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FROM EXCITED CHARGE DYNAMICS TO CLUSTER DIFFUSION: DEVELOPMENT AND APPLICATION OF TECHNIQUES BEYOND DFT AND KMC

by

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A dissertation submitted in partial fulfillment of the requirements
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ABSTRACT

This dissertation focuses on developing reliable and accurate computational techniques which enable the examination of static and dynamic properties of various activated phenomena using deterministic and stochastic approaches. To explore ultrafast electron dynamics in materials with strong electron-electron correlation, under the influence of a laser pulse, an *ab initio* electronic structure method based on time-dependent density functional theory (TDDFT) in combination with dynamical mean field theory (DMFT) is developed and applied to: 1) single-band Hubbard model; 2) multi-band metal Ni; and 3) multi-band insulator MnO. The ultrafast demagnetization in Ni reveal the importance of memory and correlation effects, leading to much better agreement with experimental data than previously obtained, while for MnO the main channels of charge response are identified. Furthermore, an analytical form of the exchange-correlation kernel is obtained for future applications, saving tremendous computational cost. In another project, size-dependent temporal and spatial evolution of homo- and hetero-epitaxial adatom islands on fcc(111) transition metals surfaces are investigated using the self-learning kinetic Monte Carlo (SLKMC) method that explores long-time dynamics unbiased by *apriori* selected diffusion processes. Novel multi-atom diffusion processes are revealed. Trends in the diffusion coefficients point to the relative role of adatom lateral interaction and island-substrate binding energy in determining island diffusivity. Moreover, analysis of the large data-base of the activation energy barriers generated for multitude of diffusion processes for variety of systems allows extraction of a set of descriptors that in turn generate predictive models for energy barrier evaluation. Finally, the kinetics of
the industrially important methanol partial oxidation reaction on a model nanocatalyst is explored using KMC supplemented by DFT energetics. Calculated thermodynamics explores the active surface sites for reaction components including different intermediates and energetics of competing probable reaction pathways, while kinetic study attends to the selectivity of products and its variation with external factors.
To my daughter, Sophia Acharya
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Shree Ram Acharya
TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... xiv

LIST OF TABLES ............................................................................................................ xxii

CHAPTER 1: INTRODUCTION ........................................................................................ 1

CHAPTER 2: THEORETICAL METHODS ...................................................................... 8
  2.1 Electronic Structure Calculation of Static System ............................................... 8
    2.1.1 Density Functional Theory ........................................................................... 12
      2.1.1.1 Hohenberg-Kohn Theorems .................................................................... 12
      2.1.1.2 Kohn-Sham Equations .......................................................................... 14
    2.1.2 Beyond Standard DFT: the Case of Strong Electron-Electron Correlation .... 16
      2.1.2.1 The Hubbard Model ............................................................................. 18
      2.1.2.2 The DMFT Solution ............................................................................. 22
      2.1.2.3 Real Systems: The DFT+DMFT Solution ............................................. 28
        2.1.2.3.1 Analytical Continuation .................................................................. 29
        2.1.2.3.2 Calculation of electronic structures .................................................. 29
    2.2 Electronic Properties Calculation of System out-of-Equilibrium .................... 32
      2.2.1 Time-Dependent Density-Functional Theory ............................................. 34
        2.2.1.1 The Case of Linear Response: Exchange-Correlation (XC) Kernel ..... 38
2.2.1.2 Calculation of XC Kernel ................................................................. 41
2.2.1.3 Bound States (Exciton) ................................................................. 43

2.3 Atomic Properties Calculation of Static System .................................. 45
2.3.1 Models for Total Energy ................................................................. 46
2.3.2 Methods to Calculate Activation Energy Barrier ............................. 47
2.3.2.1 Barrier Calculation Based on Interaction Potential ..................... 48
2.3.2.1.1 Drag Method .............................................................................. 49
2.3.2.1.2 Nudged Elastic Band Method ..................................................... 50
2.3.2.2 Barrier Calculation Based on Predictive Data-driven Approaches .... 50
2.3.2.2.1 Linear Approach: Multivariate Linear Regression (MLR) .......... 51
2.3.2.2.2 Non-linear Approach: Neural Network (NN) ............................. 53

2.4 Atomic Properties Calculation of Evolving Systems ........................... 55
2.4.1 Molecular Dynamics ..................................................................... 55
2.4.2 Kinetic Monte Carlo ...................................................................... 56
2.4.2.1 KMC for Chemical Reaction ....................................................... 59
2.4.2.2 Self-Learning KMC for Island Diffusion ................................. 64
2.4.2.2.1 Structural Model and Nomenclature ........................................ 67
2.4.2.2.2 Pattern Recognition Scheme .................................................. 72
2.4.2.2.3 Process Finder and Barrier Calculation Scheme .................. 73
CHAPTER 3: APPLICATION OF TDDFT+DMFT METHOD: ONE BAND HUBBARD MODEL

3.1 Introduction

3.2 The DFT+DMFT Solution

3.2.1 Density of States

3.2.2 Charge Susceptibility

3.3 The XC Kernel

3.3.1 Numerical Solution

3.3.2 Analytical Fitting

3.4 Applications: Ultrafast Charge Response

3.5 Conclusions

CHAPTER 4: APPLICATION OF TDDFT+DMFT METHOD: ULTRAFAST MAGNETISM ON BULK Ni

4.1 Introduction

4.2 Computational Details

4.3 Results

4.3.1 DFT+DMFT Solution: Electronic and Magnetic Properties

4.3.2 TDDFT Solution: Ultra-fast Demagnetization
4.4 Conclusions............................................................................................................. 110

CHAPTER 5: APPLICATION OF TDDFT+DMFT METHOD: CHARGE EXCITATIONS AND ULTRAFAST DYNAMICS ON BULK MnO, AN INSULATOR......................... 112

5.1 Introduction............................................................................................................. 112

5.2 Computational Details .......................................................................................... 114

5.3 Results..................................................................................................................... 117

5.3.1 DFT: Geometrical, Electronic, and Magnetic Structures ............................... 117

5.3.2 DFT+DMFT: Band Structure and Excitation Spectrum................................. 119

5.3.3 TDDFT Solution: Charge Dynamics and Bound State ............................... 123

5.4 Conclusions............................................................................................................. 126

CHAPTER 6: APPLICATION OF SLKMC: Cu ISLANDS DIFFUSION ON Ni(111). 126

6.1 Introduction............................................................................................................. 128

6.2 Computational Details .......................................................................................... 130

6.3 Results..................................................................................................................... 131

6.3.1 Validation of Approximations in SLKMC Method........................................... 132

6.3.2 Diffusion Characteristics by Island Size: Monomer to Octamer..................... 141

6.4 Conclusions............................................................................................................. 176
CHAPTER 7: ISLAND DIFFUSION KINETICS USING SLKMC: BARRIERS FROM INTERATOMIC INTERACTION TO PREDICTIVE DATA-DRIVEN APPROACHES

7.1 Introduction ........................................................................................................................................... 179
7.2 Comparison of Diffusion Characteristics: Pd/Pd(111) and Ag/Ag(111), Cu/Ni(111) and Ni/Cu(111) ................................................................................................................................. 182
7.3 Machine Learning for Diffusion Study .................................................................................................... 190
  7.3.1 Descriptor Generation .......................................................................................................................... 191
  7.3.2 Model Development ............................................................................................................................ 200
  7.3.3 Energy Barrier and Diffusion Characteristics ....................................................................................... 201
7.4 Conclusions ............................................................................................................................................... 206

CHAPTER 8: METHANOL PARTIAL OXIDATION REACTION ON Pd_{16}Zn_{16} NANOPARTICLE: A DFT+KMC STUDY .......................................................................................................................... 208
8.1 Introduction .............................................................................................................................................. 208
8.2 Computational Details .............................................................................................................................. 211
8.3 Adsorption of Reactants, Products, and Intermediates ........................................................................... 215
8.4 Reaction Pathways .................................................................................................................................. 223
8.5 Selectivity of Products ............................................................................................................................. 234
8.6 Conclusions ............................................................................................................................................ 235
LIST OF FIGURES

Figure 1 A graphical representation of Hubbard model with possible occupancy dynamics of a lattice site. ..........................................................19
Figure 2 Basic idea of DMFT solution of lattice problem. ..........................................................23
Figure 3 Flow-chart of KMC algorithm used for chemical reaction. ........................................61
Figure 4 Unit cell of face centered cubic packing of elements and its cutting along (111) plane (yellow plane). .........................................................68
Figure 5 Variation of energy per atom of Ni substrate with number of atoms arranged in fcc(111) arrangement. Note the flat portion about 256 and 1200 atoms that signify 16x16 atoms in a layer and 5 layers of them are enough for a substrate........................................69
Figure 6 (a) Top view of the fcc(111) surface. The exposed top layer (A-layer), a layer below (B-layer) and two-layers below (C-layer) are represented by big hollow green circles, filled blue circles and filled yellow circles, respectively, (b) Octamer island adsorbed on fcc sites with A-or B-type step-edge and A or B-type processes, (b) Three possible available directions for an adatom to move from an fcc (hcp) to neighboring hcp (fcc) site along with numbering convention for processes used in this article. ........................................69
Figure 7 (a) Three concentric hexagonal rings out of six such rings to uniquely specify local neighborhood of an island in pattern recognition scheme of the SLKMC-II method. Enumeration of top layer substrate atoms and adsorption sites of the fcc(111) surface to explore possible processes and store information. Initial pentamer island configuration in (a) transforms to that in (b) after execution of a 2-atom process shown by lines with arrowhead, (c) format of database that stores information about the initial island configuration, energy barrier of process and executed process The two-atom process is complemented by probable single-atom process with the same probable target site 19...........................................71
Figure 8 Variation of energy at each drag step during drag of the central adatom at site 1 of the Cu pentamer island on Ni(111) shown in Figure 7(a) to target site 19 for the single-atom process keeping other adatoms fixed (first part), and allowing all island atoms to move which results in a 2-atom process (the second part). The resulting process, final
configuration and the storage of the information in database of SLKMC simulation is shown in Figure 7.

Figure 9 Flow chart of SLKMC method.

Figure 10 The single particle Density Of States (DOS) as a function of frequency obtained for U = 1t, 2t and 4t: (a) for T = 0.16t with both the Hirsch–Fye Quantum Monte Carlo (HF-QMC) and the Iterative Perturbation Theory (IPT) approaches; (b) for T = 0.05t using IPT only.

Figure 11 Plot of spectral function at intermediate value of parameter U, U=2t, obtained by DMFT and DFT+U approaches.

Figure 12 The imaginary part of the charge susceptibility as a function of frequency obtained with the HF-QMC and the IPT approaches at U = 1t, 2t and 4t and temperature T = 0.16t.

Figure 13 The real (left column) and imaginary (right column) parts of $f_{XC}(\omega)$ for the one-band Hubbard model at different values of U and temperature T = 0.16t obtained by using the IPT and the HF-QMC approaches.

Figure 14 HF-QMC and analytical fitting results for the imaginary parts of the XC kernels from Figure 13.

Figure 15 Time dependence of the excited charge density in the one-band Hubbard model in the case of 0.8-fs laser pulse perturbation at T=0.16t at different values of U and adiabatic (A) and non-adiabatic (NA) exchange-correlation (XC) kernels.

Figure 16 Temperature-dependence of the magnetic moment of bulk Ni obtained with DMFT.

Figure 17 The DFT (dashed lines) and DFT+DMFT (continuous lines, T=216K) spin-orbital resolved density of states of bulk Ni.

Figure 18 (a) The DMFT excitation spectrum, (b) time- dependence of the DMFT XC kernel of bulk Ni.

Figure 19 The demagnetization dynamics obtained for the free particle (green curve), adiabatic LDA fxc (blue curve) and non-adiabatic TDDFT+DMFT $f_{XC}(\omega)$ (red curve) with the laser pulse (black curve) with the amplitude 0.05V/Å, duration 7.2fs and energy 2eV.
Figure 20 Orbital and spin resolved excited charge density dynamics for the pulse shown in the bottom. (b) Excited charge density dynamics that includes only selected spin transitions.

Figure 21 The time-dependence of the TDDFT+DMFT demagnetization at different (a) field amplitude, (b) pulse duration, and (c) the pulse frequency and other pulse parameters shown in the previous figure.

Figure 22 Unit cell of bulk MnO in NaCl structure consisting of two interlaced fcc (111) lattices consisting of Mn and O such that each Mn atom has six O neighbors. Lines with arrow head shows the ordered arrangement of spins of the $Mn^{2+}$ ions in MnO.

Figure 23 Spin-orbital resolved density of states of bulk MnO calculated using density functional theory method.

Figure 24 (a) Comparison of density of states obtained using DFT, DFT+DMFT, and experimental XPS valence-band and BIS conduction band from ref. [200] spectra. (b) 3-fold degenerate $t_2g$ and 2-fold degenerate $e_g$ orbitals of one Mn atom obtained using DFT+DMFT.

Figure 25 DMFT excitation spectrum of Mn.

Figure 26 Time dependence of the DMFT XC kernel of Mn.

Figure 27 Dynamics of variation of orbital resolved excited charge density in non-interacting case, (b) interacting case with adiabatic and non-adiabatic approximations, (c) orbital resolved excited charge density dynamics in non-adiabatic TDDFT.

Figure 28 Schematic representation of the mechanism of charge dynamics on bulk MnO.

Figure 29 Variation of exciton binding energy with dielectric constant in screened Slater XC kernel.

Figure 30 Variation of number of processes in the database for the tetramer island with number of KMC steps (in ln scale).

Figure 31 Cu monomer on the Ni (111) surface adsorbed on (a) an fcc site, and (b) an hcp site. The line with arrowhead pointing right (left) represents an fcc to hcp (hcp to fcc) hopping process with a number specifying the energy barrier for the process in question.

Figure 32 (a) Center of mass trajectory, (b) Mean square displacement vs. time, of Cu tetramer on the Ni (111) surface at 300K.
Figure 33 (a) Arrhenius plot for Cu islands of size 1-8 on the Ni(111) surface. (b) Variation of effective of Cu islands of size 1-8 on the Ni(111) surface with island size.

Figure 34 Variation of normalized frequency of executed single-atom, multi-atom and concerted processes on diffusion kinetics of adatom islands of size 2 to 8 with temperatures 100K to 600K.

Figure 35 Structures of a dimer island on the fcc(111) surface: (a) the energetically most favored 2F, (b) 2H, and (c) FH. Process shown using lines with arrowheads in (a) and (b) represent the most executed A-type concerted processes, (c) and (d) represent the most executed single-atom processes, (e) and (f) represent long-jump single-atom processes of 2F and 2H islands, respectively, in each of which I is B-type non-detachment process, II, III and IV are detachment processes which are not taken into account in this study of island diffusion, but are displayed to show their significantly higher energy barriers, and V is a non-detachment A-type process. The numbers with enumeration next to figures represent barriers of processes, as shown in Figure 6(c), in the enumerated directions.

Figure 36 Variation on energy of the system with distance between two Cu adatoms during (a) a B-type single-atom process, e.g., #I in Figure 35(e), (b) an A-type single-atom process, e.g., #V in Figure 35(e).

Figure 37 The compact structures of the Cu trimer island on the Ni(111) surface: (a) the energetically most favored 3F-H, (b) 3H-T, (c) 3H-F, and (d) 3F-T. The most diffusive concerted sliding processes and the most frequently executed rotational processes in trimer island diffusion are shown respectively in (a-d) and (e-f) using lines with arrowhead.

Figure 38 Single-atom processes in four different compact structures of trimer island along with their energy barriers in the four possible directions enumerated as processes I, II, III, and IV. Barrier of non-detachment process precedes the barrier of their reverse process in parenthesis.

Figure 39 Possible low barrier processes on non-compact 3H trimer, (a-b) A-type single atom processes, (c) concerted, (d) dimer-shearing, and (e) reputation. Among those processes the barrier of the A-type single-atom process that converts the non-compact structure into
compact structure is the lowest barrier processes and so are the rate-limiting processes.

Figure 40 (a) The energetically most favored rhombus shaped compact 4F island, (b) rhombus shaped compact 4H island. The numbers with enumeration next to figures specify the energy barriers of concerted processes in the enumerated directions. Lines with arrowhead in (c & d) show A-type dimer-shearing process on 4F tetramer. The shown processes along with the hcp counterpart of the dimer-shearing process are the most executed processes of Cu tetramer island diffusion on the Ni(111) surface.

Figure 41 (a) The energetically most favored long B-type step-edge 5F pentamer. The lines with arrowhead in (a-d) and (e & f) show respectively the most executed processes among concerted processes and A-type dimer-shearing multi-atom processes in pentamer island kinetics, (g) shows the rate-limiting single-atom processes that interconvert long B-type 5F pentamer shown in (h) into long A-type 5F pentamer shown in (i).

Figure 42 (a) or (c) represents the energetically most favorable 6F parallelogram structure of hexamer island with process in (a) shows the most executed concerted-sliding process that turns the island into 6H parallelogram structure shown in (b). The numbers with enumeration next to figures in (a & b) specify the energy barriers of concerted processes in the enumerated directions. Processes in (c-d) and (e) show the most executed processes among multi-atom and single atom processes in hexamer island diffusion respectively.

Figure 43 (a) or (c) represents the energetically most favorable 7F heptamer island with processes shown in (a) and (c) representing the most executed concerted and dimer-shearing processes of heptamer respectively. Process shown in (e) is the most frequently executed dimer-shearing process of non-compact 7F heptamer.

Figure 44 (a) The energetically most favored long B-type step-edge 8F island. The processes shown in (a-d) and (e-f) represent the most executed processes among concerted and multi-atom processes in octamer diffusion respectively. The corner rounding single-atom process with barriers 0.024 eV and 0.165 eV shown in (g) represent respectively the most executed and rate-limiting processes in octamer diffusion.
Figure 45 Normalized frequency of executed single-atom, multiatom, and concerted processes in the diffusion of adatom islands of size 2 to 8 in the temperature range of 100-600K of: (a) Pd (continuous line) and Ag (dotted line) adatom islands of size 2 to 8 on their respective (111) surface; (b) Ni islands on the Cu(111) surface (continuous line) and Cu islands on the Ni(111) surface (dotted line)...................................................................................183

Figure 46 Arrhenius plot of islands of size 1 to 8 of (a) Pd islands on Pd(111) (continuous line) and Ag islands on Ag(111) (dotted line) and (b) Ni islands on Cu(111) (continuous line) and Cu islands on Ni(111) (dotted line). .......................................................................188

Figure 47 Single-atom processes for a trimer island that require breaking of different number of bonds for diffusion, along with their energy barriers. ...................................................192

Figure 48 Single-atom process that converts (a) a compact trimer island into a non-compact one and, (b) its reverse process; along with their barriers. ...................................................192

Figure 49(a) Translational, and (b) rotational motion processes for a trimer island along with their barriers. ..........................................................................................................................193

Figure 50 Translational concerted processes of (a) a dimer, and (b) a trimer island, along with their barriers. ..........................................................................................................................193

Figure 51 A- and B-type processes for (a) a dimer, (b) a tetramer island, along with their barriers. ....................................................................................................................................194

Figure 52 Predicted vs. calculated barriers of most frequently executed processes for Ni islands on the Ni(111) surface, (a) when some Ni samples are used in the training of the multivariate linear model and (b) Ni samples are not used to develop the model........................................203

Figure 53 Calculated vs. predicted barriers of different processes of an island diffusion on the fcc(111)surface using a neural network; (a), (b), and (c) show plots for training, validation, and testing samples, respectively. .................................................................................204

Figure 54 Error histogram of prediction of barriers of processes using a neural network. ....205

Figure 55(a) Arrhenius plot, (b) normalized type of executed processes obtained from KMC simulation of the Ni dimer diffusion processes on the Ni(111) surface using barriers from drag method from EAM interaction (red curves) and from the trained neural network model (black curves)........................................................................................................206
Figure 56 Pd$_{16}$Zn$_{16}$ nanoparticle catalyst model in which white and blue balls represent Zn and Pd atoms, respectively. ...........................................................................................................211

Figure 57 Side view of methanol molecule (a) in free standing configuration, and (b) in the adsorbed configuration on the energetically most preferred (Pd(3)) site of Pd$_{16}$Zn$_{16}$ nanoparticle. Hydrogen, carbon, and oxygen atoms of molecule are represented using green, black, and yellow spheres, respectively. Only the top surface of the nanoparticle is shown to clearly show the adsorption geometry............................................................218

Figure 58 Side view of adsorbed oxygen molecule on the energetically most preferred (Zn(1)-Zn(1)) bridge site on Pd$_{16}$Zn$_{16}$ nanoparticle.............................................................................219

Figure 59 Side view of hydrogen molecule adsorbed on the energetically most preferred (Pd(2)) top site on Pd$_{16}$Zn$_{16}$ nanoparticle. ........................................................................................................219

Figure 60 Side view of the energetically most preferred adsorption configuration of CO molecule on (Pd(3) site on surface of Pd$_{16}$Zn$_{16}$ nanoparticle. ...........................................................220

Figure 61 Side view of the energetically most preferred adsorption configuration of CO$_{2}$ molecule on surface of Pd$_{16}$Zn$_{16}$ nanoparticle..............................................................................220

Figure 62 Side view of the energetically most preferred adsorption configuration of H$_{2}$O molecule on Pd(3) site of Pd$_{16}$Zn$_{16}$ nanoparticle. .........................................................................................221

Figure 63 Side view of the energetically most preferred adsorption configuration of CH$_{3}$O molecule on (Zn(1) - Zn(1) ) bridge site of Pd$_{16}$Zn$_{16}$ nanoparticle.................................................221

Figure 64 Side view of the energetically most preferred adsorption configuration of CH$_{2}$O molecule on Pd(3) site of Pd$_{16}$Zn$_{16}$ nanoparticle. .........................................................................................222

Figure 65 Side view of the energetically most preferred adsorption configuration of CHO molecule on (Pd(1) - Pd(2) ) bridge site of Pd$_{16}$Zn$_{16}$ nanoparticle......................................................222

Figure 66 Energetics of the dehydrogenation and the oxidation routes on Pd$_{16}$Zn$_{16}$ nanoparticle. The “*” indicates adsorbed surface species.................................................................223

Figure 67 Energy profile of CH$_{3}$OH* dehydrogenation.................................................................225

Figure 68 Energy profile of CH$_{3}$O* dehydrogenation.................................................................225

Figure 69 Energy profile of CH$_{2}$O* dehydrogenation.................................................................226

Figure 70 Energy profile of CHO* dehydrogenation.................................................................226

Figure 71 Energy profile of CH$_{3}$O* oxidation reaction.................................................................227
Figure 72 Energy profile of CH$_2$O* oxidation reaction ..............................................................228
Figure 73 Energy profile of CHO* oxidation reaction ..............................................................229
Figure 74 Energy profile of CO* oxidation reaction ..............................................................229
Figure 75 Energy profile of CH$_3$OH* hydroxylation reaction ....................................................230
Figure 76 Energy profile of CH$_3$O* hydroxylation reaction ....................................................231
Figure 77 Energy profile of CH$_2$O* hydroxylation reaction ....................................................231
Figure 78 Energy profile of CHO* hydroxylation reaction .......................................................232
Figure 79 Selectivity of products: (a) H$_2$ vs. H$_2$O, and (b) CO$_2$ vs. CO on Pd$_{16}$Zn$_{16}$ model catalyst
as a function of temperature. .........................................................................................234
LIST OF TABLES

Table 1 Fitting parameters for the analytically-approximated expression for the imaginary part of the XC kernel at different values of U. .................................................................92

Table 2 The calculated values of various ground state quantities and the values reported experimental values of the corresponding quantities........................................................117

Table 3 Values of exciton binding energy for different XC kernels in density matrix TDDFT formulation. ..........................................................................................................................126

Table 4 Energy barriers of selected processes from drag method using EAM interaction and NEB method using DFT energetics. .......................................................................................134

Table 5 Size dependent adsorption energies of the most stable island configurations and the lateral interaction of adatoms on those configurations after calculating energies based on EAM interaction and DFT method. Energies are expressed in eV unit. ......................137

Table 6 Variation of lateral interaction with dimer distance from EAM and DFT approaches. 138

Table 7 Fcc and Hcp adsorption energy difference of the most stable islands from EAM and DFT. ........................................................................................................................................139

Table 8 Percentage change in the calculated values of lnD for Pd pentamer diffusion on the Pd(111) for different pre-factors with reference to its value with pre-factor $10^{12}$ s$^{-1}$ at different temperatures ........................................................................................................................................140

Table 9 Percent variation in the bond length of island adatoms with respect to the substrate bulk nearest neighbor distance ........................................................................................................140

Table 10 Diffusion coefficients of (1-8)-atom Cu islands on Ni(111) in the temperature range 100 - 600 K. Error bars on the values of D are less than 1%. ........................................................................144

Table 11 Energy barrier of concerted processes in three possible directions of the energetically favored compact pentamers shown in Figure 41(a-d). ........................................................166

Table 12 Energy barrier of concerted processes in different directions on non-parallellogram shaped hexamer ..................................................................................................................170

Table 13 Energy barrier of concerted processes in 3 possible directions of various compact octamer island structures shown in Figure 44 (a) The energetically most favored long B-type step-edge 8F island. The processes shown in (a-d) and (e-f) represent the most executed
processes among concerted and multi-atom processes in octamer diffusion respectively. The corner rounding single-atom process with barriers 0.024 eV and 0.165 eV shown in (g) represent respectively the most executed and rate-limiting processes in octamer diffusion.(a-d). TSE abbreviates type step-edge.

Table 14 Comparison of barriers of concerted and multi-atom processes on the same adatom island configuration of different island sizes of the systems under study.

Table 15 Lateral interaction among adatoms of islands on the fcc(111) substrate for the configurations relevant to processes in Table 14.

Table 16 Effective energy barriers calculated as function of island-size using SLKMC simulation for the systems under study.

Table 17 Diffusion barriers of some selected single-atom (S), multi-atom (M), and concerted (C) processes of adatom islands on several homo-epitaxial and hetero-epitaxial fcc(111) systems.

Table 18 Size dependent adatom island binding energy on several homo-epitaxial and hetero-epitaxial systems.

Table 19 Comparison of barriers of concerted and multi-atom processes for the same adatom island configuration in homo and hetero-epitaxial systems.

Table 20 Lateral interaction among adatoms of islands on the fcc(111) substrate for the configurations relevant to processes in Table 19.

Table 21 Calculated coefficients in the linear predictive equation of activation energy barrier using 7 descriptors and value of $R^2$ for models.

Table 22 Values of correlation coefficients in the training, validation, and testing dataset of diffusion barriers using the neural network.

Table 23 Comparison of adsorption energies of reactants and products of MPO, adsorbed at various surface sites of Pd$_{16}$Zn$_{16}$. The distances are in Å and energies are in eV units.

Table 24 Comparison of adsorption energies (in eV) of intermediates of MPO adsorbed at various surface sites of Pd$_{16}$Zn$_{16}$ nanoparticle catalyst.

Table 25 Elementary reaction steps of MPO reaction included in KMC simulation.
CHAPTER 1: INTRODUCTION

All of the processes in the physical world around us are happening under the influence of static or dynamic external factors. Those factors induce activated processes that change the properties of a system, for e.g., electromagnetic energy affects motion and spin orientation of charge particles that changes transport and magnetic properties, supplied heat energy changes the structural properties of a material that leads to its phase change, catalyst changes the strength of chemical bond that changes the rate of chemical reaction, thermal energy and applied pressure also change the rate of chemical reaction. In an evolutionary process from initial to final equilibrium state under external influence, materials undergo through number of intermediate steps that may or may not be perceivable at natural time scale. Understanding of those steps is crucial to completely understand the process that is essential to design control on the process to optimize desired output or to move the evolution in the desired pathways or simply to extract output from intermediates. Due to those important possibilities of rational property design associated with microscopic static and more importantly with dynamic understanding of a phenomenon, they are the subject of interest on various fields including ultrafast electronic charge dynamics[1], surface diffusion[2; 3], and catalysis[4]. Although experimental observations of any phenomena provide realistic information and are crucial in design and testing of theoretical approaches, in most of cases they have limitations to get microscopic understanding owing to their time or spatial resolution, for e.g., one can observe only input and output without intermediates in exploration of chemical reaction process that pushes to indirectly infer details. On the other hand, theoretical studies can provide complete
microscopic understanding predicting the effect of each of the component factors in the output which enables one to rationally design a material by considering its intrinsic features or obtain desired property in a material by manipulating extrinsic parameters. However, to reliably predict the properties of systems, theoretical approach requires to use reliable, accurate, viable and the spatial and temporal dimension of considered model should be enough to mimic all details of experimental counterpart. In this dissertation, focus is on the development and application of a reliable \textit{ab initio} framework to explore charge and spin dynamics on bulk of strongly correlated materials, explore post deposition island diffusion on surface for extended time using stochastic approach, develop a data-driven approach to expedite calculation of ingredients required to study island diffusion kinetics to reduce the time gap between simulation and experimental measurement., and explore the active sites and kinetics of surface chemical reaction on a nanoparticle catalyst.

As a dynamic phenomenon under the external laser pulse perturbation, the charge and spin dynamics in materials with valence electrons in localized d orbitals (so called strongly correlated) is studied. Research in this direction is motivated by a number of novel properties\cite{5} on those materials on both static or dynamic phase due to the strong electron-electron correlation. Although density functional theory approach with local or semi-local density dependent exchange-correlation (XC) functional forms using local density approximation (LDA) or generalized gradient approximation (GGA) are viable and mostly used for material property prediction and are successful for weakly correlating s or p electron systems, they are partially or fully fail to predict features of those strongly-correlated materials even in static equilibrium calculation\cite{6; 7}. This failure becomes more severe on prediction of
the dynamical properties of those systems using the same XC potentials in the TDDFT approach[8], which, in exact formulation, requires time-dependence of the XC potential. This partial failure of those XC potentials is due to the improper treatment of those strongly localized electrons [9; 10]. Among various approaches followed to circumvent the complexity, generally followed trend to mimic such systems is to use Hubbard model that explicitly considers the on-site Coulomb interaction of electrons on those localized orbitals keeping the band dispersion of s or p orbital electrons via hopping term. The same approach is followed in this study. The model is solved in DMFT [11; 12] approach by self-consistently mapping the lattice problem into effective quantum impurity problem which is then solved using iterative perturbation theory (IPT)[13] and/or the exact quantum Monte Carlo (QMC)[14] solver. Based on the solution of dynamical susceptibility, the frequency dependent XC kernel is calculated which is then used in linear response TDDFT formulation to calculate the charge excitation dynamics. The TDDFT method is formulated in the density matrix formulation as explained in Ref. [15] and presented in Appendix D that considers only the most relevant bands which significantly simplifies the problem and speeds up the calculation. Using such approach in relatively simple case of one band Hubbard model taking different values of correlation via Coulomb interaction parameter, an analytical expression is fitted for the numerical results of the XC kernel obtained at different values of Coulomb correlation[15]. Such an XC is directly useful (without further calculating it using computationally intensive DMFT calculation) in response calculation in TDDFT for materials systems which can be mimicked by such a model. As an application of such TDDFT +DMFT [15-17] formulation, the ultrafast magnetization dynamics on bulk Ni under ultra-short laser pulse excitation is studied. Experimentally, it is
shown in ref. [18; 19] that the spin and hence magnetism on the system can be manipulated in ultra-short time scale (femtosecond) under laser pulse perturbation but the quantitative solution based on available computational techniques has remained orders of magnitudes off of experimental measurements. We provide a microscopic understanding for the observed significant change on the magnetic moment of the system under laser pulse irradiation on the basis of the orbital occupancy of different d orbitals. This study has also established that non-adiabaticity (memory) and correlation effects are important in such ultra-short processes and the ultra-fast demagnetization takes place mainly due to spin-flip transitions from occupied into unoccupied orbitals implying dynamical reduction of the exchange splitting. To study the effect of the laser-pulse parameters on such an ultrafast demagnetization process, the TDDFT Kohn-Sham equation is solved at different values of the laser pulse parameters: amplitude, energy, and duration, and show that the above scenario of the demagnetization remains valid in all the cases. Additionally, we apply the method to study the d-electron dynamics on Manganese oxide (MnO), a prototype of transition metal oxide system, and infer the main channels of the charge response. In addition, the calculation of possible bound state on the system demonstrates the existence of exciton, as predicted in experiment [20], with rather strong binding energy of order 100meV that may have practical applications.

As a dynamical multi-scale phenomenon under external thermal perturbation, the post deposition diffusion kinetics of metallic 2D islands on metallic fcc(111) surface is explored. Although the straightforward molecular dynamics (MD)[21] approach that explores the diffusion dynamics in natural way taking force and vibrational character implicitly in formulation, it is limited in attainable equivalent physical time and in most of cases cannot
attain enough time to explore the execution of rare bond-breaking diffusive processes. As a consequence, a thin film growth model just by incorporating processes explored by MD method has limited predictability. On the other hand, kinetic Monte Carlo (kMC)[22; 23] approach overcomes such limitations by being based on rate equation and explicitly incorporating individual processes in simulation. Based on our simulation of post deposition island diffusion kinetics of homo- and hetero-epitaxial systems using the self-learning kinetic Monte Carlo (SLKMC) method, we provide dominant and rate-limiting processes on small island diffusion that is expected to be crucial to understand experimental observations, to formulate a reliable growth model, to design a control measure on early stage on the evolving morphology of thin film, among many others applications. By comparing the diffusion kinetics on different systems, a general understanding about the dominancy of particular process or competition among different types of processes on an island diffusion kinetics is created. On the fundamental aspect, examination of energy barriers of processes and corresponding geometrical and energetic information enables us to uncover the reason for variation of barriers of different processes on the same island structure and of the same process on the different elements. Such an understanding gathered by dealing with processes on different structures of an island or islands of various sizes or islands of different elements is utilized to extract easily accessible geometrical and ground state energetic features to encode a process in terms of descriptors, which is necessary to train and test predictive statistical models. Simplified data-driven models based on linear and non-linear statistical approaches are developed which can make ultrafast and accurate barrier prediction which otherwise require intensive computational resources. Such a predictive model can reliably replace the computationally intensive part of
interaction based diffusion barrier calculation, a step forward to reduce the spatial-temporal gap in the multiscale problem of thin-film growth.

As a kinetic problem driven by externally controllable temperature and pressure perturbations, the chemical reaction kinetics of one of the industrially important heterogeneous chemical reaction on surface of nanoparticle model of catalyst is explored. The specific process studied is motivated by experimental observations in the laboratory of our collaborator Feng Tao’s group at University of Kansas, Kansas city. Experimentally they observe the significant variation of the performance of Pd/ZnO catalyst for methanol partial oxidation (MPO) reaction towards conversion of reactants and the selectivity of products under the low loading of Pd (singly dispersed Pd on ZnO) and relatively higher loading of Pd in which signature of formation of PdZn bimetallic nanoparticle is observed. This is an important observation that uses an economical catalyst to selectively extract hydrogen from a sulphur-free and the simplest alcohol with possible application in emerging hydrogen fuel cell technology. However, a microscopic understanding of the reason behind such an observed difference in reactivity and its variation for externally controllable temperature and pressure conditions is important. While exploring the MPO reaction on the surface of a nanoparticle catalyst model, active sites for adsorption of various intermediates of dehydrogenation, oxidation, and hydroxylation routes of reaction is reported which is followed by kinetic study to explore the variation of experimentally measurable quantities of product selectively as function of temperature and pressure. Based on the analysis using quantum mechanical DFT [24; 25] based energetics in kinetic Monte Carlo simulation [26], it is clear that the nanoparticle is
active for oxidation reaction whereas similar study of singly dispersed Pd on ZnO surface is active for successive dehydrogenation process leading ultimately for high H₂ production.

In chapter 2, I present the mathematical details of theoretical aspects of the electronic structure methods used in the dissertation: DFT, DMFT and TDDFT which is followed by the detail of the interatomic-interaction based atomic level simulation techniques: MD and the SLKMC along with their components. The application of TDDFT+DMFT method in the prototypical 1 band Hubbard model is presented in Chapter 3 (from reference [15]) and for the realistic systems of metallic bulk Ni and insulating bulk MnO are presented in chapter 4 and 5, respectively. In chapter 6, I present the application of SLKMC method for the hetero-epitaxial Cu island diffusion on the Ni(111) surface (Cu/Ni(111)) from ref. [27]. In chapter 7, I present the application of the method to compare diffusion kinetics of homo-epitaxial Pd/Pd(111) with Ag/Ag(111), and hetero-epitaxial Cu/Ni(111) with Ni/Cu(111) systems from ref. [28] along with the newly developed statistical model for the prediction of activation energy barriers. In chapter 8, I present the results of the kinetic study of MPO reaction on surface of a nanoparticle catalyst using kMC+DFT method.
CHAPTER 2: THEORETICAL METHODS

2.1 Electronic Structure Calculation of Static System

In quantum mechanical approaches, all the information about a system containing electrons and nuclei is contained in its wave function $\Psi$ which is calculated from Schrödinger equation\[29\]

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_M) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_M), \tag{1}$$

where

$$\hat{H} = -\sum_{i=1}^{N} \frac{\nabla_i^2}{2} - \sum_{A=1}^{M} \frac{Z_A}{|\mathbf{r}_{iA}|} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\mathbf{r}_{ij}|} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{|\mathbf{r}_{AB}|}, \tag{2}$$

is the Hamiltonian of a system containing $N$ electrons and $M$ nuclei in which successive terms represent the sum of the electronic and the nuclear kinetic energy operators, the attractive electron-nuclei, the repulsive electron-electron, and the repulsive nuclei-nuclei Coulomb potential energy, respectively. In the Equation, the rest of the dissertation, atomic unit ($\hbar = m_e = e = 1$) is used. In the Hamiltonian, an electron is treated as an individual entity so that $\mathbf{r}_i$ refers the position of an electron $i$ at displacement $\mathbf{r}_{ij}$ from another electron $j$ at position $\mathbf{r}_j$ and a nucleus is treated as a single charged mass so that nucleus $A$ has charge number $Z_A$ and mass $M_A$ at displacement $\mathbf{r}_{AB}$ from another nucleus $B$ with charge number $Z_B$ and mass $M_B$. Since the mass of a nucleus is thousands of times that of an electron, the Hamiltonian in Equation, is usually simplified by using Bohn-Oppenheimer approximation\[30\] in which slowly moving nuclei as compared to electrons can be treated as classical particles that allows to consider electrons as moving entities in the field of fixed nuclei. Importantly, this approximation decouples the motion of electrons and nuclei of a
system. For electron property calculation at a set of fixed nuclear coordinates, the nuclear kinetic energy term vanishes and the total energy contains the sum of electron energy and the nuclei-nuclei repulsive energy. So, after applying Bohn-Oppenheimer approximation, the Hamiltonian of a system that mimics electrons moving in a stationary potential created by frozen nuclei becomes

$$\hat{H} = -\sum_{i=1}^{N} \frac{\nabla_i^2}{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|r_{iA}|} + \sum_{i=1}^{N} \sum_{j>i} \frac{1}{|r_{ij}|} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{|r_{AB}|}. \quad (3)$$

Since the energy due to nuclear degree of freedom (lattice in solid) appears as a simple additive constant, it changes energy but not $\Psi$ of an electron and so $\Psi = \Psi(r_1, r_2, \ldots, r_N)$ i.e., the wave function of electronic Hamiltonian depends only on the electronic coordinates which can be obtained by solving

$$\hat{H}\Psi(r_1, r_2, \ldots, r_N) = E\Psi(r_1, r_2, \ldots, r_N), \quad (4)$$

where

$$\hat{H} = \sum_{i=1}^{N} \left[ -\frac{\nabla_i^2}{2} - v(r_{iA}) + \sum_{j>i} U(r_i, r_j) \right]. \quad (5)$$

The potential $v(r_{iA})$ is the term that distinguishes whether electron is on a molecule or a solid based on the boundary condition on $r_{iA}$ and the presence of last term $U(r_i, r_j)$ represents the problem as complicated many-body problem different from relatively simple one-electron problem. Up to this point, although the nuclear degrees of freedom are decoupled treating them as classical point–like particles, electronic interactions among all electrons are required to consider to get electronic structures. In addition to the discussed application scenario of electronic structure computing for given nuclear coordinates, the general scenario in the
structural optimization requires to find equilibrium positions for electrons for given ionic
distribution and the ions position updating at given electron charge distribution repeatedly
continues until total convergence for the electronic and ionic subsystems is achieved.

A straightforward quantum mechanical approach to solve Schrödinger equation is to specify
a system by choosing $v(r_{iA})$ and plug it into Schrödinger equation which is then solved for
the wave function $\Psi(r_1, r_2, ..., r_N)$ and calculate observables of interest as expectation value
of operators:

$$v(r) \xrightarrow{SE} \Psi(r_1, r_2, ..., r_N) \xrightarrow{<\Psi|\cdot|\Psi> \rightarrow \text{Observables.}}$$

In numerical calculation, storing values of $\Psi(r_1, r_2, ..., r_N)$, quantity that includes total
information about the state of the electronic system, is a difficult task. One simple estimate of
it is to imagine a real space representation of $\Psi$ on a mesh, in which each coordinate is
discretized by using 10 mesh points. In this mesh, to store $\Psi$ of 1 electron (ignoring spin and
taking it to be real instead of complex for simplicity) requires $10^3$ numbers. In general, $\Psi$ of
an N electrons system becomes a function of $3N$ spatial coordinates that requires to store big
matrix with $10^{3N}$ entries to store information of the system. For e.g., O atom with N=8 electrons
needs a big table with $10^{24}$ entries to store its $\Psi$. Using 5GB DVD that stores $5 \times 10^9$ bytes, $\Psi$
needs $2 \times 10^{14}$ DVDs. If one DVD weighs 10gm, DVD of mass $2 \times 10^{15}$ gm = $2 \times 10^9$ tons are
needed. Taking spin and real and imaginary part increases the requirement by a factor of 4 on
ground state calculation. In addition, solving the full eigenvalue equation takes $n^3$ operations
for an nxn matrix. In this way, the computation even of atomic systems with relatively few
electrons is challenging and so the computation of properties of systems that has large number
of atoms in their unit cell, for e.g., biological or nano or surface calculation, is impossible. Note that $U(r_i, r_j)$ is the only term in Equation (1) that makes the problem extremely complex many-body problem, without which it becomes a simple, exactly solvable single-body quantum mechanical problem. In the limiting case of $U(r_i, r_j) = 0$ (Hartree approximation), electrons do not interact directly with each other at which the Schrödinger equation can be splitted into collection of $N$ 1- electron Schrödinger equations which interact through mean field due to nuclei. Such a simplified equation for coordinate $r_1$ becomes

$$\left[-\frac{\nabla^2}{2} - v(r_{1A})\right] \Psi_1(r_1) = \epsilon_1 \Psi_1(r_1). \quad (7)$$

Once wave function of each electrons are separately computed, the state of the total system can be written as the product of individual electrons’ wave function

$$\Psi(r_1, r_2, \ldots, r_N) = \Psi_1(r_1)\Psi_2(r_2)\ldots\Psi_N(r_N). \quad (8)$$

The approximation keeps $\Psi(r_1, r_2, \ldots, r_N)$ symmetric (does not change sign with interchange of any two $r_i$s) and does not offer any restriction on spin degree of freedom that leads to get the same solution i.e., allowed energy values, for singlet and triplet states.

To study a real systems containing many interacting electrons, density functional theory (DFT) is a viable alternative approach, less accurate perhaps but much more versatile, since in this theory the problem is reduced to an effective one-electron problem.
2.1.1 Density Functional Theory

DFT explicitly recognizes that nonrelativistic Coulomb systems differ only by their potential \( v(\mathbf{r}) \) and provides a way to systematically map the many-body problem with many-body potential \( \mathbf{U} \) onto a single-body problem without \( \mathbf{U} \). All this is done is by selecting the particle density \( n(\mathbf{r}) \), one among many observables, as the key variable on the basis of which all other quantities are calculated. In general, the particle density is calculated by using

\[
n(\mathbf{r}) = N \int d\mathbf{r}_1 \int d\mathbf{r}_2 \ldots \int d\mathbf{r}_N \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N),
\]

To be explicit, since \( n(\mathbf{r}) \) is defined on the wave functions that obey Schrödinger equation with the external potential \( v(\mathbf{r}) \), it is also written as \( n[v](\mathbf{r}) \).

2.1.1.1 Hohenberg-Kohn Theorems

The first Hohenberg-Kohn theorem states that, in a finite, interacting \( N \)-electron system with a given particle-particle interaction there exists one-to-one correspondence between the external potential \( v(\mathbf{r}) \) and the ground state density \( n_0(\mathbf{r}) \). This statement implies that the external potential is a unique functional of the ground-state density, \( v[n_0](\mathbf{r}) \) up to an arbitrary additive constant. Since external potential of an electronic system determines all properties of system and there is unique relation to ground state density, the ground state particle density is also equally valid variable to determine the ground state properties of a system. This confirms that the many-body Hamiltonian, many body wave function and all physical observables are functionals of \( n_0(\mathbf{r}) \). So, ground state density is all one need to obtain any observable of a many-body system. Hence Hohenberg-Kohn theorem of DFT changes a complete paradigm of solving the electronic many-body problem by making the ground-state density \( n_0(\mathbf{r}) \) (a
function of three variables) as a fundamental variable instead of the wave function \( \Psi \) (a function of 3N variables). The density-functional approach can be summarized by the sequence:

\[
n(r) \Rightarrow \Psi (r_1, \ldots, r_N) \Rightarrow \nu(r).
\]  

(10)

In practice some observables can easily be expressed as explicit functional of the density whereas others not. In addition, up to this point, what is the exact ground-state density \( M_0 (r) \) of an interacting system is unclear.

Hohenberg-Kohn’s second theorem gives a recipe to get the ground state density of an interacting system. The second theorem states that the density that minimizes the total energy of an interacting system is the exact ground state density. In other words, if \( n(r) \) is the density and \( \Psi \) is the corresponding wave function then \( n(r) \) becomes the ground state density \( n_0 (r) \) only if the wave function \( \Psi \) minimizes the total energy functional \( E[n] \) with value say \( E[n_0] \), i.e., for \( n_0 (r) \) to be ground state density, the wave function \( \Psi \) corresponding to it should give minimum energy \( E[n_0] \) as

\[
\min_{\Psi \to n_0 (r)} \langle \Psi | \hat{T} + \hat{U} + \hat{V} | \Psi \rangle = E[n_0].
\]  

(11)

When this condition is satisfied, \( \Psi \) is the ground-state wave function and \( n_0 (r) \) is the exact ground state density. So, for an arbitrary density \( n(r) \) different from the ground state density

\[
\min_{\Psi \to n(r)} \langle \Psi | \hat{T} + \hat{U} + \hat{V} | \Psi \rangle = E[n]
\]  

(12)
According to the variational principle, for an arbitrary \( n(r) \) the minimum \( E[n] \) is higher than (or equal to) the ground-state energy \( E[n_0] \). However, in this formalism, the minimization of \( E[n] \) is, in general, a tough numerical problem and one needs reliable approximations for \( T[n] \) and \( U[n] \) to begin with. Kohn-Sham theorem gives an exact and more convenient method over many-body approaches and so is preferred for practical applications.

### 2.1.1.2 Kohn-Sham Equations

Kohn-Sham formulation of DFT used in this study does not follow energy minimization route, rather it brings a special kind of wave function called single particle wave-function into the picture and approximately includes all many-body effects in exchange-correlation energy \( E_{xc}[n] \) which is a part of the total energy of a system as,

\[
E[n] = T[n] + U[n] + V[n] = T_s[\varphi_i(\{n\})] + U_H[n] + E_{xc}[n], \tag{13}
\]

where \( T[n] \) is the single electron kinetic energy functional and \( U_H[n] \) is the Hartree potential energy functional. So, this method divides the K.E of a many electron system into single electron K.E. and beyond (that takes care of the difference between the interacting and non-interacting kinetic energy) and divides potential energy into Hartree potential energy and beyond (beyond takes care of interacting and non-interacting potential energies) and including all contribution beyond single independent electron into XC term (Equation (13)). In Equation (13), the K.E. of non-interacting system, \( T_s[n] \), can be obtained from the sum of K.E. of non-interacting single particle as

\[
T_s[n] = \frac{-1}{2} \sum_{i=1}^{N} \varphi_i^*(r) \nabla^2 \varphi_i(r), \tag{14}
\]
and the Hartee potential energy term $U_H[n]$ that depends on the instantaneous density at other points by nature of Coulomb interaction can be obtained as

$$U_H[n] = \int d^3r' \frac{n(r')}{|r-r'|}, \quad (15)$$

Although $E_{xc}[n]$ is unknown XC energy, it is guaranteed to be density functional from the Hohenberg-Kohn theorem.

The Kohn-Sham DFT equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + v_S(r)[n_S(r)] \right] \phi_i(r) = \epsilon_i \phi_i(r), \quad (16)$$

has form of a single-particle Schrödinger equation with the effective potential

$$v_S[n](r) = v(r) + \int d^3r' \frac{n(r')}{|r-r'|} + v_{xc}[n](r), \quad (17)$$

where the density of ground state of an interacting system $n(r)$ is approximated by the density of a non-interacting Kohn-Sham system following

$$n(r) = n_S(r) = \sum_{i=1}^N |\phi_i(r)|^2. \quad (18)$$

So, in this formalism the Kohn-Sham orbitals $\phi_i(r)$ correctly reproduce the ground-state density of interacting system but they are not required to give correct results for other observables of the interacting system.

Although Kohn-Sham equation has enormous reduction of dimensionality in comparison to Schrödinger equation or other many-body approaches, it is still a non-linear differential eigenvalue equation. If the eigenvalue problem is solved using conventional diagonalization
method for given Hamiltonian, the computational cost of each iteration step scales as $O(N^3)$, where $N$ is the number of electrons in the system. Such computational scaling is prohibitively expensive when $N$ is large, for e.g., to calculate the electronic structure for biological or nano-systems whose unit cell contains large number of atoms. In practice, instead of solving these nonlinear equations directly, one common method of finding solution is the self-consistent field (SCF) method in which the nonlinearity of the Kohn-Sham eigenvalue equations is dealt by using a nonlinear iteration scheme. At each iteration, a linear eigenvalue problem for the effective Hamiltonian corresponding the density of current iteration is solved to update the density till convergence to a self-consistent solution. The self-consistent way of solving Kohn-Sham eigenvalue problem of electronic system can be summarized as follows:

(i) Start with an initial guess for the ground-state density $n_i(r)$.

(ii) Calculate $v_s[n_i](r)$ using $n_i(r)$ and determine a new set of orbitals $\varphi_{j}^{i+1}(r)$ by solving the static Kohn-Sham equation.

(iii) Obtain new density $n_{i+1}(r)$ and quantity like energy and compare with their respective step values. If the difference is greater than some given threshold criterion, repeat step (ii) and (iii) until the criteria is satisfied.

**2.1.2 Beyond Standard DFT: the Case of Strong Electron-Electron Correlation**

For practical applications, the accuracy of Kohn-Sham theory depends on the accuracy of the XC potential for the system. Reasonably accurate potentials are available for many materials, such as metals, band semi-conductors, and insulators. However, the potentials at
hand fail to describe properties of an important class of materials that contain atoms with significantly localized charges. Examples include transition metals and rare earth atoms with localized partially filled d- and f-orbitals. The materials whose electronic configuration have valence electrons occupying 3d, 4f or 5f orbitals are the ones with flat band dispersion or equivalently localized region in the density of states plot are categorized as strongly correlated materials. These materials have a wide range of properties (magnetism, superconductivity, thermo-electricity, and magneto-resistance) relevant for technological applications. Importantly, most of these quantum phenomena have complex origin and the conventional convenient band structure methods partially or fully fail to explain the observations on those systems. So, they remain as important theoretical challenge to understand. For e.g., transition metal oxide compounds in the category are expected to be metals based on band theory due to partial occupancy of orbitals, however, they are insulators indicating that the conventional band theory based on itinerant electron concept cannot accurately predict important structural and spectroscopic features in those materials. The density functional theory based on single-particle approximation with many-body effects approximated in XC potential also cannot reproduce experimentally observed spectroscopic features on many of those materials[6; 31; 32]. This partial failure is due to the improper treatment of electrons in strongly localized orbitals that requires to incorporate strong electron-electron interaction in those orbitals.

The simplest approach to have the interaction effect is to phenomenologically introduce a parameter (U) to mimic local on-site electron-electron repulsion energy in DFT calculation, so called DFT+U method[7]. This correction leads to get correct band gap of some materials by pushing valence and conduction bands about Fermi energy. However, it cannot reproduce
some peaks in spectral function (see Figure 11 for the simplest 1 band Hubbard model), which are obtained experimentally, for e.g., in ref. [32]. The limitation of the static mean field correction necessitate to consider a dynamic electron-electron interaction.

2.1.2.1 The Hubbard Model

One of the most popular and simplest Hamiltonian that includes electron hopping kinetic term and on-site electron-electron interaction is the Hubbard Hamiltonian that in the second quantization representation can be written as:

\[
H = -\sum_{i,j,l,m,\sigma} t_{ij,\sigma} c_{i\sigma}^l c_{j\sigma}^m - \mu \sum_{i,l,\sigma} c_{i\sigma}^l c_{i\sigma}^l + \sum_{i,l,m,\sigma,\sigma'} U_{\sigma\sigma'} t_{im}^{lm} n_{i\sigma} n_{i\sigma'},
\]

where \(c, c^+\) are the electron annihilation and creation operators, \(t\) refer to the (inter- and intra-site) hopping parameters that tend to delocalize electrons and \(U_{\sigma\sigma'}^{lm}\) are the on-site Coulomb interaction energy parameters (\(i, j\) are the site, \(l, m\) are the orbitals, and \(\sigma, \sigma'\) are the spin indices) and \(\mu\) is the chemical potential that fixes the charge density in the system. In this lattice model, first terms represents the annihilation of an electron at orbital \(m\) with spin \(\sigma\) on lattice site \(j\) and creation of an electron at orbital \(l\) with the same spin \(\sigma\) on another lattice site \(i\) and the probability for the transition is given by the transfer parameter \(t_{ij,\sigma}^{lm}\). Third term represents that there can be two electrons with opposite spins \(\sigma\) and \(\sigma'\) on the same site \(i\) but need an additional energy cost of \(U\) (zero for single occupancy) that pushes every double occupancy. The graphical representation of the model is shown in Figure 1.
Figure 1 A graphical representation of Hubbard model with possible occupancy dynamics of a lattice site.

For systems with localized orbitals, t and hence band width W are small and for given U of the material, U/W becomes large that leads to limited application of perturbation theories. Exact analytical solution so far is possible only in d=1 space dimension and so various numerical approaches using diagonalization and Quantum Monte Carlo (QMC) are in use. The problem is also studied from mean field approach to field theory. In dynamical mean field approach, the problem due to presence of electron-electron interaction term is gradually removed by isolating one site or electron and include the effect of all remaining part (nuclei and other electrons) in an average way. Based on mean field approach, insight of how the interactions between electrons can give rise to insulating, magnetic, and even novel superconducting effects in a solid are explored and also predicted insulating features in metal oxides including FeO, NiO, and CoO for which band theory fails.

Note that this model takes only the onsite interaction assuming this gives the biggest interaction (neglecting the long range interaction) and approximates nuclei as fixed (no lattice vibration) which provides sites or atoms on which electrons move. A single atom is already a very complex structure in Hubbard model with many different energy levels.
Analytical solution in limiting cases

The first case when the first term of the Hamiltonian in Equation (19) vanishes i.e., no hopping or \( t=0 \) case, is equivalent to a collection of independent sites or one site problem. If there is one orbital on the site, there are only four possible occupancy on the site: empty (\( |0> \)), occupied with a single electron (spin up, \( |\sigma> \) or down, \( |\bar{\sigma}> \)) and with two electrons (\( |\sigma \bar{\sigma}> \)) with energy value 0, \(-\mu\), \(-2\mu\), \( U - 2\mu \), respectively. Since these four states are the only allowed energy states, the partition function becomes

\[
Z = \sum_{\alpha} <\alpha|e^{-\beta H}|\alpha> = 1 + 2e^{\beta\mu} + e^{-\beta(U - 2\mu)},
\]

and the energy is

\[
E = <H> = \sum_{\alpha} \frac{<\alpha|He^{-\beta H}|\alpha>}{Z} = \frac{(U - 2\mu)e^{-\beta(U - 2\mu)} - 2\mu e^{\beta\mu}}{1 + 2e^{\beta\mu} + e^{-\beta(U - 2\mu)}}.
\]  

The second limiting case when the third term of the Hamiltonian in Equation (19) vanishes corresponds to no interaction case in which the modified Hamiltonian becomes

\[
H = -\sum_{i,j,l,m,\sigma} t_{ij,\sigma}^{lm} c_{i\sigma}^{+} c_{j\sigma}^{l} - \mu \sum_{i,l,\sigma} c_{i\sigma}^{l} c_{i\sigma}^{l}.
\]

The presence of site indices \( i \) and \( j \) in the Hamiltonian implies mixing of all the different sites and so if an electron off is started from a given site, it can move to adjacent sites due to K.E. For very small system size of one or two sites, the Hamiltonian quadratic in the fermion creation and annihilation operators can be solved by diagonalizing the matrix \( t \). For larger system or small system with each site containing atom with number of energy levels, it is computationally intensive to diagonalize large matrix and so real space representation is not a
convenient framework to solve the problem. Importantly, in momentum representation the momentum k can’t be any real number on a finite lattice (basic feature of quantum system) rather has discretized values, for e.g., in 1D lattice allowed values of momentum k are 

\[ k_n = \frac{n\pi}{L} \] which are spaced \( \frac{\pi}{L} \), and so it is convenient to get solution. Defining momentum dependent operators as a linear combination of space dependent operators as

\[ c_{k\sigma}^+ = \sum_{j \sigma} \epsilon_{ij} c_{ij \sigma}^+ \frac{1}{\sqrt{N}}, \] (23)

the one dimensional Hubbard model in momentum space for \( U=0 \) becomes

\[ H = \sum_{k,\sigma} (\epsilon_k - \mu) c_{k\sigma}^+ c_{k\sigma}, \] (24)

with \( \epsilon_k = -2t \cos(ka) \), where a is the lattice constant.

This shows that the Hamiltonian is only k dependent (different from dependence on both site indices i and j in space representation) that decouples different momenta allowing to treat different modes independently. Since the Hamiltonian is a sum of independent pieces, the total partition functions is the product of the associated individual partition functions as

\[ Z = \prod_k (1 + e^{-\beta(\epsilon_k - \mu)})^{-1}. \] (25)

So, for discussed two limiting cases, single site or non-interaction, the Hubbard model can be solved exactly.

In real space representation, the Hubbard Hamiltonian has quartic electronic correlation interaction term \( c_{\sigma}^+ c_{\sigma} c_{\sigma}^+ c_{\sigma} \) even for one-orbital case. Presence of this term makes calculation complicated since one has to diagonalize large dimensional matrix. Due to conveniences of
Green function (the expectation value of a product of operators evaluated at different times) based approach to isolate and treat only the correlated part of the problem by integrating out the non-interacting part, it is generally followed approach to find the solution of Hubbard model. In addition, Green function (GF) contains the most important information of system such as the ground-state energy, linear response to external perturbation, energy and lifetime of excited states, and other thermodynamic variables. For an arbitrary system, diagonalizing the Hamiltonian that depends on orbital and spin degrees of freedom on Green function technique also becomes computationally intensive and so Hubbard model will be of no interest to study real material systems. In this context, Dynamical Mean field theory (DMFT) approach provide a way in such a complicated situation and is a milestone to hold continue interest to use Hubbard model to predict material properties.

2.1.2.2 The DMFT Solution
Metzner and Vollhardt proved that in the limit of $d \to \infty$ or $z \to \infty$ (i.e., large spatial dimension (d) or coordination (z)) electron self-energy does not depend on momentum but only on frequency[11]. In real space terminology, momentum independence means all non-local site terms $i \neq j$ of self-energy that give momentum dependence vanish and only local matrix element in $\Sigma$ are non-zero. The consequence of the theory is that the solution of equation of motion of electron on lattice obtained with neglect of spatial or inter-site correlation and taking only dynamical on-site fluctuation is exact solution. This allows one to map an interacting lattice into a lattice with non-interacting single sites and bath function (basic idea is shown graphically in Figure 2) that includes space independent and frequency dependent (non-local in time) interactions.
The framework of lattice with each site as isolated impurity (quantum impurity problem and is solvable) can be used to find the solution for the lattice with interacting electrons once isolation of sites is self-consistently confirmed from frequency dependent bath function. By solving the impurity model, the state of the single site is obtained which holds for all sites of translationally invariant lattice and thus defines the state of the lattice. Due to $\mathbf{k}$ independence (same solution for all sites, basic feature of mean field approach) and frequency dependence (dynamical) of electronic self-energy, the method is called dynamical mean field theory.

Among various kind of Green functions, one that depends on real time and can give spectral function upon Fourier transform is the most relevant to apply to solve the Hubbard model taking non-local time effects. However, DMFT approach formulated using real frequency dependence require large number of frequency points (and hence require long computational time) to converge the self-energy. In addition, in quantum mechanical approach, calculation of the time dependence of any operator requires thermal average which incorporates $e^{-\frac{H}{T}}$ term in calculation.
Time dependence is then calculated using

\[ e^{-iHt} e^{-\frac{H}{\tau}} e^{iHt}, \]  

which contains both real and imaginary exponent. To avoid the awkward practice to use both real and imaginary exponents at the same time, \( it = \tau \) (this corresponds to \( t \) being imaginary) is kept in the time dependence of operators that leads the time dependence of operators as

\[ A(\tau) = e^{-H\tau} A e^{H\tau}. \]  

In this way, if one uses only imaginary times, only real exponents occur that simplifies calculations. Unlike real time arguments, imaginary time have no direct physical meaning. Imaginary time is used for the theorists’ convenience because Green functions, the mathematical machinery used to approach the many-particle problem, have very useful mathematical properties if regarded as a function of a complex time and frequency, instead of just real times and frequencies. The imaginary time formulation is usually not used for time-dependent Hamiltonian: it would be awkward to specify how a certain time dependence translates into imaginary time. So, the imaginary-time single-particle time-ordered Green functions defined as

\[ G(k, \tau; k', \tau') = -< T_\tau \left( c_k(\tau) c^+_k(\tau') \right) >, \]  

where \( \tau \) and \( \tau' \) satisfy \( 0 < \tau, \tau' < \beta \), for \( \beta = \frac{1}{\tau} \).
The symbol $T_\tau$ is time ordering operator which puts the operators in chronological order, with the earlier time furthest to the left as

$$T_\tau \left( c_k(\tau) c_{k'}^+(\tau') \right) = \begin{cases} c_k(\tau) c_{k'}^+(\tau') & \text{if } \tau > \tau' \\ -c_{k'}^+(\tau') c_k(\tau) & \text{if } \tau' > \tau \end{cases}, \quad (29)$$

where $c_k(\tau), c_{k'}^+(\tau')$ are the operators in Heisenberg representation. If $\tau' > \tau$, the Green function is the probability amplitude to find an electron with momentum $k'$ if the electron was added to the system with momentum $k$ at time $\tau$ and if $\tau' < \tau$ the Green function describes propagation of a hole created at time $\tau$. Using definition of expectation value,

$$G(k, \tau; k', \tau') = \frac{\text{Tr}(-e^{-\beta H} T_\tau(c_k(\tau)c_{k'}^+(\tau')))}{\text{Tr}(e^{-\beta H})}, \quad (30)$$

$$G(k, \tau; k', \tau') = \frac{\text{Tr}[-e^{-\beta \int_0^\tau dr \left[u_{n_\sigma n_\sigma} + \Sigma_{i,l,\sigma} \sigma_i c_i^+ \sigma_d^+ c_d \right] \left(c_k(\tau)c_{k'}^+(\tau')\right)]}{Z}. \quad (31)$$

In the simplest example of non-interacting case, the Hamiltonian becomes

$$H = \sum_k \varepsilon_k c_k^+ c_k. \quad (32)$$

Using the definition relation

$$c_k(\tau) = e^{H\tau} c_k(0) e^{-H\tau}, \quad (33)$$

in interaction representation in the definition of $G(k; k', \tau)$ and using Fourier transform, one gets the Green function in the momentum representation as

$$G(k; \tau) = \frac{1}{i\omega_n - \varepsilon_k}. \quad (34)$$
Using the same procedure for interacting Hamiltonian which is Fourier transformed with respect to \((\tau - \tau')\), one gets Green function as

\[
G_{l\sigma}(k, i\omega_n) = \int \frac{A(\epsilon)d\epsilon}{i\omega_n + \mu - \epsilon - \Sigma_{l\sigma}(k, i\omega_n)},
\]

(35)

where \(l\) and \(\sigma\) represent the orbital and spin indices respectively, \(A(\epsilon)\) is the density of states, \(\omega_n = (2n + 1)\pi T, n = 0, \pm 1, \ldots\) are Matsubara frequencies for fermions, \(\Sigma_{l\sigma}(k, i\omega_n)\) is the electron self-energy that describes the effects of electron-electron interaction.

In DMFT approximation,

\[
\Sigma_{l\sigma}(k, i\omega_n) = \Sigma_{l\sigma}(i\omega_n),
\]

(36)

that leads Equation (35) as

\[
G_{l\sigma}(i\omega_n) = \int \frac{A(\epsilon)d\epsilon}{i\omega_n + \mu - \epsilon - \Sigma_{l\sigma}(i\omega_n)}
\]

(37)

Once one know the self-energy \(\Sigma_{l\sigma}(i\omega_n)\) and the local Green function \(G_{l\sigma}(i\omega_n)\), the effective bath Green function \(G_{MF\sigma}(i\omega_n)\) can be obtained from Dyson equation

\[
G_{l\sigma}^{-1}(i\omega_n) = G_{MF\sigma}^{-1}(i\omega_n) - \Sigma_{l\sigma}(i\omega_n)
\]

(38)
The bath Green function \( G_{MFl\sigma}(i\omega_n) \) is then used in the effective impurity model described by effective action

\[
S_{\text{eff}} = -\sum_\sigma \int_0^\beta d\tau_3 \int_0^\beta d\tau_4 \psi^*_\sigma(\tau_3) G^{-1}_{MFl\sigma}(\tau_3 - \tau_4) \psi_{\sigma}(\tau_4) + \\
\int_0^\beta d\tau_5 U_{\sigma\sigma} \psi^*_\sigma(\tau_5) \psi_{\sigma}(\tau_5) \psi^*_{\bar{\sigma}}(\tau_5) \psi_{\bar{\sigma}}(\tau_5),
\]

(39)

and the corresponding impurity Green function is given by

\[
G_{l\sigma}(\tau_i, \tau_j) = \int \mathcal{D}[\psi] \mathcal{D}[\bar{\psi}] \psi(\tau_i) \psi(\tau_j) \times \exp\left[ -\int_0^\beta d\tau_3 \int_0^\beta d\tau_4 \psi^*(\tau_3) G^{-1}_{MFl\sigma}(\tau_3, \tau_4) \psi(\tau_4) + \\
U_{l\sigma} \int_0^\beta d\tau_5 n_{\sigma}(\tau_5) n_{\bar{\sigma}}(\tau_5) \right].
\]

(40)

The impurity Green function obtained by solving the impurity problem (Equation (40)) is then used to calculate the impurity self-energy using Equation (38) which is then used to update the local lattice GF in Equation (37). This system of equations (37), (38), and (40) is solved self-consistently till the self-energy from impurity problem becomes equal to the self-energy of local lattice problem. When they are equal, the bath GF in effective single impurity model can be interpreted as that of local lattice problem that takes into account all fluctuations on all other lattice sites. So, as result of mapping, one get the single site Green function of interacting lattice with Green function of some effective single impurity model having the same on site Coulomb interaction (self-energy).

In this work, the mapped impurity problem Equation (40) is solved by using iterative impurity problem (IPT) solver (see Appendix A for detail) and Hirsch-Fye Quantum Monte Carlo (HF-QMC) solver (see Appendix B for detail).
2.1.2.3 Real Systems: The DFT+DMFT Solution

At the beginning, free electron spectrum is obtained with DFT and is used to solve correlated DMFT problem. Then following steps of iterative solution of the DMFT equations follow to find solution in the DFT+DMFT approach:

(i) Initialize lattice self-energy.

(ii) Calculate the local Green’s function with adjustment of the chemical potential such that the total number of electrons in the system remains conserved.

(iii) Calculate the dynamical mean-field function using the Dyson equation.

(iv) Use the dynamical mean-field function to solve the quantum impurity problem to find impurity Green function.

(v) Find the self-energy for the impurity problem from the Dyson equation by using the impurity Green function and the dynamical mean-field function.

(vi) Substitute the local lattice self-energy by the self-energy of impurity problem.

(vii) Continue iteration until the self-energy is converged.

Although DMFT approach enables to solve Hubbard model, it has limitations. It assumes only strong local spatial correlations of electron-electron interaction which requires it combine with method that considers non-local effects. It does not have a consistent way to calculate the parameters, U and J, needed in the formulation. At large value of $\omega$, since both $G_{MF}$ and local Green function in Equation (38) goes to zero, calculation of self-energy as difference of their
inversion requires very high precision implementation which offers numerical complexity. The low electronic temperature calculation results on small value of Matsubara frequency and so to capture energy spread of a system, one needs large number of grid points which slows down calculation significantly. After simplification of many-body problem of an infinite lattice to a local impurity problem, solving the impurity model is non-trivial and finding the solution is the most important part of the solution. Since no analytical solution exists, one has to retreat to numerical methods. Development of continuous-time quantum monte carlo (CTQMC)[33] provides exact solution but it suffers from fermion sign problem. After having solution, one needs to encounter ill-posed analytical continuation to transform from Matsubara axis to real-frequency axis.

2.1.2.3.1 Analytical Continuation

DMFT formalism in the implementation used in this study is based on imaginary time (Matsubara) Green function (GF). GF obtained on Matsubara or imaginary frequencies requires analytical continuation to real frequency, ωₙ → ω + iδ, δ being a small real number, to make them useful to study of spectral, transport or optical properties. To analytically continue the complex frequency Green’s function from the Matsubara points to the real frequency axis, N-point Pade approximation method is used (see details in Appendix C).

2.1.2.3.2 Calculation of electronic structures

The spectral function \( A^l_\sigma(\omega) \) for the orbital index l and spin-index \( \sigma \) can be calculated using

\[
A^l_\sigma(\omega) = -\frac{1}{\pi} \text{Im} G^l_\sigma(\omega),
\]

(41)
The charge susceptibility $\chi(q; \omega)$ of interacting system is given by

$$\chi(r, t; r', t') = -\langle \hat{T}n(r, t)n(r', t') \rangle,$$  \hspace{1cm} (42)

where $\hat{T}$ is the time-ordering operator and $n(r, t)$ is the charge density operator.

For multi-orbital case, $\chi(r, t; r', t')$, called also the two-particle correlation function, is a sum of the corresponding orbital spin susceptibilities, $\chi_{\sigma\sigma'}^{ll'}(r, t; r', t')$

$$\chi(r, t; r', t') = \sum l, m, \sigma, \sigma' \chi_{\sigma\sigma'}^{ll'}(r, t; r', t') \equiv -\sum l, m, \sigma, \sigma' \langle \hat{T}n_{\sigma}^{l}(r, t)n_{\sigma'}^{l'}(r', t') \rangle$$ \hspace{1cm} (43)

In general, these functions can be obtained by using the Bethe–Salpeter equation (BSE) formalism [49] as

$$\chi_{ijkl}^{abcd}(\tau_i, \tau_j, \tau_k, 0) = -\langle \hat{T}c_{i}^{a+}(\tau_i)c_{j}^{b}(\tau_j)c_{k}^{c+}(\tau_k)c_{l}^{d}(0) \rangle$$

$$+\langle \hat{T}c_{i}^{a+}(\tau_i)c_{j}^{b}(\tau_j)\rangle \langle \hat{T}c_{k}^{c+}(\tau_k)c_{l}^{d}(0) \rangle,$$ \hspace{1cm} (44)

where, $a, b, c, d$ are the spin-orbital indices and $i, j, k, l$ and $\tau_i, \tau_j, \tau_k$ are the corresponding electron site and time coordinates (one of the time arguments is made equal to zero due to time translation invariance). The frequency transform of the susceptibilities in Equation (44) becomes

$$\chi_{ijkl}^{abcd}(\omega_m, \omega_i, \omega_n) =$$

$$T^{2}\int_{0}^{\beta} d\tau_i \int_{0}^{\beta} d\tau_j \int_{0}^{\beta} d\tau_k e^{-i\tau_i \omega_m} e^{i\tau_j (\omega_m + \omega_n)} e^{-i\tau_k (\omega_i + \omega_n)} \chi_{ijkl}^{abcd}(\tau_i, \tau_j, \tau_k).$$ \hspace{1cm} (45)
In the single-site (impurity) approximation used in DMFT, one approximates the susceptibilities Equation (63) by local functions $\chi_{iili}^{abcd}(\omega_m, \omega_l, \omega_n) \equiv \chi^{abcd}(\omega_m, \omega_l, \omega_n)$.

In terms of the free-electron generalized susceptibility $\chi^{abcd(0)}(\omega_m, \omega_n)$

$$\chi^{abcd}(\omega_m, \omega_l, \omega_n) = 2T \sum_m \chi^{0}(\omega_m, \omega_n; q). \tag{46}$$

where

$$\chi^{0}(\omega_m, \omega_n; q) = \frac{1}{N} \sum_k G(\omega_m + \omega_n, k + q)G(\omega_m, k). \tag{47}$$

In local in space approximation, the Green function

$$G(\omega_m, k) = \left[\omega - \epsilon_k - \Sigma(\omega, k)\right]^{-1}, \tag{48}$$

becomes

$$G(\omega_m) = \left[\omega - \epsilon_k - \Sigma(\omega)\right]^{-1}. \tag{49}$$

Combined susceptibility for a system based on multi-orbital spin-resolved calculation can be obtained using

$$\chi(\omega) = -\sum_{\sigma,l,m} \int d\omega' G_{\sigma}^{lm}(\omega + \omega')G_{\sigma}^{ml}(\omega'). \tag{50}$$
2.2 Electronic Properties Calculation of System out-of-Equilibrium

Materials that are subjected to external perturbation reveal fascinating phenomena whose origin lies on the subtle ways electrons interact with each other. The direct approach to treat these problems is to solve time-dependent Schrödinger equation for the many-electron wave-function \( \Psi(r_1, r_2, \ldots, r_N, t) \)

\[
i \frac{\partial}{\partial t} \Psi(r_1, r_2, \ldots, r_N, t) = H(t)\Psi(r_1, r_2, \ldots, r_N, t),
\]

where \( H(t) = T + V(t) + W, \)

\[
T = \sum_{j=1}^{N} \frac{-1}{2} \nabla_j^2,
\]

\[
V(r, t) = \sum_{j=1}^{N} v(r_j, t),
\]

\[
W = \frac{1}{2} \sum_{j,k}^{N} w(|r_j - r_k|),
\]

are the kinetic energy operator, the time dependent potential energy operator which includes the potential electrons experience due to the nuclear attraction or any externally applied field to the system, and the particle-particle interaction, respectively. For electronic system that interact following Coulomb interaction,

\[
w(r_j, r_k) = \frac{1}{|r_j - r_k|}.
\]
Owing to their large mass, one can assume nuclei fixed in their position or moving along some classical path that keeps electronic system under time-dependent external potential

\[
\nu_{\text{ext}}(\mathbf{r}, t) = -\sum_{p=1}^{N_n} \frac{Z_p}{|\mathbf{r} - \mathbf{R}_p(t)|} \tag{57}
\]

where \(Z_p, R_p\), and \(N_n\) represent the atomic number, position of a nucleus, and the total number of nuclei in the system, respectively.

For system excited by laser field, the external potential term due to electric field (assuming that magnetic field is negligibly small in the dipole approximation where \(\lambda \gg a\)) is given by

\[
\nu_{\text{ext}}(\mathbf{r}, t) = d \cdot E(\mathbf{r}, t), \tag{58}
\]

where \(d\) represents the electric dipole moment of material and \(E(\mathbf{r}, t)\) is an external electric field.

To find the dynamical properties of a system in electronic level, Equation (51) is to propagate over some time interval \([t_0, t_1]\) for a given initial state \(\Psi_0(\mathbf{r}_1', \mathbf{r}_2', \ldots, \mathbf{r}_N', t_0)\). Importantly, the complete information about the many-body system at any given time \(t\) is contained in its wave function \(\Psi_t(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t)\) because the many-body Hamiltonian \(H(t)\) depends only on time \(t\); there is no memory of earlier times. As an implication, there is no need to know \(\Psi_{t'}(\mathbf{r}_1', \mathbf{r}_2', \ldots, \mathbf{r}_N', t')\) at earlier times \(t' < t\) to calculate the expectation value of any observable at time \(t\).
In Schrödinger method, each external potential $v(r, t)$ produces a time-dependent wave function $\Psi(r_1, r_2, \ldots, r_N, t)$ for a given initial state $\Psi_0(r_1', r_2', \ldots, r_N', t_0)$ and the sequence of steps in this method can be summarized as

$$ V(r, t) \xrightarrow{SE} \Psi(r_1, r_2, \ldots, r_N, t) \xrightarrow{\langle \psi| - |\psi\rangle} \text{Observables}, \quad (59) $$

i.e., specify a system by choosing $V(r, t)$, plug it into Schrödinger equation, and solve it to get wave function $\Psi$ that is used to calculate expectation value of operator of a quantity of interest.

However, due to dependence of the wave function of $N$ electron system on $3N+1$ coordinates, the wave function based approach is applicable only to systems containing few electrons.

### 2.2.1 Time-Dependent Density-Functional Theory

Time-dependent density-functional theory (TDDFT) is a promising alternative to computationally intensive many-body approaches to calculate non-equilibrium response of an electronic system. DFT formalism on time-dependent case is based on the property of wave function that Runge and Gross [8] proved which states that for a given initial ($t = 0$) state $\Psi_0$ of an interacting many-electron system with electron-electron interaction $w(r, r')$, the external time-dependent potential acting on the system is uniquely determined by the time evolution of the one-electron time-dependent density $n(r, t)$ for $t > 0$. Since the non-relativistic Coulomb systems differ only by their potential $v(r, t)$ and there is one-to-one correspondence to the time-dependent density $n(r, t)$ implies that $n(r, t)$ is equally valid as a variable which completely determines the dynamics of the system. As an immediate consequence, all physical observables including potential, many-body Hamiltonian, and thus the many-body wave
function become functional of density $n(r, t)$. In addition, Van Leeuwen [34] proved that exactly the same density $n(r, t)$ can be reproduced in a many-body system with different two-body interaction (which could be zero), starting from a different initial state $\Psi_0'$ and under the influence of a different external potential $v'(r, t)$. In his formalism, if the second system is chosen to be non-interacting, $v'(r, t) = 0$ and assume that there exists a non-interacting initial state $\Psi_0' = \Phi_0$ with the correct initial density and time derivative of the density, then Van Leeuwen theorem tells us that there is a unique potential $v_s(r, t)$ in a non-interacting system which produces $n(r, t)$ at all times $t > t_0$. As a consequence, one can replace an interacting system with an auxiliary non-interacting system (Kohn-Sham) that reproduces the same density. So, Van Leeuwen theorem guarantees that the time-dependent density $n(r, t)$ of an interacting system that evolves from an initial state $\Psi_0$ under the influence of a potential $v(r, t)$ can also be reproduced by a non-interacting system. As spirit of DFT, one can use effective potential of non-interacting system $v_s[n, \Psi_0, \Phi_0](r, t)$, a functional of the time-dependent density, the initial many-body state, and the initial state $\Phi_0$ of the non-interacting system to establish a time-dependent Kohn-Sham (TDFS) equation from which dynamics of various one-particle properties of the interacting system can obtained.

If a system is initially in ground state (general situation in practice), $\Psi_0$ and $\Phi_0$ are both functionals of the ground-state density $n_0(r)$ and hence the effective potential becomes only a density functional, $v_s[n](r, t)$. 

35
However, immediately after the initial time \( t_0 \), the time-dependent potential \( v_1(r, t) \) contribute in effective potential

\[
v_s[n](r, t) = v(r, t) + v_H[n](r, t) + v_{xc}[n](r, t),
\]

and the system starts to evolve in time under its influence. The first term in R.H.S. of Equation (88), \( v(r, t) = v_{ion}(r, t) + v_{ext}(r, t) \), represents the interaction with the nuclei and external fields, and the second term \( v_H(r, t) = \int d^3r' \frac{n(r', t)}{|r-r'|} \) represents the classical electron-electron repulsion and is called the time-dependent Hartree potential which depends only on the density at the same time \( t \) and the third term \( v_{xc}[n](r, t) \) is the XC potential and includes in principle all non-trivial multi-electron effects.

With the effective potential, the dynamics of many-body system can be explained using the single-particle Kohn-Sham orbitals \( \varphi_j(r, t) \) that satisfy the time-dependent Kohn-Sham equation

\[
\left[ -\frac{\nabla^2}{2} + v_s[n](r, t) \right] \varphi_j(r, t) = i \frac{\partial}{\partial t} \varphi_j(r, t),
\]

(61)

where the auxiliary wave function \( \varphi_j(r, t) \) reproduce the time-dependent density

\[
n(r, t) = \sum_{j=1}^{N} \left| \varphi_j(r, t) \right|^2.
\]

(62)

With the initial condition \( \varphi_j(r, t_0) = \varphi_j(r) \), the set of Equations (60), (61), and (62) form a self-consistent set of equations to solve. The complexity comes through the XC potential term whose functional form is unknown. Since the effective potential \( v_s[n](r, t) \) at point \( r \) and time \( t \) on L.H.S. of Equation (60) depends on the densities over all
space and at all times $t' < t$ and the Hartree term on R.H.S. depends only on the instantaneous density, the XC term should depend on densities at previous times or density history and initial state (both interacting or non-interacting mapping has to depend on the initial state). So, TDKS single-particle Hamiltonian has a memory dependence through the $v_{xc}[n](\mathbf{r}, t)$ term. Unfortunately, if little is known about the XC potential in static DFT, even less is known about it in the time-dependent case. A reasonable starting point in the quest for approximation to the time-dependent xc potential is to simply take the approximated xc potential functional from static DFT in the TDKS equation, but plugging the time-dependent density $n(\mathbf{r}, t)$ rather than the ground-state density $n_0(\mathbf{r})$. This defines the adiabatic approximation, \begin{equation}
abla^A_{xc}(\mathbf{r}, t) = v^0_{xc}[n_0](\mathbf{r})|n_0(\mathbf{r}) = n(\mathbf{r}, t), \tag{63}\end{equation}
$v^A_{xc}(\mathbf{r}, t)$ becomes exact in the limit where the system remains in its instantaneous eigenstate i.e., adiabatic process which occurs if a perturbation acting on it is slow. In such a situation, the functional dependence of the XC potential at time $t$ only on the density at the very same time i.e., without memory consideration, is valid. Most of the existing applications of XC on TDDFT are using the static functional form of XC potential formulated based on local or gradient density dependence with space and so are adiabatic in time dependence. The simplest of the adiabatic approximation is the adiabatic local density approximation[35]. Despite the crudeness of these approximations, optical spectra calculated are in some cases almost as accurate as those obtained from more computationally demanding many-body approaches. However, truly adiabatic time evolution of quantum systems occurs only in exceptional cases and most situations of practical interest are non-adiabatic at least to some degree. There are
attempts to develop functional for time dependent xc potential beyond adiabatic approximation [36-43] to apply in TDDFT Calculations with approximations beyond the adiabatic approximation including memory effects is an important goal but the progress is very slow in developing those potential that can be applied to real systems[43].

2.2.1.1 The Case of Linear Response: Exchange-Correlation (XC) Kernel

When the perturbing field is weak, which is the case in normal spectroscopic experiments, perturbation theory applies. Instead of requiring knowledge of $v_{xc}$ for densities that are changing significantly with time, one needs to know only this potential for densities close to that of the initial state and express time dependent density as $n(r,t) = n_{GS}(r) + \delta n(r,t)$, then

$$v_{xc}[n_{GS} + \delta n](r,t) = v_{xc}[n_{GS}](r) + \int dt' \int d^3r' f_{xc}[n_{GS}](r,r',t-t')\delta n(r',t'),$$

(64)

where $f_{xc}$ is called the exchange-correlation kernel, evaluated on the ground-state density:

$$f_{xc}[n_{GS}](r,r',t-t') = \left. \frac{\delta v_{xc}(r,t)}{\delta n(r',t')} \right|_{n = n_{GS}}.$$

(65)

The exchange-correlation kernel is much more manageable than the full time-dependent exchange-correlation potential because it is a functional of the ground-state density alone in its exact form. Still, to replace XC potential by XC kernel, one needs non-local space dependent and memory dependent XC kernel and updated density at every time.
After replacing the XC potential by XC kernel (linear approximation), TDKS equation becomes

\[
\frac{-1}{2} \nabla^2 + v_{\text{ion}}(\mathbf{r}, t) + v_H[n](\mathbf{r}, t) + v_{\text{XC}}[n](\mathbf{r}, t = t_0) + \int_{t'>t_0} f_{\text{XC}}(t-t') \delta n(\mathbf{r}, t') dt' + v_{\text{ext}}(\mathbf{r}, t) \right] \psi_k(\mathbf{r}, t) = i \frac{\partial}{\partial t} \psi_k(\mathbf{r}, t), \quad (66)
\]

(here \(t_0\) refers to the origin for time and \(v_{\text{XC}}[n](\mathbf{r}, t = t_0)\) is a part of static \(H_{KS}(\mathbf{r})\). Although TDKS equation has enormously reduce the dimensionality required in Schrödinger equation, it is still a self-consistent (density dependence of effective potential), non-linear partial differential equation. Like the time-dependent Schrödinger equation, it is an initial-value problem that propagates initial Kohn-Sham wave function forward in time. Splitting XC into static and dynamic contribution, external potential for the electronic system into pulse and ionic part assuming the ionic potential is constant in time, \(v_{\text{ion}}(\mathbf{r}, t) = v_{\text{ion}}(\mathbf{r})\) (this approximation avoids lattice vibration or phonon effect which is a reasonable approximation in the ultrafast electronic dynamics study at femtosecond time scale) and taking

\[
\frac{-1}{2} \nabla^2 + v_{\text{ion}}(\mathbf{r}) + v_H[n](\mathbf{r}, t = 0) + v_{\text{XC}}[n](\mathbf{r}, t = 0) = H_{KS}(\mathbf{r}), \quad (67)
\]

and rest as \(H_{\text{int}}\), TDKS Equation (66) becomes

\[
[H_{KS}(\mathbf{r}) + H_{\text{int}}] \psi_k(\mathbf{r}, t) = i \frac{\partial}{\partial t} \psi_k(\mathbf{r}, t). \quad (68)
\]
In conventional TDDFT approach, the initial Kohn-Sham wave function

\[ \Psi_k(r, 0) = \prod_{j=1}^{N} \varphi_{kj}^{mj}(r), \tag{69} \]

where \( H_{KS}(r) \varphi_{kj}^{mj}(r) = \varepsilon_{kj}^{mj} \varphi_{kj}^{mj}(r). \) \( \tag{70} \)

where \( \varepsilon_{kj}^{mj}, \varphi_{kj}^{mj}(r), k, \) and \( m \) represent the static Kohn-Sham energy levels, eigen-function, momentum, and bands, respectively and \( j=1,2,...,N \) represents electrons number. In this approach, only the \( N \) initially occupied orbitals are propagated. There is always question about how the approach can show all possible excitation processes. This issue is overcome in density matrix TDDFT formalism.

In density matrix TDDFT approach, Kohn-Sham wave function \( \Psi_k(r, t) \) is expressed as linear combination of static Kohn-Sham eigenstates \( \varphi_{kj}^{mj}(r) \),

\[ \Psi_k(r, t) = \sum_m c_k^m(t) \varphi_{kj}^{mj}(r). \tag{71} \]

Substituting Equation (71) in Equation (68), multiplying by \( \varphi_q^{l\ast}(r) \) and integrating over \( dr \) one get

\[ \varepsilon_q c_q^l(t) + \sum_n c_k^n(t) H_{qk}^{ln}(t) = i \frac{\varphi}{\alpha} c_q^l(t). \tag{72} \]
Defining the one electron density matrix kernel as
\[ \rho_{kl}^{m}(t) = C_{k}^{m}(t)C_{q}^{l*}(t), \]  
(73)
whose differentiation w.r.t. time and using Equation (157), one gets
\[ i \frac{\partial \rho_{kl}^{m}(t)}{\partial t} = (\epsilon_{k}^{m} - \epsilon_{q}^{l})\rho_{kl}^{m}(t) + \sum_{n}[H_{kq}^{mn}(t)\rho_{qq}^{nl}(t) - \rho_{kk}^{mn}(t)H_{kq}^{nl}(t)]. \]  
(74)
Substituting change in density in terms of density matrix, time-dependent Liouville equation becomes (for complete derivation, see Appendix C)
\[ i \frac{\partial \rho_{kl}^{m}(t)}{\partial t} = (\epsilon_{k}^{m} - \epsilon_{q}^{l})\rho_{kl}^{m}(t) + \sum_{n}[H_{kq}^{mn}(t)\rho_{qq}^{nl}(t) - \rho_{kk}^{mn}(t)H_{kq}^{nl}(t)] - \rho_{kk}^{mn}(t)F_{kq}^{ned}(t, t')[\rho_{k}^{ed}(t') - \rho_{k}^{ed}(0)] + \sum_{n}d_{kq}^{mn}(t)\rho_{qq}^{nl}(t) - \sum_{n}d_{kq}^{nl}(t)\rho_{qq}^{nl}(t), \]  
(75)
where
\[ d_{kq}^{mn} = \int dr\varphi_{q}^{*}(r)r\varphi_{k}^{m}(r).E(t), \]  
(76)
\[ F_{kq}^{ned}(t, t') = \int d\mathbf{r} d\mathbf{r}'\varphi_{q}^{*}(\mathbf{r})\varphi_{k}^{e}(\mathbf{r})f_{XC}(\mathbf{r}, t, t', \mathbf{r}', \mathbf{r}'). \]  
2.2.1.2 Calculation of XC Kernel
To derive an expression for the XC kernel, \( f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) \), let an unperturbed inhomogeneous electronic system of density \( n_{0}(\mathbf{r}) \) at the static potential \( \nu_{0}(\mathbf{r}) \) be perturbed by small perturbing potential \( \nu_{1}(\mathbf{r}, t) \) that creates density \( n_{1}(\mathbf{r}, t) \). The associated Fourier components \( \nu_{1}(\mathbf{r}, \omega) \) and \( n_{1}(\mathbf{r}, \omega) \) are then related through density-density response function \( \chi(\mathbf{r}, \mathbf{r}'; \omega) \) by the equation
\[ n_{1}(\mathbf{r}, \omega) = \int d^{3}\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}'; \omega)\nu_{1}(\mathbf{r}', \omega). \]  
(77)
In the spirit of density-functional theory, the density \( n_0(r) + n_1(r,t) \) is non-interacting \( v \)-representable i.e., can be reproduced by a system of non-interacting electrons in an appropriate single-particle potential \( v_0^{\text{eff}}(r) + v_1^{\text{eff}}(r,t) \), then

\[
n_1(r, \omega) = \int d^3r' \chi_{\text{KS}}(r,r'; \omega) v_1^{\text{eff}}(r', \omega),
\]

(78)

where \( \chi_{\text{KS}}(r,r'; \omega) \) is the density-density response function of the non-interacting Kohn-Sham system corresponding to \( v_1^{\text{eff}} \). It is given by

\[
\chi_{\text{KS}}(r,r'; \omega) = \sum_{i,j} \frac{(f_i-f_j)\varphi_i^*(r)\varphi_j(r)\varphi_j^*(r')\varphi_i(r')}{\omega-(\varepsilon_i-\varepsilon_j)+i\delta},
\]

(79)

where \( \varphi_i(r) \) and \( \varepsilon_i \) are the Kohn-Sham eigen-functions and eigenvalues and the \( f_i = 0 \) or 1 are the occupation numbers.

In Kohn-Sham formulation \( v_1^{\text{eff}}(r,t) \) contains the Hartree, external, and XC part as

\[
v_1^{\text{eff}}(r, \omega) = v_1(r, \omega) + \int \frac{n_1(r', \omega)}{|r-r'|} d^3r' + v_{1,\text{xc}}(r, \omega),
\]

(80)

Note that without XC part, it yields the time-dependent Hartree response. In the spirit of density-functional theory, expressing \( v_{1,\text{xc}}(r, \omega) \) as a linear functional of \( n_1(r, \omega) \) as

\[
v_{1,\text{xc}}(r, \omega) = \int d^3r' f_{\text{xc}}(r,r'; \omega)n_1(r', \omega),
\]

(81)

where \( f_{\text{xc}}(r,r'; \omega) \) depends on the unperturbed ground state density \( n_0(r) \).
\[ v_1^{\text{eff}}(\mathbf{r}, \omega) = v_1(\mathbf{r}, \omega) + \int \frac{n_1(\mathbf{r'}, \omega)}{|\mathbf{r} - \mathbf{r'}|} \, d^3\mathbf{r'} + \int d^3\mathbf{r'} \, f_{xc}(\mathbf{r}, \mathbf{r'}; \omega)n_1(\mathbf{r'}, \omega), \]  
\[ \int d^3\mathbf{r'} \chi_{KS}^{-1}(\mathbf{r}, \mathbf{r'}; \omega)n_1(\mathbf{r'}, \omega) = \int d^3\mathbf{r'} \chi^{-1}(\mathbf{r}, \mathbf{r'}; \omega)n_1(\mathbf{r'}, \omega) + \int \frac{n_1(\mathbf{r}, \omega)}{|\mathbf{r} - \mathbf{r'}|} \, d^3\mathbf{r'} + \int d^3\mathbf{r'} \, f_{xc}(\mathbf{r}, \mathbf{r'}; \omega)n_1(\mathbf{r'}, \omega), \]
\[ f_{xc}(\mathbf{r}, \mathbf{r'}; \omega) = \chi_{KS}^{-1}(\mathbf{r}, \mathbf{r'}; \omega) - \chi^{-1}(\mathbf{r}, \mathbf{r'}; \omega) - \frac{1}{|\mathbf{r} - \mathbf{r'}|} \]

provided that the inverse response functions \( \chi_{KS}^{-1}(\mathbf{r}, \mathbf{r'}; \omega) \) and \( \chi^{-1}(\mathbf{r}, \mathbf{r'}; \omega) \) exist.

In local in space interaction approximation, calculation of \( f_{xc}(\mathbf{r}, \mathbf{r'}; \omega) \) becomes \( f_{xc}(\omega) \) and is given by

\[ f_{xc}(\omega) = \chi_{KS}^{-1}(\omega) - \chi^{-1}(\omega). \]

In Equation (85), \( \chi_{KS}(\omega) \) is the “non-interacting” DFT on-site Kohn-Sham susceptibility. In the case of strong electron-electron correlation, \( \chi \) is calculated using Equation (46).

### 2.2.1.3 Bound States (Exciton)

Under an external perturbation, e.g., absorption of a photon with energy equal to or higher than the fundamental band gap or thermal energy at high temperature, an electron can excite from the valence band (VB) to the conduction band (CB) of a semiconductor or insulator. As a result, CB contains one electron and VB consists of many electrons and lack of an electron that creates a quasi-particle called hole. Since electron and hole have opposite charges, they interact via a Coulomb potential and form an electron-hole pair called exciton (a quasi-particle). Property like the exciton binding energy gives its stability against thermal dissociation and so large value opens up the possibility of using exciton based application even
at room temperature. Although exciton has kinetic energy, it is not as broad as the free carrier spectrum and so creates a narrow energy spread which is highly attractive for optical devices, for e.g., it is easier to build lasers on a material which has a narrow discrete density of states than the one which shows a broad continuum.

Since exciton is formed with one electron in CB and hole and many electrons in VB, explanation of properties of excitons requires to incorporate all important details in many-body effects which is not feasible. As an alternative ab initio approach TDDFT method based on effective charge density that includes all effects of electron-electron interactions in exchange-correlation potential (whose exact form is unknown), is in use. Different XC potential are formulated to be used in TDDFT even including the static and dynamic screenings defined by the other charges in parametric form to explain exciton properties (see Appendix E for detail).

Using linearized Equation (74) under the vertical or direct transition at the same momentum value, \( k=q \), (this is the case for negligible photon momentum in momentum conservation equation) in two band approximation, one gets the following eigenvalue equation for excitonic binding energy

\[
\Sigma_q (\varepsilon_q^m - \varepsilon_q^l) \delta_{kq} + F_{kq}^{mllm}(\omega) \rho_q^{ml}(\omega) = \omega \rho_k^{ml}(\omega),
\]

(86)

where

\[
F_{k\mathbf{k}k'\mathbf{k}'}^{mllm} = \iint d\mathbf{r} d\mathbf{r}' \varphi_k^{m*}(\mathbf{r}) \varphi_k^l(\mathbf{r}) f_{XC}(\mathbf{r}, \mathbf{r}', \omega) \varphi_{k'}^{l*}(\mathbf{r}') \varphi_{k'}^m(\mathbf{r}'),
\]

(87)

describes the electron-hole interaction and is known if one knows the static Kohn-Sham orbitals and XC kernel. For given \( f_{XC} \), if negative solution of the Equation (86) if it exists represents an exciton binding energy. Exciton binding energy reduces the band gap
energy due to the formation of a bound e-hole state. However, no excitonic Rydberg series is produced. So, TDDFT with relatively simple XC kernel is capable of producing bound excitons.

In this study, we compare results using generally used XC potentials, successful to reproduce various other features of materials, including adiabatic local density approximation (LDA), generalized gradient approximation (GGA). Following the success of functional that contain a Coulomb singularity of the long range electron-hole type interaction to explain the excitonic effects on bulk and 2D materials, I try a phenomenological long range kernel. Results using parameter free kernel with a Coulomb singularity exact-exchange (EXX) kernel is also reported. The details of formalism to calculate the exciton BE in density-matrix TDDFT formulation and mathematical form of various XC kernels used in this study are presented in detail in Appendix E.

2.3 Atomic Properties Calculation of Static System

The electronic structure methods discussed in sections 2.1 and 2.2 are applicable to systems containing up to few hundred atoms and time up to few hundred femtoseconds due to necessity to calculate properties by manipulating electronic degree of freedom. So, these approaches provide understanding about the phenomenon in microscopic level but are not suitable to explore properties of an extended systems both in static and the spatial-temporal evolution cases. However, to reliably predict the properties of experimental systems, theoretical model requires to be close in spatial and temporal extent to experimental counterpart. Use of reliable atomic interaction can avoid the necessity of electronic level resolution of calculation and so
extends the spatial limit of system that can be dealt and the temporal limit of analysis of a phenomena. Use of expedited approaches (without loss of accuracy) in the prediction of quantity of interest can contribute to fill the gap of those multi-scale problems.

Here I explore an example multi-scale problem of island diffusion kinetics. The following ingredients are required for atomic level simulation for both the static and the dynamical exploration using an expedited kinetic approach.

2.3.1 Models for Total Energy

Once the geometrical structure of an atomic model of interest is set up, mimicking the interaction among atoms on it is the most challenging part of a system set up. Obviously, the interaction terms that combined in an energy function require to incorporate all possible types of interaction in a system, which in the simplest case may be, for e.g., the sum of the pair interactions. The empirical Lennard-Jones (LJ)[44], Morse[45] or semi-empirical embedding atom method[46], Tersoff interatomic interaction[47] functions are some of the interactions that are successful in different material systems to reproduce experimental results.

Semi-empirical embedded atom method (EAM) potential function that views system energy as the energy obtained by embedding an atom into the local electron density provided by remaining atoms of the system is able to reproduce qualitatively and semi-quantitatively correct results for metallic systems[46; 48; 49] and is the one used for to mimic interaction among metal atoms in this study reported in this dissertation.
In EAM model, the interaction energy ($E_i$) between atoms $i$ of type $\alpha$ and $j$ of type $\beta$ at separation $r_{ij}$ is given by

$$E_i = F_\alpha(\sum_{j\neq i} \rho_\beta(r_{ij})) + \sum_i \sum_{j>i} \phi_{\alpha\beta}(r_{ij}),$$

(88)

where the first term is the embedding energy (many-body term) and the second is the pair repulsion term. In first term, $\rho_\beta(r_{ij})$ is electron density contributed by atom $j$ of type $\beta$ at the position of atom $i$ and so $\sum_{j\neq i} \rho_\beta(r_{ij})$ represents the host electron density at atom $i$ due to remaining atoms of the system. The first term $F_\alpha(\sum_{j\neq i} \rho_\beta(r_{ij}))$ represents the energy required to embed atom $i$ into the background electron density. In actual implementation, both summation are over all neighbors $j$ of atom $i$ within a cutoff distance. Second term is the pair repulsion term which is expressed as

$$\phi_{\alpha\beta}(r_{ij}) = \frac{Z_\alpha(r_{ij})Z_\beta(r_{ij})}{r_{ij}},$$

(89)

where

$$Z_\alpha(r_{ij}) = Z_0 (1 + \beta r_{ij} \gamma) e^{-\alpha' r_{ij}} - Z_{\text{cutoff}},$$

(90)

$$Z_{\text{cutoff}}(r_{ij}) = Z_0 (1 + \beta r_{ijc} \gamma) e^{-\alpha' r_{ijc}}$$

(91)

2.3.2 Methods to Calculate Activation Energy Barrier

The activation energy barrier ($E_a$) of a process is the difference in energy between the maximum energy along the minimum energy path (MEP) of a process and the energy of initial configuration. It is a quantity of interest for us because of its necessity to study the kinetics of any phenomenon for long-time using kinetic Monte Carlo (KMC) method.
2.3.2.1 Barrier Calculation Based on Interaction Potential

For given initial and final configurations, various methods are used to find the MEP, for e.g., drag[50], NEB[51], CINEB[52], dimer[53]. The common feature in those methods is that a number of images are interpolated between the initial and the final configurations which are connected by springs that avoids collapsing of images upon relaxation. Here image corresponds to a specific geometrical configuration of atoms or a snapshot on an artificial path from initial to final configuration. Using an energy expression corresponding to objects connected by spring with spring constant $k$, the energy of an image configuration $R_i$, $E(R_i)$, due to inter-image spring interaction is given by

$$E(R_i) = \frac{(k/2)(R_i - R_{(i-1)})^2 + (k/2)(R_i - R_{(i+1)})^2}{r^2},$$ (92)

The position of atoms in each of intermediate images $R_2, R_3, ..., R_{N-1}$ between the initial configuration $R_1$ and the final configuration $R_N$ are adjusted so that resultant force due to interatomic interaction and the spring force are zero or below a selected threshold value. Additionally, in order to make sure the natural tendency of any isolated system to be in equilibrium, the initial and final configurations of a process requires to have zero force. The force acting on a system on which atoms interact via EAM interaction is given by

$$F_i = -\nabla_{\vec{F}_i} \sum_i E_i = -\nabla_{\vec{F}_i} \left[ F_i(\rho_i) + \sum_{j \neq i} F_j(\rho_j) + \sum_{j \neq ij} \phi_{ij}(r_{ij}) \right],$$

$$= \sum_{j \neq i} \left[ \frac{\partial F_i(\rho_i)}{\partial \rho_i} \frac{\partial f_j(r_{ij})}{\partial r_{ij}} + \frac{\partial F_j(\rho_j)}{\partial \rho_j} \frac{\partial f_i(r_{ij})}{\partial r_{ij}} + \frac{\partial \phi_{ij}(r_{ij})}{\partial r_{ij}} \frac{(r_i - r_j)}{r_{ij}} \right].$$
Sequence of minimum energy configurations from initial to final configuration form the minimum energy path (MEP).

2.3.2.1.1 Drag Method

In the drag method, the energy of system containing N atoms is minimized in (3N-1) dimensional hyperplane keeping the reaction coordinate direction (direction of vector connecting a relaxed intermediate image to final configuration) fixed that corresponds to connecting images in the direction by rod or spring with high spring constant. Due to strong stiffness, the spring forces on the two sides of each intermediate images always cancel and the total force on the system results only from the interatomic interaction. To ensure each image is in minimum energy configuration (no further motion) and there is no force along reaction coordinate from interatomic interaction, atomic positions on each images are adjusted until resultant force in the direction perpendicular to reaction coordinate becomes below assigned threshold. To make efficient calculation, once the first image is relaxed, the initial configuration of 2\textsuperscript{nd} intermediate image is updated in the direction of vector from relaxed first image to the final configuration and the procedure is successively followed for additional images. In this way, system is dragged from the reactant to product configuration following a MEP. Since the force towards adjacent images always cancel due to stiffness, this approximate method becomes efficient to calculate barriers of a number of possible processes. However, one needs cross check the reliability of the calculated barriers of some selected processes with computationally reliable method. Details of the implemented drag method is explained in sec 2.4.2.2.3.
2.3.2.1.2 Nudged Elastic Band Method

In contrast to the drag method, in nudged elastic band (NEB) method images are connected using spring (mimicking of elastic band) that additionally allows relaxation along the direction of connection of images (reaction direction). Each image feels resultant force due to spring and interatomic interaction force and convergence requires minimization of resultant force. Since the direction of the spring force is the direction of the reaction coordinate, it has only parallel component and can become zero when two images on both sides of an image are equidistant. In a relaxed image, the force due to potential require to be below assigned threshold close to zero along reaction direction (that avoids possibility of motion of image along that direction) and in perpendicular direction that confirms the image is in minimum energy configuration.

2.3.2.2 Barrier Calculation Based on Predictive Data-driven Approaches

Finding the minimum energy path (MEP) and then the activation energy barriers of processes using the previously mentioned method is the most time consuming part of simulation. Efficient calculation of $E_a$s is the bottleneck to overcome the time gap between the theoretical prediction using kinetic approaches and experimental observation. Although study of 2D island diffusion using the state of the art SLKMC approach gives gain in simulation time by avoiding repeated calculation of barriers of the same or symmetrical processes, still one time calculation of $E_a$s of hundreds of possible processes in asymmetrical configurations is remaining as computationally time consuming part of the simulation. Once barriers to train a model are available, a data-driven descriptor based approach can be a viable route to avoid
further calculation of such computationally intensive quantities by using previously used methods.

2.3.2.2.1 Linear Approach: Multivariate Linear Regression (MLR)

For $Y_i$ representing a dependent variable ($E_a$ of a process in this study) and $Xs$ representing independent variables, consider a linear dependence of $Y$ on $X$ as

$$ Y_i = \beta_0 + \beta_1 X_{i1} + \beta_2 X_{i2} + \ldots + \beta_p X_{ip} + \epsilon_i, \quad (93) $$

where $\beta_0$ and $\beta_p$s are parameters to determined that represent an intercept and regression coefficients, respectively.

For ‘n’ number of samples, the equation can be represented in a matrix form as

$$ Y = X\beta + \epsilon, \quad (94) $$

where

$$ Y = \begin{pmatrix} Y_1 \\ Y_2 \\ \vdots \\ Y_n \end{pmatrix}, \quad X = \begin{pmatrix} 1 & X_{11} & X_{12} & \ldots & \ldots & X_{1p} \\ 1 & X_{21} & X_{22} & \ldots & \ldots & X_{2p} \\ \vdots & \vdots & \vdots & \ddots & \ddots & \vdots \\ 1 & X_{n1} & X_{n2} & \ldots & \ldots & X_{np} \end{pmatrix}, \quad \beta = \begin{pmatrix} \beta_0 \\ \beta_1 \\ \beta_2 \\ \ldots \\ \beta_p \end{pmatrix}, \quad \epsilon = \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ \ldots \\ \epsilon_n \end{pmatrix}, $$

and $\epsilon$ are to be determined to minimize an error function.
Define error function (ERF) as

$$ERF = \sum_{i=1}^{n} \epsilon_i^2,$$

and applying the condition of its minimization with respect to $\beta$s, one gets

$$\hat{\beta} = (X^T X)^{-1} X^T Y,$$ (95)

as the minimized matrix, where $T$ refers to the transpose of the matrix. Then the predictive equation for the dependent variable becomes

$$\hat{Y} = X\hat{\beta}.$$ (96)

In addition of predicting the values of the dependent variable ($Y$) for samples whose values are used for training of a model, it can be used to predict values of the same dependent variable for unused samples, say P, which indicates generality of a model. The predictive capacity of the model can be measured in terms of the Pearson’s correlation coefficient between the calculated barrier ($Y'$) of the dependent variable of the data unused for training and the corresponding predicted values (P) of dependent variable using

$$R = \frac{N \sum Y'P - \sum Y' \sum P}{\sqrt{[N \sum Y'^2 - (\sum Y')^2][N \sum P^2 - (\sum P)^2]}},$$ (97)

where N represents the number of samples in $Y'$ or P. The value of correlation coefficient is an indication of the relationship between the outputs and targets. The value close to 1 indicates that there is an exact linear relationship between the outputs and targets.
2.3.2.2.2 Non-linear Approach: Neural Network (NN)

Neural network is a non-linear data fitting approach whose basic mechanism can be summarized in an example case as

\[ f(y_i) = \frac{1}{(1+e^{-y_i})}, \]  \hspace{1cm} (98)

where

\[ y_i = \sum_{j=1}^{s} w_{ij} x_j + b_{i0}, \]  \hspace{1cm} (99)

represents the weighted sum of inputs on node \( i \) that contains the bias input \( b_{i0} \) and the sum of inputs \( x_j \) from node \( j \) of the previous layer containing \( s \) nodes weighted by fitting parameters \( w_{ij} \) and \( f \) is a transfer function. If \( x^1_j, x^2_k, \) and \( x^3_l \) represent neuron values in 1\(^{st}\), 2\(^{nd}\), and 3\(^{rd}\) hidden layers, respectively, then explicitly expressing Equation (98) and Equation (99) for input descriptor \( x_i, i=1,2,...,p \) in zeroth layer, the relation can be expressed as

\[ f\{ \sum_{i} (w^1_{ij} x_i + b^1_j) \} = x^1_j, \]

\[ f\{ \sum_{j} (w^2_{kj} x^1_j + b^2_k) \} = x^2_k, \]

\[ f\{ \sum_{k} (w^3_{lk} x^2_k + b^3_l) \} = x^3_l, \]  \hspace{1cm} (100)

where the superscript denotes the layer, \( w^l_{ik} \) represents the weight matrix that connects neurons from layer 2 to the layer 3 and \( b^3_l \) represents the bias for neuron \( l \) in layer 3.
In terms of values of input descriptors, \( x_i, \ i=1,2,\ldots,p \) in zeroth layer, the mathematical expression of an output on the third layer \( (x_i^3 = o_i^3) \) in a network containing four layers becomes

\[
a_i^3 = f \{ \sum_k w_{ik}^3 f \{ \sum_j w_{jk}^2 f \{ \sum_i x_i + b_j^1 \} + b_k^2 \} + b_k^3 \}
\]

If mean squared error (MSE) calculated as

\[
MSE = \sum_{l=1}^N \frac{(x_l^3 - t_l^3)^2}{N} = \sum_{l=1}^N \frac{(f(\sum_k w_{lk}^3 x_k^2 + b_k^3)z - t_l^3)^2}{N},
\]

where \( t_l^3 \) is a target value (a constant), \( N \) is the number of neurons in the output layer, is defined as performance function, the weights and biases are required to adjust to optimize the function (called training process) that converts the neural network training problem into an optimization problem. Differentiating performance function with respect to neuron value and weight value in \( 2^{\text{nd}} \) and \( 1^{\text{st}} \) hidden layer using chain rule of differentiation, one gets

\[
\frac{\partial MSE}{\partial x_k^2} = \sum_{l=1}^N \frac{\partial MSE}{\partial x_l^3} \frac{\partial x_l^3}{\partial x_k^2} = \sum_{l=1}^N \frac{\partial MSE}{\partial x_l^3} f'(x_k^2),
\]

\[
\frac{\partial MSE}{\partial w_{kj}^2} = \sum_{l=1}^N \frac{\partial MSE}{\partial x_l^3} \frac{\partial x_l^3}{\partial w_{kj}^2} = \sum_{l=1}^N \frac{\partial MSE}{\partial x_l^3} f'(x_k^2) w_{lk}^3, 
\]

\[
\frac{\partial MSE}{\partial w_{ji}^1} = \sum_{l=1}^N \frac{\partial MSE}{\partial x_l^3} \frac{\partial x_l^3}{\partial w_{ji}^1} = \sum_{l=1}^N \frac{\partial MSE}{\partial x_l^3} \frac{\partial x_l^3}{\partial w_{ji}^1},
\]

So, gradient values with respect to any neuron value or weight can be calculated recursively using \( \frac{\partial MSE}{\partial x_i^3} \) and other partial derivatives while propagating backward. Define
\[
J_F = \frac{\partial(e_1, e_2, \ldots, e_{547})}{\partial(w_1, w_2, \ldots, w_{11487})} = \begin{pmatrix}
\frac{\partial e_1}{\partial w_1} & \frac{\partial e_1}{\partial w_2} & \cdots & \frac{\partial e_1}{\partial w_{11487}} \\
\frac{\partial e_{547}}{\partial w_1} & \frac{\partial e_{547}}{\partial w_2} & \cdots & \frac{\partial e_{547}}{\partial w_{11487}}
\end{pmatrix},
\]

(105)

is the Jacobian of performance function with respect to weights and biases of the second hidden layer,

\[
JJ = (J_F)^T J_F,
\]

(106)

\[
Je = (J_F)^T E,
\]

(107)

\(E\) being a matrix of all errors.

Levenberg-Marquardt algorithm[54; 55] is used as optimizer in which the current weight and bias vector \((x_k)\) is updated to vector \(x_{k+1}\) following

\[
x_{k+1} = x_k - (JJ + I \star \mu)J_e,
\]

(108)

where \(I\) is identity matrix and \(\mu\) is a training rate parameter which influences the rate of weight and bias adjustment. Note that during training, derivative of each weight and bias is subtracted from its value.

### 2.4 Atomic Properties Calculation of Evolving Systems

#### 2.4.1 Molecular Dynamics

One of the mostly used and straightforward tool for studying dynamic evolution of a physical system at atomic resolution is molecular dynamics (MD) simulation[21]. In MD, the time evolution of a system is deterministically calculated by numerical integration of classical Newton's equations of motion. To get atomic positions and velocities at close time steps for
given interaction \((U_i)\) among atoms (force, \(f_i = -\frac{\partial U_i}{\partial r_i}\)), many methods exist, for e.g., in velocity Verlet algorithm, momentum \((p_i(t))\) and position \((r_i(t))\) are updated as

\[
p_i\left(t + \frac{\Delta t}{2}\right) = p_i(t) + \frac{\Delta t}{2} f_i(t),
\]

\[
r_i(t + \Delta t) = r_i(t) + \Delta t \frac{p_i(t + \frac{\Delta t}{2})}{m_i},
\]

\[
p_i(t + \Delta t) = p_i\left(t + \frac{\Delta t}{2}\right) + f_i(t + \Delta t) \frac{\Delta t}{2}.
\]

In this method, thermodynamic state of a system is obtained from information at microscopic level including atomic positions and velocities and macroscopic properties are calculated using statistical mechanical tools. However, due to necessity to take time step in femtosecond to resolve atomic vibrational motion that occurs in pico-second time scale, MD method is limited to few hundred nanoseconds of real time and hence fails to explore many processes which are infrequent in that time scale. Since huge computational steps are spent in a vibrational motion in a state in comparison to the time it takes to jump from one state to another, the diffusion trajectory obtained using MD method is short.

### 2.4.2 Kinetic Monte Carlo

Kinetic Monte Carlo (kMC) approach\cite{22; 23} overcomes the time-limitation of MD simulation by treating evolution of a system as succession of execution of process among given set of processes based on probability that is calculated using rates. For the state to state dynamics, the rate used to transit from state \(i\) to state \(j\) is independent of what state preceded state \(i\). This approximation valids in the study the evolution of activated processes like
diffusion or chemical reaction on which system spends long time on minimum energy basin by executing vibrational motion before jump to another basin and so forgets information of how it got there. Since the transition probability per unit time depends only on the transition probabilities of different processes on current configuration, the dynamics of such process follows relation of the form

\[ \frac{dP}{dt} \propto P, \quad (111) \]

\[-\ln P = \text{Rate} \times t,\]

that enables to update time using

\[ t \rightarrow t - \frac{\ln(P)}{\text{Rate}}. \quad (112)\]

If \( r_i \) refers to the rate of transition from a configuration ‘i’ to another configuration ‘j’ and \( n_i \) is the number of symmetrical ways for the transition, then total rate becomes \( \sum_i n_i r_i \).

The most important theoretical approach in analyzing the rate of rare events is the transition state theory (TST) [56; 57] which is valid if the time taken to cross the transition state (TS) is very short compared with the transition time from reactant (R) to product (P). Transition of atoms from one energy basin to another in diffusion process is rare event since it is many orders of magnitude slower than the vibrations of atoms. Since atoms vibrate about fixed average position, the region of the potential surface that is of the great importance can be represented by harmonic approximation[57].
Under the harmonic approximation, the transition rate \( r_{ij} \) from initial state \( i \) to final state \( j \) is given by

\[
 r_{ij}^{HTST} = \frac{1}{2\pi} \frac{\prod_{i=1}^{N} \omega_i^R}{\prod_{i=1}^{N-1} \omega_{TS,i}^R} e^{-\frac{(V_{SP} - V_{min})}{k_B T}},
\]

(113)

where \( V_{SP} - V_{min} = E_B \) is the energy difference between the saddle point and the minimum configuration corresponding to the reactant region is the activation energy barrier of a process, \( N \) is the number of atoms, \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. Imaginary frequency corresponding to unstable vibrational mode at the saddle point is left out from the product in the denominator.

In BKL scheme of KMC simulation[22], a \((j-1)^{th}\) process among \( N_e \) possible processes is executed in the current KMC step if following the condition is satisfied

\[
 (\sum_{i=1}^{j-1} n_i r_i) < \rho_1 * S_{N_e} < (\sum_{i=1}^{j} n_i r_i),
\]

(114)

where \( \rho_1 \epsilon (0,1] \) and

\[
 S_{N_e} = \sum_{i=1}^{N_e} n_i r_i.
\]

(115)

Time is updated by \( t \rightarrow t \frac{\ln(\rho_2)}{S_{N_e}} \), where \( \rho_2 \) is a random number. With the execution of the process thus selected, a new configuration results, and this KMC step ends. In this way, the system evolves by performing a process of its choice from among the multitude of possible provided processes. KMC can simulate the evolution of rather large atomic system, up to experimentally resolvable time scales within a reasonable computational time and resources
and provides a description that allows direct comparison with experimental characterizations. As explained, since the probability of selecting a process and the time advanced both depend on the rate of processes, the full range of processes and an accurate rate of occurrence of each is necessary in advance.

2.4.2.1 KMC for Chemical Reaction
Determining the major products of chemical reactions for given input reactants and conditions such as temperature and pressure is a fundamental problem in chemistry. Because of the time resolution, experimental measurements cannot track the complete reaction pathways, rather know only reactants, products and their proportion at different external conditions. This limitation on experimental approaches necessitate computational approach to better understand the microscopic detail of a chemical reaction. Although exploration of microscopic reality requires time dependent quantum mechanical solution, it is not currently computationally viable. Computational studies create understanding about a reaction via calculation of minimum energy path and saddle point between stable configurations on a high-dimensional potential energy surface. Calculation of transition state with ab-initio approach and exploration of reaction as competition among different possible routes is one of the popular approach. In the followed approach, the energy barrier for probable processes are calculated using NEB method discussed in section 2.3.2.1 with ab-initio energetics obtained using DFT approach followed by the reaction kinetics study using KMC approach, whose detail is explained in ref.[26].
The rate constants for reactions, desorption, and diffusion of species are calculated using the Arrhenius relation following transition state theory using

\[
\text{Rate (R)} = A e^{\frac{-E_a}{k_B T}},
\]

(116)

and the rate constants for adsorption of reactant species are calculated using:

\[
\text{Rate (R)} = \frac{s^* P}{\sigma \sqrt{2\pi M k_B T}} e^{\frac{-E_a}{k_B T}},
\]

(117)

where \(A, E_a, k_B, T\) in Equation (116) are the pre-exponential factor, an activation energy barrier of a process, the Boltzmann constant, and the reaction temperature in absolute scale, respectively and \(s^*, \sigma, P,\) and \(M\) in Equation (117) are the sticking coefficient, site density, pressure, and mass of the reactant species, respectively. Note that the rate is function of interaction and external factors.

The total reaction rate \(R(k)\) at KMC step \(k\) is calculated by summing over the total site rates \(\Gamma_n(k)\) at each site \(n\), which in turn is the sum of rates of the individual process \((i)\), \(\Gamma_n^{(i)}(k)\), at site \(n\) as

\[
R(k) = \sum_{n} \Gamma_n(k) = \sum_{n} \sum_{\text{total-sites}} \sum_{\text{total-processes}} \Gamma_n^{(i)}(k).
\]

The rate is used to select a site ‘\(s\)’ if the following condition is satisfied

\[
\sum_{n} \Gamma_n(k) < r_1 R(k) \leq \sum_{n} \Gamma_n(k)
\]

for a random number \(0 < r_1 < 1\).
Once a site is chosen, the selection of a process on the site among different possibilities on it is made in a similar manner by generating another random number $r_2$. Right after the execution of the selected process at the chosen site ‘s’, the system clock is forwarded by average time-step of $1/R$: $t(k)\rightarrow t(k-1)+1/R(k)$. The local space around the process executed site is scanned to update the total site rate ($\Gamma_n(k)$) for those scanned sites and the total reaction rate $R(k)$ since rest of system remains as it was before. Flow chart of the steps is presented in Figure 3.

The followed procedure can be summarized as below.

1. Choose one site on the surface following the explained BKL algorithm. Update the process database per site before checking for conditions to select a process. The sites with no executable process have zero total site rate and should not be considered to select a process in the step.
(2) If there is a possible instantaneous event on the site selected in step (1), check its local neighboring sites for its products. If there is no any available site, terminate the process, otherwise execute it. In the case of more than one possible instantaneous events on a site, one of them is chosen randomly and is executed. The neighborhood of the site is changed according to the event.

(3) If condition (2) is not satisfied, choose a process (i) from the list of possible processes on the site following the explained BKL algorithm.

(4) Perform the reaction event (i) selected in step (3) taking care of the type of process as follows:

**Adsorption**

- If the adsorption of a reactant is selected and the site selected in step (1) is empty, the event is successful. If the site is occupied, the attempt is terminated.

- If a dissociative adsorption of reactant is selected and the site selected in step (1) is empty, a neighboring site is chosen randomly next to the first site. If the later site is empty, the event is successful and individual products are adsorbed on each of the two sites. If either site is occupied, the attempt is terminated.

**Desorption**

- If the desorption of reactant or product is selected and the site selected in step (1) is occupied by them, the event is successfully executed, the site then becomes empty. If the site is not occupied by the desorbing species, the attempt is terminated.
• If the associative desorption of product is selected and the site selected in step (1) is occupied by a radical of the product, a neighboring site is then chosen randomly next to the first site. If the later site is occupied by the required radical, the event is successfully executed and the two sites are kept empty. If either site is not occupied by required radicals, the attempt is terminated.

**Surface Reaction**

• If a surface reaction process is selected (combination reaction) and the site selected in step (1) is occupied by a particle corresponding to one of the reactants, a neighboring site is then chosen randomly next to the first site. If the latter site is occupied by the other species of the same reaction, the reaction event is successful and one particle is replaced by a product particle and the other site is empty. If the reaction ends on two product species, each are placed on one of those sites randomly. If both sites are not occupied by the appropriate reactants, the attempt is terminated.

**Surface reaction and desorption**

• If the surface reaction and desorption event is selected, the procedure is analogous to a surface reaction event but a product molecule leaves the surface and the site becomes empty.

**Diffusion**

One site from the surface is randomly chosen. If the site is occupied by a diffusive species, and a randomly chosen neighboring site is empty, the diffusion process is executed.
For any of the executed process, time is updated following: $t \rightarrow t - \frac{\ln \rho_2}{S_{Ne}}$, where $\rho_2 \in (0, 1]$ is a uniformly distributed random number and $S_{Ne} = \left( \sum_{i=1}^{N_e} n_i r_i \right)$. Every KMC iteration will execute a process as long as the total rate is non-zero. If total rate is zero (there is no process to execute) which is the situation when all sites are occupied and desorption process can’t be executed due to absence of product molecule on surface, the KMC simulation will stop. If any of the stop condition: the number of kMC steps or all surface sites are occupied, the simulation stops.

2.4.2.2 Self-Learning KMC for Island Diffusion

There is preponderance of evidence that the variation of evolving morphology during thin-film growth on a surface, e.g. experimental observation of growth modes as cluster, fractal, or dendritic on fcc(111) surface[58-60], results from competition among several phenomena including surface diffusion. In fact, diffusion of adatom islands on surfaces provides important insights not only in thin-film growth[61-63] but also in surface chemical reactions[64], mass transport[65], deformation[66], and corrosion[67] and so making it a focus of many experimental and theoretical investigations. In thin film growth in particular, a complete understanding of its morphological evolution requires atomic-level understanding of the processes executed at early stages. Experimental observations (using scanning tunneling microscopy [STM] or field ion microscopy [FIM]) of various diffusion mechanisms of islands on a surface such as edge diffusion[68; 69], dimer-shearing[70; 71], and concerted gliding[72; 73] have already pointed to the factors that may control a growth mode. However, because of insufficient time resolution these experimental findings cannot uncover complete pathways of
short-lived diffusion process; instead, on the basis of experimental evidence alone, those processes must be inferred indirectly. In contrast, theoretical atomistic simulations are capable of determining directly the diffusion pathways and so play an important role in revealing the processes driving morphological evolution of the nanostructures. Among the available simulation techniques, one of the widely used tool at atomic resolution is molecular dynamics (MD) simulation[21] which implicitly includes system vibrational and structural information in the formulation. It also incorporates anharmonic effects that may come into play. However, the necessity of short simulation time step (~femtosecond) to resolve atomic vibrations makes MD an inefficient tool for studying the long-time evolution of a system triggered by rare events such as bond-breaking, as a large number of computational steps are required even to capture a single diffusive process. The most successful framework to bridge the time scale gap is transition state theory (TST)[57][74] in which rare events are explained in terms of the rate of crossing an energy surface separating an initial and a final configuration. Once rate of processes are known, the kinetic Monte Carlo (KMC)[22; 23] method that treats evolution as succession of state-to-state Markov walks dictated by rates of the possible processes becomes a method of choice to explore long-time evolution of a system.

By treating the support as static during the simulation, KMC is able to simulate the evolution of rather large atomic system, up to experimentally resolvable time scales, within a reasonable computational time frame and resources to provide a description that allows direct comparison with experiments. In KMC, the probability of selecting a process is proportional to its rate constant and the time advanced after each successful transition depends inversely on the sum of rate constants of all possible processes in the system. So, for this method to yield reliable
results, it is crucial to know in advance the full range of processes and an accurate rate of occurrence of each. In standard KMC, no special attempts are made to overcome the first challenge and information about the possible processes are postulated (and ultimately guessed) before the simulation is undertaken. This may be reasonable when the number of possible processes is relatively small (e.g. simple chemical reactions in vacuum, or diffusion of islands containing no more than three adatoms) because chances of imagining all possible processes are higher and the calculation-intensive task of determining the activation energy barrier ($E_a$) for all of them is not prohibitively expensive. But when the number of possible processes is huge (e.g. simulation of diffusion of islands containing more than three adatoms), building such a library of processes and their respective energy barriers in advance is not only unreliable (since the chance of leaving out some processes increases as the number of possible configurations increases) but inefficient (since only few processes will dominate in the simulation).

To economize addressing of the completeness challenge of input into KMC simulations, an on-the-fly method was developed that treats only processes corresponding to a configuration that shows up in the KMC step as a possibility. In this method, the $E_a$ of a given possible process is calculated each time it appears in the simulation[75]. Since it is not stored, it has to be calculated every time the process is picked. To avoid such redundancy in the calculation, a Self-Learning Kinetic Monte Carlo (SLKMC) [76] [75] method was developed. In SLKMC[76], a pattern-recognition scheme[77] is used for efficient storage and subsequent retrieval of information about possible processes and their corresponding $E_a$s. For each process generated by KMC, SLKMC consults the evolving database to determine if that process or its
symmetrical equivalent is already stored; if it is, the stored $E_a$ is used to calculate the rate of occurrence; if not, the $E_a$ for the new process is calculated on-the-fly. In the last decade, a number of studies using SLKMC have provided a microscopic understanding on the diffusion kinetics of adatom islands on metal surfaces. For example, study of the diffusion of Cu islands containing 19-100 atoms on the Cu(111) surface, a scaling relation between diffusion coefficient ($D$) with the number of atoms in the island ($N$) was found to be $D \propto (N^{-1.57})$[76]. Furthermore, a crossover from domination of multi-atom processes to that of involving single atoms was also found. In subsequent work detailed attention to the diffusion kinetics of small island sizes containing up to 10 adatoms in homo-epitaxial [78-80] and hetero-epitaxial systems[27] revealed a number of diffusion processes, including their relative significance in island diffusion characteristics. The method was extended to off-lattice systems using the set of relative position of atoms in pattern recognition scheme and has successfully uncovered a number of novel mechanisms in the diffusion of Cu island on Ag(111)[81]. The on-site SLKMC was further improved to incorporate both fcc- and hcp-occupancy sites on the fcc(111) surface (SLKMC-II), first following manual incorporation of processes[78] and later automatic incorporation using extended pattern recognition scheme[79].

### 2.4.2.2.1 Structural Model and Nomenclature

In a computational study of properties of a system, designing of a structural atomic model to mimic a system of interest is the first and an important step. The transition metal elements, which are the system studied in this dissertation, crystallize in face centered cubic (fcc) structure. Figure 4 shows the unit cell a fcc structure that contains eight atoms at the corners of a cube and six atoms at the center of each face of cube.
Among various surface cut of fcc crystals, the six-fold symmetric (111) surface is the most compact one with a relatively flat potential-energy surface which makes it the substrate of choice for the growth of nanoscale films. To make a reliable substrate model to calculate the diffusion barriers of adatom islands, we test the number of atoms on a layer and the number of layers such that the system mimics the stacking on the bulk structure and contains enough lateral dimension to avoid the interaction among adatoms and its image while using periodic boundary condition to mimic infinite surface. For that purpose, the number of considered atoms in a layer to form fcc(111) surface is increased till relaxed energy per atom converged followed by convergence test with respect to increase in the number of layers. Such a plot is shown in Figure 5. A substrate of 5 layers with 256 atoms per layer converges in relaxed energy, as shown for Ni substrate in Figure 6 that justifies to take 16x16x5 substrate geometry. Two bottom layers are kept fixed to avoid motion of the sample as a whole and to mimic bulk system. To mimic infinite system, periodic boundary conditions are applied that avoids edge effect.
Figure 5 Variation of energy per atom of Ni substrate with number of atoms arranged in fcc(111) arrangement. Note the flat portion about 256 and 1200 atoms that signify 16x16 atoms in a layer and 5 layers of them are enough for a substrate.

Figure 6 (a) Top view of the fcc(111) surface. The exposed top layer (A-layer), a layer below (B-layer) and two-layers below (C-layer) are represented by big hollow green circles, filled blue circles and filled yellow circles, respectively, (b) Octamer island adsorbed on fcc sites with A-or B-type step-edge and A or B-type processes, (b) Three possible available directions for an adatom to move from an fcc (hcp) to neighboring hcp (fcc) site along with numbering convention for processes used in this article.

In Figure 6 (a), we show the top view of the fcc(111) surface that displays the topmost three layers, namely A, B, and C represented by hollow green circles, filled blue circles, and filled
yellow circles respectively, leaving two possible 3-fold hollow adsorption sites: one on top of blue circle whose nucleation leads to the ABAB stacking fault that constitutes a hexagonal close-packed (hcp) site and another on top of the filled yellow circle whose occupancy maintains the crystal stacking order ABCABC as in its bulk structure that constitutes a face-centered cubic (fcc) site. Schematically, an hcp site (H) comprises three A-layer atoms that form a downward pointing triangle whereas an fcc site (F) comprises three A-layer atoms that form an upward pointing triangle as shown in Figure 6(c). This difference in the orientation of the A-layer atoms on fcc and hcp sites is used in the rest of this article to identify whether an island is adsorbed on an fcc or hcp site. Here an island is defined as a group of adatoms of which any two are connected directly or indirectly through other adatoms by the nearest neighbor bonds. To introduce various terminology, in Figure 6 (b) we show an example of an octamer island in which the row containing 4 adatoms (neglect presence of the single-atom showing A-type process) forms (100) micro-facet (aka an A-type step-edge) and the short edge forms (111) micro-facet (aka a B-type step-edge). An adatom island on an fcc(111) surface can form compact or non-compact geometries with their boundaries forming A- and B-type step edges of equal or different edge lengths. The activation energy barriers of various processes also depend upon whether a top-layer substrate atom lies in between adatoms during the process (which we henceforth call an A-type process) or not (a B-type process), as shown in Figure 6(b). An adatom(s) of an island can move in three directions as shown in Figure 6(c) whose numbering convention used in this article for an island on an fcc and an hcp occupancy is shown there. From now on, in all our figures, we show only the adatoms (represented by filled red circles) and their neighboring atoms of the top-most substrate layer (A-layer).
Several steps need to be undertaken before we begin our simulations. Because of the application of the pattern recognition scheme, we need to first label the atoms in the adatom island whose diffusion pathways and activation energy barriers need to be calculated as reliably as feasible. To begin with we arrange the substrate atoms in the fcc(111) configuration on which an initial island of a given size is adsorbed.

To label the initial island configuration (and also to explore possible processes), we assign, for example, as shown in Figure 7(a), site 1 as the fcc hollow site with one adsorbed adatom.

Figure 7 (a) Three concentric hexagonal rings out of six such rings to uniquely specify local neighborhood of an island in pattern recognition scheme of the SLKMC-II method. Enumeration of top layer substrate atoms and adsorption sites of the fcc(111) surface to explore possible processes and store information. Initial pentamer island configuration in (a) transforms to that in (b) after execution of a 2-atom process shown by lines with arrowhead, (c) format of database that stores information about the initial island configuration, energy barrier of process and executed process The two-atom process is complemented by probable single-atom process with the same probable target site 19.

To label the initial island configuration (and also to explore possible processes), we assign, for example, as shown in Figure 7(a), site 1 as the fcc hollow site with one adsorbed adatom.
The top layer substrate atoms, the fcc and hcp adsorption sites in the top substrate layer are then enumerated around it so that sites on first, second, third, ..., up to sixth hexagonal rings are assigned numbers from 2 to 7, 8 to 19, 20 to 37, ..., 91 to 127, respectively. The adatom on site 1 is called “central” adatom, not in terms of the geometry of the island but in virtue of its initiating role to explore processes. Since the available adsorption sites on the first ring (sites numbered 2, 4, and 6 in Figure 7(a)) are within the nearest neighbor distance from the central adatom, they cannot be energetically occupied by other adatoms so that the initial dimer island occupies sites 1 and 9, initial trimer island occupies sites 1, 9, and 11 and so on. Once an adatom island is labeled, ionic relaxation of the atoms in the top three substrate layers and those in the island is carried out by keeping the atoms in the bottom two layers of the substrate fixed to mimic the bulk structure taking energy convergence of $10^{-4}$ eV and the temperature corresponding to velocities in the projected velocity verlet algorithm[82] of $10^{-4}$ K. Note that ionic relaxation for all atoms in the island and in the top three substrate layers (island atoms + 256x3 substrate atoms) is performed for the calculation of all diffusion pathways and activation energy barriers, following the procedure described in section 2.4.2.2.3.

2.4.2.2 Pattern Recognition Scheme

For an island configuration, a pattern of binary bits (pattern-recognition scheme[77]) is assigned based on the occupancy of sites on the six hexagonal rings around a central adatom to store and retrieve information. As a convention, for the first ring the binary number 1 is assigned for every top substrate sites and number 0 is assigned for hollow sites whereas, for higher rings, number 1 is assigned for sites with adatoms adsorbed on them and number 0 is assigned for both the top layer substrate atoms and the unoccupied hollow sites. Following the
convention, the binary bit patterns of the first, second, and third rings in Figure 7(a) become 101010₂ (=42₁₀), 001010100000₂ (=67₂₁₀), and 000001000000000000₂ (=4096₁₀), respectively and those of higher rings become 0 due to the absence of adatoms on those rings. Because of the difference in neighboring geometry, if the central adatom is on an hcp site, the decimal equivalent of the bit pattern of its first ring becomes 2₁₀. A set of 6 numbers which uniquely specify a configuration becomes (42  67₂  4096  0  0  0) for the pentamer island shown in Figure 7(a).

2.4.2.2.3 Process Finder and Barrier Calculation Scheme

After determining the initial configuration of the system, in each step of the on-the-fly KMC, the second task is to determine all the possible processes that could be executed in that configuration. For that purpose, all the sites in the second ring around the central adatom (sites at the nearest neighbor distance from it) are checked in the ascending order of enumeration as possible sites to diffuse. In the pentamer island configuration in Figure 7(a), the pre-occupancy of sites 13, 15, and 17 with adatoms leads to checking of sites 9, 11, and 19 consecutively as possible sites. Among these sites, only those that give non-symmetrical island configuration upon diffusion of central adatom to them are considered to calculate Eₐ of the process. On the fcc(111) surface, five types of operations can give the same island configurations: mirror reflection, clockwise rotation of 120° and 240°, mirror reflection after clockwise rotation of 120° and 240° about an axis passing through the central adatom. The Eₐ of process corresponding to each provisional final sites is calculated using the drag method[76] whose details for considering the site 19 as final site is presented below.
As outlined above, study of the kinetics of any phenomenon using KMC requires activation energy barriers of possible processes which are calculated in the SLKMC in on-the-fly mode using the drag method. The interaction among atoms is modeled using many-body semi-empirical Embedded-Atom Method (EAM) [48] which has been shown to produce qualitatively and semi-quantitatively reliable results for metallic system[46; 48] including island diffusion barriers on fcc (111)[27] and other surfaces[83]. In EAM, the interaction energy (\(E_i\)) between two atoms i and j of types \(\alpha\) and \(\beta\), respectively at separation \(r_{ij}\) is given by

\[
E_i = F_\alpha \left( \sum_{j \neq i} \rho_\beta(r_{ij}) \right) + \sum_i \sum_{j>i} \Phi_{\alpha\beta}(r_{ij})
\] (4)

In Equation (4) the first term is the embedding energy (many-body term) which gives the amount of energy required to embed an atom in the local electron density of other atoms and the second term is the pair repulsion term.

To illustrate the drag method for the calculation of the diffusion energy barrier, we consider the example of the pentamer island in Figure 7(a). The total energy of the system with all atoms (pentamer + substrate) in ionically relaxed positions is taken as reference energy (the first data point in Figure 8). To get started, the site numbered 19 on the second hexagonal ring, for example, is taken as a provisional final site for the central adatom to diffuse. With the above information in hand, the drag method implemented in the SLKMC consists of two parts: the first treats diffusion of the central adatom to the provisional final site as a single-atom process which requires keeping all other adatoms fixed during exploration of the minimum energy
path, while the second part allows all other adatoms to move naturally, following the central atom or in any other way. In both parts, the central adatom is constrained to move step by step with increment of 0.05Å towards the target site, at each step of which the unfixed degrees of freedom of the system are relaxed. In Figure 8, the first (up to drag step about 50) and second curves correspond to first and the second part, respectively. To be clear, the second data point in the first curve in Figure 8 represents the relative energy of the relaxed 1st intermediate configuration (keeping other adatoms, bottom 2-layers, and reaction coordinate fixed). Once the 1st intermediate relaxed configuration is obtained, the direction of the reaction coordinate is updated from it to the target configuration. The above procedure is repeated until the energy difference between successive intermediates is less than 10⁻⁴ eV or intermediate image is 0.05 Å from the provisional target site. Once the condition is attained, the entire system (except for the bottom two layers of the slab) is relaxed. The height of the energy plot of the first curve in FIG.5 gives the $E_a$ of the single-atom process. So, 0.56eV is the energy barrier for the central adatom to move to site 19 in Figure 7. To start the second part of search, the initial configuration of the system is restored (see energy of system at drag step 50 equals to the reference energy in Figure 8) and the same procedure as in first part is repeated with the difference that all adatoms are allowed to move. Once the condition for relaxation of system, energetic or distance from target, is attained, the final position of the central adatom may or may not be the same as the one initially settled on as the provisional final site, e.g. the central adatom can occupy an hcp site when it is dragged from an fcc to another fcc site. A multi-atom process results if, on checking their position after relaxation, more than one adatom change their initially occupied sites as they follow the motion of the central adatom, while a concerted
process results if all the adatoms end up on new sites. As a result, the drag method is capable of revealing single, multiple atoms and island concerted motion processes during the calculation without have any apriori bias. In the example process considered here in reference to the configuration in Figure 7(a), a multi-atom process containing two- atoms emerges from the drag in which the central adatom diffuses from site 1 to site 19 and the adatom on site 13 diffuses to site 1 (Figure 7(b) becomes the final configuration). The height of the second peak in the plot of minimum energy path (MEP) in Figure 8 gives the energy barrier of the two-atom process. The information about the initial and final island configurations and the activation energy barriers of the processes are stored in the database in the format presented in Figure 7(c).

![Figure 8 Variation of energy at each drag step during drag of the central adatom at site 1 of the Cu pentamer island on Ni(111) shown in Figure 7(a) to target site 19 for the single-atom process keeping other adatoms fixed (first part), and allowing all island atoms to move which results in a 2-atom process (the second part). The resulting process, final configuration and the storage of the information in database of SLKMC simulation is shown in Figure 7.](image)

In summary, the flow chart of SLKMC method is presented in Figure 9.
2.4.2.4 Calculation of Diffusion Properties

With the explained procedure in section 2.4.2.2, the system evolves by performing a process of its choice, from the multitude of possible single- or multi-atom processes made in the succession of KMC steps. At each step, the executed process is tracked that allows ultimately to calculate the frequency of execution of any process and also to collect the execution of single- or multi-atom and concerted process for an island at the given temperature. The simulation run for a given island size at a given temperature is halt at certain KMC steps, mostly $10^7$. For good statistics, for each island size, $10^7$ KMC steps are divided into $10^5$ simulations each with 100 KMC steps (running consecutively). For each 100 KMC steps, the coordinates of each adatom in the island before execution of the process and after are taken to calculate the center-of-mass of the island and the square displacement of the island resulting from the executed process. The square displacement for each step for 100 steps is stored, along with that step’s corresponding time; the position of the island at the end 100 steps becomes the origin for the
succeeding 100 KMC steps. The mean square displacement (MSD) is now calculated and mean
time by ensemble averaging: ensemble 1 consists of all the 1st steps (each of which has a
different origin, as explained above) in each 100 KMC steps, ensemble 2 of all of the 2nd KMC
steps of the same, …, ensemble 100 of each 100th steps, etc.); and the mean t for each ensemble
consists of the sum of the times of 10^5 KMC steps of that ensemble divided by 10^5. With the
resulting 100 MSDs and 100 mean equivalent times, a graph of the successive MSDs over
cumulative t is plotted. If the trace of center of mass of an island at a given temperature is
random, then one can calculate its diffusion-coefficient (D) using Einstein relation between
MSD and equivalent time for random motion as

\[ D = \frac{\langle (r_{cm}(t) - r_{cm}(t_0))^2 \rangle}{2dt}, \]  

(118)
where \( r_{cm}(t_0) \) and \( r_{cm}(t) \) are the center of mass of the island at time \( t_0 \) and \( t \) respectively, and \( d \) is the dimensionality of the system, which in the current case is 2. If the plot of the ln(D) for
each island varies linearly with 1/T, T being temperature, then one can fit relation between D
and T as

\[ D = D_0 e^{ \frac{E_{\text{effective}}}{k_B T} }, \]  

(119)
where \( E_{\text{effective}} \) refers to the effective energy barrier of an island.
CHAPTER 3: APPLICATION OF TDDFT+DMFT METHOD: ONE BAND HUBBARD MODEL

In this chapter, the expression for the XC kernel is derived for the one-band Hubbard model by solving DMFT equations via two approaches, the Hirsch–Fye Quantum Monte Carlo (HF-QMC) and an approximate low-cost perturbation theory approach, and demonstrate that the latter gives results that are comparable to the exact HF-QMC solution. Furthermore, through a variety of applications, we propose a simple analytical formula for the XC kernel. Additionally, we use the exact and approximate kernels to examine the nonhomogeneous ultrafast response of a one-band Hubbard model. We show that the frequency dependence of the kernel, i.e., memory effects, is important for dynamics at the femtosecond timescale.

3.1 Introduction

Materials with strong electron-electron correlations form an important class of condensed matter systems with unusual physical properties and numerous technological applications (see, for example, [84]), which are expected to significantly increase with advances in nanotechnologies [85-89]. The non-equilibrium properties of these strongly-correlated materials are particularly interesting for several reasons: (1) they allow better understanding of the excitation spectrum, orbital occupancies, lattice potential profile, and other “inherent” properties of the unperturbed system; (2) systems may be driven into new phases that cannot be achieved when in equilibrium [90]; (3) potential applications in “bulk-” and nanotechnologies, such as switches[91], microelectromechanical system (MEMS) devices [92], biosensors[93], and ultrafast lithium storage batteries [94].
An accurate theoretical description of experimental results, as well as the prediction of the desired properties of Strongly-Correlated Materials (SCMs) out of equilibrium is a very complex task. The power of many-body approaches is remarkably limited in this case, since one needs to deal with multi-orbital systems with no translational and temporal invariance. As a result, the corresponding simulations, which involve very large (especially for nanoscale systems) Green’s function matrices with multiple arguments (atom coordinate, electron orbital and spin indices and complex time variable), are extremely slow. As an alternative, the ab initio Time-Dependent Density-Functional Theory (TDDFT) approach[8], because of its technical simplicity, seems to be a better candidate for the purposes mentioned above. However, to make TDDFT applicable to SCMs, one needs to construct an appropriate exchange-correlation (XC) potential, since the available ones are not very successful in describing these systems, even in the static (DFT) case.

The most straightforward way to construct such a potential is to use a many-body theory approach in which some of the strongly-correlated problems can be solved either exactly or by using an accurate and physically-transparent approximation. In this case, the XC potential (kernel) is found by taking functional derivative(s) of the obtained XC action with respect to the electron charge density \( n(\mathbf{r}, t) \) with the corresponding boundary terms arising from the requirements of causality (in the adiabatic case, one differentiates the XC energy with no boundary terms). Indeed, most of the progress in building the XC potential for SCMs has been made for the exactly-solvable systems (using, e.g., the Bethe ansatz approach [95]) or systems that can be solved with a high numerical accuracy: small clusters [96-103], including one- and
a few-impurity junctions[104-107], and one-dimensional systems [97; 103; 108-110] (for an over-review of the relationship between static DFT and the two-site Hubbard model, see [111]). Thus, so far, most of the results have been obtained for “small” systems: small clusters and chains. Nevertheless, these results already give an idea about the structure of the XC potential and XC kernel needed for SCMs and the possible physical phenomena that may be described within TDDFT. In order to “converge” to a universal potential (kernel) valid in all dimensions, further analytical and/or numerical studies, especially of two-dimensional systems, surface and bulk materials, are required. The power of the analytical methods for “large” (extended) strongly-correlated systems is mainly constrained to some limiting cases, such as systems with low particle densities for which it is possible to obtain an accurate result for the exchange-correlation energy [112; 113].

Probably, the most powerful, modern, numerical, many-body approach to study extended SCMs is Dynamical Mean-Field Theory (DMFT) [11; 114]. In particular, combined with DFT (DFT+DMFT) [12; 115], it was successfully applied to analyze the equilibrium properties of bulk systems and films [116; 117] and recently even nanostructures (see, e.g., [118; 119]). The success of DMFT is based on an “impurity approximation”, i.e., neglecting the non-local correction to the electron self-energy, which is an accurate approximation for systems with a large atomic coordination number (or in high dimensions). This approximation enables one to solve strongly-correlated problems with reasonable computational resources. Recently, the approach was also generalized to examine systems in non-equilibrium [5; 120-122], though the application has so far been restricted to systems with computational super-cells that contain less than ten non-equivalent atoms. On the other hand, one can use the equilibrium DMFT
solution to construct the XC potential, which could be used to examine the non-equilibrium response of SCMs within TDDFT. In this regard, Karlsson et al. applied DMFT to obtain the adiabatic XC potential for the three-dimensional one-band Hubbard model[123]. To test the theory, the authors used the exact numerical solution for a $5 \times 5 \times 5$ cubic cluster with a finite local Coulomb repulsion on the central atom. In this important work, the authors showed that their adiabatic TDDFT + DMFT can successfully describe the response of the system when correlations are not very strong and/or the electron density is not very close to half-filling. Since memory effects (non-adiabaticity or frequency dependence of the XC potential) were neglected in their approach, one expects that inclusion of these effects into the theory will make it more robust.

The importance of non-adiabatic effects has already been demonstrated for some strongly correlated systems of different sizes and geometries. For example, in the case of the Hubbard dimer, it has been demonstrated [99] that the non-adiabaticity of the XC kernel is essential for obtaining an electronic spectrum with the characteristic satellite peaks resulting from dynamical (time-resolved) local interactions between electrons. Furthermore, Fuks and Maitra [100; 101] showed that the adiabatic approximation leads to the wrong results for the charge-transfer dynamics for the Hubbard dimer. In the case of the Hubbard chain, it was indicated that non-adiabatic effects are important at some values of doping [110]. Recently, it a non-adiabatic TDDFT + DMFT approach[16; 17] is proposed, which allows one to take into account non-adiabatic effects in practically all types of systems, from clusters to bulk materials. In this approach, the XC kernel is obtained from the charge susceptibility for an
effective (many-body theory) Hubbard model solved using DMFT. We have also applied this TDDFT + DMFT method to the bulk Hubbard model and demonstrated that non-adiabatic effects significantly modify the adiabatic results for the excitation spectrum and the non-equilibrium charge response of the system.

In this chapter, the derivation of the numerical results for the XC kernel for the 3D one-band Hubbard model by using two routes to solve the DMFT equations, a numerically-exact Hirsch–Fye Quantum Monte Carlo (HF-QMC) and an approximate, computationally-efficient Iterative Perturbation Theory (IPT) approach, and show that the latter is a reasonable approximation for getting preliminary, semi-quantitative or even quantitative results, as well as insight into the properties of the system. We also propose an analytical fitting formula for the frequency dependence of the XC kernel for the 3D one-band Hubbard model. Next, we compare some results obtained with the XC kernel, solved using the HF-QMC and IPT approaches for the prototypical 1 band Hubbard model, focusing on the role of non-adiabatic effects in the response of the systems (excited charge density and conductivity).

3.2 The DFT+DMFT Solution

As a prototypical case, the DFT+DMFT method discussed in section 2.1.2 is applied to the one-band bulk Hubbard model (Equation (19) with $l=m=1, \sigma = 1$) with a Gaussian free electron Density of States (DOS):

$$\rho(\varepsilon) = \frac{e^{-\left(\varepsilon/t\right)^2}}{\sqrt{\pi}}$$ (120)
A system with such a DOS is the most relevant to DMFT, since it corresponds to a cubic lattice with infinite coordination number. In this case, the electron self-energy is momentum independent, and the DMFT solution is the exact one [33]. On the other hand, the Gaussian DOS corresponds to a general physical situation of a narrow-band system with the bandwidth of order of several t’s (where \( t \approx 1 \) eV is the hopping parameter). Below, we analyze the most important case of half-filling, assuming that the system is in the paramagnetic phase.

### 3.2.1 Density of States

The results of the density of states (DOS), obtained from the local Green’s function using Equation (41) at different values of U and temperature by using the IPT and HF-QMC approaches are presented in Figure 10(a) and (b).

![Figure 10](image)

Figure 10 The single particle Density Of States (DOS) as a function of frequency obtained for \( U = 1t, 2t \) and \( 4t \): (a) for \( T = 0.16t \) with both the Hirsch–Fye Quantum Monte Carlo (HF-QMC) and the Iterative Perturbation Theory (IPT) approaches; (b) for \( T = 0.05t \) using IPT only.
In Figure 10(a) the results for the DOS for $U = 1t$, $2t$, and $4t$ obtained within these two approaches are presented at temperature $T = 0.16t$ (this corresponds to the low temperature regime, since the temperature is much smaller than two other energy scales in the system: $T \ll t, U$). Only the positive frequency part of the DOS is shown, since at half-filling, $A(\omega)$ is an even function of frequency. Figure 10(a) shows that the two approaches give qualitatively and semi-quantitatively the same dependence of the DOS on $U$: at small $U$’s (red curves), it is close to the non-interacting electron Gaussian DOS; at larger $U$’ (green curves), three quasi-bands (actually, peaks of the redistributed electron spectral function) emerge: two Hubbard quasi-bands, with the peaks separated by a frequency $\omega \sim U$ and the central quasi-particle peak around zero frequency. More importantly, such a peak, known to play a very important role in the properties of many SCMs, cannot be obtained with DFT + U and other “non-dynamic” approximations, as shown in Figure 11. Finally, at large $U$’s (blue curves), the system is in a Mott insulator regime with the two Hubbard sub-bands separated by the gap $\sim U$.

Figure 11 Plot of spectral function at intermediate value of parameter $U$, $U=2t$, obtained by DMFT and DFT+U approaches.
The difference between the exact HF-QMC and approximated IPT DOS increases with U, though the shape of the curves remains the same. It is important that the computationally-inexpensive IPT solution gives results similar to the exact ones, except the case \( U = 4t \). A good performance of IPT can be especially beneficial for complex systems with many non-equivalent atoms and orbitals, for which IPT can be used relatively easily as the first approximation to get an intuitive insight on the general features of the XC kernel and even on the properties of the materials. We will focus on the exact HF-QMC results, presenting the IPT solutions, only to gauge its accuracy at different strengths of correlations. We also used the IPT solution to check the temperature dependence of the results (Figure 10(b)). It follows from Figure 10(a) & (b) that the IPT DOS for \( T = 0.16t \) and \( T = 0.05t \) are very similar, except for a large \( U (U = 4t) \). At a lower temperature, the gap opens in the spectrum due to suppression of the central peak, while other parts of the spectrum remain the same. Since in the HF-QMC case, the gap is already open at \( U = 4t, T = 0.16t \), one does not expect to get any difference in the spectrum at lower temperatures, which are computationally much more demanding, within this approach.

### 3.2.2 Charge Susceptibility

As the next step, the excitation spectrum of the system for parameters used in Figure 10(a) is obtained by calculating the imaginary part of the one-loop susceptibility in the local-in-space approximation (Equation (47)), and results are shown in Figure 12.
Figure 12 The imaginary part of the charge susceptibility as a function of frequency obtained with the HF-QMC and the IPT approaches at $U = 1t$, $2t$ and $4t$ and temperature $T = 0.16t$.

It follows from Figure 12 that the excitation spectrum is in agreement with the DOS of the system. That is, at small $U$’s (red), the main excitation processes take place around zero frequency (“Fermi level”) states, at which the DOS has the sharp peak. At medium $U$’s (green), for which the DOS is three-peaked, the excitations mainly take place around the central (“Fermi level”) quasi-particle peak, though now, this peak is much lower compared to the small-$U$ case as a result of reduced zero-frequency DOS. In addition, there is another pronounced type of the excitations at intermediate $U$’s, between the left and right Hubbard sub-bands, revealed in the (not very sharp) peak of $-\text{Im}\chi$ at $\omega \sim 2.4t \sim U$. Finally, at large $U$’s (blue), the excitation spectrum is dominated by the transitions between the Hubbard sub-bands, separated by the energy $\sim U$. Again, qualitatively and semi-quantitatively, the HF-QMC and IPT results are rather similar, which is not surprising since they are the consequence of very similar results for the DOS in Figure 10.
3.3 The XC Kernel

We calculate the XC kernel using Equation (85).

3.3.1 Numerical Solution

In Figure 13, the real (left column) and imaginary (right column) parts of $f_{XC}(\omega)$ are shown for the one-band Hubbard model at different values of $U$ and temperature $T = 0.16t$ obtained by using the IPT and the HF-QMC approaches.

![Figure 13](image)

Figure 13 The real (first row) and imaginary (second row) parts of $f_{XC}(\omega)$ for the one-band Hubbard model at different values of $U$ and temperature $T = 0.16t$ obtained by using the IPT and the HF-QMC approaches.

One can make several conclusions about the qualitative frequency dependence of the XC kernel: (1) the magnitude of the kernel grows with $U$; (2) the real part of XC is a decaying oscillating function of frequency with the oscillation period proportional to $U$; (3) its imaginary
part has one peak at a frequency \( \omega \sim U \) and also decays at large frequencies; (4) in all cases (surprisingly), both the real and imaginary parts decay with approximately the same decay constant \( \sim 10t \). Again, the IPT and the HF-QMC results are in a good qualitative and semi-quantitative agreement with each other. The physical interpretation of the shape of the XC kernel is as follows: in real-time representation, the kernel is an oscillating function of time with the period of oscillations \( \sim U \), which corresponds to scattering between singly- and doubly-occupied “sub-bands” separated in energy by approximately \( U \). The decay constant corresponds to the memory (scattering) time of the system, defined by the XC kernel. Indeed, our kernel includes the effects of time-resolved electron-electron interactions successfully captured by DMFT. Comparison of the results for the XC kernel with another available rare result for the frequency-dependent XC kernel for strongly-correlated systems, namely for a cubic \( 3 \times 3 \) cluster,[96] shows that despite significant differences between the system considered in this work and [96], both kernels share several similarities: a peak in the imaginary part of the kernel and an oscillatory (rather irregular in the case of the cluster) feature of the real part of the kernel, with oscillation and decay periods \( \sim U \) (though in the case of the cluster, the proportionality coefficients are a couple of times larger than in the extended system). Given these generalities, we were motivated to find an analytical (and at least semi-quantitatively correct) frequency-dependent kernel common for systems of different sizes and geometries. It is also important to mention that in constructing an accurate analytical kernel, one also needs to take into account known constraints that come from many-body theory, such as the generalized translational invariance and the zero-force theorem (see [103] for some discussion in this regard).
3.3.2 Analytical Fitting

To accompany the numerical results for the XC kernel in Figure 13 with a simple analytical fitting expression, we begin with the approximate Gross–Kohn XC kernel for the Homogeneous Electron Gas (HEG) [36; 124] with the imaginary part $\text{Im}[f_{\text{XC}}(\omega)] = \frac{a\omega}{[1+b\omega^2]^{5/2}}$ (the real part can be found by using the Kramers–Kronig relation). This kernel has correct analytically derived low- and high-frequency asymptotes obtained for the HEG (see also [125] for an over-review of the subject).

Since the imaginary $f_{\text{XC}}(\omega)$ has intercept on ordinate whose value depends on value of correlation, we start with an expression

$$\text{Im}[f_{\text{XC}}(\omega)] = \frac{a(\omega+\alpha)}{[1+b\omega^2]^{5/4}},$$

which has 3 fitting parameters $a$, $\alpha$, and $b$.

At $\omega = 0, f_{\text{XC}}(0) = aa$,

$$\alpha = \frac{f_{\text{XC}}(0)}{a}.$$  \hspace{1cm} (122)

Substituting Equation (122) into Equation (121)

$$\text{Im}[f_{\text{XC}}(\omega)] = \frac{a(\omega+f_{\text{XC}}(0))}{[1+b\omega^2]^{5/4}},$$

(123)
Let \( b_0 \left[ 1 + \frac{U^2}{\delta^2} \right] = b \).

To use the minimum value of \( \text{Im}[f_{XC}(\omega)] \), after differentiating it with respect to \( \omega \) and taking \( \omega_m \) as the value of \( \omega \) at which the minimum exists, the solution gives value of \( b \) as

\[
\frac{1}{2\omega_m^2 + \frac{5}{2} \frac{f_{XC}(0)}{a} \omega_m} = b_0 \left[ 1 + \frac{U^2}{\delta^2} \right],
\]

and the minimum value of \( \text{Im}[f_{XC}(\omega)] = f_m \) becomes

\[
f_m = \frac{a(\omega_m + \frac{f_{XC}(0)}{a})}{\left\{ 1 + b_0 \left[ 1 + \frac{U^2}{\delta^2} \right] \omega_m^2 \right\}^{\frac{5}{2}}},
\]

For known values of \( \omega_m, f_{XC}(0), \) and \( f_m \), Equation (124) and Equation (125) give \( a \) and \( b \), which when substituted in Equation (122) gives value of \( \alpha \). For given value of \( U \), one can calculate the value of \( \delta \) by taking any two values of \( \omega \) and their corresponding values of \( \text{Im}[f_{XC}(\omega)] \) in Equation (123). But since the values of other quantities depend on the values of \( \delta \), it becomes a self-consistent calculation of all parameters. It appears that one can reproduce the numerical curves in Figure 13 reasonably accurately by using the following simple kernel:

\[
\text{Im}[f_{XC}(\omega)] = \frac{(a \omega + \text{Im}[f_{XC}(0)])}{\left[ 1 + \frac{5}{2} b^2 \omega^2 \right]^{\frac{5}{2}}} \left\{ e^{-U \omega / 12} + \left( 1 - e^{-U \omega / 12} \right) e^{-U \omega^4 / 576} \right\},
\]

which is obtained by multiplying the Gross–Kohn kernel by the term consisting of two exponential parts and shifting the zero-frequency value (Figure 14). The fitting parameters at different \( U \)'s are given in Table 1.
Figure 14 HF-QMC and analytical fitting results for the imaginary parts of the XC kernels from Figure 13.

Table 1 Fitting parameters for the analytically-approximated expression for the imaginary part of the XC kernel at different values of $U$.

<table>
<thead>
<tr>
<th>$U/t$</th>
<th>$a$</th>
<th>Im$f_{xc}(0)$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−0.40</td>
<td>1.56</td>
<td>0.14</td>
</tr>
<tr>
<td>2</td>
<td>−1.32</td>
<td>1.93</td>
<td>0.09</td>
</tr>
<tr>
<td>4</td>
<td>−1.14</td>
<td>22.42</td>
<td>0.01</td>
</tr>
</tbody>
</table>

From the fitting formula, it is clear that the kernel decays faster with the frequency growth when the electron charge density is strongly nonhomogeneous (in SCMs, it is mostly localized around the atoms, i.e., the situation is opposite that for HEG). Such a difference between the kernels of the homogeneous and nonhomogeneous electron gases might be explained by stronger scattering effects at short times (large frequencies) in the nonhomogeneous case (since the scattering time is proportional to $1/U$), which leads to a weaker dependence on frequency at large frequencies. Otherwise, the structures of the kernel are rather similar.

Further, thorough examination of the structure of the DMFT XC kernel for SCMs, especially for systems with reduced dimensionality and/or many electron orbitals, is needed in
order to arrive at an analytical formula for $f_{\text{XC}}(\omega)$ that is proven to be accurate. However, despite the over-simplified fitting above, one can already get an intuitive feeling of the connection between the frequency dependence of the XC kernel and the strong spatial non-homogeneity of the electronic charge distribution (charges localized around the atoms).

### 3.4 Applications: Ultrafast Charge Response

As the first application of the kernels in Figure 13, we analyze the charge response of the Hubbard system excited by a homogeneous electric laser pulse (the electric field $E(t) = E_0 e^{-t^2/\tau^2}$, the field magnitude $E_0 = 0.1$ eV/Bohr, the pulse duration $\tau = 0.8$ fs). Here and in the next subsection, we solved Liouville Equation (75). The results for the excited change density in the case of different $U$’s and approximations for the XC kernel are shown in Figure 15.

Figure 15 Time dependence of the excited charge density in the one-band Hubbard model in the case of 0.8-fs laser pulse perturbation at $T=0.16t$ at different values of $U$ and adiabatic (A) and non-adiabatic (NA) exchange-correlation (XC) kernels.

Several conclusions can be made from Figure 15. First, the electrons get “quasi-ballistically” excited during the pulse excitation. Then, the excited charge density starts to decrease, but at the time scale an order of magnitude longer, as compared to the charge
pumping time. This indicates that the main process at this stage is not repopulation of the lower band, but excitation relaxation of the electronic system to a new quasi-equilibrium state with high electronic temperature. The duration of this process strongly depends on the value of $U$ and may vary from several to hundreds of femtoseconds. These results are in a qualitative and (very probably) semi-quantitative agreement with recent experimental results on the ultrafast breakdown of the Mott insulating state in VO$_2$ [126], where at initial times, the electronic and lattice subsystems are disentangled (i.e., the lattice is frozen at times below $\sim$100 fs), and the metallization happens without the lattice transformation. The last process takes place on a ps to ns time scale, when the lattice undergoes a transformation to the stable (metallic, high-temperature) rutile phase. Theoretical analysis based on the solution of phenomenological (spatially-averaged) Bloch equations is also in agreement with this scenario [127]. The advantage of the TDDFT + DMFT approach is that it can be easily applied to study also a spatially non-homogeneous response by properly taking the exact electronic structure of the material. To study the longer time response, one needs to include the lattice dynamics, which is one of our primary tasks for the near future. On comparing the results for the system response for different XC kernels, one can find from Figure 15 that the HF-QMC gives a faster relaxation of the system, though the order of the timescales of the excitation and relaxation stages for both HF-QMC and IPT solutions are the same. Finally, the difference between the solutions with the full kernel and its instant (adiabatic) approximation is discussed, when the non-adiabatic effects are neglected, i.e., when $f_{\text{XC}}(t - t') \sim \delta(t - t')$ or the kernel is frequency independent. This is the case of the DFT + U approximation. It follows from our calculations above that the memory (dynamical) effects slow down the relaxation of the system, since the
scattering is more efficient on “frozen” electrons (for the complex role of “movable” and “frozen” (heavy) charges and between both subsystems, see, e.g., [128]). Thus, it appears that consideration of non-adiabaticity is important even at the femtosecond time scale.

3.5 Conclusions

The key element of the TDDFT+DMFT theory, the XC kernel, applicable for SCMs is defined by the DMFT self-energy of the electron. The main features of the dependence of the kernel on frequency is established by solving the DMFT equations exactly with HF-QMC and by using an approximate (IPT) approach and demonstrated that both results are in reasonable agreement, which makes the computationally-efficient IPT solver attractive for initial considerations of systems of interest. We also proposed a simple analytical expression for the XC kernel. We used the XC kernels calculated with both approaches to study the ultrafast electronic response and found that the inclusion of the non-adiabatic, or memory, effects significantly modifies the femtosecond response.
CHAPTER 4: APPLICATION OF TDDFT+DMFT METHOD: ULTRAFAST MAGNETISM ON BULK Ni

In this chapter, the ultrafast charge and spin dynamics in bulk ferromagnetic Ni excited by a laser pulse is analyzed using a combined Time-Dependent Density-Functional Theory and Dynamical Mean-Field Theory (TDDFT+DMFT) approach that takes into account electron-electron correlations and non-adiabatic effects via a newly developed exchange correlation kernel. It is shown that the TDDFT+DMFT results for the time-dependent demagnetization of the system are much closer to experimental data than those obtained from the standard adiabatic TDLDA method, which in most cases underestimates the change of the magnetization. Apart from attesting to the importance of non-adiabatic (memory) effects, the calculations show that the ultrafast demagnetization results mainly from spin-flip transitions from occupied to unoccupied orbitals implying a dynamical reduction of exchange splitting. The conclusions above are found to be valid for a large range of laser pulse parameters: amplitude, energy, and duration.

4.1 Introduction

Ultrafast tuning of the magnetization in transition-metal ferromagnets by short laser pulses is an intense topic of research because of possible applications in ultrafast data storage, switches, and spintronics, to name some. The unusual accompanying physical effects, such as a very fast-femto-second- demagnetization and possible non-trivial combined contribution of the electron, spin and lattice subsystems to the response, including orbital momentum transfer between the subsystems, have also called for theoretical explanations (for an over-review, see Ref.[129]). Beginning with the pioneering experimental work of Beaurepaire et al. on
nickel,[18] which displays an ultrafast (femtosecond) demagnetization when excited by an ultrashort laser pulse, the subject continues to be examined both experimentally and theoretically. Based on experimental observations[18; 130-140], it is now well-established that the laser-induced demagnetization in bulk and thin film ferromagnetic Ni takes place at the sub-picosecond time scale. Theoretical studies have attempted to provide an understanding of the factors connecting this demagnetization to the electronic and spin structure of the system. Probably the simplest is the phenomenological three-temperature (3T) model introduced in ref. [18], in which the magnetization dynamics is characterized by an effective spin temperature, which equilibrates through energy exchange between the spin subsystem with the electron and phonon baths. Although this model can be used to fit experimentally measured electron and spin temperatures, it does not provide a microscopic understanding of the processes involved in the demagnetization, except for the possible role of phonons which occurs at the post picosecond stage. A modified 3T model that includes spin-relaxation in the form of Elliot-Yafet[141; 142] phonon-mediated scattering (that leads to a dissipation of the angular momentum)[143] thus concluded that thermalization of the electron system is required to obtain the experimentally observed ultrafast demagnetization. Other studies [140; 144] concluded that spin-phonon interaction is the reason for the demagnetization on the picosecond (ps) or longer timescales. Employing dynamical feed-back exchange splitting model[145] it was argued that the spin-flip scattering effects are needed to be included in order to properly describe the magnetization dynamics at the ps timescale.

In the experiments of Gudde et al., however, the magneto-optical signal decays already in 50fs [132], much before the involvement of lattice phonons. To account for this ultrafast decay,
Zhang et al. [146] analyzed the problem using a model Hamiltonian that did not include a phonon-assisted spin relaxation and concluded that the demagnetization is a combined effect of the external laser field and the spin-orbit coupling in the system, a conclusion later corroborated in Ref. [140]. These Hubbard-model based studies [146-148] have also aimed at understanding the role of electron correlations in the demagnetization. However, the interaction parameters (fitted to the spectroscopic data) used in these are quiet different from those obtained computationally[149; 150], which when used by Lichtenstein et al.[151] in DMFT calculations provided good agreement with experimental data on the Ni Curie temperature and high temperature magnetic moment.

In Ref.[140] , the authors have shown the coherent coupling between the magnetic and optical response in demagnetization process. On the other hand, in ref.[138] it was experimentally shown that the demagnetization involves a femto-second quenching of the electron spins and their subsequent transfer to the lattice. Another possible reason for the demagnetization is an ultrafast laser pulse-induced change of the magnetic exchange splitting (an ultrafast modification of the band structure for both spin-up and spin-down electrons). In particular, time-resolved photoemission spectroscopy measurements on Ni films on W(110)[135] demonstrated a collapse of the magnetic exchange splitting under laser-pulse excitation due to an electron-spin energy transfer during times from 300fs to 2ps, depending on other involved excitations (i.e., magnons).

Thus, as it follows from different phenomenological model studies, electron, spin and lattice subsystems together with photons can contribute to different, often excluding each other,
scenarios of the ultrafast demagnetization in Ni. To describe the demagnetization dynamics in materials in a “non ad hoc” (parameter free) way, *ab initio* approaches, including TDDFT, that take into account important microscopic properties of the system, such as spatially-resolved screening, multi-orbital effects, etc. have also been applied to study this problem of time dependent demagnetization. One of the most popular DFT approaches is the method of the rigid band approximation with fixed band structure (and hence with fixed exchange splitting, see, for example, ref. [19]). However, there are some serious indications[152] that this approximation cannot reproduce the experimental data. In the case of spin DFT, it was shown that magnon-electron interaction plays an important role in the demagnetization.[153] Among the works that employ TDDFT, that with the local density approximation (LDA) for the exchange-correlation kernel [154] showed that after excitation both spin-up and spin-down (majority and minority) bands shift towards the Fermi level, reducing the exchange splitting. This reduction corresponds to 10% or less decrease of the spin moment of Ni atoms, which is significantly below the experimental value (~57% [18]) suggesting that non-adiabaticity can be important. Another adiabatic, spin TDDFT, study based on the non-collinear local spin density approximation for the XC potential, [155] demonstrated that the demagnetization in Ni can take place in a few dozens of femtoseconds. Large decrease of the magnetic moment (~43%) in Ni under an applied laser pulse was shown to be a result of spin flipping of the initially excited electrons because of spin-orbit interactions with the remaining non-excited electrons (as a matter of fact, to a similar conclusion was reached for Fe [156]). However, the pulses amplitude used in the work [155]were much stronger that the ones used experimentally.
Thus, the question whether TDDFT can describe the demagnetization in the case of experimentally-used pulses remains open.

To answer this question, one needs to take additional elements into account beyond the present TDDFT investigation. Among them, one of the most important ones is the strong electron-electron correlation effect, relevant in the case of transition metals with partially-filled d-orbitals. Another open question is the role of the memory effects in the process of demagnetization. Indeed, since the corresponding electron transitions take place at the fs time scale, the time-resolved details of these transitions can be very important (see, e.g., Ref.[157]). For example as it was shown in the case of Au clusters,[43] the memory effects significantly modify the plasmonic properties of these systems.

While the role of the memory effects in the ultrafast demagnetization of Ni was overlooked by the theoretical and computational communities, the electron correlations attracted attention of theorists that analyzed them in the framework of many-body theory. In particular, in a set of papers (see, e.g., [146-148]) Zhang et al. have raised the question of whether the electron-electron correlations can affect the initial magnetization dynamics, and questioned the roles of the spin- versus orbital momentum in the magnetization dynamics by using an effective Hubbard model. In these studies some rather serious approximation to solve the Hubbard model, like the exact diagonalization with the two excited hole basis, was made. On the other hand, it is known that to include properly the correlation effects in Ni, like to describe the photoemission spectrum of the material (see, e.g., ref. [84]), one needs to use the DMFT solution for the Hubbard model in the framework of the ab initio+many body DFT+DMFT
approach. As it was also shown in the works [151; 158; 159], one needs to include strong correlations in DMFT in order to reproduce a satellite peak in the DOS at ~-6eV (for a recent DMFT result showing that alternatively the non-local correlations can be important, see Ref. [160]). DMFT is shown to be the state-of-art approach to study the systems where strong electron correlation effects. Its success is from properly taking into account local-in-space (i.e., on-site) time-resolved charge interactions, that play the dominant role in the physics of such materials [45, 47].

These facts are some of the our motivation to analyze the problem within our recently proposed non-adiabatic TDDFT+DMFT approach [15; 17]. This approach is a pure charge TDDFT theory, i.e. simpler than spin TDDFT used in ref. [153]. In TDDFT+DMFT, the static properties of the system, like band structure that defines photoemission spectrum, are treated with DFT+DMFT, i.e. taking into account strong electron-electron correlations, while the dynamics, including demagnetization processes, is analyzed with a non-adiabatic TDDFT with the XC kernel obtained from the DMFT charge susceptibility. Besides inclusion of the correlation effects, we have another goals with DMFT XC kernel applied to analyze the magnetic response of Ni at the femtosecond time scale – the orbital-resolved spin dynamics. As demonstrate below, both strong electron correlations and the non-adiabaticity (memory) effects play an important role in the multi-orbital magnetic response of the system. Naturally, the approach is valid only at the fs time scale, where the lattice effects can be neglected. To include them one needs to consider the dynamics at longer times (for a combined effect of the electronic and structural dynamics on the demagnetization in Ni, see a recent paper [161]).
4.2 Computational Details

DFT calculation

As the first step in the TDDFT+DMFT approach, a spin-polarized DFT[24; 25] calculation is performed to obtain the electronic properties of the “non-correlated” system: the spin-resolved orbital DOS, the band structure and the corresponding Kohn-Sham eigen functions. For the DFT calculations, the Quantum Espresso package[162] is used with the PBE XC potential,[163] the ultra-soft pseudopotentials, the energy cutoff 35 Ry, and the 15x15x15 k-points mesh for the face centered cubic unit cell (one atom in the cell). Using the total energy and the force convergences of $10^{-4}$ Ry and $10^{-3}$ Ry/Å, respectively, the lattice constant was found to be 3.52Å, in agreement with the experimental data[164] and previously reported DFT calculation [165; 166]. In the post-processing calculations of the DOS, 20 bands were used.

DFT+DMFT calculation

The static “correlated” properties of the system were calculated by solving the many-body problem, described by the Hubbard multi-band Hamiltonian (Equation (22)) for the subsystem of the d-electrons. The following often-used values for the on-site Coulomb repulsion parameter (U) and the exchange parameter (J) are chosen for the Hamiltonian for bulk Ni: U=3.0 eV, J=0.9eV (see, e.g., refs. [151; 166] where these values were obtained by using constrained DFT calculation [149; 150] and also ref. [167], were it was argued that such values are needed to properly describe the effects of the electron-electron correlations in the system). So, $U= 3$ eV for two electrons on the same orbital with different spins; $U - J$ for different orbitals with the different spins and $U-2J$ for the different orbitals with the same spin. The
Equation (22) is solved by finding the spin- and orbital-dependent single-electron Green’s functions $G^{\sigma\sigma}_{\sigma\sigma}(\mathbf{k}, \omega)$ within DMFT[11; 12], where the self-energy of the interacting electrons $\Sigma^{\sigma\sigma}_{\sigma\sigma}(\omega)$ is assumed to be frequency-dependent and local-in-space (momentum-independent). Locality in space of the self-energy allows one to map the problem on the single-impurity problem that can be solved numerically with a reasonable computational costs. In this study, we solve the impurity problem approximately using the multi-orbital iterative perturbation theory (MO-IPT) approximation.[13] Detailed information on the DFT+DMFT approach can be found elsewhere, [117] here we describe only the following important steps. The lattice model, Equation (22), is self-consistently mapped on a multi-orbital Anderson impurity model requiring that the local impurity Green function is equal to the local Green function on the lattice (Equation (37) for which the electron spin-orbital self-energies are defined in the MO-IPT approximation using Equation (139). So, the Equations (37), (38), and (139) are solved in a more convenient Matsubara (imaginary) frequency representation, with $i\omega_n = i\pi T(2n + 1)$ being the discrete Matsubara frequencies, $T$ – temperature keeping 0.02eV (216 K), and $n$ – integer numbers refers number of the Matsubara frequencies. To choose the proper number for $n$, the DMFT solution is tested by simulating the temperature dependence of the magnetization. It is found that for 250 frequencies, the magnetic moment $0.64\mu_B$ decreases with increasing temperature and becomes zero at temperature $T_c \approx 627K$, in a good agreement with the experimental value of Curie temperature of 631K [164] (Figure 16).
Real-frequency dependencies of the Green’s function and other functions can be found by performing analytical continuation as $i\omega_n \rightarrow \omega + i\delta$, where $i\delta$ is a small imaginary term. In this paper, the analytical continuation is performed by using the Pade approximation approach[168] explained in Appendix C. Once DMFT Green’s functions are found, the orbital spectral functions are calculated using Equation (41) and the excitation spectrum of the system from the imaginary part of the DMFT on-site susceptibility, Equation (50).

**TDDFT calculation**

The susceptibility function is then used to calculate the frequency-dependent part of the DMFT XC kernel using Equation (85) that is used in the TDDFT calculations to get local in space XC kernel ($f_{xc}(r, t, r', t')$) as

$$f_{xc}(r, t, r', t') = A\delta(r - r')f_{xc}^{DMFT}(t - t'),$$  \hspace{1cm} (127)
with $f_{xc}^{\text{DMFT}}(t - t')$ is the Fourier transform of the kernel in Equation (85) and the parameter $A$ (see Appendix D for derivation of its expression) represents the strength of the on-site Coulomb repulsion calculated in the DMFT XC kernel corresponds averaging of the following matrices over the orbital and spin variables:

$$A = \int d^3r \phi_k^{l(0)*}(r) \phi_k^{m(0)}(r) \phi_q^{n(0)*}(r) \phi_q^{s(0)}(r), \quad (128)$$

($\phi^{0}(0)$ are the Kohn-Sham wave functions, with top indices corresponding to the bands and bottom ones to the momenta). The calculated values of $A$ for the DMFT kernels is 0.05. We also perform calculations with the adiabatic LDA XC kernel, where the frequency dependent part of the kernel is delta function and

$$A = \int d^3r \phi_k^{l(0)*}(r) \phi_k^{m(0)}(r) \frac{1}{(9\pi n(r)^2)^{\frac{1}{3}}} \phi_q^{n(0)*}(r) \phi_q^{s(0)}(r), \quad (129)$$

The calculated values of $A$ for the LDA kernel is -0.06. The external potential is chosen in the form $v_{\text{ext}}(r, t) = d.E(t)$ ($d$ is the dipole moment) and the time-evolving electric field is approximated to be spatially uniform in the mathematical form

$$E(r, t) = E_0 e^{-\frac{t^2}{\tau^2}} \cos(\omega t), \quad (130)$$

where $E_0, \tau$ and $\omega$ represent the field intensity, duration, and frequency respectively of the laser field. Dipole moment in each direction is calculated using

$$d = \int d^3r \phi_k^{l(0)*}(r)r \phi_q^{s(0)}(r), \quad (131)$$
where l, s refer band indices, k, q refer momentum indices and \( \varphi^{(0)} \) refers to the static Kohn-Sham eigen functions. Once memory dependent XC term and the external field term are known, dynamics of the spin-orbital occupancies is obtained by propagating density-matrix TDDFT Equation (75).

4.3 Results

4.3.1 DFT+DMFT Solution: Electronic and Magnetic Properties

The DFT and DMFT spin-orbital resolved DOS for the d-orbitals are shown in Figure 17. As it follows from Figure 17, the degeneracies of the DFT bands survive also in the DMFT case.

![Figure 17](image)

Figure 17 The DFT (dashed lines) and DFT+DMFT (continuous lines, \( T=216K \)) spin-orbital resolved density of states of bulk Ni.

As an effect of the local Coulomb interaction, DMFT solution shifts the DFT peaks to the left with respect to \( E_F \). The magnetic moments of the nickel unit cell are 0.64\( \mu_B \) (DFT) and 0.563\( \mu_B \) (DMFT), which is close to experimental value of 0.57\( \mu_B \) [169], and different theoretical results: 0.55\( \mu_B \) (GW)[170], 0.57\( \mu_B \) (KKR-DMFT),[171] and more different from the reported
value of $0.47 \mu_B$ obtained with the LDA+DMFT-IPT [166] (probably, due to different DFT XC potential), and $0.42 \mu_B$ [172] that comes from the EMTO-DMFT calculations and ARPES measurements[173; 174]. The reduced DMFT magnetic moment in comparison to DFT value is due the reduction of the number of the spin-up electrons from 4.56 to 4.48 and increase of the spin-down electrons from 3.90 to 3.98 that comes, in particular, from the frequency dependence of the on-site self-energy. As can be notices in Figure 17, down spin $d_{xy}, d_{yz}, d_{zx}$ orbitals have unoccupied peak close to the Fermi level, which is suppressed in DMFT spectrum.

The DMFT excitation spectrum is shown in Figure 18(a). As it follows from this Figure, the excitation spectrum covers a rather wide range of frequencies, suggesting a complex response of the system to external perturbations. The presence of the satellite peak at ~5eV in the DMFT excitation spectrum in Figure 18(a) (see also the inset) is the well-known satellite peak in Ni spectrum[175; 176] that is missed in the DFT spectrum.

![Figure 18](image)

Figure 18 (a) The DMFT excitation spectrum, (b) time- dependence of the DMFT XC kernel of bulk Ni.
In Figure 18(b) we show the time-dependence of the DMFT XC kernel for Ni. As it follows from Figure 18(b), the memory effects in the system are important for times \( \sim 1.5 \text{fs} \), though the oscillating tail of the kernel spreads up to much longer times, and will appear to be rather important for the system response.

### 4.3.2 TDDFT Solution: Ultra-fast Demagnetization

![Graph of demagnetization dynamics](image)

Figure 19 The demagnetization dynamics obtained for the free particle (green curve), adiabatic LDA fxc (blue curve) and non-adiabatic TDDFT+DMFT \( f_{XC}(\omega) \) (red curve) with the laser pulse (black curve) with the amplitude 0.05V/Å, duration 7.2fs and energy 2eV.

As it follows from the calculations, for a pulse with parameters give in the caption to Figure 19, the change in magnetization obtained with the adiabatic TDLDA with is about \( 0.002\mu_B \), in a close agreement to the value reported in ref. [19] obtained also with the adiabatic TDLDA and the same intensity and frequency of the pulse, but slightly different duration of the laser pulse. The demagnetization is only 0.3% of reported experimental value. Using the non-adiabatic DMFT XC kernel, we get a significantly larger change of the magnetization, which is 34% of initial static magnetization for which the experimental value reported in ref. [18] is 57%. This indicates importance of the memory effects in the ultrafast properties of Ni. Note
that we are limited to time-scale of 8fs at current implementation due to necessity to integrate Liouville Equation (189) in non-Markovian approach by considering every early time point to integrate for a given time point taking hundreds of time grid points to avoiding blowing up of solution.

Figure 20 Orbital and spin resolved excited charge density dynamics for the pulse shown in the bottom. (b) Excited charge density dynamics that includes only selected spin transitions.

In Figure 20 (a), the spin-resolved results for the excited charge density dynamics is shown in the case of DMFT XC kernel, indicating stronger response of the \(d_{xy}, d_{yz}, \) and \(d_{zx}\) electrons as compared to the \(d_{z^2}, d_{x^2-y^2}\) charges. Note that the plot offers only qualitative understanding since the effect of only a pair orbitals in a specific combination, for e.g., up to up or so on, is considered on each calculation. As it follows from Figure 20 (b), the charge excitation happens mainly due to excitation of from up or down spin orbitals into spin down orbitals. The density of excited charge from spin-up to spin-down orbitals is higher than from the occupied to unoccupied spin-down orbitals, which indicates importance of the spin-
flipping processes (that may involve spin-orbit coupling to remaining localized electrons (see, e.g., ref.[34])) and a dynamical reduction of the spin-exchange.

Figure 21 The time-dependence of the TDDFT+DMFT demagnetization at different (a) field amplitude, (b) pulse duration, and (c) the pulse frequency and other pulse parameters shown in the previous figure.

Further analysis of the pulse dependence of the demagnetization (Figure 21), show strong dependence of the demagnetization on the pulse parameters. This conclusion agrees with the experimental data for different pulse [143; 177; 178] and pump fluences.[179] On the other hand, one might expect importance of the phonons at longer times,[143] which makes the demagnetization independent of the field strength[154] and requires studies beyond the pure electron scenario.

4.4 Conclusions

In this work, we have performed a TDDFT+DMFT analysis of the demagnetization dynamics in bulk Ni after perturbation by a laser pulse. It is demonstrated that strong electron-electron correlation effects lead to a significant change of the spin-down density of states at
the Fermi level, which results in an increased change of the magnetization as compared to the DFT results. On the other hand, the non-adiabaticity (memory) effects play an important role in the femtosecond dynamics and also lead to a significant increase of the demagnetization as compared to the adiabatic results.

There are some open questions that need to be answered in the framework of TDDFT+DMFT, and probably the most important of them is strongly non-linear response (when one needs to go beyond the XC kernel approximation) and the longer-time dynamics, which requires efficient implementation of the formalism. In addition, implementation of exact CTQMC solver of impurity problem in multi-orbital formalism, which is under development, enhances the reliability of the TDDFT+DMFT approach.
CHAPTER 5: APPLICATION OF TDDFT+DMFT METHOD: CHARGE EXCITATIONS AND ULTRAFAST DYNAMICS ON BULK MnO, AN INSULATOR

In this chapter, the results of exploration of ultrafast d-electron dynamics in the insulating antiferromagnet MnO when perturbed by a laser pulse are presented. To take properly into account the effects of electron correlations, \textit{ab initio} (TDDFT+DMFT) \cite{15, 16} approach is used. Details of the ultrafast charge dynamics allowed to identify the main channels of the charge response, dominated by the inter-orbital d-electron transitions. In addition, analysis of the excitation spectrum of the system demonstrates the existence of bound excitonic states with rather strong binding energy in an order of 100meV.

5.1 Introduction

The advances in ultrafast science has opened the possibility of investigating the non-equilibrium dynamics of charge, spin, and orbital degrees of freedom that enables to develop understanding on many fundamental questions in condensed matter physics and shows phenomena that otherwise are not seen on the equilibrium state. Transition metal oxide (TMO) systems that possess number of unexpected features including being in insulating state at static case, although they have partially filled 3d orbitals set them as new kind of materials with new possibility that might be of technological importance. On the other hand, they possess considerable theoretical challenge since successful approaches that can reproduce the static experimental properties of other conventional materials cannot reproduce their experimental properties for e.g., the band gap and the photoemission spectra, .Improper treatment of localized d-orbital electrons is one of the problem and so requires to rely on methods that can
handle the itinerant s- and p- electrons and localized d-electrons properties explicitly in formulation. Using those approaches it is now established that most of the peculiar static properties of such systems are consequence of localized d-orbitals of the system. In addition, there are experimental observation that show the possibility to manipulate the band gap of these materials used in solar cells or photo catalysts by manipulating the d-band of the transition metal atom [180-182] [183-187]. It is common understanding that the adsorption intensity in solar spectral region and the dynamics of photo-induced carriers on those systems depend on the d-electron dynamics. Due to localization effects, photo excited d-electron may behave rather differently from the free-carrier-like electron that occupy s- and p- bands in those materials. In spite of those fundamentally different features of d-electrons, the d-electron dynamics in transition metal oxides remains rather poorly understood topic. Therefore, it is important to investigate the relaxation dynamics of d-electrons on TMOs.

Following the success of methodologies that take short range Coulomb interaction directly into calculation to explain the static properties of such systems, their extension to the time-dependent case is a straightforward choice. Introduction of dynamical variables makes the study of those systems more complex. Many-body approaches to study non-equilibrium dynamics on those systems have limitation due to the computational complexity. In this scenario, time-dependent density functional theory (TDDFT) is a viable alternative but it requires approximation for an exchange-correlation (XC) potential. Failure of the prevalent LDA and GGA approximation of XC potential to reproduce the experimentally measured features of the TMO systems at static calculation implies that the prediction of non-equilibrium properties of those SCMs are even more off. Success of many-body dynamical mean field
theory (DMFT) approach to tackle the localized d-electrons in combination of DFT method for its input (DFT+DMFT method, as explained in section 2.1.2.3) to reproduce correctly the experimental properties of such TMO systems implies to have necessary inputs in the non-equilibrium study from that approach. In this study, we apply the TDDFT +DMFT approach to study the d-electron dynamics of TMO that calculate the XC potential necessary for TDDFT approach based on the DMFT approach. On the best of my knowledge, there is not any study dealing with the dynamics of the d-orbital occupancy on TMOs. Manganese oxide (MnO) is the simplest and representative of 3d TMOs in antiferromagnetic insulating state in which the exchange-splitting of the d bands is more than the d-band width and 5 valence electrons of Mn$^{2+}$ half fill each of the $t_{2g}$ and $e_g$ orbitals making MnO a Mott insulator [188; 189]. Using optical pump-THz probe (OPTP) measurement, Nishitani et al.[20] observed various features in the d-electron dynamics on MnO: (a) significant charge excitation with a no time delay observed in picosecond spectroscopy, (b) longer excitation of electrons excited in the first d-state in the antiferromagnetic phase of MnO in comparison to higher excited states, and are interpreted as due to the formation of excitonic state during the de-excitation from 1$^{st}$ excited state. Obtaining microscopic understanding on the photo excited d-electron dynamics including relaxation time is therefore of great importance. In addition, we report here the binding energy of exciton.

5.2 Computational Details

At an initial step, spin-resolved DFT calculation in Kohn-Sham formulation is preformed using PBE functional for exchange-correlation (XC) potential and ultra-soft norm-conserving pseudopotential for the core valence interactions in Quantum Espresso package. The structural
model of bulk MnO system consists 32 Mn atoms and 32 O atoms arranged in rock-salt unit cell structure as shown in Figure 22. Note that the unit cell contains double of the number of atoms as required for chemical unit cell due to antiferromagnetic arrangement of Mn atoms. The valence electron wave functions are expanded in plane-wave basis set taking an energy cutoff of 80 Ry and k points mesh density is taken 5x5x5. Structure optimization is carried out with the total energy and force convergence of $10^{-4}$ Ry and $10^{-3}$ Ry/Å, respectively. To calculate the free electron spectrum and its corresponding Green function to start the self-consistent DMFT calculation, spin-polarized non-SCF calculation is performed taking 450 number of bands and denser 7x7x7 k-points grid, however, we don’t get any difference from 5x5x5 case. The density of states obtained by taking an energy cut off of 70 Ry is found to be same as while using 50 Ry cut off.

The correlated d electrons of Mn on MnO are calculated by solving the Hubbard multi-band Hamiltonian (Equation (22)). In the self-consistent DFT+DMFT calculations, the numerical values[7] of $U=6.9\text{eV}$ and $J=0.86 \text{ eV}$ are chosen which are obtained by the constrained LDA method[190], which are also used for other studies of the system [191]. Equation (22) is solved in DMFT approach in which the self-energy of interacting electrons is assumed to be function of frequency but not of spatial coordinates i.e., $\Sigma_{ij}(i\omega_n) = 0$ for $i\neq j$ which is a reasonable approximation for localized orbitals and is exact in infinite dimension, so that the problem of locally interacting electrons on a lattice in the multi-band Hubbard model is mapped to the numerically solvable single impurity Anderson model. In this study, the impurity problem is solved approximately using the multi-orbital iterative perturbation theory (MO- IPT) (see
Appendix A). The DMFT problem is solved self-consistently by requiring that Green function of the local impurity problem is the same as the local Green function of the lattice problem (Equation (37)). So, we solve the Equations (37), (38), and (139) in a more convenient Matsubara (imaginary) frequency representation, with $i\omega_n = i\pi T(2n + 1)$ being the discrete Matsubara frequencies, $T$ – temperature keeping 0.0022eV (22.8K), and $n=250$ is the number of the Matsubara frequencies. Real-frequency dependencies of the Green’s function and other functions can be found by performing analytical continuation as $i\omega_n \rightarrow \omega + i\delta$, where $i\delta$ is a small imaginary term. In this study, the analytical continuation is performed by using the Pade approximation approach[168] explained in Appendix C. Once DMFT Green’s functions are found, the orbital spectral functions are calculated using Equation (41) and the excitation spectrum of the system from the imaginary part of the DMFT on-site susceptibility, Equation (50). The space dependence of kernel (kernel strength A) calculated using Equations (128) & (129) comes out to be 0.06 and the calculated value of the dipole moment using Equation (131) comes out to be 1.0.

The density-matrix TDDFT Equation (75) is propagated to calculate the dynamics of the spin-orbital occupancies for given XC and external potential in dipole approximation. Since the XC term is density dependent, not density matrix, when we assemble the density, only the diagonal element $\rho_{i,i,k}$ are considered and calculate charge density using $n(r, t)= \Sigma_{i,k} \rho_{i,i,k}$. To calculate the density matrix elements, we take the product of bands that are 1.0
eV below and above the Fermi energy. To make fine grid, we divide the time of 16 fs into 1200 intervals of equal width.

5.3 Results

5.3.1 DFT: Geometrical,Electronic, and Magnetic Structures

Figure 22 Unit cell of bulk MnO in NaCl structure consisting of two interlaced fcc (111) lattices consisting of Mn and O such that each Mn atom has six O neighbors. Lines with arrow head shows the ordered arrangement of spins of the Mn$^{2+}$ ions in MnO.

Calculated values of various structural, magnetic, and electronic properties of MnO within DFT are presented in Table 2 along with the reported experimental values. The lattice constant is within 3.5%, the rhombohedral distortion angle, and total magnetization are exact with the experimental value whereas band gap is 25% off from the experimental value.

Table 2 The calculated values of various ground state quantities and the values reported experimental values of the corresponding quantities.

<table>
<thead>
<tr>
<th>Physical Quantity</th>
<th>DFT calculation</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>4.60</td>
<td>4.44[192]</td>
</tr>
<tr>
<td>Band Gap (eV)</td>
<td>4.5</td>
<td>3.6-4.2</td>
</tr>
<tr>
<td>Rhombohedral distortion angle: α</td>
<td>0.62$^0$</td>
<td>0.62$^0$ [193]</td>
</tr>
</tbody>
</table>
The orbital and spin resolved density of states are shown in Figure 23. In Figure 23(a), the spin-resolved density of states of MnO is shown by multiplying DOS of spin down components by -1. The symmetry of up and down spin DOS implies that the system is in antiferromagnetic state, which is also reflected with the total magnetization value of 0 in Table 2.

<table>
<thead>
<tr>
<th>Total magnetization ($\mu_B$)</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute Magnetization ($\mu_B$/atom)</td>
<td>4.88</td>
<td>4.79</td>
</tr>
</tbody>
</table>

Figure 23 Spin-orbital resolved density of states of bulk MnO calculated using density functional theory method.

From Figure 23 (a), one can see that MnO is in insulating phase owing to lack of any states at the Fermi level. In addition, the occupied bands are within a narrow energy range from Fermi level. In Figure 23(b), the different orbitals resolved density of states of one Mn and one O atom of MnO are shown. The partially filled 3d orbitals of Mn atom energetically overlap with the oxygen 2p orbitals. Figure 23 (b) shows that the weight of s and p orbitals of Mn atom near the Fermi level are negligibly small in comparison to weight of 3d orbital. Spin up component of that Mn atom are all occupied whereas the spin down components of it are completely unoccupied whereas for another Mn atom on different plane, the trend reverses. This occupancy indicates that the Mn atoms of MnO have changed electronic configuration from...
that of neutral Mn atom ([Ar] 3d⁵ 4s²) into Mn²⁺ ions which has half-filled 3d⁵ shells. Interestingly, the p orbitals of O atoms are mostly occupied and lie close to the Fermi level hybridizing with the Mn d orbitals with magnitude comparable to that of Mn atoms. All these features ensure that MnO is in antiferromagnetic phase and electrons in Mn d orbitals and O p orbitals are to be taken into account in the charge dynamics. Figure 23(c) presents the orbital resolution of occupancy of d-orbital of MnO which shows that the five-fold degeneracy of the 3d level is split into triply degenerate out of plane states $t_{2g}$ and doubly degenerate in plane $e_g$ states. Occupancy of all the parallel spin states of the $t_{2g}$ and $e_g$ states of Mn²⁺ by keeping opposite spin states completely empty indicates the favor of parallel spin alignment creating high-spin nature of the 3d electrons. Occupancy of in plane doubly degenerate states have peak about 1eV below $E_F$, and three fold degenerate out of plane orbitals are almost non-hybridized and have peak occupancy about 3 eV below the $E_F$ and both of them have significantly less unoccupied states within 1.0eV above $E_F$. Three p orbitals of O atom are degenerate. In 3d orbitals, the states are localized that reduces the overlapping between the electronic wave functions and so the band width becomes small. The partial failure of semi-local GGA to capture band gaps and photoemission spectra is due to the strong localization of the TM 3d electrons. Cohen et.al [194] calculated the energy and magnetic moment using only LDA based interaction in which MnO is predicted to be in metallic phase.

5.3.2 DFT+DMFT: Band Structure and Excitation Spectrum

Since the system is insulating in contrary of expectation to be metallic due to half-filling of the 3d orbitals, one needs to consider the correlation induced Mott localization which can be
characterized by the Coulomb repulsion energy $U$ of two electrons on the same atomic site and is treated explicitly in Hubbard model. The prediction of LDA+U method is found to be affected by magnetic order. Various methods have been suggested to overcome the deficiencies of the local approximation including DMFT [11; 12; 195] to better understand those systems[6; 31; 116-118; 196-199].

Figure 24 (a) Comparison of density of states obtained using DFT, DFT+DMFT, and experimental XPS valence-band and BIS conduction band from ref. [200] spectra. (b) 3-fold degenerate t$_{2g}$ and 2-fold degenerate e$_{g}$ orbitals of one Mn atom obtained using DFT+DMFT.

The plot of spectral function in Figure 24(a) shows that the one obtained using DMFT method is qualitatively different form that based on DFT approach and captures features of experimental measurement of both valence and conduction band. As effect of interaction, the peak of occupied states are shifted away from $E_F$. As shown in Figure 24(a), for the present choice of parameters, the spectral distribution broadens as effect of self-energy. The broadening is comparable to the experimental measurement. In Figure 24 (b), we show the
Degeneracy of in and out of plane states obtained in DFT+DMFT calculation. If compare with experiment, the A feature appears due to three-fold degenerate orbitals while the main peak (B feature) appears due to Mn two-fold degenerate orbitals. There is very small occupancy of orbitals at Fermi level, which was zero in DFT calculation.

**Excitation Spectrum**

![Figure 25 DMFT excitation spectrum of Mn.](image)

In Figure 25, the imaginary part of the response function is shown. The spectrum shows zero excitation at up to 2 eV that corresponds to the insulating nature of the material, sharp increase of spectrum for positive energy within 2-4eV, broadening with width of 3eV corresponds to significantly large density of states with energy difference of 4-7eV due to peaks within that range in valence and conduction bands and continuous smoothly decreasing and almost constant spectrum for energy values beyond 16eV.
In Figure 26, the time dependence of the XC kernel is shown which is used in linear response TDDFT calculation. There are number of striking features in the plot. First, the kernel has the main peak for the instantaneous interaction, which decreases sharply with delay in time after interaction for 2fs. There another small peak about 2 fs and 2.5fs. There is fluctuation in the strength of interaction for 6fs after which the strength remains independent of time and becomes zero.
5.3.3 TDDFT Solution: Charge Dynamics and Bound State

Figure 27 Dynamics of variation of orbital resolved excited charge density in non-interacting case, (b) interacting case with adiabatic and non-adiabatic approximations, (c) orbital resolved excited charge density dynamics in non-adiabatic TDDFT.

As shown in Figure 27, for a given Gaussian pulse with amplitude 1V/Å and duration 0.01fs, there is instantaneous charge excitation on MnO. The orbital resolved excited charge density shows that the orbitals with relatively higher unoccupied states near the Fermi level has higher excited charge density whereas the double degenerate orbitals which has high intensity of dos on the occupied sites has relatively less excited charge density. The degeneracy of orbitals can be seen even on the dynamical calculation. In Figure 27(b), we show the dynamics including
electronic interaction in adiabatic and non-adiabatic approximation. Charge still undergoes instantaneous excitation under the pulse and the amount of excited charge is the same as in free case. There is hardly any difference in the charge relaxation till 7fs, after which the system gains memory and the relaxation while taking memory effect is quiet faster than the one in adiabatic approximation. The relaxation time calculated as the time the system takes to attain half of the maximum excited charge density comes out to be about 700fs in adiabatic approximation and about 200fs in non-adiabatic approximation. Figure 27(c) shows variation on the relaxation time of charge on different orbitals. The relaxation dynamics is faster on the 3-fold degenerate orbitals in comparison to 2-fold degenerate orbitals. Faster relaxation is due to the presence of 3-fold degenerate orbitals close to the Fermi level in previously unoccupied sites.

Based on the density of states plot and the variation on the relaxation time from different orbitals, we plot a model for d-orbitals charge excitation on MnO, whose sketch is shown in Figure 28. Since electron easily excite from 3-fold degenerate orbitals and electronic relaxation time is long in 2-fold degenerate orbitals, an excitation can be formed by hole in 3-fold degenerate orbitals and electron in 2-fold degenerate orbitals. So, dynamics includes spin flip excitation from occupied to unoccupied orbitals and formation of exciton.
To calculate the binding energy of this electron-hole pair, we use screen Slater XC kernel. At the screening parameter of 3, the exciton binding energy comes out to be 280 meV whereas the experimentally reported value is 330 meV. Figure 29 shows the variation of binding energy with dielectric constant. Since exciton is a Coulomb correlated electron-hole pair, we calculate its binding energy as the energy of its ionization to a non-correlated electron-hole couple.
Values of exciton binding energy calculated with different XC kernels whose mathematical formula are presented in Appendix E are presented in Table 3.

Table 3 Values of exciton binding energy for different XC kernels in density matrix TDDFT formulation.

<table>
<thead>
<tr>
<th>XC Kernel</th>
<th>Exciton Binding Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>112</td>
</tr>
<tr>
<td>PBE</td>
<td>220</td>
</tr>
<tr>
<td>PW91</td>
<td>4</td>
</tr>
<tr>
<td>Local</td>
<td>22</td>
</tr>
<tr>
<td>Long Range</td>
<td>690</td>
</tr>
</tbody>
</table>

5.4 Conclusions

In this chapter, we show the results of TDDFT+DMFT calculation of femtosecond response of d-electrons of MnO to an ultrafast lase pulse perturbation. Based on the relaxation stages of the excited electrons, the main channel of the charge response is explored which is dominated by the inter-orbital transitions. We have also analyzed the possibility of the bound state and found that the exciton binding energy in the order of 100 meV. In future, one can explore non-equilibrium charge dynamics including exciton into formulation.

CHAPTER 6: APPLICATION OF SLKMC: Cu ISLANDS DIFFUSION ON Ni(111)
In this chapter, we elucidate the diffusion kinetics of a heteroepitaxial system consisting of two-dimensional small (1-8 atoms) Cu islands on the Ni(111) surface at (100-600) K using the Self-Learning Kinetic Monte Carlo (SLKMC-II) method. Study of the statics of the system shows that compact Cu$_N$ (3≤N≤8) clusters made up of triangular units on fcc occupancy sites are the energetically most stable structures of those clusters. Interestingly, we find a correlation between the height of the activation energy barrier and the location of the transition state (TS). The activation-energy barriers ($E_a$) of processes for Cu islands on the Ni(111) surface are in general smaller than those of their counterpart Ni islands on the same surface. We find this difference to correlate with the relative strength of the lateral interaction of the island atoms in the two systems. While the SLKMC database consists of hundreds of possible processes, we identify and discuss the energetics of those that are the most dominant, or are rate-limiting, or most contributory to the diffusion of the islands. Since the energy barriers of single- and multi-atom processes that convert compact island shapes into non-compact ones (owing to a significantly smaller barrier for their reverse processes) are larger than that for the collective (concerted) motion of the island, the later dominate in the system kinetics -- except for the cases of the dimer, pentamer, and octamer. Short-jump involving one atom, long jump dimer-shearing, and long-jump corner shearing (via a single-atom) are, respectively, the dominating processes in the diffusion of the dimer, pentamer and octamer. Furthermore single-atom corner-rounding and edge-shearing are, respectively, the rate limiting processes for the pentamer and the octamer. Comparison of the energetics of selected processes and lateral interactions obtained from semi-empirical interatomic potentials with those from density functional theory show minor quantitative differences and overall qualitative agreement.
6.1 Introduction

Surface diffusion of adatom islands plays an important role in many phenomena of interest for fundamental science and technological applications including thin-film growth, surface chemical reactions, catalysis and mass transport. In understanding thin-film growth in particular, the stability and kinetics of the adatom islands are the major predictors of the growth modes on a surface. Experimental observations (using scanning tunneling microscopy [STM] or field ion microscopy [FIM]) of various diffusion mechanisms of islands on a surface, such as edge diffusion[68; 69], dimer-shearing[70; 71] and concerted gliding [72; 73] have been crucial in understanding diffusion dynamics. However, because of their insufficient time resolution, they cannot uncover complete pathways of these short-lived diffusion process; instead, on the basis of experimental evidence alone, those processes must be inferred indirectly. In contrast, theoretical calculations are capable of determining directly the diffusion pathways along with their transition states. On the basis of such computational approaches as molecular dynamics based on model interaction potentials, Voter[23] proposed single-atom edge-running process of a cluster as the dominant mechanism for diffusion; V. Chirita et al. [201] inferred that reptation competes with concerted motion for adatom islands of size less than 7 atoms; Hamilton et al. [202] revealed the dislocation mechanism for diffusion of adatom islands of size 4-50 on fcc(111) surfaces; A. Singor et al. [73] have shown that direct- and dislocation-mediated concerted gliding-diffusion process of islands are necessary to reproduce the experimentally predicted barriers; Z. Shi et al. [203] presented dimer-shearing as an important process for interpreting mobility of compact clusters; Marinica et al.[204] have highlighted the role of concerted motion of islands to explain the observed diffusion of islands
at very short time scale; and Muller et al.[205] have obtained good agreement with experimental data after including concerted motion for simulating stacking-fault formation on Ir(111). While a number of experimental and theoretical studies[68; 76; 78-80; 201; 204; 206-211] helped to understand the diffusion kinetics of small adatom islands in homoepitaxial systems, information about their far more numerous heteroepitaxial counterparts are still scarce [59; 73; 81; 212-233]. Owing to the differences in the various microscopic mechanisms responsible for diffusion in metal-on-metal systems, much work remains to be done, especially on heteroepitaxial systems whose prospects for tuning properties are especially promising for devising essential components in such applications as laser diodes, solar cells, and magnetic- and optical-storage devices.

Previous studies exploring diffusion dynamics of heteroepitaxial systems on fcc(111) surfaces (but not of Cu/Ni(111) ) are based on MD simulation for shorter overall durations[213; 214; 219], or on KMC methods[78] or Monte Carlo method[221]. None of them have pinpointed the most important diffusive processes for a particular cluster size and their respective diffusion barriers nor determined how often they are executed for a given temperature. Computation that directly incorporates information about the multifarious possible single-atom, multi-atom or concerted mechanisms in simulation enables one to point out quantitatively the most executed, rate-limiting and the most diffusive processes for an island at a given temperature. The reliability of such prediction can be enhanced by exploring system dynamics over a time long enough that even infrequent processes come into existence. Such an understanding of the mechanisms of clusters’ diffusion on a surface is crucial in formulating realistic models of thin-film growth. In addition, the numerical accessibility of
relative frequencies of different types of processes enables one to rationalize the calculated
diffusion coefficients of a cluster size at the various temperatures under study. The present
study is designed to provide this information for the small Cu islands on the Ni(111) surface
at temperature range of (100-600)K.

6.2 Computational Details

Small Cu islands on the Ni(111) surface is a good system for opening up an investigation
of the kinetics of diffusion in heterometallic systems owing to its small lattice mismatch
(2.56%), its stability, its tendency towards segregation on the surface of the mixed system[234]
due to the lower surface energy of Cu than that of Ni – 1.9 $J/m^2$ for Cu/Ni(111) vs. 2.4 $J/m^2$ for
Ni/Cu(111)[235] – and the fact that its strain is relatively low (the shift of the atomic position
from that in registry is less than 3% of that in the relaxed structure in any direction).

To study diffusion of small Cu islands on the Ni(111) surface, the simulation starts by
placing a compact fcc/hcp island of a given size on the adsorption sites of Ni(111) surface
(atomic size (16x16) with the bottom two of a total of five layers fixed and interacting through
the many-body semi-empirical Embedded-Atom Method (EAM) potential[48] for all static
calculations) on concentric rings as explained in section 2.4.2.2. A system evolves by
performing a process of its choice, from the multitude of possible single- or multi-atom
processes made in the succession of KMC steps as explained in the same section. The
simulation run for a given island size at a given temperature is halted at $10^7$ KMC steps –
although we observe that the database gets saturated after a few thousand steps (that is, hardly
any new configurations appear), as shown in case of tetramer in Figure 30.
For good statistics, for each island size we divide $10^7$ KMC steps into 100 simulations each with $10^5$ KMC steps and calculate the average of square displacement and equivalent time. From the thus-generated trace of the center of mass of an island at a given temperature, I calculate its diffusion-coefficient and then the effective energy barriers using Equation (118) and Equation (119), respectively. In this study, we ran simulations for Cu/Ni(111) systems of island size 1-to-8 and at temperatures of (100-600) K in increments of 100K.

**6.3 Results**

For each island size, we mention the energetically most favored configuration by comparing the relaxed energy of various configurations of the island adsorbed on the Ni(111) surface stored in our database. Out of a number of processes executed during our KMC simulation, we present here only the key processes that are executed the most, or are rate-limiting, or are the most diffusive, along with their $E_a$s. We map the potential energy surface of the system resulting from each step of drag as a function of the distance between an adatom to another adatom which lies closest to its target position and present it as a descriptor to understand the
variation in energy barriers of A- and B- type processes. In addition, we compare the energy barriers of key diffusion processes of the Cu islands on the Ni(111) system with their counterparts on the Ni islands on the same Ni(111) surface, tracing the differences to the variation of the strength of lateral interaction of the adatoms with Ni(111) as the substrate. We report key differences on kinetics of Cu islands on the Ni(111) surface with Ni islands on the Ni(111) surface and Cu islands on the Cu(111) surface reported on references [79] and [206], respectively while discussing each island size.

6.3.1 Validation of Approximations in SLKMC Method

The reliability of our results depends on the defensibility of various necessary approximations. We should comment about the accuracy of the $E_a$s calculated using the drag method and EAM potentials. Ideally, with the methods available so far, the most reliable path would be to use density functional theory[24; 25] based methods for calculation of the total energy and a robust technique such as the nudged-elastic band (NEB) method[51] or its variant the “dimer” method[53] for calculating the energy barriers. Since the first step in SLKMC is to saturate the database with all imaginable diffusion processes and their energy barriers, for each cluster size, it entails calculation of several thousand such quantities, many of which the system never selects for execution. DFT+NEB based calculations of thousands of energy barriers is a computationally formidable task, even with the advances that have been made. Using EAM+NEB is also 100 times slower than using EAM+drag. We have thus kept EAM+drag as our work horse for populating the database with diffusion processes and their barriers. Once we find the trends and extract the processes that the system prefers to execute.
for diffusion, we check the accuracy of the stored energy barriers using not only NEB, but also DFT +NEB. The comparisons so far have displayed only minor differences between the barriers calculated using the EAM+drag method and that using EAM+NEB, as we discuss for Cu islands on the Cu(111) in ref.[76]. Additional comparison of selected diffusion barriers for Cu islands on the Ni(111) surface calculated using the EAM+drag method with those obtained using DFT+NEB presented in ref.[27] show minor quantitative difference.

To check the validity and reliability of the predictions which are based on the semi-empirical EAM interaction we compare, (1) the energy barriers of some selected processes, (2) the lateral interaction energy of adatoms in the energetically most favored structures, and (3) the difference in the adsorption energy of the most stable Cu clusters on the fcc and on the hcp occupancy sites on the Ni(111) surface, with those obtained using first-principles density functional theory (DFT). The Kohn-Sham formulated DFT [24; 25] calculation is performed using the VASP package [236] employing the projector-augmented wave approach [237; 238] to describe the core-valence interactions and the plane wave basis functions to expand the valence electrons wave functions. The energy cutoff for plane-wave expansion is set at 350 eV to achieve total energy convergence to within $10^{-5}$ eV. The exchange-correlation contributions to the total energy is treated in the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE)[163] functional. The Ni(111) slab is mimicked by 6x6x5 unit cell with 22 Å vacuum. The k-points mesh density is taken to be 3x3x1 for the Brillouin zone integration for one surface unit cell. The atomic positions of the unit cell are relaxed until all components of force acting on each atom converges to $10^{-2}$ eV/Å.
Table 4 Energy barriers of selected processes from drag method using EAM interaction and NEB method using DFT energetics.

<table>
<thead>
<tr>
<th>Island Size</th>
<th>Process</th>
<th>Energy Barrier (eV)</th>
<th>Drag (EAM)</th>
<th>NEB (DFT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>F to H [Figure 31(a)]</td>
<td>0.052</td>
<td>0.048</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>H to F [Figure 31(b)]</td>
<td>0.049</td>
<td>0.036</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>F to F long jump A-type[Figure 35 (e) process 5]</td>
<td>0.038</td>
<td>0.028</td>
<td></td>
</tr>
</tbody>
</table>
To calculate the activation energy barrier of diffusion process, the Nudged Elastic Band (NEB) method [51] (explained in section 2.3.2) as implemented in VASP package is used. Six images between the initial and final structure are taken and the spring constant is approximated to be $-5\text{eV/Å}^2$. In Table 4, we present a comparison of the energy barriers of selected single-atom, multi-atom and concerted processes obtained using drag method with the EAM interaction that is used in SLKMC simulation and NEB method with energetics based on DFT. The selected processes of monomer, dimer, tetramer, and heptamer are short-jump single-atom, long-jump single-atom, multi-atom, and concerted processes, respectively. From the
comparison, one can see that the energy barrier of processes calculated from two different approaches agree qualitatively and semi-quantitatively. The significant difference in energy barriers of the A- and B-type processes obtained on the basis of EAM interaction are predicted with the same trend in NEB-DFT method.

In Table 5, we present a comparison of adsorption energies (E\text{ad}) of the most stable island configurations and the strength of the lateral interaction (L.I.) energy (E\text{lat}) of adatoms on those configurations calculated using relations

\begin{align}
E_{\text{ad}} &= E_{\text{cl+sub.}} - (E_{\text{cl.}} + E_{\text{sub.}}), \\
E_{\text{lat}} &= E_{\text{cl+sub}} - n \times E_{\text{mono+sub}} + (n-1) \times E_{\text{sub}},
\end{align}

where $E_{\text{cl+sub}}$, $E_{\text{mono+sub}}$, $E_{\text{cl}}$ and $E_{\text{sub}}$ are the energy of relaxed system containing substrate with adsorbed n-adatom cluster on its most stable configuration, substrate with adsorbed monomer, isolated cluster, and isolated substrate, respectively. In the Table 5, one can see that values of the adsorption and lateral interaction energies calculated using EAM interaction follow the same trend as those calculated from DFT approach. From both approaches, the adsorption energy of each cluster is found to be stronger than the lateral interaction energy among adatoms. The strength of lateral interaction energies of Ni adatoms of a Ni cluster are larger than that of the Cu adatoms of Cu cluster on the Ni(111) surface.
Table 5 Size dependent adsorption energies of the most stable island configurations and the lateral interaction of adatoms on those configurations after calculating energies based on EAM interaction and DFT method. Energies are expressed in eV unit.

<table>
<thead>
<tr>
<th>Island Size</th>
<th>Occupancy site</th>
<th>Cu/Ni(111)</th>
<th>Ni/Ni(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>EAM</td>
<td>DFT</td>
</tr>
<tr>
<td>1</td>
<td>F [Figure 31(a)]</td>
<td>-3.21</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2F[Figure 35(a)]</td>
<td>-3.29</td>
<td>-3.91</td>
</tr>
<tr>
<td>3</td>
<td>3F[Figure 37(a)]</td>
<td>-4.24</td>
<td>-6.07</td>
</tr>
<tr>
<td>4</td>
<td>4F[Figure 40(a)]</td>
<td>-5.37</td>
<td>-6.78</td>
</tr>
<tr>
<td>5</td>
<td>5F[Figure 41(a)]</td>
<td>-6.54</td>
<td>-7.99</td>
</tr>
<tr>
<td>6</td>
<td>6F[Figure 42(a)]</td>
<td>-7.71</td>
<td>-9.58</td>
</tr>
<tr>
<td>7</td>
<td>7F[Figure 43(a)]</td>
<td>-8.67</td>
<td>-10.4</td>
</tr>
</tbody>
</table>
In Table 6, we present the variation of lateral interaction energy with the distance between the adatoms of the Cu dimer island adsorbed on various configurations on the Ni(111) surface from which one can see that both approaches predict the lateral interaction energy to be attractive for short distances whose magnitude decreases with distance and becomes insignificant if adatoms are spaced beyond 5Å.

Table 6 Variation of lateral interaction with dimer distance from EAM and DFT approaches.

<table>
<thead>
<tr>
<th>EAM</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance (Å)</td>
<td>Lateral interaction energy (eV)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2.46</td>
<td>-0.39</td>
</tr>
<tr>
<td>2.49</td>
<td>-0.38</td>
</tr>
<tr>
<td>4.31</td>
<td>-0.01</td>
</tr>
<tr>
<td>4.98</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

In Table 7, we present the comparison of the difference in adsorption energies of the most stable Cu clusters on the fcc and the hcp occupancy sites of the Ni(111) surface. The positive values of difference in Table 7 from both approaches imply that adsorption of cluster on fcc site is energetically favored than on hcp site and also justifies the necessity of treating them as different sites in KMC simulation. The difference is underestimated in EAM interaction in
comparison to DFT calculation, however, they show the same trend of site preference of islands.

Table 7 Fcc and Hcp adsorption energy difference of the most stable islands from EAM and DFT.

<table>
<thead>
<tr>
<th>Island Size</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>[E(Fcc)-E(Hcp)] (eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EAM</td>
<td>0.003</td>
<td>0.006</td>
<td>0.010</td>
<td>0.014</td>
<td>0.018</td>
<td>0.024</td>
<td>0.024</td>
</tr>
<tr>
<td>DFT</td>
<td>0.013</td>
<td>0.025</td>
<td>0.043</td>
<td>0.046</td>
<td>0.078</td>
<td>0.105</td>
<td>0.095</td>
</tr>
</tbody>
</table>

In addition, for every process (at no matter what temperature), we approximate attempt frequency or the pre-exponential factor ($r_0$) in Equation (114) as $10^{12}$ s$^{-1}$, which is a reasonable approximation in reference to the calculated value of attempt frequency based on experimental observations [73]; [223; 232] and theoretical calculations[239; 240]. We are aware that the assumption of the “normal” value for the pre-exponential factor may be questionable and may hide some important physical implications of those processes with either too large or too small a value compared to the normal. To check the dependence of the results on the choice of the pre-factor, we have carried out calculations assigning the pre-factor values of $10^{11}$, $10^{13}$, and $10^{15}$ s$^{-1}$ for all single-atom, multi-atom, and concerted processes for the case of Pd pentamer diffusion on the Pd(111) surface in the temperature range 100K to 600K. We find that the result for normalized frequency of execution of different processes is not affected and neither is the effective energy barrier for the Pd pentamer diffusion. Naturally, the value of diffusion coefficient changes. The percentage change in values of lnD with corresponding values obtained on using pre-factor $10^{12}$ s$^{-1}$ in our calculation are presented in Table 8.
Table 8 Percentage change in the calculated values of lnD for Pd pentamer diffusion on the Pd(111) with pre-factors as referenced to $10^{12}$ s$^{-1}$ at different temperatures.

<table>
<thead>
<tr>
<th>Temp(K)</th>
<th>Pre-factor (s$^{-1}$)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>$E_{\text{effective}}$(meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{11}$</td>
<td></td>
<td>0.07</td>
<td>0.71</td>
<td>0.02</td>
<td>0.12</td>
<td>0.17</td>
<td>0.24</td>
<td>196</td>
</tr>
<tr>
<td>$10^{13}$</td>
<td></td>
<td>40.6</td>
<td>13.52</td>
<td>10.52</td>
<td>9.84</td>
<td>9.4</td>
<td>9.1</td>
<td>195</td>
</tr>
<tr>
<td>$10^{15}$</td>
<td></td>
<td>120</td>
<td>37.4</td>
<td>24.68</td>
<td>30.55</td>
<td>22.53</td>
<td>28.74</td>
<td>197</td>
</tr>
</tbody>
</table>

In the on-lattice KMC approach, some strain is to be expected even for homo-epitaxial systems since the bond lengths between the adatoms are not be the same as the nearest neighbor distance of the substrate atoms in the bulk. To estimate the bias due to such an assumption, we calculate the percentage deviation in the average bond length in islands of different sizes in their relaxed configuration from the substrate bulk nearest neighbor distance. The results presented in Table 9 show that the deviation is not significant, implying that the results based on the on-lattice approximation are reliable.

Table 9 Percent variation in the bond length of island adatoms with respect to the substrate bulk nearest neighbor distance.

<table>
<thead>
<tr>
<th>System</th>
<th>Dimer</th>
<th>Trimer</th>
<th>Tetramer</th>
<th>Pentamer</th>
<th>Hexamer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Pd(111)</td>
<td>6.8</td>
<td>5.6</td>
<td>4.64</td>
<td>4.22</td>
<td>3.14</td>
</tr>
<tr>
<td>Ag/Ag(111)</td>
<td>5.49</td>
<td>4.15</td>
<td>3.25</td>
<td>2.83</td>
<td>1.97</td>
</tr>
<tr>
<td>Cu/Ni(111)</td>
<td>1.2</td>
<td>0.15</td>
<td>0.48</td>
<td>0.02</td>
<td>1.84</td>
</tr>
<tr>
<td>Ni/Cu(111)</td>
<td>8.18</td>
<td>6.82</td>
<td>5.76</td>
<td>5.39</td>
<td>4.22</td>
</tr>
</tbody>
</table>
Note also that in this study, we consider only fcc and hcp adsorption sites because on other sites (top or bridge) islands become unstable and so immediately occupy hcp or fcc adsorption sites upon relaxation. As a possible mechanism of diffusion, we checked the probability of diffusion of a vacancy on the Ni (111) surface using the NEB method for the same EAM interaction. Since the calculated energy barriers of diffusion processes for a single vacancy turns out to be 0.85eV -- significantly higher than the 0.05 eV barrier of adatom hopping on the Ni(111) surface and conclude that there is thus little justification for considering the possibility of diffusion via vacancies.

Although there is no infallible method for discovering all possible processes, we are confident (given the fact that the generation of new configurations virtually ceased around a few thousand steps, as shown in Figure 30) that the database generated in $10^7$ steps at 600K did virtually entirely exhaust the search for possible non-detachment processes.

6.3.2 Diffusion Characteristics by Island Size: Monomer to Octamer

**General trend with example of monomer**

In this section, we summarize the general findings for the diffusion coefficients and the frequency of execution of different types of processes as a function of temperature as well as the effective energy barriers ($E_{\text{effective}}$) for the islands under consideration here. With the example of Cu monomer, the procedure for obtaining the characteristics of interest is explained. In subsequent sections discuss the special features in the diffusion of islands of larger size.
Figure 31 Cu monomer on the Ni (111) surface adsorbed on (a) an fcc site, and (b) an hcp site. The line with arrowhead pointing right (left) represents an fcc to hcp (hcp to fcc) hopping process with a number specifying the energy barrier for the process in question.

The Cu monomer adsorbs either on an fcc or an hcp hollow site of the Ni(111) surface. Adsorption on an fcc site (Figure 31(a)) is found to be slightly favored (by 0.003 eV) over that on an hcp site (Figure 31(b)) (Note that the uncertainty in reported energy values on the basis of EAM interaction is in the fraction of meV), the difference is 0.013 eV based on the Density Functional Theory (DFT) calculation, cf. Table 7.

The monomer diffuses only by a short-jump process, i.e., from F to H or vice versa. The energy barriers of the F-to-H and reverse processes as calculated by the drag method are 0.052eV and 0.049eV, respectively -- in nearly exact agreement with the ones obtained via NEB method using the same interaction potential: 0.051eV and 0.048eV respectively. Using minimization of classical action to search for the minimum energy path, Kim et al.[241] found the $E_a$ for diffusion of a Cu monomer on the Ni(111) surface to be 0.050eV. The corresponding barriers for the Ni/Ni(111) system as reported in [79] are 0.059eV and 0.057eV. So, the barriers of Cu monomer diffusion on the Ni(111) surface are smaller than those of Ni monomer diffusion on the same Ni(111) surface. Not only in the case of monomer, but also for other island sizes considered here, the $E_a$ of a diffusion process of a Cu islands on the Ni(111) surface
is smaller than that of the corresponding process for Ni island on the Ni(111) surface. For comparison purpose, from here onwards a number representing the barrier of some key process for Cu/Ni(111) is followed by that for the corresponding process for the Ni/Ni(111) in square brackets (make a distinction that if the second number is in parenthesis, it represents the barrier of reverse of a process on Cu/Ni(111) system). Such a variation correlates with the relatively lower strength of the lateral interaction of Cu atoms of the Cu cluster as compared to that of the Ni atoms of the Ni cluster on the Ni(111) surface (see Table 5).

Not only for the monomer island but for each island at each temperature under study, the center of mass follows a random trajectory and the mean square displacement (MSD) varies linearly with time (an example of tetramer island diffusion at 300K is shown in Figure 32). Hence we use Equation (118) to calculate the diffusion coefficient (D). Calculated values of D for islands of sizes and at temperatures under study are presented in Table 10.

As expected, the diffusivity of the islands shown in Table 10 increases with increase in temperature but at any particular temperature, it decreases with increase in island size. The rationale for such variation will be explained while discussing each islands separately.
Figure 32 (a) Center of mass trajectory, (b) Mean square displacement vs. time, of Cu tetramer on the Ni (111) surface at 300K.

The tabulated values of D of studied Cu islands on the Ni(111) surface at various temperatures under study are larger than those of Ni islands on the same substrate (reported upon earlier in ref.[79] using the same method).

Table 10 Diffusion coefficients of (1-8)-atom Cu islands on Ni(111) in the temperature range 100 - 600 K. Error bars on the values of D are less than 1%.

<table>
<thead>
<tr>
<th>Temp.(K)</th>
<th>Island Size</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>E_{\text{effective}} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.60x10^9</td>
<td>8.71x10^{10}</td>
<td>2.32x10^{11}</td>
<td>3.87x10^{11}</td>
<td>5.07x10^{11}</td>
<td>6.17x10^{11}</td>
<td>0.051</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8.64x10^5</td>
<td>1.88x10^9</td>
<td>2.37x10^{10}</td>
<td>8.12x10^{10}</td>
<td>1.66x10^{11}</td>
<td>2.68x10^{11}</td>
<td>0.131</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.01x10^4</td>
<td>1.51x10^8</td>
<td>3.88x10^9</td>
<td>1.71x10^{10}</td>
<td>5.02x10^{10}</td>
<td>8.18x10^{10}</td>
<td>0.165</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.99x10^3</td>
<td>6.53x10^7</td>
<td>2.06x10^9</td>
<td>1.26x10^{10}</td>
<td>3.71x10^{10}</td>
<td>8.09x10^{10}</td>
<td>0.180</td>
<td></td>
</tr>
</tbody>
</table>
As shown in Figure 33, ln(D) for each island under study varies linearly with 1/T and so we calculate the $E_{\text{effective}}$ from the slope of the Arrhenius plot. For the monomer, the $E_{\text{effective}}$ turns out to be 0.05eV and appears as the first data point in Figure 33(b). The corresponding values are reported to be 0.058eV for Ni/Ni(111)[79], 0.026eV for Cu/Cu(111)[78], 0.059eV for Ag/Ag(111)[80] using Arrhenius plot resulting from SLKMC simulation and 0.059eV for Cu/Ag(111)[213] using the Arrhenius plot from MD simulation. The variation of $E_{\text{effective}}$ with island size is shown in Figure 33(b).
For islands containing more than one atom, single, multi-atom and concerted processes are to be expected. Even for islands of the same size, there is variation in the execution frequency of the single-atom, multi-atom and concerted processes at the various temperatures under study. A plot of such a variation for island sizes (mentioned at the top of each column) under study is shown in Figure 34. Atomic processes which are the most contributory to the diffusion of those islands are discussed when exploring diffusion characteristics of islands of each size.

Figure 34 Variation of normalized frequency of executed single-atom, multi-atom and concerted processes on diffusion kinetics of adatom islands of size 2 to 8 with temperatures 100K to 600K.

**Dimer**
There are three possible configurations of dimer islands on the fcc(111) surface: both adatoms occupying fcc sites (a 2F-dimer, Figure 35(a)), both occupying hcp sites (a 2H-dimer, Figure 35(a)), both occupying hcp sites (a 2H-dimer, Figure 35(a)),
Figure 35(b)) or one occupying an fcc site and the other occupying an hcp site (an FH-dimer,

Figure 35 Structures of a dimer island on the fcc(111) surface: (a) the energetically most favored 2F, (b) 2H, and (c) FH. Process shown using lines with arrowheads in (a) and (b) represent the most executed A-type concerted processes, (c) and (d) represent the most executed single-atom processes, (e) and (f) represent long-jump single-atom processes of 2F and 2H islands, respectively, in each of which I is B-type non-detachment process, II, III and
IV are detachment processes which are not taken into account in this study of island diffusion, but are displayed to show their significantly higher energy barriers, and V is a non-detachment A-type process. The numbers with enumeration next to figures represent barriers of processes, as shown in Figure 6(c), in the enumerated directions.

Figure 36 Variation on energy of the system with distance between two Cu adatoms during (a) B-type single-atom process, e.g., \#1 in
Figure 35(e), (b) an A-type single-atom process, e.g., #V in Figure 35(e).

For Cu/Ni (111), we find the 2F-dimer to be energetically favored over the 2H-dimer by 0.006 eV and over the FH-dimer by 0.002 eV; whereas for Cu/Cu(111)[78] and Ni/Ni(111)[79] FH and 2F, respectively, have been reported to be the energetically most favored configurations.
From comparison of barriers of the concerted processes along directions 1, 2, and 3 on 2F or 2H structures (see enumeration next to Figure 35(a-b)) or barriers of long jump single-atom processes enumerated in different directions on the same 2F or 2H structures (Figure 35(e-f)), there is significant difference in the barriers of A- and B-type concerted or single-atom processes. Such a variation correlates with two distinct dynamic patterns: in one the TS occurs at the minimum distance between two adatoms; in the other, it occurs after that.
minimum distance has been traversed. For the B-type single-adatom process (process I in Figure 35(e) with the relatively high barrier of 0.290eV), the TS – represented by the peak of the black curve in Figure 36(a) – occurs at inter-adatom distance of 2.33Å, which is the minimum distance between them during the process as shown by the blue curve in Figure 36(a); in contrast, for the A-type process (with the same initial and symmetrical final configuration, process #V in
Figure 35(e) with a relatively small barrier of 0.038 eV, the TS (peak of black curve in Figure 36(b)) occurs when the adatoms are at distance of 2.50Å while the minimum distance between them during the process is 2.45Å, as shown by blue curve in Figure 36(b). Following the similar trend, the B-type concerted processes, for e.g., along directions 2 or 3 in Figure 35(a) but not shown by line with arrowhead, has barrier of 0.136eV, the two adatoms are at their minimum distance of 2.41Å at TS, while in the A-type process in the same structure, represented by arrows in
Figure 35(a) with an $E_a$ of 0.062 eV, the two adatoms are at distance of 2.43Å at TS though their minimum distance is 2.42Å.

As shown in Figure 34 (the column labeled “2”), single-atom processes are executed in significant fraction at temperatures under study: 99% at 100K, and 78% at 600K. Among single-atom processes, the greatest contribution among executed processes is made by processes that transform 2H-dimer into HF-dimer (process shown in Figure 35(d)) and its hcp counterparts converting 2F-dimer into FH-dimer with barrier of 0.029 eV(0.027 eV) and the remaining part is consists of the long-jump A-type processes.
Figure 35(e & f). As shown in Figure 34, the execution of concerted processes increases with increase in temperature. These processes are the A-type short-jump dimer gliding processes on the 2F structure (process shown in Figure 35(a)) and its reverse, and the B-type concerted process along direction 2 or 3 with a barrier of 0.136 eV [0.148 eV] and their counterparts on the 2H structure, barriers of 0.056 eV [0.066 eV] and 0.124 eV [0.143 eV] respectively. We note in passing that in the case of the
Ni/Ni (111) system, the concerted gliding A-type process on 2F or 2H structure is reported in [79] to turn into a rotational process.

Short-jump single-atom processes do not change the center of mass of a system significantly and so are less diffusive. At temperature of 100K, the relatively small diffusion coefficient of 8.64x10^5 Å²/s (cf. Table 10) of dimer island diffusion as compared to that of the same island at higher temperatures can be rationalized on the basis of small MSD owing to the higher execution of those less diffusive processes (84% among executed processes) and the general trend of long time equivalent for simulation at low temperature (time equivalent is inversely proportional to rate and the rate of execution of the same process becomes low at low temperature than at relatively high temperature). At 200K, execution of the short-jump single-atom processes falls to 73% with the increase in the execution of long-jump single-atom processes to 21% along with 6% execution of concerted-processes (those represented by arrows in Figure 35(a & b)). This results in increased MSD and an increase in the diffusion coefficient (D) to 1.88x10^9 Å²/s. From row two of Table 10, we see that the D of the dimer diffusion
keeps increasing with temperature with value $2.37 \times 10^{10} \text{Å}^2/\text{s}$ at 300K to $2.68 \times 10^{11} \text{Å}^2/\text{s}$ at 600K. The $D_s$ of Cu on the Ni(111) surface are increased by 191% and 137% over those of Ni on the Ni(111) surface reported in [15] at 300K and 600K, respectively. The $E_{\text{effective}}$ calculated for dimer island diffusion from the Arrhenius plot is displayed in Figure 33(b) whose value is 0.131 eV, which is close in value to the $E_a$ of concerted processes despite the fact that these are, in virtue of their higher $E_a$, significantly less frequent.

**Trimer**

Figure 37 The compact structures of the Cu trimer island on the Ni(111) surface: (a) the energetically most favored 3F-H, (b) 3H-T, (c) 3H-F, and (d) 3F-T. The most diffusive
concerted sliding processes and the most frequently executed rotational processes in trimer island diffusion are shown respectively in (a-d) and (e-f) using lines with arrowhead.

The compact configurations of the Cu trimer on the Ni(111) surface are found to be energetically favored over the non-compact ones. The compact 3F-H configuration (Figure 37(a)) having 3 adatoms occupying fcc sites around an hcp site is the energetically most favorable configuration – by 0.002 eV over the 3F-T configuration (Figure 37(d)) centered around a top layer substrate atom (T), by 0.01 eV over the 3H-F configuration (Figure 37(c)), by 0.011 eV over the 3H-T configuration (Figure 37(b)). In addition, any of those compact island structures are energetically favored over other non-compact structures, for e.g., the difference in system energy with the most favored island structure and a linear 3F and 3H trimer island structures are 0.335 eV and 0.346 eV respectively. In contrast, in case of Ni trimer on the Ni (111) surface 3F-T configuration is reported in ref. [79] to be the energetically most favored structure.

As shown in Figure 34 (the column labeled “3”), the concerted processes are executed more than 97% among the executed processes at all temperatures under study.
Figure 38 Single-atom processes in four different compact structures of trimer island along with their energy barriers in the four possible directions enumerated as processes I, II, III, and IV. Barrier of non-detachment process precedes the barrier of their reverse process in parenthesis.

The concerted processes belonging to the four compact structures shown in Figure 37 are executed 100% up to 300K and 97% at 600K, however, database includes single-atom, multi-atom or concerted processes on additional 18 non-compact configurations. Based on the static and the kinetic features, Cu trimer on the Ni(111) surface shows a strong tendency for maintaining a compact shape at the temperature range under study in this work.

The dominancy of concerted processes of a few compact structures in diffusion kinetics is attributed to two features that hold even for other larger size islands where concerted processes dominate in their kinetics. First, the barriers of the non-concerted processes on those energetically favored structures are significantly higher than those of the concerted processes (compare the barriers of non-detachment single-atom processes represented by I and IV in
Figure 38(a-d) to those of concerted processes on the corresponding structures in Figure 37). Such an observation is also reported for processes of Cu trimer on the Cu (111) surface [78; 204]. Second, as shown in Figure 39 with an example of a non-compact 3H trimer, the barrier of a process that turns the non-compact structure again into compact structure (A-type single-atom process shown in Figure 39(a)) is the lowest barrier process among processes of various kinds possible on non-compact structure. The A-type single-atom process on compact trimer structures centered about F or H sites (processes I and IV in Figure 38(a & c) with relatively lower barriers than B-type single atom processes are the ones whose execution is necessary to obtain the non-compact structures and thereby opening the possibility of execution of various processes.
Figure 39 Possible low barrier processes on non-compact 3H trimer, (a-b) A-type single atom processes, (c) concerted, (d) dimer-shearing, and (e) reputation. Among those processes the barrier of the A-type single-atom process that converts the non-compact structure into compact structure is the lowest barrier processes and so are the rate-limiting processes.

Among the executed concerted processes of few compact structures, the concerted rotational processes from 3F-T configuration into 3H-T configuration and its reverse as represented by line with arrowheads in Figure 37(e & f) are the most executed processes at all temperatures under study: 68 % at 100K, 56% at 300K, and 55% at 600K. Note that the clusters that have those rotational concerted processes are the ones that are centered on a top surface-layer atom. The concerted-sliding processes that convert the 3F-H configuration into the 3H-T configuration (represented by lines with arrowhead in Figure 37(a)) or 3H-F configuration into the 3F-T configuration (lines with arrowhead in Figure 37(b)) are executed about 8% each at 100K, 11% each at 300K, and 12% each at 600K. The concerted sliding processes that transform the 3H-T into 3F-H (represented by lines with arrowhead in Figure 37(b)) and the 3F-T into 3H-F (represented by lines with arrowhead in Figure 37(d)) are executed 16% of total executed process at 100K, 22% at 300K, and 22% at 600K. Based on the analysis, at 100K the non-diffusive concerted rotational and diffusive concerted sliding processes are executed 68% and 32% respectively of the executed processes. The small diffusion coefficient of 1.01x10^4 Å²/s at 100K can be rationalized on the basis of small MSD owing to the higher execution of non-diffusive processes and long time equivalent for simulation at small temperature. At 300K, increase in MSD (owing to 44% execution of diffusive processes) and relatively short time equivalent of simulation than at 100K results into
high value of diffusion coefficient of $3.88 \times 10^9 \ \text{Å}^2 / \text{s}$. Contribution of concerted sliding processes in the island diffusion is also reflected in the value of $E_{\text{effective}}$ of trimer, 0.168 eV, value closer to the $E_a$ of those processes than those of the most frequently executed rotational processes.

**Tetramer**

Among various distinct compact and non-compact tetramer islands, the compact rhombus shape structure in which all adatoms are adsorbed on fcc sites (Figure 40(a)) is found to be the energetically most favorable structure, by 0.014 eV over the rhombus structure with all adatoms on hcp sites (Figure 40(b)).

Figure 40 (a) The energetically most favored rhombus shaped compact 4F island, (b) rhombus shaped compact 4H island. The numbers with enumeration next to figures specify the energy barriers of concerted processes in the enumerated directions. Lines with arrowhead in (c & d) show A-type dimer-shearing process on 4F tetramer. The shown
processes along with the hcp counterpart of the dimer-shearing process are the most executed processes of Cu tetramer island diffusion on the Ni(111) surface.

The energy barriers of concerted processes in three possible directions on compact structures are enumerated next to the corresponding structures in Figure 40(a & b). As discussed in the case of dimer, the variation in values of $E_a$ correlates with whether the distance of an adatom at TS to the neighboring adatom initially closest to its target position is the minimum distance between them during the process or not. For the concerted process along direction 1 of the 4H structure with relatively small barrier of 0.167 eV, the distance at TS is 2.45 Å while the minimum distance is 2.42 Å; whereas for the process along direction 3 with barrier of 0.274 eV, the TS occurs at the minimum distance of 2.43 Å between adatoms during the process.

Although our database includes various single-atom, multi-atom and concerted processes, the processes shown in Figure 40 on the compact shaped tetramers along with hcp counterpart of the A-type dimer-shearing process are executed more than 99% of simulation. On the dimer-shearing mechanism of diffusion that executes starting on tetramer island of the system (initially reported in ref. [71]), two atoms on the A-type step-edge of the compact tetramer islands undergo long jump A-type process whose barriers are 0.205 eV [0.285] on 4F (Figure 40(c-d)) and 0.191 eV [0.276] on 4H with equal barrier for reverse process. However, the barriers of B-type dimer-shearing processes are significantly large: 0.478 eV and 0.492 eV on 4H and 4F respectively. Such a significant difference on barriers of dimer-shearing processes in case of tetramer and higher islands has also been reported in Ref. [16] (calling the processes as along A and B steps) and is qualitatively justified in terms of presence or absence of vacant
site that provides room for atoms to move. We find the difference to be more general and presents for processes in small islands with no step edges as well as for single atom, multi-atom, and concerted processes. The processes mentioned as along A and B steps in ref. [16] are equivalent to A- and B-type processes respectively in general explanation. The execution of the most frequent concerted sliding processes on rhombus-shaped tetramer structures decreases with increase in temperature: 96.2% at 100K, 81.2% at 300K, and 73.4% at 600K, and that of the A-type dimer-shearing process increases with temperature: 3.8% at 100K, 18.7% at 300K, and 24.8% at 600K. For comparison, in case of Ni tetramer island diffusion on Ni(111), dimer-shearing is reported in ref. [15] to turn only 5% of total executed processes. An obvious reason for such a difference is the relatively large difference in the energy barriers between the A-type dimer-shearing and the concerted processes, for e.g., the difference is 0.072 eV on 4F structure on Ni on the Ni(111) while it is only 0.023eV for Cu on Ni(111). Concerted processes are reported in ref. [14] to be the only executed processes in the kinetics of Cu tetramer diffusion on the Cu(111) surface.

Pentamer
Figure 41 (a) The energetically most favored long B-type step-edge 5F pentamer. The lines with arrowhead in (a-d) and (e & f) show respectively the most executed processes among concerted processes and A-type dimer-shearing multi-atom processes in pentamer island kinetics, (g) shows the rate-limiting single-atom processes that interconvert long B-type 5F pentamer shown in (h) into long A-type 5F pentamer shown in (i).

Compact pentamer structures that are obtained on adding an adatom to a rhombus-shaped tetramer are found to be energetically more favorable than all other compact or non-compact pentamers. Moreover, pentamers having all adatoms on fcc sites are found to be energetically more favorable than their hcp counterparts or those occupying both kinds of occupancy sites. The 5F pentamer having a long B-type step-edge (Figure 41(a)) is found to be the energetically most favorable configuration — by 0.004 eV over the 5F structure with a long A-type step-edge (Figure 41(c)), by 0.018 eV over the 5H with a long B-type step-edge (Figure 41(d)), and by 0.021 eV over the 5H with a long A-type step-edge (Figure 41(b)). In contrary, in case of
Ni/Ni(111), long A-type step-edge 5F is reported in ref. [15] to be the most stable configuration.

At 100K, the long jump, A-type dimer-shearing process on the long A-type step-edge 5H pentamer (process not shown but is hcp equivalent of the process shown in Figure 41 (e)) that convers the structure (Figure 41(b)) again into the same long A-type step-edge 5H structure with barrier of 0.183eV and its reverse process with the same barrier (being symmetrical) are executed 98% and the concerted process converting the structure into long B-type step-edge 5F structure (process shown in Figure 41(b)) and its reverse are executed 2% of the executed processes. Although 5F configuration with long A-type step-edge also has the A-type dimer-shearing processes with comparable small energy barrier of 0.196 eV(Figure 41(e-f)), they are not executed at lower temperatures due to high barriers of the necessary intermediate processes, so called rate-limiting processes, to get to the structure.

Table 11 Energy barrier of concerted processes in three possible directions of the energetically favored compact pentamers shown in Figure 41(a-d).

<table>
<thead>
<tr>
<th>Direction</th>
<th>Fcc long-B</th>
<th>Hcp long-A</th>
<th>Fcc long -A</th>
<th>Hcp long -B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.375</td>
<td>0.275</td>
<td>0.290</td>
<td>0.198</td>
</tr>
<tr>
<td>2</td>
<td>0.323</td>
<td>0.275</td>
<td>0.290</td>
<td>0.213</td>
</tr>
<tr>
<td>3</td>
<td>0.222</td>
<td>0.224</td>
<td>0.234</td>
<td>0.294</td>
</tr>
</tbody>
</table>
The rate-limiting processes to convert the long B-type step-edge 5F (Figure 41(a) or equivalently Figure 41(h)) into long A-type step-edge 5F (Figure 41(e)) are: (1) the A-type long jump single-atom process with barriers of 0.353 eV that turns the most stable pentamer structure shown in Figure 41(h) into the one shown in Figure 41(g)); (2) the B-type single-atom process with barrier of 0.153eV that turns structure shown in Figure 41(g) into structure shown in Figure 41(i). The rate-limiting single atom process of step 1 has reverse process with significantly small barrier of 0.022 eV on the structure shown in Figure 41(g). The process with barrier 0.022 eV is executed at all times when rate limiting process “1” is executed till 200K avoiding the execution of rate limiting process “2” and so execution of any processes on long A-type step-edge 5F including the low barrier dimer-shearing processes and long B-type step-edge 5H. At 200K, dimer-shearing processes continue on dominating in the kinetics but the concerted processes shown in Figure 41(a-b) have slightly increased execution to 10%. At 300K, the rate-limiting process “2” is also rarely executed and so processes on the long A-type step-edge 5F and the long B-type step-edge 5H structures constitute 34% of total executed processes, out of which 97.5% is dimer-shearing process shown in Figure 41(e) and 2.5% is concerted processes shown in Figure 41(c-d). With increase in temperature, owing to their relatively small $E_a$s, A-type dimer-shearing processes are executed in significant fraction of executed processes: 80% at 300K and 53% at 600K. At all temperatures under study, the executed concerted processes are the ones in the four compact pentamer structures shown in Figure 41(a-d) with barriers presented in Table 11.

As shown in Figure 34, execution of single-atom processes increase with increase in temperature: 3% at 400K to 9% at 600K. They are the long jump A-type corner rounding
processes on the long B-type step-edge 5F (rate-limiting process “1” and its reverse process shown in Figure 41(g-h)) or their hcp counterpart. Those features seen in the diffusion kinetics of Cu pentamer island on Ni(111) are different than the reported features in case of the homoepitaxial diffusion of Ni or Cu pentamer islands. In contrary to the dominance of A-type dimer-shearing process (multi-atom) in Cu pentamer island on the Ni(111), concerted processes are reported to be the most executed processes in homoepitaxial diffusion kinetics of Cu[14] and Ni[15] pentamers respectively. Specifically, in case of Ni pentamer diffusion on the Ni(111) surface, more than 90% of the executed processes are reported to be concerted and rest is constituted by single-atom processes with negligible execution of multi-atom processes even at high temperature of 700K. In case of Cu pentamer island diffusion on Cu(111), more than 95% of executed processes are reported to be concerted processes with multi-atom processes constituting less than 5% at temperature of 700K.

**Hexamer**
Figure 42 (a) or (c) represents the energetically most favorable 6F parallelogram structure of hexamer island with process in (a) shows the most executed concerted-sliding process that turns the island into 6H parallelogram structure shown in (b). The numbers with enumeration next to figures in (a & b) specify the energy barriers of concerted processes in the enumerated directions. Processes in (c-d) and (e) show the most executed processes among multi-atom and single atom processes in hexamer island diffusion respectively.

Hexamer of parallelogram shape with all adatoms on fcc sites (Figure 42(a)) is the energetically most favorable configuration, by 0.023 eV over similar structure with all adatoms on the hcp sites (Figure 42(b)). On those compact hexamers, one long edge forms A-type step-edge and another forms B-type step-edge.
Up to temperature of 200K, the executed processes of hexamer island are either of the following two processes of the compact parallelogram structure: (1) short-jump concerted sliding process from the 6F parallelogram into the 6H-parallelogram along direction 1 and its reverse (represented by line with arrowhead in Figure 42(a-b), (note the relatively higher barriers of concerted processes in other two directions), and (2) the long jump A-type dimer-shearing process, which for 6F structure is shown by line with arrowhead in Figure 42(c-d) having barrier of 0.202 eV(0.221 eV). The process for 6H parallelogram has an \( E_a \) of 0.211 eV (0.196 eV). After 300K, the proportion of execution of the dimer-shearing processes remains nearly constant while execution of long jump corner rounding single-atom processes increase from 4% at 300K to 12% at 600K. The structures on which single-atom processes are mostly executed are the ones resulted after execution of dimer-shearing process on 6F or 6H parallelogram structures, one such 6F structure (named 6F-down in Table 12) with the most executed single-atom processes on it (\( E_a \) of reverse processes equal to their respective forward processes) is shown in Figure 42(e).

<table>
<thead>
<tr>
<th>Direction</th>
<th>6H-down</th>
<th>6F-down</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.275</td>
<td>0.297</td>
</tr>
<tr>
<td>2</td>
<td>0.279</td>
<td>0.301</td>
</tr>
<tr>
<td>3</td>
<td>0.299</td>
<td>0.320</td>
</tr>
</tbody>
</table>

In contrary to the preference of concerted process along direction 1 and then the dimer-shearing process in parallelogram structures, the 6F- or 6H-down structures has the lowest barriers for the dimer shearing processes (Figure 42(d) for 6F) and then the A-type single-atom
process (0.239 eV on 6F (Figure 42(e)) and 0.225 eV on 6H) and then only the concerted processes (see Table 12 for barriers of concerted processes). Owing to the relatively small barriers of dimer-shearing processes than single-atom processes on the 6F or the 6H-down structures, they are the only executed processes on those structures till 200K and the most executed processes on those structures at temperatures beyond 200K. The relatively smaller barriers of A-type single-atom processes than those of concerted processes on 6F-down or 6H-down structures explain the observed result of increasing execution of single-atom processes at temperature beyond 300K (Figure 34). On the basis of the type of executed processes, the diffusion kinetics of Cu hexamer island on the Ni(111) surface is close to that of Cu hexamer on the Cu(111), however, significantly different than that of Ni hexamer on the Ni(111). In case of Ni hexamer island diffusion on the Ni(111) surface[15], single-atom processes are reported to be the most executed processes with no execution of multi-atom processes.

**Heptamer**

Among various structures of heptamer island, the compact closed-shell fcc structure with 6 adatoms at the corner of a regular hexagon surrounding an adatom at their center (Figure 43(a)) is found to be the energetically most favorable configuration and is favored over similar structure on hcp occupancy by 0.024 eV.
Figure 43 (a) or (c) represent the energetically most favorable 7F heptamer island with processes shown in (a) and (c) representing the most executed concerted and dimer-shearing processes of heptamer respectively. Process shown in (e) is the most frequently executed dimer-shearing process of non-compact 7F heptamer.

At 100K, only the forward and reverse of the short-jump concerted sliding process that converts 7F into 7H island in 3 possible symmetrical directions (one of the process at direction 1 is shown in Figure 43(a)) are executed. Due to execution of the concerted processes in different directions, the MSD of the system is large with value of $3.86 \times 10^5 \text{ Å}^2$ even at low temperature of 100K. However, due to high barriers of those processes, the rate of execution
of those processes at 100K is very low, in the order of $10^{-8}$/s. Since the rate of execution is small but one of them has to be executed at every step on the rejection free KMC simulation, the equivalent time for the simulation becomes large. Although MSD has significant value, the large value of time equivalent for the simulation results into small $D$ of $2.74 \times 10^{-8}$ Å²/s (cf. Table 10). At 300K, execution of those concerted processes decreases to 83.5% and the long jump A-type dimer-shearing processes on compact and non-compact 7F heptamer that are shown in Figure 43(c-d) and Figure 43(e-f) and their hcp counterparts are executed 16.5%. The barriers of the frequently executed dimer-shearing processes on 7H structures are 0.458 eV (reverse barrier 0.169 eV) and 0.190 eV (reverse barrier of 0.200 eV). As shown in Figure 34, even at higher temperatures, the execution of concerted processes keeps decreasing while that of dimer–shearing processes keeps increasing in the diffusion of heptamer. As a result of the increases in execution of dimer-shearing processes, the MSD of the heptamer island diffusion decreases. Even for decreasing MSD, the diffusivity of heptamer increases with increase in temperature (see Table 10) due to the significant decrease in the time equivalent for increase in temperature and relatively small barrier of two-atom processes. In contrast to the execution of concerted, multi-atom and single-atom processes in diffusion of Cu heptamer on the Ni(111) surface, concerted processes are reported as the only executed processes for homoepitaxial island diffusion of Cu or Ni heptamer on their (111) surface in ref. [14] and [15] respectively up to temperature of 700K.
Figure 44 (a) The energetically most favored long B-type step-edge 8F island. The processes shown in (a-d) and (e-f) represent the most executed processes among concerted and multi-atom processes in octamer diffusion respectively. The corner rounding single-atom process with barriers 0.024 eV and 0.165 eV shown in (g) represent respectively the most executed and rate-limiting processes in octamer diffusion.

A compact 8F octamer island obtained on adding one adatom at the corner of the compact 7F heptamer so that the octamer structure has the long B-type step-edge (Figure 44(a)) is found
to be the energetically most favored structure, favored over 8F structure with long A-type step-edge island (Figure 44(c)) by 0.007 eV, long B-type step-edge 8H island (Figure 44(d)) by 0.022 eV, and long A-type step-edge 8H island (Figure 44(b)) by 0.035 eV. In contrary, for Ni octamer on the Ni(111) surface, the long A-type step-edge 8F is reported in ref. [15] to be the most energetically favored configuration.

Table 13 Energy barrier of concerted processes in 3 possible directions of various compact octamer island structures shown in Figure 44 (a) The energetically most favored long B-type step-edge 8F island. The processes shown in (a-d) and (e-f) represent the most executed processes among concerted and multi-atom processes in octamer diffusion respectively. The corner rounding single-atom process with barriers 0.024 eV and 0.165 eV shown in (g) represent respectively the most executed and rate-limiting processes in octamer diffusion.(a-d). TSE abbreviates type step-edge.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Fcc-long B-TSE</th>
<th>Hcp-long A-TSE</th>
<th>Fcc-long A-TSE</th>
<th>Hcp-long B-TSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.378</td>
<td>0.340</td>
<td>0.372</td>
<td>0.354</td>
</tr>
<tr>
<td>2</td>
<td>0.378</td>
<td>0.340</td>
<td>0.372</td>
<td>0.354</td>
</tr>
<tr>
<td>3</td>
<td>0.468</td>
<td>0.430</td>
<td>0.460</td>
<td>0.437</td>
</tr>
</tbody>
</table>

At 100K, the A-type corner rounding single-atom processes on the long B-type step-edge 8F octamer with barriers of 0.325 eV and its reverse process with significantly small barrier (0.024 eV, shown in Figure 44(g)) dominate in system kinetics with execution of 99.5% the concerted process along direction 1 or 2 (Figure 44(a-b) shows the process along directions 2) that turn the structure into long A-type step-edge 8H and its reverse process are executed 0.3%, and the 3-atom shearing processes on the long A-type 8H structure (not shown but are hcp counterpart
of processes shown in Figure 44(e-f)) with barrier of 0.347 eV are executed 0.2%. The execution of the B-type single-atom processes on 8F structure (shown in Figure 44(g)) with barrier 0.165 eV after the execution of the most executed A-type single-atom process is necessary to convert the long B-type step-edge 8F into the long A-type step-edge 8F and is rate-limiting process. When temperature increases, the execution of concerted and 3-atom shearing processes increases while that of single-atom processes decreases, as shown in Figure 34. At 600K, the single-atom, concerted, and the 3-atom shearing processes are executed 61.2%, 26%, and 12.8% respectively of the total executed processes. In contrary to the reported kinetics of Ni octamer on the Ni(111) surface in ref. [15], trimer shearing processes are executed in significant fraction in this system, however, the trend of dominancy of single-atom processes and increase of execution of concerted processes with temperature is common on both systems. In contrary to both systems, concerted processes are reported in ref. [14] to be the dominating processes in diffusion of Cu octamer island on the Cu(111) surface with negligible execution of multi-atom processes up to temperature of 700K.

6.4 Conclusions

The Self-Learning Kinetic Monte Carlo (SLKMC-II) method is employed for the first time to study the thermally activated diffusion kinetics of a hetero-metallic system - in this case, the two dimensional small Cu islands of size 1 to 8 on the Ni(111) surface in the temperature range of 100K-600K. Energetically most favored islands structures are compact fcc structures with equal number of A- and B-type step-edges in tetramer, hexamer and heptamer islands whereas with long B-type step-edge in trimer, pentamer and octamer islands. Among multitude of processes of various types present in our database for various island sizes, we have reported
the most dominant, rate-limiting and diffusive ones and discussed their energetics. We find that short jump single-atom processes, concerted rotational processes and single-atom corner rounding processes dominate in diffusion kinetics of dimer, trimer and octamer islands respectively, concerted sliding processes dominate in tetramer, hexamer and heptamer islands whereas dimer-shearing processes dominate in diffusion of pentamer island at the temperature range of study. Dimer and trimer-shearing process of A-type are the most executed multi-atom processes in islands of size (4-7) and 8 respectively. Corner rounding single-atom processes are found to be the rate-limiting processes on pentamer and octamer islands. We expect that such an understanding of diffusion process at atomic level enables one to understand experimentally observed diffusion mechanisms and formulate reliable growth model. In future, we are planning to extend the methodology considering off-lattice positions to study kinetics of large lattice mismatched systems.

On the fundamental aspect, we correlate the significant variation on barriers of A- and B-type processes with the position of transition state either at minimum distance between adatom and another adatom closest to its target position during the process or beyond. Such a feature can be used as an important descriptor during training process in supervised (machine) learning methods in designing precise predictive model for computationally intensive activation energy barrier calculation. Comparatively smaller energy barrier of a processes of Cu diffusion over Ni diffusion on the same Ni(111) surface is attributed to the relatively lower lateral interaction of adatoms of Cu islands than Ni islands. Such a variation on Eₐₛ explains the higher diffusion of Cu than Ni islands at all temperatures under study.
CHAPTER 7: ISLAND DIFFUSION KINETICS USING SLKMC: BARRIERS FROM INTERATOMIC INTERACTION TO PREDICTIVE DATA-DRIVEN APPROACHES

In this chapter, we will present results of application of the SLKMC technique to explore the diffusion kinetics of homo-epitaxial Pd islands on the Pd(111) surface (Pd/Pd(111)) and Ag/Ag(111) systems and hetero-epitaxial Cu/Ni(111) and Ni/Cu(111) systems with special attention to the executed processes. We will trace the dominance of concerted processes in Pd/Pd(111) and Ni/Cu(111) and competition among concerted, multi-atom and single-atom processes in Ag/Ag(111) and Cu/Ni(111) to the strength of the lateral interaction of adatoms on these systems. Furthermore, we present predictive models of the activation energy barriers of diffusion processes of adatom islands using machine learning techniques. A set of easily accessible features, geometric and energetic, that are extracted using physical insight by noticing the variation of activation energy barriers of various processes on different homo-epitaxial metallic systems are encoded and used along with activation energy barrier to train and test linear and non-linear models. A non-linear model developed based on neural network technique explains 99% of the variations and possesses correlation coefficient of 99%. The developed model is used to predict the barriers of processes of Ni island diffusion on the Ni(111) surface which are then used to study kinetics of the its dimer island at the temperature range (100-700)K. No significant difference in the kinetic parameters such as the executed processes, diffusion coefficients as function of temperature, and the effective energy barriers of islands is obtained as compared to the kinetics study of the same system obtained using the
straightforward self-learning kinetic Monte Carlo (SLKMC) technique that does KMC simulation based on energy barriers calculated using interatomic interaction potential.

7.1 Introduction

There is preponderance of evidence that the variation of evolving morphology during thin-film growth on a surface, for e.g., experimental observation of growth as cluster, fractal, or dendritic modes on fcc(111) surface[58-60], results from competition among several phenomena including surface diffusion. In fact, diffusion of adatom islands on surface provides important insights into not just to thin-film growth[61-63], but also to surface chemical reactions[64], mass transport[65], deformation[66], and corrosion[67] of metal surfaces making it a focus of many experimental and theoretical investigations. In thin film growth in particular, a complete understanding of its morphological evolution requires atomic-level understanding of the processes executed at early stages. A number of studies using SLKMC have created an understanding for the island diffusion kinetics by exploring it for long time being unbiased by chosen processes apriori. For example, study on the Cu(111) surface, a scaling relation between diffusion coefficient (D) with the number of atoms in the island (N) was found to be $D \propto N^{-1.57}$ in ref.[76]. Furthermore, a crossover from domination of multi-atom process to that of involving single atoms was also found. In the subsequent work, detailed attention to the diffusion kinetics of small island sizes containing up to 10 adatoms in homo-epitaxial[78-80] and hetero-epitaxial systems[27] revealed a number of diffusion processes, including their relative significance in island diffusion characteristics. However, no any attempt is reported to gather a general understanding regarding the variation on the mode of diffusion on different systems. In this chapter, we report its application to explore the
diffusion kinetics of small (2-8 atoms) two-dimensional islands of Ag and Pd on their respective fcc(111) surfaces (two homo-epitaxial systems) and that of small Ni islands on Cu(111) and Cu islands on Ni(111) (two hetero-epitaxial systems). We pay special attention to the type of processes that are executed in the two sets and provide rationale for trends in the diffusion characteristics in terms of an energy descriptor. We also compare my results to the few experimental and computational results that are available.

The understanding gathered from the exploration alongwith including other factors is used to develop a predictive model for barriers of diffusion processes. Although the study of island diffusion using the SLKMC approach enables long-time simulation by avoiding repeated calculation of barriers of the same or symmetrical processes, it is hampered by calculation of $E_a$ s of hundreds of possible processes in different asymmetrical configurations on the same system. In addition, one need to calculate barriers of processes for every system. We think reliably generate descriptors and use them in predictive model can overcome both challenges. Once model be developed to predict $E_a$ s based on the already stored information that can extend the time equivalent obtained using kinetic Monte Carlo simulations. The challenge is to come up with a model that correlate the variation on barrier of processes with other factors. It is interesting to see if the same mathematical relation holds for different types of processes, for e.g., single-atom or multi-atom or concerted island motion.

Reported studies to calculate barriers of processes, but not of metal island diffusion processes, can broadly be classified as methods that infer $E_a$ from other quantities and those that directly predict $E_a$. Along the first category, Anand et al. [242] proposed that there is a
simple correlation between the diffusion barrier of atomic or molecular species and their binding energy on transition metal surfaces and quantitatively conclude that the diffusion barrier can be estimated by approximating it as 12% of the binding energy of the adsorbed state. To infer $E_a$, Kang et al. [243] used the energy of end state and R. Kutner et al. [244] used the energy difference between the final and initial configurations. Such inferences around in chemical reaction studies: Michaelides et al. [245] predicted $E_a$s of dissociative reactions in heterogeneous catalysis using enthalpy change, others [246-248] explored the bond breaking reaction of diatomic molecules on surface catalysts and reported a linear correlation between the transition state and the final state energies in elementary steps. These correlations provide a convenient tool for prediction of barriers which would enable screening of catalyst computationally. In the second category, calculation of $E_a$ using simplified approaches based on the counting of broken and newly formed bonds [249-252] and others based on the sophisticated mathematical techniques such as cluster expansion [253; 254], genetic programming [255], and artificial neural network [256; 257] are proposed. Because of the ability of neural network (NN) [258] to identify underlying highly complex and non-linear relationships on input-output data, it is becoming a method of interest for data fitting purpose.

In second part of this chapter, we develop predictive models for calculation of barriers of diffusion processes by using data-driven approaches. Barriers of a number of processes of metallic island diffusion and easily accessible local geometrical and energetic features of the systems are used to train, validate, and test models in linear approximation using multivariate linear regression and non-linear approximation using the neural network approach. We compare results of diffusion kinetics in a test case of Ni dimer diffusion on the Ni(111) surface
obtained from KMC simulation using such predicted barriers with that obtained using interatomic interaction potential.

7.2 Comparison of Diffusion Characteristics: Pd/Pd(111) and Ag/Ag(111), Cu/Ni(111) and Ni/Cu(111)

In this section, we present results of SLKMC-II simulations for island diffusion of two sets of systems. In one, we compare the homo-epitaxial systems: Ag islands on Ag(111) and Pd islands on Pd(111), while in the other we focus on the comparison of the hetero-epitaxial systems: Ni islands on Cu(111) and Cu islands on Ni(111). We have chosen to examine the Cu-Ni and Ag-Pd systems, for both homo- and hetero-epitaxial diffusion as the lattice mismatch in the two sets of systems is not very large (Cu-Ni mismatch ~2.5%; Ag-Pd mismatch~ 4.6%). Since the present SLKMC-II formulation is on-lattice, larger mismatch than noted above would have led to more strain in the systems, adding an additional complexity that is left for the future. An estimate of the error introduced due to assumption of on-lattice sites has already been discussed in section 6.3.1. Note that some results for Cu islands on Ni(111) have already been presented in chapter 6 and we have included them here for comparison and for completeness.

As in earlier chapters, the general findings using SLKMC method consists of a tabulation of the frequency of execution of the different types of processes: single- and multi-atom, and concerted processes. We also compare for these systems the island-size dependent diffusion coefficients as a function of temperature and their effective energy barrier ($E_{\text{effective}}$).
Figure 45 Normalized frequency of executed single-atom, multiatom, and concerted processes in the diffusion of adatom islands of size 2 to 8 in the temperature range of 100-600K of: (a) Pd (continuous line) and Ag (dotted line) adatom islands of size 2 to 8 on their respective (111) surface; (b) Ni islands on the Cu(111) surface (continuous line) and Cu islands on the Ni(111) surface (dotted line).

As shown in Figure 45(a), except in the case of the dimer, concerted processes constitute more than 80% of the executed processes for Pd island diffusion (filled green squares connected by a green line), at all temperatures considered in this study. Furthermore, this fraction is consistently higher than the execution percentage of the same type of process in Ag island diffusion (represented by green squares connected by a dotted line). Note that some of our results compare well with previous calculations. For example, molecular dynamics
simulation of the diffusion of heptamer island of Pd on the Pd(111) surface show [259] that the symmetrical form of the cluster is maintained during cluster diffusion from one stable site to the next, in qualitative agreement with our finding of the dominancy of execution of concerted process for the same system. The diffusion processes revealed for small Pd islands on Pd(111) in MD simulations [260] are also to be found in our database, which naturally contains many more processes that could be revealed in MD.

For Ag islands, the pentamer and the heptamer show interesting crossover behavior, as a function of temperature. Notice also that for Ag octamers, single-atom processes are dominant at all temperatures, in contrast to the behavior of Pd octamers on Pd(111). A similar difference in the dominancy of concerted processes is observed in the diffusion kinetics study of Ni islands on the Cu(111) surface as shown in Figure 45(b). On the other hand, competition among concerted, multi-atom and single-atom processes is obtained for Cu islands on the Ni(111) surface (see Figure 45(b)).
Table 14 Comparison of barriers of concerted and multi-atom processes on the same adatom island configuration of different island sizes of the systems under study.

<table>
<thead>
<tr>
<th>Island Size</th>
<th>Energy barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd/Pd</td>
</tr>
<tr>
<td></td>
<td>Concerted</td>
</tr>
<tr>
<td>4</td>
<td>0.186</td>
</tr>
<tr>
<td>5</td>
<td>0.277</td>
</tr>
<tr>
<td>6</td>
<td>0.364</td>
</tr>
<tr>
<td>7</td>
<td>0.327</td>
</tr>
<tr>
<td>8</td>
<td>0.416</td>
</tr>
</tbody>
</table>

Comparison of the energy barriers of some frequently-executed multi-atom and concerted processes of islands of different sizes for four different systems explored in this study, as summarized in Table 14, show that the order of difference between barriers for multi-atom and concerted motion for the same island configuration to be Ni/Cu, Pd/Pd, Cu/Ni, and Ag/Ag. For Pd islands on Pd(111) and Ni islands on Cu(111), we see that the barrier for concerted motion are much smaller than those for the other type of processes, and hence the obvious rationale for their dominancy in diffusion kinetics at all temperatures under study. On the other hand, there is relatively small difference in the barriers of various kinds of diffusion processes for all
configurations of Ag islands on Ag(111) and Cu islands on Ni(111), resulting in a competition amongst them. Note that for most island sizes the most dominant concerted processes are the ones for their compact structures and the competing multi-atom processes are the A-type dimer shearing for the tetramer to the heptamer and A-type trimer shearing process for an octamer.

Some insights into the relative difference in the barriers of multi-atom and concerted processes for the considered systems can be obtained from the comparison of the lateral interaction among adatoms, since the effect of a substrate is the same for all processes for islands with the same configuration. Such an understanding follows from our work on Cu on Ni(111) system presented in chapter 6 in which we had emphasized the role of lateral interaction to understand the relatively smaller barriers of the diffusion processes of Cu adatom islands on the Ni(111) substrate. To examine the role of lateral interactions in a general manner, we calculate the lateral interaction energy \( E_{L,I} \) amongst the adatoms in the island configuration of which barriers of multi-atom and concerted processes are compared in Table 14 using \( E_{L,I} = E_{\text{island+sub.}} - nE_{\text{mono+sub.}} + (n - 1)E_{\text{sub.}} \) where \( E_{\text{island+sub.}} \), \( E_{\text{mono+sub.}} \), and \( E_{\text{sub.}} \) are the total energy of the system with the island adsorbed on the substrate, a monomer adsorbed on the substrate, and that of the isolated substrate, respectively. The calculated values of \( E_{L,I} \) for four different systems are presented in Table 15.
Table 15 Lateral interaction among adatoms of islands on the fcc(111) substrate for the configurations relevant to processes in Table 14.

<table>
<thead>
<tr>
<th>Island Size</th>
<th>Lateral interaction energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd/Pd</td>
</tr>
<tr>
<td>2</td>
<td>-0.54</td>
</tr>
<tr>
<td>3</td>
<td>-1.49</td>
</tr>
<tr>
<td>4</td>
<td>-2.42</td>
</tr>
<tr>
<td>5</td>
<td>-3.29</td>
</tr>
<tr>
<td>6</td>
<td>-4.2</td>
</tr>
<tr>
<td>7</td>
<td>-5.45</td>
</tr>
<tr>
<td>8</td>
<td>-6.33</td>
</tr>
</tbody>
</table>

Clearly, Pd/Pd(111) and Ni/Cu(111) systems, which have relatively large difference in the barriers for concerted and multi-atom processes have strong lateral interactions among adatoms, whereas the Ag/Ag(111) and Cu/Ni(111) systems have relatively weak interaction among adatoms.
Figure 46 Arrhenius plot of islands of size 1 to 8 of (a) Pd islands on Pd(111) (continuous line) and Ag islands on Ag(111) (dotted line) and (b) Ni islands on Cu(111) (continuous line) and Cu islands on Ni(111) (dotted line).

The Arrhenius plot of each island size under study for the homo- and hetero-epitaxial systems, plotted in Figure 46(a) & (b) displays the expected linear dependence from which one can calculate the effective energy barrier ($E_{\text{effective}}$) for each island size (from the slope of the curve). The values of the so-extracted $E_{\text{effective}}$ are presented in Table 16.

Table 16 Effective energy barriers calculated as function of island-size using SLKMC simulation for the systems under study.

<table>
<thead>
<tr>
<th>System/Size</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Pd(111)</td>
<td>0.038</td>
<td>0.103</td>
<td>0.177</td>
<td>0.172</td>
<td>0.195</td>
<td>0.282</td>
<td>0.421</td>
<td>0.385</td>
</tr>
<tr>
<td>Ag/Ag(111)</td>
<td>0.058</td>
<td>0.112</td>
<td>0.173</td>
<td>0.201</td>
<td>0.276</td>
<td>0.301</td>
<td>0.401</td>
<td>0.394</td>
</tr>
<tr>
<td>Ni/Cu(111)</td>
<td>0.028</td>
<td>0.102</td>
<td>0.140</td>
<td>0.139</td>
<td>0.197</td>
<td>0.236</td>
<td>0.356</td>
<td>0.400</td>
</tr>
<tr>
<td>Cu/Ni(111)</td>
<td>0.051</td>
<td>0.131</td>
<td>0.165</td>
<td>0.180</td>
<td>0.285</td>
<td>0.316</td>
<td>0.399</td>
<td>0.378</td>
</tr>
</tbody>
</table>
The Arrhenius behavior of Pd adatom diffusion on the Pd(111) surface is also reported using MD simulations [260; 261], from which an effective energy barrier were calculated. Note that on every island their values are higher than those obtained by us. This difference could be attributed to the types of diffusion processes that were revealed in MD simulation. Some difference could also arise from the differences in the interaction potential. The noticeably large change in the effective energy barrier from the hexamer to the heptamer seen in my result in Table 16 was also observed Liu et al. [260]. My result of dominancy of concerted processes for compact configurations of Pd trimer and heptamer on Pd(111) are also in agreement with observation in ref. [260], however, their results for the rate of occurrence of concerted and multiatom processes of compact configurations of other small islands is different from mine, although our database includes those processes. The slight decrease of effective energy barrier in case of tetramer in comparison to that of trimer and pentamer island diffusion of Pd/Pd(111) and Ni/Cu(111) in my result in Table 16 is consistent to the result reported in ref. [208]. Note also that the effective energy barrier increases relatively less from trimer to tetramer islands diffusion in case of Ag/Ag(111) and Cu/Ni(111) systems too. The values of effective energy barriers of Pd/Pd(111) and Ag/Ag(111) systems compare well with the reported values of free diffusion energy in ref. [208].

For completeness we include here the comparison of the diffusion characteristics of the monomer with those already reported in the literature. Using another form of the semi-empirical potential [262], Liu et al. [239] calculated the activation energy barrier of Pd adatom diffusion on the Pd(111) surface to be 0.031 eV with 0.001 eV difference in binding stability on fcc and hcp sites comparing well we my value of 0.037eV with the corresponding difference
of 0.002 eV. Furthermore, the calculated diffusion pre-factor of $5 \times 10^{12} \text{Å}^2/\text{s}$ compares well with our value of $2 \times 10^{12} \text{Å}^2/\text{s}$, respectively. Similarly, for Ag monomer diffusion on Ag(111), Liu et al. get activation energy barriers of 0.059eV and $D_0$ of $5 \times 10^{12}$ comparing well with my value of 0.059eV and $2.24 \times 10^{12} \text{Å}^2/\text{s}$, respectively. The value of effective energy barrier of Ag monomer diffusion on Ag(111) obtained from Arrhenius plot of monomer after SLKMC simulation is close to the reported experimental value of diffusion energy of $(0.051 \pm 0.024)$ eV in ref. [263]. In addition, the calculated values of vibrational frequencies of different modes by Liu et al. in the range $10^{11}$ to $10^{13} \text{ s}^{-1}$ imply my assumed value of $10^{12} \text{ s}^{-1}$ for attempt frequency is reasonable. The main message from these comparisons with previous work is that my results here for the simple case of monomer diffusion are in accord with what has already been observed. From the few results available for (2-8 atom) islands, the main difference is in the magnitude of the effective energy barriers and the types of processes revealed during the simulation.

### 7.3 Machine Learning for Diffusion Study

In this study, we develop predictive models for calculation of activation energy barrier for the multitude of diffusion processes using data-driven approaches. Barriers of number of metallic island diffusion and easily accessible local geometrical and energetic features of the system are used to train, validate and test models.

The first step in developing predictive model is generation of descriptors for which we have taken physical insights that we have obtained from our systematic investigations of the processes most responsible for the diffusion of small (2-8 adatom) islands on the (111) surfaces.
of Ag, Cu, Ni, and Pd. Below we discuss these descriptors using specific examples from SLKMC database.

### 7.3.1 Descriptor Generation

The first task is to analyze the database of energy barriers and initial and final state configurations of the island and top substrate layer for single, multi-atom, and concerted motion process of adatom islands of Ag, Pd, Cu, and Ni on their respective (111) surfaces which are calculated and stored using the procedure explained in section 2.4.2.2. While the dependence of the activation energy barrier for a particular process on the local geometry is subtle, some systematic trends can be found through analyses of certain microscopic factors that we will discuss in this section. The selection of these factors is, of course, very crucial to designing a reliable model that predicts barriers with high correlation with the calculated ones. The rational used in the identification of such descriptors is explained in this section through examples of some frequently occurring diffusion processes.

i) Number of bonds change ($x_1$)

For the trimer island shown in Figure 47 with 3 initial internal bonds, the execution of process I with an energy barrier of 0.629eV reduces the number of bonds among adatoms to 2 (i.e. a net loss (change) of 1 bond). On the other hand, the process II with an energy barrier of 1.147eV involves a change of 2 bonds. This is not surprising, as it costs energy to break a bond, larger the number of bonds to be broken, the higher the energy cost. Comparison of energy barriers of the type represented in this example in Figure 47 for adatom islands of other sizes and shape, we find a general trend in the relative strength of the barrier on the number of
bonds that are broken in the diffusion process. So, the change in the number of bonds associated with a diffusion process can be an important descriptor of the energy barrier.

Figure 47 Single-atom processes for a trimer island that require breaking of different number of bonds for diffusion, along with their energy barriers.

ii) Change in average distance from center of mass ($x_2$)

Figure 48 Single-atom process that converts (a) a compact trimer island into a non-compact one and, (b) its reverse process; along with their barriers.

Figure 48(a) illustrates a single atom process that converts a compact trimer into a non-compact one with a calculated barrier of 0.629 eV whereas Figure 48(b) shows its reverse process that converts the non-compact island configuration into the compact one with a significantly small energy barrier of 0.023eV. In the example, another quantity of interest is the average distance of adatoms in the initial and final configurations from their center of mass (CM) divided by the number of atoms in the island. The variation in this average distance may also be used to encode information about the change in shape of configuration, or compactness
of the island before and after execution of a process. In case of multi-atom or concerted process (no island shape change in concerted process), this descriptor encodes the information of whether they are on the compact or non-compact configuration.

iii) Shifted distance of center of mass of an island ($x_3$)

Figure 49  (a) Translational, and (b) rotational motion processes for a trimer island along with their barriers.

Figure 49 shows the variation of barriers of translational and rotational concerted processes for the same triangular 3H-T (3 adatoms adsorbed on hcp sites centered about a top (T) site) island configuration. In terms of geometrical variables, these two processes have different values for the distance by which the center of mass of the island shifts: zero and non-zero for rotational and translational processes, respectively. In the case of a single-atom process, there is also variation on the barriers of short and long-jump processes. So, the distance of the moving adatom from the center of mass of adatoms at the initial and final configurations encodes such information.
iv) Number of atoms involved in a process ($x_4$)

![Image of dimer and trimer islands](image)

Figure 50 Translational concerted processes of (a) a dimer, and (b) a trimer island, along with their barriers.

For small islands, concerted motion of the island as a whole is an important contributor to the diffusivity of the island. In Figure 50, we show the variation in the barriers of such processes with the number of atoms in the island, with the example of dimer and trimer islands. To encode such information, the number of atoms involved in a diffusion process is taken as an additional descriptor. The encoding is obvious for single-atom and multi-atom processes.

v) A-or B-type process ($x_5$)

![Image of A and B-type processes](image)

Figure 51 A-and B-type processes for (a) a dimer, (b) a tetramer island, along with their barriers.

In Figure 51, we have shown the dependence of the energy barrier of processes on whether the executed move is an A-type and B-type processes (as defined in Figure 6(b)) with an example of single atom processes in dimer diffusion (Figure 51 (a)) and two-atom processes in case for a tetramer (Figure 51(b)). For each island, both A- and B-type of processes start on the same initial island configuration and form the same final island configuration after
executing those processes. To explain such variations, a binary variable is introduced that has
value 1 if the process is A-type and 0 if it is B-type.

vi) Binding energy of island ($x_6$)

As shown in ref. [27], the energy barriers of diffusion processes of Ni island on Ni(111) are
in general larger than those of the corresponding processes of Cu islands on the same Ni(111)
substrate. In fact, such trends are also to be found when comparing Ag and Pd systems, as seen
in Table 17 in which we have summarized the energy barriers of some representative processes
for several homo-epitaxial and hetero-epitaxial systems. Although the current data used only
consists of homo-epitaxial system, we show the same general trend in case of hetero-epitaxial
system too.

Table 17 Diffusion barriers of some selected single-atom (S), multi-atom (M), and concerted (C)
processes of adatom islands on several homo-epitaxial and hetero-epitaxial fcc(111)
systems.

<table>
<thead>
<tr>
<th>Island</th>
<th>Energy barrier(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu/Ni</td>
</tr>
<tr>
<td>1</td>
<td>0.052</td>
</tr>
<tr>
<td>2(S)</td>
<td>0.029</td>
</tr>
<tr>
<td>2(C)</td>
<td>0.059</td>
</tr>
<tr>
<td>3(C)</td>
<td>0.152</td>
</tr>
<tr>
<td>4(M)</td>
<td>0.191</td>
</tr>
</tbody>
</table>
Table 18  Size dependent adatom island binding energy on several homo-epitaxial and hetero-epitaxial systems.

<table>
<thead>
<tr>
<th>Island</th>
<th>Island binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu/Ni</td>
</tr>
<tr>
<td>2</td>
<td>-3.29</td>
</tr>
<tr>
<td>3</td>
<td>-4.24</td>
</tr>
<tr>
<td>4</td>
<td>-5.37</td>
</tr>
<tr>
<td>5</td>
<td>-6.54</td>
</tr>
<tr>
<td>8</td>
<td>-10.60</td>
</tr>
</tbody>
</table>

Comparison of energy barrier in the first four columns in Table 17 shows that those for the diffusion of Cu islands on either Cu(111) or Ni(111) are lower than those of the corresponding Ni islands on the same substrate. A similar relation holds for Ag islands having relatively higher barriers than Pd islands on both Pd(111) and Ag(111) as presented in last four columns in the Table 17. To obtain some qualitative understanding of the above trends, we present in Table 18 the binding energy (B.E.) of adatom islands on respective surface mentioned in Table 17. These have been calculated using

\[
\text{B.E.} = E_{\text{island}+\text{subs}} - E_{\text{island}} - E_{\text{subs}},
\]

where \(E_{\text{island}+\text{subs}}, E_{\text{island}}, E_{\text{subs}}\) are the total energy of a system containing the adatom island adsorbed on the substrate, the isolated adatom island, and the isolated substrate, respectively.
We conclude from Table 18 that B.E. of the Cu islands on Ni(111) are somewhat higher than that of Ni islands on the same surface, while that of Pd islands are larger than that of Ag islands on the same substrate. We thus conclude that the binding energy of the adatom island on the substrate and may be taken as an additional descriptor.

vii) Lateral interaction energy among adatoms ($\chi_7$)

In chapter 6, we had emphasized the role of lateral interaction to understand the relatively smaller barriers of the diffusion processes of Cu adatom islands than that of Ni on the Ni(111) substrate. The slight difference in the binding energy of Cu and Ni islands on Ni(111) (first 2 columns of Table 18) also indicates that several factors beyond binding energy are responsible for the noticeable differences in diffusion barriers for otherwise similar processes of the Cu and Ni islands on Ni(111). To examine the role of lateral interactions in a general manner we turn here to a comparison of some frequently-executed multi-atom and concerted processes of islands of different sizes for four different systems explored in this study, in Table 19.
Table 19  Comparison of barriers of concerted and multi-atom processes for the same adatom island configuration in homo and hetero-epitaxial systems.

<table>
<thead>
<tr>
<th>Island Size</th>
<th>Energy barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd/Pd</td>
</tr>
<tr>
<td></td>
<td>Concerted Multi-Atom</td>
</tr>
<tr>
<td>4</td>
<td>0.186</td>
</tr>
<tr>
<td>5</td>
<td>0.277</td>
</tr>
<tr>
<td>6</td>
<td>0.284</td>
</tr>
<tr>
<td>7</td>
<td>0.327</td>
</tr>
<tr>
<td>8</td>
<td>0.416</td>
</tr>
</tbody>
</table>

From Table 19, one can make two observations: there is a noticeable difference in the barriers of concerted and the multi-atom processes for the same island configuration and that the magnitude of the difference is system dependent. We find the order to be Ni/Cu, Pd/Pd, Cu/Ni, and Ag/Ag i.e., the difference is in general large in Ni/Cu and Pd/Pd systems. Such a difference might be understood from the interatomic interaction among adatoms. One quantitative measure of such is the lateral interaction amongst the adatoms in the island which is given by

\[ E_{LL} = E_{\text{island+sub.}} - nE_{\text{mono+sub.}} + (n - 1)E_{\text{sub.}} \]  

(135)

where \( E_{\text{island+sub.}}, E_{\text{mono+sub.}}, \text{and } E_{\text{sub.}} \) are the total energy of the system with the island adsorbed on the substrate, a monomer adsorbed on the substrate, and that of the isolated
substrate, respectively. The calculated values of $E_{LI}$ for four different systems whose energy barriers are in Table 19 are presented in Table 20. In Table 20, one can see that the Pd/Pd and Ni/Cu systems which have the relatively large difference between barriers of concerted and multi-atom processes, with low barriers of concerted processes, have strong lateral interactions among adatoms whereas the Ag/Ag and Cu/Ni systems have relatively weak interaction among adatoms. We may thus conclude that the lateral interaction energy of adatoms may be taken as an additional descriptor.

Table 20 Lateral interaction among adatoms of islands on the fcc(111) substrate for the configurations relevant to processes in Table 19.

<table>
<thead>
<tr>
<th>Island Size</th>
<th>Lateral interaction energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd/Pd</td>
</tr>
<tr>
<td>2</td>
<td>-0.54</td>
</tr>
<tr>
<td>3</td>
<td>-1.49</td>
</tr>
<tr>
<td>4</td>
<td>-2.42</td>
</tr>
<tr>
<td>5</td>
<td>-3.29</td>
</tr>
<tr>
<td>6</td>
<td>-4.2</td>
</tr>
<tr>
<td>7</td>
<td>-5.45</td>
</tr>
<tr>
<td>8</td>
<td>-6.33</td>
</tr>
</tbody>
</table>

With the above seven descriptors in hand, a large database of these descriptors for the systems of interest here, we now proceed to develop a data-enabled model for predicting the
diffusion barriers in question. Some details of the modeling approaches follow in the next section.

7.3.2 Model Development

As an initial step, a predictive model is developed using multivariate linear regression technique as explained in section 2.3.2.2. In any model, \( E_a \) of a diffusion process is taken as dependent variable and 7 descriptors explained above are taken as independent input variables. For the purpose here we consider 168 barriers for Cu, 191 for Ag, 156 for Pd, and 328 for Ni collected from dimer to tetramer islands from our SLKMC database. Those descriptors along with the energy barrier of the corresponding process are used to train and test our models. To compare the importance of each descriptor, values for each is normalized. In the first set of calculation, all 844 samples of the input-output pair are used to develop a model.

A non-linear statistical modeling is performed using neural network toolbox of MATLAB software. The structural organization of the NN consists of 4 layers of which the first layer is input layer with 7 nodes corresponding to 7 input features, 2 hidden layers containing 10 nodes in each layer and output layer containing 1 node with outputs \( o_1^3 \), the predicted energy barrier. The sigmoid function is taken as transfer function between first and second, and second and third layers, and linear function between third and output layer. The mean square error (MSE) calculated using Equation (101) is taken as optimizing function. Levenberg-Marquardt algorithm[54; 55] is used as optimizer whose update equation is given in Equation (108) in which the current weight and bias vector (\( x_k \)) is updated to vector \( x_{k+1} \) following \( x_{k+1} = x_k - (J^T J + I * \mu)J e \), where I is an identity matrix, \( \mu \) is a training
rate parameter which influences the rate of weight and bias adjustment and $JJ = (J_F)^T(J_F)$ for $J_F$ being the Jacobian of performance function with respect to weights and biases. In this study, the initial weight and biases are randomly selected and the initial value of the learning rate parameter $\mu$ is taken as 0.001 which is increased by a factor of 10 until the updated $x_{k+1}$ results in a reduced performance after which $\mu$ is decreased by a factor of 0.1. During training, the network performance in the validation vectors is checked every epoch and if it is less in the previous step and higher or constant in the current step (fails to improve) for 6 additional epochs in a row, training is stopped after 6 steps. In addition, if the performance error is 0 or the gradient of the error is less than $10^{-7}$, the calculation terminates.

In both of the approaches, we first perform calculation taking only one elemental system at a time. After four such sets of calculation, prediction are made using all systems combined. After that only Cu, Pd, and Ag are used to make a model which is then used to predict barriers of Ni system. In first 3 sets of calculation, the input samples of all four systems are randomly divided into training, validation, and testing set. In the fourth set of calculation, the barriers of Cu, Ag, and Pd systems are used for the training and the validation sets whereas those of Ni system are used only for the testing set.

7.3.3 Energy Barrier and Diffusion Characteristics

The value of $R^2$ between the calculated and predicted values of activation energy barrier is calculated as a measure of goodness of the prediction along with the coefficients in the expansion of barrier linearly with 7 descriptors are presented in Table 21.
Table 21. Calculated coefficients in the linear predictive equation of activation energy barrier using 7 descriptors and value of $R^2$ for models.

<table>
<thead>
<tr>
<th>System</th>
<th>Sample Size</th>
<th>Coefficients</th>
<th>Intercept</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\beta_1$  $\beta_2$ $\beta_3$ $\beta_4$ $\beta_5$ $\beta_6$ $\beta_7$ $\beta_0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>168</td>
<td>0.92         -0.09 0.20 0.19 0.11 0.08 0.003 -0.44 0.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>191</td>
<td>0.78         -0.15 0.11 0.16 0.13 0.28 -0.29 -0.11 0.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>157</td>
<td>1.22         -0.36 0.23 0.15 0.23 -0.08 0.11 -0.24 0.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>328</td>
<td>1.51         -0.11 0.24 0.17 0.14 0.08 -0.04 -0.63 0.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuAgPdNi</td>
<td>844</td>
<td>1.38         -0.23 0.19 0.11 0.14 -0.31 0.07 -0.31 0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuAgPd</td>
<td>516</td>
<td>1.35         -0.28 0.20 0.14 0.14 -0.50 0.24 -0.28 0.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni using CuAgPd</td>
<td>328</td>
<td>0.887</td>
<td></td>
<td>0.04</td>
</tr>
</tbody>
</table>

As a second scenario, we use the dataset of Cu, Ag, and Pd systems that contains 516 samples to develop a model and test its predictive capacity for the Ni system. The coefficients of such a predictive equation are plotted in the row labeled CuAgPd in Table 21. The Pearson’s correlation coefficient between the calculated and the predicted values of Ni barriers using such a trained model is found to be 0.86. The high value of correlation coefficient indicates that the 7 descriptors used in this study are sufficient to predict the value of an activation energy barrier with reliable accuracy. The calculated and predicted activation energy barriers of the Ni system in the first and scenario are plotted in Figure 52(a) & (b) respectively. The black continuous line represents an ideal case.
Figure 52 Predicted vs. calculated barriers of most frequently executed processes for Ni islands on the Ni(111) surface, (a) when some Ni samples are used in the training of the multivariate linear model and (b) Ni samples are not used to develop the model.

The values of the regression coefficients between calculated and predicted barriers on training, validation, and testing data sets for modeling using different samples are presented in Table 22.

Table 22 Values of correlation coefficients in the training, validation, and testing dataset of diffusion barriers using the neural network.

<table>
<thead>
<tr>
<th>System</th>
<th>Sample Size</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Training</td>
</tr>
<tr>
<td>Cu</td>
<td>168</td>
<td>0.99</td>
</tr>
<tr>
<td>Ag</td>
<td>191</td>
<td>0.99</td>
</tr>
<tr>
<td>Pd</td>
<td>157</td>
<td>0.99</td>
</tr>
<tr>
<td>Ni</td>
<td>328</td>
<td>0.99</td>
</tr>
<tr>
<td>CuAgPdNi</td>
<td>844</td>
<td>0.97</td>
</tr>
</tbody>
</table>
The plots of the predicted vs. computed values of barriers of processes for training, validation, and testing data are shown in Figure 53.

Figure 53 Calculated vs. predicted barriers of different processes of an island diffusion on the fcc(111)surface using a neural network; (a), (b), and (c) show plots for training, validation, and testing samples, respectively.

Significantly larger value of $R^2$ indicates that the used variables are sufficient to explain the variability at 99% on the output variable. The regression analysis of the model gave a 0.99 correlation coefficient and the mean square error of 0.005. A histogram plot of the error of predictions is shown in Figure 54. Note that there are significant instances where the error lies within few meV of the calculated values and the instances with increasing error magnitude
decrease with increase in error value. Note that every result might change slightly because of the random setting of the initial weights and biases and different divisions of data into training, validation, and test sets. This has demonstrated that artificial neural networks have good potential for predicting activation energy barriers of any transition metal elements from easily available structural descriptors of homo-epitaxial systems.

Figure 54 Error histogram of prediction of barriers of processes using a neural network.

To test the generality of the model, we predict the activation energy barriers of processes for the Ni dimer excluding the barriers of the system in the training and validation process. Those predicted barriers are then used to explore the diffusion properties of the island using the kinetic part of the SLKMC method. The Arrhenius plot and the normalized type of executed processes in the simulation of dimer island diffusion in the temperature range 200K to 600K are presented in Figure 55.
Figure 55 (a) Arrhenius plot, (b) normalized type of executed processes obtained from KMC simulation of the Ni dimer diffusion processes on the Ni(111) surface using barriers from drag method from EAM interaction (red curves) and from the trained neural network model (black curves).

The reasonably close values of the quantities plotted in Figure 55 imply that the predictive approach can be used to find quantitatively and qualitatively reliable diffusion characteristics of islands of any size of any element in the set of metallic systems considered here, with a significant gain in computational time.

**7.4 Conclusions**

From a systematic analysis of the diffusion characteristics of a set of small (1-8 atoms) 2D islands of Cu, Ag, Ni and Pd on their respective (111) surfaces, and in a few cases on hetero combinations, we conclude that whether concerted process dominate or there exists competition among other types of processes (involving single and multiple atoms) depends on the lateral interaction among the island atoms. In case of systems with large lateral interaction, the concerted motion of the island is found to be the dominating process at low or high...
temperatures. On the other hand, for systems with relatively low lateral interaction, multi-atom and single-atom processes also compete with concerted processes at low temperatures whereas the concerted motion dominates the dynamics at high temperatures. Furthermore, we introduced and applied a data-driven approach for ultrafast prediction of activation energy barriers for island diffusion processes. Once the descriptors that can explain the variation of activation energy barriers of processes are determined and encoded with sufficient physical insight, such a model may be used to predict barriers with remarkable accuracy. These results are very promising for application of tools suitable for multi-scale modeling of thin film growth and morphological evolution of nanostructured systems.

It is important to stress that one can perform simulation of the growth pattern of islands of different systems with significantly different lateral interaction by incorporating the barriers of various possible processes and predict the possible variation on experimentally observable time and spatial dimension. In addition, one can compare the diffusion characteristics of islands of different systems using predicted barriers with the result obtained with well tested methods. Implementation of neural network approach on-the-fly for the barrier calculation in SLKMC method can extend the time-limit accessible using state of the art SLKMC approach and might disclose novel rare processes.
CHAPTER 8: METHANOL PARTIAL OXIDATION REACTION ON Pd_{16}Zn_{16} NANOPARTICLE: A DFT+KMC STUDY

In this chapter, we discuss results of performing ab initio density functional theory (DFT) calculations of energetics for several elementary pathways associated with methanol partial oxidation (MPO) reaction (CH$_3$OH + $\frac{1}{2}$ O$_2$ → CO$_2$ + 2H$_2$) on a 32-atom Pd$_{16}$Zn$_{16}$ nanoparticle catalyst and use them in the kinetic Monte Carlo simulations for elucidating reaction rates. We determine the geometry of active sites for adsorption and the strength of binding of reactants, products, and various intermediates of the reaction on different adsorption sites on the surface of the catalyst by calculating adsorption energetics. The activation energy barriers of probable reactions including oxidation and hydroxylation of decomposed CH$_3$OH are determined. KMC simulations show that the catalyst yields no selectivity for H$_2$ but almost perfect, temperature-independent selectivity (~100%) for CO$_2$ and H$_2$O leading to full oxidation of methanol. Such a result can be rationalized as the availability of O* following the breaking of O$_2^*$ with small barrier and almost spontaneous conversion of H$_2^*$ into H*.

8.1 Introduction

Extraction of chemical energy stored in hydrogen molecule using proton exchange membrane fuel cell is taken as an alternative to non-renewable and environmentally unfriendly petroleum fuels. H$_2$, however, does not appear in abundant quantities in nature, and therefore, must be obtained by processing another molecule. Methanol, the simplest alcoholic hydrocarbon molecule, has the highest hydrogen density, can be easily produced from biomass or coal-driven syngas, is sulfur free, and does not have C-C bonds that avoids the risk of
catalyst coking, can be activated at temperature less than 300\(^{\circ}\)C due to absence of C-C bond[264] and so is taken as one better option for H\(_2\) production from its transformation. H\(_2\) can be extracted from CH\(_3\)OH from its decomposition: CH\(_3\)OH \(\rightarrow\) CO + 2H\(_2\) or partial oxidation (MPO): CH\(_3\)OH + \(\frac{1}{2}\) O\(_2\) \(\rightarrow\) CO\(_2\) + 2H\(_2\) or steam reforming (MSR): CH\(_3\)OH + H\(_2\)O \(\rightarrow\) CO\(_2\) + 3H\(_2\). Among those transformations, MSR produces higher H\(_2\)/CO\(_2\) and produces CO free H\(_2\) and Cu based catalyst are regarded the best catalyst for MSR (see review [265]) due to high CO\(_2\) selectivity (avoiding poisoning) that keeps H\(_2\) production. They have limited long term stability due to sintering at elevated temperatures [266-268]. It is reported that Pd/ZnO system shows exceptional performance in MSR [269; 270] and dehydrogenation. Pd/ZnO exhibits much higher thermal stability than the Cu catalyst [271; 272]. The high activity of Pd/ZnO is attributed the formation of PdZn alloy at the metal-support interface[272; 273]. It is shown in ref. [274] that PdZn catalyst offers high conversion on MSR reaction even at low temperature. Interestingly, PdZn alloy has a similar local valence d-band DOS as that of Cu[275] and X-ray photoelectron spectroscopy (XPS) valence band spectra[276; 277]. However, MSR is energetically less attractive since it requires to produce steam (heat energy). Since the partial oxidation reaction requires oxygen (air), is an exothermic reaction, and produces CO free H\(_2\), it can be important pathways for H\(_2\) production. However, lesser studies are reported of Pd/ZnO catalyst for MPO [278; 279] and there is no any reported MPO reaction on PdZn system, although some processes remain the same as in MSR studies reported in ref. [280] (see review [281]).
In comparison to bulk and an extended surface, nanoparticles have unique properties, for e.g., bulk and extended Au surfaces are inert [282], but small Au nanoparticles are active for different reactions [283-285]. The unique properties have been attributed to various under-coordinated sites, strain developed on facets etc. Recently, one of our experimental collaborator has shown that low loading of Pd on ZnO becomes an active catalyst for H₂ production with high selectivity (higher than 90%) under MPO condition, which decreases with higher Pd loading that generates PdZn nanoparticle. Since reaction intermediates are difficult to observe directly in experiment, if not impossible, the study requires theoretical input to conclusively determine the mechanism. It is also interesting to develop an energetic understanding about difference in activity with Pd loading. Experimental observations of signature of formation of PdZn nanocluster ([277; 286]) when Pd loaded on ZnO under reaction condition require to explore its effect for any reaction, including MPO. Due to computational requirement, unsupported PdZn nanoparticle is taken as a model catalyst system to explore the product selectivity with an objective to devise an optimum catalytic condition in terms of externally controlling factors of temperature and pressure in reliable kinetic modeling.

In this chapter, we present result of exploration of active surface sites for adsorption of reactants, products, and intermediates along with the adsorption energy and geometry of corresponding species on those sites. The energetics of various reaction pathways of the MPO reaction including hydroxylation and oxidations on the catalyst are explored. The selectivity of products using the kinetic Monte Carlo simulation explained in section 2.4.2.1 is reported as function of temperature and pressure.
8.2 Computational Details

To construct a structural model of the catalyst, we are guided from experimental observations that report formation of nanoparticle with 1:1 ratio of Pd and Zn \([287-289]\), thermal stability of such a nanoparticle in the temperature range of 473–873 K\([286]\) and the most stability of (111) surface of PdZn\([288-290]\). We form CuAu \(L1_0\)-type tetragonal bulk PdZn crystal structure that has 1:1 Pd-Zn ratio taking the lattice parameters of \(a=4.11 \text{ Å}\) and \(c=3.35 \text{ Å}\) from ref. \([291]\) and cut the structure around its center with a radius of 5 Å that results into bimetallic structure containing 16 Zn and 16 Pd atoms exposing six (111) facets, which is shown in Figure 56.

Figure 56 Pd\(_{16}\)Zn\(_{16}\) nanoparticle catalyst model in which white and blue balls represent Zn and Pd atoms, respectively.

Although one needs to consider all possible sites on different facets as active sites, we chose stable (111) facet as an active site model for the sake of computational efficiency. The considered facet, labeled in Figure 56, exposes four Zn atoms and four Pd atoms for molecular adsorption. The variation of local neighborhood and presence of edge sites provides heterogeneous adsorption sites with varying number of homo- and hetero-nearest neighboring bonds and so various species can show their preference, either on Zn or Pd or bridge site. The
symbol convention used to refer the non-equivalent top sites, 5 in number, is shown in Figure 56 and bridge sites will be explained as pair of such sites. Such a structure is placed in a cubical cell of size of 25 Å so that a vacuum space of 18.91 Å along x- and y-axis, and 16.75 Å along z-axis is used in super cell to isolate the nanoparticle from its repeated images.

*Ab-initio* calculations are performed in the density functional theory (DFT)[24; 25] approach by using VASP[236] package. The valence electrons are represented by plane wave functions with kinetic energy cut off of 350 eV and their interactions with ionic cores are treated using the projector-augmented wave (PAW)[238] method. The exchange correlation contribution of electron-electron interaction to the total energy is treated in the generalized-gradient approximation with Perdew, Burke, and Ernzerhof (PBE) functional[163]. For integration over the Brillouin zone, the k-point mesh density of 1x1x1 is taken with irreducible k-point generation according to the Monkhorst-Pack scheme[292]. The atomic structures are relaxed using the conjugate algorithm until the energy difference between successive electronic iterations is $10^{-4}$ eV and the force on each atom reduces to 0.01 eV/Å. The binding of a species on the substrate is quantified using the adsorption energy ($E_{ad}$) which is calculated using

$$E_{ad} = E_{\text{Adsorbate/nanocluster}} - E_{\text{Adsorbate}} - E_{\text{nanocluster}},$$

(136)

where $E_{\text{Adsorbate/nanocluster}}$, $E_{\text{Adsorbate}}$, and $E_{\text{nanocluster}}$ represent the total energies of adsorbate/nanocluster, isolated adsorbate, and isolated nanocluster, respectively. The positive (negative) values of $E_{ad}$ indicate that the adsorbate does not (does) adsorb on the nanocluster.
For the exploration of long-time kinetics of a phenomenon like chemical reaction using kinetic approach using transition state theory[57; 74], the activation energy barriers of possible processes is a necessary ingredient. After finding the reactant and product states of each elementary step, we calculate the activation energy barrier of corresponding process. The initial guess for the path connecting the reactant and product is formed by linear interpolation between them with 5 or 7 images. The reaction pathways of various reactions are initially calculated using the Nudged Elastic Band (NEB) method[51] and then use the climbing-Image NEB method[52] for the final minimum energy path. The activation energy barrier of forward process is then obtained as the energy difference between maximum energy along the MEP and the initial equilibrium state of the reactants and the energy barrier of the reverse process as the energy difference between the maximum of the MEP and the product state. The energy difference between the final and the initial configurations of a process gives its reaction energy (ΔE).

A flow chart of standard KMC algorithm[22; 293] from ref. [26] used in this study to explore kinetics of the reaction is shown in Figure 3. We have considered 42 processes, which include dehydrogenation, oxidation, hydrogenation, and hydroxylation of intermediates and are presented in Table 25. The surface mesh considered for kMC simulation consists of 20X20 lattice points i.e., 20 alternating columns of Zn and Pd, each chain being made up of 20 equivalent sites with each site having coordination number of 4. The feed ratio of reactants O$_2$ and CH$_3$OH is kept at 1:2 keeping the partial pressure of 1x10$^{-4}$ bar and 2x10$^{-4}$ bar, respectively and the temperature effect are studied by varying it in the range 282$^0$C to 352$^0$C in step of 15$^0$C. The pre-exponential factor is taken to be a normal value of 10$^{13}$ s$^{-1}$ for every reaction in the
KMC simulation. It is argued in ref. [294] that for surface reactions where bond breaking-forming involves high vibrational frequency mode (such as C-H, O-H bonds), the pre-exponential factor on rate calculation in the order of $10^{12}$–$10^{13}$ s$^{-1}$ is reasonable value. In addition, this argument is also valid in calculated value of pre-factor for processes associated with water-gas shift reaction on Cu/ZnO in ref.[295]. In this context, it is also reasonable to assume pre-factor of $10^{13}$ s$^{-1}$ in the rate calculation for various reaction steps of MPO reaction on nanoparticle catalyst. The above-mentioned procedure is repeated for $2 \times 10^{10}$ KMC iterations. In order to ascertain the randomness of generated numbers, the pseudorandom number generator is reset in every $10^6$ steps. At each temperature and pressure, $10^{10}$ MC steps are performed out of $10^9$ iterations are taken to attain the system to steady-state at which the production rate and the fractional coverages are nearly constant after which various quantities of interest including the reaction rate are collected. Results of various physical quantities are calculated by taking average over the subsequent $9 \times 10^9$ steps. If $R_{H_2}$, $R_{H_2O}$, $R_{CO}$ and $R_{CO_2}$ are the production or reaction rate of products $H_2$, $H_2O$, $CO$, and $CO_2$ respectively, measured as the number of them produced per site in a unit time, the selectivity of desired products over competing undesired product is calculated using

$$S_{H_2} = \frac{R_{H_2}}{R_{H_2} + R_{H_2O}}$$

$$S_{CO_2} = \frac{R_{CO_2}}{R_{CO_2} + R_{CO}}$$

(137)

KMC used in this study does not use a site-specific grid, i.e., a homogeneous grid which treats all sites, both Pd and Zn sites, alike. In this sense, KMC grid is more or less a
mathematical grid for solving the master equation for the entire reaction network made up of the elementary steps.

**8.3 Adsorption of Reactants, Products, and Intermediates**

An adsorption energetics and geometrical information of adsorption of reactants, intermediate species, and products of MPO reaction at different sites on the surface of Pd\(_{16}\)Zn\(_{16}\) nanoparticle catalyst are presented in Table 23.

Table 23 Comparison of adsorption energies of reactants and products of MPO, adsorbed at various surface sites of Pd\(_{16}\)Zn\(_{16}\). The distances are in Å and energies are in eV units.

<table>
<thead>
<tr>
<th>Adsorbates</th>
<th>Sites</th>
<th>Pd(<em>{16})Zn(</em>{16})</th>
<th>Reported PdZn(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)OH</td>
<td>Zn</td>
<td>-0.21 (Zn(_{11}))</td>
<td>-0.32 [296]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d(\text{O-Zn(1)})=2.38, d(\text{O-C})=1.44, d(\text{O-H})=0.99)</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td></td>
<td>-0.40 (Pd(_3))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d(\text{O-Pd(3)})=2.33, d(\text{O-C})=1.45, d(\text{O-H})=0.97)</td>
<td></td>
</tr>
<tr>
<td>Pd-Zn</td>
<td></td>
<td>-0.10 (Pd(<em>3)-Zn(</em>{2\text{Z}}))</td>
<td>-0.18 [296]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d(\text{O-Zn(2)})=2.58, d(\text{O-Pd(3)})=3.17, d(\text{O-C})=1.44, d(\text{O-H})=0.99)</td>
<td></td>
</tr>
<tr>
<td>O(_2)</td>
<td>Zn-Zn</td>
<td>-1.13 (Zn(<em>{1\text{Z}})-Zn(</em>{1\text{Z}}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d(\text{O-Zn(1)})=1.92, d(\text{O-C})=1.42)</td>
<td></td>
</tr>
<tr>
<td>Pd-Pd</td>
<td></td>
<td>-0.79 Pd(<em>{1\text{Z}})-Pd(</em>{1\text{Z}})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d(\text{O-Pd(1)})=2.05, d(\text{O-Pd(2)})=2.06, d(\text{O-C})=1.37)</td>
<td></td>
</tr>
<tr>
<td>Pd-Zn</td>
<td></td>
<td>-1.35 (Pd(<em>3)-Zn(</em>{2\text{Z}}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d(\text{O-Pd(3)})=2.02, d(\text{O-Zn(2)})=2.03, d(\text{O-C})=1.48)</td>
<td></td>
</tr>
<tr>
<td>Adsorbates</td>
<td>Sites</td>
<td>Pd$<em>{16}$Zn$</em>{16}$</td>
<td>Reported PdZn(111)</td>
</tr>
<tr>
<td>------------</td>
<td>-------</td>
<td>------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td><strong>CO</strong></td>
<td>Zn</td>
<td>-0.25 (Zn$_{(1)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d_{(C-Zn(1))}=2.03$, $d_{(O-C)}=1.15$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-1.53 (Pd$_{(3)}$)</td>
<td>-1.11 [297]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d_{(C-Pd(1))}=1.91$, $d_{(O-C)}=1.16$</td>
<td></td>
</tr>
<tr>
<td><strong>CO$_2$</strong></td>
<td>Zn</td>
<td>-0.01(Zn$_{(2)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-0.10 (Pd$_{(3)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d_{(O-Pd(3))}=2.55$, $d_{(O-C)}=1.17$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Zn</td>
<td>-0.12 (Pd$<em>{(3)}$-Zn$</em>{(2)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d_{(O-Zn(2))}=2.03$, $d_{(C-Pd(3))}=2.13$, $d_{(O-C)}=1.21$</td>
<td></td>
</tr>
<tr>
<td><strong>H$_2$</strong></td>
<td>Zn</td>
<td>-0.04 (Zn$_{(2)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-0.21 (Pd$_{(2)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d_{(H-Pd(2))}=1.77$, $d_{(H-H)}=0.87$</td>
<td></td>
</tr>
<tr>
<td><strong>H$_2$O</strong></td>
<td>Zn</td>
<td>-0.24 (Zn$_{(1)}$)</td>
<td>-0.24[296]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d_{(O-Zn(1))}=2.26$, $d_{(O-H)}=1.02$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-0.42(Pd$_{(3)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d_{(O-Pd(3))}=2.35$, $d_{(O-H)}=0.98$</td>
<td></td>
</tr>
</tbody>
</table>
Table 24  Comparison of adsorption energies (in eV) of intermediates of MPO adsorbed at various surface sites of Pd$_{16}$Zn$_{16}$ nanoparticle catalyst.

<table>
<thead>
<tr>
<th>Adsorbates</th>
<th>Sites</th>
<th>Pd$<em>{16}$Zn$</em>{16}$</th>
<th>Reported PdZn(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O</td>
<td>Zn</td>
<td>-3.04 (Zn$<em>{(1)}$)- (Zn$</em>{(1)}$)</td>
<td>-2.28</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-2.70 (Pd$<em>{(1)}$)- (Pd$</em>{(2)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Zn</td>
<td>-2.72 (Zn$<em>{(1)}$)- (Pd$</em>{(1)}$)</td>
<td>-2.30</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>Zn</td>
<td>-0.27 (Zn$<em>{(1)}$)- (Zn$</em>{(1)}$)</td>
<td>-0.13</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-0.68 (Pd$_{(3)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Zn</td>
<td>-0.12 ((Pd$<em>{(2)}$)-Zn$</em>{(1)}$)</td>
<td>-0.21</td>
</tr>
<tr>
<td>CHO</td>
<td>Zn</td>
<td>-1.61 (Zn$<em>{(1)}$)- (Zn$</em>{(1)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-2.18 (Pd$<em>{(1)}$)- (Pd$</em>{(2)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Zn</td>
<td>-1.48 (Zn$<em>{(1)}$)- (Pd$</em>{(1)}$)</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Zn</td>
<td>-3.18 (Zn$_{(1)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-3.72 (Pd$<em>{(1)}$)- (Pd$</em>{(2)}$)</td>
<td>-2.45</td>
</tr>
<tr>
<td></td>
<td>Pd-Zn</td>
<td>-3.49 ((Pd$<em>{(2)}$)-Zn$</em>{(1)}$)</td>
<td>-2.50</td>
</tr>
<tr>
<td>O</td>
<td>Zn</td>
<td>-6.6 (Zn$<em>{(1)}$)- (Zn$</em>{(1)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-5.9 (Pd$<em>{(1)}$)- (Pd$</em>{(2)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Zn</td>
<td>-6.04 (Zn$<em>{(1)}$)- (Pd$</em>{(1)}$)</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>Zn</td>
<td>-4.45 (Zn$<em>{(1)}$)- (Zn$</em>{(1)}$)</td>
<td>-3.14</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-3.70 (Pd$_{(3)}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Zn</td>
<td>-4.13 (Zn$<em>{(1)}$)- (Pd$</em>{(1)}$)</td>
<td>-2.93</td>
</tr>
</tbody>
</table>
Methanol molecule (CH₃OH)

Figure 57 Side view of methanol molecule (a) in free standing configuration, and (b) in the adsorbed configuration on the energetically most preferred (Pd(3)) site of Pd₁₆Zn₁₆ nanoparticle. Hydrogen, carbon, and oxygen atoms of molecule are represented using green, black, and yellow spheres, respectively. Only the top surface of the nanoparticle is shown to clearly show the adsorption geometry.

In Figure 57(a) & (b), the free standing and adsorbed CH₃OH molecule on Zn₁₆Pd₁₆ nanoparticle are shown, respectively. In molecular form, all 3 hydrogen (H) atoms are equally spaced from carbon atom (C) at distance 1.1 Å, longer than distance 0.97 Å of a hydrogen atom bonded with oxygen atom. The distance between carbon and oxygen atom is 1.43 Å. On the energetically most favored configuration, the molecule binds on top of low coordinated Pd site (Pd(3)) of the nanoparticle through O atom with d(O-Pd(3))=2.337Å. The adsorption energy on other sites and the summary of geometrical information of this and other adsorbates are presented in Table 23 and Table 24.

Comparison of the adsorption energies of CH₃OH molecule on various probable active sites show that it prefers to adsorb on top sites than bridge sites and among the top sites, it prefers those on edge having low coordination. Upon adsorption, the C-O bond length elongates slightly to 1.446 Å keeping the O-H and C-O bond of the same length. The molecule adsorbs on a tilted configuration that has C-O axis bent at 61.2° towards nanoparticle surface. The
molecule weakly adsorbs on the surface with the binding energy of -0.40eV on the most strongly bonded site. The small value of binding energy of the molecule and large distance from molecule from surface indicates the molecule is on the physisorbed form.

**Oxygen molecule (O₂)**

![Figure 58 Side view of adsorbed oxygen molecule on the energetically most preferred (Zn₁₋₋₋Zn₁₋₋₋) bridge site on Pd₁₆Zn₁₆ nanoparticle.](image)

The O₂ molecule adsorbed on horizontal orientation on the nanoparticle is found to be energetically favored over that on vertical orientation on each site of the nanoparticle. The molecule preferentially adsorbs on bridge Zn₁₋₋₋-Zn₁₋₋₋ site as shown in Figure 58 with adsorption energy of -1.13 eV (chemisorbed) having d(Zn₁₋₋₋-O) = 1.92Å as distance of each O atom from nearby Zn atom. Upon adsorption, the bond length elongates to 1.423 Å (free molecule: 1.236Å). Comparison of O₂ binding energy at different sites indicates that the binding energy decreases with increase in coordination with surface Pd atoms.

**Hydrogen molecule (H₂)**

![Figure 59 Side view of hydrogen molecule adsorbed on the energetically most preferred (Pd₁₋₋₋) top site on Pd₁₆Zn₁₆ nanoparticle.](image)
The horizontally oriented adsorption of H₂ molecule is found to be energetically favored over vertically oriented adsorption on each site of the nanoparticle surface. The energetically most favored adsorption geometry of H₂ molecule on Pd₂ site of nanoparticle is shown in Figure 59 where the adsorption energy is -0.212eV and d(H-H)=0.835 Å, elongated in comparison to free molecule (0.75 Å) and d(Pd-H)=1.80 Å.

**Carbon mono-oxide molecule (CO)**

![CO molecule](image)

Figure 60 Side view of the energetically most preferred adsorption configuration of CO molecule on (Pd₃) site on surface of Pd₁₆Zn₁₆ nanoparticle.

The CO molecule adsorbed on vertical tilted orientation on the nanoparticle (Figure 60) is found to be energetically favored at which d(Pd-C)= 1.91 Å and adsorption energy -1.529 eV. Interestingly, the C-O bond length (1.16 Å) on the energetically most favored adsorption on the top of Pd atoms on edge of the nanoparticle remains same as in the case of free CO molecule, although the adsorption energy is significant.

**Carbon di-oxide molecule (CO₂)**

![CO₂ molecule](image)

Figure 61 Side view of the energetically most preferred adsorption configuration of CO₂ molecule on surface of Pd₁₆Zn₁₆ nanoparticle.
In free molecule, two O atoms are symmetrically located about O atom with C-O bond length 1.177Å. On Pd_{16}Zn_{16} nanoparticle, the molecule desorbs which is reflected on the positive adsorption energy of 0.155eV on the energetically favored top Pd_{(3)} site (Figure 61).

**Water molecule (H_{2}O)**

![Side view of the energetically most preferred adsorption configuration of H_{2}O molecule on Pd_{(3)} site of Pd_{16}Zn_{16} nanoparticle.](image)

In free molecular form, both H atoms of H_{2}O molecule locate symmetrically about O atom with bond length of 0.973Å. On the energetically most favored adsorption on top of Pd_{(3)} site on Pd_{16}Zn_{16} nanoparticle (Figure 62), it adsorbs with adsorption energy of -0.235eV, physisorbed phase with H-O distance of 0.975Å each and Pd-O distance of 2.349Å. Note that the H-O bond length in the adsorbed configuration has value pretty close to that on free molecular case.

**Methoxy molecule (CH_{3}O)**

![Side view of the energetically most preferred adsorption configuration of CH_{3}O molecule on (Zn_{(1)} - Zn_{(1)}) bridge site of Pd_{16}Zn_{16} nanoparticle.](image)
CH$_3$O is adsorbed vertically on Zn$_{(1)}$-Zn$_{(1)}$ bridge of with an adsorption energy of -3.04 eV. The distance of O atom from each of the Zn atoms of the substrate is 2.00 Å, d(C-O) is 1.435 Å, and 3 H atoms form equilateral triangle with d(C-H) = 1.103 Å. The angle (C-O-Zn) is 123°.

**Formaldehyde molecule (CH$_2$O)**

![Formaldehyde molecule](image)

Figure 64 Side view of the energetically most preferred adsorption configuration of CH$_2$O molecule on Pd$_{(3)}$ site of Pd$_{16}$Zn$_{16}$ nanoparticle.

Out of various configurations of CH$_2$O molecule, one having C and O on top of Pd$_{(3)}$ site on tilted orientation (Figure 64) is found to be energetically favorable that has an adsorption energy of -0.272 eV. The distance of O atom from Pd$_{(3)}$ atom is 2.164 Å, d(C-Pd)=2.206 Å and d (O-C)=1.276 Å. Two H atoms are at 1.109 Å each from C atom.

**Formyl molecule (CHO)**

![Formyl molecule](image)

Figure 65 Side view of the energetically most preferred adsorption configuration of CHO molecule on (Pd$_{(1)}$ - Pd$_{(2)}$ ) bridge site of Pd$_{16}$Zn$_{16}$ nanoparticle.

Out of various configurations of CHO molecule, one configuration that has O and H atom on two sides of C atom adsorbed on bridge Pd$_{(1)}$-Pd$_{(2)}$ of the nanoparticle surface (Figure 65)
is found to be energetically favorable which has an adsorption energy of -2.18eV. In the configuration, the distances of C atom from surface Pd are 2.101 Å and 2.212 Å and d(C-O)=1.233 Å and d(H-C)=1.121 Å.

A plot of the energetics taking energies of the most stable configurations of species corresponding to MPO reaction on the catalyst is presented in Figure 66. The plot shows the reaction is exothermic and so is energetically favorable. However, the reaction might still be hindered by high activation energy barrier of a process in between every fill square points.

Figure 66 Energetics of the dehydrogenation and the oxidation routes on Pd\textsubscript{16}Zn\textsubscript{16} nanoparticle. The “*” indicates adsorbed surface species.

8.4 Reaction Pathways

Here, we discuss various possible reaction pathways from reactants to product in MPO reaction. Here we assume successive dehydrogenation, oxidation, and hydroxylation of intermediate species obtained from decomposed CH\textsubscript{3}OH as possible pathways. In the
following, we describe the DFT-calculated energetics for those pathways by calculating the transition state (TS) from conversion from the initial state (IS) to the final state (FS). The most stable configurations of species were used as the initial and final configurations in the calculation of energy barriers, wherever possible. If the lowest energy states of reactants and products are far away, the second energetically most favored adsorption site is considered.

**Dehydrogenation of Methanol**

Dehydrogenation of methanol is one of the key step in MPO. For the hydrogen abstraction from CH$_3$OH* molecule, there can be two possibilities: C-H bond scission and O-H bond scission. The CH$_3$O* molecule that forms after O-H bond scission has adsorption energy 0.76eV lower than that of CH$_2$OH* formed after C-H bond scission and co-adsorbed CH$_3$O*+H* is preferred over CH$_2$OH*+H* by 0.3eV. In addition, the energy of CH$_2$OH*+H* is 0.3eV higher than that of CH$_3$OH* whereas that of CH$_3$O*+H* is rather 0.005eV lower in energy. These comparisons hint that formation of CH$_3$O* is preferred over formation of CH$_2$OH*. Since the distance that the detached H* requires to move to generate the most energetically favored final co-adsorbed configuration of product is far (> 5Å), we consider the CH$_3$OH* on the second energetically favored Zn(1) site as the initial configuration. The barrier of the elementary process is calculated to be 0.56eV and the reaction becomes exothermic with $\Delta E = 0.21$eV. The calculated value is comparable to the reported value of 0.88eV of same process on PdZn(111) surface in ref.[296]. The energy profile for the process with geometry of initial, transition state, and final configurations is shown in Figure 67.
The C-H bond scission of CH$_3$O$^*$ starts with an initial state at bridge Zn$_{(1)}$-Zn$_{(1)}$ site at which each O-Zn$_{(1)}$ distance is 2 Å, and proceeds to have CH$_2$O$^*$ at top Zn$_{(1)}$ site and H$^*$ on its most favored Pd$_{(2)}$ site. The reaction is endothermic with $\Delta E$ about 1 eV and the barrier calculates to be 0.70 eV. As a consequence of C-H bond scission, the height of CH$_2$O$^*$ is 0.2 Å more than that of CH$_3$O$^*$ and CH$_2$O$^*$ tilts more to the surface. On PdZn(111) surface, the barrier of the process is reported to be 1.21 eV in ref. [296]. The energy profile of the process is shown in Figure 68.
The C-H bond scission of CH$_2$O* starts with almost horizontal initial configuration with distance of C or O atom from the closest surface Zn$_{(1)}$ atom to be 2.8Å. The reaction is endothermic with $\Delta E$ of 0.16eV. At transition state, as a consequence of C-H bond scission, O atom moves away from Zn$_{(1)}$ atom whereas C atom moves close to it. This reaction has barrier of 0.37eV and the energy profile is shown in Figure 69.

Figure 69 Energy profile of CH$_2$O* dehydrogenation.

Before C-H bond scission, CHO* molecule forms almost V-shape configuration with angle O-C-H being 120$^\circ$ at bridge Pd$_{(1)}$-Pd$_{(2)}$ site with d(C-Pd)= 2.1 Å and after ends forming vertical CO* at the same site getting slightly close to surface with d(C-Pd)= 2.0 Å and H* moves to its most favored Pd$_{(2)}$ site. This reaction has barrier of 0.44eV and is exothermic with $\Delta E$ of 0.85eV. The energy profile of the reaction is shown in Figure 70.

Figure 70 Energy profile of CHO* dehydrogenation.
Elementary oxidation reactions

The abstraction of hydrogen by breaking O-H bond of CH$_3$OH$^*$ to react with O$^*$ yielding CH$_3$O$^*$ and OH$^*$ is spontaneous process. Although H of O-H bond of CH$_3$OH$^*$ and O$^*$ are initially far away (distance=3.0Å), the bond breaks during the relaxation of initial configuration in presence of O$^*$ and forms the product configuration with no significant movement of CH$_3$O$^*$. The spontaneous process means that the reaction immediately runs though the reactant within no time and it significantly increases the conversion of reactants. It is a much faster kinetic process dominating the occurrence of any other competing possible reaction using the same reactants.

The energy profile of elementary reaction step of oxidation of CH$_3$O$^*$ that proceeds via abstraction of hydrogen from CH$_3$O$^*$ forming CH$_2$O$^*$ and OH$^*$ is shown in Figure 71. The reaction is exothermic with $\Delta E$=0.38 eV and has significantly high barrier of 1.33eV. As a consequence of C-H bond breaking, C atom comes close to surface which is reflected in value of distance $d$(Zn-C)=3.08Å, 2.76Å, and 2.67Å at initial, transition state and final configuration, respectively. The process has the highest energy barrier among different oxidation reactions of different intermediates of MPO reaction.

Figure 71  Energy profile of CH$_3$O$^*$ oxidation reaction.
The energy profile of elementary reaction step of oxidation of CH$_2$O* that proceeds via abstraction of hydrogen from CH$_2$O* forming CHO* and OH* is shown in Figure 72. The reaction is exothermic with significantly large energy release of $\Delta E=1.11$eV and barrier calculates to be 0.72eV. As a consequence of C-H bond breaking, C atom comes close to surface which is reflected in value of distance d(Pd-C)=2.16Å, 2.13Å, and 2.01Å at initial, transition state, and final configuration, respectively.

Figure 72 Energy profile of CH$_2$O* oxidation reaction.

The energy profile of elementary reaction step of oxidation of CHO* that proceeds via abstraction of hydrogen from CHO* forming CO* and OH* is shown in Figure 73. The reaction is exothermic with significantly large energy release of $\Delta E=1.62$eV and barrier calculates to be 0.41eV. After C-H bond breaking, CO* becomes vertical and get adsorbs on bridge Pd sites at distance 2.0Å from each Pd atom.
Figure 73 Energy profile of CHO\(^{\ast}\) oxidation reaction.

The energy profile of elementary reaction step of oxidation of CO\(^{\ast}\) to form CO\(_{2}\)\(^{\ast}\) is shown in Figure 74. The reaction is slightly exothermic with energy release of \(\Delta E=0.07\text{eV}\) and has barrier of 0.49eV. With the O\(^{\ast}\) attachment with initially vertically adsorbed CO\(^{\ast}\), the resultant CO\(_{2}\)\(^{\ast}\) molecule takes V-shape configuration having 2 oxygen atoms almost symmetrically arranged about C atom and making angle O-C-O of 133\(^{\circ}\).

Figure 74 Energy profile of CO\(^{\ast}\) oxidation reaction.
Elementary hydroxylation reactions

As is clear from discussion of the oxidation process, adsorbed hydroxide radical (OH*) forms on every elementary oxidation reaction when detached hydrogen from intermediates of decomposed CH₃OH* molecule reacts with O*. When OH* reacts with H*, it forms stable H₂O* molecule as one of the product of the reaction.

The energy profile of elementary reaction of abstraction of hydrogen from CH₃OH* by breaking O-H bond in presence of OH* yielding CH₃O* and H₂O* is shown in Figure 75. The reaction is endothermic with energy 0.62eV and its barrier comes out to be 0.62eV. At transition or final state, H₂O molecule desorbs and CH₃O* adsorbs on the bridge Zn(1)-Zn(1) site.

Figure 75 Energy profile of CH₃OH* hydroxylation reaction.

The energy profile of elementary reaction of hydrogen abstraction from CH₃O* by breaking C-H bond in presence of OH* yielding CH₂O* and H₂O* is shown in Figure 76. The reaction is endothermic with ΔE of 1.14eV and calculates out to have high barrier of 1.73eV. The H₂O* molecule desorbs and the CH₂O* molecule moves from bridge Zn(1)-Zn(1) site to on top Zn(1) site after C-H bond breaking.
Figure 76 Energy profile of CH$_3$O* hydroxylation reaction.

The energy profile of elementary reaction of abstraction of hydrogen from CH$_2$O* by breaking C-H bond in presence of OH* yielding CHO* and H$_2$O* is shown in Figure 77. The process is exothermic with energy release of 0.36eV and has barrier of 0.76eV. At transient state, hydrogen detaches from CH$_2$O* and C atom of resulted CHO* comes closer to surface by 0.3Å. H$_2$O* adsorbs on top Zn$_{(1)}$ site with d(Zn-O) equals 2.0Å.

Figure 77 Energy profile of CH$_2$O* hydroxylation reaction.

The energy profile of elementary reaction of abstraction of hydrogen from CHO* by breaking C-H bond in presence of OH* yielding CO* and H$_2$O* is shown in Figure 78. The CHO* radical adsorbed on V-shape configuration with angle O-C-H of 119° at Pd$_{(2)}$ site reacts with OH* on bridge Zn$_{(1)}$-Zn$_{(1)}$ site. After H release by breaking C-H bond, CO* becomes
vertical and H\textsubscript{2}O desorbs. The process has barrier of 0.54eV and is exothermic with energy release of 0.29eV.

Figure 78 Energy profile of CHO* hydroxylation reaction

Summary of reaction energies and activation energy barrier of different elementary steps of MPO reaction on the (111) surface of Pd\textsubscript{16}Zn\textsubscript{16} nanoparticle catalyst are provided in Table 25. As presented in Table 25, 22 processes (column 2) and the reverse of processes except desorption of products that counts 18 are considered in kinetic model whose barriers are presented in column 3 and assumed pre-factor in column 4. The processes include adsorption, dissociation, oxidation, hydroxylation, and desorption. Processes R1 and R2 represent an instantaneous adsorption of reactants CH\textsubscript{3}OH and O\textsubscript{2} on surface. Processes R3 and R4-R7 represent the dissociation of O\textsubscript{2}* and successive dehydrogenation of hydrocarbon species, respectively. Reaction R8 and R9 represent the desorption and oxidation of CO* whereas R10 represents desorption of CO\textsubscript{2}*. Reactions (R11, R12) and (R13, R14) represent formation and desorption of H\textsubscript{2} and H\textsubscript{2}O, respectively. Reactions (R15, R17, R19, R21) and (R16, R18, R20, R22) represent oxidation and hydro-oxidation of methanol, methoxy, formaldehyde, and formyl, respectively.
Table 25 Elementary reaction steps of MPO reaction included in KMC simulation.

<table>
<thead>
<tr>
<th>Reactions steps [Processes]</th>
<th>Barrier of forward (Reverse) process (eV)</th>
<th>Prefactor (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1  CH$_3$OH(g) + * → CH$_3$OH*</td>
<td>0.0 (0.40)</td>
<td>1(1.0×10$^{13}$)</td>
</tr>
<tr>
<td>R2  O$_2$(g)+* → O$_2$*</td>
<td>0.0(1.48)</td>
<td>1(1.0×10$^{13}$)</td>
</tr>
<tr>
<td>R3  O$_2$<em>+</em> → O*+O*</td>
<td>0.36(2.35)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R4  CH$_3$OH*+* → CH$_3$O*+H*</td>
<td>0.60(0.81)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R5  CH$_3$O*+* → CH$_2$O*+H*</td>
<td>0.70 (0.24)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R6  CH$_2$O*+* → CHO*+H*</td>
<td>0.37(0.21)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R7  CHO*+* → CO*+H*</td>
<td>0.44 (1.29)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R8  CO* → CO(g)+*</td>
<td>1.53</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R9  CO*+O* → CO$_2$<em>+</em></td>
<td>0.49(0.56)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R10 CO$_2$* → CO$_2$(g)+*</td>
<td>0.09</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R11 H*+H* → H$_2$<em>+</em></td>
<td>0.56(0.10)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R12 H$_2$* → H$_2$(g)+*</td>
<td>0.56</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R13 H*+OH* → H$_2$O*+*</td>
<td>0.47(0.17)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R14 H$_2$O* → H$_2$O(g)+*</td>
<td>0.42</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R15 CH$_3$OH*+O* → CH$_3$O*+OH*</td>
<td>0.0(0.74)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R16 CH$_3$OH*+OH* → CH$_2$O*+H$_2$O*</td>
<td>0.21 (0.47)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>R17 CH$_3$O*+O* → CH$_2$O*+OH*</td>
<td>1.33 (1.71)</td>
<td>1.0×10$^{13}$</td>
</tr>
<tr>
<td>Reactions steps [Processes]</td>
<td>Barrier of forward (Reverse) process (eV)</td>
<td>Prefactor (s(^{-1}))</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>R18 ( \text{CH}_3\text{O}^<em>+\text{OH}^</em>\rightarrow\text{CH}_2\text{O}^<em>+\text{H}_2\text{O}^</em> )</td>
<td>1.30(0.16)</td>
<td>1.0×10(^{13})</td>
</tr>
<tr>
<td>R19 ( \text{CH}_2\text{O}^<em>+\text{O}^</em>\rightarrow\text{CHO}^<em>+\text{OH}^</em> )</td>
<td>0.72(1.83)</td>
<td>1.0×10(^{13})</td>
</tr>
<tr>
<td>R20 ( \text{CH}_2\text{O}^<em>+\text{OH}^</em>\rightarrow\text{CHO}^<em>+\text{H}_2\text{O}^</em> )</td>
<td>0.76 (1.12)</td>
<td>1.0×10(^{13})</td>
</tr>
<tr>
<td>R21 ( \text{CHO}^<em>+\text{O}^</em>\rightarrow\text{CO}^<em>+\text{OH}^</em> )</td>
<td>0.41 (2.03)</td>
<td>1.0×10(^{13})</td>
</tr>
<tr>
<td>R22 ( \text{CHO}^<em>+\text{OH}^</em>\rightarrow\text{CO}^<em>+\text{H}_2\text{O}^</em> )</td>
<td>0.54 (0.83)</td>
<td>1.0×10(^{13})</td>
</tr>
</tbody>
</table>

Note that the dissociation of \( \text{O}_2^* \) and \( \text{H}_2^* \) is with significantly low barrier on the nanoparticle.

The rate of adsorption processes R1 and R2 are calculated using Equation (117) taking sticking coefficient 1 whereas that of remaining processes are calculated using the Arrhenius relation in Equation (116).

### 8.5 Selectivity of Products

![Selectivity of products](image-url)

Figure 79 Selectivity of products: (a) \( \text{H}_2 \) vs. \( \text{H}_2\text{O} \), and (b) \( \text{CO}_2 \) vs. \( \text{CO} \) on \( \text{Pd}_{16}\text{Zn}_{16} \) model catalyst as a function of temperature.

In Figure 79, we have shown the result about the selectivity of outputs in the temperature range of study and at the mentioned pressure obtained using kMC simulation. As shown in
Figure 79 (a), the selectivity for H₂ is nearly 0% and that for H₂O is nearly 100%, which does not change with temperature in the temperature range of study. This can be rationalized on the basis of almost spontaneous dissociation of adsorbed H₂ (reverse of reaction R11 in Table 25) rather than its desorption (reaction R12) and the availability of OH* (initially from the spontaneous oxidation of CH₃OH*) that reacts with O* producing H₂O*(reaction R13) that desorbs (reaction R14). As shown in Figure 79(b), the selectivity for CO₂ is nearly 100% whereas that of CO is nearly 0% that does not change with temperature. The significantly higher energy barrier for desorption of CO* from surface (reaction R8) whereas negligibly small barrier of CO₂* desorption (reaction R10) after its formation following CO* oxidization (reaction R9) rationalizes higher CO₂ selectivity.

**8.6 Conclusions**

In this chapter, we have explored the adsorption properties of reactants, products, and intermediates of methanol partial oxidation reaction on Pd₁₆Zn₁₆ nanoparticle catalyst. Binding of each of the species on the catalyst indicate that the catalyst is active for MPO reaction that does not desorb intermediate. In addition, we have performed extensive DFT-based calculation to calculate energetics of several probable pathways corresponding to the hydrogen abstraction from CH₃OH, reactions of each intermediates with O* and OH*. Although dehydrogenation pathways and oxidation pathways compete in reaction kinetics, spontaneous dissociation of H₂* formed and hard to desorb CO* due to strong binding leads to get 100% selectivity of products H₂O and CO₂ over H₂ and CO respectively, irrespective of variation on temperature.
In future, to mimic the real catalytic situation in reservoir, one needs to consider nanoparticle adsorbed on the surface of ZnO surface and consider the possibility of reaction of different species on all there geometries: nanoparticle, substrate, and interface between them. Comparison of such study with current study can assist to explore substrate effect on the reaction. Rather than KMC study based on some guessed reactions, one can design an on-the-fly approach that can better mimics the reality.
APPENDIX A: IPT SOLVER
Finding the solution of Hubbard model (Equation (19) means to calculate the electronic Green function in interacting lattice. Once the self-energy of the single-electron impurity model equals to that of lattice model, the impurity Green function gives the seeking solution for given value of bath function. So finding the electron self-energy in impurity problem is the main part of solution. In the second order self-consistent iterative perturbation approximation[298], expansion of the local impurity dynamical self-energy $\Sigma_l(\omega)$ of impurity particle in one-band model at half-filling as mentioned in ref. [13] becomes

$$
\Sigma_l(\omega_n) = U n_{l\sigma} - U^2 T^2 \sum_{m} G_{l\sigma}(\omega_m) G_{l\bar{\sigma}}(\omega_l) G_{l\bar{\sigma}}(\omega_m + \omega_l - \omega_n),
$$

where $l$ is orbital index, $\sigma$ is spin-index, $n_{l\sigma}$ are the on-site spin-orbital occupancies and $G_{l\sigma}(\omega_m)$is the dynamical mean-field that describes the effect of the bath on the impurity electrons. Generalization of Equation (138) within the extended multi-orbital iterated-perturbation theory (MO-IPT) approximation [299] as derived in ref.[13] which expresses the orbital- and spin-dependent self-energy $\Sigma_l(\omega)$ of electron as

$$
\Sigma_l(\omega) = U n_{l\sigma} + \frac{A_{l\sigma} \Sigma^{(2)}_{l\sigma}(\omega)}{1 - B_{l\sigma} \Sigma^{(2)}_{l\sigma}(\omega)},
$$

where

$$
\Sigma^{(2)}_{l\sigma}(\omega_n) = U^2 T^2 \sum_{m} G_{l\sigma}(\omega_m) G_{l\bar{\sigma}}(\omega_l) G_{l\bar{\sigma}}(\omega_m + \omega_l - \omega_n)
$$

is second order self-energy and

$$
A_{l\sigma} = \frac{n_{l\sigma}(1-n_{l\sigma}) + D_{l\sigma} n_{l\bar{\sigma}}}{n_{l\sigma}(1-n_{l\sigma})}, \quad B_{l\sigma} = \frac{(1-2n_{l\sigma})}{n_{l\sigma}(1-n_{l\sigma})},
$$

are the coefficients, $n_{l\sigma}$ and $n_{l\sigma}^{(0)}$ are the on-site spin-orbital occupations in the case of lattice and non-interacting impurity electrons, respectively calculated using
\[ n_{l\sigma} = \frac{-i}{\pi} \int d\omega G_{l\sigma}(\omega) = \frac{1}{2} + T \sum_n G_{l\sigma}(\omega_n) \]

\[ n_{l\sigma}^{(0)} = \frac{-i}{\pi} \int d\omega \tilde{G}_{l\sigma}(\omega) = \frac{1}{2} + T \sum_n \tilde{G}_{l\sigma}(\omega_n) \tag{142} \]

\[ D_{l\sigma, l'\sigma'} = \langle n_{l\sigma} n_{l'\sigma'} \rangle = U_{l\sigma, l'\sigma'} T \sum_n \Sigma_{l\sigma}(\omega_n) G_{l\sigma}(\omega_n) \tag{143} \]

is the density-density correlation function. The choice of A leads to the correct high-frequency behavior of the self-energy while that of B leads to the correct atomic limit of this quantity. Generally speaking, for extended systems IPT is regarded as a valid approximation for small and large values of U, IPT may still be valid as it reproduces important features, such as the central quasiparticle peak and the Hubbard bands in the density of states of extended systems in agreement with more accurate solutions. The approximation was used by different groups and, despite its limitations, led to encouraging results, even in the case of systems with reduced dimensionality (see, e.g., [300; 301]).
APPENDIX B: HF-QMC SOLVER
Quantum Monte Carlo (QMC) methods are used in finding the solution of Hubbard model by converting quartic term into quadratic terms. In doing so, the thermos-dynamical time interval is divided into L segments that allows to approximate infinite dimensional path integrals by finite dimensional integrals. The main idea of QMC is to write Anderson model electronic GF as an integral over fluctuating fields. Interacting electrons system is converted into non-interacting particles that move in fluctuating in time field defined by a set of spin for every L segments in $\tau$ intervals. So, GF is determined as a sum over all possible pseudo-spin configurations. As number of configurations grows exponentially with L following $2^L$ dependence, direct summation is not possible for large L and is replaced by stochastic Monte Carlo method of many dimensional integral evaluations.

Here, some detail of the HF-QMC formalism [14] used in this study to calculate numerically exact impurity Green’s function is explained. The main idea of this approach is to split the effective action in the exponent of the impurity Equation (40) into the free and interacting part with the identity due to Hirsch [302] in Equation (144) for fermion system, called Hubbard–Stratonovich transformation, of the “interacting” parts of the exponent

$$e^{-\Delta \tau U n_\uparrow n_\downarrow + (\Delta \tau U/2)(n_\uparrow + n_\downarrow)} = \frac{1}{2} \sum_{s_\tau = \pm 1} e^{\lambda s_\tau (n_\uparrow - n_\downarrow)}$$

(144)

where $\lambda = \text{arccosh}(e^{\Delta \tau U/2})$ and $s_\tau = \pm 1$ are the “Ising spin” variables for each of the L time point of the discretized time contour in Equation (40). In this case, the effective action in the exponent is quadratic in operators,
\[ G_{ab}(\tau_1 - \tau_2) = \frac{1}{Z} \int D[\psi] D[\psi^*] \psi_a(\tau_1) \psi_b^*(\tau_2) \exp \left[ - \int_0^\beta d\tau_3 \int_0^\beta d\tau_4 \psi_c^*(\tau_3) G_{cd}^{-1}(\tau_3 - \tau_4) \psi_d(\tau_4) + \int_0^\beta d\tau_5 \psi_e^*(\tau_5) \psi_e(\tau_5) \psi_f(\tau_5) \psi_f^*(\tau_5) \exp \right] \]

one can easily perform the path integration and get

\[ G_\sigma(\tau, \tau') = \frac{1}{Z} \sum_{\{s_1, s_2, \ldots, s_L\} = \pm 1} \det[g_{1\uparrow}^{-1}(s_1, \ldots, s_L)] \det[g_{L\downarrow}^{-1}(s_1, \ldots, s_L)] g_\sigma(s_1, \ldots, s_L; \tau, \tau') \]  \hspace{1cm} (146)

\[ Z = \sum_{\{s_1, s_2, \ldots, s_L\} = \pm 1} \det[g_{1\uparrow}^{-1}(s_1, \ldots, s_L)] \det[g_{L\downarrow}^{-1}(s_1, \ldots, s_L)] \]  \hspace{1cm} (147)

In the last two equations, \( g_\sigma(s_1, \ldots, s_L; \tau, \tau') \) are the time matrices that depend on both time and Ising spin variables \( \{s_1, s_2, \ldots, s_L\} \). The explicit form of the inverse of these matrices is:

\[ g_\sigma^{-1}(s_1, \ldots, s_L; \tau, \tau') = G_\sigma^{-1}(\tau, \tau') + \sigma \lambda s_\tau \delta_{\tau, \tau'+1}, \]  \hspace{1cm} (148)

where:

\[ \delta_{l, l'+1} = \begin{cases} 1, & \text{for } l = 2, \ldots, L - 1 \text{ and } l' = l - 1 \\ -1, & \text{for } l = 1 \text{ and } l' = L \\ 0, & \text{otherwise.} \end{cases} \]  \hspace{1cm} (149)

Thus, the problem is reduced to calculating the inverses of \( L \times L \) matrix Equation (148) for all possible Ising spin configurations \( \{s_1 = \pm 1, s_2 = \pm 1, \ldots, s_L = \pm 1\} \) in the “L-atom time chain” and summing up the corresponding terms in Equations (146) and (147). Since the computational time increases with \( L \) as \( \sim 2^L \), the exact calculations are usually performed only at \( L \sim 10 - 20 \). For practical needs, at temperatures of order of room or lower, one typically needs \( L \)’s of order one to several hundreds. Therefore, the summations in Equation (146) and
Equation (147) are usually performed for a randomly-chosen set of configurations \( \{s_1, s_2, ..., s_L\} \), i.e., by using QMC methods (for details, see, e.g., [12]).
For given \( u_i \) \((i = 1,2, \ldots, N)\) being the N values of a complex function (self-energy in our case) calculated at N complex points \( Z_i \) the coefficients \( a_i \)s are calculated to express dependent variable as a rational polynomial

\[
C_N(Z_N) = u_N = \frac{a_1}{1+} \frac{a_2(Z_N-Z_1)}{1+} \ldots \ldots \ldots \ldots \frac{a_N(Z_N-Z_{N-1})}{1} \frac{A_N(x)}{B_N(x)}
\]  \tag{150}

using the recursion

\[
a_i = g_i(z_i), g_1(z_i) = u_i, i = 1,2, \ldots, N, \tag{151}
\]

Note that all the \( g_1 \) are known from given data and the required \( g_i \) to calculate \( a_i \) are calculated using

\[
g_i(z) = \frac{g_{i-1}(z_{i-1}) - g_{i-1}(z)}{(z - z_{i-1})g_{i-1}(z)}, i \geq 2, \tag{152}
\]

that enables to directly calculate the value at a given point. Once the rational polynomial \( C_N(Z_N) \) is obtained in terms of coefficients \( a_i \)s, the polynomial yields an estimation of \( C_N(x) \), \( x \) being a real frequency. In principle, the method should work for any desired frequency range and resolution. However, the further away we are from the interpolation points \((i\omega)\), the less trustworthy the generated values will be. By interpolating data, the method does not take into account any statistical errors which may lead to artificial features in the output. The method is used in the current study to get real frequency dependence of self-energy from calculated equally spaced Matshubara frequency dependence.
APPENDIX D: DENSITY MATRIX TDDFT FORMALISM
We approximately expressed $\Psi_k(r, t)$ (Note only initial) as linear combination of static Kohn-Sham eigenstates $\varphi_k^m(r)$,

$$\Psi_k(r, t) = \sum_m C_k^m(t) \varphi_k^m(r)$$  \hspace{1cm} (153)

such that all the time dependence comes through coefficients. Substituting $\Psi_k(r, t)$

$$[H_{KS}(r) + H_{int}] \sum_m C_k^m(t) \varphi_k^m(r) = i \frac{\partial}{\partial t} \sum_m C_k^m(t) \varphi_k^m(r)$$  \hspace{1cm} (154)

Multiplying by $\varphi_l^{ls}(r)$ and integrating over $dr$, we get

$$\varepsilon_{kl} C_k^l(t) + \sum_m C_k^m(t) H_{kl}^m(t) = i \frac{\partial}{\partial t} C_k^l(t)$$  \hspace{1cm} (155)

$$\varepsilon_l C_l^l(t) + \sum_m C_k^m(t) H_{kl}^m(t) = i \frac{\partial}{\partial t} C_l^l(t)$$  \hspace{1cm} (156)

Since $m$ is dummy variable, changing $m$ to $n$ (but can’t change $l$, $q$)

$$\varepsilon_{ql} C_q^l(t) + \sum_n C_k^n(t) H_{ql}^n(t) = i \frac{\partial}{\partial t} C_q^l(t)$$  \hspace{1cm} (157)

Similarly,

$$\varepsilon_k^m C_k^m(t) + \sum_p C_q^n(t) H_{kp}^{mp}(t) = i \frac{\partial}{\partial t} C_k^m(t)$$  \hspace{1cm} (158)

where $H_{kl}^{ln}(t) = \int dr \varphi_l^{ls}(r) H_{int} \varphi_k^n(r)$  \hspace{1cm} (159)

Defining the one electron density matrix kernel as

$$\rho_{kl}^{ml}(t) = C_k^m(t) C_q^{ls}(t)$$  \hspace{1cm} (160)
Its differentiation w.r.t. time becomes

\[
i \frac{\partial \rho_{kq}^{ml}(t)}{\partial t} = i \frac{\partial c_{k}^{m}(t)}{\partial t} . C_{q}^{l*}(t) + i \frac{\partial c_{q}^{l*}(t)}{\partial t} . C_{k}^{m}(t), \tag{161}\]

Using above equation

\[
i \frac{\partial \rho_{kq}^{ml}(t)}{\partial t} = C_{q}^{l*}(t) [\varepsilon_{k}^{m} C_{k}^{m}(t) + \sum_{p} C_{p}^{m}(t) H_{kp}^{mp}(t)] - C_{k}^{m}(t) [\varepsilon_{q}^{l} C_{q}^{l*}(t) + \sum_{n} C_{k}^{n*}(t) H_{qn}^{ln*}(t)], \tag{162}\]

\[
i \frac{\partial \rho_{kq}^{ml}(t)}{\partial t} = \varepsilon_{k}^{m} \rho_{kq}^{ml}(t) + \sum_{p} H_{kp}^{mp}(t) \rho_{pq}^{pl}(t) - \varepsilon_{q}^{l} \rho_{kq}^{ml}(t) - \sum_{n} H_{kq}^{ln*}(t) \rho_{kn}^{mn}(t), \tag{163}\]

With \(H_{qk}^{ln*} = H_{kq}^{nl}\) and taking dummy variable \(p=n\), we get

\[
i \frac{\partial \rho_{kq}^{ml}(t)}{\partial t} = (\varepsilon_{k}^{m} - \varepsilon_{q}^{l}) \rho_{kq}^{ml}(t) + \sum_{n} [H_{kq}^{mn}(t) \rho_{qn}^{nl}(t) - \rho_{kn}^{mn}(t) H_{kq}^{nl}(t)], \tag{164}\]

(Note that the product of matrices on RHS satisfies convolution property of matrices) where

\[
H_{kq}^{mn}(t) = \iint dr \; dr' \frac{\varphi_{q}^{*n}(r) \varphi_{k}^{m}(r)}{|r-r'|} [n(r', t) - n(r', 0)] + \iint dr \; dr' \varphi_{q}^{*n}(r) \varphi_{k}^{m}(r) \int_{-\infty}^{t} dt' f_{XC}(r, t, r', t') [n(r', t') - n(r', 0)] + \int dr \varphi_{q}^{*n}(r) \varphi_{k}^{m}(r) . E(t), \tag{165}\]

General expression for XC term is

\[
f_{XC}(r, t, r', t') = f_{XC}^{DMFT}(t, t') - \frac{1}{|r-r'|} \tag{166}\]
In the strongly-correlated systems we will use the formalism for, for \( f_{XC}(r,t,r',t') \) we use \( f_{XC}^{DMFT}(t,t') \) with the assumption that \( \frac{1}{\mid r-r' \mid} \) is small for those systems. To be consistent with neglect of \( \frac{1}{\mid r-r' \mid} \) term, we also neglect the dynamic part of the Hartree term (Note the static part of Hartree is included in \( H_{KS}(r) \) that gives energy eigenvalues.)

To calculate \( \delta n(r',t') \) in the XC term of \( H_{mn}^{kq}(t) \) in TDKS equation, we use the following formalism.

\[
\delta n(r',t') = n(r',t') - n(r',0)
\]

(167)

From definition,

\[
n(r',t') = \sum_{k \leq k_F} |\Psi_k(r',t')|^2
\]

(168)

(Note that due to square of the same KS wavefunction, \( n(r',t') \) term depends on only one momentum \( k \))

\[
= \sum_{k \leq k_F} \sum_e C_k^e(t') \phi_k^e(r') \sum_d C_k^d(t') \phi_k^d(r')
\]

(169)

\[
n(r',t') = \sum_{k \leq k_F} \sum_e \sum_d C_k^e(t') C_k^d(t') \phi_k^e(r') \phi_k^d(r')
\]

(170)

Using definition, \( \rho_{k}^{ed}(t') = C_k^e(t') C_k^d(t') \), density matrix (not density)

\[
n(r',t') = \sum_{k \leq k_F} \sum_e \sum_d \rho_{k}^{ed}(t') \phi_k^e(r') \phi_k^d(r')
\]

(171)

Since the eigenstates \( \phi_k^e(r') \) and \( \phi_k^d(r') \) are on the same momentum (\( k \)) and for Bloch lattice

\[
\phi_k^e(r') = e^{-ik \cdot r'} \phi_0^e(r')
\]

(172)
\[ \varphi_k^d(r') = e^{ik \cdot r'} \varphi_0^d(r') \]  

(173)

\[ \varphi_k^{e*}(r') \varphi_k^d(r') = \varphi_0^{e*}(r') \varphi_0^d(r'), \] we get

\[ n(r', t') = \sum_{k \leq k_F} \sum_e \sum_d \rho_k^{ed}(t') \varphi_0^{e*}(r') \varphi_0^d(r') = \sum_{k \leq k_F} \sum_e \sum_d \rho_k^{ed}(0) \varphi_0^{e*}(r') \varphi_0^d(r') \]  

(174)

Since RHS does not have product of terms with different k, we can solve TDKS equations for each k separately and can add over k finally to get \( n(r', t') \) for each time point \( t' \). This significantly reduces computational efficient otherwise the matrix \( \rho_k^{ed} \) corresponding to e and d for each k becomes too big. Substituting \( n(r', t') \), we get

\[ \delta n(r', t') = n(r', t') - n(r', 0) \]

\[ \delta n(r', t') = \sum_{k \leq k_F} \sum_e \sum_{de} \rho_k^{ee}(t') \varphi_0^{e*}(r') \varphi_0^e(r') - \sum_{k \leq k_F} \sum_e \sum_d \rho_k^{ed}(0) \varphi_0^{e*}(r') \varphi_0^d(r') \]

(175)

(Writing this way people might say rho does not have r dependence).

\[ \delta n(r', t') = \sum_{k \leq k_F} \sum_{e \neq v} \sum_{d \neq c} \left[ \begin{array}{cc} \rho_k^{ee}(t') & 0 \\ 0 & \rho_k^{dd}(t') \end{array} \right] \varphi_0^{e*}(r') \varphi_0^d(r'), \]

Note that v and c refers to the valence and conduction band and we don’t allow transition from valence to valence or conduction to conduction assigning the index \( l \) for any of the valence orbital and \( m \) only for any of the conduction orbital. To get the term \( \delta n(r', t') \) in TDKS
equation, it is enough to get the cross valence-conduction terms which avoids the inter-valence and inter-conduction states transition or polarization terms. The diagonal elements of this matrix \( \rho_{k}^{ed}(t') \) describe the time-resolved or dynamical state occupancies and the non-diagonal elements describe dynamical polarizability. Note that this term has to be calculated for each time step \( t' \).

The elements of the density matrix, \( \rho_{k}^{lm}(t') \) in XC term is iteratively calculated up to that time propagating the Liouville matrix equation

\[
\frac{i}{\hbar} \hat{\rho}_{kq}^{ml}(t) = (\varepsilon_{k}^{m} - \varepsilon_{q}^{l})\rho_{kq}^{ml}(t) + \sum_{n}[H_{kq}^{mn}(t)\rho_{qq}^{nl}(t) - \rho_{kk}^{mn}(t)H_{kq}^{nl}(t)],
\]

where

\[
H_{kq}^{mn}(t) = \int d\mathbf{r} d\mathbf{r}' \varphi_{q}^{n\ast}(\mathbf{r})\varphi_{k}^{m}(\mathbf{r}) \int_{-\infty}^{t} dt' f_{XC}(\mathbf{r}, t, \mathbf{r}', t') \delta n(\mathbf{r}', t') + \int d\mathbf{r} \varphi_{q}^{n\ast}(\mathbf{r}) \mathbf{r} \varphi_{k}^{m}(\mathbf{r}). E(t),
\]

Substituting the value of \( \delta n(\mathbf{r}', t') \)

\[
\delta n(\mathbf{r}', t') = \sum_{k \leq k_F} \sum_{d e} \sum_{e e c} \varphi_{k}^{e\ast}(\mathbf{r}')\varphi_{k}^{d}(\mathbf{r}')[\rho_{k}^{ed}(t') - \rho_{k}^{ed}(0)]
\]

\[
H_{kq}^{mn}(t) = \int d\mathbf{r} d\mathbf{r}' \varphi_{q}^{n\ast}(\mathbf{r})\varphi_{k}^{m}(\mathbf{r}) \int_{-\infty}^{t} dt' f_{XC}(\mathbf{r}, t, \mathbf{r}', t') \sum_{k \leq k_F} \sum_{d e} \sum_{e e c} \varphi_{k}^{e\ast}(\mathbf{r}')\varphi_{k}^{d}(\mathbf{r}')[\rho_{k}^{ed}(t') - \rho_{k}^{ed}(0)]
\]

\[
+ \int d\mathbf{r} \varphi_{q}^{n\ast}(\mathbf{r}) \mathbf{r} \varphi_{k}^{m}(\mathbf{r}). E(t),
\]

Defining

\[
d_{kq}^{mn} = \int d\mathbf{r} \varphi_{q}^{n\ast}(\mathbf{r}) \mathbf{r} \varphi_{k}^{m}(\mathbf{r}). E(t),
\]
\[ F_{kq}^{mned}(t, t') = \iint dr dr' \varphi_{q}^{n*}(r) \varphi_{k}^{m}(r) f_{XC}(r, t, r', t') \varphi_{k}^{e*}(r') \varphi_{k}^{d}(r'), \] (182)

Note that all \( \varphi \)s are included in the coefficients. So, the DMFT XC kernel corresponds averaging of the XC kernel matrices over the orbital and spin variables.

With coefficients, Liouville equation becomes

\[
i \frac{\dot{\rho}_{kq}(t)}{\alpha} = (\varepsilon_{k}^{m} - \varepsilon_{q}^{l}) \rho_{kq}^{ml}(t) + \sum_{k' \leq k} \sum_{l} \int_{0}^{t} \rho_{q}^{nl}(t') \rho_{kq}^{ed}(t, t') \rho_{q}^{ed}(0) + \sum_{n} d_{kq}^{nln}(t) \rho_{q}^{ed}(t) - \sum_{n} d_{kq}^{nl}(t) \rho_{q}^{ed}(0), \]

(183)

The equation has to be solved with the initial condition

\[
\rho_{kq}^{ml}(t' = 0) = \delta^{ml} \rho_{k}^{m}, \]

(184)

where \( \rho_{k}^{m} \) are the initial state occupancies.

No approximation within the density-matrix formalism has been made so far. In the case of DGA we use, \( f_{XC}(r, t; r', t') = \delta(r - r')f_{XC}(t - t') \), which gives the following simplified expressions for the matrix elements

\[ F_{kq}^{edmn}(t, t') = A_{kq}^{edmn} f_{XC}(t - t'), \]

(185)

where

\[ A_{kq}^{edmn}(t, t') = \iint dr dr' \varphi_{q}^{n*}(r) \varphi_{k}^{m}(r) \varphi_{k}^{e*}(r') \varphi_{k}^{d}(r'), \]

(186)

are static coefficients. In the calculations we also assume that \( A_{kq}^{edmn} \) are momentum independent, \( A_{kq}^{edmn} = A^{edmn} \), (this is equivalent to the standard Bloch wave-function...
approximation: $\varphi_k^m(r) \approx e^{-ikr}\varphi_{k=0}^m(r)$. This approximation means we assume all the transition occur at the given momentum (optical transition) that don’t require additional momentum due to phonon. From the structure of the integral of $A_{kq}^{edm}(t, t')$, one can also see that the following approximation may be used: $A^{edm} \approx \delta^{ed} \delta^{mn} A^{emm}$, since the product of two conjugated functions has maximal overlap when they are same-orbital functions. For the same reason, one can make further simplification: $A^{emm} \approx \delta^{me} A^m$, which gives

$$F_{kq}^{edm}(t, t') \approx \delta^{edm} A^m f_{XC}(t - t'),$$

where

$$A^m = \int dr |\varphi_{k=0}^m(r)|^4,$$  \hspace{1cm} (187)

These numbers may be regarded as spatial strength of the XC kernel, which we used in our calculations (more explicitly we used one averaged over the orbitals parameter $A$).

With continuous representation, sum over all momenta $k \leq k_F$ can be replaced by integration over energy $\varepsilon$ of valence band and then the excited charge density to conduction band or equivalently the changed charge density on the valence band at time $t'$ is given by

$$\delta n(r', t') = \int d\varepsilon A(\varepsilon) \sum_{0} \sum_{m} \rho_{k}^{im}(t') \varphi_{0}^{l}(r') \varphi_{0}^{m}(r'),$$  \hspace{1cm} (188)

where $A(\varepsilon)$ represents density of states obtained from DFT calculation.

XC term of TDKS equation becomes,

$$\sum_{lev} \sum_{mec} [\rho_{k}^{im}(t') - \rho_{k}^{im}(0)] \int_{-\infty}^{t} dt' f_{xc}(t - t') \int d\varepsilon' d\varepsilon A'(\varepsilon) A^m(\varepsilon'),$$  \hspace{1cm} (189)
APPENDIX E: BOUND STATE (EXCITON) BINDING ENERGY AND AVAILABLE XC KERNELS FOR ITS CALCULATION
TDDFT-DM formalism begins with Kohn-Sham TDDFT equation

\[
\left[ -\frac{\nabla^2}{2} + v_s[n](r, t) \right] \Psi_k(r, t) = i \frac{\partial}{\partial t} \Psi_k(r, t),
\]  

(190)

\[v_s[n](r, t) = v_H[n](r, t) + v_{xc}[n](r, t) + v(r, t)\]  

(191)

\[n(r, t) = \sum_{|k|<k_F} |\Psi_k(r, t)|^2,\]  

(192)

Expanding \(\Psi_k(r, t)\) in terms of static KS wave functions \(\varphi^m_k(r)\) keeping all time dependence in coefficient as

\[\Psi_k(r, t) = \sum_m C_k^m(t) \varphi_k^m(r),\]  

(193)

Substituting \(\Psi_k(r, t)\)

\[\left[ H_{KS}(r) + H_{int} \right] \sum_m C_k^m(t) \varphi_k^m(r) = i \frac{\hbar}{\alpha} \sum_m C_k^m(t) \varphi_k^m(r),\]  

(194)

Multiplying by \(\varphi_q^l(r)\) and integrating over \(dr\), we get

\[\delta_{kq}^m \epsilon_k^m C_k^m(t) + \sum_m C_k^m(t) H_{qk}^{lm}(t) = i \frac{\hbar}{\alpha} C_q^l(t),\]  

(195)

\[\epsilon_q^l C_q^l(t) + \sum_m C_k^m(t) H_{qk}^{lm}(t) = i \frac{\hbar}{\alpha} C_q^l(t),\]  

(196)

Since \(m\) is dummy variable, changing \(m\) to \(n\) (but can’t change \(l, q\))

\[\epsilon_q^l C_q^l(t) + \sum_n C_k^n(t) H_{qk}^{ln}(t) = i \frac{\hbar}{\alpha} C_q^l(t),\]  

(197)
To explain the system response including intermixing of different orbitals, it is convenient to define combination of c-coefficients called the density matrix kernel of one electron as

$$\rho_{kq}^{ml}(t) = C_k^m(t)C_q^l(t),$$  \hspace{1cm} (198)

Its differentiation w.r.t. time becomes

$$i \frac{\partial \rho_{kq}^{ml}(t)}{\partial t} = i \frac{\partial C_k^m(t)}{\partial t}C_q^l(t) + i \frac{\partial C_q^l(t)}{\partial t}C_k^m(t),$$ \hspace{1cm} (199)

Substituting the values of terms, we get

$$i \frac{\partial \rho_{kq}^{ml}(t)}{\partial t} = (\varepsilon_k^m - \varepsilon_q^l)\rho_{kq}^{ml}(t) + \sum_n[H_{kq}^{mn}(t)\rho_{qq}^{nl}(t) - \rho_{kk}^{mn}(t)H_{kq}^{nl}(t)],$$ \hspace{1cm} (200)

$$H_{kq}^{mn}(t) = \iint \frac{\varphi_q^* \varphi_k}{|r-r'|} |n(r',t)-n(r',0)| + \iint \frac{\varphi_q^* \varphi_k}{|r-r'|} \int_{-\infty}^{t} dt' f_{XC}(r, t, r', t') [n(r', t') - n(r', 0)] + \int \varphi_q^* \varphi_k E(r), \hspace{1cm} (201)$$

Considering vertical or direct transition at the same momentum value, k=q, (this is the case for negligible photon momentum in momentum conservation equation) then

$$i \frac{\partial \rho_{kq}^{ml}(t)}{\partial t} = (\varepsilon_k^m - \varepsilon_k^l)\rho_{kq}^{ml}(t) + \sum_n[H_{kq}^{mn}(t)\rho_{kq}^{nl}(t) - \rho_{kq}^{mn}(t)H_{kq}^{nl}(t)],$$ \hspace{1cm} (202)

To calculate the excitonic binding energies, we drop the time-dependent external-field term. The Hartree term causes only minor local-field corrections and does not lead to any excitonic binding. We therefore keep only the XC contribution and the expansion of the charge density fluctuation in the XC term in terms of the density matrix elements gives
\[
\delta n(r', t') = \sum_{k \leq k_F} \sum_{\text{eev}} \sum_{\text{dec}} \left[ \begin{array}{cc} 0 & \rho_{k}^{ed}(t') \\ \rho_{de}^{ed}(t) & 0 \end{array} \right] \varphi_0^*(r') \varphi_0^d(r'),
\]

(203)

Note that \( v \) and \( c \) refers to the valence and conduction band and we don’t allow transition from valence to valence or conduction to conduction assigning the index \( l \) for any of the valence orbital and \( m \) only for any of the conduction orbital. So, in such two band situation and even tougher by taking only vertical transition, the TDDFT equation after Fourier transformation becomes

\[
\sum_q (\epsilon^m_q - \epsilon^l_q) \delta_{kkq} + F_{kk\sigma\tau}(\omega) \rho_{q}^{ml}(\omega) = \omega \rho_{k}^{ml}(\omega),
\]

(204)

where

\[
F_{kk\sigma\tau}(\omega) = \iint d\mathbf{r} \, d\mathbf{r}' \, \varphi_k^m(\mathbf{r}) \varphi_k^*(\mathbf{r}) f_{XC}(\mathbf{r}, \mathbf{r}', \omega) \varphi_k'^l(\mathbf{r}) \varphi_k'^*(\mathbf{r}),
\]

(205)

describes the electron-hole interaction and is known if we know the static Kohn-Sham orbitals and XC kernel.

For given \( f_{XC} \), if negative solution of the equation if it exists represents an exciton binding energy. However, no excitonic Rydberg series is produced. So, TDDFT with relatively simple XC kernel is capable of producing bound excitons.

Available XC Kernels

The effective electron-hole interaction in TDDFT and thus the exciton binding energies depend crucially on the approximate XC kernel. In the following, we shall implement several simple frequency-independent XC kernels and test their performance in our formalism.
To calculate the exciton binding energy, we solve the Equation (204) using eight XC kernels which can be classified as local, gradient density corrected, and long range kernels. The details about the XC kernels is available in ref. [303]

Adiabatic local XC Kernels

Adiabatic approximation of kernel neglects all memory effects. Although the memory effect does not play a decisive role, they can significantly modify the binding energy.

The simplest adiabatic XC kernel is the XC kernel that is local in both space and time and called contact interaction which is expressed as

\[ f_{XC}^{contact}(\vec{r}, \vec{r}', \omega) = -4\pi A \delta(\vec{r} - \vec{r'}), \]  

(206)

where A is a parameter that describes the effect of local charge interaction and so it is a phenomenological kernel.

The exchange-only adiabatic local density approximate (ALDA) kernel is given by

\[ f_{XC}^{ALDA}(\vec{r}, \vec{r}', \omega) = -\frac{1}{(9\pi n_0^2(\vec{r}))^{\frac{3}{2}}} \delta(\vec{r} - \vec{r'}), \]  

(207)

where \( n_0(\vec{r}) \) is the equilibrium electron density. As expected, the ALDA does not produce any bound excitons. LDA lead to strongly underestimated binding energies. Comparing LDA result to the contact kernel, one can suggest that the spatial constraint may be important for the excitons in this system.
Gradient-corrected XC Kernels

These kernels take into account the effects of possible strong spatial variation of the electronic charge, and hence the spatial-dependence of the local electron-hole interaction.

We also found that charge-gradient correction does not improve the situation significantly. The GEA and PW91 binding energies are even lower than LDA ones. Though PBE gives much larger energy than LDA, it is still much lower that the experimental value.

Long Range (LR) Kernels

These kernels take into account the Coulomb nature of the interaction (a kernel with \( \frac{1}{r^2} \) singularity). The simplest LR kernel is the phenomenological LR kernel

\[
f^{LR}_{XC}(\vec{r},\vec{r'}) = \frac{-1}{\epsilon |r-r'|}
\]  

(208)

where \( \epsilon \) is the effective screening parameter (dielectric constant). Unscreened (\( \epsilon = 1 \)) LR kernel gives somewhat underestimated value of the binding energy.

The Slater exchange kernel is given by

\[
f^{Slater}_{X}(r,r') = \frac{-2|\sum_j \epsilon |r-r'|\psi_j(r)\psi^*_j(r)|^2}{|r-r'|n_0(r)n_0(r')}
\]  

(209)

This kernel exhibits some degree of long-range behavior but not the ultra-nonlocality. The long-range contribution can be explicitly taken into account using the term

\[
f^{LRX}_{X}(r,r') = \frac{-\alpha}{4\pi|r-r'|}
\]  

(210)
Bootstrap Kernel

Another type of kernel that takes into account the effects of long-range interaction and is physically motivated by its close connection to the experimental quantity—dielectric function, the so-called Bootstrap (BO) kernel was proposed in ref. [304]. The basic motivation for the choice of the kernel was that: (1) it must have a Coulomb singularity,

\[ f_{XC\tilde{G}'GZ}^\text{boot}(\vec{k} \to 0, \omega) \to \frac{-\alpha_{XC}}{k^2}, \]

in which case the dielectric function \( \varepsilon(\vec{k} \to 0, \omega) \) may have an exciton pole at finite frequency, and (2) at \( \vec{k} \to 0 \), the kernel \( f_{XC\tilde{G}'GZ}^\text{boot} \) gives static dielectric function close to RPA, that reproduces the experimental data well.

The postulated kernel has the following structure:

\[
f_{XC\tilde{G}'GZ}^\text{boot}(\vec{k}, \omega) = \frac{\varepsilon_{G\tilde{G}'GZ}^{-1}(\vec{k}, \omega=0)v_{GZ}(\vec{k})}{\varepsilon_{00}^{-1}(\vec{k}, \omega=0) - 1} = \frac{\varepsilon_{G\tilde{G}'GZ}^{-1}(\vec{k}, \omega=0)}{\chi_{00}^{-1}(\vec{k}, \omega=0)}, \tag{211}
\]

A significant advantage of the BO kernel is its \textit{ab initio} form (i.e., it is essentially defined by the Kohn-Sham wave functions), relative technical simplicity of calculation as compared, e.g., to the EXX kernel.
REFERENCES


