Collisions of electrons with polyatomic molecules: Electron-methane scattering by the complex Kohn variational method

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The complex Kohn variational method, which is an anomaly-free algebraic variational procedure, is implemented for the case of collisions of electrons with polyatomic molecules. The complex Kohn method requires only Hamiltonian matrix elements and, in this formulation, does not require any exchange matrix elements involving continuum functions. Direct matrix elements of the scattering potential(s) which involve continuum functions are evaluated by an adaptive three-dimensional quadrature scheme. The entire procedure is applied to elastic electron-methane scattering at the static-exchange level and proves to be both efficient and accurate. No Ramsauer-Townsend minimum is found at low energies, and it is concluded that this feature of the experimental cross section cannot be described theoretically without the inclusion of target polarization.

I. INTRODUCTION

Although theoretical treatments of collisions with diatomic or linear triatomic molecules have reached a level of sophistication and reliability,[1] theoretical calculations on electronic collisions with nonlinear polyatomic molecules are still at a relatively primitive stage. This is the state of affairs in spite of the fact that these systems are intrinsically more interesting than diatomics because they possess an expanded range of energy-transfer possibilities between electronic and vibrational degrees of freedom as well as more complicated electronic structure. Pioneering calculations at the static-exchange level have been performed,[2-4] but electronic close-coupling or *ab initio* treatments of target polarization for polyatomic targets are still daunting computational challenges, and results of such calculations have not yet been published. Some successful efforts have been made to attack this problem through the use of local approximations for exchange and polarization interactions.[5-9] Although those calculations may be successful at reproducing experimental elastic cross sections, their great sensitivity at low energies to the approximations used for exchange potentials makes them poor starting points for reliable treatments of electronically inelastic processes.

At the core of this dilemma is the need for an extremely efficient and reliable approach to scattering from arbitrarily nonspherical targets in the presence of nonlocal potentials. Such a technique will provide an essential tool for solving close-coupling equations and performing accurate calculations for polyatomics. In this study we present such a procedure and test it by computing elastic scattering cross sections for electron-methane scattering.

A procedure which is generally applicable to electron-polyatomic molecule scattering should not become much more complicated as the size of the molecule or the number of nuclei increases. For that reason, we have sought to avoid the expansion of the scattering wave function in spherical harmonics about a single center. Simply stretching a bond increases the number of terms in such an expansion. Furthermore, for the sake of efficiency, we have avoided approaches which require evaluating Green's function matrix elements.[10] The essential features of the method which we demonstrate in this study and its principal advantages can be summarized briefly.

(1) It is based on the complex Kohn variational principle.[11,12] This starting point provides a computationally stable approach while avoiding the computation of Green's function matrix elements. Only matrix elements of the Hamiltonian appear in the calculation.

(2) It employs a trial function which expands the scattering wave function in Gaussian basis functions in the interaction region together with the proper asymptotic form in terms of Bessel functions.[13] This choice allows appropriate flexibility near the nuclei and facilitates the use of standard target wave functions from bound-state quantum chemistry.

(3) Exchange matrix elements with respect to continuum functions (so-called free-free and bound-free matrix elements) are eliminated rigorously.[14] The only approximation involved is that nonlocal potentials, including coupling potentials between electronic channels, are approximated by separable expansions in terms of Gaussian basis functions.

(4) All direct matrix elements of the Hamiltonian [which always appear in this formulation in the combination $(H - E)$, where E denotes the total energy of the collision system] involving continuum functions are evaluated with a three-dimensional (3D) adaptive quadrature scheme. This pivotal feature of the method eliminates the need for the single-center expansion of the scattering

wave function.

In Sec. II we describe the theoretical basis of the method, and in Sec. III we discuss the evaluation of the necessary matrix elements. Calculations on electron-methane elastic scattering are described in Sec. IV, and discussed further in Sec. V together with the application of this approach to electronically inelastic collisions.

II. THEORY

A. Trial wave function and variational principle

The first step in the formulation of the method is to choose the trial scattering wave function which is to be used in the variational principle. We have chosen the trial function to have the form[13]

$$\psi_{\Gamma'}(\mathbf{r}_1, \ldots, \mathbf{r}_{N+1}) = \sum_{\Gamma} A(\chi_\Gamma(\mathbf{r}_1, \ldots, \mathbf{r}_N) F_{\Gamma\Gamma'}(\mathbf{r}_{N+1}))$$

$$+ \sum_{\mu} d_\mu^{\Gamma'} \Theta_\mu(\mathbf{r}_1, \ldots, \mathbf{r}_{N+1}) , \qquad (1)$$

where the first sum runs over open channels, denoted by the normalized functions χ_Γ. The Θ_μ are an orthonormal set of antisymmetric, square-integrable $(N+1)$-electron functions. The target functions χ_Γ may be single or multiconfiguration descriptions of the bound states of the target molecule provided by an adequate (or manageable) level of standard quantum chemistry techniques. The second sum can contain closed channel functions and will also include $(N+1)$ electron configurations which compensate for the orthogonality constraints discussed below.

The channel continuum functions $F_{\Gamma\Gamma'}$ are further expanded as

$$rF_{\Gamma\Gamma'}(\mathbf{r}) = \sum_l [f_l^\Gamma(r)\delta_{ll'}\delta_{mm'}\delta_{\Gamma\Gamma'} + T_{lm\,l'm'}^{\Gamma\,\Gamma'} g_l^\Gamma(r)] Y_{lm}(\hat{\mathbf{r}})$$

$$+ \sum_k c_k^{\Gamma\Gamma'} \varphi_k^\Gamma(\mathbf{r}) , \qquad (2)$$

where $Y_{lm}(\hat{\mathbf{r}})$ is a spherical harmonic and $\varphi_k^\Gamma(\mathbf{r})$ denotes a square-integrable basis function which is generally a linear combination of Gaussians. The continuum functions appearing in the expansion are regular and outgoing Ricatti-Bessel functions defined by

$$f_l^\Gamma(r) = h(r)j_l(k_\Gamma r)/\sqrt{k_\Gamma} = \sin(k_\Gamma r - l\pi/2)/\sqrt{k_\Gamma}$$

$$\text{as } r \to \infty , \qquad (3)$$

$$g_l^\Gamma(r) = ih(r)[j_l(k_\Gamma r) + in_l(k_\Gamma r)c(r)]/\sqrt{k_\Gamma}$$

$$= \exp[i(k_\Gamma r - l\pi/2)]/\sqrt{k_\Gamma} \text{ as } r \to \infty .$$

The functions $c(r)$ and $h(r)$ are cutoff functions; $c(r)$ is chosen to regularize n_l at $r=0$ and $h(r)$ can further exclude both the regular and irregular functions from the inner portion of the interaction region. These are chosen as

$$c(r) = (1 - e^{-\alpha r})^{(2l+1)} , \qquad (4)$$

$$h(r) = (1 - e^{-\gamma r})^n . \qquad (5)$$

Finally, the channel momenta k_Γ are defined by

$$k_\Gamma^2/2 = E - E_\Gamma , \qquad (6)$$

where E_Γ is the energy of target state χ_Γ. The T-matrix elements which we desire to compute, and which provide both differential and integral scattering information, are the coefficients $T_{lm\,l'm'}^{\Gamma\,\Gamma'}$ in the expansion in Eq. (2).

There are several important points to be made about the trial function in Eq. (1). First of all, the number of l's and m's in the sum in Eq. (2) is the number needed to provide conserved cross sections and is determined by the asymptotics. There is no attempt being made to expand the scattering wave function about a single center. In the case of methane the maximum l value required was 4 while in a typical diatomic case values as high as 10 or 12 might be necessary for scattering below 30 eV. In general the calculation will be separable in irreducible representations of the molecular point group. In each such symmetry a particular subset of the l's and m's will appear. The cutoff functions in Eqs. (4) and (5) not only regularize the Bessel functions at the origin, but partially exclude the continuum functions from the inner part of the scattering region. There, such features as nuclear cusps are represented by the square-integrable functions (sums of Gaussians) $\varphi_k^\Gamma(\mathbf{r})$.

The coefficients in these expansions, $T_{lm\,l'm'}^{\Gamma\,\Gamma'}$, $c_k^{\Gamma\Gamma'}$, and $d_\mu^{\Gamma'}$, can be determined as variational parameters in the complex Kohn variational principle.[12,13] At this point it is convenient (but not strictly necessary) to restrict the application of the variational principle to the open-channel subspace. To enforce this separation of open- and closed-channel subspaces we employ Feshbach partitioning.[15]

The correlation functions Θ_μ can be formally incorporated into an effective optical potential. If Q is defined as the operator that projects onto the subspace defined by the functions Θ_μ and P is its orthogonal complement, then we can manipulate the Schrödinger equation in a standard way to produce a modified Hamiltonian,

$$H_{\text{eff}} = H_{PP} + (H-E)_{PQ}(E-H)_{QQ}^{-1}(H-E)_{QP}$$

$$\equiv H_{PP} + V_{\text{opt}} . \qquad (7)$$

The terms Θ_μ no longer appear in $\Psi_{\Gamma'}$, and the coefficients $d_\mu^{\Gamma'}$ need not be computed.

The remaining coefficients $T_{lm\,l'm'}^{\Gamma\,\Gamma'}$ and $c_k^{\Gamma\Gamma'}$ in the trial function $\psi_{\Gamma'}$ can be treated as variational parameters whose values are to be determined from a stationary principle. The Kohn principle can be used to characterize the T matrix as the stationary value of the functional,

$$[T^{\Gamma\Gamma'}] = T^{\Gamma\Gamma'} - 2\int \Psi_\Gamma (H_{\text{eff}} - E)\Psi_{\Gamma'} . \qquad (8)$$

The result of the variation is

$$[T] = -2(M_{00} - M_{q0}M_{qq}^{-1}M_{q0}) \qquad (9)$$

where the elements of M_{00} are defined as

$$(M_{00})_{lm\,l'm'}^{\Gamma\,\Gamma'} = \int A(\chi_\Gamma f_l^\Gamma Y_{lm})(H_{\text{eff}} - E)A(\chi_{\Gamma'} f_{l'}^{\Gamma'} Y_{l'm'})$$

$$\qquad (10)$$

and $\underline{M}_{q0}$ and $\underline{M}_{qq}$ are similarly defined as matrix elements

of $(H_{\text{eff}} - E)$ with q referring to the subspace spanned by the functions $A(\chi_\Gamma g_l^\Gamma Y_{lm})$ and $A(\chi_\Gamma \varphi_k^\Gamma)$. Because of the outgoing-wave definition of the functions g_l^Γ, the matrix $\underline{M}_{qq}$ is complex symmetric and *its inverse is nonsingular for real energies.*[11,12]

B. Orthogonality and the rigorous elimination of continuum exchange matrix elements

For practical calculations on many-electron systems, it is essential to work with an orthogonal basis. A property of the Kohn principle that has been discussed previously,[14,16] called transfer invariance, is that the T matrix is unchanged by any unitary transformation between the functions φ_k^Γ and the continuum orbitals f_l^Γ and g_l^Γ and that they can thus be taken to be mutually orthogonal. In additional, we will construct the φ_k^Γ to be orthogonal to the set of molecular orbitals used to form both the target states χ_Γ and the correlation terms Θ_μ. This latter prescription imposes a strong orthogonality condition between the continuum channel functions and the target wave functions. In cases where this latter condition does represent a constraint, additional terms can always be added to the list Θ_μ to relax the constraint.[14]

If the orbitals and continuum functions which make up the various terms in Eq. (1) were not orthogonal the first difficulty which would arise would be in writing formulas for the matrix elements of the many-electron Hamiltonian. For example, Slater's rules would not apply and we would meet complexities like those encountered in configuration-interaction calculations using nonorthogo-

nal orbitals.

If we use a separable approximation for exchange interactions, an additional premium beyond the absence of overlap factors in matrix elements is gained. First, however, let us dispense with the other integrals which contribute to Eq. (9).

The matrices $\underline{M}_{qq}$, $\underline{M}_{00}$, and $\underline{M}_{q0}$ can be formed from one- and two-electron integrals. Integrals involving only bound functions may be extracted from standard electronic structure codes. These are called bound-bound integrals. Integrals involving one continuum function (bound-free integrals) or two continuum functions (free-free integrals) are more problematic because there are in general no analytic formulas available for them. Moreover, we maintain maximum flexibility in the procedure (to treat Coulomb scattering, for example) if the bound-free and free-free integrals do not rely on particular analytic techniques.

Direct integrals of the electron repulsion potential may be expressed in terms of the local, one-particle transition potentials $V_{\Gamma\Gamma'}$,

$$V_{\Gamma\Gamma'}(\mathbf{r}) = \sum_{q=1,\ldots,N} \int \chi_\Gamma(\mathbf{r}_1, \ldots, \mathbf{r}_N) \frac{1}{|\mathbf{r} - \mathbf{r}_q|} \times \chi_{\Gamma'}(\mathbf{r}_1, \ldots, \mathbf{r}_N) d\mathbf{r}_1 \cdots d\mathbf{r}_N . \quad (11)$$

Matrix elements of $V_{\Gamma\Gamma'}(\mathbf{r})$, and those of the nuclear attraction potential and kinetic energy, are evaluated by the three-dimensional adaptive quadrature scheme discussed in Sec. III. For example,

$$\langle A(\chi_\Gamma f_l^\Gamma Y_{lm}) | (H - E) | A(\chi_{\Gamma'} g_{l'}^{\Gamma'} Y_{l'm'}) \rangle_{\text{direct}} = \delta_{\Gamma\Gamma'} \delta_{ll'} \delta_{mm'} \langle f_l^\Gamma | -\frac{1}{2} \frac{d^2}{dr^2} + E_\Gamma - E | g_l^{\Gamma'} \rangle$$
$$+ \langle f_l^\Gamma Y_{lm} | V_{\Gamma\Gamma'} + \delta_{\Gamma\Gamma'} V_{\text{nuc}} | g_{l'}^{\Gamma'} Y_{l'm'} \rangle . \quad (12)$$

The exchange-type integrals remain. A simple approximation for exchange interactions which has been proven reliable in numerous electron scattering studies is to approximate such operators by separable expansions.[17,18] The exchange portion of H_{PP} can be approximated by

$$H_{PP}^{\text{exch}} = \sum_{\substack{k,k' \\ \Gamma,\Gamma'}} |\varphi_k^\Gamma\rangle \langle \varphi_k^\Gamma | H_{PP}^{\text{exch}} | \varphi_{k'}^{\Gamma'} \rangle \langle \varphi_{k'}^{\Gamma'} | . \quad (13)$$

This definition does not change any bound-bound matrix elements. However, since all the continuum functions, f_l^Γ and g_l^Γ, have been orthogonalized to the bound functions, φ_k^Γ, any matrix element of exchange involving free functions simply vanishes.

This device, which was first proposed by Rescigno and Schneider,[14] lies at the heart of a practical algorithm for polyatomics, because it opens the way for the quadrature scheme in Sec. III to be applied to all nonzero interaction matrix elements involving free functions.

Although we do not employ an optical potential in the calculations reported here, it is worth noting that the same separable approximation can be made for the optical potential V_{opt} in Eq. (7). With that approximation,

we have specified how all the matrix elements appearing in the working equation for the T matrix, Eq. (9), are to be evaluated.

III. THREE-DIMENSIONAL ADAPTIVE QUADRATURE

The quadrature scheme we describe in this section is applied only to the evaluation of the bound-free and free-free matrix elements of direct potential operators and of the kinetic energy. This procedure provides a set of points and weights in the space $\mathbf{r} = (x,y,z)$. The prerequisite for the quadrature is that we be able to construct the integrand at points in three space. For example, for a bound-free potential matrix element

$$\langle \varphi_k^\Gamma | V_{\Gamma\Gamma'} + \delta_{\Gamma\Gamma'} V_{\text{nuc}} | g_{l'}^{\Gamma'} Y_{l'm'} \rangle$$

we need Gaussian basis functions which contribute to φ_k^Γ, a Riccati Bessel function defined in Eq. (3), and a spherical harmonic evaluated at the points in r space, as well as the potential $V_{\Gamma\Gamma'}(\mathbf{r})$. The Gaussian functions and nuclear attraction potential V_{nuc} are of course given by simple formulas and the Bessel and spherical harmonic func-

tions can be evaluated by straightforward recursion schemes.

The direct potential from Eq. (11) can be written in terms of a one-electron density matrix (or transition density matrix if $\Gamma \neq \Gamma'$),

$$V_{\Gamma\Gamma'}(\mathbf{r}) = \sum_{k,k'} \rho_{kk'}^{\Gamma\Gamma'} \int \frac{\varphi_k^{\Gamma}(\mathbf{r}')\varphi_{k'}^{\Gamma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' \ . \tag{14}$$

The bound functions φ_k^{Γ} appearing in Eq. (14) are simply sums of Gaussians so the integrals appearing in this equation are identical to nuclear attraction integrals with a nucleus at the position $\mathbf{r}$. These integrals are one-electron integrals which appear in any quantum chemistry computer code.[19] An efficient algorithm can be constructed which computes these for the $\mathbf{r}$ points in the quadrature grid, and which can easily make use of vectorization on vector architecture supercomputers.

Thus we can construct the factors of the integrands of the bound-free and free-free integrals which we require at points in a three-dimensional quadrature grid. We now turn our attention to the construction of the points and weights of that grid.

We will choose a single grid with which to quadrature all integrals involving free functions. The integrands of many of those integrals involve nuclear singularities or bound functions which are strongly peaked at the nuclei, so we must adapt our quadrature accordingly. It is near the integrable singularities of the nuclear potentials that we must use the greatest care to avoid quadrature errors. Asymptotically, however, the integrands of many of our integrals, the free-free integrals, become separable in spherical coordinates. For large r the potential ultimately is proportional to a single spherical harmonic (the largest term in a multipole expansion) and the free functions are products of Bessel functions and spherical harmonics. So our grid should make a smooth transition from local spherical symmetry around each nuclear singularity to global spherical symmetry around the center of charge of the molecule.

To construct such a quadrature, consider the general three-dimensional integral

$$I = \int F(\mathbf{r}) d^3r \tag{15}$$

and define the change of variable,

$$\mathbf{r}(\mathbf{q}) = \mathbf{q} - \sum_{\text{nuc}} (\mathbf{q} - \mathbf{R}_{\text{nuc}}) S_{\text{nuc}}(\mathbf{q}) \ , \tag{16}$$

where $S_{\text{nuc}}(\mathbf{q})$ is a strength function depending on the distance of a point from the nuclear position $\mathbf{R}_{\text{nuc}}$. The function $S_{\text{nuc}}(\mathbf{q})$ may be chosen in any number of ways, but it must have the property that

$$S_{\text{nuc}}(\mathbf{q}) \xrightarrow[q \to \infty]{} 0 \ . \tag{17}$$

This property is necessary so that the transformation in Eq. (16) will reduce to the identity, and $\mathbf{r}$ will be the same as $\mathbf{q}$ at large distances from the molecule. A flexible and effective form for our purposes is

$$S_{\text{nuc}}(\mathbf{q}) = P(|\mathbf{q} - \mathbf{R}_{\text{nuc}}|)^2 \Big/ \sum_{\text{nuc}'} P(|\mathbf{q} - \mathbf{R}_{\text{nuc}'}|) \ , \tag{18}$$

where the sum is over all nuclei in the molecule and

$$P(\zeta) = e^{-\mu\zeta^2} \ . \tag{19}$$

The effect of this transformation is to draw points in $\mathbf{q}$ space toward $\mathbf{R}_{\text{nuc}}$ if they lie roughly within a radius of $1/\mu$ of $\mathbf{R}_{\text{nuc}}$ and to leave them unaffected otherwise. With this change of variable the integral we wish to evaluate becomes

$$I = \int F(\mathbf{r}(\mathbf{q})) \left| \frac{\partial \mathbf{r}}{\partial \mathbf{q}} \right| d^3q \ . \tag{20}$$

This equation is equivalent to Eq. (15) only if the transformation from $\mathbf{q}$ to $\mathbf{r}$ is one to one. The particular form we have chosen for $S_{\text{nuc}}(\mathbf{q})$ makes this constraint easy to accomplish. We have found that for values of μ between 5 and 20 the transformation is well beyond for internuclear distances of 2-bohr radii and up.

The first step in developing an optimum and efficient grid for a particular molecule is to choose a separable (q, θ_q, φ_q) grid consisting of shells of points chosen from standard 1D quadratures. In these calculations we have used Gauss-Legendre quadratures on subintervals of q and $\cos(\theta_q)$ and Simpson's rule for φ_q. Although this grid is separable, it can be adapted to the molecular framework by choosing the (q, θ_q, φ_q) grid to have a denser spacing of points in those subshells which contain the nuclei, as shown in the two-dimensional projection of
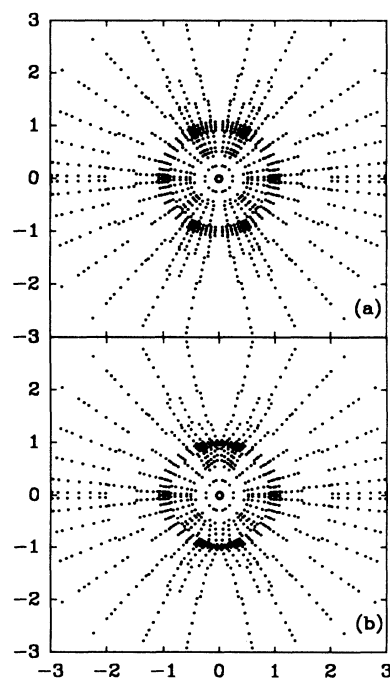

FIG. 1. (a) Sample untransformed (separable) grid for a case with two atoms. Atoms are located 1 a_0 above and below the center of the figure. (b) Same grid transformed (nonseparable), showing the condensation of points near the atoms with no distortion of the grid elsewhere.

TABLE I. Convergence of sample molecular integral in Eq. (23) evaluated using both transformed and untransformed grids. The value of μ in Eq. (19) is 15 and the exact value of the integral is 11.170 107.

No. of points	Untransformed	Transformed
982	11.086 045	11.158 258
1030	11.135 080	11.168 904
1280	11.158 680	11.170 610
1388	11.157 628	11.170 075
1460	11.165 517	11.170 092
1640	11.166 771	11.170 107
2000	11.166 784	11.170 107
3376	11.167 401	11.170 107

such a grid in Fig. 1(a). Then, upon evaluating the Jacobian of the transformation at each point and defining

$$w_p = w_{q_p} w_{\theta_{q_p}} w_{\varphi_{q_p}} , \qquad (21)$$

we obtain

$$I = \sum_p F(\mathbf{r}(\mathbf{q}_p)) \left| \frac{\partial \mathbf{r}}{\partial \mathbf{q}_p} \right| w_p , \qquad (22)$$

where the sum is over points in the q grid.

Equation (22) defines a nonseparable, adaptive 3D quadrature with effective weight $|\partial \mathbf{r}/\partial \mathbf{q}_p| w_p$ at each grid point. Figure 1(b) shows the transformed grid $\mathbf{r}(\mathbf{q})$ for a sample grid. The effectiveness of this transformation in treating nuclear singularities in the integrand is demonstrated in Table I. There we show the results from the untransformed grid with r equal to q and the transformed grid for a test integral of the form

$$I = \int \left[\frac{e^{-1.5|\mathbf{r}-\mathbf{A}|}}{|\mathbf{r}-\mathbf{A}|} + \frac{e^{-1.5|\mathbf{r}+\mathbf{A}|}}{|\mathbf{r}+\mathbf{A}|} \right] d^3r , \qquad (23)$$

with $\mathbf{A}=(0,0,1.034)$. The integrand in Eq. (23) has axial symmetry so the grid can be chosen to lie entirely in a plane containing the nuclei. To make the most meaningful comparison possible, the number of grid points in Table I was increased from 982 to 3376 by adding points only in the regions near the nuclei (within $0.5a_0$), where the transformation strongly affects the grid. The results show that the transformed grid produces eight significant figures in the integral with 1640 points where the un-

TABLE II. Exponents of Gaussian functions added to methane target basis to form the square-integrable part of scattering basis in Eq. (2).

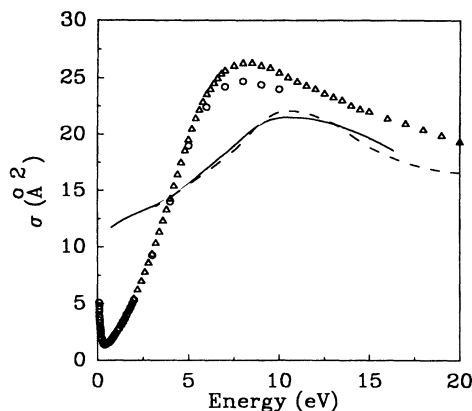| Center	Exponents
Carbon s (a_1 symmetry)	3.0,1.0,0.3,0.075,0.03,0.01
Carbon p (t_2 symmetry)	2.0,0.5,0.2,0.05,0.02
Carbon d (t_2 symmetry)	2.4,0.6,0.15,0.0375
Carbon d (e symmetry)	5.0,2.0,0.8,0.32,0.128,0.0512, 0.02048,0.00819
Hydrogen s (a_1 and t_2 symmetries)	1.0,0.25,0.05

FIG. 2. Total elastic cross section for CH_4 in $\overset{\circ}{A}^2$. ———, present results; — — —, results of Lima et al. (Ref. 2); $\bigcirc$, experiments of Ferch et al. (Ref. 22); $\triangle$, experiments of Lohmann et al. (Ref. 23).

transformed grid produces only four. The most important feature of Table I, however, is that further doubling the number of points does not improve the performance of the untransformed grid because of its lack of spherical symmetry around the nuclear singularities.

IV. ELECTRON-METHANE CROSS SECTIONS AT THE STATIC-EXCHANGE LEVEL

In a static-exchange calculation, the initial-state target wave function defines the scattering problem. For these calculations, methane is described by the Hartree-Fock wave function for its ground state in a $(9s,5p)$ basis contracted to $[5s,3p]$ on the carbon and a $4s$ basis contracted to $3s$ on the hydrogens. The contraction coefficients and exponents are those given by Dunning.[20] In this basis the ground-state energy is $-40.183\ 14E_h$, which is to be compared with $-40.2124E_h$ from the more extensive calculation of Meyer[21] at the same carbon-hydrogen internuclear distance of $2.05a_0$.

The scattering trial function is defined by specifying the square-integrable basis functions φ_k^Γ and the continuum basis in Eq. (2). In these calculations, the square-integrable part of the scattering basis consists of the tar-
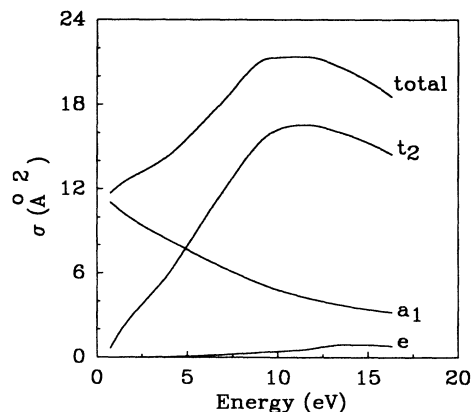

FIG. 3. Contributions to total elastic cross section for CH_4 from a_1, t_2, and e symmetries.

get basis described above augmented by the Gaussian functions listed in Table II. To complete the specification of the trial function, we must specify the continuum basis of Bessel functions multiplied by spherical harmonics which appear in Eq. (2). These functions are necessary only to describe the long-range behavior of the scattering wave function. Methane is not a strongly asymmetrical target in the sense that it does not strongly couple a large number of partial waves in electron scattering. We found it sufficient to include continuum functions with l up to 4. The parameters for the cutoff functions in Eqs. (4) and (5), which modify the continuum functions near the origin, were chosen such that both α and γ were 1.0 and n was 1.

Molecular symmetry simplifies the working equations of the complex Kohn variational method in a familiar and predictable way. In this case, we may solve separately for the contributions to the trial function in Eqs. (1) and (2) which transform with different irreducible representations of the tetrahedral point group T_d. Of the five irreducible representations of T_d, only three contribute significantly to the elastic scattering cross sections we compute here. Those irreducible representations and the l values which contribute to them are

$$a_1, \; l = 0,3,4 \; ;$$

$$t_2, \; l = 1,2,3,4 \; ;$$

$$e, \; l = 2,4 \; .$$

The total numbers of square-integrable basis functions in each of these symmetries in these calculations are 17 in a_1, 18 in t_2, and 8 in e symmetry.

Beyond specifying the target and scattering basis sets, all that remains to describe the calculations on methane completely is to describe the adaptive grid chosen to perform the bound-bound and bound-free integrals as discussed in Sec. III. We may also use symmetry to reduce the number of points in the grid. Because of constraints imposed by the electronic structure codes we used to compute the bound-bound integrals, the calculations were actually performed in the lower symmetry point group C_{2v}, which is abelian. For this reason, the grid could be restricted to one quarter of a sphere, which was chosen to have a radial extent of $40a_0$. The grid in that quadrant was chosen adaptively as described in Sec. III, and consisted of 63 301 points in r space. As we will demonstrate below, that grid contains vastly more points than are necessary to obtain accurate results.

The total elastic cross section from these calculations is shown in Fig. 2 together with the static-exchange calculations of Lima et al.[2] and the results of two experimental determinations.[22,23] The calculations of Lima et al. were performed using the Schwinger variational method. Assuming that the scattering trial function in their calculations is adequate, the results of the Schwinger calculations should differ from the present results only to the extent that these calculations are sensitive to the differences in the basis sets used to describe the target wave functions for methane. Lima et al. used a somewhat larger target basis which included d functions on the carbon. It

TABLE III. Contributions to total cross section from t_2 symmetry for large (63 301) and small (21 323) grids used in quadrature of bound-free and free-free integrals. Cross sections are in a_0^2 and incident energies are in Hartrees.

E	Small grid	Large grid
0.15	6.150	6.151
0.35	15.875	15.904
0.425	16.560	16.584

is clear from Fig. 2 that the resulting differences in the total cross sections are minor indeed. In Fig. 3 we show the contributions to the total cross section from the three molecular symmetries included in the present calculations.

To test the dependence of the computed cross sections on the selection of grid points we performed calculations using a much small grid than the one described above. The smaller grid contained 21 323 points, roughly one-third the number in the larger grid. The results of the two calculations for the contributions to t_2 symmetry to the total cross section at three energies are compared in Table III. The cross sections from the two grids differ over this energy range only in the fourth significant figure. It is worth noting that the differences in individual bound-free or free-free matrix elements may be somewhat larger than the differences in the final T-matrix values. Thus, in part, the relative insensitivity to the number of grid points which we observe is a manifestation of the variational stability of the Kohn method.

V. DISCUSSION

It is apparent from Fig. 2 that the results of the static-exchange calculations presented here show no indication of the Ramsauer-Townsend minimum which is observed in the experimental elastic scattering cross section.[22,23] The effects of target polarization evidently play a critical role in the physics of this phenomenon in methane. To verify that this is the case we performed calculations for
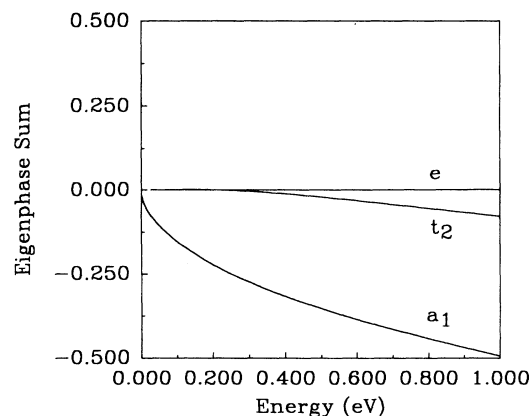
FIG. 4. Eigenphase sums for a_1, t_2 and e symmetries for low incident energies.

energies below 1 eV, for which the eigenphase sums are plotted in Fig. 4. At very low energies the cross section is dominated by the s-wave contribution and the eigenphase sum for a_1 symmetry essentially becomes the s-wave phase shift. A Ramsauer-Townsend minimum occurs in the cross section when this phase shift passes through 0 or a multiple of π at a low, but nonzero, value of the incident energy.

The a_1 eigenphase sum in Fig. 4 shows no such behavior. Nonetheless, Gianturco et al.[6] were able to produce a Ramsauer-Townsend minimum in the methane cross section in calculations which omitted polarization effects but which employed local approximations for the exchange interaction. The fact that, at low energies in particular, electron scattering cross sections are sensitive to subtle changes in the effective interaction underlines the need for reliable ab initio methods for this problem. Moreover, such sensitivity is to be expected near every inelastic threshold, and the feasibility of extending these methods to electronically inelastic processes is a central question.

The implementation of the complex Kohn variational method we have described in this work is designed to eliminate barriers to its application to electronic close-coupling calculations on polyatomics. First of all, no matrix elements of nonlocal operators involving continuum functions will be required. The exchange part of each coupling potential and of the Feshbach optical potential appearing in such calculations will be treated in exactly the same way that exchange is treated in the static-exchange calculation we present here. By using separable representations of those nonlocal potentials, and orthogonalizing the free functions in each channel to the square-integrable functions used in the multichannel analog to Eq. (13), the effects of these terms are shifted to bound-bound portions of the computation.

The adaptive three-dimensional quadrature used in these calculations can be applied easily to the calculation of all of the remaining integrals involving free functions.

As we demonstrated in Sec. IV, where dropping two-thirds of the grid points used in these calculations left the results essentially unchanged, there is considerable room for reducing the number of grid points even further. A reasonable question to ask is whether this quadrature scheme will be successful in the presence of long-range polarization and coupling potentials or for molecules with large permanent multipole moments. Actually, extending the grid to large distances from the molecule adds very few quadrature points. At large distances the potentials are dominated by a few (low) multipole terms. The angular grid necessary is therefore quite small, because there are in general only a handful of partial waves which contribute to the scattering wave function asymptotically. Using five or six radial points per oscillation in the continuum functions at large distances (the point density used in these calculations), the grid for methane can be extended from 40 to 100 bohr by adding roughly 5000 points.

Thus the principal barrier to calculations including several electronic channels is the construction of compact descriptions of several target states which involve reasonable numbers of configurations constructed out of a single orbital basis. At this point the problems are in efficiently representing the physics of target response—even at incident energies of only a few eV—rather than in solving the resulting close-coupling equations.

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