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Electronic excitation of atoms and molecules using the linear-algebraic method

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The linear-algebraic method for electron-molecule scattering is generalized to treat inelastic collisions involving a set of primary coupled channels. The coupling between these channels is expanded in separable form using a set of Cartesian Gaussian functions. As a consequence of the separable expansion, we need only to solve a set of *uncoupled*, homogeneous and inhomogeneous equations in each channel to obtain the basis in which the final solution is expanded. The separable form of the coupling allows the physical solution to be obtained with use of the matrix elements of the interaction and the overlap integrals between the solutions and the basis used for the separable expansion. The method is applied to inelastic scattering from H, He, H_2^+, and H_2. Comparison with exact solutions of the close-coupling equations indicates that the method is quite accurate, provided that the basis set used in the separable expansion is flexible enough to span the interaction region.

I. INTRODUCTION

The development of reliable theoretical methods to calculate the excitation cross section of molecular targets has proven to be a formidable task. In fact, it is only in the last two or three years that techniques which were used for elastic scattering have been sufficiently generalized to account for inelastic transitions.[1-5] Previously, one had to rely on Born, Born-Ochkur-Rudge,[6-8] or distorted-wave calculations[9,10] for the generation of cross-section information for most molecular systems. In one or two cases (H_2,N_2) there were some limited two-state close-coupling calculations[11,12] with which to compare, but the difficulties of the calculations as well as the experiments demanded further study. Of the newer more general approaches, three methods [the linear-algebraic method (LAM),[5] Schwinger variational method,[4] and R matrix methods[2]] have already provided inelastic scattering cross sections, albeit in a limited number of cases. The purpose of this paper is to provide some further insight into the application of the LAM to inelastic scattering and to suggest some refinements of the present approach, which we feel may be necessary for some inelastic transitions. Consequently, the present study was designed to test the separable-potential approach discussed in a recent paper[5] for a number of atomic and molecular systems. Except for the calculations on the $b\,^3\Sigma_u^+$ state of H_2,[13] the authors did not attempt an exhaustive study of any single inelastic transition. In fact, all of the cases were deliberately chosen to mimic as closely as possible calculations which could be performed by other methods. Even with the above limitations, it was difficult in certain cases to compare our results with those in the literature. To do so in the case of $e + H_2$ scattering required us to write a specialized close-coupling program for two-electron targets. The results of our calculations not only provide us with new insights into our own methods but uncovered a number of difficulties with other results in the literature. The above discussion only underlines the difficulties and uncertainties of the inelastic electron-molecule scattering problem and the need for a cooperation between researchers in this field.

The remaining parts of the paper are devoted to a discussion of the theory of the linear-algebraic separable-potential (LASP) approach and its application to $e + H$, $e + He$, $e + H_2^+$, and $e + H_2$ scattering. All of the calculations involved just two physical states. In the case of H_2 and H_2^+ both optically allowed and optically forbidden transitions were studied. The results of the calculations and a comparison with other methods appear in the final section of the paper.

II. THEORY

In the LAM,[14] as in the R-matrix theory, physical space is divided into an internal $(r \leq a)$ and external $(r \geq a)$ region. The internal region is characterized by the presence of strong, nonlocal forces between the incident and bound electrons. In the outer region the two systems are more or less separate, and the scattering electron is subject to the long-range multipole potentials of the charge distribution of the target. Additionally, the vibrational and rotational degrees of freedom of the target can become as important as the electrostatic potentials and cannot be ignored. Since our purpose is to compare our results with other fixed-nuclei calculations, we have assumed that the nuclei can be considered as frozen during the scattering event. Inside the R-matrix sphere, the Schrödinger equation can be written as

$$(\mathscr{H}+\mathscr{L}_b-E)\,|\,\psi\rangle=\mathscr{L}_b\,|\,\psi\rangle\ . \tag{1a}$$

The Hamiltonian H for the total $(N+1)$-electron system has the form

$$H=T_e+H_N+V\ , \tag{1b}$$

where T_e is the kinetic-energy operator of the continuum electron. H_N is the Hamiltonian for the N-electron target molecule, and V is the interaction potential between the scattered electron and the molecule. The total system wave function ψ is given by

$$\psi(1,2,\ldots,N+1)=A\sum_{c=1}^{m}\phi_c(1,2,\ldots,N)F_c(N+1)+\sum_{\alpha}d_\alpha\chi_\alpha(1,2,\ldots,N+1)\ , \tag{1c}$$

where $\phi_c(1,2,\ldots,N)$ is an eigenstate of the target molecule

$$H_N\phi_c(1,2,\ldots,N)=\epsilon_c\phi_c(1,2,\ldots,N)\ , \tag{1d}$$

$F_c(N+1)$ represents the continuum wave function labeled by the target state c, and A is the antisymmetry operator. We assume that the continuum functions are orthogonal to all orbitals φ_q used to construct the target wave function ϕ_c. In order to relax this strong orthogonality constraint we introduce fully antisymmetric, $(N+1)$-electron "correlation" functions χ_α for completeness. These correlation functions may take a more general form and represent certain compound states omitted from the sum in the first term. We usually make a partial-wave decomposition of the target and continuum orbitals and thus also label the scattering function by the orbital angular momentum l_c and its projection on the internuclear axis m_c. The Bloch operator $\mathscr{L}_b$ given by

$$\mathscr{L}_b=\tfrac{1}{2}\sum_{c,l_c,m_c}|\,cl_cm_c)\delta(r-a)\left[\frac{\partial}{\partial r}-b\right](cl_cm_c\,| \tag{1e}$$

is introduced to enforce the proper logarithmic boundary conditions at $r=a$.

We place the scattering equation (1) in a more convenient form by introducing the projection operators

$$P=\sum|\,A[\phi_c(1,2,\ldots,N)F_c(N+1)]\rangle\times\langle A\,|\,[\phi_c(1,2,\ldots,N)F_c(N+1)]\,|\ ,$$

$$Q=1-P\ ,$$

such that

$$|\,\psi\rangle=(P+Q)\,|\,\psi\rangle\ .$$

This allows us to express the Schrödinger equation[15] as the pair of coupled equations

$$(\mathscr{H}_{PP}-E)P\,|\,\psi\rangle+\mathscr{H}_{PQ}Q\,|\,\psi\rangle=\mathscr{L}_bP\,|\,\psi\rangle\ , \tag{2a}$$

$$(\mathscr{H}_{QQ}-E)Q\,|\,\psi\rangle+\mathscr{H}_{QP}P\,|\,\psi\rangle=0\ , \tag{2b}$$

where $\mathscr{H}=\mathscr{H}+\mathscr{L}_b$. Solving for $Q\,|\,\psi\rangle$ in (2b) and substituting into (2a), we obtain

$$(\mathscr{H}_{PP}-E)P\,|\,\psi\rangle+\mathscr{H}_{PQ}(E-\mathscr{H}_{QQ})^{-1}\mathscr{H}_{QP}P\,|\,\psi\rangle=0 \tag{3a}$$

or

$$(\mathscr{H}_{PP}+\mathscr{L}_b-E)P\,|\,\psi\rangle+U^{\text{opt}}P\,|\,\psi\rangle=\mathscr{L}_bP\,|\,\psi\rangle\ , \tag{3b}$$

where the optical potential U^{opt} is defined as

$$U^{\text{opt}}=\mathscr{H}_{PQ}(E-\mathscr{H}_{QQ})^{-1}\mathscr{H}_{QP}\ . \tag{3c}$$

In practice, we manipulate Eq. (3) to retain the projection operator P only in the term containing the optical potential. For calculations, P is replaced by the expression

$$P=\sum_{c,\alpha}|\,A[\phi_c(1,2,\ldots,N)F_\alpha(N+1)]\rangle\times\langle A[\phi_c(1,2,\ldots,N)F_\alpha(N+1)]\,|\ , \tag{4}$$

where we have introduced an additional expansion of the channel wave functions F_c in terms of a complete set of states F_α. By taking components with respect to the open target states, we obtain a set of coupled, integro-differential equations

$$(h_c+\mathscr{L}_{bc}-\tfrac{1}{2}k_c^2)\,|\,F_c\rangle+\sum_{c'}\sum_{\alpha,\beta}|\,F_\alpha\rangle\langle F_\alpha\,|\,U_{cc'}^{\text{opt}}\,|\,F_\beta\rangle\langle F_\beta\,|\,F_{c'}\rangle=\mathscr{L}_{bc}\,|\,F_c\rangle+\sum_q\lambda_{cq}\,|\,\varphi_q\rangle\ , \tag{5a}$$

where

$$h_c=-\tfrac{1}{2}\nabla^2+U_{cc}^{\text{opt}}\ , \tag{5b}$$

$$\mathscr{L}_{bc}\equiv\tfrac{1}{2}\sum_{l_c,m_c}|\,l_cm_c)\delta(r-a)\left[\frac{\partial}{\partial r}-b\right](l_cm_c\,|\ , \tag{5c}$$

k_c^2 is the energy of target state c, and $|\,\varphi_q\rangle$ are the bound orbitals orthogonal to $|\,F_c\rangle$. The Lagrange multipliers λ_{cq} are needed to ensure the orthogonality condition to the $|\,\varphi_q\rangle$. All of the diagonal interactions are placed in the operator h_c. The reason for this division is that the diagonal static potentials are strong and converge quite slowly in a basis set. On the other hand, the introduction of the basis set F_α leads to a matrix or separable expansion of the off-diagonal channel interactions. This has the possibility of rapid convergence in a conventional L^2 basis set. Similar observations were made with the exchange[16,17] and polarization parts[15,18] of the interaction potential in elastic scattering. Separable forms were used to give highly accurate cross sections for electron-H_2 and -N_2 scattering as well as precise resonance parameters for electron-$H_2{}^+$ collisions. Equations (5) may be recast as a set of coupled, integral equations by using the Green's operator

$$g_c=(h_c+\mathscr{L}_b-\tfrac{1}{2}k_c^2)^{-1}\ ,$$

containing only the diagonal interactions. This gives

$$|\,F_c\rangle+\sum_{c'}\sum_{\alpha,\beta}|\,F_{c\alpha}\rangle\langle F_\alpha\,|\,U_{cc'}^{\text{opt}}\,|\,F_\beta\rangle\langle F_\beta\,|\,F_{c'}\rangle=\sum_q|\,F_{cq}\rangle\lambda_{cq}+\tfrac{1}{2}\sum_{l_c,m_c}|\,F_{cl_cm_c}^0\rangle\left[\frac{\partial F_{cl_cm_c}}{\partial r}-bF_{cl_cm_c}\right]_a\ , \tag{6a}$$

where

$$F_{cl_cm_c}^0(\mathbf{r})=\int d\Omega'\,g_c(\mathbf{r}\,|\,a,\Omega')Y_{l_cm_c}(\Omega')\ , \tag{6b}$$

$$F_{c\alpha}(\mathbf{r})=\int g_c(\mathbf{r}\,|\,\mathbf{r}')F_\alpha(\mathbf{r}')d\mathbf{r}'\ , \tag{6c}$$

$$F_{cq}(\mathbf{r})=\int g_c(\mathbf{r}\,|\,\mathbf{r}')\varphi_q(\mathbf{r}')d\mathbf{r}'\ . \tag{6d}$$

Each of Eqs. (6a)–(6d) may be reduced to a set of coupled, radial integral equations by expanding in a set of spherical harmonics Y_{lm}. These equations are converted to LA form by introducing a quadrature in r space. An important point about these equations is that they are *uncoupled* in the physical channel index c. This means that the dimensionality of the equations that need to be solved is identical to that of the elastic scattering equations. Of course, the calculations must be performed for each physical channel and for all α,q within the channel. However, the quantities associated with the separable optical potential, the Bloch operator, and the Lagrange multipliers appear as simple inhomogeneous terms. Since the computational procedure reduces the coupled integral equations to a set of linear-algebraic equations, the presence of a number of inhomogeneties introduces little additional complications. The major computational step is the $\underline{L}\,\underline{U}$ factorization of the algebraic matrix, not the back solution for the right-hand sides.

Projecting Eqs. (6a) onto a set of spherical harmonics, we find

$$\begin{aligned} F_{cl_cm_c}(r)+\sum_{c'\,(\neq c)}\sum_{\alpha,\beta}F_{c\alpha l_cm_c}(r)\langle F_\alpha\,|\,U^{\rm opt}_{cc'}\,|\,F_\beta\rangle\langle F_\beta\,|\,F_{c'}\rangle &= \sum_q F_{cql_cm_c}(r)\lambda_{cq}+\tfrac{1}{2}\sum_{l_{c'},m_{c'}}F^0_{cl_cm_c,l_{c'}m_{c'}}(r) \\ &\quad\times\left[\frac{\partial F_{cl_{c'}m_{c'}}}{\partial r}-bF_{cl_{c'}m_{c'}}\right]_a . \end{aligned} \tag{7}$$

Expression (7) gives the standard equation that we must solve for the continuum channel wave functions $F_{cl_cm_c}$. However, this equation still depends on two unknown quantities $\langle F_\alpha\,|\,F_c\rangle$ and λ_{cq}. Since neither of these quantities explicitly depends on the angular momentum expansion (l_cm_c), we may determine them from a direct projection onto the three-dimensional equation (6a). We derive two equations. The first is determined by projecting Eq. (6a) onto the general L^2 expansion basis $\{\,|F_\alpha\rangle\}$ while the second arises from a projection with respect to the bound orbitals φ_q of the same symmetry as the continuum function. This latter constraint enforces the strong orthogonality condition assumed throughout the derivation. We proceed by defining the following vectors and matrices:

$$\begin{aligned} &X_{\alpha c}=\langle F_\alpha\,|\,F_c\rangle,\quad X_{qc}=\lambda_{cq}\ , \\ &N_{\alpha c,\beta c'}=\sum_\gamma\langle F_\alpha\,|\,F_{c\gamma}\rangle\langle F_\gamma\,|\,U^{\rm opt}_{cc'}\,|\,F_\beta\rangle\ , \\ &N_{\gamma,cq}=\langle F_\gamma\,|\,F_{cq}\rangle,\quad N_{\gamma,cl_cm_c}=\langle F_\gamma\,|\,F^0_{cl_cm_c}\rangle\ , \\ &N_{qc,\beta c'}=\sum_\alpha\langle\varphi_q\,|\,F_{c\alpha}\rangle\langle F_\alpha\,|\,U^{\rm opt}_{cc'}\,|\,F_\beta\rangle\ , \\ &N_{q,cq'}=\langle\varphi_q\,|\,F_{cq'}\rangle,\quad N_{q,cl_cm_c}=\langle\varphi_q\,|\,F^0_{cl_cm_c}\rangle\ . \end{aligned} \tag{8}$$

The set of equations which determines the unknowns $X_{\alpha c}$ and X_{qc} are

$$X_{\gamma c}+\sum_{c'\,(\neq c)}\sum_\beta N_{\gamma c,\beta c'}X_{\beta c'} =\sum_q N_{\gamma,cq}X_{qc}+\tfrac{1}{2}\sum_{l_c,m_c}N_{\gamma,cl_cm_c}\left[\frac{\partial F_{cl_cm_c}}{\partial r}-bF_{cl_cm_c}\right]_a , \tag{9a}$$

$$\begin{aligned} \sum_{c\,(\neq c')}\sum_\beta N_{qc,\beta c'}X_{\beta c'} &=\sum_{q'}N_{q,cq'}X_{q'c} \\ &\quad+\tfrac{1}{2}\sum_{l_c,m_c}N_{q,cl_cm_c}\left[\frac{\partial F_{cl_cm_c}}{\partial r}-bF_{cl_cm_c}\right]_a . \end{aligned} \tag{9b}$$

In Eq. (9b), the first term vanishes due to the assumed orthogonality $\langle q\,|\,F_c\rangle=0$.

In order to cast Eq. (9) in standard form, we add a channel label and an appropriate sum where needed. We then define a new set of matrices as

$$A_{ic,jc'}=\begin{cases}\delta_{ij}\delta_{cc'}+N_{ic,jc'}, & i,j\in\alpha\\ N_{i,c'j}\delta_{cc'}, & i\in\alpha \text{ and } j\in q\\ N_{ic,jc'}, & i\in q \text{ and } j\in\alpha\\ N_{i,c'j}\delta_{cc'}, & i,j\in q\end{cases} \tag{10a}$$

$$B_{i,cl_cm_c}=N_{i,cl_cm_c}\ , \tag{10b}$$

to get

$$\sum_{j,c'}A_{ic,jc'}X_{jc'}=\tfrac{1}{2}\sum B_{i,cl_cm_c}\left[\frac{\partial F_{cl_cm_c}}{\partial r}-bF_{cl_cm_c}\right]_a . \tag{11}$$

The dimensionality of the matrix $\underline{A}$ is determined by the number of target states c times the number of basis functions i. The (l_cm_c) labels play no direct role. They determine the number of independent solutions of the algebraic set of equations which are required for the final solution. Formally, we may write

$$\begin{aligned} X_{ic}&=\tfrac{1}{2}\sum_{l_{c'},m_{c'}}\sum_{c',j}A^{-1}_{ic,jc'}B_{j,c'l_{c'}m_{c'}}\left[\frac{\partial F_{c'l_{c'}m_{c'}}}{\partial r}-bF_{c'l_{c'}m_{c'}}\right]_a \\ &=\tfrac{1}{2}\sum_{c',l_{c'},m_{c'}}T_{ic,c'l_{c'}m_{c'}}\left[\frac{\partial F_{c'l_{c'}m_{c'}}}{\partial r}-bF_{c'l_{c'}m_{c'}}\right]_a . \end{aligned} \tag{12}$$

Substituting Eq. (12) into Eq. (7) and setting $r=a$, we find

$$F_{cl_cm_c}(a)=\sum_{c',l_{c'},m_{c'}}R_{cl_cm_cc'l_{c'}m_{c'}}\left[\frac{\partial F_{c'l_{c'}m_{c'}}}{\partial r}-bF_{c'l_{c'}m_{c'}}\right]_a , \tag{13a}$$

where

$$R_{cl_cm_cc'l_{c'}m_{c'}}=\frac{1}{2}\left[\sum_q F_{cql_cm_c}(a)T_{qc,c'l_{c'}m_{c'}}+\delta_{cc'}F^0_{cl_cm_{c'}l_{c'}m_{c'}}(a)\right.$$
$$\left.-\sum_{\bar{c}}\sum_{\alpha,\beta}F_{c\alpha l_cm_c}(a)U^{\text{opt}}_{\alpha c,\beta\bar{c}}T_{\beta\bar{c},c'l_{c'}m_{c'}}\right]. \tag{13b}$$

This completes the formal derivation. Once we have obtained $\underline{R}$, it is possible by a simple matching procedure to extract the scattering information. Alternatively, it is straightforward to devise numerical procedures which propagate $\underline{R}$ from $r=a$ to very large values of the radial coordinate.[19] At these values a matching to free or coulomb waves is possible. In the outer region this propagation step can be made very efficient when the potentials are slowly varying as would be the case for multipolar electrostatic forces.

Before turning to the numerical results, a few comments on the derivation and the physical implications are in order. In earlier publications we have shown the difficulty of expanding the direct diagonal interaction, which contains the strong nuclear coupling, in an L^2 basis. By moving this term into Green's function, we hope to avoid the difficulties of the earlier R- and T-matrix methods. The residual interaction has both local and nonlocal parts. There is little doubt that the exchange interactions, which are short range, can be efficiently expanded in separable form. Indeed we have demonstrated that it is possible in elastic scattering to expand both the exchange and optical potential interactions in a conventional set of L^2 Cartesian Gaussian orbitals.[18,20] The reduction of the elastic scattering problem to a set of coupled, inhomogeneous algebraic equations using the linear-algebraic method has proven to be a most efficient technique. These equations are readily solved on present-day computers but are particularly suited to the architecture of the new vector machines such as the Cray Research, Inc. Cray XMP and Control Data Corporation Cyber 205. By generalizing these methods to the inelastic problem, we can perform equivalent calculations with an effort proportional to the number of channels in the open channel space. The inclusion of optical potentials does increase the complexity of the calculation, but the methodology is still quite efficient. The real question, of course, is the efficacy of the separable expansion of the off-diagonal interactions. It is essential to be able to place both the direct and exchange parts of the off-diagonal terms in separable form. Only in this way will the problem be reduced to a set of *uncoupled, elastic* scattering equations. The exchange potential presents no particular difficulty but the direct potential can contain some rather unpleasant long-range terms, which converge rather slowly in a conventional L^2 basis. This is particularly true for optically allowed transitions in which dipolelike potentials dominate the coupling matrix. In an earlier publication,[5] the authors implemented and tested these ideas on the three-state $1s$-$2s$-$2p$ close-coupling equations for $e+\text{H}$ atom scattering. This case was chosen because of the well-known strong dipole coupling and the Rydberg nature of the excited states. We felt that if this approach were effective for $e+\text{H}$ collisions, then it might also be valid for the molecular case. The results of that calculation proved it was indeed possible and practical to use our approach for inelastic electronic scattering. However, it was necessary to make the L^2 basis sets flexible enough to span the large interaction region. In more practical molecular problems, where one is limited to Cartesian Gaussians as a basis, convergence could be a problem. Encourage by our success in the $e+\text{H}$ atom case, we embarked on the more general treatment in this paper. The results of our calculations appear in the next section.

III. APPLICATIONS

Before describing our various calculations, we first establish some notational conventions. We shall let the number of states be given by n_s and the number of partial waves included in *each* state by n_c. Thus, for $n_s=2$ and $n_c=4$, we have a set of eight coupled integro-differential equations. We divide the radial variable into two regions at the point r_a. We solve the LA equation in the inner region ($r\leq r_a$) by the methods described in the previous section by introducing a Gauss-Legendre mesh of n_p points. The local coupled equations in the outer region are solved to $r=r_m$ by an R-matrix propagator method. For the traditional or "exact" treatment of exchange, we must also note the number of expansion terms for the bound (n_b) and continuum orbitals (n_e) explicitly included in the calculation of the exchange term. Since both atomic calculations involve total S symmetries and s states, we always have $n_c=1$.

A. $1s$-$2s$ $e+\text{H}$ scattering

The $1s$-$2s$ close-coupling calculation in $e+\text{H}$ scattering is a natural first choice for our new theory. Many other calculations of this transition can be found in the literature, and we had our own earlier results[5] for comparison. The calculations were performed on the ^1S symmetry state of the composite system. Thus, both the incident and final channel continuum waves are of s type. Since our calculational methods require that the continuum functions be orthogonal to both the $1s$ and $2s$ functions, we added the ($1s^2$), ($1s2s$), and ($2s^2$) configurations as an optical potential into the coupling matrix element. This is easily accomplished using our new separable-potential techniques and adds no complexity other than an energy dependence to the coupling potential. The coupling matrix element does not contain any long-range potential but the rather extensive nature of the $2s$ state requires a large R-matrix radius ($20a_0$) to contain the exchange region. This in turn forces us to use a large basis set to span the interaction region over the energy range of interest. For this transition, we examined the cross section from threshold to 4 Ry incident electron energy. Over this range, we used a basis which built on the Gaussian expansions of the $1s$ and $2s$ hydrogen functions given by Huzinaga.[21] To his most extensive basis, we added functions whose exponents were in a geometric progression of two starting with his most diffuse exponent of 0.0165 and ending at 0.000 06. In addition, some compact exponents were also included to better span the valence region. This set was found to produce cross sections to within 10% or less of our earlier calculations. At this point in our study we were only examining our computer codes for gross errors and no systematic attempt was made to improve these results. A rather cursory examination of several smaller basis sets revealed some sensitivity but no dramatic deterioration of the results was found to occur. A comparison of our calculation and exact close coupling[22] is found in Table I.

B. $1s^2-1s2s\,(^2S)$ $e+\mathrm{He}$ scattering

Another simple test of the LAM is inelastic $e+\mathrm{He}$ scattering. We performed calculations using the separable expansion of the coupling interaction and compared our results with exact close coupling.[22] In both cases we ignored the correlation terms and forced orthogonality to the $1s$ and $2s$ He orbitals which were calculated using the IVO prescription.[23] As for hydrogen, the major difficulty was the extended nature of the excited $2s$ orbital. Since we studied overall ^2S symmetry of the scattering system, only s waves were present in our continuum solutions. Two prescriptions were used to choose the basis sets in the calculation. The first was identical to that used in the electron-hydrogen problem. The second started from an exponent of 0.0001 and added functions in a geometric progression of 1.5 until an exponent of 4974 was reached. Both basis sets produced results at low energies to within 15% of the exact close-coupling calculations. At higher energies the agreement was considerably better. Table II contains the results of our calculations using the two basis sets at four energies. The reason for the larger errors at lower incident energies is somewhat mystifying to us since the usual trend in the use of separable expansions is in the opposite direction. Considering the different character of the two basis sets, the results are even more puzzling. Perhaps this is a consequence of the extended nature of the $2s$ orbital or the diffuse form of the direct potential. We hope to return to this transition at a later date to better understand these effects.

C. $e+\mathrm{H}_2{}^+$ scattering

We performed two-state close-coupling calculations on two transitions in $\mathrm{H}_2{}^+$: $1\sigma_g$-$2\sigma g$ and $1\sigma_g$-$1\sigma_u$. In both cases we examined overall $^1\Sigma_g$ symmetry and added into the coupling matrix those configurations needed to relax any orthogonality constraints on the scattering functions.

TABLE I. Comparison of LASP method with exact treatment of exchange for e-H atom scattering in the ^1S symmetry for a $1s$-$2s$ close-coupling case. Cross sections (Q) in units of πa_0^2. Parameters: $n_s=2$, $n_c=1$, $n_e=n_b=1$, $n_p=65$, $r_a=r_m=20a_0$.

	$Q(1s\rightarrow 2s)$	
k^2 (Ry)	LASP	Exact (Ref. 26)
1.0	0.072 86	0.072 32
2.0	0.031 38	0.030 33
3.0	0.013 50	0.013 48
4.0	0.007 96	0.007 25

TABLE II. Comparison of the LASP method with the exact treatment of exchange for e-He scattering in the ^2S symmetry for a two-state close-coupling prescription ($1s^2$, $1s2s$). Cross sections (Q) in units of a_0^2. Parameters: $n_s=2$, $n_c=n_e=n_b=1$, $n_p=65$, $r_a=r_m=20a_0$.

	$Q(1s^2\rightarrow 1s2s)$		
	Exact	LASP	
k^2 (Ry)	(Ref. 26)	Basis 1	Basis 2
1.8375	0.034	0.038	0.040
2.2049	0.032	0.027	0.031
2.5724	0.026	0.026	0.025
2.9399	0.023	0.022	0.018

In both calculations a number of basis sets were examined. All of the basis sets started with the two-center basis used by Hazi and us in earlier calculations[20] of the resonances of $^1\Sigma_g$ symmetry of H_2. The basis was augmented by increasing the orbitals on both centers and at the midpoint of the molecule. Our initial attempts at calculating the cross section for these transitions was disappointing. The reasons for this are different for the two transitions. In both cases the excitation cross sections were small, and we had difficulty in obtaining high accuracy with small basis sets. In the former transition, we found it necessary, as in the $1s$-$2s$ hydrogen case, to use a large R-matrix radius ($20a_0$). The long-range coulomb force helps in reducing the basis-set size, but it is essential to include both s, p, and d type functions in the augmented basis for very accurate calculations. The need for such a large basis set is even more important in the case of $1\sigma_g\rightarrow 1\sigma_u$ excitation. Here the transition is optically allowed, and a significant

TABLE III. Basis set for $e+\mathrm{H}_2{}^+$ calculations: experimental coefficients.

s type, $R=\pm1.0a_0$
82.474, 12.3980, 2.8391, 0.814 72, 0.582 74, 0.271 84, 0.099 483, 0.042 726, 0.0165
pz type, $R=\pm1.0a_0$ 1.253 48, 0.291 528, 0.078 125
dz^2 type, $R=\pm1.0a_0$ 0.078 899
s type, $R=0.0a_0$ 104.8576, 52.5288, 26.2144, 13.1072, 6.5536, 3.2768, 1.6384, 0.8192, 0.4096, 0.2048, 0.1024, 0.0512, 0.0256, 0.0128, 0.0064, 0.0032, 0.0016, 0.0008, 0.0004, 0.0002, 0.0001
pz type, $R=0.0a_0$ Same as above
dz^2 type, $R=0.0a_0$ 0.52, 0.26, 0.128, 0.064, 0.032, 0.016, 0.0053, 0.0018, 0.0005, 0.0002

TABLE IV. Comparison of the LASP method with the exact treatment of exchange for e-H_2^+ collisions in the $^1\Sigma_g$ symmetry for two two-state close-coupling cases $[(1\sigma_g, 1\sigma_u)$ and $(1\sigma_g, 2\sigma_g)]$. Cross sections in units of a_0^2. Parameters: $n_s=2$, $n_c=4$, $n_p=50$, $r_m=r_a=10(1\sigma_u)$, $20(2\sigma_g)$, $n_e=n_b=3$ (exact).

k^2 (Ry)	Exact[a]	LASP
	$Q(1\sigma_g \rightarrow 2\sigma_g)$	
0.9	0.4274	0.4293
2.0	0.2070	0.2085
	$Q(1\sigma_g \rightarrow 1\sigma)$	
1.5	0.0809	0.0762
2.0	0.0763	0.0722
3.0	0.0439	0.0516
4.0	0.0278	0.0314

[a] Close-coupling calculations similar to those in Reference 26.

fraction of the transition probability comes from the long-range part of the coupling potential. The basis set used in the best calculation is given in Table III. The results for the two calculations are given in Table IV.[22]

The calculations show that it is essential to use a large, single-center basis set to achieve accurate results. The need to include a significant number of these orbitals for each angular momentum which contributes substantially to the cross sections leads to quite large basis sets. Since our current configuration-interaction programs are limited to a total of 60 molecular orbitals, we could not expand the calculations any further. The overall agreement with the exact close coupling[22] is about 5% for the $1\sigma_u$ transition and 5–15% for the $2\sigma_g$ transition. The $2\sigma_g$ transition suffers from the same difficulty as the $2s$ transition in H and He. The large R-matrix radius requires a large basis set. The $1\sigma_u$ transition is optically allowed but the compact nature of the excited state allows us to span the interaction region with our basis set quite well. The overall conclusions of our study suggest that the basic methodology and computer programs are sound. What is needed is a better basis set and/or a more flexible configuration-interaction program. Both of these are actively being investigated and results will be presented in forthcoming publications.

D. Excitation of the $b\,^3\Sigma_u^+$ of H_2

One of the few transitions which has been studied by a wide variety of theoretical techniques is the $b\,^3\Sigma_u^+$ state of H_2.[4,8,9,11–13,24,25] The transition may be described, to zeroth order, as the excitation of a $1\sigma_g$ orbital of the ground-state configuration to a $1\sigma_u$ orbital, which is triplet coupled to the remaining $1\sigma_g$ function. In our calculations, we generated the $1\sigma_u$ orbital using the IVO technique where the potential was that appropriate to triplet coupling. The remainder of the basis was generated in the field of the ground-state target using several primitive sets. The valence character of the $1\sigma_u$ orbital does not require a very large R-matrix radius $(10a_0)$, and there are no long-range coupling parts to the interaction potential. In fact, the coupling matrix is purely due to the exchange interaction and is quite short ranged. Again as in the previous tests, we investigated a number of basis sets for the scattering electron. These ranged from some quite simple Cartesian Gaussian orbitals to very large extended sets chosen as in the $e+H_2^+$ calculation. Very little sensitivity was observed in the results, and the bulk of the calculations were performed using a set given by Lima *et al.*[4] in a recent Schwinger variational calculation of the transition under discussion. As a first check for this system, we compared with several earlier two-state close-coupling calculations[8,11,12] that enforced the orthogonality constraint of bound and continuum orbitals but failed to relax this condition with the introduction of correlation terms [orthogonalized static exchange (OSE) method]. Therefore, we omitted the $1\sigma_g 1\sigma_u^2$ $(1\sigma_g^2 1\sigma_u)$ correlation terms from our calculations of the $^2\Sigma_g$ $(^2\Sigma_u)$ total scattering symmetry. We found fairly good agreement with Chung and Lin[8] in all symmetries except the $^2\Sigma_g$. In this symmetry, our cross section was almost an order of magnitude larger. In order to further test our method, we formulated a completely independent computer program specifically designed to treat two-electron targets. This program had the capabilities of solving the close-coupling equations within the strong orthogonality constraint but not the flexibility to include correlation terms. We found excellent agreement between the results of this program and our more general code, if the correlation terms were neglected, for *all* scattering symmetries. Since the $^2\Sigma_g$ symmetry makes a small contribution to the total scattering, our total integrated cross sections are in fairly good agreement with Chung and Lin.[8]

Once the correlation terms are introduced into the two-state calculation [static exchange plus correlation (SEC) method], this agreement with the earlier results[4,8,11,12] vanishes. Factor-of-2 disagreements in some symmetries were observed. New calculations[25] by Lima *et al.*, who found some problems with their earlier results,[4] and by

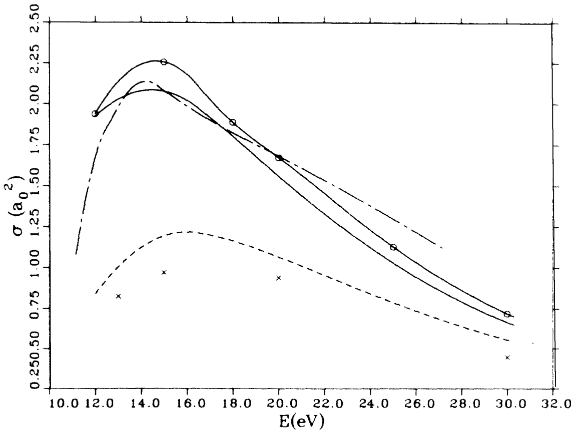

FIG. 1. Comparison of theoretical calculations of the $X\,^1\Sigma_g$-$b\,^3\Sigma_u$ total excitation cross sections as a function of incident electron energy for e-H_2 scattering. ——, present SEC calculations; — — —, present OSE; —·—, SEC (Baluja *et al.*, 1985); —○—, SEC (Lima *et al.*, 1985); ×, OSE (Holley *et al.*, 1981).

Baluja, Noble, and Tennyson[24] are in excellent agreement with our full two-state results.[13] We compare these various calculations in Fig. 1. We note the importance at low energies of including the correlation terms and relaxing the strong orthogonality constraint. Although the older experimental results[26,27] are in disagreement with one another, the latest evidence strongly supports the results of the theoretical calculations of Refs. 13, 24, and 25.

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