Electron-Molecule Scattering above the Ionization Threshold

T. N. Rescigno and C. W. McCurdy
Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550

(Received 6 June 1994)

We show how to extend close-coupling calculations into the intermediate energy region without explicitly including a large number of inelastic channels. By discretizing the target continuum in a suitably chosen set of complex functions, we can construct convergent representations of a Feshbach optical potential that represents open inelastic channels including the ionization continuum. The method can be implemented for electron scattering by atomic or molecular targets with minimal modifications to existing electronic structure codes. The method is illustrated by applying it to $e^- + \mathrm{Li}_2$ elastic scattering.

PACS numbers: 34.80.Gs

The close-coupling formalism is the centerpiece of time-independent scattering theory and has formed the basis of most *ab initio* work on low-energy electron-atom and electron-molecule scattering. The essence of the method is an expansion of the total wave function, describing the composite target + projectile system, in a complete set of internal states of the target, including the continuum. Scattering information is extracted from an examination of the asymptotic behavior of the channel functions, which are the coefficients of the target eigenstates in the total wave function. Obviously, the complete set of target states must be truncated to finite size in actual computations, and the continuum states, if included, must be appropriately discretized. Some time ago [1] it was learned that, in the low energy region below the ionization threshold, convergence could be accelerated by including energy pseudostates above that threshold in the expansion, typically obtained by diagonalizing the target Hamiltonian in a basis of square-integrable (L^2) functions.

The intermediate energy region, extending from the ionization threshold to an energy of a few hundred eV presents a formidable challenge for *ab initio* theory. The infinity of open channels precludes us, even in principle, from writing down a wave function that describes all possible scattering events and is simply a reflection of the fact that the ionization problem persists as one of the fundamentally unsolved problems of atomic collision theory. Close-coupling expansions that include pseudostates, when extended to the intermediate energy region, typically encounter unphysical resonances near pseudostate thresholds [2], although their effect appears to diminish with increasing number of states [3]. As computer power has increased over the years, so has the number of target states that could be included in close-coupling expansions, allowing some exploration of their convergence properties.

Recently, Bray and Stelbovics [4] demonstrated, quite convincingly, that the close-coupling method does in fact converge at intermediate energies if enough states are included in the expansion. By including up to thirty target states in calculations on $e^- + \mathrm{H}$ scattering, they found that the pseudoresonance behavior eventually disappears. The intermediate energy R-matrix method [5] offers a similar approach to the problem but has not been able to obtain convergence without the need for averaging over dense pseudoresonance structure. Without detracting from the importance of these demonstrations, it remains to be seen whether such approaches will be applicable to electron scattering from complex atomic or molecular targets, where the number of terms needed to achieve convergence is likely to be far greater than what is currently feasible.

The Holy Grail of *ab initio* time-independent scattering theory is a method which requires specification only of the initial and final states of the target for calculating a particular elastic or inelastic cross section and, thereby, avoids the close-coupling expansion. Progress along these lines has usually involved the use of analyticity. Early efforts, dating back to the work of Schwartz and Schlessinger [6], involved calculations of the T matrix at negative or complex [7] energies, where asymptotic boundary conditions need not be enforced, followed by analytic continuation or extrapolation to physical energies of interest. From these early methods a variety of techniques later emerged [8,9], which attempt to move the continuous spectrum of the Hamiltonian off the real energy axis, thereby enabling the computation of scattering quantities without specification of asymptotic boundary conditions. While such techniques have been refined into powerful tools for computing resonance states [10], their application to nonresonant electron scattering has been less successful. With applications in electron scattering largely confined to model potentials and simple atomic problems and the failure of any widely applicable, practical computational schemes to emerge, these approaches have largely remained a formal, if intriguing, curiosity.

The Feshbach optical potential formalism [11] provides a framework for singling out one or more discrete scattering channels and treating the remainder implicitly. By partitioning the total space into P- and Q-space parts, where P projects onto the asymptotic states of interest, one can derive an effective Hamiltonian that determines $P\Psi$. The effective Hamiltonian is the sum of PHP and

0031-9007/94/73(26)/3524(4)$06.00

an optical potential V_{opt} which takes the form

$$V_{\text{opt}} = \lim_{\varepsilon \to 0} PHQ \frac{1}{E - QHQ + i\varepsilon} QHP \,. \tag{1}$$

Feshbach partitioning can easily be used in conjunction with a close-coupling expansion. If P space includes all open channels, then the optical potential is real and can be expanded in a straightforward way as

$$V_{\text{opt}} = \sum_i PH|\Phi_i\rangle \frac{1}{E - E_i} \langle \Phi_i|HP \,, \tag{2}$$

where E_i and Φ_i are the eigenvalues and eigenfunctions of QHQ obtained in a basis of square-integrable terms. However, the optical potential of Eq. (2) is not appropriate for cases where Q contains open channels. In such cases, the optical potential should be complex, reflecting loss of flux to open channels included in Q. In contrast, V_{opt} of Eq. (2) is real and has singularities at energies in the discretized continuous spectrum of QHQ. This gives rise to the pseudoresonance behavior discussed above.

The idea of using complex coordinates to obtain a convergent representation of Eq. (2) was recently applied to a model problem (the radial limit of elastic $e^- +$ H scattering) by Bhatia, Schneider, and Temkin [12], who computed converged elastic cross sections above the ionization threshold. However, the complex rotation method they used must be modified to be practical for many-electron targets. That modification is outlined in this Letter, where we propose a simple scheme for implementing a complex basis function method to represent the optical potential in a form akin to that of Eq. (2), but which is valid at any real value of E.

The complex basis function technique [9] is a generalization of the coordinate rotation method [8]. The latter, for a many-body Coulomb system, simply corresponds to a scaling of all interparticle coordinates according to the prescription $r_{ij} \to r_{ij}e^{i\theta}, \theta > 0$. This transformation has the formal property of leaving the discrete spectrum of the Hamiltonian unchanged, while rotating the continuous spectra of the system into the complex energy plane. In order to appreciate the problems that arise when coordinate rotation is applied to many-electron systems in general [13] and to molecular targets in particular [14], consider a case where the target wave function is well described by a determinantal function of the form

$$\Psi_0 \sim A(\phi_1(r_1) \cdots \phi_N(r_N)) \tag{3}$$

After coordinate rotation, the function that gives the same value for the target energy is simply that given in Eq. (3) but with all coordinates replaced by $r_i e^{i\theta}$. The generic problem is that the core orbitals oscillate rapidly under this transformation and are difficult to represent by standard basis sets. In a molecular case, nonanalyticities appear at the nuclei, *vide infra,* and the difficulties are worse still. The basic difficulty was discovered some time ago in attempts to use the method to find resonance positions and lifetimes of complex atoms. A method was needed for applying complex rotation only to the coordinates of the outer valence electrons, while leaving the inner orbitals unchanged [13]. To accomplish that end, consider the matrix element

$$\langle \chi_i|H(\mathbf{r}e^{i\theta})|\chi_j\rangle \equiv \int_0^\infty r^2\,dr \int d\hat{r}\,\chi_i^*(\mathbf{r})H(\mathbf{r}e^{i\theta})\chi_j(\mathbf{r}) \tag{4}$$

where χ_i is an L^2 basis function. By distorting the contour for the radial integration in Eq. (4) onto a complex, rotated path, it can be shown that

$$\langle \chi_i|H(\mathbf{r}e^{i\theta})|\chi_j\rangle = e^{-3i\theta} \int_0^\infty r^2\,dr \int d\hat{r}\,\chi_i^* \times (\mathbf{r}e^{i\theta})H(\mathbf{r})\chi_j(\mathbf{r}e^{-i\theta}) \,, \tag{5}$$

that is, coordinate rotation is equivalent to using a real Hamiltonian and basis functions whose coordinates are scaled by $e^{-i\theta}$. Note that the usual definition of the scalar product must be modified so that there is no complex conjugation of the factor $e^{-i\theta}$ associated with the transformation. Generalizing to a many-electron problem, we can speed convergence by using real basis functions to expand the core orbitals and by employing complex basis functions only to describe valence electrons. This generalization of the method no longer corresponds to any simple scaling of the variables in the Hamiltonian.

For molecules, we must go farther. If we use the Born-Oppenheimer approximation, then the nuclear coordinates are treated as fixed parameters in the electronic Hamiltonian, not dynamical variables. However, if the nuclear coordinates are left real and the electronic coordinates scaled $\mathbf{r} \to \mathbf{r}e^{i\theta}$, then the electron-nuclear attraction terms in the Born-Oppenheimer Hamiltonian,

$$\sum_{i,\alpha} |\mathbf{r}_i e^{i\theta} - \mathbf{R}_\alpha|^{-1},$$

render it a nonanalytic operator. The solution again is to use complex basis functions, but to associate a scale factor $e^{-i\theta}$ with the orbital exponents and not the electronic coordinates [14]. For example, if one is using nuclear-centered Cartesian Gaussian functions, then one would simply choose functions of the form

$$\chi_{lmn}(\mathbf{r}, \alpha e^{-i\theta}, \mathbf{A}) = (x - A_x)^l (y - A_y)^m (z - A_z)^n \times \exp[-\alpha e^{-i\theta}(\mathbf{r} - \mathbf{A})^2] \tag{6}$$

to expand the valence orbitals, again defining the scalar product without complex conjugation. This prescription corresponds to an *asymptotic* scaling of the electronic coordinates which rotates the continuous spectrum of the Born-Oppenheimer Hamiltonian off the real axis.

In this Letter, we apply the complex basis function method only to the Q-space part of the partitioned wave function, to obtain a discrete, complex representation of the operator (E-QHQ), which can be inverted to give an approximation to the optical potential that is valid at any real energy E. One could use this complex optical potential in any conventional variational method. We use the complex Kohn method as previously developed [15], with a trial function that includes continuum functions only for those channels delineated in P space. This contrasts with previous attempts to use complex basis functions to solve the entire scattering problem without enforcing asymptotic boundary conditions [16]. The present approach is far less demanding of the complex variational basis, since the channels of interest are treated by a conventional formalism, and the complex basis expansion is only used to construct that part of the interaction potential that represents the effect of other channels on those between which we are computing the scattering amplitudes.

While there is no formal difficulty with forming a matrix representation of QHQ in a complex basis, practical considerations led us to a simplification which avoids the need to compute the Hamiltonian matrix elements involving complex functions directly. Without loss of generality, we can represent the complex matrix elements in the denominator of Eq. (1) by using a complete *real* basis to expand any complex orbitals that appear in the representation of QHQ. The denominator matrix takes the form

$$(E - QHQ)_{\tilde{m},\tilde{m}'} \approx E\delta_{\tilde{m},\tilde{m}'} - \sum_{n}^{N}\sum_{n'}^{N} \times (\tilde{m}|n\rangle\langle n|QHQ|n'\rangle\langle n'|\tilde{m}'), \quad (7)$$

where $|\tilde{m})$ and $|\tilde{m}')$ denote configurations containing complex orbitals. The sums over the real basis must be larger than the order of the denominator matrix. This is in fact a general procedure which can be applied to the calculation of resolvent matrix elements.

For an initial demonstration, we look at elastic $e^- +$ Li_2 scattering in overall ${}^2\Sigma_u^+$ symmetry. The Li_2 dimer has very low-lying excited states and an ionization potential of only 5 eV [17]. Moreover, from our previous study [18], we know that the ${}^2\Sigma_u^+$ partial cross section has a pronounced minimum near 0.1 eV which is sensitive to polarization effects and that the static-exchange approximation grossly overestimates the cross section in the energy range below 1 eV. In the present calculation, we describe the Li_2 molecule in its ground state by a self-consistent field (SCF) wave function, which has the configuration $\Phi_0 = 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2, {}^2\Sigma_g^+$, in a $4s4p1d$ contracted basis of Gaussian functions. The P-space function then has the form

$$P\Psi = \Phi_0 \otimes f_{\sigma_u}. \quad (8)$$

The variational basis used to expand f_{σ_u} consisted of the unoccupied σ_u orbitals obtained from the SCF calculation, an additional four s- and five p-type Gaussians on each atom, and continuum functions up to $l = 5$.

To construct the Q-space part of Ψ, we form $(N + 1)$-electron configuration state functions (CSF) as the direct product of a configuration obtained by promoting a $2\sigma_g$ valence electron into a complex orbital and an additional complex orbital to describe the scattered electron, i.e., we use terms of the form $1\sigma_g^2 1\sigma_u^2 2\sigma_g n\chi\, m\chi$, where the orbitals χ are formed from complex basis functions of the type defined in Eq. (6), orthogonalized to the occupied orbitals, and orthonormalized with respect to a scalar product defined without complex conjugation. It is important to note that each CSF contains *two* complex orbitals: we wish to rotate not only the continua associated with each excited state, but also the ionization continuum which is being represented by the discretized pseudostates.

In order to avoid the substantial recoding effort that would be required to calculate, transform, and process complex one- and two-electron integrals in an electronic structure code, we implemented Eq. (7) by expanding the complex orbitals in the basis of real virtual orbitals, i.e., we use the approximation

$$\chi_{lmn}(\mathbf{r}, \alpha e^{-i\theta}, \mathbf{A}) \approx \sum_{\beta} c_{\beta}^{\alpha} \chi_{lmn}(\mathbf{r}, b, \mathbf{A}), \quad (9)$$

where the coefficients c_{β}^{α} are simply the overlaps between the complex and real functions. To insure that no resulting error is introduced, we must be certain that the real basis is large enough to represent the complex orbitals. In these calculations, we picked approximately half of the original real basis functions to make complex via the transformation $\alpha \rightarrow \alpha e^{-i\theta}$, while using the entire basis of real orbitals to carry out the expansion in Eq. (9). This approximation allows us to form QHQ in a real basis of CSF's without modifying any structure codes and subsequently transform to the complex basis representation using only the complex overlap matrix elements. We can represent the transformation symbolically as

$$\langle\alpha\beta|QHQ|\gamma\delta\rangle_{\mathrm{complex}} = \sum_{\kappa\lambda\mu\nu} c_{\kappa}^{\alpha} c_{\lambda}^{\beta} \times \langle\kappa\lambda|QHQ|\mu\nu\rangle_{\mathrm{real}} c_{\mu}^{\gamma} c_{\nu}^{\delta}, \quad (10)$$

which not coincidentally has the form of a two-electron integral transformation. We carry out an analogous transformation to obtain the complex matrix elements of PHQ and then construct the optical potential by simply inverting the complex matrix $(E\text{-}QHQ)$.

Figure 1 shows the ${}^2\Sigma_u^+$ elastic cross section from 0.02 to 10 eV. In the frozen core approximation we are using, the first excited state of Li_2 lies at 0.7 eV, and the ionization energy is 4.9 eV. Three results are plotted. The static-exchange result, which is obtained by dropping the optical potential, grossly overestimates the cross section in the low-energy region below the first excited state. The static-exchange interaction is incapable of binding an electron in ${}^2\Sigma_u^+$ symmetry ($\mathrm{Li}_2{}^-$ is bound in this symmetry), but produces instead a spurious low-energy shape resonance. Two curves from calculations employing an optical potential are plotted, one obtained solely with real functions and the other corresponding

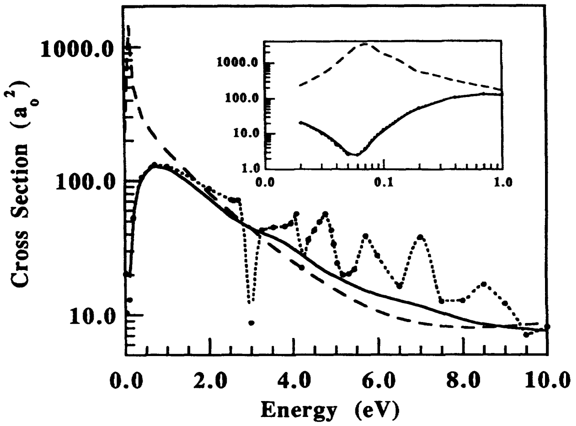

FIG. 1. Elastic cross sections for $e^- + \text{Li}_2$ scattering in $^2\Sigma_u^+$ symmetry. Solid curve: complex optical potential result; dotted curve with data points: optical potential results using real basis function; dashed curve: static-exchange result. Inset: cross sections in the low energy region below 1 eV.

to a rotation angle $\theta = 20°$. It is gratifying to see that the two curves are virtually identical in the region below the first excitation threshold, as of course they should be, while the complex basis set results remain smooth as the energy increases up to and above the ionization threshold. In contrast, the optical potential results obtained with real functions display characteristic pseudoresonance behavior in this region. We have varied the rotation angle and verified that the results are indeed stable. Figure 2 shows the complex eigenvalue spectrum of *QHQ* corresponding to the results plotted in Fig. 1. There is evidently no tendency for eigenvalues to bunch near pseudostate thresholds in the ionization continuum and the eigenvalues that represent the ionization cut move well into the complex plane.

In conclusion, the complex optical potential method we have outlined is clearly capable of extracting useful cross section information from finite pseudostate close-coupling calculations at energies where traditional methods can be plagued by spurious pseudoresonances. By relying on a complex basis function formalism, rather than coordinate rotation, we have demonstrated a method that is practical and readily applicable to many-electron atomic or molecular targets. And finally, we have shown that, by reexpanding the complex basis functions in a set of real functions with complex overlap coefficients, we can construct the quantities of interest without extensively modifying or rewriting standard electronic structure codes.

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

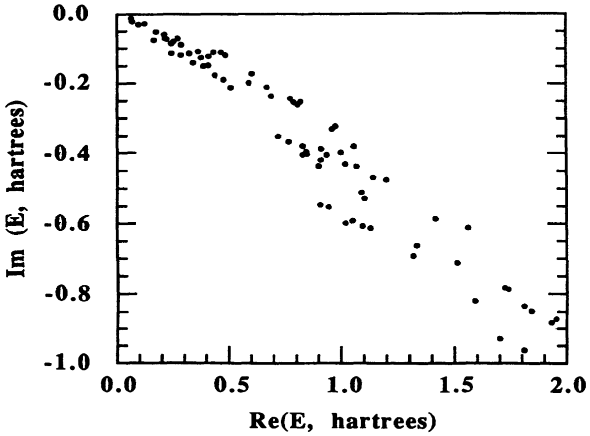

FIG. 2. Complex eigenvalue spectrum of *QHQ* obtained with a rotation angle of 20°.

[1] P. G. Burke, D. F. Gallaher, and S. Geltman, J. Phys. B **2**, 1142 (1969).
[2] P. G. Burke and J. F. B. Mitchell, J. Phys. B. **6**, 320 (1973).
[3] D. H. Oza and J. Callaway, Phys. Rev. **27**, 2840 (1983); D. H. Oza, Phys. Rev. **30**, 1101 (1984).
[4] I. Bray and A. T. Stelbovics, Phys. Rev. Lett. **69**, 53 (1992); **70**, 746 (1993).
[5] T. T. Scholz, H. R. J. Walters, and P. G. Burke, J. Phys. B **23**, L467 (1990).
[6] L. Schlessinger and C. Schwartz, Phys. Rev. Lett. **16**, 1173 (1966); L. Schlessinger, Phys. Rev. **168**, 1411 (1968).
[7] F. A. McDonald and J. Nuttall, Phys. Rev. Lett. **23**, 361 (1969); Phys. Rev. A **4**, 1821 (1971).
[8] J. Nuttall and H. L. Cohen, Phys. Rev. **188**, 1542 (1969); T. N. Rescigno and W. P. Reinhardt, Phys. Rev. A **10**, 2240 (1974); T. N. Rescigno and V. McKoy, Phys. Rev. A **12**, 522 (1975); S. I. Chu and W. P. Reinhardt, Phys. Rev. Lett. **39**, 1195 (1977).
[9] T. N. Rescigno and W. P. Reinhardt, Phys. Rev. A **8**, 2828 (1973); T. N. Rescigno and C. W. McCurdy, Phys. Rev. A **31**, 624 (1985).
[10] C. W. McCurdy, in *Autoionization*, edited by A. Temkin (Plenum, New York, 1985), p. 135; W. P. Reinhardt, Annu. Rev. Phys. Chem. **33**, 223 (1982).
[11] H. Feshbach, Ann. Phys. (Paris) **5**, 357 (1958); **19**, 287 (1962).
[12] A. K. Bhatia, B. I. Schneider, and A. Temkin, Phys. Rev. Lett. **70**, 1936 (1993).
[13] T. N. Rescigno, C. W. McCurdy, and A. E. Orel, Phys. Rev. A **17**, 1931 (1978).
[14] C. W. McCurdy and T. N. Rescigno, Phys. Rev. Lett. **41**, 1364 (1978).
[15] See, for example, T. N. Rescigno, in *Electronic and Atomic Collisions, Proceedings of the XVII ICPEAC, Invited Papers,* edited by W. R. MacGillivray, I. E. McCarthy, and M. C. Standage (IOP, Bristol, 1992).
[16] T. N. Rescigno and C. W. McCurdy, Chem. Phys. Lett. **140**, 232 (1987).
[17] D. D. Konowalow and J. L. Fish, Chem. Phys. **84**, 463 (1984).
[18] T. J. Gil, C. W. McCurdy, T. N. Rescigno, and B. H. Lengsfield, Phys. Rev. A **47**, 255 (1993).