Discrete-basis-set method for electron-molecule continuum wave functions

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We present a method for calculating the continuum wave function in electron-molecule scattering for an $N \times N$ discrete-basis-set representation of the potential. The method is based on the T-matrix method introduced by Rescigno, McCurdy, and McKoy. In this work, the wave function is used in a prescription for the variationally corrected partial-wave K matrix analogous to Kohn's variational formula for the scattering amplitude in three dimensions. Results presented for e^--H_2 scattering in the static-exchange approximation are in good agreement with other accurate calculations.

I. INTRODUCTION

There is currently a need for the development of accurate *ab initio* methods for electron-molecule scattering calculations. Discrete-basis-set methods are of particular interest due to the success of these methods in molecular-bound-state calculations and in spherical potential scattering calculations. Unfortunately, the standard variational methods for scattering introduced by Hulthén,[1] Kohn,[2] and Rubinow[3] are not readily applied to nonspherical potential scattering. Recently, several new basis-set methods have been introduced which avoid the technical difficulties encountered in the standard methods. Accurate results for elastic electron-molecule scattering have been obtained by Schneider and co-workers[4,5] by applying the R-matrix method introduced by Wigner and Eisenbud.[6] In this approach, configuration space is divided into two regions and a set of square-integrable basis functions is used to describe the scattering wave function in the inner region. Another approach is to represent the potential by its projection onto a subspace of square-integrable functions,

$$U^t = \sum_{\alpha,\beta=1}^{N} |\alpha\rangle \langle \alpha|U|\beta\rangle \langle \beta|, \tag{1}$$

and solve the scattering problem exactly for U^t. This is the approach used in the J-matrix method of Heller and Yamani[7] and in the T-matrix method for electron-molecule scattering introduced by Rescigno, McCurdy, and McKoy.[8]

In the T-matrix method, the scattering problem is expressed by the Lippmann-Schwinger equation for the transition matrix,

$$T = U + UG_0T. \tag{2}$$

In actual calculations it is more convenient to work with the K matrix, which is obtained by using the principal value free-particle Green's function G_0^P in Eq. (2). Inserting the separable potential

U^t into Eq. (2) then leads to a finite matrix equation,

$$\langle \alpha|K|\beta\rangle = \langle \alpha|U|\beta\rangle + \sum_{\gamma,\delta=1}^{N} \langle \alpha|U|\gamma\rangle \langle \gamma|G_0^P|\delta\rangle \langle \delta|K|\beta\rangle, \tag{3}$$

which has the solution

$$K^t = (1 - U^t G_0^P)^{-1} U^t. \tag{4}$$

The on-shell partial-wave K matrix is obtained by the transformation

$$\langle klm|K|kl'm'\rangle = -k \sum_{\alpha\beta}\langle kl\,m\,|\alpha\rangle \langle \alpha|K|\beta\rangle \langle \beta|kl'm'\rangle. \tag{5}$$

As discussed previously,[8] the truncated potential U^t can be constructed for a multicenter Gaussian basis set using standard molecular-bound-state computer codes. Equation (3) involves Gaussian matrix elements of the free-particle Green's function. As shown by Ostlund[9] and by Levin *et al*,,[10] these matrix elements can be reduced to expressions involving the complex error function for which efficient algorithms exist.[11] The Bessel-Gaussian overlap-matrix elements occurring in Eq. (5) can also be reduced analytically to closed-form expressions.[12] Thus all the matrix elements needed to compute the partial-wave K matrix for the truncated multicenter potential U^t can be obtained without numerical quadrature, even for polyatomic targets.

By solving Eq. (3), one obtains scattering information without calculating the scattering wave function for the associated Schrödinger equation (in a.u.)

$$(-\nabla^2 + U^t - k^2)\psi_{\vec{k}} = 0. \tag{6}$$

However, it is often desirable to have a representation of the wave function itself. An important application is the correction of $\langle klm|K|kl'm'\rangle^t$ through first order for errors due to the difference $U - U^t$. This involves the following variational

formula:

$$\langle klm|K|kl'm'\rangle^s = \langle klm|K|kl'm'\rangle^t$$

$$+ k\langle \psi^t_{klm}|(U - U^t)|\psi^t_{kl'm'}\rangle . \qquad (7)$$

Equation (7) for the variationally stable partial-wave K matrix is analogous to Kohn's formula for the scattering amplitude in three dimensions.[2] A representation of the wave function is also of interest for the calculation of distorted-wave-approximation matrix elements, which occur in electronic excitation by electron impact and other electron-molecule continuum processes.

In this paper we present an efficient technique for generating the scattering wave function ψ^t_{klm} from the solution of Eq. (3). The method involves the numerical solution of a set of *uncoupled* inhomogeneous, one-dimensional ordinary differential equations, and does not require a single-center expansion of the potential. To show the utility of the method, variationally stable K-matrix elements are presented for e^--H_2 scattering in the static-exchange approximation. These results include Σ_g-symmetry K-matrix elements for incident momenta from 0.1 to 1.0 a.u. Examples of Σ_u and Π_u symmetry results are also given. These results are in good agreement with the results of other accurate calculations.[4,13]

II. THEORY

In the fixed-nuclei approximation the Schrödinger equation for an elastically scattered electron is of the form

$$[-\nabla^2 + U(R, \vec{r}) - k^2]\psi_{\vec{k}}(\vec{r}) = 0 , \qquad (8)$$

where $U(R, \vec{r})$ is an optical potential for the effective interaction between the target and the scattered electron. The potential depends parametrically on the relative coordinates of the target nuclei, denoted by R. The vector subscript $\vec{k}$ indicates the dependence of the wave function on the direction as well as the magnitude of the incident momentum. Except as noted, atomic units are assumed throughout. Imposing the standing-wave boundary condition leads to the asymptotic form

$$\psi_{\vec{k}}(\vec{r}) \to \frac{1}{(2\pi)^{3/2}}\left(e^{i\vec{k}\cdot\vec{r}} - 2\pi^2\langle\vec{k}'|K|\vec{k}\rangle\frac{\cos kr}{r} \right) \qquad (9)$$

as $r \to \infty$, where $\vec{k}' = k\hat{r}$ and we have chosen the normalization

$$\langle\psi_{\vec{k}}|\psi_{\vec{k}'}\rangle = \delta(\vec{k} - \vec{k}') . \qquad (10)$$

The incident-direction dependence of the scattering wave function may be expanded in the partial-wave series

$$\psi_{\vec{k}}(\vec{r}) = \left(\frac{2}{\pi}\right)^{1/2}\sum_{lm} i^l \psi_{klm}(\vec{r}) Y^*_{lm}(\hat{k}) . \qquad (11)$$

The function $\psi_{klm}(\vec{r})$ is the scattering wave function when a particular incident partial wave is specified. For a linear target molecule with internuclear axis along the z axis, $\psi_{klm}(\vec{r})$ may in turn be expanded in the partial-wave series

$$\psi_{klm}(\vec{r}) = \sum_{l'} g_{ll'm}(k, r) Y_{l'm}(\hat{r}) . \qquad (12)$$

Equation (12) defines a set of radial continuum functions with the asymptotic form

$$g_{ll'm}(k, r) \to j_{l'}(kr)\delta_{ll'} - y_{l'}(kr)\langle kl'm|K|klm\rangle \qquad (13)$$

as $r \to \infty$, where $j_l(kr), y_l(kr)$ are the regular and irregular spherical Bessel functions. The partial-wave K matrix is related to the plane-wave-representation K matrix according to

$$\langle\vec{k}'|K|\vec{k}\rangle = -\frac{1}{k}\sum_{ll'mm'} i^{l-l'}\langle kl'm'|K|klm\rangle$$

$$\times Y_{l'm'}(\hat{k}')Y^*_{lm}(\hat{k}) , \qquad (14)$$

where the set $|\vec{k}\rangle$ denotes the normalized plane-wave state

$$\phi_{\vec{k}} = \frac{1}{(2\pi)^{3/2}}e^{i\vec{k}\cdot\vec{r}} . $$

If the exact potential is replaced by the truncated potential U^t, the scattering wave function satisfies Eq. (6) and, equivalently, the Lippmann-Schwinger equation for the wave function,

$$\psi^t_{klm} = \phi_{klm} + G^P_0(k)U^t\psi^t_{klm} , \qquad (15)$$

where $\phi_{klm} \equiv j_l(kr)Y_{lm}(\hat{r})$. Substituting the identity

$$K^t\phi_{klm} = U^t\psi^t_{klm} \qquad (16)$$

into Eq. (15) yields an expression for ψ^t_{klm} in terms of the solution of Eq. (3):

$$\psi^t_{klm} = \phi_{klm} + G^P_0(k)K^t\phi_{klm} . \qquad (17)$$

Substituting the partial-wave expansion of the principal-value free-particle Green's function

$$G^P_0(k; \vec{r}, \vec{r}') = \sum_{lm} kj_l(kr_<)y_l(kr_>)Y_{lm}(\hat{r})Y^*_{lm}(\hat{r}') \qquad (18)$$

into Eq. (17) leads to the asymptotic form

$$\psi^t_{klm}(\vec{r}) \to \sum_{l'} [j_{l'}(kr)\delta_{l'l}$$

$$- y_{l'}(kr)\langle kl'm|K|klm\rangle^t] Y_{l'm}(\hat{r}) \qquad (19)$$

as $r \to \infty$. Comparison of Eqs. (12), (13), and (19) shows that ψ^t_{klm} satisfies the same asymptotic boundary condition as the exact scattering function except for the replacement of $\langle kl'm|K|klm\rangle$

by $\langle k l'm | K | k l m \rangle^t$.

To calculate a numerical representation of ψ^t_{klm}, Eq. (16) is substituted into Eq. (6) yielding the inhomogeneous equation

$$(-\nabla^2 - k^2)\psi^t_{klm} = K^t \phi_{klm} . \qquad (20)$$

Substituting the single-center expansion

$$\psi^t_{klm} = \sum_{l'} g^t_{ll'm}(k,r) Y_{l'm}(\hat{r}) \qquad (21)$$

into Eq. (20), multiplying on the left by $Y^*_{l'm}(\hat{r})$, and integrating with respect to $\hat{r}$ leads to a set of *uncoupled* ordinary differential equations,

$$\left(-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} - k^2\right) r g^t_{ll'm}(k,r)$$

$$= r \langle Y_{l'm} | K^t | klm \rangle , \qquad (22)$$

where

$$\langle Y_{l'm} | K^t | klm \rangle = \sum_{\alpha\beta} \langle Y_{l'm} | \alpha \rangle \langle \alpha | K | \beta \rangle \langle \beta | j_l Y_{lm} \rangle . \qquad (23)$$

A prescription for obtaining a numerical solution of Eq. (22) subject to the boundary conditions

$$\lim_{r \to 0} r g^t_{ll'm}(k,r) = 0 , \qquad (24a)$$

and

$$g^t_{ll'm}(k,r) \to j_{l'}(kr)\delta_{ll'} - y_{l'}(kr)\langle k l'm | K | klm \rangle^t \qquad (24b)$$

as $r \to \infty$, is given in the Appendix. As discussed previously,[12,14] the matrix elements $\langle Y_{lm} | \alpha \rangle$ and $\langle \alpha | j_l Y_{lm} \rangle$ can be evaluated analytically for arbitrary Guassians.

This technique for calculating electron-molecule continuum functions involves considerably less computational effort than direct numerical integration of the Schrödinger equation [Eq. (8)] for the exact potential U, particularly when exchange is included. Moreover, it avoids the severe convergence problem which occurs when the dynamical solution is obtained via a single-center expansion of U. In the T-matrix method the dynamical solution is obtained in terms of multicenter Gaussian functions. The price for computational simplicity relative to an exact numerical solution of the Schrödinger equation is the lack of point-by-point variational stability in the functions $g^t_{ll'm}(k,r)$. However, the function $g^t_{ll'm}$ and the K-matrix element $\langle klm | K | kl'm \rangle^t$ should converge uniformly to the exact results as the basis set is increased. One does not expect to find pseudoresonances in the behavior of the approximate K-matrix elements $\langle klm | K | kl'm \rangle^t$ of the type which occur in the standard variational methods for scattering of Hulthén, Kohn, and

Rubinow.[15] This feature of our approach is discussed by Heller and Yamani[7] in the context of the J-matrix method. For an extensive discussion of algebraic variational methods, see Truhlar *et al.*[16]

To verify the variational formula [Eq. (7)] for the partial-wave K matrix we follow Mott and Massey[17] and define the functional

$$I = \int \psi_2 L \psi_1 \, d\tau , \qquad (25)$$

where $\psi_1 = \psi_{kl_1m}$, $\psi_2 = \psi^*_{kl_2m}$, $L = \nabla^2 + k^2 - U$, and ψ_1, ψ_2 are solutions of Eq. (8) subject to the boundary condition given in Eqs. (12) and (13). Consider the variation of I due to variations in ψ_1 and ψ_2 which preserve their asymptotic form, i.e.,

$$\delta\psi_1 \to \sum_{l'} - \delta\langle k l'm | K | kl_1m \rangle y_{l'} Y_{l'm} \qquad (26)$$

as $r \to \infty$. Since $L\psi_1 = L\psi_2 = 0$, we have

$$\delta I = \int [\psi_2 \nabla^2(\delta\psi_1) - \delta\psi_1 \nabla^2 \psi_2] \, d\tau \qquad (27)$$

through first order in $\delta\psi$. Using Green's theorem gives

$$\delta I = \int_S \left(\psi_2 \frac{\partial}{\partial r}(\delta\psi_1) - \delta\psi_1 \frac{\partial}{\partial r}(\psi_2) \right) dS , \qquad (28)$$

where S is the surface of a sphere centered at the origin and of such large radius that ψ_1 and ψ_2 have taken up their asymptotic forms. Using the asymptotic forms of the Bessel functions

$$j_l(kr) \to \sin(kr - \tfrac{1}{2}l\pi)/kr , \qquad (29a)$$

$$y_l(kr) \to -\cos(kr - \tfrac{1}{2}l\pi)/kr \qquad (29b)$$

as $r \to \infty$, we substitute the asymptotic forms of $\delta\psi_1$ and ψ_2 into Eq. (28). Then we integrate over angles and, neglecting terms of order $1/r$, we obtain

$$\delta I = -(1/k)\delta\langle kl_2m | K | kl_1m \rangle . \qquad (30)$$

Since I vanishes if ψ_1 is an exact solution of Eq. (8) and

$$\delta\langle kl_2m | K | kl_1m \rangle \equiv \langle kl_2m | K | kl_1m \rangle^t - \langle kl_2m | K | kl_1m \rangle , \qquad (31)$$

it follows that the variationally corrected K matrix is given by

$$\langle kl_2m | K | kl_1m \rangle^s = \langle kl_2m | K | kl_1m \rangle^t + kI . \qquad (32)$$

The distorted-wave-approximation form of Eq. (32) given in Eq. (7) follows from the exact treatment of the free-particle Hamiltonian in Eq. (6).[18]

For a closed-shell diatomic molecule the static-

exchange potential is of the form

$$U = -\frac{2Z}{|\vec{r} - \vec{A}|} - \frac{2Z}{|\vec{r} + \vec{A}|} + 2 \sum_{\sigma=1}^{N} (2J_\sigma - K_\sigma), \quad (33)$$

where the Coulomb operator

$$J_\sigma(\vec{r}) = \int d^3r' \frac{\phi_\sigma^*(\vec{r}')\phi_\sigma(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (34)$$

and K_σ is the corresponding exchange operator. The nuclear charge is denoted by Z, the nuclear centers are located at $\pm\vec{A}$, and N is the number of occupied orbitals ϕ_σ. Equation (7) involves the matrix elements $\langle \psi_{klm}^t | U | \psi_{kl'm}^t \rangle$ and $\langle \psi_{klm}^t | U^t | \psi_{kl'm}^t \rangle$. The latter is given by

$$\langle \psi_{klm}^t | U^t | \psi_{kl'm}^t \rangle = \langle klm | (K^t G_0^P + 1) U^t (1 + G_0^P K^t) | kl'm \rangle \quad (35)$$

and involves only components of K, G_0^P, and U within the subspace $\{|\alpha\rangle\}$. To evaluate the matrix element

$$\langle \psi_{klm}^t | U | \psi_{kl'm}^t \rangle = \sum_{pq} \langle g_{lpm}^t Y_{pm} | (U^{(s)} - U^{(ex)}) | \times g_{l'qm}^t Y_{qm} \rangle, \quad (36)$$

we use the single-center expansion method formulated by Faisal[19] for the static potential $U^{(s)}$, and by Burke and Sinfailam[20] for the exchange part $U^{(ex)}$. Expressions for the matrix elements $\langle g_{lpm}^t Y_{pm} | U^{(i)} | g_{l'qm}^t Y_{qm} \rangle$, $U^{(i)} = U^{(s)}, U^{(ex)}$ are given in Ref. 14. These expressions involve a multipole expansion of the static potential

$$U^{(s)} = 2 \sum_\lambda V_\lambda P_\lambda(\hat{r}), \quad (37)$$

where P_λ is a Legendre polynomial, and a single-center expansion of each occupied orbital:

$$\phi_\sigma(\vec{r}) = \sum_s \phi_{sm\sigma}(r) Y_{sm\sigma}(\hat{r}). \quad (38)$$

In this work we use Cartesian Gaussian functions of the form

$$\mu_{pqs}^{\alpha\vec{A}}(\vec{r}) = N_{pqs}(x - A_x)^p (y - A_y)^q (z - A_z)^s e^{-\alpha|\vec{r} - \vec{A}|^2} \quad (39)$$

where N_{pqs} is a normalization coefficient.

III. CALCULATIONS AND RESULTS

To determine the state-exchange potential for H_2, we carried out a self-consistent-field (SCF) calculation for the σ_g occupied orbital at an internuclear separation of 1.4006 a.u. The SCF basis consists of a $(10s5p_z)$ set of primitive Gaussians on each nucleus contracted to $[7s5p_z]$. The Huzinaga[21] exponents and contraction coefficients for this basis are given in Ref. 14. The quadru-

pole moment of the H_2 ground state in this basis is 0.478 a.u.

For a closed-shell homonuclear diatomic, the static-exchange potential is diagonal in m_l, the projection of the scattered-electron orbital angular momentum along the internuclear axis, and the inversion symmetry of the scattering wave function. The truncated potential U^t is constructed for each irreducible symmetry by projecting the exact static-exchange potential, defined in Eq. (33), onto a subspace of Gaussian functions. These functions approximate the Hilbert space of the scattering potential. When the scattering symmetry is the same as the symmetry of an occupied orbital, the scattering basis includes the primitive basis used to represent the occupied orbital. The scattering subspace also includes basis functions not normally used in bound-state calculations such as very diffuse functions. A discussion of scattering basis sets is given in the recent R-matrix calculation by Morrison and Schneider.[5] The scattering basis sets used in this work are listed in Table I.

Our prescription for the matrix element $\langle \psi_{klm}^t | U | \psi_{kl'm}^t \rangle$ involves single-center expansions for the σ_g occupied orbital, Eq. (38), and the static potential, Eq. (37). In this calculation we obtained adequate convergence by including $l = 0, 2, \ldots, 10$ in Eq. (38) and $\lambda = 0, 2, \ldots, 10$ in Eq. (37). Similarly, we included six partial waves in the expansion of the scattering wave function: $l' = 0, 2, \ldots, 10$ for the Σ_g symmetry and $l' = 1, 3, \ldots, 11$ for the Σ_u and Π_u symmetries. The one- and two-dimensional radial integrals occurring in the expansions for $\langle \psi_{klm}^t | U | \psi_{kl'm}^t \rangle$ are evaluated by Simpson's-rule quadrature. The expansions are converged to three significant figures.

Our results for zero order and variationally corrected K-matrix elements are shown in Table II. The agreement between corrected and uncorrected s-wave ($l = l' = 0$) matrix elements is good but some of the higher partial-wave matrix elements differ by more than a factor of 2 at low incident momenta. The Σ_g-symmetry K-matrix results in Table II were obtained using basis set A, Table I; the Σ_u and Π_u results were obtained using basis sets B and C, Table I, respectively. Table III compares variationally corrected and uncorrected results of this calculation with previously obtained[14] approximately corrected and uncorrected results. The present results were calculated using basis set B, Table I. The basis set used to obtain the results from Ref. 14 is similar to set B so that most of the difference between the present corrected results and the corrected results from Ref. 14 is attributable to the neglect

TABLE I. Scattering basis sets. $\vec{A}$ denotes the coordinates of the centers and (p, q, s) the symmetry type of the basis function $\mu_{pqs}^{\alpha \vec{A}}$.

A. $\vec{A}=(0, 0, \pm 0.7003)$ $(p, q, s)=(0, 0, 0)$	$(0, 0, \pm 0.7003)$ $(0, 0, 1)$	$(0, 0, 0)$ $(0, 0, 0)$	$(0, 0, 0)$ $(0, 0, 2)$
1685.517	4.8	1.0	1.0
249.958 4	2.53	0.5	0.5
55.658 34	1.33	0.25	0.25
15.274 3	0.701	0.15	0.15
4.862 28	0.369	0.09	0.09
1.731 6		0.054	0.054
0.668 05		0.03	0.03
0.274 37		0.02	0.02
0.116 98		0.01	0.01
0.041 133		0.005	
		0.002	
		0.0006	

B. $\vec{A}=(0, 0, \pm 0.7003)$ $(p, q, s)=(0, 0, 0)$	$(0, 0, \pm 0.7003)$ $(0, 0, 1)$	C. $\vec{A}=(0, 0, \pm 0.7003)$ $(p, q, s)=(1, 0, 0)$
1685.517	4.8	15.274 3
249.958 4	2.53	4.862 8
55.658 34	1.33	1.731 6
15.274 3	0.701	0.668 05
4.862 28	0.369	0.274 37
1.731 6	0.2	0.116 98
0.668 05	0.1	0.041 133
0.274 37		0.027
0.116 98		0.016 9
0.041 133		0.010 6
0.018		0.006 63
0.008 3		0.004 14
0.003 8		0.002 58
0.001 7		0.001 61
0.000 8		0.001 01

TABLE II. K-matrix results. [a,b]

k (a.u.)	K_{000}^{t}	K_{000}^{s}	K_{020}^{t}	K_{020}^{s}	K_{220}^{t}	K_{220}^{s}
0.1	−0.2165	−0.2160	3.30(−3)	4.44(−3)	1.67(−2)	8.1 (−4)
0.2	−0.4391	−0.4537	4.30(−3)	7.64(−3)	2.04(−2)	4.15(−3)
0.3	−0.7146	−0.7207	1.14(−2)	1.02(−2)	2.54(−2)	6.27(−3)
0.4	−1.063	−1.066	1.42(−2)	1.31(−2)	1.14(−2)	1.14(−2)
0.5	−1.522	−1.549	9.23(−3)	1.52(−2)	3.67(−2)	1.67(−2)
0.6	−2.290	−2.313	1.31(−2)	1.46(−2)	2.71(−2)	2.65(−2)
0.7	−3.765	−3.824	1.07(−2)	8.37(−3)	5.85(−2)	3.78(−2)
1.0	8.26	8.13	0.142	0.116	0.103	9.27(−2)

	K_{110}^{t}	K_{110}^{s}	K_{111}^{t}	K_{111}^{s}
0.6	0.652	0.589	0.164	0.162

[a] Σ_g-symmetry results are for basis set A, Table I; $p\sigma$ and $p\pi$ results are for basis sets B and C, Table I, respectively.
[b] $K_{ll'm} \equiv \langle klm|K|kl'm\rangle$.

TABLE III. K-matrix results.

k	This calculation[a]		Ref. 14[b]	
	K_{000}^t	K_{000}^s	K_{000}^t	K_{000}^s
0.5	−1.433	−1.555	−1.540	−1.512
0.7	−3.803	−3.823	−3.531	−3.646
	K_{020}^t	K_{020}^s	K_{020}^t	K_{020}^s
0.5	1.95(−2)	1.55(−2)	2.32(−2)	1.36(−2)
0.7	1.30(−2)	8.29(−3)	9.59(−3)	6.77(−3)
	K_{220}^t	K_{220}^s	K_{220}^t	K_{220}^s
0.5	5.98(−2)	1.50(−2)	6.02(−2)	1.54(−2)
0.7	4.60(−2)	3.83(−2)	4.64(−2)	3.83(−2)

[a] Basis set B, Table I.
[b] Basis set C, Table II.

of the matrix element $\langle klm|K^t G_0^P(U - U^t)G_0^P K^t|kl'm\rangle$ in the latter. The accuracy of the corrected results depends on the agreement between the uncorrected and corrected matrix elements. The best agreement and hence most accurate results are obtained for diagonal s-wave matrix elements. We estimate that the s-wave results are accurate to 0.1%, and that the other results given in Table II are accurate to 5%.

Table IV compares our "s" and "$d\sigma$" variationally corrected eigenphase results with R-matrix static-exchange eigenphases calculated by Schneider[4] and with the static-exchange diagonal phase shifts of Tully and Berry.[13] The off-diagonal K-matrix elements for the cases considered here are small enough that our eigenphases are essentially equal to our diagonal phase shifts. Our s

TABLE IV. Eigenphase results.

k	Calc.	s	$d\sigma$
0.1	FM[a]	2.929	9.0 (−4)
	S[b]	2.931	
	TB[c]	2.939	
0.2	FM	2.716	4.28(−3)
	S	2.721	
	TB	2.737	
0.3	FM	2.517	6.41(−3)
	S	2.513	2.2 (−3)
	TB	2.541	3 (−3)
0.4	FM	2.324	1.16(−2)
	S	2.312	5.7 (−3)
	TB	2.352	7 (−3)
0.5	FM	2.144	1.68(−2)
	S	2.122	1.01(−2)
	TB	2.174	1.2 (−2)
0.6	FM	1.949	1.83(−2)
	S	1.949	1.83(−2)
	TB	2.006	2.0 (−2)
0.7	FM	1.827	3.78(−2)
	S	1.797	3.33(−2)
1.0	FM	1.45	9.10(−2)
	S	1.418	7.29(−2)

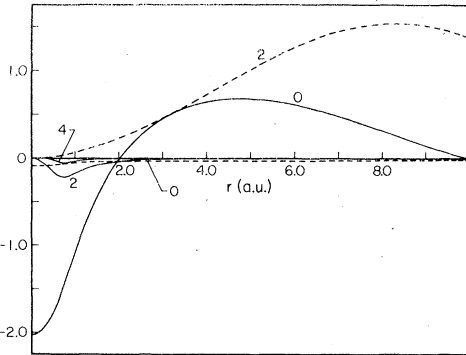| k	Calc.	$p\sigma$	$p\pi$
0.6	FM	0.532	0.161
	S	0.561	0.1628
	TB	0.537	0.162

[a] This work.
[b] Schneider, Ref. 4.
[c] Tully and Berry, Ref. 13.

FIG. 1. Solid lines: radial components $g_{0l'0}^t$, $l' = 0$, 2, 4 of s wave function for $k = 0.4$ and basis set A, Table I; dashed lines: radial components $g_{2l'0}^t$, $l = 0$, 2 components of $d\sigma$ wave function for $k = 0.4$ and basis set A multiplied by 5.

eigenphases agree very well with the other calculations. The agreement of our $d\sigma$ eigenphases with the other results is not as good, but the agreement improves as k increases and the $d\sigma$ eigenphases become larger. The differences in the calculated results may be due to the use of slightly different target wave functions in the calculations. However, we expect that our SCF result for the H_2 σ_g occupied orbital is close to the Hartree-Fock limit.

Figure 1 shows the first three components $g_{0l'0}^t$, $l' = 0, 2, 4$ of the s-wave scattering function ψ_{k00}^t at incident momentum $k = 0.4$ calculated using basis set A, Table I. The components g_{200}^t and g_{220}^t of the $d\sigma$ wave function ψ_{k20}^t at $k = 0.4$ and the same basis are also shown in Fig. 1 scaled by a factor of 5. Figure 2 shows the components $g_{1l'0}^t$, $l' = 1, 3, 5$ of the $p\sigma$ wave function ψ_{k10}^t, $k = 0.6$, for basis set B, Table I, and the components g_{111}^t and g_{131}^t of the $p\pi$ wave function ψ_{k11}^t, $k = 0.6$, for basis set C.
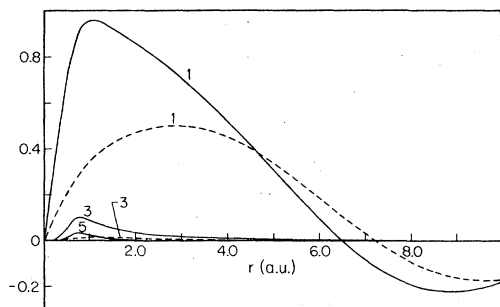
FIG. 2. Solid lines: radial components $g^t_{1l'0}$, $l'=1$, 3, 5, of $p\sigma$ wave function for $k=0.6$ and basis set B, Table I; dashed lines: radial components $g^t_{1l'1}$, $l'=1$, 3 of $p\pi$ wave function for $k=0.6$ and basis set C.

When the total scattering wave function can be expressed as a single Slater determinant, the continuum function may be chosen orthogonal to occupied orbitals of the same symmetry without introducing additional constraints. In the present approach this choice is implied by the form of the static-exchange potential given in Eq. (33) but is not otherwise imposed during the calculation. Thus the deviation from zero of the overlap-matrix element $\langle\phi_\sigma|\psi^t_{kl0}\rangle$, where ϕ_σ is the H_2 occupied orbital, is another measure of the accuracy of Σ_g continuum functions. Our results for this matrix element are given in Table V.

IV. DISCUSSION AND CONCLUSIONS

We have presented an efficient method for computing electron-molecule continuum wave functions. Two advantages of this method are (a) the nonspherical character of the scattering potential is accounted for in a natural way by means of multicenter basis functions, and (b) the important exchange effect is treated on an equal footing with the direct interaction. We have compared the s and $d\sigma$ continuum wave functions shown in

TABLE V. Orthogonality overlap matrix $\langle\phi_\sigma|\psi^t_{kl0}\rangle$ results for basis set A, Table I.

k	$l=0$	$l=2$
0.1	−2.06(−2)	−1.42(−1)
0.2	−1.55(−1)	−5.07(−2)
0.3	−3.58(−2)	6.46(−2)
0.4	−2.16(−3)	4.00(−2)
0.5	−8.24(−3)	2.11(−2)
0.6	−4.23(−2)	5.68(−2)
0.7	−1.66(−2)	7.01(−2)
1.0	−1.25(−2)	1.95(−2)

Fig. 1 and the $p\pi$ wave function shown in Fig. 2 with the tabulated results of Tully and Berry.[13] We find good agreement for diagonal components and qualitative agreement for off-diagonal components. However, our wave functions are not directly comparable with those of Tully and Berry who use a Weinbaum function[22] for the H_2 target instead of a Hartree-Fock wave function. Application of this method to the calculation of electronic excitation cross sections for H_2 in the distorted-wave approximation will be treated in a forthcoming paper.

We have demonstrated an effective method for calculating variationally stable K-matrix elements for elastic scattering. The results presented here for e^--H_2 scattering in the static-exchange approximation are in good agreement with other calculations for s-wave eigenphases. Our results for $d\sigma$-wave eigenphases appear to be more accurate than other published results. In addition, our reported results for off-diagonal K-matrix elements are of interest because they significantly affect rotational excitation cross sections.[23] The variationally corrected results presented here are more accurate than the results obtained by our recently proposed approximate variational correction method.[14] Of perhaps greater importance is that the present method is more straightforward and much less time consuming to apply.

An important physical effect not treated in this work is the polarization of the target by the scattered electron. Several calculations have shown that an approximate treatment of long-range polarization and exchange effects qualitatively accounts for many features observed in low-energy electron-molecule scattering.[24,25] Unfortunately, these calculations have led to confusion concerning the relative importance of exchange and polarization effects. Therefore, accurate static-exchange results are of interest as a preliminary toward a from-first-principles treatment of polarization. Moreover, the static-exchange approximation is itself a useful *ab initio* method which accounts, at least qualitatively, for many processes in electron-molecule scattering.

The approach to scattering described here is valid when long-range potential effects are small. This is clearly not the case for scattering from ions and strongly polar molecules. The generalization of our techniques to treat these systems is in progress.

ACKNOWLEDGMENT

APPENDIX

To apply the Numerov finite-difference method,[26] we write Eq. (23) in the form

$$\frac{d^2}{dr^2}u(r) = F(r) + G(r),\tag{A1}$$

where $u(r) = rg^t_{ll'm}(k,r)$,

$$F(r) = \frac{l'(l'+1)}{r^2} - k^2,\tag{A2}$$

and

$$G(r) = -r\langle Y_{l'm}|K^t|klm\rangle\tag{A3}$$

Let h be the constant step size of r,

$$r_h = nh, \quad n = 0, 1, 2, \ldots$$

and define $u_n = u(r_n)$, $F_n = F(r_n)$, and $G_n = G(r_n)$. Then the Numerov formula may be written in the form

$$(1 - \tfrac{1}{12}h^2 F_{n-1})u_{n-1} + (-2 - \tfrac{10}{12}F_n)u_n + (1 - \tfrac{1}{12}h^2 F_{n+1})u_{n+1}$$

$$= \tfrac{1}{12}h^2(G_{n-1} + 10G_n + G_{n+1}).\tag{A4}$$

For sufficiently large r, say, r_N, $G(r)$ vanishes and $u(r)$ is determined by Eq. (24b). From Eq. (24a), $u(r_0) = 0$; in addition, $G(r_0) = 0$. Thus we obtain a finite, tridiagonal matrix equation

$$AP = B\tag{A5}$$

for the vector P,

$$P_n = u_n, \quad n = 1, \ldots, N-1,\tag{A6}$$

where

$$A_{11} = -2 - \tfrac{10}{12}h^2 F_1,\tag{A7a}$$

$$A_{12} = 1 - \tfrac{1}{12}h^2 F_2,\tag{A7b}$$

$$B_1 = \tfrac{1}{12}h^2(10G_1 + G_2),\tag{A7c}$$

$$A_{n,n-1} = 1 - \tfrac{1}{12}h^2 F_{n-1},\tag{A7d}$$

$$A_{n,n} = -2 - \tfrac{10}{12}F_n,\tag{A7e}$$

$$A_{n,n+1} = 1 - \tfrac{1}{12}F_{n+1},\tag{A7f}$$

$$B_n = \tfrac{1}{12}h^2(G_{n-1} + 10G_n + G_{n+1})\tag{A7g}$$

for $n = 2, \ldots, N-2$; and

$$A_{N-2,N-1} = 1 - \tfrac{1}{12}h^2 F_{N-2},\tag{A7h}$$

$$A_{N-1,N-1} = -2 - \tfrac{10}{12}h^2 F_{N-1},\tag{A7i}$$

$$B_{N-1} = \tfrac{1}{12}h^2(G_{N-2} + 10G_{N-1}) - (1 - \tfrac{1}{12}h^2 F_N)u_N.\tag{A7j}$$

Equations (A7a)–(A7j) are readily generalized for multiple step sizes.

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