1-1-1991

Multiconfiguration Hartree-Fock Calculation Of The Photoionization Of The Excited N 2P(2)3P 2S State

H. P. Saha
University of Central Florida

Find similar works at: <https://stars.library.ucf.edu/facultybib1990>
University of Central Florida Libraries <http://library.ucf.edu>

This Note is brought to you for free and open access by the Faculty Bibliography at STARS. It has been accepted for inclusion in Faculty Bibliography 1990s by an authorized administrator of STARS. For more information, please contact STARS@ucf.edu.

Recommended Citation

Saha, H. P., "Multiconfiguration Hartree-Fock Calculation Of The Photoionization Of The Excited N 2P(2)3P 2S State" (1991). *Faculty Bibliography 1990s*. 325.
<https://stars.library.ucf.edu/facultybib1990/325>

Multiconfiguration Hartree-Fock calculation of the photoionization of the excited N $2p^23p\ ^2S$ state

H. P. Saha

Department of Physics, University of Central Florida, Orlando, Florida 32816

(Received 22 February 1991; revised manuscript received 17 July 1991)

The partial photoionization cross sections and asymmetry parameter of the excited state $2p^23p\ ^2S$ of nitrogen have been calculated using the multiconfiguration Hartree-Fock method for continuum wave functions. The effects of electron correlation on the excited initial state, the ionic core state, and the final continuum state have been taken into account in an *ab initio* manner through the configuration-interaction procedure. It is found that the correlations do not change the result significantly from that obtained with Hartree-Slater and Hartree-Fock calculations. The present result of the asymmetry parameter is seen to be in excellent agreement with the experimental measurement of Pratt, Dehmer, and Dehmer [Phys. Rev. A **36**, 1702 (1987)] performed at a single photon energy.

PACS number(s): 32.80.Fb

The photoionization of atoms in excited states has received increasing attention from both experimentalists and theoreticians in the past few years as a rich source of information on detailed atomic structure and processes. Excited-state photoionization is of importance in controlled thermonuclear research plasmas and in regions of high temperature, such as stellar atmospheres. This is also important in the inverse process, radiative recombination.

Photoionization of molecules by lasers has proven to be a powerful technique for the production of open-shell, first-row atoms. There are many studies of resonantly enhanced multiphoton ionization (REMPI). In some experiments, REMPI can be described as one- or more-photon ionization of an excited state. Studies of this type have been recently performed on nitrogen. Pratt, Dehmer, and Dehmer [1] produced two-photon resonant, three-photon ($2+1$) ionization spectrum of atomic nitrogen by photodissociation of nitrous oxide. They found an anisotropic angular distribution of photoelectrons emitted from the excited state $2p^23p\ ^2S$ of nitrogen. This photoelectron spectrum via the 2S state displays a single N^+ photoelectron peak corresponding to the production of the $2p^2\ ^3P$ ground state.

In fact, there is very little experimental work on excited-state photoionization cross sections due to various technical difficulties associated with the production of excited-state targets in the laboratory and even less which covers a significant energy range. To judge the accuracy of the theoretical work, experimental data for a wide range of energies are of great importance. Cross sections at a single photon energy, although useful, are not sufficient for verification of the theoretical results. Pratt, Dehmer, and Dehmer [1] measured the asymmetry parameter for the photoionization of the excited nitrogen at a single photon energy, 4.61 eV. They found the asymmetry parameter to be -0.2 ± 0.1 at this photon energy.

Recently Theodosiou [2] calculated the $3p$ photoioniza-

tion cross section and asymmetry parameter of the excited state $2p^23p\ ^2S$ of nitrogen using the Hartree-Slater approximation and obtained the asymmetry parameter $\beta = -0.25$ which is in excellent agreement with the experimental value of -0.2 ± 0.1 measured at a single photon energy 4.61 eV. Manson [3] also performed a similar calculation for the photoionization cross section and the photoelectron angular distribution resulting from N $3p$ photoionization using the central-field Hartree-Slater method and obtained reasonably good agreement with experiment. Very recently Nahar and Manson [4] calculated the photoelectron angular distribution asymmetry parameter for the excited $2p^23p\ ^2S$ state of atomic nitrogen using Hartree-Fock approximation. They used the relaxed-core wave functions for both the initial discrete and the final continuum states. They found reasonably good agreement with the experimental measurement [1].

Although some calculations [2-4] have been performed on the central-field level and also on the Hartree-Fock level, which neglects the electron-electron correlation completely, a more accurate calculation that takes into account the electron correlation very efficiently is needed to understand the physics of the problem and also to explain the behavior of the photoelectron angular distribution quantitatively.

Recently we applied the multiconfiguration Hartree-Fock (MCHF) method to the calculation of the photoionization cross section and the photoelectron asymmetry parameter of the excited state of cesium [5]. This method employs procedures that allow optimization at each kinetic energy of the important core-polarization effects on the continuum function as well as for the incorporation of target and the ionic core configuration mixing effects.

The main aim of this paper is to investigate the behavior of the photoionization cross section and the photoelectron asymmetry parameter for the excited state N $3p$ by performing calculations in the MCHF approximation. The emphasis in this study is to take into account the

electron-electron correlation effects *ab initio* in order to obtain accurate photoionization cross section and the photoelectron angular distribution and compare them with the recent experimental measurement [1]. The calculations have been performed using both the simple Hartree-Fock (HF) and the more sophisticated MCHF wave function of the initial discrete excited state, the final discrete ionic state, and the continuum state.

The photoionization cross section for a transition from an initial bound state i to a final continuum state f is given, in the dipole approximation by

$$\sigma(\omega) = 4\pi^2 \alpha a_0^2 \omega \sum_{f,m} |\langle \Psi_f | T | \Psi_i \rangle|^2.$$

The dipole transition operator T is given by

$$T = T_L = \sum_{j=1}^n Z_j$$

in the length form and

$$T = T_V = \sum_{j=1}^n \frac{\nabla_j^z}{i\omega}$$

in the velocity form.

The asymmetry parameter, in the Cooper-Zare model, is given by [6]

$$\beta_{nl}(\omega) = \frac{l(l-1)T_{l-1}^2(\omega) + (l+1)(l+2)T_{l+1}^2(\omega) - 6l(l+1)T_{l-1}(\omega)T_{l+1}(\omega)\cos(\epsilon_{l+1} - \epsilon_{l-1})}{(2l+1)[lT_{l-1}^2(\omega) + (l+1)T_{l+1}^2(\omega)]}$$

where $T_{l-1}(\omega)$ and $T_{l+1}(\omega)$ are the radial parts of the dipole matrix element corresponding to the $l-1$ and $l+1$ channels, respectively, and $\epsilon_l(\omega)$ is the total phase shift of the l th channel.

The final MCHF wave function for the continuum state with label γ , energy E , and the term LS is expanded in a series of the form

$$\Psi(\gamma LS; N+1) = \sum_{j=1}^{m_c} a_j \Phi(\gamma_j L_c S_c; N) \phi_{kl} + \sum_{i=1}^m c_i \Phi(\gamma_i LS; N+1).$$

A set of radial functions $P_i(r)$, $i=1, 2, \dots, m$, which defines the above MCHF wave function, is a solution of the coupled integro-differential equations of the form

$$\left[\frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{l(l+1)}{r^2} \right] P_i(r) = \frac{2}{r} [Y_i(r)P_i(r) + X_i(r) + I_i(r)] + \sum_{i'} \epsilon_{ii'} P_{i'}(r).$$

These coupled integro-differential equations are solved

numerically by the iterative method described in detail earlier [5].

Both HF and MCHF calculations were performed to determine the effects of correlation. The main emphasis in this study is to take into account the electron correlation effect *ab initio*. To simplify the evaluation of the electric dipole matrix elements, the $1s$, $2s$, and $2p$ radial functions for both the states are obtained from the HF calculation of the core $2s^2 2p^2 {}^3P$ state, for the HF calculation, and from the MCHF calculation of core $(2s^2 2p^2 + 2p^4) {}^3P$ state, for the MCHF calculation. The $2s^2 2p^2 {}^3P$ state of the core mixes strongly with the $2p^4 {}^3P$ state. Mixing coefficients are, respectively, 0.989 902 7 and -0.141 748 3.

The MCHF wave-function expansion of the initial excited bound-state wave function is over the set of three configuration states coupled to form a 2S term,

$$\{2s^2 2p^2 3p, 2p^4 3p, 2s^2 3p 3d^2\} {}^2S.$$

The initial excited bound-state radial functions are obtained from the MCHF calculation [7] varying $3p$ and $3d$ orbitals simultaneously with $1s$, $2s$, and $2p$ the same as the MCHF wave function of the core.

The final MCHF continuum-wave-function expansion for the $2s^2 2p^2 kd {}^2P$ state is over the 108 configurations coupled to form a 2P term,

$$\{2s^2 2p^2 kd_1, 2p^4 kd_1, 2s^2 2p^2 3d, 2p^4 3d, 2s 2p^2 3d^2, 2p^2 3s 3d^2, 2s^2 3s 3d^2, 2s 2p^2 3s 3d, 2s 2p 3s 3p 3d, 2p^2 3s^2 3d,$$

$$2p^3 3p 3d, 2p^3 3s 3p, 2s 2p^2 3p^2, 2p^2 3s 3p^2, 2s 2p^2 3s^2, 2p^2 3p^2 3d, 2s^2 3d^3, 2p^2 3d^3, 2s^2 4d_2^3, 2p^2 4d_2^3\} {}^2P.$$

The radial functions $3s$, $4d_2$, and kd_1 are varied simultaneously for each kinetic energy of the photoelectron.

For the final continuum state $2s^2 2p^2 ks {}^2P$, the MCHF expansion was over the set of 65 configuration states,

$$\{2s^2 2p^2 ks_1, 2p^4 ks_1, 2s^2 2p^2 3d, 2p^4 3d, 2s 2p^2 3d^2, 2p^3 3p 3d, 2s 2p^2 3p^2, 2p^2 3p^2 3d, 2s^2 3d^3, 2p^2 3d^3, 2p^2 3p^2 3s_2\}^2P.$$

In this expansion, $3s_2$, $3p$, and ks_1 are varied simultaneously for each kinetic energy of the photoelectron. In all cases, $1s$, $2s$, and $2p$ wave functions are kept the same as the MCHF wave functions of the core and the $3d$ orbital is taken from the MCHF wave function of the initial state.

The photoionization cross sections, and the photoelectron angular distribution asymmetry parameters were calculated using both the HF and the correlated wave functions.

In the HF approximation, zero in the dipole matrix element for the $3p \rightarrow kd$ transition, in the length form appears at 0.125 Ry whereas the dipole matrix element in the velocity form shows zero at a slightly lower energy, 0.12 Ry. The correlated dipole matrix elements behave in a similar manner to that of the HF results but the length and the velocity dipole matrix elements reach zero between 0.10 and 0.11 Ry.

The calculated photoionization threshold of the N $3p$ state in the HF approximation is 0.1039 a.u. whereas in the MCHF approximation it is found to be 0.1087 a.u.

FIG. 1. Partial N $3p \rightarrow kd$ photoionization cross section as a function of photoelectron energy (Ry), using Hartree-Fock (HF) and correlated wave functions in both length and velocity formulations.

which is in excellent agreement with the experimental [8] value of 0.1083 a.u.

The photoionization cross sections for the $3p \rightarrow kd$ transition are shown in Fig. 1. The HF length and velocity results go to zero at about 0.125 and 0.12 Ry, respectively. The present HF results for this transition agree very well with the HF results obtained by Nahar and Manson [4], except for minor differences due to the different numerical methods used to compute the HF continuum wave functions. The cross section for this transition in the correlated approximation shows the same general qualitative behavior as that in the HF approximation. In this case minima occur between 0.10 and 0.11 (both length and velocity). In Fig. 2, the cross sections for the $3p \rightarrow kd$ transition are presented in an expanded diagram to show the differences between the HF and the correlated results at very low energies close to the minimum.

It should be mentioned that the present correlated partial cross-section results agreed very well with the work of Theodosiou which used an excited configuration self-consistent Hartree-Slater potential to describe the initial and the final states where correlations are completely neglected. This suggests that correlations do not appreciably change the results of the cross sections.

The asymmetry parameter $\beta_{nl}(\omega)$ for the N $3p$ photoionization is shown in Fig. 3. From the figure it is seen that both HF length and velocity results decrease sharply

FIG. 2. Same as Fig. 1.

FIG. 3. Photoelectron angular distribution asymmetry parameter β for N $3p$ in both length and velocity formulations, using Hartree-Fock (HF) and correlated (MCHF) wave functions.

from $\beta=2.0$ to a minimum at 0.17 Ry, and then increase smoothly with the increase of energy. The present HF results show very good agreement with that obtained by Nahar and Manson [4] except for the slight differences due to different numerical methods used for the calculation of the continuum wave function. The correlated length and velocity results show similar qualitative behavior. The minimum occurs at 0.15 Ry. The experimental asymmetry parameter ($\beta=-0.2\pm0.1$) obtained by Pratt, Dehmer, and Dehmer [1] at a single photon en-

ergy of 4.61 eV is in excellent agreement with the correlated result ($\beta=-0.18$). The result obtained by Theodosiou ($\beta=-0.25$) using the Hartree-Slater approximation agreed very well with the experimental value. However, there is a considerable difference in the value of the asymmetry parameter, in particular, around the minimum where it varies rapidly with energy. Based on his graphical results, since the numerical data of Theodosiou is not available, we found that Theodosiou obtained a minimum of less than -0.5 at a photon energy of about 5.27 eV, whereas the present correlated calculation shows a minimum of -0.29 around 5.00 eV photon energy. Also, the second zero in β occurs at about 6 eV according to the present approximation, whereas Theodosiou obtained the second zero around 6.8 eV.

Finally we conclude that the MCHF method, which takes into account the electron correlation effect very accurately and in an *ab initio* manner through the configuration interaction procedure, does not produce considerable change in the results in the present case over the central-field and the HF calculation where this effect is completely neglected. Although there is excellent agreement between the calculated and the experimental asymmetry parameter at a single photon energy, more experimental data over a larger energy range would be extremely desirable.

This research was supported by grants from the National Science Foundation and in part by the Petroleum Research Fund, administered by the American Chemical Society. This research was also supported by the Florida State University through time granted on its ETA-10 and CRAY-YMP Supercomputers.

- [1] S. T. Pratt, J. L. Dehmer, and P. M. Dehmer, Phys. Rev. A **36**, 1702 (1987).
- [2] C. E. Theodosiou, Phys. Rev. A **37**, 1795 (1988).
- [3] S. T. Manson, Phys. Rev. A **38**, 126 (1988).
- [4] S. N. Nahar and S. T. Manson, Phys. Rev. A **40**, 5017 (1989).
- [5] H. P. Saha, Phys. Rev. A **41**, 174 (1990).
- [6] J. Cooper and R. N. Zare, in *Lectures in Theoretical Phys-*

- ics*, edited by S. Geltman, K. Mahanthappa, and W. Britten (Gordon and Breach, New York, 1969), Vol. 11c, pp. 317-337.
- [7] C. Froese Fischer, Comput. Phys. Commun. **14**, 145 (1978).
- [8] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. Ref. Data Ser. Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, DC, 1949).