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Analytically derived switching functions for exact H_2^+ eigenstates

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Electron translation factors (ETF's) appropriate for slow atomic collisions may be constructed using switching functions. In this paper we derive a set of switching functions for the H_2^+ system by an analytical "two-center decomposition" of the exact molecular eigenstates. These switching functions are closely approximated by the simple form $f = \tanh b\eta$, where η is the "angle variable" of prolate spheroidal coordinates. For given united atom angular momentum quantum numbers (l, m) , the characteristic parameter b_{lm} depends only on the quantity $c^2 = -\epsilon R^2/2$, where ϵ is the electronic binding energy and R the internuclear distance in a.u. The resulting parameters are in excellent agreement with those found in our earlier work by a heuristic "optimization" scheme based on a study of coupling matrix-element behavior for a number of H_2^+ states. An approximate extension to asymmetric cases (HeH^{2+}) has also been made. Nonadiabatic couplings based on these switching functions have been used in recent close-coupling calculations for $H^+-H(1s)$ collisions and $He^{2+}-H(1s)$ collisions at energies 1.0–20 keV.

I. MOLECULAR-STATE TRANSLATION FACTORS

To satisfy scattering boundary conditions and translational invariance requirements in atomic-collision problems, electronic basis functions must include a description of electron translation due to nuclear motion with respect to the reference origin chosen for electron coordinates.¹⁻⁷ In applications of the perturbed-stationary-states (PSS) method, inclusion of these electron translation factors (ETF's) is especially important, since they produce substantial corrections to the nonadiabatic couplings responsible for electronic transitions, and their neglect results in couplings which can depend strongly on the choice of reference origin and exhibit incorrect, unphysical behavior.⁵⁻¹²

For basis functions centered on a single nucleus (e.g., atomic orbitals), the proper ETF's are uniquely and simply defined^{1,2,12} (as in Ref. 12, we call these *single-center* or *Bates-McCarroll* ETF's). But for basis states with genuinely molecular, *two-center* character, choice of an appropriate ETF is more problematic, since the electron is partially "attached" to both nuclei.

For asymmetric systems, each molecular state is asymptotically correlated to one atomic state, and it has been frequent practice to associate with each such state the Bates-McCarroll ETF proper to the corresponding atomic state.^{1,2,13-15} This guarantees that asymptotic boundary conditions and translational invariance requirements are met, and removes the more obvious defects from PSS coupling matrix elements (such as constant values as $R \rightarrow \infty$), so a formally correct theory is obtained. However, it often happens that a state

asymptotically correlated to one center acquires substantial two-center character at finite internuclear separations; a good example is the $2p\sigma$ orbital in the HeH^{2+} system, which corresponds asymptotically to $He^{2+} + H(1s)$, but has very large contributions from $He^*(2s, 2p) + H^+$ at finite R values.¹¹ In such a case it seems clear that a single-center ETF, though correct for the asymptotic state, is physically inappropriate at finite distances.

For symmetric systems (e.g., H_2^+) a further complication arises because the molecular states have g or u symmetry and do not correlate in one-to-one fashion with atomic states on a single center. It is possible to correct the asymptotic behavior and meet translational invariance by defining linear combinations of pairs of g and u states which correspond asymptotically to single-center states, associating to these fragments the corresponding Bates-McCarroll ETF's, and recombining the fragments to give "molecular states."^{1,3,16,17} However, the same physical criticism may be made as before—is the combination of a pair of g and u molecular states really a single-center state at finite internuclear separations? Moreover, it can be shown that such a scheme is simply an approximate way to simulate the effects of a switching function (cf. Sec. II G).

Thorson and Delos^{6,7} have shown that ETF's appropriate for molecular states can be constructed using *switching functions*.^{4,18} In effect, these describe an electron translation which is a function of the electron's local behavior; alternatively they can be viewed as defining a local reference origin for an electron adapted to its "degree of attachment" to one or the other of the nuclei. The

resulting formulation meets all requirements of translational invariance and scattering boundary conditions. Bates-McCarroll ETF's for one-center states are effectively recovered as a special limiting case, but the flexibility in the switching function permits ETF's to reflect the two-center character in a molecular state. Symmetric and asymmetric systems can be treated on a common footing and the resulting basis states have rigorous g or u symmetry.

Formulation of collision theory with ETF's based on switching functions does not place constraints on these functions, other than those imposed by asymptotic boundary conditions (i.e., as internuclear distance $R \rightarrow \infty$, a switching function f must have the effective limiting values $f = -1$ in any finite neighborhood of nucleus A and $f = +1$ in any finite neighborhood of nucleus B [see Eqs. (2.34), Ref. 6]). This arbitrariness in f is *formally* irrelevant, since, provided the expansion basis used is complete, the resulting scattering amplitudes must be invariant to the choice used for f . In real life, though, with basis sets which are finite and far from complete, the selection of appropriate switching functions is an important problem. PSS coupling matrix elements can be very sensitive to the choice taken for f , both for couplings between discrete states and, markedly, for ionizing transitions.⁹⁻¹¹ The differences in couplings can produce significant differences in computed excitation cross sections for individual states, and also affect total cross sections (to lesser extent); moreover, results as a function of increasing basis size may appear to "converge" on different limits for different choices for f . Work recently completed in this laboratory^{19,20} gives examples of all these effects and provides the practical motivation for studies of the sort presented here.

The formulation of Refs. 6 and 7 assumes that a single switching function may be used for all electronic states of a given system, and at least one collision study has been reported, based on this assumption,²¹ but there is a great deal of evidence which shows that switching functions which are distinct for each molecular state are more appropriate.^{10,11} A formulation based on this more general assumption has been given by Delos and Thorson¹² in the framework of a classical-trajectory collision theory; more recently, Delos²² has extended the formulation to a fully quantum-mechanical framework, and a somewhat different formulation with such features has been given by Green.²³ It can be shown that the non-Hermitian character of nonadiabatic coupling matrix elements which results from different f 's for different states is required to maintain probability

conservation^{24,12}; it is not correct to replace the distinct forward and reverse couplings by their Hermitian averages as has sometimes been done.^{16,17}

Formal variational principles may be used to obtain conditions for optimum ETF's for a given electronic basis set, and Riley and Green²⁵ have employed the Euler-Lagrange method to do this. Using ETF's of single-center type, but with variable parameters, they show that the Bates-McCarroll ETF's are obtained as the exact solutions when atomic functions are the basis states, and they obtain coupled equations valid when ETF's of this type are associated with more general (molecular) basis states.²⁶ In principle, their scheme can be extended to obtain conditions for optimum ETF's based on switching functions,^{23,27} but the resulting systems of coupled equations appeared to us to be too complicated for convenient application in the context of our present studies.

One scheme for selecting switching functions for molecular states is based on the fact that the non-adiabatic couplings from a bound molecular state to continuum states are extremely sensitive to variations in the switching function used. For one-electron systems (H_2^+ and HeH^{2+}), Rankin and Thorson¹¹ used a switching function of the form

$$f_\mu = \tanh[\beta_\mu R(\eta - \eta_0^\mu)] \quad (1)$$

for the molecular state ψ_μ , where $\eta = (r_A - r_B)/R$, and β_μ , η_0^μ are parameters which may depend on R . For each bound state they found that there are specific values for β_μ and η_0^μ which spectacularly reduce the magnitudes of couplings to all continuum states (relative to uncorrected PSS values), except for the first few partial waves. The "optimum parameters" so obtained depend neither upon the energy or other properties of the continuum states involved, nor upon the type of coupling considered (radial or angular). Relative to uncorrected PSS values, couplings to higher continuum partial waves are reduced by factors 10^3 – 10^5 . The implication is that the switching functions obtained are in some way characteristic of the bound states involved.

Unpublished work in this laboratory (by Kimura) has extended such studies to discrete-discrete-state couplings, with partial success. Some families of coupling elements (notably those to sequences of Rydberg states) show a strong sensitivity to switching function variations similar to that exhibited by continuum couplings, but other couplings are relatively insensitive, or have an irregular behavior complicated by the existence of nodal zeroes in the matrix elements. Neverthe-

less, it is possible to obtain general confirmation of the optimum parameters found by Rankin and Thorson; when the effects on both discrete- and continuum-state couplings are considered, the values obtained for β_μ tend to be somewhat larger (~ 5 – 10% at most) than those of Ref. 11, and have a slightly larger uncertainty. (In one case, $3d\sigma$, a quite different set of β values is found from a study of the discrete-state couplings, and reexamination of the continuum couplings shows that a secondary minimum occurs for this case at these values.)

While these results are strongly suggestive, the procedure used to obtain them is heuristic and has not been derived formally from any variational principle.²⁸ Moreover, the calculations involved are extensive and are only feasible for the exactly solvable one-electron systems. It would be an important advance if these "characteristic switching functions" could be deduced directly in some well-defined way from an analysis of the bound states themselves, and in this paper we show that this can be done.

Still another approach to the construction of a molecular-state switching function has been given in Ref. 12; it is based on the fact that the proper ETF for an atomic (single-center) orbital is uniquely defined. Let us assume that molecular orbitals ψ_μ can be expressed as linear combinations of atomic orbitals $\{\phi_n\}$ (LCAO-MO),

$$\psi_\mu = \sum_n U_{n\mu} \phi_n, \quad (2)$$

where the transformation U is invertible. Then, the requirement that the physical description of a collision in the molecular-state basis shall be identical in the low-velocity limit to that obtained in the supporting atomic-state basis, leads to a definition of the switching function f_μ for state ψ_μ as

$$f_\mu \psi_\mu = \sum_n U_{n\mu} f_n \phi_n, \quad (3)$$

where $f_n = -1$ if ϕ_n is centered on nucleus A , and $f_n = +1$ if ϕ_n is centered on B . This shows how a switching function reflects a local "degree of attachment" to one or the other center, indicates that, in general, it will be different for each molecular state, and also provides a rationalization for the form used in Eq. (1): A simple LCAO-MO approximation to the $1s\sigma_g$ state of H_2^+ is

$$\psi_{1s\sigma_g} = C(e^{-\beta r_A} + e^{-\beta r_B})$$

and this gives [via Eq. (3)]

$$f_{1s\sigma_g} = \tanh \beta R \eta$$

(with $\beta = 0.5$ as $R \rightarrow \infty$; the heuristic method described earlier yields $\beta = 0.45$ – 0.46 at $R = 12.0$ a.u.).

Equation (3) gives a consistent definition of switching functions for molecular states *explicitly constructed by the LCAO procedure from one-center states as a starting point*, but it says nothing about either the *adequacy* or the *uniqueness* of the LCAO expansion [Eq. (2)] as a representation of a molecular state. In particular, for one-electron systems like H_2^+ or HeH^{2+} where we know the molecular states exactly, the failings of LCAO expansions in these respects become quite evident. In other unpublished work (by Knudson) we have studied LCAO expansions of the exact H_2^+ states ($1s\sigma_g$, $2p\sigma_u$) in an effort to deduce switching functions via Eq. (3). The results were as follows.

(1) Variational calculations were performed for the $1s\sigma_g$ state using up to 10–12 σ_g LCAO-MO's with variable orbital exponents. Although the calculated energies are accurate to more than eight significant figures, the wave function on the internuclear axis is represented to only 5–10% accuracy for $2.0 \leq R \leq 8.0$ a.u. Moreover, for $R < 2.0$ a.u., redundancy in the basis set becomes increasingly severe, and the resulting instability of the expansion coefficients in Eq. (2) leads to a much greater instability in Eq. (3). For $R > 2.0$ a.u., however, the *switching function* obtained agrees closely (5% or better) with that found by the heuristic optimization process described previously—and the computed coupling matrix elements are also in similar agreement.

(2) For the $2p\sigma_u$ state, variational calculations were performed using up to 8 σ_u LCAO-MO's with variable orbital exponents (if additional basis functions are used, instability due to basis-set redundancy becomes severe). Again the computed energies are very accurate, but the wave function is reproduced even more poorly than for $1s\sigma_g$ ($\sim 25\%$ or more error on the internuclear axis for $4 < R < 8$ a.u.) and severe redundancy and/or stability problems appear for $R \lesssim 4$ a.u. For $R > 4$ a.u., an approximate switching function can be deduced via Eq. (3), but since the $2p\sigma_u$ state has a node at $\eta = 0$, this has a completely different form from that of Eq. (1); in particular, it is singular at $\eta = 0$. Nevertheless the resulting *coupling matrix elements* agree reasonably well with those computed using the switching function of form (1) found by the heuristic optimization scheme, for internuclear separations $R \gtrsim 6$ a.u. For $R < 6$ a.u., however, they diverge from and become much larger than the optimized couplings.

From these studies we concluded that Eq. (3) provides important insight about the nature of switching functions but cannot be used as a rigorous

scheme for constructing them from molecular states as a starting point; in particular, there are difficulties with Eq. (3) (especially as $R \rightarrow 0$) if the wave function has zeroes on the internuclear axis.

In this paper we show that an analytical "two-center decomposition" of the exact molecular states of H_2^+ can be made along lines suggested by Eq. (3); this decomposition is based on a different analytical form for the "angular" part of the separable wave function from those commonly used. The decomposition leads to well-defined switching functions for each state, whose form is closely approximated by Eq. (1), and, moreover, the values of parameters β determined by this analysis are in excellent agreement with those found using the heuristic optimization scheme described above. The same ideas may be extended in an approximate way to asymmetric systems (e.g., HeH^{2+}) and we briefly describe this extension in Sec. III.

II. ANALYSIS

As is well known, the two-center Coulomb problem is separable in prolate spheroidal coordinates ($1 \leq \xi < \infty$; $-1 \leq \eta \leq 1$; $0 \leq \phi < 2\pi$). ξ is analogous to a radius, and information about two-center decomposition will be found only in the "angular" wave function $S(\eta)$, which obeys the equation

$$\frac{d}{d\eta} (1 - \eta^2) \frac{dS}{d\eta} + \left(c^2 \eta^2 + p\eta - A - \frac{m^2}{1 - \eta^2} \right) S = 0. \quad (4)$$

Here m is the azimuthal quantum number, c is the energy parameter ($c^2 = -\epsilon R^2/2$, ϵ , R in a.u.), $p = R(Z_B - Z_A)$ is a charge asymmetry parameter, and A is the angular separation constant; in the united-atom limit $R \rightarrow 0$, A takes limiting values $-l(l+1)$, $l = |m|, |m|+1, \dots$, and the corresponding $S_{lm}(\eta)$ are the associated Legendre functions $P_l^m(\eta)$ (we label the eigenstates at all R with l, m). We remove azimuthal nodes by writing

$$S_{lm}(\eta) = (1 - \eta^2)^{|m|/2} h_{lm}(\eta),$$

where (assume $m \geq 0$)

$$(1 - \eta^2) h_{lm}'' - 2(m+1)\eta h_{lm}' + \{ -[A_{lm} + m(m+1)] + c^2 \eta^2 + p\eta \} h_{lm} = 0, \quad (5)$$

and h_{lm} has $(l-m)$ zeroes ($-1 < \eta < +1$). In this section we consider the symmetric case $p=0$.

A. H_2^+ $1s\sigma_g$ state

For simplicity we look first at the case $m=0$, $l=0$ where $h_{lm}(\eta)$ is a nodeless function. We have already seen that in this case Eq. (3) may be applied with at least some success via the LCAO-MO scheme; we now look for a decomposition

of $h_{00}(\eta)$ on similar lines.

Solutions to Eq. (4) in the form^{29,30}

$$S_{lm}(\eta) = \exp(\pm c\eta) \sum_{k=1}^{\infty} d_k^{lm} P_k^{lm}(\eta) \quad (6)$$

lead to a three-term recursion relation for the coefficients $\{d_k^{lm}\}$ (commonly used to determine eigenvalues in the asymmetric case). A simple reflection rule connects the coefficients d_k^{lm} for an expansion using $e^{-c\eta}$ as a prefactor, to those for one using $e^{+c\eta}$. However, it is well known²⁹⁻³¹ that Eqs. (6) give poorly convergent representations of the eigenfunctions, especially as R increases; expansions like

$$S_{lm}(\eta) = \sum_{j=1}^{\infty} b_j^{lm} P_j^{lm}(\eta), \quad (7)$$

or a power series for $h_{lm}(\eta)$, are used instead.³¹⁻³⁴

The evident asymmetry of the expansions (6) suggests the reason for their poor convergence. They are analogous to one-center expansions, respectively, about $\eta = \pm 1$ (B, A), and the well-known difficulties of one-center LCAO expansions are also latent here. A form in which contributions from both centers are present on an equal footing is needed for an "even-tempered" expansion. The simplest LCAO-MO approximation gives us the zero-order form

$$h_{00}^{(0)} = \cosh b\eta,$$

but the proper choice for b is *not* $b=c$ as in Eqs. (6); matching the second derivative of $h_{00}(\eta)$ at $\eta=0$ yields $b^2 = A_{00}$ [asymptotically, A_{00} is well approximated by the series

$$A_{00} = (c-1)^2 + \frac{1}{4}(c-1)^{-1} + \frac{1}{8}(c-1)^{-3} + \dots, \quad (8)$$

so that $b \rightarrow c$ when $R \rightarrow \infty$, as the LCAO-MO result predicts]. Interpreting this zero-order form on lines suggested by Eq. (3), i.e., associating $f_n = +1$ with $e^{+b\eta}$ and $f_n = -1$ with $e^{-b\eta}$, we obtain the switching function

$$f_{00}^{(0)} = \tanh \beta R \eta$$

with $\beta R = b$. The resulting values for β (e.g., $\beta = 0.456$ at $R = 12.0$ a.u.) are in excellent agreement with those determined by the optimization procedure and also with those found by the LCAO-MO computations on the $1s\sigma_g$ state described in Sec. I.

A numerically accurate representation of the $s\sigma_g$ eigenfunction can be given in the form (cf. Sec. IIE)

$$h_{00}(\eta) = (1 + G_4 \eta^4 + G_6 \eta^6 + \dots) \cosh b\eta + (G_3 \eta^3 + G_5 \eta^5 + \dots) \sinh b\eta, \quad (9a)$$

and the corresponding switching function is then defined by

$$f_{00}(\eta)h_{00}(\eta) = (1 + G_4\eta^4 + G_6\eta^6 + \dots) \sinh b\eta \\ + (G_3\eta^3 + G_5\eta^5 + \dots) \cosh b\eta \quad (9b)$$

with $h_{00}(\eta)$ given by (9a). However, for reasons of simplicity we have chosen to represent $h_{00}(\eta)$ in the slightly different form

$$h_{00}(\eta) = \cosh \theta_{00}(\eta), \quad (10)$$

so that the switching function is just given by

$$f_{00}(\eta) = \tanh \theta_{00}(\eta). \quad (11)$$

The function $\theta_{00}(\eta)$ may be written

$$\theta_{00}(\eta) = \beta R \eta [1 + \chi_{00}(\eta^2)] \quad (12)$$

and is found to deviate only slightly from strict linearity (at most about 6%—see Sec. IIE below). All $s\sigma_g$ states, as well as $p\pi_u$, $d\delta_g$, etc., states, for which $(l-m)=0$ and h_{lm} is a nodeless function, may be analyzed in the same fashion.

B. Nodes and the $2p\sigma_u$ state

Analysis of the $2p\sigma_u$ state raises the problem of nodes in $h_{lm}(\eta)$. Analogy with the $s\sigma_g$ case suggests two different zero-order forms, either

$$h^{(0)} = \sinh \tilde{b}\eta \quad (13a)$$

or

$$h^{(0)} = \eta \cosh \tilde{b}\eta, \quad (13b)$$

where we find (by matching the third derivative at $\eta=0$) that $\tilde{b}^2 = 3b^2 = A_{10} + 2$. Numerically accurate representations of the $p\sigma_u$ eigenfunction may be based on either form, but they lead to quite different switching functions: Again interpreting components $e^{\pm b\eta}$ in Eqs. (13) as contributions, respectively, from centers B and A, the corresponding zero-order switching functions are

$$f^{(0)} = \coth \tilde{b}\eta \quad (14a)$$

or

$$f^{(0)} = \tanh \tilde{b}\eta \quad (14b)$$

and the numerically accurate results do not differ much from these. This shows very clearly that a two-center decomposition—and the switching function associated with it—depends on the specific form taken to represent the eigenfunction.

However, we find that the values $\beta = b/R$ obtained from Eq. (14b) are in excellent agreement with the heuristic optimization procedure values for the $2p\sigma_u$ state. Moreover, calculations of the coupling matrix elements obtained with the two types of switching functions also lead us to favor the form (13b) as the appropriate base for representation. We find that for internuclear distances $R \gtrsim 6$ a.u., couplings computed using either form are in reasonably close agreement. However, for decreasing

R , couplings generated by (14a) rapidly diverge from those computed from (14b), and they become very large even in comparison to the *uncorrected* PSS couplings, with singularities at $R \rightarrow 0$. This behavior obviously arises from the singularity in (14a) at $\eta=0$. By contrast, the couplings generated by the switching function (14b) are well behaved everywhere and typically smaller than the uncorrected PSS couplings. Evidently also, the previously described problems with LCAO-MO calculations on the $2p\sigma_u$ state and the nonadiabatic couplings are explicable in terms of these same ambiguities of representation.

We conclude that the appropriate representation of the eigenfunction $S_{lm}(\eta)$ requires explicit factorization of the nodal structure which is associated as $R \rightarrow 0$ with orbital angular momentum of the electron. For $p\sigma_u$, $d\pi_g$, $f\delta_u$, etc., states, this factor is just η , and we write

$$h_{10}(\eta) = \eta g_{10}(\eta), \quad (15)$$

where

$$g_{10}(\eta) = \cosh \theta_{10}(\eta) \quad (16)$$

is, again, a nodeless amplitude function and is treated in the same way as the $s\sigma_g$ states; the switching function is

$$f_{10}(\eta) = \tanh \theta_{10}(\eta) \quad (17)$$

and the deviation of $\theta_{10}(\eta)$ from strict linearity, though larger than for $s\sigma$ states, is unimportant in Eq. (17) (see Sec. IIE).

C. General case

For general (l, m) ($m \geq 0$) we write

$$h_{lm}(\eta) = \Pi_{lm}(\eta) g_{lm}(\eta), \quad (18)$$

where $\Pi_{lm}(\eta)$ is a polynomial of order $(l-m)$, even or odd according to the parity s of $(l-m)$ ($s=0, 1$). The $(l-m)$ zeroes of $\Pi_{lm}(\eta)$ are arranged symmetrically about $\eta=0$, and $g_{lm}(\eta)$ is a nodeless amplitude function like $h_{00}(\eta)$. As $R \rightarrow 0$,

$$\lim_{R \rightarrow 0} [(1 - \eta^2)^{l-m}/2 \Pi_{lm}(\eta)] = (\text{const}) P_l^{lm}(\eta), \quad (19)$$

which determines the limiting zeroes. Given the zeroes of $\Pi_{lm}(\eta)$, we may determine the function $g_{lm}(\eta)$, which we write as in Eqs. (10) and (16):

$$g_{lm}(\eta) = \cosh \theta_{lm}(\eta). \quad (20)$$

The switching function is then always of the form

$$f_{lm}(\eta) = \tanh \theta_{lm}(\eta). \quad (21)$$

$\theta_{lm}(\eta)$ may be written

$$\theta_{lm}(\eta) = b_{lm} \eta [1 + \chi_{lm}(\eta^2)], \quad (22)$$

FIG. 1. Parameter β vs R for five H_2^+ states. Solid curves show analytical results. All data points are values from optimization calculations ($\bullet$, $\blacktriangle$, $\boxtimes$, values of Rankin and Thorson for $1s\sigma_g$, $2s\sigma_g$, $2p\pi_u$, and $3d\sigma_g$; $\circ$, $\square$, $\triangle$, $\times$, as modified by inclusion of discrete-state coupling effects). Error bars indicate uncertainties in the latter.

FIG. 2. $(b/c)^2$ vs c^2 for various (l, m) in H_2^+ . Solid curves, σ states; dashed, π states; dotted, $d\delta$ states.

and in essentially *all* cases (Sec. II E) the linear approximation to θ_{lm} is *adequate* for use in Eq. (21).

D. Switching function parameters b_{lm}

Characteristic parameters b_{lm} may be computed, given the eigenvalues A_{lm} and the zeroes of $\Pi_{lm}(\eta)$. If $s(=0, 1)$ is the parity of $(l - m)$, $\Pi_{lm}(\eta)$ has $(l - m - s)$ nonzero roots in pairs $\eta_i^* = \pm(1/D_i)$, $i = 1, \dots, (l - m - s)/2$. The b_{lm} may be computed by the formula

$$b_{lm}^2 = [A_{lm} + l(l + 1)] / (2s + 1) - \Delta_{lm}, \quad (23)$$

where

$$\Delta_{lm} = \frac{(l - m - s)(l + m + s + 1)}{(2s + 1)} - 2 \left(\sum_i D_i^2 \right) \quad (24)$$

$[\Delta_{lm} \sim O(c^2)$ as $c^2 \rightarrow 0$].

Figure 1 shows values of $\beta_{lm} = b_{lm}/R$ vs R for a number of H_2^+ states. For comparison, the values found by the heuristic optimization procedure are also shown and it can be seen that the agreement is excellent (Rankin and Thorson's¹¹ values for the $3d\sigma$ state are the only exception).

For given (l, m) , angular eigenfunction properties can depend only on the parameter $c^2 = -\epsilon R^2/2$. Figure 2 depicts $(b_{lm}/c)^2$ vs c^2 for those (l, m) of common interest in H_2^+ . Except for $s\sigma$, and to some extent $p\pi$ states, this ratio is almost con-

stant for those c^2 values corresponding to inter-nuclear distances $R < 12$ a.u. in H_2^+ ; the variations in β_{lm} which appear in Fig. 1 mostly reflect bonding and antibonding effects on the electronic energies ϵ vs R . It is also interesting that $(b_{lm}/c)^2$ is a much less strongly varying function of c^2 than either the separation constant A_{lm} or roots parameter Δ_{lm} . For small c^2 ,

$$(b_{lm}/c)^2 = 1/(2l+3) + C_2 c^2 + \dots; \quad (25)$$

for $(l-m) = 0, 1$,

$$C_2 = \frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)^3(2l+5)}, \quad (26)$$

but a more complicated result holds for $(l-m) \geq 2$.

Rational polynomial approximations to $(b_{lm}/c)^2$ as functions of c^2 are given in Table I for the (l, m) values of common interest. Except for certain couplings involving $d\sigma$ states (see Sec. II F), this information is sufficient to construct switching

functions and calculate ETF-corrected couplings for H_2^+ states.

E. Deviation of $\theta_{lm}(\eta)$ from linearity

The purpose of this work was to construct well-defined switching functions by analytical two-center decomposition of the molecular states, since the heuristic optimization studies clearly indicated their existence. However, we have seen that the concept of a two-center decomposition cannot be uniquely defined by purely formal means; it depends on the specific form chosen to represent the eigenfunctions. This is clearly illustrated by the case of the $p\sigma$ state and the problem of nodes in h_{lm} , but can be demonstrated even more radically. For example, if we perversely chose to construct $h_{lm}(\eta)$ by taking symmetric combinations of the one-center expansions of Eqs. (6), we would find the resulting switching function is identically zero everywhere. However, by the analytical procedure described above—including the decision to factor

TABLE I. Rational polynomial approximations to switching function parameters $(b_{lm}/c)^2 = (2l+3)^{-1} + c^2 F_2(c^2)$, where $F_2(x) = P(x)/Q(x)$. $P(x)$ and $Q(x)$ are polynomials: $P(x) = \sum_n P_n x^n$ and $Q(x) = \sum_n Q_n x^n$.

$l=0$ $m=0$ $(s\sigma)$			$l=1$ $m=0$ $(p\sigma)$		
n	P_n	Q_n	n	P_n	Q_n
0	$0.148\,148\,15 \times 10^{-1}$	$0.100\,000\,00 \times 10^1$	0	$0.228\,571\,43 \times 10^{-2}$	$0.100\,000\,00 \times 10^1$
1	$0.104\,231\,29 \times 10^{-2}$	$0.384\,799\,15 \times 10^{-1}$	1	$0.721\,572\,11 \times 10^{-4}$	$0.404\,602\,66 \times 10^{-1}$
2	$0.125\,194\,06 \times 10^{-3}$	$0.829\,064\,60 \times 10^{-2}$	2	$0.230\,721\,83 \times 10^{-5}$	$0.174\,476\,71 \times 10^{-2}$
3	$0.751\,754\,02 \times 10^{-5}$	$0.386\,795\,62 \times 10^{-3}$	3	$-0.478\,846\,84 \times 10^{-8}$	$0.165\,013\,91 \times 10^{-4}$
4	$0.207\,896\,89 \times 10^{-7}$	$0.166\,179\,14 \times 10^{-4}$	4	$0.235\,773\,33 \times 10^{-10}$	
5	$-0.840\,382\,60 \times 10^{-10}$				
$l=2$ $m=0$ $(d\sigma)$			$l=3$ $m=0$ $(f\sigma)$		
n	P_n	Q_n	n	P_n	Q_n
0	$0.107\,979\,71 \times 10^{-2}$	$0.100\,000\,00 \times 10^1$	0	$0.548\,696\,85 \times 10^{-3}$	$0.100\,000\,00 \times 10^1$
1	$-0.116\,736\,39 \times 10^{-4}$	$-0.419\,433\,38 \times 10^{-1}$	1	$-0.120\,561\,07 \times 10^{-3}$	$-0.232\,761\,17 \times 10^0$
2	$0.755\,590\,94 \times 10^{-5}$	$0.663\,759\,54 \times 10^{-2}$	2	$-0.665\,566\,14 \times 10^{-5}$	$-0.911\,462\,18 \times 10^{-2}$
3	$-0.109\,310\,43 \times 10^{-7}$	$-0.175\,819\,97 \times 10^{-3}$	3	$-0.102\,240\,79 \times 10^{-6}$	$-0.545\,801\,87 \times 10^{-4}$
4	$-0.408\,022\,29 \times 10^{-9}$	$0.251\,198\,96 \times 10^{-5}$	4	$0.737\,805\,07 \times 10^{-9}$	
5	$0.544\,151\,20 \times 10^{-10}$				
$l=1$ $m=1$ $(p\pi)$			$l=2$ $m=1$ $(d\pi)$		
n	P_n	Q_n	n	P_n	Q_n
0	$0.457\,142\,86 \times 10^{-2}$	$0.100\,000\,00 \times 10^1$	0	$0.129\,575\,64 \times 10^{-2}$	$0.100\,000\,00 \times 10^1$
1	$-0.117\,243\,65 \times 10^{-3}$	$-0.523\,114\,23 \times 10^{-1}$	1	$0.633\,211\,92 \times 10^{-4}$	$0.451\,567\,36 \times 10^{-1}$
2	$0.836\,276\,71 \times 10^{-5}$	$0.276\,182\,60 \times 10^{-2}$	2	$0.662\,170\,65 \times 10^{-6}$	$0.490\,206\,10 \times 10^{-3}$
3	$0.933\,746\,54 \times 10^{-8}$	$-0.421\,855\,98 \times 10^{-4}$	3	$0.187\,817\,14 \times 10^{-7}$	$0.211\,012\,04 \times 10^{-4}$
4	$0.399\,926\,90 \times 10^{-8}$	$0.107\,950\,75 \times 10^{-5}$	4	$-0.689\,086\,65 \times 10^{-10}$	
5	$-0.873\,093\,73 \times 10^{-11}$				
$l=3$ $m=1$ $(f\pi)$			$l=2$ $m=2$ $(d\delta)$		
n	P_n	Q_n	n	P_n	Q_n
0	$0.598\,578\,38 \times 10^{-3}$	$0.100\,000\,00 \times 10^1$	0	$0.194\,363\,46 \times 10^{-2}$	$0.100\,000\,00 \times 10^1$
1	$-0.957\,328\,22 \times 10^{-5}$	$-0.251\,795\,26 \times 10^{-1}$	1	$0.413\,124\,20 \times 10^{-3}$	$0.194\,023\,14 \times 10^0$
2	$0.242\,347\,87 \times 10^{-5}$	$0.383\,764\,08 \times 10^{-2}$	2	$-0.461\,338\,08 \times 10^{-5}$	$-0.628\,789\,21 \times 10^{-2}$
3	$0.358\,945\,97 \times 10^{-7}$	$0.434\,500\,43 \times 10^{-4}$	3	$0.113\,755\,34 \times 10^{-6}$	$0.117\,210\,61 \times 10^{-3}$
4	$0.199\,029\,60 \times 10^{-8}$		4	$0.214\,611\,91 \times 10^{-8}$	

out nodal structure in the polynomial $\pi_{im}(\eta)$ —nearly all this ambiguity has been removed: The parameter b_{im} is fixed by the second derivative of the nodeless amplitude function $g_{im}(\eta)$ at $\eta=0$, and is therefore precisely defined by analytical methods. Moreover, the switching functions obtained coincide with those arrived at by the heuristic studies. Therefore, insofar as accurate switching functions are provided by the linear approximation to $\theta_{im}(\eta)$ in Eq. (21), we have achieved our objective, although of course, the utility of such switching functions can only be shown by their effects on cross-section calculations, which we present in Refs. 19 and 20.

A (less serious) problem of uniqueness reappears if we attempt to prescribe $g_{im}(\eta)$ —and the associated switching function—exactly. The $s\sigma_g$ case provides the paradigm. An expansion like (9a) comprehends a whole class of solutions of the form

$$g_{im}(\eta) = \rho_{im}(\eta) \cosh \phi_{im}(\eta), \quad (27a)$$

where ϕ_{im} and ρ_{im} are a generalized phase and amplitude; the associated switching function depends only on the phase

$$f_{im}(\eta) = \tanh \phi_{im}(\eta). \quad (27b)$$

By imposing the constraint $\rho_{im}(\eta) \equiv 1$ in Eqs. (10) and (20), we have made a particular limiting

FIG. 3. Deviation of the phase angle $\theta_{im}(\eta)$ from linearity as indicated by $\theta_{im}(\eta=1)/b_{im}$ vs c .

choice, but of course there is no guarantee that this is the “appropriate” one. The problem could perhaps be defined mathematically as the selection of an efficient asymptotic expansion, but a rigorous investigation on such lines is beyond the scope of this work. Fortunately, for nearly all cases, this residual ambiguity has no practical importance.

FIG. 4. Significant effects of deviation from linearity in the $3d\sigma_g$ state, as shown in couplings. Radial couplings are shown for $3d\sigma_g \rightarrow 1s\sigma_g$ (a small effect) and for $3d\sigma_g \rightarrow 4d\sigma_g$ (a significant effect).

Deviation of $\theta_{lm}(\eta)$ from linearity is depicted in Fig. 3, which shows $\theta_{lm}(\eta=1)/b_{lm}$ vs c for several (l, m) . Behavior of the hyperbolic functions should be kept in mind to interpret this figure. A small deviation of θ_{lm} from linearity can be very important for an accurate description of $g_{lm}(\eta)$ in Eq. (20), but unimportant for predicting $f_{lm}(\eta)$ in Eq. (21), since $|\tanh \theta|$ rapidly approaches 1 for increasing $|\theta|$. For the $p\sigma$ state, for example, even though very large deviations of $\theta_{lm}(\eta)$ from linearity are indicated by Fig. 3, errors in the switching function $f_{10}(\eta)$ arising from the linear approximation are everywhere less than 2.5%, and effects on coupling matrix elements are similarly small. For highly excited levels, the values of c relevant for the H_2^+ collision problem are very small and the deviation of θ_{lm} from linearity is then small also. For the study of $H^+ - H$ collisions presented in Ref. 19, we found that only for the $3d\sigma_g$ state does the deviation of $\theta_{lm}(\eta)$ from linearity have a significant effect on coupling matrix elements.

F. $3d\sigma_g$ state couplings

Coupling matrix elements computed using the exact switching function and using the linear approximation to $\theta_{lm}(\eta)$ are compared, for two representative transitions from the $3d\sigma_g$ state, in Fig. 4. Use of the exact $f_{20}(\eta)$ substantially reduces the size of the coupling $3d\sigma_g \rightarrow 4d\sigma_g$ but has a smaller effect on $3d\sigma_g \rightarrow 1s\sigma_g$ coupling; also, we found that convergence of cross-section results as a function of basis size, is improved using the exact $3d\sigma_g$ switching function.

G. Switching functions of Crothers and Hughes (Ref. 16) and Ponce (Ref. 27)

Crothers and Hughes¹⁶ have computed corrected coupling matrix elements for H_2^+ by a procedure based on Bates-McCarroll-type ETF's for approximate one-center fragments (as described in the introduction to this paper). Although they criticize the idea of a switching function as somehow implying a violation of the uncertainty principle, it can be shown that their procedure is equivalent to a particular choice for the switching function, in the low-velocity limit. We shall illustrate this for the case of the pair of molecular states ($1s\sigma_g$ and $2p\sigma_u$) for H_2^+ .

For this case, Crothers and Hughes construct fragments

$$\phi_J = 2^{-1/2}(\psi_{1s\sigma_g} \pm \psi_{2p\sigma_u}); \quad (28a)$$

in the limit $R \rightarrow \infty$, ϕ_J become $1s$ atomic orbitals on nuclei B and A . To these fragments they can attach a single-center ETF,

$$\Phi_J = \phi_J \exp[\pm(im/2\hbar)\lambda(R)\hat{v} \cdot \hat{r}], \quad (28b)$$

where $\hat{v}$ is the relative nuclear velocity and $\lambda(R)$ is an adjustable parameter which may vary with R . These fragments are then recombined to form molecular-basis functions for the close-coupling treatment,

$$\chi_{1s\sigma_g, 2p\sigma_u} = 2^{-1/2}(\Phi_B \pm \Phi_A). \quad (28c)$$

Finally, $\lambda(R)$ is determined by the Euler-Lagrange variational method of Riley and Green,²⁵ and Crothers and Hughes show a graph depicting $\lambda(R)$ obtained for this pair of states.

If we expand Eq. (28c) in powers of the velocity $\hat{v}$ we find, for $\chi_{1s\sigma_g}$,

$$\begin{aligned} \chi_{1s\sigma_g} = & \psi_{1s\sigma_g} + (im/2\hbar)\lambda(R)\hat{v} \cdot \hat{r}\psi_{2p\sigma_u} \\ & + \frac{1}{2}[(im/2\hbar)\lambda(R)\hat{v} \cdot \hat{r}]^2\psi_{1s\sigma_g} + \dots, \end{aligned} \quad (29)$$

and analogously for $2p\sigma_u$. The first-order term gives rise to the lowest-order ETF corrections to nonadiabatic couplings, and higher-order terms to velocity dependence in these couplings, etc. Comparing this expansion with that obtained using a switching function explicitly,

$$\begin{aligned} \Psi_{1s\sigma_g} = & \psi_{1s\sigma_g} \exp[(im/2\hbar)\hat{v} \cdot \hat{r}\psi_{1s\sigma_g}] \\ = & \psi_{1s\sigma_g} + (im/2\hbar)\hat{v} \cdot \hat{r}\psi_{1s\sigma_g} \\ & + \frac{1}{2}[(im/2\hbar)\hat{v} \cdot \hat{r}]^2\psi_{1s\sigma_g} + \dots, \end{aligned} \quad (30)$$

the first-order terms are seen to be identical, provided

$$\tilde{f}_{1s\sigma_g} = \lambda(R)(\psi_{2p\sigma_u}/\psi_{1s\sigma_g}) \quad (31a)$$

and similarly

$$\tilde{f}_{2p\sigma_u} = \lambda(R)(\psi_{1s\sigma_g}/\psi_{2p\sigma_u}). \quad (31b)$$

We may compare $\tilde{f}_{1s\sigma_g}$ with the analytical switching functions we have derived for the $1s\sigma_g$ state. The exact wave functions are separable into radial and angular factors, so

$$\tilde{f}_{1s\sigma_g} = \lambda(R)[S_{2p\sigma_u}(\eta)/S_{1s\sigma_g}(\eta)][F_{2p\sigma_u}(\xi)/F_{1s\sigma_g}(\xi)] \quad (32)$$

[$F_\mu(\xi)$ are the radial functions]. The radial factor in (32) varies from ~ 0.75 to ~ 1.3 for ξ values where F_μ have appreciable amplitude; for purposes of comparison we have simply replaced this factor by an average value of 1.0. The comparison of the remaining factors with our analytically derived $f_{1s\sigma_g}(\eta)$ is shown in Fig. 5 for $R = 12.0, 4.0$, and 2.0 a.u. The agreement is remarkable, especially when the differences in method used are considered.

For the $2p\sigma_u$ state, Eq. (31b) shows that the Crothers-Hughes switching function has a singularity at $\eta = 0$. It belongs to the class of switching functions we considered, but discarded, for the $2p\sigma_u$ state [Eq. (14a)]. Crothers and Hughes found that $\lambda(R)$ as determined by the Euler-Lagrange

FIG. 5. Comparison of $1s\sigma_g$ switching functions for H_2^+ at $R=12.0$, 4.0 , and 2.0 a.u. Solid curves, analytically derived results; open circles, effective switching functions of Crothers and Hughes. Also shown for comparison is an analogous function derived by Ponce (Ref. 27).

scheme decreases sharply to zero as $R \rightarrow 0$; such behavior is necessary to avoid the singular couplings arising from forms like (14a) and (31b) as $R \rightarrow 0$. The coupling matrix elements computed by Crothers and Hughes for $2p\sigma_u$ and $2p\pi_u$ states are generally somewhat different from ours (see Ref. 19).

We may also compare our switching functions with some results obtained by Ponce²⁷ using a

type of switching function determined by the Euler-Lagrange scheme. Since he uses Cartesian coordinates for the electron, his velocity-field distributions are not strictly comparable with our switching functions, but a general similarity is observed between his function $g_s(z, R)$ and our $f(\eta)$ on the internuclear line, where $\eta = 2z/R$ (for $\eta \leq 1$), and $2g_s$ is to be compared with f . Ponce's values for $1s\sigma_g$ at $R=2.0$ and 4.0 a.u. are depicted in Fig. 5, showing that they generally do not agree closely with ours and those of Crothers and Hughes. On the other hand, for the $2p\sigma_u$ state Ponce's function agrees at least qualitatively with ours, since it generally resembles the form (14b), even though the quantitative discrepancies are similar to those shown for the $1s\sigma_g$ case. (In view of the approximate nature of Ponce's derivation and his use of Cartesian coordinates, we do not agree with his conclusion that the switching function should properly exceed a magnitude of unity; a comparison of variationally derived forms using spheroidal coordinates would be of much more significance.)

III. ASYMMETRIC CASE

These ideas may be extended in an approximate way to an asymmetric system such as HeH^{2+} . As for the symmetric case, the nodal structure associated with orbital angular momentum is first removed, by writing $S_{lm}(\eta)$ in the form

$$S_{lm}(\eta) = (1 - \eta^2)^{|m|/2} \Pi_{lm}(\eta) g_{lm}(\eta), \quad (33)$$

FIG. 6. Parameters β_{lm} vs R for three states of HeH^{2+} ; data points show optimized values for comparison.

FIG. 7. Parameters η_0^{lm} vs R for three states of HeH^{2+} ; data points show optimized values for comparison. Note behavior $\eta_0 \sim R^{-1}$ as $R \rightarrow 0$, as is appropriate if system translates with center of charge in the united-atom limit.

where $\pi_{lm}(\eta)$ is a polynomial of order $(l-m)$ which reduces to the appropriate Legendre polynomial as $R \rightarrow 0$, and $g_{lm}(\eta)$ is a nodeless amplitude function, which we wish to represent in a suitable two-center decomposition. However, in this case the eigenvalues and eigenfunctions depend on two parameters (c^2, p), and $g_{lm}(\eta)$ is no longer symmetric about $\eta=0$; a corresponding variety of plausible forms for $g_{lm}(\eta)$ may be suggested.

One scheme that appears to work fairly well for the more genuinely "molecular" states is again based on the zero-order form

$$g_{lm}^{(0)} = C_0 \cosh b(\eta - \eta_0)$$

which leads to the switching function form used by Rankin and Thorson¹¹ [i.e., Eq. (1)]. An exact solution may be written as

$$g_{lm}(\eta) = C_0 \cosh \theta_{lm}(\eta - \eta_0), \quad (34a)$$

where η_0 is such that $g'_{lm}(\eta_0) = 0$; θ_{lm} may be expanded to

$$\theta_{lm} = b_{lm}(\eta - \eta_0) + c_2(\eta - \eta_0)^2 + \dots \quad (34b)$$

and

$$b_{lm}^2 = g''_{lm}(\eta_0) / g_{lm}(\eta_0). \quad (34c)$$

The corresponding switching function would then be

$$f_{lm}(\eta) = \tanh \theta_{lm}(\eta - \eta_0), \quad (35)$$

and in many cases it is well approximated by taking only the linear term in Eq. (34b). For those cases in which g_{lm} exhibits a minimum in the range $-1 \lesssim \eta_0 \lesssim +1$, we find there is reasonably good agreement of the parameters $\beta_{lm} = (b_{lm}/R)$ and η_0^{lm} , with those found in optimization studies (including both continuum and discrete-state couplings from the bound state in question). An indication of this agreement is shown in Figs. 6 and 7. States with genuinely two-center character are those for which η_0 lies between -1 and $+1$, and in these cases it appears that an analysis on the above lines is at least qualitatively correct. On the other hand, states for which $g_{lm}(\eta)$ has no minimum between the two nuclei (e.g., $ns\sigma$, $np\pi$, etc.) appear to be almost entirely "He⁺ atomic states" in character, and for these cases we find poor agreement between the parameters obtained using this analysis and those found by the optimization of couplings. Fortunately, for these states the switching functions are very close to the simple Bates-McCarroll value of -1 , and neither coupling matrix elements nor the calculated collision cross sections²⁰ are significantly affected by these discrepancies.

It can be shown that in the united atom limit $R \rightarrow 0$ the bound electron should translate with the center of charge, rather than the geometric center, of the system³⁵; for HeH^{2+} we should then expect a limiting mean value of $-\frac{1}{3}$ for $f_{lm}(\eta)$. From the form given in Eq. (1), one might expect a limiting value of zero, but, as shown in Fig. 7, we find that η_0 (as determined either by the above analysis or by the optimization scheme) increases very rapidly for small R ; if $\eta_0 \sim R^{-1}$ as $R \rightarrow 0$, a nonzero expectation value for $f_{lm}(\eta)$ will result.

For the more tightly bound states in HeH^{2+} ($1s\sigma$, $2s\sigma$, $2p\sigma$, $2p\pi$) we find that even at the smallest internuclear distance we considered ($R = 0.5$ a.u.), the limiting behavior is not yet observed, since the atomic orbitals involved do not fully overlap both nuclei. For more diffuse states (e.g., $3d\sigma$, $3d\pi$, etc.), however, we find that the expectation values of $f_{lm}(\eta)$ over these states appear to be changing in a manner consistent with this prediction; for example, $\langle f_{3d\sigma} \rangle$ is decreasing from its limiting atomic He⁺ value of -1 at $R \rightarrow \infty$, to a value of ~ -0.7 at $R = 0.5$ a.u., and most of this decrease occurs at smaller R values.

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