

Electron-molecule close coupling with correlated target wave functions: Application to impact dissociation of F_2

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An analysis of the close-coupling method as it is traditionally formulated for electron-scattering problems shows that it can give rise to spurious resonances at intermediate energies when multiconfiguration target states are used. These resonances are associated with excited states of the target that are not explicitly included in the close-coupling expansion. We develop a modification of the close-coupling technique that allows one to isolate and systematically eliminate terms from the total wave function which are responsible for the spurious behavior. We have applied this technique to the study of electron-impact dissociation of F_2 through its two lowest excited states. The complex Kohn variational calculations we have performed on this system incorporate accurate, multiconfiguration descriptions of the target wave functions.

I. INTRODUCTION

Many theoretical methods for studying electron-impact excitation of atoms and molecules are based on the close-coupling formalism [1], in which the total $(N+1)$ -electron wave function is expanded as a sum of (antisymmetrized) products of N -electron target wave functions and single-electron channel orbitals. In principle, this sum should include all energetically open channels. However, as the incident energy in a collision is increased toward the ionization energy, the number of open channels approaches infinity. Practical considerations generally limit the number of target states that can be included in a close-coupling calculation. Moreover, in many applications one is only interested in cross sections for excitation to low-lying excited states and physical considerations can be used as a guide in determining which excited states should be explicitly included in the close-coupling expansion. Nonetheless, one frequently requires these cross sections well above the thresholds of other low-lying states, so it is natural to inquire about the effect of neglected channels at intermediate collision energies and to examine whether there is anything about the close-coupling formulation that might lead to pathological results.

Fundamental questions about the convergence of close-coupling expansions pose formidable theoretical problems even for the simplest atomic systems. Our interest here is in electron-molecule collisions. In contrast to the electron-atom problem, the entire body of *ab initio* studies that have treated electronic excitation of molecules is quite small [2] and the target states employed have been, with a few recent exceptions [3,4], quite simple. Our purpose here is to investigate aspects of the coupled-channel problem which arise when multiconfiguration target states are employed. Although the focus will be on molecular problems, the points we address in this study are applicable to electron-atom collisions as well. The particular computational method we

employ is the complex Kohn variational method [5], but this fact will not limit the treatment. The aspects of the close-coupling formulation we will discuss are quite general and the methods we develop here can be incorporated into other expansion and/or numerical integration methods.

With the exception of single-electron atoms and ions, exact target states are not known and approximate wave functions must be used. These are generally expressed as linear combinations of configuration state functions (CSF's) built from a specified list of "target" orbitals. To simplify the formulation of the collision problem and the evaluation of many-electron matrix elements, the channel scattering functions are generally required to be orthogonal to all of the target orbitals. It is well known that this strong orthogonality constraint can lead to physically incorrect results if it is not relaxed. Indeed, early calculations [6,7] on electron-impact dissociation of H_2 were subsequently shown to be incorrect for precisely this reason. The standard remedy [8-10] for removing the orthogonality constraints is to include $(N+1)$ -electron functions or "penetration terms" built exclusively from target orbitals in the close-coupling expansion. This set of functions is chosen by taking the direct product of the target orbitals and all the N -electron configurations used in building the target wave functions. One then retains all such terms that are consistent with the Pauli exclusion principle and that have the same symmetry as the total wave function.

Because the coefficients of the individual penetration terms are chosen variationally, this procedure can, in the case of multiconfiguration target states, provide more flexibility than the minimum needed to compensate for any orthogonality constraints and can actually incorporate additional correlation effects. In effect, the penetration terms built from N -electron configurations that contribute weakly to the target states explicitly chosen can represent excited pseudostates and can give rise to broad unphysical resonances at intermediate energies where no

structure is expected.

We can illustrate this phenomenon with the simple example of elastic scattering of an electron from H_2 in $^2\Sigma_g^+$ symmetry. For the ground-state $X^1\Sigma_g^+$ wave function, we use a simple configuration-interaction (CI) wave function of the form $(C_1 1\sigma_g^2 + C_2 1\sigma_u^2)$, with $C_1=0.9968$ and $C_2=0.0799$. We included the single penetration term $1\sigma_u^2 1\sigma_g$ in the trial wave function to relax the orthogonality constraint on the scattering wave function with respect to the $1\sigma_g$ orbital and used the complex Kohn method to solve for the elastic cross section. The result is shown in Fig. 1. There is evidently a broad resonance near 16 eV. Elastic scattering cross sections obtained with a simple self-consistent-field (SCF) target wave function, which differs only slightly from the target CI wave function we used, show no such structure. When the calculation is performed without the $1\sigma_u^2 1\sigma_g$ term, the resonance disappears. This result is also shown in Fig. 1.

The $1\sigma_u^2 1\sigma_g$ term can be thought of as a doubly excited negative-ion term whose parent is the $(1\sigma_g 1\sigma_u)$, $b^3\Sigma_u^+$ state of H_2 . This state is physically open at energies above 10 eV, but is not properly included in the single-channel calculation. To demonstrate this, we performed a third calculation in which the $X^1\Sigma_g^+$ and $b^3\Sigma_u^+$ states were both included in the open-channel portion of the trial function and the single-penetration term was again retained. The resulting elastic cross section, shown in Fig. 1, is evidently quite close to the smooth result obtained from the single-channel calculations in which the penetration term was dropped. This simple example serves to show how excited states, which are not explicitly included in the close-coupling expansion, can enter the problem in an indirect way when correlated target wave functions are used. In this simple case, it is possible to easily identify the cause of the trouble and remove the term responsible for this behavior from the single-channel trial function.

In this paper we will show that it is possible to develop a procedure for incorporating the penetration terms in

the expansion of the total wave function in fixed linear combinations that are consistent with the approximate target state that are being employed. This contraction of the Hilbert-space component of the total wave function then allows us to develop a procedure for identifying and eliminating the terms in the trial wave function that will give rise to pseudoresonances. This procedure effectively allows one to meaningfully apply the close-coupling method at intermediate energies even when elaborate multireference target states are employed.

To illustrate this discussion, we present cross sections for electron-impact dissociation of F_2 from 5 to 30 eV through its first excited ($^3\Pi_u$ and $^1\Pi_u$) states. We chose to study F_2 for several reasons. The dissociation cross sections turn out to be quite small and are consequently very sensitive to approximations made in the dynamics. Moreover, the total wave function used in the scattering problem must reflect the fact that the F_2^- negative ion is bound in $^2\Sigma_u^+$ symmetry [11]. Electron-target correlation is consequently very important in this system. Finally there is a need for accurate $e^- + F_2$ dissociation cross sections in modeling several important types of lasers (HF, KrF) and only one previous theoretical study has been performed using the distorted-wave approximation [12].

The details of our formulation will be presented in Sec. II. Section III presents the results of our calculations on $e^- + F_2$. We conclude with a brief discussion.

II. THEORY

The scattering of an electron by an N -electron target can be described by a wave function of the form

$$\Psi_\Gamma = \sum_{\Gamma'} \mathcal{A} \chi_{\Gamma'} F_{\Gamma'} + \sum_{\mu} d_{\mu}^{\Gamma} \Theta_{\mu}, \quad (1)$$

where $\chi_{\Gamma'}$ is a normalized N -electron target wave function, $F_{\Gamma'}$ is a one-electron function which describes the scattering of an electron, incident in channel Γ , into channel Γ' , and \mathcal{A} antisymmetrizes the product $\chi_{\Gamma'} F_{\Gamma'}$. The target states are expressed as linear combinations of configuration state functions,

$$\chi_{\Gamma} = \sum_i C_i^{\Gamma} \Phi_i, \quad (2)$$

which are in turn constructed from a set of orthonormal orbitals, φ_{σ} $\{\sigma=1, n\}$. The functions Θ_{μ} , which make up the Hilbert-space component of the total wave function, are $(N+1)$ -electron functions constructed from the same set of molecular orbitals φ_{σ} , while the functions $F_{\Gamma'}$ are, by construction, orthogonal to the set φ_{σ} . The orthogonality of these functions ensures that the first term in Eq. (1) is orthogonal to the Hilbert-space component of Ψ . The functions Θ_{μ} are introduced in order to allow the scattering function to penetrate the target wave function, that is, to compensate for the orthogonality constraint imposed on $F_{\Gamma'}$, and to introduce correlation and/or polarization effects into the scattering wave function.

The expansion given by Eq. (1) is quite general and is common to many close coupling formulations [8–10]. In algebraic variational methods, such as the complex Kohn

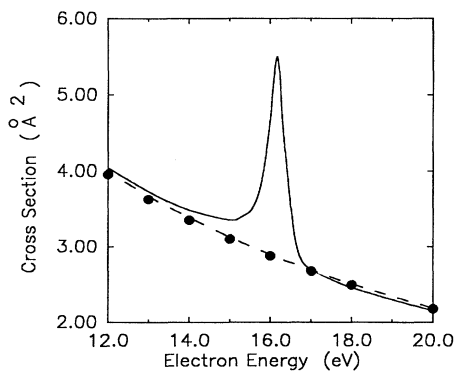


FIG. 1. $e^- + H_2 \Sigma_g^+$ elastic cross section. Solid curve, static exchange plus penetration term; dashed curve, static exchange without penetration term; solid circles, two-channel calculation including penetration term.

method, which we employ in our electron-molecule scattering work [5,13], the one-electron functions $F_{\Gamma\Gamma'}$ are further expanded in terms of a complementary set of molecular orbitals, φ_s $\{s = n + 1, m\}$ as well as continuum functions that satisfy appropriate incoming and outgoing asymptotic boundary conditions. The expansion coefficients are determined from a variational principle. However, the particular method employed to determine the scattering functions is not central to this discussion and our remarks will also apply to methods in which the functions $F_{\Gamma\Gamma'}$ are determined by numerical integration. We shall refer to methods which use a wave-function expansion of the type given by Eq. (1) as close-coupling plus correlation (CCPC) methods.

It is convenient to adopt the language of Feshbach partitioning theory [14] at this point. The open-channel component of the total wave function is assigned to P space and the variational terms weighting the $(N + 1)$ -electron CSF's, Θ_μ , are assigned to Q space. It is the contribution of these $(N + 1)$ -electron terms which can give rise to spurious features in the computed cross sections when certain open channels have not been included in the close-coupling expansion.

Our intention is to introduce a formalism which can systematically eliminate the terms which give rise to this spurious behavior. Instead of the general CCPC expansion, we introduce a multiconfiguration-close-coupling (MC-CC) expansion of the total wave function where the terms comprising Q space are restricted to the penetration terms which arise by taking the direct product of the target wave function and occupied orbitals:

$$\begin{aligned} \Psi_\Gamma &= \sum_{\Gamma'} \mathcal{A} \chi_{\Gamma'} F_{\Gamma\Gamma'} + \sum_{\Gamma', \sigma} d_{\sigma}^{\Gamma\Gamma'} \mathcal{A} \chi_{\Gamma'} \varphi_\sigma \\ &= \sum_{\Gamma'} \mathcal{A} \chi_{\Gamma'} F_{\Gamma\Gamma'} + \sum_{\sigma, \Gamma'} d_{\sigma}^{\Gamma\Gamma'} \sum_{\mu} T_{\sigma\mu}^{\Gamma'} \Theta_\mu \\ &= \sum_{\Gamma'} \mathcal{A} \chi_{\Gamma'} F_{\Gamma\Gamma'} + \sum_{\sigma, \Gamma'} d_{\sigma}^{\Gamma\Gamma'} \omega_{\sigma}^{\Gamma'} . \end{aligned} \quad (3)$$

Thus there will be one Q -space term for each *partially* occupied orbital in the target wave function $\chi_{\Gamma'}$ (the product $\mathcal{A} \chi_{\Gamma'} \varphi_\sigma$ vanishes if φ_σ is doubly occupied in every CSF used in the expansion of $\chi_{\Gamma'}$). The Q -space configurations, Θ_μ used in a CCPC expansion are generated by taking the direct product of an occupied orbital and every CSF appearing in the target wave function, whereas the Q -space terms appearing in the MC-CC wave function are the direct product of occupied orbitals and the linear combination of CSF's that define the target states. Thus, penetration terms that appear in the multiconfiguration close-coupling wave function can be expressed as a contraction of the Q -space terms in the CCPC trial function.

While it is a simple matter to build the list of $(N + 1)$ -electron CSF's Θ_μ , needed in the CCPC wave function that are consistent with the Pauli exclusion principle, the construction of the transformation matrix, $T_{\sigma\mu}^{\Gamma'}$ used to build the Q -space CSF's employed in the MC-CC wave function requires some additional effort. However, the construction of these terms is neither a formal nor a computational problem of note. In fact, we show in Appen-

dix A that this matrix can be constructed by modifying the transition-density code present in most modern electronic-structure packages.

The basic idea underlying the close-coupling method is that the set of target states included in the expansion of the total wave function can be extended toward completeness. In practice, the expansion must be severely truncated so that physical considerations must dictate which target states to include. One consequence of this truncation, as noted previously, is that spurious resonances can arise in the cross sections obtained in CCPC calculations as a consequence of excluding certain open channels from the close-coupling expansion. The consequence of truncating the CCPC expansion is that there may be terms in Q space which are the direct product of major components of missing open-channel wave functions and occupied orbitals. These terms can be identified with eigenvalues of the Q -space Hamiltonian, which give rise to spurious resonances. There are also poles in the optical potential constructed from the Q -space Hamiltonian associated with open channels which have been included in the close-coupling expansion, but these terms do not give rise to any spurious features in the computed cross sections. The contraction of Q space inherent in the multiconfiguration close-coupling Hamiltonian eliminates most, but not all, of these spurious poles. In order to understand the types of terms which arise by contracting Q space, consider a single-channel (static-exchange) calculation, which employs the following target wave function:

$$\chi = C_1 \mathcal{A} \varphi_1^2 + C_2 \mathcal{A} \{ \varphi_2, \varphi_3 \}_{\text{singlet}} , \quad (4)$$

where $C_1 \cong 0.9$ and $C_2 \cong 0.4$. Then the unnormalized Q -space CSF's would be

$$\begin{aligned} \omega_1 &= C_2 \mathcal{A} \varphi_1 \{ \varphi_2, \varphi_3 \}_{\text{singlet}} , \\ \omega_2 &= C_1 \mathcal{A} \varphi_1^2 \varphi_2 - (1/\sqrt{2}) C_2 \mathcal{A} \varphi_2^2 \varphi_3 , \\ \omega_3 &= C_1 \mathcal{A} \varphi_1^2 \varphi_3 - (1/\sqrt{2}) C_2 \mathcal{A} \varphi_2 \varphi_3^2 . \end{aligned} \quad (5)$$

The direct product of the strongly occupied orbital, φ_1 , with the target wave function can be associated with an excited state whose principal CSF is $\varphi_2 \varphi_3$, while the direct products of the weakly occupied orbitals, φ_2 and φ_3 , and the target wave function give rise to Q -space CSF's associated with the target wave function itself. The norm of these direct-product CSF's also reflects this dichotomy of terms. The terms associated with the target wave function have norms which are close to 1, while the term associated with an excited state will have a norm close to zero. The excited-state terms that lead to spurious resonances are now easily identified and can be removed from Q space.

This procedure is based upon the notion that the excited states, associated with the small components of the physical states included, are not strongly coupled to those states that have been included in the trial function. We wish to emphasize that we are not now referring to spectroscopic states of the target which may have physical resonances associated with their thresholds, but rather

the broad structures generated by pseudostates that occur at energies above the ionization threshold of the target, where no such behavior is expected.

One can test this procedure by performing close-coupling plus correlation calculations at low incident-electron energies, where all of the penetration terms can be included in the problem, and by comparing the results to MC-CC calculations with and without terms being excluded from Q space. Such a series of calculations will be discussed in Sec. III.

A note about the target orbitals bears further comment. In the examples we have considered, as well as in the calculations we will describe next, the target wave functions are assumed to have a compact representation in terms of the orbital set chosen so that it is easy to identify a principal configuration for each target state. If this were not the case, then it might be necessary to carry out a rotation of the target orbitals, on a state-by-state basis, to obtain the desired representation of the ω basis. Such a procedure, which is described in Appendix B, guarantees that the MC-CC results will not depend on the way in which the target orbitals are defined.

III. CALCULATIONS

We have applied the formalism outlined in the preceding section to study electron-impact dissociation of F_2 . This is an important process in electrically excited gas mixtures containing fluorine and plays an important role in the modeling of several gas lasers.

Fluorine is a closed-shell molecule with a $^1\Sigma_g^+$ ground state. The two lowest excited electronic states are the dissociative $^3\Pi_u$ and $^1\Pi_u$ states which correspond, in a simple molecular-orbital picture, to the promotion of an electron from the doubly occupied π_g orbital to the low-lying $3\sigma_u$ orbital. Previous theoretical calculations [15] place the vertical excitation energies of these states from the ground state at 3.32 and 4.64 eV, respectively. The only previous theoretical investigation of dissociative excitation of F_2 is the distorted-wave study of Fliflet,

McKoy, and Rescigno [12], which considered excitation of the $^3\Pi_u$ state. The cross sections they found were rather small, with a peak value of $\sim 1.5 \times 10^{-17}$ cm² at an energy of 10 eV. No previous study of excitation of the $^1\Pi_u$ state has been carried out, but since the transition moment between this state and the ground state is known to be anomalously small in the Franck-Condon region [15], one also expects the excitation cross section to be weak.

We have carried out three-state calculations including the $1^1\Sigma_g^+$, $1^3\Pi_u$, and $1^1\Pi_u$ states using the complex Kohn variational method. This technique has been fully discussed in preceding publications [4,5,13,16] and these derivations will not be repeated here.

The target wave functions were determined in the following manner. We began with a SCF calculation on the ground state of F_2 using the basis of contracted Gaussian functions given in Table I. All calculations were carried out at the equilibrium internuclear separation of 2.68 bohr. We then carried out a configuration-interaction calculation which included all single excitations from the two dominant configurations for the ground state ($3\sigma_g^2$ and $3\sigma_u^2$) and the excited $^1\Pi_u$ state ($\pi_g^3 3\sigma_u$ and $\pi_u^3 3\sigma_g$) [15]. From this calculation we obtained natural orbitals of the averaged one-particle density matrices for the ground and $^1\Pi_u$ states. This orbital set was truncated on the basis of occupation number to a final target basis consisting of four σ_g , four σ_u , two π_g , and two π_u orbitals. To generate the target wave functions for the scattering calculations, the CI calculations were repeated using this compact set of natural orbitals. The final excitation energies we obtained for the $X \rightarrow ^3\Pi_u$ and $X \rightarrow ^1\Pi_u$ transitions were 3.28 and 4.56 eV, respectively, which are in good agreement with the values obtained by Cartwright and Hay [15].

We augmented the functions listed in Table I with additional Gaussian functions, depending on the total symmetry being studied, in order to generate the square-integrable basis orbitals for the complex Kohn variational calculations. These additional functions are listed in Table II. Finally, we included partial-wave continuum

TABLE I. Contracted Gaussian basis for F_2 target states.

	Fluorine				D type
	S type	P type			
9994.79	0.006 431	44.3555	0.042 011	0.9	1.0
1506.03	0.048 757	10.082	0.261 899		
350.269	0.233 065	2.9959	0.797 662		
104.053	0.785 549	0.9383	1.0		
		0.2733	1.0		
34.8432	0.802 728				
4.3688	0.317 752	0.07	1.0		
12.2078	1.0	0.02	1.0		
1.2078	1.0				
0.3634	1.0				
0.036	1.0				

TABLE II. Uncontracted supplementary basis for augmenting basis in Table I.

Fluorine S type	Fluorine D type	Bond-center S type	Bond-center P type	Bond-center D type
5.0	5.0	0.1	0.15	0.015
0.12	1.5	0.036	0.05	0.005
	0.5	0.012	0.01	
	0.15	0.004	0.0065	
	0.05		0.002	

basis functions up to $l=6$ in our calculations. Details about the numerical schemes used in the evaluation of bound-free and free-free matrix elements [17], as well as other technical aspects of the complex Kohn method [4,13], have been given elsewhere.

The total and differential cross sections we report include contributions from ${}^2\Sigma_g^+$, ${}^2\Sigma_u^+$, ${}^2\Pi_g$, ${}^2\Pi_u$, and ${}^2\Delta_g$ symmetry. We carried out both CCPC calculations using all the Q -space penetration terms generated from the occupied target orbitals, as well MC-CC calculations using the Q -space contraction scheme previously outlined. We shall use the case of total ${}^2\Sigma_g^+$ symmetry to illustrate the way the calculations were performed. Because the spacial symmetries of the target states are Σ_g^+ and Π_u , the only penetration terms we need consider in this symmetry are those formed from the direct product of a target-state configuration and target orbitals of σ_g , π_{ux} , or π_{uy} symmetry. Moreover, the $1\sigma_g$ and $2\sigma_g$ orbitals were doubly occupied in all the target configurations, so they generate no Q -space terms. The ground state gives rise to two Q -space vectors, $\omega_{3\sigma_g}^{1\Sigma_g^+}$ and $\omega_{4\sigma_g}^{1\Sigma_g^+}$, while the excited states give rise to the vectors $\omega_{1\pi_{ux}}^{1\Pi_{ux}}$, $\omega_{2\pi_{ux}}^{1\Pi_{ux}}$, $\omega_{1\pi_{ux}}^{3\Pi_{ux}}$, $\omega_{2\pi_{ux}}^{3\Pi_{ux}}$ + ($x \leftrightarrow y$). Because the ground state of F_2 is dominated by the configuration (core) $1\pi_u^4 1\pi_g^4 3\sigma_g^2$, the vector $\omega_{4\sigma_g}^{1\Sigma_g^+}$ will have a norm close to unity, whereas the norm of $\omega_{3\sigma_g}^{1\Sigma_g^+}$ will be small. The norms of the vectors generated from the $1\pi_u$ orbitals will also be small, since the principal occupancy in the excited Π_u states is (core) $1\pi_u^4 1\pi_g^3 3\sigma_g^2 3\sigma_u$. In the MC-CC calculations we performed, the ω vectors with small norms were not used in contracting the Q -space Hamiltonian. Similar considerations were used in carrying out calculations in other symmetries.

The ${}^2\Sigma_u^+$ component of the total wave function is more complicated and requires special consideration. The F_2^- ion is actually bound at internuclear distances greater than 2.68 a.u. in ${}^2\Sigma_u^+$ symmetry [11]. However, previous state-exchange calculations on $e^- + F_2$ show a broad shape resonance in the elastic cross section at 2.2 eV in ${}^2\Sigma_u$ symmetry [18]. This is a reflection of the fact that the frozen-core potential is not attractive enough to bind an electron and instead produces an unbound resonance state. We found that the three-state MC-CC calculations lower this resonance energy, but still do not provide sufficient core relaxation to make it disappear entirely.

As a result, there is an artificially large enhancement in the ${}^2\Sigma_u^+$ -symmetry component of the excitation cross sections. This phenomenon was also noticed in the early distorted-wave calculations [12] and was dealt with in a somewhat *ad hoc* fashion by modifying the distorted-wave potential to make it more attractive. The uncontracted CCPC calculations we performed did produce a bound F_2^- state (the lowest eigenvalue of H_{QQ} is, in fact, the F_2^- ground state), at the expense of producing pseudo-resonances at higher energies. This suggested a simple modification of the MC-CC procedure to handle cases where there is a bound negative ion. We simply determine the lowest eigenvalue of the Q -space Hamiltonian and add the corresponding eigenvector to the set of transformation vectors used to contract H_{QQ} . We found that MC-CC calculations performed with this one additional vector give smooth cross sections that were very close to the CCPC results at energies away from pseudo-resonances in the latter.

In Figs. 2 and 3 we show the total cross sections obtained for the $1^1\Sigma_g^+ \rightarrow 1^3\Pi_u$ and $1^1\Sigma_g^+ \rightarrow 1^1\Pi_u$ transitions using both the CCPC method and the MC-CC technique with selected transformation vectors deleted, as previously outlined. Evidently, the modified MC-CC technique does a good job of averaging over the pseudo-resonances that are evident in the CCPC cross section and extracts the underlying background results.

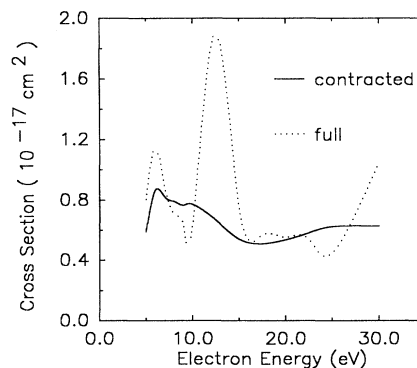


FIG. 2. Total cross sections for $e^- + F_2$, $X^1\Sigma_g^+ \rightarrow 1^3\Pi_u$. Comparison of CCPC and MC-CC results.

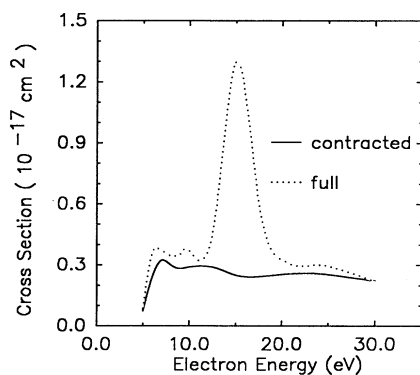


FIG. 3. As in Fig. 2, for $X^1\Sigma_g^+ \rightarrow 1^1\Pi_u$.

In Fig. 4 we show the MC-CC results for the two individual transitions along with the total dissociation cross section. The singlet-triplet contribution is seen to dominate the total dissociation cross section. It is interesting that the cross sections we have obtained here are approximately $2\frac{1}{2}$ times smaller than the distorted-wave results of Fliflet *et al.* [12], which are the only other theoretical results available for comparison. Fliflet *et al.* speculated that the distorted-wave results were likely to be 2–3 times too large, based on results from other systems and limited experimental evidence for F_2 . Our calculations appear to confirm these older estimates.

In Figs. 5 and 6 we present differential cross sections for the $1^1\Sigma_g^+ \rightarrow 1^3\Pi_u^+$ and $1^1\Sigma_g^+ \rightarrow 1^1\Pi_u$ transitions. These too are typical of what one expects to find: the singlet-triplet cross sections show significant scattering at large angles, associated classically with small impact parameters, while the singlet-singlet cross sections do not show the large backward peak.

IV. DISCUSSION

The intermediate-energy region in electron-scattering problems is the most difficult to treat theoretically be-

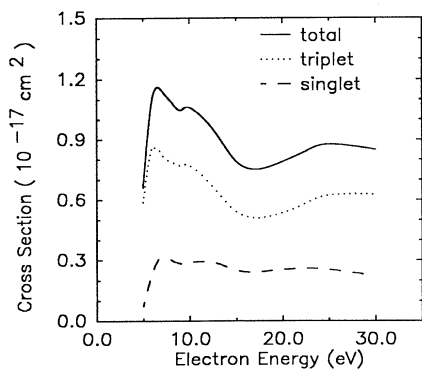


FIG. 4. MC-CC total cross sections for $e^- + F_2$.

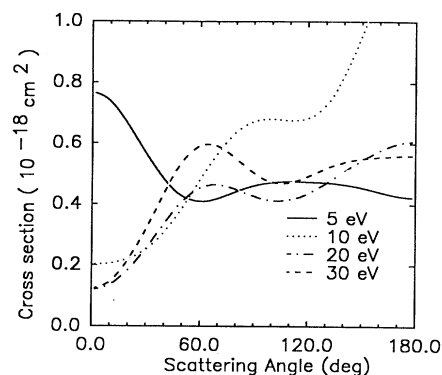


FIG. 5. Differential cross sections for $e^- + F_2$, $X^1\Sigma_g^+ \rightarrow 1^3\Pi_u$.

cause the number of open channels is infinite, but the energy may not be high enough for perturbative methods to be valid. We have analyzed the close-coupling method as it is traditionally formulated and we have shown that it can produce spurious structures when correlated target wave functions are used. These structures are associated with open channels that are not explicitly delineated in the close-coupling expansion, but which nevertheless enter the trial wave function indirectly through correlation terms. As the description of the target wave functions is improved, the number of such pseudoresonances will grow.

We have outlined a general method for contracting the penetration terms into linear combinations consistent with the approximate target-state wave functions being employed. This makes it possible to systematically identify and eliminate the terms responsible for the spurious structure. We have illustrated this procedure with a simple $e^- + H_2$ example and extensive calculations on the $e^- + F_2$ system.

We should mention that other methods have been proposed for dealing with the problems we have raised. Burke and co-workers [19] have proposed an intermediate-energy R -matrix theory in which one takes

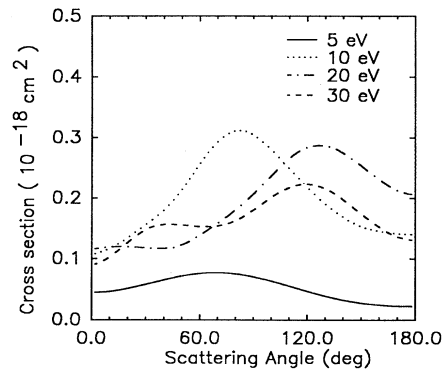


FIG. 6. As in Fig. 5, for $X^1\Sigma_g^+ \rightarrow 1^1\Pi_u$.

the opposite approach from that proposed here. Namely, one tries to effectively saturate the continuum by incorporating many configurations built from discretized pseudostates [20,21]. The idea is to make the number of pseudoresonances in the intermediate-energy region so dense that a meaningful average can be taken. The claim is that this technique will converge, in principle, to the correct result. This idea has only been applied to the simplest atomic systems. It is not clear whether the approach can be made practical for complicated atomic or molecular targets. The method we have proposed represents a practical, approximate alternative.

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APPENDIX A

In this section we develop an algorithm to construct the transformation matrix that we use to contract the Q -space configurations which appear in our trial scattering function. Such a (nonsquare) transformation matrix can be easily constructed if we expand the CSF's in terms of determinants, but a more efficient scheme is desired if we wish to exploit the power of the current generation of electronic-structure codes. We show that one can devise such a method by modifying the density code present in most state-of-the-art electronic structure packages.

We need consider only that portion of the trial scattering function, χ_t , which gives rise to penetration terms in the MC-CC method

$$\Psi_t = \mathcal{A}\chi_t(N)f(N+1) \quad (\text{A1})$$

where the one-electron scattering function is now expanded only in terms of occupied orbitals, $f = \sum_{\sigma} C_{\sigma} \varphi_{\sigma}$. We can rewrite this portion of the trial scattering function as

$$\Psi_t = \sum_{\sigma} C_{\sigma} \sum_{\mu} T_{\mu\sigma} \Theta_{\mu}(N+1), \quad (\text{A2})$$

where we now have a sum over antisymmetric $(N+1)$ -electron configuration-state functions. To obtain elements of the transformation matrix $T_{\mu\sigma}$, we only need consider the contributions from one of the occupied orbitals,

$$T_{\mu\sigma} = \langle \mathcal{A}\chi_t \varphi_{\sigma} | \Theta_{\mu} \rangle. \quad (\text{A3})$$

This matrix element is obtained by replacing the occupied orbital φ_{σ} from the one-electron scattering function, f , with an arbitrary scattering orbital φ_s . This arbitrary scattering orbital is orthogonal to all of the occupied orbitals. This orbital is used to represent the one-electron scattering function f in the computation of the transition density matrix that we will use to construct the $T_{\mu\sigma}$ transformation matrix. We then compute the one-particle transition density matrix between these functions:

$$\begin{aligned} d^{\mu}(1,1') &= \langle \Theta_{\mu} | \mathcal{A}\chi_t \varphi_s \rangle_1 \\ &\equiv \int \Theta_{\mu}(1, \dots, N+1) \mathcal{A}\chi_t(1', \dots, N) \\ &\quad \times \varphi_s(N+1) d2, \dots, dN+1. \end{aligned} \quad (\text{A4})$$

The nonzero matrix elements of this density must involve the scattering orbital φ_s since none of the $(N+1)$ -electron CSF's comprising Q space, Θ_{μ} , contain this orbital. Thus, the only nonzero elements in this matrix are of the form $d^{\mu}_{\sigma s}$. We will show that these density matrix elements are components of the transformation matrix we need to contract Q space, that is

$$T_{\mu\sigma} = d^{\mu}_{\sigma s}. \quad (\text{A5})$$

In order to obtain a nonzero between a Q -space configuration state function, Θ_{μ} , and the target wave function, the trace of the density defined in Eq. (A4) must be nonzero. This means a nonzero overlap of these functions will result if the prototype scattering orbital, φ_s , is replaced by the occupied orbital φ_{σ} in the direct-product wave function. This can be easily seen by expanding the CSF's used to build the target wave function and the Q -space CSF's in terms of determinants. Now consider what occurs on a determinant-by-determinant basis when we construct a direct-product wave function as a target determinant $\Phi_t = \mathcal{A}\varphi_1^{\alpha}\varphi_2^{\alpha}\varphi_3^{\beta}$ times a target orbital. If the direct-product function does not violate the Pauli principle, then the overlap can be only 1, -1 , or 0 with a Q -space determinant. Consider the example

$$\begin{aligned} \mathcal{A}\Phi_t \varphi_3^{\alpha} &\equiv \mathcal{A}\varphi_1^{\alpha}\varphi_2^{\alpha}\varphi_3^{\beta}\varphi_3^{\alpha} \\ &\equiv \Theta_1 \end{aligned} \quad (\text{A6})$$

and the density matrix that results when the occupied orbital φ_3^{α} is replaced by a scattering orbital φ_s^{α} ,

$$\langle \mathcal{A}\Phi_t \varphi_s^{\alpha} | \Theta_1 \rangle_1 = |\varphi_s^{\alpha}\varphi_3^{\alpha}|. \quad (\text{A7})$$

In this case the matrix element, d^1_{3s} , is 1. Now if we consider another Q -space determinant,

$$\Theta_2 = \mathcal{A}\varphi_1^{\alpha}\varphi_2^{\alpha}\varphi_2^{\beta}\varphi_3^{\alpha}, \quad (\text{A8})$$

then a zero matrix element would ensue,

$$\langle \mathcal{A}\Phi_t \varphi_s^{\alpha} | \Theta_2 \rangle_1 = 0, \quad (\text{A9})$$

which is again the desired result. Since a phase factor in the overlap results in the same phase factor in the density, these are the only two cases we need consider. Because we can expand a wave function expressed in terms of CSF's as one expanded in terms of determinants, the fact that each determinant-determinant interaction is treated correctly means that we can obtain the desired transformation matrix, $T_{\mu\sigma}$, by computing density matrix elements between CSF's.

APPENDIX B

The $(N+1)$ -electron contracted functions [ω basis defined in Eq. (3)] are generated by taking the direct

product of occupied orbitals and target wave functions. In a multichannel calculation, it may not be possible to generate a *single* set of orthogonal orbitals that provides a compact representation of *all* of the states to be included in the scattering calculation. This was not a problem in the F_2 calculations reported in this paper since the averaged natural orbitals we used did provide such a compact description of the target states. However, when there are excited states that have mixed valence-Rydberg character, such as the B state of H_2 , it is not always possible to achieve a compact representation of the ground and excited states using a single orbital set. In such a case our prescription for identifying excited pseudostates, which is based on the norm of a contracted $(N+1)$ -electron function, might fail. However, this problem can be remedied by rotating the orbitals used to define the ω basis. Such a procedure is outline below.

We do not have to use the same occupied orbital basis in constructing the one-electron scattering function [$f(N+1)$ in Eq. (A1)] that we employ in the target wave function. For each target state in the scattering calculation, these orbitals can be chosen so as to extremize the

norm of the contracted $(N+1)$ -electron functions. We can simply form the overlap matrix for the set of ω vectors generated by a particular target state and diagonalize it. This procedure then defines a new transformation of the contracted Q -space Hamiltonian. We note that this transformation does not introduce any additional complexities into the construction of the optical potential since the linear combinations of $(N+1)$ -electron CSF's comprising the ω basis are not, in general, orthogonal.

This transformation provides a unique definition of these contracted functions which is independent of the orbital basis used to define the target wave functions. We tested the procedure of F_2 by choosing a smaller basis than that reported previously and using full CI target wave functions, which are invariant to the choice of occupied orbitals. We first performed MC-CC calculations using natural orbitals as the occupied orbitals. We then generated a new set of orbitals by rotating one strongly occupied and one weakly occupied natural orbital by 45° . By diagonalizing the new ω -overlap matrix, we recovered the original ω basis and the same cross sections were obtained in both calculations.

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