PHYSICAL REVIEW A VOLUME 22, NUMBER 6 DECEMBER 1980

Iterative static-exchange techniques applied to low-energy collisions of electrons with molecular ions: $H_2{}^+$, CH^+, and $N_2{}^+$

W. D. Robb and L. A. Collins

Theoretical Division (MS 212), Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

(Received 21 May 1980)

An iterative static-exchange single-center close-coupling procedure is applied to electron collisions with molecular ions. The method is taken *mutatus mutandus* from a procedure used previously to study electron neutral-molecule collisions. The procedure is found to be both stable and efficient for calculating static-exchange level wave functions and eigenphases. The method is applied to electron collisions with $H_2{}^+$, CH^+, and $N_2{}^+$. In addition, ro-vibrational-excitation cross sections for $e + H_2{}^+$ collisions in the adiabatic nuclei approximation and photoionization cross sections for H_2 and N_2 are reported.

I. INTRODUCTION

The understanding of such processes as photoionization,[1] dissociative recombination,[2] and rotational excitation of interstellar species[3] depends on a knowledge of electron scattering from molecular ions. While the long-range Coulomb potential plays an important role in this scattering process, short-range effects such as exchange and correlation must be included, especially at low energies, for an accurate treatment of the dynamics. The scattering of electrons by $H_2{}^+$ has received much attention both for its simplicity and for its relation to photoionization[1] of H_2. Temkin and co-workers[4a,4b] were the first to include aspects of the static, exchange, and polarization interactions for elastic scattering of electrons by $H_2{}^+$. Their single-center close-coupling calculations were performed in the static-exchange and polarized orbital approximations. In the static-exchange approximation, the target molecule is frozen in the ground state. No excitations (virtual or real) are permitted, although full account is taken of the nonlocal nature of the exchange interaction in the elastic channel. The polarized orbital method allows relaxation or distortion effects to be included through a perturbative scheme. Recently, Takagi and Nakamura[5] have included correlation effects more accurately for e-$H_2{}^+$ collisions through a nonperturbative Kohn variational technique. The treatment of more complex molecular ions has been made possible by the quite recent development of a number of powerful computational methods such as the iterative[6] and noniterative[7,4] close-coupling, R-matrix,[8a] T-matrix,[8b] and Schwinger[8c] and Kohn[5,9] variational techniques. While these methods have been implemented primarily at the static-exchange level, a few studies of electronic excitation[10a] have been performed. The noniterative close-coupling method has already been applied to e-$H_2{}^+$ (Ref. 4), $N_2{}^+$ (Ref. 4c), and CH^+ (Ref. 7) in the static-exchange approximation. The results of these calculations have been employed to calculate photoionization cross sections and capture widths. Endeavors to extend the other methods to ionic systems are presently under way.

In this paper, we extend the iterative close-coupling method[6] for electron neutral-molecule collisions to electron scattering from molecular ions. We take as our starting point the formulation of the method for neutrals as described in an earlier paper[6b] (hereafter referred to as Paper I) and indicate where changes must be made in order to extend the procedure to molecular ions. This formulation is presented in Sec. II at the level of the static-exchange approximation. In Sec. II we also briefly outline procedures for calculating vibrational-excitation cross sections in the adiabatic-nuclei approximation and photoionization cross sections in the frozen-core approximation. We apply the method to three molecular ions, $H_2{}^+$, CH^+, and $N_2{}^+$ and present our results in Sec. III. In addition, we present photoionization cross sections for H_2 and N_2 and vibrational-excitation cross sections for $H_2{}^+$. We reserve Sec. IV for a summary of our findings.

II. THEORY

A. Static-exchange equations

1. Formulation

All scattering calculations were performed in the body frame within the fixed-nuclei approximation.[4,11] In addition, we made the static-exchange approximation by which the series expansion of the total system wave function ψ in terms of a set of electronic state Φ of the target molecule is truncated at a single state (the ground state). The wave function Φ for the N-electron target molecule is represented by a single determinant as

$$\Phi(\vec{r}_1,\ldots,\vec{r}_N)=\left|\bar{\phi}_1(\vec{r}_1)\cdots\bar{\phi}_N(\vec{r}_N)\right|, \tag{2.1}$$

with $\bar{\phi}_i$ an occupied spin orbital with spatial part $\phi_i^{m_i}(\vec{r})$ and spin part χ_i. The continuum wave function $\underline{F}$ is likewise decomposed into spatial $F(\vec{r}_{N+1})$ and spin χ_{N+1} parts. The total system wave function in the static-exchange approximation can then be represented as

$$\Psi=A\Phi F\ , \tag{2.2}$$

where A is the antisymmetry operator.

We further choose to represent the collision with respect to a single center.[4] This is accomplished by expanding the bound and continuum orbitals in spherical harmonics about the center-of-mass of the molecule as

$$\phi_i^{m_i}(\vec{r})=\frac{1}{r}\sum_{l_i}\phi_{l_i}^{m_i}(\hat{r})Y_{l_i m_i}(\hat{r})\,, \tag{2.3a}$$

$$F(\vec{R})=\frac{1}{R}\sum_{lm}F_l^m(R)Y_{lm}(\hat{R})\,, \tag{2.3b}$$

where we have replaced r_{N+1} with R, the coordinate of the incident electron. We have assumed implicitly in Eq. (2.3a) that the molecular orbitals are uniquely labeled by symmetry, [e.g., $m_i=0(\sigma),1(\pi)$]. In Eq. (2.3b), the orbital angular momentum l of the incident electron forms a channel label, which is coupled by the asymmetric field of the molecule.

Substituting Eq. (2.2) into the Schrödinger equation, multiplying through by $Y^*_{l'm'}(\hat{R})\chi^{+}_{N+1}$, and integrating over angular and spin coordinates, we obtain a set of coupled integro-differential equations which are block diagonal in m. Thus, in the fixed-nuclei approximation for target molecular states of Σ symmetry m, the symmetry of the continuum orbital, becomes a "good" quantum number. This set of coupled equations is formally of infinite order. To reduce the collision problem to a tractable form, we impose the close-coupling approximation by which we truncate the expansions in Eqs. (2.3) at a finite number of terms, say N_i and N_c, respectively. The resulting set of order N_c coupled integro-differential equations can be written in matrix notation as

$$(\underline{\Delta}-\underline{V})\underline{F}=\sum_{i=1}^{N_0}p_i\left[W_i(\underline{\phi}_i\underline{F})+\delta_{mm_i}(2\epsilon_i-k^2)\Delta(\phi_i\underline{F})\right]\ , \tag{2.4}$$

where

$$(\underline{\Delta})_{ll'}\equiv\left(\frac{d^2}{dR^2}-l(l+1)R^{-2}+k^2\right)\delta_{ll'}\ , \tag{2.5a}$$

$$(\underline{V})_{ll'}\equiv\langle lm\,|\,V_{st}\,|\,l'm\rangle\ , \tag{2.5b}$$

$$[\,W_i(\phi_{\underline{i}}\underline{F})]_{ll_0}\equiv{\sum_{l'\,l''\,l'''\,\lambda}}'\phi_{l_i''}^{m_i}(R)\,g_\lambda(ll'l''l'''\,|\,mm_i)\times Y_\lambda(\phi_{l_i'''}^{m_i}F_{l'l_0}\,|\,R)\,, \tag{2.5c}$$

$$\Delta(\phi_iF)\equiv\int_0^\infty\phi_i(r)\underline{F}(r)\,dr\,, \tag{2.5d}$$

$$Y_\lambda(\phi_{l_i'''}^{m_i}F_{l'l_0})\equiv\int_0^\infty\phi_{l_i'''}^{m_i}(r)\,\frac{r_<^\lambda}{r_>^{\lambda+1}}\,F_{l'l_0}(r)\,dr\ , \tag{2.5e}$$

with $r_>(r_<)$ the greater (lesser) of R and r, and g_λ defined in Ref. 12. The continuum orbital $\underline{F}$ is a $N_c\times N_c$ matrix whose rows are labeled by the scattering channels l and whose columns are labeled by the N_c linearly independent solutions. Each bound orbital is represented by a row vector whose components are the N_i radial expansion coefficients. The averaged electrostatic potential energy for the interaction of an electron with the molecule is given by V_{st}. The two-electron nonlocal energy-dependent exchange term is represented by $\underline{W}$. The above equations are valid for electron scattering from either closed- or open-shell target molecules, whose wave function can be represented as a single determinant. For the open-shell case, we assume that *only one* molecular orbital is singly occupied. With this caveat, the variable p_i in Eq. (2.4) has the following form:

$$p_i=\begin{cases}-1, & \text{all doubly occupied orbitals}\\ -1, & \text{singly occupied orbitals—triplet scattering}\\ +1, & \text{singly occupied orbitals—singlet scattering}\,.\end{cases}$$

2. *Method of solution*

The general method employed to solve an equation of the form of (2.4) with only local potentials is the direct outward propagation of the solution by some standard numerical algorithm. The presence of a nonlocal term in (2.4) obviates this approach. We circumvent this problem by solving the set of coupled equations iteratively.[13] To better illustrate this procedure, we represent equation (2.4) in the following schematic form:

$$(\underline{\Delta}-\underline{V})\underline{F}=\underline{W}(\underline{F})\,, \tag{2.6}$$

where $\underline{W}$ now represents all terms on the right-hand side of equation (2.4). We begin the iterative procedure with the solution $\underline{F}^0$ to Eq. (2.6) with $\underline{W}=0$. We then use $\underline{F}^0$ to calculate an approximate $\underline{W}(\underline{F}^0)$ which in turn is used in Eq. (2.6) to derive a new solution $\underline{F}^1$. The iterative procedure is continued until cross sections or eigenphase sums at subsequent iterations agree to within some specified tolerance ϵ, (e.g., $|\sigma(n)-\sigma(n-1)|<\epsilon$).

The iteratative method can be summarized as the solution to the following sequence of equations,

$$
\begin{aligned}
&(\underline{\Delta}-\underline{V})\underline{F}^0=0\,,\\
&(\underline{\Delta}-\underline{V})\underline{F}^1=\underline{W}(\underline{F}^0)\\
&\qquad\cdot\\
&\qquad\cdot\\
&\qquad\cdot\\
&(\underline{\Delta}-\underline{V})\underline{F}^n=\underline{W}(\underline{F}^{n-1})\,.
\end{aligned}
\tag{2.7}
$$

One can either proceed to solve the inhomogeneous equations (2.7) directly or one can convert each to a local form using the identity

$$[\underline{F}^{n-1}]^{-1}\cdot\underline{F}^n=\underline{1}\,,\tag{2.7$'$}$$

which is valid for the converged solution. Multiplying Eq. (2.7) by Eq. (2.7′), we have

$$
\begin{aligned}
&(\underline{\Delta}-\underline{V})\underline{F}^n=\underline{W}(\underline{F}^{n-1})\simeq\{\underline{W}(\underline{F}^{n-1})[\underline{F}^{n-1}]^{-1}\}\underline{F}^n\\
&\text{or}\\
&(\underline{\Delta}-\underline{V}-\underline{V}_{\text{ex}}^{n-1})\underline{F}^n=0\,,
\end{aligned}
\tag{2.8}
$$

where $\underline{V}_{\text{ex}}^{n-1}\equiv\underline{W}(\underline{F}^{n-1})[\underline{F}^{n-1}]^{-1}$. Equation (2.8) is exact only at the *n*th or "converged" iteration. Thus, each inhomogeneous equation in (2.7) is converted to a local one by the procedure in Eq. (2.8). We have termed the technique the WF-inverse or WFI method. The technique is similar to one applied by Tully and Berry[14] to $e+\mathrm{H}_2$ collisions and is described in more detail in Paper I.

For scattering of electrons from closed-shell neutral molecules, we found[6] that, in the case of a continuum orbital with the same symmetry as the bound orbitals, enforcing orthogonality of bound and continuum orbitals at each iteration greatly accelerates the convergence of the iterative procedure. This may be viewed in some sense as forcing the correct nodal structure on the continuum orbital. For closed-shell ions and triplet scattering from open-shell ions, we find that the orthogonality procedure implemented for the neutrals is equally beneficial in accelerating convergence. The procedure must be modified slightly to treat singlet scattering.

For doublet (triplet) scattering from closed (open)-shell ions, the solution of the static-exchange equations is independent of whether or not the one-electron terms are included. In other words, the cross sections calculated from solutions of Eq. (2.4) with or without the $(2\epsilon_i-k^2)\Delta(\underline{\phi}_i\underline{F})$ terms will be equal. Therefore, a solution $\underline{F}'$ that is orthogonal to the bound orbitals of its symmetry is a valid solution to Eq. (2.4). We generate this solution at each iteration by the method of Lagrange undetermined multipliers (LUM). At each iteration we wish to solve an equation of the form

$$(\underline{\Delta}-\underline{V}-\underline{V}_{\text{cx}})\underline{F}'=\sum_i\underline{\phi}_i\underline{\lambda}_i\,,\tag{2.9}$$

where the sum runs over all bound orbitals of the same symmetry as $\underline{F}'$, and where the $\underline{\lambda}_i$ are row vectors of the LUM components. We find a general solution of (2.9) of the form

$$\underline{F}'=\underline{F}+\sum_i\underline{P}_i\underline{\lambda}_i\,,\tag{2.10a}$$

such that

$$(\underline{\Delta}-\underline{V}-\underline{V}_{\text{ex}})\underline{F}=0\,,\tag{2.10b}$$

$$(\underline{\Delta}-\underline{V}-\underline{V}_{\text{cx}})\underline{P}_i=\underline{\phi}_i\,.\tag{2.10c}$$

The $\underline{\lambda}_i$ coefficients can then be determined from the condition that the continuum orbital $\underline{F}'$ and bound orbitals $\underline{\phi}_i$ of its symmetry be orthogonal:

$$\Delta(\underline{\phi}_i\underline{F}')=0\,,\tag{2.11}$$

for all $m_i=m$. This orthogonality procedure is employed as a numerical convenience to accelerate convergence with iteration. A more detailed discussion of the orthogonality question can be found elsewhere.[15]

For a singlet scattering from an open-shell ion, the continuum solution is not independent of the one-electron term arising from the partially filled molecular orbital. This term must be retained in some form in order to obtain the correct solution for the case in which the continuum and singly occupied bound orbitals have the same symmetry. For the doubly occupied bound orbitals with the same symmetry as the continuum solution, the orthogonality prescription of the previous paragraph applies. The procedure which ensures the fastest acceleration of the iterative procedure in the present case is to force orthogonality to all doubly occupied orbitals and self-consistency of the LUM for the *one* singly occupied orbital. At the *n*th iteration, we seek a solution to an equation of the form

$$(\underline{\Delta}-\underline{V}-\underline{V}_{\text{ex}})\underline{F}'=\sum_i\underline{\phi}_i\underline{\lambda}_i\,,\tag{2.12}$$

where the sum runs over *all* bound orbitals of the same symmetry as $\underline{F}'$. A general solution of Eq. (2.12) has the form

$$\underline{F}'=\underline{F}+\sum_i\underline{P}_i\underline{\lambda}_i\,,\tag{2.13a}$$

such that

$$(\underline{\Delta}-\underline{V}-V_{\text{ex}})\underline{F}=0\,,\tag{2.13b}$$

$$(\underline{\Delta} - \underline{V} - \underline{V}_{\mathrm{ex}})\underline{P}_i = \underline{\phi}_i, \quad \text{doubly occupied}$$
$$= \underline{\phi}_i(2\epsilon_i - k^2), \quad \text{singly occupied}. \tag{2.13c}$$

We calculate the $\underline{\lambda}_i$ terms by the following two prescriptions depending on whether the bound orbital is filled or open:

$$\Delta(\underline{\phi}_i \underline{F}') = 0, \quad \phi_i \text{ doubly occupied}, \tag{2.14a}$$

$$\Delta(\underline{\phi}_j \underline{F}') = \underline{\lambda}_j, \quad \phi_j \text{ singly occupied}. \tag{2.14b}$$

These two conditions can be translated into more convenient computational forms by substituting Eq. (2.13a) into Eqs. (2.14) to obtain

$$\sum_k \Delta(\underline{\phi}_i \underline{P}_k)\underline{\lambda}_k = -\Delta(\underline{\phi}_i \underline{F}), \quad \text{doubly occupied } i, \tag{2.15a}$$

$$\sum_k [\delta_{kj} - \Delta(\underline{\phi}_j \underline{P}_k)]\underline{\lambda}_k = +\Delta(\underline{\phi}_j \underline{F}), \quad \text{singly occupied } j. \tag{2.15b}$$

Equations (2.15) are solved simultaneously for the $\underline{\lambda}_k$ terms.

Before leaving this section, we briefly outline the algorithms which we employ to solve the coupled differential equations of (2.10) or (2.13). More thorough treatments are given elsewhere[16] but a condensed formulation will aid in the later description of the photoionization process.

We solve the set of coupled differential equations by converting it to a set of coupled integral equations. We write the differential equations of Eqs. (2.10) or (2.13) in the general form

$$(\underline{\Delta} - \underline{V})\underline{F} = 0, \tag{2.16}$$

where VF is either $(V + V_{\mathrm{ex}}^{n-1})F$ or $(V + V_{\mathrm{ex}}^{n-1})F + \phi_i$. A general solution to Eq. (2.16) can be written as

$$\underline{\bar{F}}(R) = \underline{G}^1(R)\underline{I}^2(R) - \underline{G}^2(R)\underline{I}^1(R), \tag{2.17}$$

with

$$\underline{F}(R) = \underline{\bar{F}}(R)[\underline{I}^2(\infty)]^{-1}, \tag{2.18a}$$

$$\underline{I}^j(R) = \underline{1}\delta_{j2} + \int_0^R \underline{G}^j(r)\underline{V}(r)\underline{F}(r)\,dr, \tag{2.18b}$$

$$\underline{L}\,\underline{G}^j(R) = 0. \tag{2.18c}$$

For neutral systems, we take $\underline{L} = \underline{\Delta}$ of Eq. (2.5a). The solutions to Eq. (2.18c) are then the spherical Bessel (G^1) and Neumann (G^2) functions. For ions, we add Z/R to $\underline{L}$ and its negative to $\underline{V}$ in Eq. (2.16). The solutions to the new $\underline{L} = \underline{\Delta} + Z/R$ are the regular (G^1) and irregular (G^2) Coulomb functions.[17] The lowest-order long-range moment of $\underline{V}$ is now the dipole (quadrupole) for polar (nonpolar) systems. With this choice of the Coulomb Green's function, the K matrix may be determined simply from the relationship

$$\underline{K} = \underline{I}^1(\infty)[\underline{I}^2(\infty)]^{-1}. \tag{2.19}$$

We have assumed the F goes asymptotically as $[\underline{S}(R) + \underline{K}\,\underline{C}(R)]/\sqrt{k}$, where $[\underline{S}(R)]_{ll'} = \sin(kr + l\pi/2 + \sigma_l)\delta_{ll'}$ and $[\underline{C}(R)]_{ll'} = \cos(kR + l\pi/2 + \sigma_l)$ with σ_l the Coulomb phase. Equations (2.17) and (2.18) are solved with a trapezoidal quadrature. A description of the numerical techniques employed to guarantee stable, linearly independent solutions are discussed in Paper I and Ref. 15.

In the close-coupling approximation, we obtain an accurate, though approximate, solution to the infinite order set of coupled equations by systematically increasing the number of terms in the expansions in Eqs. (2.3) until subsequent values of the cross section agree to within a specified tolerance. The number of terms N_c or channels retained in the expansion of the continuum orbital [Eq. (2.3a)] determines the order of the coupled equations and thus the size of the matrix equations which must be propagated in order to determine the continuum wave function $\underline{F}$ [Eq. (2.4)]. In the single-center expansion the order of the equations is determined principally by the nuclear component of the static potential $\underline{V}_{\mathrm{st}}$. While the contribution of the high-order partial waves (large l-value channels) in Eq. (2.3a) to the total cross section is small, they are necessary to ensure an accurate representation of the continuum wave function in the region of strong coupling near the nuclei. The exchange term $\underline{W}$, on the other hand, does not involve such a singularity as is found in the nuclear interaction, and thus an accurate representation of this term can be obtained with a small number of terms in the expansions of both the continuum and bound wave functions. This is fortunate since the time to calculate the exchange terms increases rapidly with addition of channels. In order to describe the collision calculation, we define the following parameters:

(1) l_m = maximum value of the channel label l needed to converge the continuum orbital $\underline{F}$;

(2) n_c^{ex} = number of continuum channels included in the evaluation or the exchange term;

(3) n_i^{ex} = number of projects of the ith bound orbital included in evaluating the exchange term;

(4) λ_m = maximum order of the Legendre expansion of the static potential retained;

(5) r_m = matching radius.

B. Vibrational excitation

We calculate vibrational-excitation cross sections for e-H_2^+ collisions in the adiabatic-nuclei approximation.[18] The space-fixed frame rovibrational cross sections $\sigma(vj \rightarrow v'j')$ are obtained from the body-frame fixed-nuclei K-matrix elements $K^{m}_{ll'}$, calculated from the methods discussed in Section II A, by a set of transformations. The transformation for the vibrational excitation involves an integration of the body-frame T-matrix elements and the initial and final state vibrational wave functions over internuclear separation. The rotational transformation simply involves performing angular momentum algebra.

The method may be implemented in the following manner. First, at each of a set of internuclear separations $\{s_i\}$ of the target molecule, we perform a body-frame fixed-nuclei static-exchange electron-scattering calculation which produces a body-frame K-matrix, $K^{m}_{ll'}(s_i)$. We then convert the body-frame K-matrix to T-matrix elements as

$$\underline{T}(s_i) = 2i\underline{K}(s_i)[\underline{1} - i\underline{K}(s_i)]^{-1}.$$

The space-fixed frame T-matrix elements are then found by

$$\underline{T}(vj \rightarrow v'j') = \int \chi_{v'j'}(s)\underline{T}(s)\chi_{vj}(s)\,ds\,, \qquad (2.20)$$

where χ_{vj} is vibrational wave function for a molecule in vibrational state v and rotational state j. The ro-vibrational cross sections can then be calculated from these transformed $\underline{T}$-matrix elements. A more detailed description of the calculational procedures involved in the adiabatic-nuclei approximation is given by Henry.[19]

C. Photoionization

For H_2 and N_2 we present photoionization cross sections in the "frozen (relaxed) core" and static-exchange approximations. Since the procedure we follow to calculate photoionization cross sections at the equilibrium separation of the neutral system from the electron-molecule ion static-exchange continuum wave function closely parallels those described by Chapman[20] and Raseev,[21] we present only a brief outline of the method.

The photoionization cross section in the dipole radiation approximation is given by[19]

$$\sigma_{\text{tot}} = \frac{8\pi^2\alpha\hbar\omega}{9}\sum_{ml_0}|d_{l_0m}|^2, \qquad (2.21)$$

where α is the fine-structure constant, $\hbar\omega$ is the energy of the incident photon in Rydbergs, and d_{l_0m} is the dipole matrix element. The dipole matrix element is labeled by the symmetry m and a particular linearly independent solution l_0 of the continuum orbital, which represents the collision of an electron with the molecular ion. The explicit form of this term is given by

$$d_{l_0m} = \sum_i \sum_l \sum_{l_i} \langle Y_{lm} | Y_{lm''} | Y_{l_im_i}\rangle \langle f_{ll_0} | r | \phi^{m_i}_{l_i}\rangle\,, \qquad (2.22)$$

where Y_{lm} is a spherical harmonic, $\phi^{m_i}_{l_i}$ is the radial expansion coefficient of the ith bound orbital of the neutral system from which an electron is ionized [see Eq. (2.3a)], the brackets represent angular and radial integrals, and f_{ll_0} is a component of the continuum scattering orbital (electron-molecular ion) with $\underline{S}$-matrix boundary conditions and m'' takes on the values 0 or ±1 depending on the values of m and m_i. The continuum orbital with K-matrix boundary conditions described in Sec. II A can be converted to one with S-matrix boundary conditions by

$$\underline{f}(R) = 2\underline{F}(R)(-i\underline{1} + \underline{K})^{-1}\,, \qquad (2.23)$$

where $\underline{F}$ is given by Eq. (2.18a). The more general form of the matrix element in Eq. (2.22) would be $\langle \Phi_{A_2} | \vec{r} | f\Phi_{A_2^+}\rangle$, where Φ_{A_2} is the wave function for the neutral A_2 system, f is the wave function for the electron $+A_2^+$ collision, and $\Phi_{A_2^+}$ is the wave function of the molecular ion. The product $f\Phi_{A_2^+}$ implicitly assumes a fully antisymmetric final state function. In general, Φ_{A_2} and $\Phi_{A_2^+}$ can be determined from independent structure calculations which have allowed complete relaxation in each system. In this case, the dipole matrix element has a more complex form than in Eq. (2.22) since the orbitals of the neutral and ion need not be orthonormal.[21] We shall refer to this formulation as the "relaxed core" approximation.

In the frozen core approximation, we use the molecular orbitals of the neutral for the molecular ion. In this case, the orthonormality of the neutral and ion orbitals (since they are identical) causes the dipole matrix element to collapse to the form in Eq. (2.22). In this form, we need only calculate dipole integrals over the continuum orbital and the molecular orbital of the neutral from which the electron was ionized. The static-exchange approximation applies to the calculation of the scattering of the electron by the molecular ion. The procedure for performing this calculation is described in Sec. II A.

For a system which is represented by a single molecular orbital, for example H_2, the relaxed core approximation assumes a particularly simple form. We obtain the *relaxed core* form of the photoionization cross section in this special case by replacing the "frozen core" dipole matrix element $\langle \Phi_{H_2} | r | f\rangle$ by $\langle \Phi_{H_2^+} | \Phi_{H_2^+}\rangle \langle \Phi_{H_2} | r | f'\rangle$. The fully relaxed neutral and ion H_2 wave functions are represented by Φ_{H_2} and $\Phi_{H_2^+}$ respectively. We distinguish between the two continuum solutions since they represent scattering in two different potentials. The frozen core continuum wave function represents scattering from an ionic potential determined by the *neutral* H_2 molecular orbital, while the relaxed core f' represents scattering from a potential determined by the molecular orbital of the H_{2^+} ion. We shall investigate the consequences of these approximations in more detail in Sec. III.

III. RESULTS

A. Electron-H_2^+ scattering

We present the results of static-exchange calculations for electrons scattering from H_2^+. These results are then used in calculations of vibrational excitation and photoionization cross sections.

1. Static-exchange calculations

We have performed calculations of the eigenphase sum as a function of continuum symmetry, energy, and internuclear separation for electron-H_2^+ collisions in the static-exchange approximation. The ground $X\,{}^2\Sigma_g^+$ state of H_2^+ was represented by the linear combination of atomic orbitals-molecular orbitals-self-consistent-field (LCAO-MO-SCF) wave function of Cohen and Bardsley.[22] This wave function used a $1s2s2p$ STO basis with full variation of the linear and exponential coefficients. The orbital parameters are given in Table I for three representative internuclear separations: $R=2.0a_0$, the equilibrium distance of H_2^+, $R=1.4a_0$, the equilibrium distance of H_2, and $R=2.6a_0$. The calculated orbital energies agree quite well with those from the exact H_2^+ ground state wave function of Bates, Ledsham, and Stewart.[23] (See Table I).

We present in Table II (b) the results of a convergence study for e-H_2^+ collisions at $R=2.a_0$ for the sigma symmetries. We also compare our one- and two-channel[4] results with those with no polarization of Temkin and Vasavada[4a] (TV) and Temkin, Vasavada, Chang, and Silver[4b] (TVCS), using as a standard our six-channel calculations. The differences between the two sets of calculations arise mainly from the different choice of target H_2^+ wave functions. In the two-channel case, we have used a slightly larger expansion of the static potential ($\lambda_m=4$ to $\lambda_m=2$) than Temkin *et al.* Still, the two sets of calculations are in rather good agreement, and the predicted trends in the eigenphase sums are generally consistent. For the Σ_u symmetries, only a modest correction to the one-channel results is introduced by the addition of more channels. This is due principally to the centrifugal barrier terms that appear in *all* the scattering channels and that exclude the electron to some extent from the region of strong coupling around the proton. For the Σ_g symmetries, which have no barriers in the s-wave channel, the effects of including additional channels are more pronounced. In all symmetries, the contribution from the higher partial waves becomes more important as the collisional energy is increased. This is due primarily to the deeper penetration of the higher partial waves. From this table, we conclude that accurate e-H_2^+ cross sections can be obtained only with expansions of the continuum wave function that are larger than two terms.

TABLE I. LCAO-MO-SCF molecular orbitals of the $X\,{}^2\Sigma_g^+$ ground state of H_2^+ as a function of internuclear distance. Linear C_i and exponential α_i coefficients for $1s2s2p$ STO basis.

$R(a_0)$	STO	C_i	α_i	Orbital energy (Ry)
1.40	$1s\sigma$	0.597 40	1.271 02	−2.566 255
	$2s\sigma$	−0.079 54	1.080 57	(−2.568 53) [a]
	$2p\sigma$	0.059 75	1.815 16	
2.0	$1s\sigma$	0.632 45	1.126 44	−2.203 008
	$2s\sigma$	−0.096 33	0.977 71	(−2.205 25)
	$2p\sigma$	0.070 199	1.550 92	
2.60	$1s\sigma$	0.656 92	1.042 66	−1.949 790
	$2s\sigma$	−0.099 143	0.907 06	(−1.950 90)
	$2p\sigma$	0.075 51	1.360 43	

[a] Exact value from Ref. 23.

We present in Table II (b) the results of e-H_2^+ collision calculations at the three internuclear distances of Table I. The collision parameters for $g(u)$ symmetries were selected as the following: $l_m=10(11)$, $n_c^{\text{ex}}=3$, $n_1^{\text{ex}}=3$, $\lambda_m=2l_m$, $r_m=50.0a_0$. This choice guaranteed a global convergence[12] to better than 3%. Our results at $R=1.4a_0$ are in good agreement with those of Dutta *et al.*,[1a] who employed an iterative static-exchange method similar to ours. We do not, however, obtain very close agreement with the results of Tambe and Ritchie[24a]; however, there appears to be some question as to the accuracy of their results.[24b] We have also performed static-exchange calculations with the above parameters at several additional internuclear distances ($R=1.2$, 1.6, 1.8, 2.2, 2.4, and $2.8a_0$) for use in the vibrational-excitation calculation of Sec. III A 1.

2. Vibrational excitation of H_2^+

We calculated the vibrational-excitation cross sections for electron-H_2^+ collisions in the adiabatic-nuclei approximation by the procedure outlined in Sec. II B. The body-frame K-matrix elements were calculated in the static-exchange ap-

TABLE II. (a) Comparison of eigenphase sums for $e^- + H_2^+$ collisions at $R_{eq} = 2.0a_0$. (b) Electron-H_2^+ scattering: Static exchange approximation. Eigenphase sum as a function of energy (Rydberg) and internuclear distance (Bohr).

			(a) δ_{sum} (rad)		
k^2 (Ry)	One channel		Two channel		Six channel
0.01	TV[a]	RC[b]	TVCS[c]	RC	RC
$^1\Sigma_g$	−0.597	−0.540	−0.356	−0.399	−0.357
$^1\Sigma_\mu$	0.318	0.352		0.314	0.349
$^3\Sigma_g$	0.021	−0.016	0.243	0.190	0.237
$^3\Sigma_\mu$	1.210	1.110		1.381	1.431
0.10					
$^1\Sigma_g$	−0.609	−0.560	−0.373	−0.417	−0.368
$^1\Sigma_\mu$	0.325	0.357		0.330	0.371
$^3\Sigma_g$	0.00	−0.036	0.247	0.186	0.241
$^3\Sigma_\mu$	1.150	1.063		1.328	1.383
1.00					
$^1\Sigma_g$	−0.632	−0.614	−0.404	−0.431	−0.346
$^1\Sigma_\mu$	0.386	0.4022		0.466	0.534
$^3\Sigma_g$	−0.148	−0.192	0.255	0.155	0.257
$^3\Sigma_\mu$	0.830	0.772		1.011	1.084
				1.000	1.000
	$l_m = 0(1)$		$l_m = 2(3)$		$l_m = 10(11)$
	$n_1^{ex} = 1$		$n_1^{ex} = 2$		$n_1^{ex} = 3$
	$n_c^{ex} = 1$		$n_c^{ex} = 2$		$n_c^{ex} = 3$

				(b) δ_{sum} (rad)					
$r(a_0)$	K^2 (Ry)	$^1\Sigma_g$	$^1\Sigma_\mu$	$^1\Pi_g$	$^1\Pi_\mu$	$^3\Sigma_g$	$^3\Sigma_\mu$	$^3\Pi_g$	$^3\Pi_\mu$
1.4	0.01	−0.1631	0.1404	0.0235	−0.2479	0.3997	1.1116	0.04813	0.2100
	0.09	−0.1757	0.1530	0.0243	−0.2444	0.3949	1.0842	0.0562	0.2128
	0.25	−0.1938	0.1804	0.0248	−0.2386	0.3852	1.0392	0.0703	0.2128
	0.49	−0.2071	0.2231	0.0254	−0.2282	0.3712	0.9881	0.0887	0.2079
	0.81	−0.2098	0.2758	0.0272	−0.2121	0.3546	0.9381	0.1088	0.1986
2.0	0.01	−0.3569	0.3490	0.0450	−0.3488	0.2368	1.4313	0.0917	0.1537
	0.09	−0.3682	0.3712	0.0467	−0.3397	0.2407	1.3828	0.1058	0.1563
	0.25	−0.3807	0.4134	0.0482	−0.3257	0.2464	1.3028	0.1210	0.1537
	0.49	−0.3806	0.4663	0.0507	−0.3055	0.2517	1.2125	0.1565	0.1451
	0.81	−0.3619	0.5150	0.0558	−0.2791	0.2557	1.1250	0.1835	0.1332
2.6	0.01	−0.5071	0.5144	0.0681	−0.4430	0.1409	1.5425	0.1465	0.0762
	0.09	−0.5149	0.5380	0.0701	−0.4272	0.1599	1.4832	0.1667	0.0806
	0.25	−0.5172	0.5758	0.0720	−0.4036	0.1908	1.3848	0.1979	0.0791
	0.49	−0.4969	0.6112	0.0757	−0.3728	0.2240	1.2757	0.2308	0.0722
	0.81	−0.4479	0.6295	0.0832	−0.3364	0.2524	1.1661	0.2587	0.0636

[a] Temkin and Vasavada, Ref. 4a.

[b] This work.

[c] Temkin *et al*., Ref. 4b.

proximation (see Sec. IIIA 1) at nine internuclear distances ($1.2 \leq R \leq 2.8$ in increments of $0.2a_0$). The vibrational wave functions were calculated in the H_2^+ potential-energy curve given by the SCF $X\ ^2\Sigma_g$ wave function described in Sec. IIIA1. The energy splittings of the lowest few vibrational states for this potential were found to be $\Delta E(v = 0-1) = 2185.27\ \text{cm}^{-1}$ and $\Delta E(v = 0-2)$ 4247.79 cm^{-1}. The cross sections were calculated using the code VIBAD[19] from the Computer Physics Communications library. The singlet (σ^s) and triplet (σ^T) cases were calculated separately, and a spin-averaged cross section determined by $(\sigma^s + 3\sigma^T)/4$. All Σ, Π, Δ, g, and u symmetries were included from the continuum functions.

In Table III, we present vibrational-excitation cross sections for singlet and triplet scattering for the $v=0$ to $v'=1$, $\Delta j=0$, transition as a function of the energy of the incident electron. A more extensive set of $\Delta v=1$ spin-averaged cross sections is presented in Fig. 1. The results for the $\Delta v=1$ cross sections are in qualitative agreement with an earlier Coulomb-Born calculation.[25] In addition, the spin-averaged $j=0$ to $j=2$ $(\Delta v=0)$ rotational-excitation cross sections agree to within ten percent with those of Chang and Temkin.[26] The differences probably arise from the larger number of terms retained in the continuum and bound orbital expansions in the present calculations. We note that for para- and ortho-H_2^+ $\Delta v=1$ transitions, the cross sections for $\Delta j=0$ are a factor of two to four larger than those for $\Delta j=2$. In addition, the $\Delta v=1$ transitions from $v=1$ are a factor of two larger than those originating from $v=0$. This behavior is observed in the Born approximation vibration-excitation cross section which scales as $v+1$. The $\Delta v=2$ transition cross sections are down by an order of magnitude from those for $\Delta v=1$. Finally, we note that preliminary calculations with our iterative-exchange electronic excitation program support earlier findings[27,10] that the region from a few tenths to one Rydberg is sprinkled with a number of narrow Feshbach resonances which will to some extent affect the vibrational-excitation cross section. These resonances, which have been most recently examined by Takagi and Nakamara,[5] do not appear in our present static-exchange calculations since no allowance has been made for correlation and multistate effects. We leave the quantitative findings of our multiple-state close-coupling calculations from this study to a later paper.[27a]

TABLE III. Vibrational-excitation cross sections $\sigma(v0 \rightarrow V'0)$ for e-H_2^+ collisions.

k^2 (Ry)	$\sigma(00\rightarrow 10)$ (Å^2) Singlet	Triplet
0.04	0.6559	0.8014
0.09	0.3637	0.4428
0.16	0.2169	0.2646
0.25	0.1416	0.1749
0.36	0.0983	0.1244
0.49	0.0712	0.0936
0.64	0.0533	0.0735
1.00	0.0326	0.0495

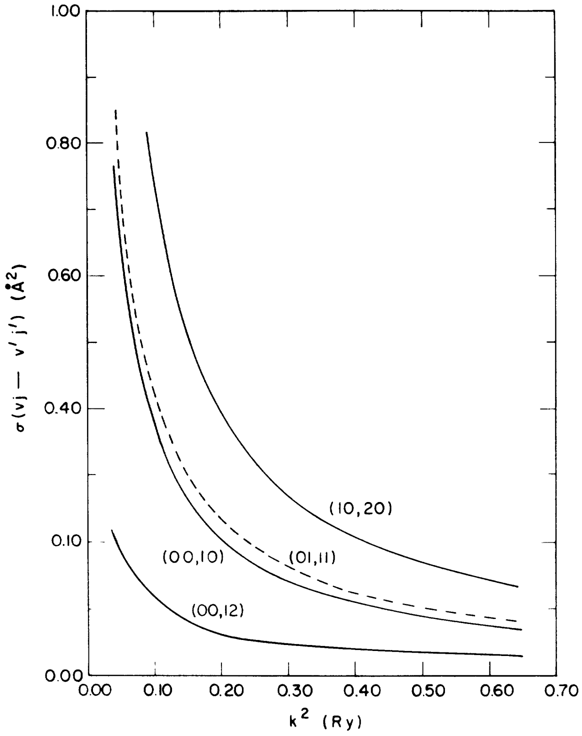

FIG. 1. Spin-averaged vibrational-excitation cross sections $\sigma(vj-v'j')$ for electron-H_2^+ collisions in the static-exchange approximation.

3. Photoionization of H_2

As a test of our photoionization program, we applied it to two atomic systems, H and He. For photoionization of the 1s state of H, we obtain excellent agreement with the analytical expression given by Sobelman.[28] For the photoionization of the ground state of He, we compare against the results of Lucchese and McKoy.[29] We apply the frozen-core approximation using the Hartree-Fock He orbital of Clementi for both the neutral and ionic systems. The scattering calculation for e-He^+ was performed in the static-exchange approximation. We obtain photoionization cross sections of 7.75 and 5.84 Mb at photon energies of 24.75 and 30.6 eV (ionization potential (IP) $=0.9034$ hartrees) respectively, while Lucchese and McKoy report values of 7.59 and 5.76 Mb at the corresponding energies. The differences can probably be attributed to the use of fully relaxed He and He^+ wave functions by Lucchese and McKoy and of the frozen-core approximation in our case.

We calculated photoionization cross sections for ground-state molecular hydrogen $(H_2\,{}^1\Sigma_g^+)$ in the frozen and relaxed core and static-exchange and Coulomb wave collisional approximations. The results of these calculations are summarized in Table IV. All calculations employed the Fraga and

TABLE IV. Total photoionization cross sections for H_2 in megabarns (Mb): Comparison of various approximations.

Approximation [a]	Photon energy (eV)		
	20	30	40
Frozen Core [b]	8.252	2.850	1.201
Relaxed Core			
$1s2s2p/c$ [c]	6.816	2.523	1.183
$1s2s2p$/SE [d]	7.738	3.006	1.375
$1s$/SE [e]	8.103	3.046	1.344
Dutta *et al.*	8.213	3.176	1.421

[a] All approximations employ the SCF $^1\Sigma_g^+$ H_2 neutral ground-state wave function of Fraga and Ransil for Φ_{A_2}.

[b] $\Phi_{A_2^+}$ = Fraga-Ransil H_2 wave function; static-exchange collision.

[c] $\Phi_{A_2^+}$ = Cohen-Bardsley H_2^+ wave function of Table I, Coulomb collision.

[d] $\Phi_{A_2^+}$ = Cohen-Bardsley H_2^+ wave function; static-exchange collision.

[e] $\Phi_{A_2^+}$ = Dutta *et al.* H_2^+ wave function, static-exchange collision.

Ransil[30] LCAO-MO-SCF $X^1\Sigma_g$ ground state H_2 wave function at $R=1.4a_0$ to represent the neutral system (Φ_{H_2}). In the frozen-core approximation, we use this neutral wave function to represent the molecular orbital of the ion. In calculating the scattering potential for the electron-ion interaction, we remove one electron from the neutral orbital so that the static potential will approach the correct asymptotic limit ($-1/R$). For the relaxed core case, we use two different wave functions to represent the molecular ion ($\Phi_{H_2^+}$). The first is the LCAO-MO-SCF function of Cohen and Bardsley given in Table I at $R=1.4a_0$. This function consists of a $1s2s2p$ STO basis. For comparison, we also use the orbital of Dutta *et al.*[1a] which is formed from a single $1s$ STO basis. Finally, we employ two approximations to the calculation of the continuum orbital which describes the e-H_2^+ collision. The first is the static-exchange (SE) approximation which is described in Secs. II and III A 1. As another approximation, we represent the continuum orbital as a Coulomb wave (CW). We thus allow only for the distortion effects of the long-range contributions from the full molecular potential.

We compare our calculations with those of other authors. The relaxed core calculation using the H_2^+ $1s$ STO function is identical with that of Dutta *et al.*[1a] except in the representation of the H_2 neutral function. Both employ a $1s2s2p$ STO basis but use slightly different exponents. The Fraga and Ransil $X^1\Sigma_g^+$ function has a total energy of $-1.133\,49$ hartrees while that of Dutta *et al.* yields $-1.133\,23$ hartrees. The slight differences in the two calculations arise from this slight difference in the neutral wave functions and the choice of convergence parameters. For all e-H_2^+ collisions, we used $l_m=7$, $n_1^{ex}=2$, $n_c^{ex}=2$, $\lambda_m=14$, and $r_m=50.a_0$. Dutta, Chapman, and Hayes included channels with l less than or equal to 5. We compare the relaxed core-Coulomb wave results with those of Ford *et al.*[31] These authors used a multiconfigurational representation of the H_2 and H_2^+ systems. At a photon wavelength of 584 Å (21.24 eV), they report a total photoionization cross section of 6.82 Mb, while we calculate for our single configuration target functions a value of 6.80 Mb at 20 eV. This agreement is to some extent fortuitous as at higher photon energies our single-configuration results are lower by a factor of 20%. We note that the effects of relaxing the core, of accurately representing the continuum wave function, and of improving the accuracy of the molecular ion wave function are most pronounced near threshold. As the photon energy increases, these various effects become less important.

B. Electron-CH^+ collisions

We have performed static-exchange calculations for electron scattering from CH^+. We use the LCAO-MO-SCF $X^1\Sigma^+$ ground-state wave function of Cade and Huo[32] at an equilibrium distance of 2.137 a_0. The dipole and quadrupole moments produced by the charge density of this wave function are 0.756 and 0.281 a.u., respectively. The collision calculations were performed at a number of energies with the following parameters for $\Sigma(\Pi)$ scattering symmetry: $l_m=6$, $n_e^{ex}=3$, $n_{1-3}^{ex}=3$, $\lambda=2l_m$, and $r_m=32a_0$. Orthogonality to all three bound orbitals was enforced in the Σ scattering symmetry. The results are in good agreement

TABLE V. Electron-CH^+ collisions in the static-exchange approximation: eigenphase sums as a function of energy for Σ and π scattering symmetries.

k^2 (Ry)	δ_{sum} (rad) Σ	mod (π) π
0.01	2.5300	1.8562
0.05	2.5474	1.8548
0.10	2.5615	1.8583
0.20	2.5691	1.8619
0.40	2.5375	1.8732
0.60	2.4649	1.8811
0.80	2.3880	1.8882
1.00	2.3113	1.8936
l_m	6	6
n_c^{ex}/n_{1-3}^{ex}	3/3	3/3
r_m (a_0)	32	32

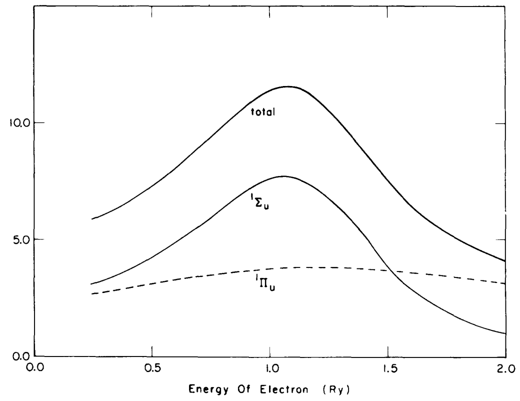

FIG. 2. Total and partial photoionization cross sections for N_2 in the frozen core and static-exchange approximations.

with those of Raseev *et al.*[7] for the Π symmetry. This choice of parameters guaranteed eigenphase sums globally converged to better than 10%. We present the eigenphase sums for the Σ and Π symmetries as a function of energy in Table V. Raseev *et al.* get a Π eigenphase 1.82 compared to our 1.85, at 0.00735 eV.

C. Photoionization of N_2

We have calculated cross sections for the photoionization of N_2 from the valence $3\sigma_g$ orbital in the frozen core and static-exchange approximations. The N_2 $X\,{}^1\Sigma_g^+$ ground-state LCAO-MO-SCF wave function of Nesbet[33] was used. The same orbitals were used to describe the N_2^+ system with one electron removed from the $3\sigma_g$ orbital. The electron-N_2^+ calculation was performed in the static-exchange approximation for the ${}^1\Sigma_u$ and ${}^1\Pi_u$ symmetries, the only two symmetries coupled to the $3\sigma_g$ orbital by the dipole term of the radiation field. The parameters used in the collision calculation were as follows: $l_m = 13$, $n_e^{ex} = 2$, $n_{1-6}^{ex} = 2$, $\lambda = 2l_m$, and $r_m = 85a_0$. We enforced orthogonality of the ${}^1\Sigma_u$ and ${}^1\Pi_u$ continuum orbitals to the bound orbitals of the same symmetry. The ionization potential was taken, according to Koopman's theorem, to be the $3\sigma_g$ orbital energy. In Fig. 2, we present the total photoionization cross section of N_2 as a function of the energy of the ionized electron. The results are in excellent agreement with those of Raseev *et al.*[21]

IV. SUMMARY

We have presented a prescription for extending an iterative static-exchange single-center method for electron scattering from neutral molecules to electron-molecular ion collisions. The procedure is found to be both stable and fast, requiring less than five iterations in most cases to obtain cross sections converged to better than three significant figures. For molecular ions, we found that the WF-inverse procedure, by which the inhomogeneous exchange term is converted, at each iteration, to a local potential by dividing through by the continuum orbital of the previous iteration, is the most stable and efficient. For cases in which there are bound orbitals of the same symmetry as the continuum function, we find, as with the neutrals, that the iterative procedure can be accelerated by forcing these orbitals to be orthogonal. To demonstrate the efficiecy of the technique, we have applied it to electron collisions with H_2^+, CH^+, and N_2^+. In particular, we have calculated vibrational-excitation cross sections for e-H_2^+ collisions and photoionization cross sections for H_2 and N_2.

ACKNOWLEDGMENTS

We wish to thank Dr. J. S. Cohen and Professor N. Bardsley for providing us with their H_2^+ wave function and Dr. B. Liu for providing us with a preliminary CH^+ wave function. Discussions on various aspects of this project with Dr. A. Hazi, Dr. V. McKoy, Dr. R. Martin, and Dr. M. A. Morrison are gratefully acknowledged. Support for this project was provided through the Theoretical Division of the Los Alamos Scientific Laboratory.

---

[1] (a) C. M. Dutta, F. M. Chapman, and E. F. Hayes, J. Chem. Phys. 67, 1904 (1977); (b) H. P. Kelly, Chem. Phys. Lett. 20, 547 (1973); B. Ritchie, J. Chem. Phys. 63, 1351 (1975), and references therein; S. V. O Neil and W. P. Reinhardt, J. Chem. Phys. 69, 2126 (1978).

[2] J. N. Bardsley and M. Biondi, Adv. At. and Mol. Phys. 6, 1 (1970); A. Giusti-Suzor and H. Lefebvre-Brion, Astrophys. J. 214, L101 (1977); C. Bottcher, Proc. R. Soc. London, Ser. A 340, 301 (1974).

[3] A. Dalgarno, in *Atomic Processes and Applications*, edited by P. G. Burke and B. L. Moiseivitsch (North-Holland, Amsterdam, 1976), Chap. 5.

[4] (a) A. Temkin and K. V. Vasavada, Phys. Rev. 160, 109 (1967); (b) A. Temkin, K. V. Vasavada, E. S. Chang, and A. Silver, Phys. Rev. 186, 57 (1969); (c) G. Raseev, H. Le Rouzo, and H. Lefebvre-Brion, J. Chem. Phys. 72, 5701 (1980).

[5] H. Takagi and H. Nakamura, *Symposium on Electron-Molecule Collisions, University of Tokyo*, 1979 (University of Tokyo Press, Tokyo, 1979); J. Phys. B 11, L675 (1978).

[6] L. A. Collins, W. D. Robb, and M. A. Morrison, (a) J.

Phys. B 12, L777 (1978); (b) Phys. Rev. A 21, 488 (1980).

[7] G. Raseev, A. Giusti-Suzor, and H. Lefebvre-Brion, J. Phys. B 11, 2735 (1978); B. D. Buckley and P. G. Burke, J. Phys. B 10, 725 (1977).

[8] (a) B. I. Schneider, M. LeDourneuf, and Vo Ky Lan, Phys. Rev. Lett. 43, 1926 (1979); B. I. Schneider and M. A. Morrison, Phys. Rev. A 16, 1003 (1977); B. I. Schneider and P. J. Hay, *ibid.* 13, 2049 (1976); (b) A.W. Fliflet, D. A. Levin, M. Ma, and V. McKoy, Phys. Rev. A 17, 160 (1978); T. N. Rescigno, C. W. McCurdy, and V. McKoy, *ibid.* 11, 825 (1975); (c) R. R. Lucchese and V. McKoy, Phys. Rev. A 21, 112 (1980); D. Watson and V. McKoy *ibid.* (in press).

[9] L. A. Collins and W. D. Robb, J. Phys. B 1 (in press).

[10] (a) S. Chung and C. C. Lin, Phys. Rev. A 17, 1874 (1978); A. Fliflet and V. McKoy, *ibid.* (in press); (b) N. F. Lane, Rev. Mod. Phys. 52, 29 (1980).

[11] S. Hara, J. Phys. Soc. Jpn. 27, 1009 (1969).

[12] M. A. Morrison and L. A. Collins, Phys. Rev. A 17, 918 (1978).

[13] M. J. Seaton, Phil. Trans. R. Soc. London 245, 496 (1953); H. E. Saraph and M. J. Seaton, Proc. Phys. Soc. London 80, 1057 (1962).

[14] J. C. Tully and R. S. Berry, J. Chem. Phys. 51, 2956 (1969).

[15] M. E. Riley and D. G. Truhlar, J. Chem. Phys. 63, 2182 (1975); M. A. Morrison, in *Electron and Photon-Molecule Collisions*, edited by T. N. Rescigno, B. V. McKoy, and B. I. Schneider (Plenum, New York, 1979).

[16] (a) M. A. Morrison, N. F. Lane, L. A. Collins, Phys. Rev. A 15, 2186 (1977); (b) W. N. Sams and D. J. Kouri, J. Chem. Phys. 51, 4815 (1969); 51, 5809 (1969).

[17] S. P. Rountree, T. Burnett, R. J. W. Henry, and C. A. Weatherford, Comput. Phys. Commun. 11, 27 (1976).

[18] F. H. M. Faisal and A. Temkin, Phys. Rev. Lett. 28, 203 (1972); R. J. W. Henry and E. S. Chang, Phys. Rev. A 5, 276 (1972); E. S. Chang and U. Fano, *ibid.* 6, 173 (1972); A. Temkin and E. C. Sullivan, Phys. Rev. Lett. 33, 1057 (1974).

[19] R. J. W. Henry, Comput. Phys. Commun. 10, 375 (1975).

[20] F. M. Chapman, J. Chem. Phys. 63, 2101 (1975).

[21] G. Raseev, J. Phys. B (in press).

[22] J. S. Cohen and N. Bardsley (private communication).

[23] D. R. Bates, K. Ledsham, and A. L. Stewart, Proc. R. Soc. London 246, 28 (1953).

[24] (a) B. R. Tambe and B. Ritchie, J. Chem. Phys. (in press); (b) B. Ritchie (private communication).

[25] R. F. Boykova and V. D. Ob"edkov, Zh. Eksp. Teor. Fiz. 53, 1327 (1967) [Sov. Phys.—JETP 27, 772 (1968)].

[26] E. S. Chang and A. Temkin, J. Phys. Soc. Jpn. 29, 172 (1970).

[27] (a) W. D. Robb and L. A. Collins, Phys. Rev. A (to be published); (b) T. F. O'Malley, J. Chem. Phys. 51, 322 (1969); C. Bottcher and K. Docken, J. Phys. B 7, L5 (1974); C. Bottcher, *ibid.* 7, L352 (1974).

[28] I. I. Sobelman, *Introduction to the Theory of Atomic Spectra* (Pergamon, New York, 1972), p. 364.

[29] R. R. Lucchese and V. McKoy, Phys. Rev. A 21, 112 (1980).

[30] S. Fraga and B. Ransil, J. Chem. Phys. 35, 1967 (1961).

[31] A. L. Ford, K. K. Docken, and A. Dalgarno, Astrophys. J. 195, 819 (1975).

[32] P. E. Cade and W. Huo, At. Data Nucl. Data Tables 12, 429 (1973).

[33] R. K. Nesbet, Phys. Rev. 179, 60 (1969).