

Complex Kohn variational method: Application to low-energy electron-molecule collisions

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An algebraic variational method, based on application of the Kohn principle to the T matrix, is formulated for multichannel scattering problems and applied to the case of low-energy electron-molecule collisions. The method requires only Hamiltonian matrix elements and is anomaly-free. The present formulation is noteworthy in that it requires no bound-free nor free-free exchange matrix elements. The new technique is illustrated by application to $e^- + \text{H}_2$ scattering in both the static-exchange and the two-state approximations. The method is found to be both efficient and accurate.

I. INTRODUCTION

The development of reliable and efficient theoretical methods for the *ab initio* determination of low-energy electron-molecule scattering cross sections has proved to be a difficult undertaking. Three techniques in particular have been the focus of much developmental work over the past five years and have been generalized to the point where they are now beginning to provide cross sections for electronic excitation of a number of first-row diatomic molecules. These techniques are the linear-algebraic method,¹ the multichannel Schwinger variational method,² and the R -matrix method.³ Although these techniques differ rather widely in both philosophy and numerical detail, they share the common property of relying heavily on bound-state computational technology for much of their implementation. Indeed, the "hybrid" nature of an approach that combines both numerical and discrete-basis-set techniques seems to be a hallmark of the most successful *ab initio* approaches to electron-molecule collisions.

Traditional algebraic variational methods,⁴ such as the Kohn method, also draw heavily on bound-state methodology. Although extensively used in electron-atom scattering problems,⁵ these methods have been virtually ignored in molecular applications. However, there has been a rekindling of interest in the Kohn method. Recent^{6,7} work has shown that application of the Kohn variational method to the T matrix rather than the K matrix, which simply involves a change to complex, outgoing-wave boundary conditions, eliminates the spurious singularities⁸ that can plague the traditional method. Another stumbling block which undoubtedly hampered application of the Kohn method to molecules involves the practical difficulties associated with the computation of certain continuum matrix elements. However, in a recent paper,⁹ we showed that the method can be formulated within a separable-potential approach in such a way as to completely eliminate the need for computing bound-free and free-free exchange matrix elements. Correlation

and polarization effects can also be systematically included in the treatment through the use of optical-potential techniques.¹⁰ In light of these developments, the complex Kohn method seems ideally suited for application to low-energy electron-molecule collisions. The purpose of this paper is to provide a computational formulation of the multichannel complex Kohn method and present some preliminary results.

In Sec. II we present a brief formulation of the complex Kohn variational method for multichannel scattering. We also outline the simplifications brought about by the judicious use of separable expansions for certain parts of the electron-target interaction potential. Section III presents the results of computations on $e^- + \text{H}_2$ scattering in both the static-exchange and two-state approximations. Section IV contains some concluding remarks.

II. THEORY

A. Choice of trial wave function

The problem we consider is scattering of low-energy electrons by an N -electron target molecule. We will formulate the problem in body-frame coordinates within the framework of the fixed-nuclei approximation. To describe the scattering of an electron, incident in a channel denoted by the label Γ^1 , we use an antisymmetrical trial wave function of the form

$$\psi_{\Gamma^1} = \sum_{\Gamma} A(\chi_{\Gamma} F_{\Gamma\Gamma^1}) + \sum_{\mu} d_{\mu}^{\Gamma^1} \otimes_{\mu}, \quad (1)$$

where the first sum runs over the energetically open N -electron target states, denoted by the normalized functions χ_{Γ} , and the operator A antisymmetrizes the orbital functions $F_{\Gamma\Gamma^1}$ into the functions χ_{Γ} . The \otimes_{μ} are an orthonormal set of antisymmetric, square-integrable $(N+1)$ -electron functions used to represent polarization and correlation effects not included in the first summation. We are using the symbol Γ to label all the quantum numbers needed to represent a physical state of the com-

posite system, i.e., the internal state of the target molecule as well as the energy and orbital angular momentum of the scattered electron.

To calculate physical differential cross sections, it is necessary to express the scattering amplitude in the laboratory frame. This is most easily accomplished by projecting the T matrix onto a set of angular functions. To this end, the channel continuum functions $F_{\Gamma\Gamma'}$ are further expanded as

$$rF_{\Gamma\Gamma'}(\mathbf{r}) = \sum_{l,m} [f_l^\Gamma(r)\delta_{ll'}\delta_{mm'}\delta_{\Gamma\Gamma'} + T_{lm'l'm'}^{\Gamma\Gamma'} g_l^\Gamma(r)] Y_{lm}(\hat{\mathbf{r}}) + \sum_k c_k^{\Gamma\Gamma'} \varphi_k^\Gamma(\mathbf{r}), \quad (2)$$

where Y_{lm} is a normalized spherical harmonic, the φ_k^Γ are a set of square-integrable functions, and the functions f_l^Γ and g_l^Γ are linearly independent continuum orbitals which are regular at the origin (i.e., go to zero at least as fast as r^{l+1}) and, in the case of neutral targets, behave asymptotically as regular and outgoing Riccati-Bessel functions, respectively,

$$\begin{aligned} f_l^\Gamma(r) &= j_l(k_\Gamma r) / \sqrt{k_\Gamma} \\ &= \sin(k_\Gamma r - l\pi/2) / \sqrt{k_\Gamma} \quad (r \rightarrow \infty), \\ g_l^\Gamma(r) &= i[j_l(k_\Gamma r) + in_l(k_\Gamma r)c(r)] / \sqrt{k_\Gamma} \\ &= \exp[i(k_\Gamma r - l\pi/2)] / \sqrt{k_\Gamma} \quad (r \rightarrow \infty). \end{aligned} \quad (3)$$

The function $c(r)$, which makes g_l^Γ regular at the origin, is chosen to be $[1 - \exp(-ar)]^{2l+1}$. The channel moment k_Γ (in a.u.) are determined by energy conservation,

$$k_\Gamma^2/2 = E - E_\Gamma, \quad (4)$$

where E is the total energy of the composite system and E_Γ is the energy of the target molecule corresponding to χ_Γ . The functions f_l^Γ and g_l^Γ may be modified to Coulomb form to treat ionic targets. The coefficients $T_{lm'l'm'}^{\Gamma\Gamma'}$ are elements of the T matrix and are the fundamental dynamical quantities that determine scattering amplitudes and cross sections.

The sum over angular quantum numbers l and m that appears in Eq. (2) will, in general, be restricted by the symmetry of the target molecule under consideration. For example, in linear molecules, m is a good quantum number and the sum over m collapses to the single term with $m = m'$. Moreover, the sum over l values can be restricted to the number of "asymptotic l 's" needed to represent the channel wave function at large distances and to provide converged cross sections at a particular energy.¹¹ The reader should note that we are *not* attempting a complete single-center expansion of the channel wave function. The burden of representing the short-range, high- l components of the wave function near the nuclei is carried by the square-integrable functions $\varphi_k^\Gamma(\mathbf{r})$.

B. Variational formulation

The coefficients $T_{lm'l'm'}^{\Gamma\Gamma'}$, $c_k^{\Gamma\Gamma'}$ and $d_\mu^{\Gamma'}$ that appear in Eqs. (1) and (2) can be treated as variational parameters

whose values are to be determined from a stationary principle. In view of approximations to be introduced in the following, it will be desirable to work in the subspace defined solely by the open-channel target functions. The effect of the closed-channel correlation functions \otimes_μ can be formally incorporated into an effective optical potential by using Feshbach partitioning techniques.¹² If Q is defined as the operator that projects onto the subspace defined by the functions \otimes_μ , and P is its orthogonal complement, then we can manipulate the Schrödinger equation in a standard way to produce a modified Hamiltonian,

$$\begin{aligned} H_{\text{eff}} &= H_{PP} + (H - E)_{PQ} (E - H)_{QQ}^{-1} (H - E)_{QP} \\ &\equiv H_{PP} + V_{\text{opt}}. \end{aligned} \quad (5)$$

The Kohn principle¹³ can be used to characterize the T matrix as the stationary value of the functional,

$$[\underline{T}^{\Gamma\Gamma'}] = \underline{T}^{\Gamma\Gamma'} - 2 \int \Psi_\Gamma (H_{\text{eff}} - E) \Psi_{\Gamma'}^{-1}, \quad (6)$$

where the terms \otimes_μ no longer appear in Ψ_Γ . Trial values for the coefficients $\underline{T}^{\Gamma\Gamma'}$ and $\underline{c}^{\Gamma\Gamma'}$ are determined from the equations obtained by requiring that the derivatives of $[\underline{T}^{\Gamma\Gamma'}]$ with respect to these parameters vanish. These coefficients, when substituted back into Eq. (6), give a stationary expression for the T matrix. In a condensed matrix notation, in which open-channel indices are suppressed, the result can be written⁵

$$[\underline{T}] = -2(\underline{M}_{oo} - \underline{M}_{oq} \underline{M}_{qq}^{-1} \underline{M}_{oq}), \quad (7)$$

where the elements of \underline{M}_{oo} are defined as

$$(\underline{M}_{oo})_{lm'l'm'}^{\Gamma\Gamma'} = \int A(\chi_\Gamma f_l^\Gamma Y_{lm})(H_{\text{eff}} - E) A(\chi_{\Gamma'} f_{l'}^{\Gamma'} Y_{l'm'}), \quad (8)$$

and \underline{M}_{oq} 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 behavior of the functions g_l^Γ , the matrix \underline{M}_{qq} will be complex symmetric and thus its inverse will be nonsingular for real energies. The fact that this choice of outgoing-wave boundary conditions in the Kohn method leads to an anomaly-free expression for the T matrix has been previously discussed.^{6,7}

It is easy to see from the structure of Eq. (7) that the variationally determined T matrix is symmetric. The traditional Kohn principle likewise produces a real, symmetric K matrix and any real, symmetric K matrix will produce a unitary S matrix. A symmetric T matrix, on the other hand, does not in itself guarantee a unitary S matrix. In fact, we can use the unitarity of the computed S matrix in the complex Kohn method as a measure of the completeness of the expansion basis employed. In all the testing we have carried out on model problems, our experience has been that a unitary result is always the correct result.

C. Orthogonality and separable expansions

For practical calculations on many-electron systems, it is computationally essential to work with an orthogonal

basis. In previous work⁹ we discussed the fact that the *transfer invariance*⁵ of the total wave function guarantees that the T -matrix elements given by Eq. (7) are unchanged by any unitary transformation between the bound 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 addition, we will construct the φ_k^l to be orthogonal to the set of molecular orbitals used to form both the target states χ_Γ and the correlation terms \otimes_μ . This prescription imposes a strong orthogonality condition between the continuum channel functions and the target wave functions. We have also previously pointed out^{9,14} that there are instances where this latter procedure *does* represent a constraint on the wave function which, in this formulation, must be relaxed by the addition of appropriate terms to the set \otimes_μ used to construct V_{opt} .

All of the matrix elements needed to construct \hat{M}_{qq} , \hat{M}_{oo} , and \hat{M}_{oq} can be formed from one- and two-electron integrals. The integrals involving purely bound functions may be extracted from standard electronic structure programs. Of the two-electron integrals involving either one (bound-free) or two (free-free) continuum functions, it is useful to distinguish between direct integrals and exchange integrals, which arise from interchange of "bound-" and "free-" electron coordinates. The direct integrals may be expressed in terms of a one-particle transition potential. For example, in the case of a free-free integral, we can write

$$\begin{aligned} & \langle A(\chi_\Gamma f_l^\Gamma Y_{lm}) | (H - E) | A(\chi_\Gamma g_{l'}^{\Gamma'} Y_{l'm'}) \rangle_{\text{direct}} \\ &= \delta_{\Gamma\Gamma'} \delta_{ll'} \delta_{mm'} \left\langle f_l^\Gamma \left| -\frac{1}{2} \frac{d^2}{dr^2} + E_\Gamma - E \right| g_{l'}^{\Gamma'} \right\rangle \\ &+ \langle f_l^\Gamma Y_{lm} | V_{\Gamma\Gamma'} | g_{l'}^{\Gamma'} Y_{l'm'} \rangle, \end{aligned} \quad (9)$$

where

$$\begin{aligned} V_{\Gamma\Gamma'}(\mathbf{r}) &= \sum_{q=1}^N \int \chi_\Gamma(\mathbf{r}_1 \cdots \mathbf{r}_N) \frac{1}{|\mathbf{r} - \mathbf{r}_q|} \chi_{\Gamma'}(\mathbf{r}_1 \cdots \mathbf{r}_N) \\ &\times d\mathbf{r}_1 \cdots d\mathbf{r}_N. \end{aligned} \quad (10)$$

By using a single-center decomposition of the transition potential

$$V_{\Gamma\Gamma'}(\mathbf{r}) = \sum_{l,m} V_{lm}^{\Gamma\Gamma'}(r) Y_{lm}(\hat{\mathbf{r}}), \quad (11)$$

the direct matrix element of Eq. (9) can be reduced to a sum of radial integrals times angular factors. A similar reduction is possible for the case of direct, bound-free integrals. The exchange-type integrals, however, are considerably more difficult to evaluate and, for the case of Gaussian-type orbitals which are the natural choice for molecular targets, no analytic treatment appears to be feasible.

We have previously shown⁹ how the formulation of the Kohn method is simplified by using a separable representation^{15,16} of the exchange components of H_{pp} which,

owing to the short-range nature of the exchange interaction, converge quite rapidly. If, in making up the $(N+1)$ -electron configurations with which to form the separable representation of H_{pp}^{exch} , we use the same set of square-integrable functions to which the free functions f_l^Γ and g_l^Γ have been orthogonalized, then all *free-free* and *bound-free exchange integrals* will simply *vanish* as a consequence of the strict orthogonality condition we have imposed on the trial wave function. The entire effect of exchange is thus carried by the bound-bound components of H_{eff} . Since the effect of the orthogonalization procedure is to "eat a hole" in the continuum orbitals at small r where exchange interactions are important, this procedure effectively eliminates all bound-free and free-free integrals from the calculation. In evaluating matrix elements of the optical potential, this same separable expansion is used. This eliminates all bound-free and free-free matrix elements of V_{opt} from consideration as well. The final working expression for $[\mathcal{I}]$ becomes

$$[\mathcal{I}] \simeq -2(\hat{M}_{oo} - \hat{M}_{oq} \hat{M}_{qq}^{-1} \hat{M}_{oq}), \quad (12)$$

where

$$\begin{aligned} (\hat{M}_{oo})_{lm'l'm'}^{\Gamma\Gamma'} &= \delta_{\Gamma\Gamma'} \delta_{ll'} \delta_{mm'} \left\langle f_l^\Gamma \left| -\frac{2}{2} \frac{d^2}{dr^2} + E_\Gamma - E \right| f_{l'}^{\Gamma'} \right\rangle \\ &+ \langle f_l^\Gamma Y_{lm} | V_{\Gamma\Gamma'} | f_{l'}^{\Gamma'} Y_{l'm'} \rangle. \end{aligned} \quad (13)$$

\hat{M}_{oq} is similarly defined, with the subscript q again referring to the subspace spanned by the functions $A(\chi_\Gamma g_l^\Gamma Y_{lm})$ and $A(\chi_\Gamma \varphi_k^\Gamma)$. Note again the absence of exchange and optical-potential terms in \hat{M}_{oo} and \hat{M}_{oq} . These only appear in the bound-bound components of \hat{M}_{qq} are defined as

$$(\hat{M}_{qq})_{kk'}^{\Gamma\Gamma'} = \int A(\chi_\Gamma \varphi_k^\Gamma) (H_{pp} + V_{\text{opt}} - E) A(\chi_\Gamma \varphi_{k'}^{\Gamma'}) . \quad (14)$$

These matrix elements were extracted from electronic structure codes. All other matrix elements were evaluated by numerical quadrature.

III. EXAMPLES

The computational steps involved in an electron-molecule calculation with the complex Kohn method can be summarized as follows.

(i) Choice of target basis and eigenstates. We must first decide how many physical target states χ to include in the expansion of the total wave function and the level at which they are to be approximated (self-consistent field, configuration-interaction, etc.). We must also decide on a molecular-orbital (MO) basis for this part of the computation. The MO's are expressed as linear combinations of Cartesian Gaussian functions.

(ii) Q -space configurations. The open-channel (P -space) part of the total wave function is to be expressed as a sum of antisymmetrized products of target states $\chi(\mathbf{r}_1 \cdots \mathbf{r}_N)$ and channel functions $F(\mathbf{r})$ which are strongly orthogo-

nal to χ . For every open-shell orbital of the same symmetry as $F(\mathbf{r})$ that appears in the expansion of χ and to which $F(\mathbf{r})$ is singlet coupled, an appropriate $(N+1)$ -electron configuration must be added to the Q -space configurations from which the optical potential is to be constructed.^{9,14} This relaxes the strong orthogonality constraint imposed on the channel functions. The set \otimes_{μ} of Eq. (1) will thus contain all "orthogonality-relaxing" configurations, as well as any additional correlation terms we may wish to include. These configurations are again built from the same set of MO's that were generated in step (i).

(iii) Choice of scattering basis. We must choose an additional set of MO's, $\varphi_k^{\Gamma}(\mathbf{r})$, to serve, in effect, in Eq. (2) as an expansion basis for the inner part of the channel functions. This set must be orthogonal to the basis of MO's used in steps (i) and (ii). Additionally, we must decide on how many continuum functions f_l^{Γ} and g_l^{Γ} to include in the expansion of the channel functions.

(iv) Single-center expansion of static potential and scattering basis. To facilitate the computation of the direct matrix elements over continuum functions, the static potentials [Eq. (10)] are expanded onto a single center, as in Eq. (11), as are the scattering functions $\varphi_k^{\Gamma}(\mathbf{r})$ chosen in step (iii). The radial components of the expansions are all expressed on a common mesh of grid points. The continuum functions are Schmidt orthogonalized to the scattering functions.

(v) Computation of direct matrix elements. Bound-free and free-free *direct* matrix elements [Eq. (13)] are constructed by appropriately assembling products of angular factors, which are readily expressed in closed form, and radial integrals over the functions calculated in step (iv). The latter are evaluated by Gauss-Legendre quadrature.

(vi) Bound-bound matrix. The entire bound-bound Hamiltonian matrix over the configurations $A(\chi_{\Gamma}\varphi_k^{\Gamma})$ and \otimes_{μ} , which is extracted from the calculations performed in steps (i) and (ii), is partitioned into P - and Q -space subblocks and manipulated to form the optical-potential matrix required in Eq. (14).

(vii) Computation of T matrix. Using the matrix elements assembled from steps (v) and (vi), the T matrix is calculated from Eq. (12) using standard linear-algebraic techniques. In practice, the bound-bound portion of \underline{M}_{qq} , which generally has the largest dimensionality of any matrix in the problem and is also purely real, is partitioned off and either preinverted or diagonalized. This allows us to confine the use of complex arithmetic only to the portions of the computation where it is actually needed.

A. $e^{-} + \text{H}_2$ static-exchange calculations

For the first application of the complex Kohn method to a molecular problem, we chose to study $e^{-} + \text{H}_2$ in the static-exchange approximation, largely as a test of the computational procedures we have developed. This problem has been thoroughly examined by a variety of computational techniques and good results are available for comparison. The calculations were performed on the ${}^2\Sigma_g^{+}$ symmetry component of the composite system. In the static-exchange approximation, the total wave func-

tion is approximated as an antisymmetrized product of a continuum function and the ground-state wave function for H_2 . With reference to Eq. (1), this means the first sum is truncated to a single term. For the ground state, we used a single configuration ($1\sigma_g^2$), self-consistent-field (SCF) wave function. This was obtained with an uncontracted ($12s4p7d$) Cartesian-Gaussian basis at an internuclear separation of $1.4a_1$. The SCF energy in this basis is -1.1331 a.u. and the quadrupole moment is 0.494 a.u. The 22 σ_g virtual orbitals, orthogonal to the occupied $1\sigma_g$ orbital, which were obtained from this calculation constituted the expansion basis χ_k^{Γ} for the T matrix in ${}^2\Sigma_g^{+}$ symmetry. No orthogonality relaxing configurations are required for single-configuration, closed-shell target calculations such as this, and consequently no optical potential is required at the static-exchange level. Six asymptotic channels ($m=0, l=0, 2, \dots, 10$) were included in calculating the T matrix. Terms up to $l=12$ were retained in the single-center expansions of the MO's and the static potential.

The results of this computation at three different energies are summarized in Table I. For comparison, we also performed calculations with the linear-algebraic method¹ using the same static-potential and separable-exchange expansions, as well as the same number of l values. This insured that any differences we found could not be attributed to the dynamical models being used. The results are found to be in good agreement. The point of this comparison was to verify the accuracy of the basis-set expansion procedures being used in the Kohn method. The accuracy of the separable expansion for exchange in this problem has already been well established,^{15,16} these results are in good agreement with other exact static-exchange calculations.

TABLE I. ${}^2\Sigma_g^{+}$ Eigenphases and partial cross sections for $e^{-} + \text{H}_2$ scattering in the static-exchange approximation. k values and cross sections are in a.u. Eigenphases are in radians. Exponents are given in square brackets.

Eigenphase	Kohn	Linear-algebraic
$k^2=0.01$		
1	-0.213	-0.214
2	0.355[-2]	0.320[-2]
3	0.586[-3]	0.572[-3]
4	-0.798[-4]	-0.827[-4]
Cross section	56.270	56.481
$k^2=0.25$		
1	-0.993	-0.993
2	0.187[-1]	0.191[-1]
3	0.336[-2]	0.337[-2]
4	0.143[-2]	0.144[-2]
Cross section	35.290	35.298
$k^2=1.0$		
1	1.456	1.454
2	0.928[-1]	0.949[-1]
3	0.940[-2]	0.796[-2]
4	0.321[-2]	0.307[-2]
Cross section	12.511	12.510

TABLE II. ${}^2\Sigma_g^+$ eigenphases and partial cross sections for $e^- + \text{H}_2$ scattering in a two-state approximation. Cross sections are in a.u. Eigenphases are in radians. Exponents are given in square brackets.

Eigenphase	Kohn	Linear-algebraic
Incident energy = 12 eV		
1	1.522	1.525
2	0.391	0.395
3	0.319[-1]	0.322[-1]
4	-0.322[-1]	-0.359[-1]
5	-0.107[-1]	-0.109[-1]
6	0.672[-2]	0.674[-2]
Cross sections		
$\sigma_{1 \rightarrow 1}$	14.294	14.300
$\sigma_{1 \rightarrow 2}$	0.430	0.435
$\sigma_{2 \rightarrow 2}$	6.917	7.094
Incident energy = 15 eV		
Eigenphase		
1	1.399	1.402
2	0.532	0.534
3	-0.544[-1]	-0.532[-1]
4	0.319[-1]	0.304[-1]
5	-0.171[-1]	-0.171[-1]
6	0.767[-2]	0.764[-2]
Cross sections		
$\sigma_{1 \rightarrow 1}$	11.140	11.151
$\sigma_{1 \rightarrow 2}$	0.534	0.528
$\sigma_{1 \rightarrow 2}$	5.492	5.567
Incident energy = 18 eV		
Eigenphase		
1	1.300	1.303
2	0.577	0.579
3	-0.615[-1]	-0.606[-1]
4	0.344[-1]	0.345[-1]
5	-0.210[-1]	-0.210[-1]
6	-0.104[-1]	-0.103[-1]
Cross sections		
$\sigma_{1 \rightarrow 1}$	8.922	8.939
$\sigma_{1 \rightarrow 2}$	0.482	0.485
$\sigma_{2 \rightarrow 2}$	4.072	4.091
Incident energy = 20 eV		
Eigenphase		
1	1.242	1.246
2	0.606	0.607
3	-0.618[-1]	-0.600[-1]
4	0.438[-1]	0.433[-1]
5	-0.227[-1]	-0.226[-1]
6	-0.114[-1]	-0.112[-1]
Cross sections		
$\sigma_{1 \rightarrow 1}$	7.783	7.802
$\sigma_{1 \rightarrow 2}$	0.431	0.435
$\sigma_{2 \rightarrow 2}$	3.676	3.670

B. $e^- + \text{H}_2$ two-state calculations

Excitation of the $b\ {}^3\Sigma_u^+$ state of H_2 has recently been studied with three different theoretical methods at the same level of approximation and the results are all in good mutual accord.¹⁷⁻¹⁹ We again calculated T -matrix

elements for this problem in ${}^2\Sigma_g^+$ symmetry and compared the results to those of linear-algebraic calculations employing the same target states, l expansions, etc. The ground state of H_2 was again taken to be the $1\sigma_g^2$ SCF wave function and the b state was described by the single configuration $1\sigma_g 1\sigma_u, {}^3\Sigma_u^+$. The $1\sigma_u$ orbital was generated in the V^{N-1} field of the frozen $1\sigma_g$ orbital, which is the usual improved virtual orbital (IVO) procedure.²⁰ An uncontracted set of (16s14p) basis functions was used. The value obtained for the vertical electronic excitation energy in our calculation was 9.98 eV, to be compared with the accurate value of 10.14 eV obtained by Kolos and Wolniewicz.²¹ From this basis, 23, σ_g and 24 σ_u orbitals could be formed. The functions (φ_k) used in the expansion of the trial wave function consisted of the 22 σ_g and 23 σ_u MO's, orthogonal to $1\sigma_g$ and $1\sigma_u$, respectively.

The open-channel configurations include terms of the form $1\sigma_g^2 n\sigma_g$ and $1\sigma_g 1\sigma_u n\sigma_u$, $n \neq 1$. For the latter class of configurations, two linearly independent spin functions can be formed. We used only those configurations corresponding to a triplet coupling of the $1\sigma_g 1\sigma_u$ core. Also included were the continuum terms $1\sigma_g^2 f_{2l}$, $1\sigma_g^2 g_{2l}$, $1\sigma_g 1\sigma_u f_{2l+1}$ and $1\sigma_g 1\sigma_u g_{2l+1}$, with $l=0, 1, \dots, 5$. Previous calculations on this problem had shown that the strong orthogonality¹ constraint had a large effect on the computed results. In ${}^2\Sigma_g^+$ symmetry, the configuration $1\sigma_g 1\sigma_u^2$ must be included to relax this constraint. This single term was carried in the optical potential. The calculation was carried out as outlined above. Table II summarizes the results. Again, the agreement found with the linear-algebraic results is good.

IV. CONCLUSIONS

We have outlined a multichannel, algebraic variational method that is anomaly-free and readily adaptable to low-energy ($e^- + \text{molecule}$) collisions. A noteworthy feature of the method is the elimination of all bound-free and free-free exchange matrix elements through the use of separable expansions. The preliminary results on H_2 presented here are quite promising, although further calculations on more complicated target molecules will have to be carried out to see if our initial optimism about the method will be justified.

The Kohn method, based as it is on the differential form of the Schrödinger equation, only requires Hamiltonian matrix elements. In this respect, it is similar to the basis-set R -matrix method. The rapid convergence of the Kohn method is associated with the fact that the wave function is expanded in terms of both bound and continuum basis functions, whereas the R -matrix method is generally implemented only with square-integrable functions which must consequently be capable of describing the scattering wave function over a finite volume. Variational principles based on the integral form of the Schrödinger equation, such as the Schwinger principle, require Green's-function matrix elements as well. While there is evidence^{22,23} that the Kohn-type methods require more basis functions than variational methods of the Schwinger type to achieve comparable accuracy, the rela-

tive simplicity of the computations required in the Kohn method may more than compensate for the larger number of functions required. The computational schemes we have used here proved to be quite efficient. The numerical quadrature of the direct integrals was the most time consuming aspect of the computations here, but these operations, as well as the matrix algebra manipulations, are ideally suited for the vector architecture of today's computers. For the two-state ($e^- + \text{H}_2$) calculations, which were performed on a Cray XMP, the actual scattering computations required about 4 sec per energy. This does not include the time spent on the electronic structure parts of the computation.

The linear-algebraic method, like the Schwinger method, is also based on the integral form of the Schrödinger equation. For the examples we studied here, the Kohn method was slightly faster, although the differences in timings we found were not large. We believe that the real advantages of the Kohn method may become more obvious in calculations on larger molecules and polyatomics, where the fact that the number of continuum functions in the trial wave function is determined

only by the asymptotics and not by the number of single-center terms required to expand the wave function at short distances is a key advantage. Finally, we note that the radial quadratures required in the Kohn method can be accurately performed with rapidly convergent Gauss quadrature schemes, whereas recent work²⁴ has pointed to convergence problems that can be encountered in representing a coordinate space Green's function on a discontinuity in the derivative at $r=r'$, unless higher-order quadrature schemes are employed. This discontinuity in the Green's function, however, evidently causes a problem only when highly accurate results (better than a few percent) are required.²⁵

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