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Modified method of perturbed stationary states. I. Wave-theoretic formulation

T. A. Green
Sandia Laboratories, Albuquerque, New Mexico 87185

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The reaction-coordinate approach of Mittleman is used to generalize the method of perturbed stationary states. A reaction coordinate and an associated electron coordinate are defined for each state in the scattering expansion in terms of scalar parameters which depend on the internuclear separation. These are to be determined from a variational principle described by Demkov. The choice of parameters, the scattering expansion, and the Lagrangian for the radial scattering functions are given for a heteropolar one-electron system.

I. INTRODUCTION

Inelastic atom-atom collisions continue to be of practical importance over a large range of impact velocities. Charge-exchange and energy-transfer cross sections are required, for example, as basic data in models of gas lasers, ion-beam propagation, and for applications to the interstellar medium. Currently, charge exchange between highly stripped ions and hydrogen atoms is of significance to the operation of magnetic fusion energy devices. In the latter case, H-atom energies from a few eV to a few hundred keV are of interest.

The work described below is concerned with the energy regime, usually below about 25 keV per nucleon, where the impact velocity does not exceed the orbital velocity of the active electron. This is the natural region of application of the method of perturbed stationary states (pss). Much has been written about the problems associated with the method, and these points will not be repeated here except where they relate directly to this paper. Among the earlier papers on the subject the author has found Refs. 1–5 instructive for physical insight and technical formalism. In particular, the paragraph starting on page 440 of the paper by Bates, Massey, and Stewart[1] describes the need to change coordinates as one proceeds from the separated-atom limit to the united-atom limit. That need is central to the work which follows. Riera and Salin[6] have critically reviewed work on the pss method.

This paper proposes a new wave-theoretic modification of the pss method for diatomic systems. It was most directly influenced by the work of Bates and McCarroll[2] on the one hand and by that of Mittleman[7] on the other. Although it was developed independently, the theory reported here is also closely related to the work of Thorson and Delos.[8] The theory is similar to Refs. 7 and 8 in that following Mittleman a reaction coordinate is introduced in place of the internuclear separation in such a way that the individual terms in the modified pss expansion can become solutions of the time-independent Schrödinger equation in the limit of separated atoms. In this limit a reaction coordinate must tend toward the distance between the atomic centers of mass.[1] The theory departs from Refs. 7 and 8 in that, instead of having a single reaction coordinate for all terms in the expansion, there is one for each term in the expansion.[9] This difference is fundamental, as can be seen most readily from the semiclassical limits of the theories. When a single reaction coordinate is used, the coupling matrix elements in the semiclassical equations do not contain Bates-McCarroll-type plane-wave translational factors in the integrands. For the theory described below, modified Bates-McCarroll factors do appear, and, in the separated-atom limit, the present expansion is equivalent to an atomic expansion with the usual factors[2] included.

This work seeks to improve on the original theory of Bates and McCarroll[2] in two ways. First, thanks to the reaction-coordinate point of view, it is not necessary to introduce any external vectors, such as the initial-state separated-atom velocity, into the expansion basis of the theory. Scalar functions of the internal configuration-space variables of the system are introduced instead. These define a transformation from the original pss center-of-mass variables to a new set, one of which is the reaction coordinate.[7,8,10] This approach guarantees that the conservation laws are obeyed and resolves all questions related to Galilean invariance automatically.[11] Second, the scalar transformation parameters introduced into the scattering expansion can be determined from the variational principle for inelastic collisions described by Demkov.[12] The use of a variational procedure avoids a completely *a priori* choice of parameters, and can lead to variationally determined values for the parameters at all internuclear separations.[13 15] The present work shows that in the semiclassical approximation these parameters appear in translational factors of the Bates-Mc-

Carroll form. These agree with those of Bates and McCarroll in the separated-atom limit but generally disagree elsewhere.

The use of translational plane-wave factors in connection with a molecular expansion complicates the structure of the scattering equations and makes the high-velocity matrix elements more expensive to compute. For this reason many researchers currently prefer to utilize molecular approaches based on a single-reaction coordinate or on its semiclassical equivalent. This author's interest in the more difficult Bates-McCarroll approach is based on the following observations.

(1) The use of Bates-McCarroll translational factors in connection with small and large atomic expansions in impact-parameter theory has been shown to be both necessary and feasible, despite the nonorthogonality of the basis and despite the need to compute new coupling matrix elements for each energy and impact parameter.[16-22] The development of comparable computer codes using a molecular basis is technically more difficult but still feasible.

(2) Experience with atomic basis expansions at energies below about 10 keV per nucleon suggests that while they are still very useful, a basis with molecular character inside the separated atom region could be even better.[18,19] It is of interest, therefore, to develop a molecular expansion which in the separated atom region is as close as possible to the atomic expansions referred to above. With such an expansion, one can hope to provide quantitative results up to energies of the order of 25 keV per nucleon. In the absence of supporting calculations, it is hard to believe[23] that the approaches based upon an overall translational factor[24-26] can yield the correct energy dependence for charge exchange at the upper end of this energy region. By contrast, in the cases where molecular-basis calculations utilizing Bates-McCarroll translational factors, or the Piacentini and Salin approximation thereto, have been carried out at high energies, they have been encouraging.[27-30]

(3) At low energy, theories with translational factors of the Bates-McCarroll type can be simplified to the point where they are no more complicated to evaluate than theories based on a single-reaction coordinate. In addition, where the Bates-McCarroll approach has been used in molecular expansions at low energies[31-33] the results have agreed closely[34] with those obtained[26] through the use of an overall translational factor of the type defined by Schneiderman and Russek[24] or by Levy and Thorson.[25]

The third statement above is in contradiction to the conclusions of some researchers[8,26] who seem to regard the use of nonorthogonal expansions as undesirable at low energies. We disagree with this point of view. In the case of the rotational transition considered in Refs. 26 and 31–33, it was shown some time ago that if terms up to first order in velocity were retained in the matrix elements, coupled equations with diagonal overlap and Hermitian symmetric coupling could be obtained for the Bates-Williams theory[31] in a simple way.[36] Thus, the equations of a theory based on Bates-McCarroll-type translational factors need not be more complicated at low energies than the theories used in Refs. 8 and 26. It is only at higher velocities, where electron momentum transfer is important, that the coupled equations become more complicated—in essentially the same way that those based on atomic expansions are complicated.

In summary, there is reason to believe that a theory of the Bates-McCarroll type offers interesting possibilities for quantitative calculations of atom-atom collisions in the energy range up to about 25 keV per nucleon. There is no actual evidence against the use of such a theory. The author feels that the arguments about complexity given against its use are not compelling.

The use of the variational principle is central to this work. As in Refs. 7 and 8, we rely primarily on the established validity of the molecular electronic eigenfunctions. The modifications introduced by the additional coordinate transformation parameters are intended to be minimal ones sufficient to make the equations decouple in the separated-atom limit and still be physically reasonable at all internuclear separations. It is only in the form of the transformation that this work differs from that in Refs. 7 and 8. We will introduce a coordinate transformation for each adiabatic or diabatic state. In this way the expansion will be flexible enough to cope with the differences between the lower-lying and higher-lying states included in it. The transformation will depend on two parameters, functions of internuclear separation. These parameters can be related in the semiclassical limit to the two components of a Bates-McCarroll-type vector translation factor in the scattering plane.

There is a problem connected with our use of the variational principle. The transformation parameters are postulated to be slowly varying functions of internuclear separation, dependent primarily on electronic structure. As the result of applying the variational principle directly, one naturally obtains coupled equations linking the transformation parameters to the radial scattering functions for the several electronic states in the expansion. Inevitably, the simultaneous solution of these equations induces high-frequency oscillations into the supposedly slowly varying parameters. This definition and solution of the variational problem is not exactly what we are looking for. Rather, we want to satisfy the variational equations as best we can with slowly varying parameters.

We do not know the best way to formulate such a problem. One approach[7] is to introduce specific, slowly varying functions depending on constants, as is done in the Kohn and Hulthen methods. This could be done here; however, we have elected another approach which yields reasonable results but which could stand further investigation. Briefly, at low or high energies, we use adiabatic or diabatic basis sets designed to make the coupling between basis states relatively weak. This allows one to decouple the determination of the variational parameters from that of the radial scattering functions. The resulting parameters then depend primarily on electronic structure.

The diabatic states just referred to are defined in terms of linear combinations of electronic eigenfunctions of the same symmetry. These states, which may be called interpolating states to avoid possible confusion with other definitions, are defined for localized avoided crossings by a method similar to that proposed by Smith, but using a finite set of electronic states.[37,38] The details are presented in the Appendix.

The results of this work are divided into two papers. This paper is concerned with the derivation of the Lagrangian functional for the radial scattering functions in a wave-theoretic context. In Sec. II, the transformation which defines the new scattering variables of the theory is developed for a one-electron heteropolar system. Section III lays the groundwork for the exact treatment of angular momentum conservation through a special choice of coordinates for the electronic basis functions. This allows one to derive the exact coupled equations for the radial scattering functions without making a semiclassical approximation or introducing an eikonal approximation with its restrictions to small-angle scattering.[39] In Sec. IV the construction of the scattering expansion and the derivation of the Lagrangian are carried out in detail. Section V contains a brief discussion of the results.

The second paper is also concerned with one-electron heteropolar systems and starts with the Lagrangian of Sec. IV. Its purpose is to reduce the integro-differential equations of the present paper to approximate ordinary differential equations which are amenable to computation. A semiclassical approximation is considered. It is shown that plane-wave translational factors of the Bates-McCarroll type result from the formulation of the present paper. In the same approximation, variational formulas for the transformation parameters are also derived.[40]

II. THE INTRODUCTION OF A STATE-DEPENDENT REACTION COORDINATE AND THE TRANSFORMATION OF THE SYSTEM KINETIC ENERGY

Consider the creation of an electronic basis set for slow collisions between atom A and atom B. The logical functions to use are those of the pss method, i.e., the fixed-nucleus electronic eigenfunctions χ_G for the AB molecule. The well-known difficulty with this method is that with a scattering function $F_G(\vec{R})$ depending on the internuclear separation $\vec{R}$, the individual terms in the expansion do not become exact solutions of the Schrödinger equation as $R\rightarrow\infty$. The differential equations obtained for the $F_G(\vec{R})$ have nonzero coupling for all R among all channels which are connected by dipole-allowed transitions. Bates and McCarroll[2] showed that, as in the case of atomic eigenfunction expansions, translational factors multiplied into the fixed-nucleus molecular eigenfunctions suffice to eliminate the undesired long-range coupling.[41]

In this paper, starting with $\vec{R}$ and the electron coordinate $\vec{r}$, for each state G in the scattering expansion, there are introduced a reaction coordinate $\vec{\xi}(\vec{R},\vec{r})$ and an electron coordinate $\vec{\eta}(\vec{R},\vec{r})$. The terms in the scattering expansion are then introduced as functions of $\vec{\xi}$ and $\vec{\eta}$. Once these terms have been constructed, the next step is to apply the system Hamiltonian H to the expansion and derive the Lagrangian functional. At this point, it becomes useful to express H in terms of $\vec{\xi},\vec{\eta}$ so that the actual equations for the unknowns $F_G(\vec{\xi})$ for each term can be deduced. The rest of this section will therefore be concerned with the transformation defined in Eq. (1) below and with its influence on the form of the kinetic energy operator. The discussion is essential, but tedious, and leads to Eqs. (18) and (23).

The electron coordinate $\vec{\eta}$ and the reaction coordinate $\vec{\xi}$ for a particular term in a scattering expansion are defined by the transformation

$$\vec{\xi}=\alpha\vec{R}+\beta\vec{r}\,,$$
$$\vec{\eta}=\gamma\vec{R}+\delta\vec{r}\,. \tag{1}$$

The original electron coordinate $\vec{r}$ is referred to the center of mass of the nuclei. Later, a subscript G will be introduced to keep track of the different transformations for different terms in a scattering expansion. The quantities α, β, γ, and δ are the transformation parameters mentioned in the Introduction. They are scalar functions of R, r, and $s\equiv\vec{r}\cdot\vec{R}$. Only scalar functions are introduced, so the expression for the total orbital angular momentum

$$-i\hbar\left(\vec{\mathrm{R}}\times\frac{\vec{\partial}}{\partial R}+\vec{\mathrm{r}}\times\frac{\vec{\partial}}{\partial r}\right)\equiv-i\hbar\left(\vec{\xi}\times\frac{\vec{\partial}}{\partial\vec{\xi}}+\vec{\eta}\times\frac{\vec{\partial}}{\partial\eta}\right)\qquad(2)$$

is form invariant. The model for the transformation used in this paper is suggested by the transformation to separated-atom, center-of-mass variables.[42] This transformation will now be discussed. Suppose that the electron is attached to nucleus A. Let $p=M_B/(M_A+M_B)$ where M_A and M_B are the nuclear masses, let m be the electron mass, and define

$$\begin{aligned}\vec{\eta}&=\vec{\mathrm{r}}+p\vec{\mathrm{R}}=\vec{\mathrm{r}}_A\,,\\ \vec{\xi}&=\vec{\mathrm{R}}-\frac{m}{(M_A+m)}(\vec{\mathrm{r}}+p\vec{\mathrm{R}})\\ &=\vec{\mathrm{R}}_{AB}\,.\end{aligned}\qquad(3)$$

The definition of p is such that $\vec{\mathrm{r}}+p\vec{\mathrm{R}}$ is the vector $\vec{\mathrm{r}}_A$ from nucleus A to the electron. The reaction coordinate $\vec{\xi}$ is just $\vec{\mathrm{R}}_{AB}$, the vector from the center of mass of atom A to that of nucleus B. The Jacobian of the transformation (3) is unity. The special thing about transformation (3) is that the transformed system kinetic energy is separable with respect to $\vec{\mathrm{R}}_{AB}$ and $\vec{\mathrm{r}}_A$. That is, there are no cross-derivative terms in the kinetic energy.[5]

Using Eq. (3) as a model we seek transformation of the form (1) such that the scattering equations decouple in the separated-atom region. This is not a unique process, and it is most easy to discuss after the form of the kinetic energy operator has been obtained. At this point, however, one restriction on the coefficients is introduced so that no large distortions of the volume element are allowed. We require that the Jacobian of the transformation (1) be unity to at least first order in m/M. This condition is imposed by assuming that

$$\begin{aligned}\alpha&=1+(m/M)g\,,\\ \beta&=(m/M)h\,,\\ \delta&=1+(m/M)f.\end{aligned}\qquad(4)$$

In Eq. (4) M is the reduced mass of the nuclei. In Eqs. (1) and (4) γ, g, h, and f are all assumed to be $O(1)$ or smaller as (m/M) approaches zero.

The result of Eqs. (4) is that through transformation (1), $\vec{\xi}=\vec{\mathrm{R}}$ up to terms of order m/M and $\vec{\eta}=\gamma\vec{\mathrm{R}}+\vec{\mathrm{r}}$ up to terms of order m/M. Thus, the reaction coordinate is kept close to $\vec{\mathrm{R}}$, and the electron is nearly located with respect to a point shifted by $-\gamma\vec{\mathrm{R}}$ along the internuclear line from the center of mass of the nuclei. As Bates and McCarroll[2] showed, the order m/M change from $\vec{\mathrm{R}}$ to $\vec{\xi}$ is important because in the scattering functions, $\vec{\xi}$ or $\vec{\mathrm{R}}$ is multiplied by the heavy-particle momentum, $M\vec{\mathrm{v}}$.

The next step in the program is to express the kinetic energy T in terms of the new variables defined in Eqs. (1) and (4). The result can be written

$$\begin{aligned}\frac{-2}{\hbar^2}T&=A_{kj}\frac{\partial}{\partial\xi_k}\frac{\partial}{\partial\xi_j}+B_{jk}\frac{\partial}{\partial\xi_j}\frac{\partial}{\partial\eta_k}\\ &\quad+C_{jk}\frac{\partial}{\partial\eta_j}\frac{\partial}{\partial\eta_k}+D_j\frac{\partial}{\partial\eta_j}\,.\end{aligned}\qquad(5)$$

In Eq. (5) the subscripts designate space-fixed vector components and the Einstein summation convention is used. The coefficient A_{kj} is

$$\begin{aligned}A_{kj}=\frac{1}{M}&\left[\left(1+\frac{m}{M}g\right)\delta_{ij}+\frac{m}{M}\frac{\partial g}{\partial R_i}R_j+\frac{m}{M}\frac{\partial h}{\partial R_i}r_j\right]\left[\left(1+\frac{m}{M}g\right)\delta_{ik}+\frac{m}{M}\frac{\partial g}{\partial R_i}R_k+\frac{m}{M}\frac{\partial h}{\partial R_i}r_k\right]\\ &+\frac{1}{m}\left(\frac{m}{M}\right)^2\left(\frac{\partial g}{\partial r_i}R_j\frac{\partial h}{\partial r_i}r_j+\delta_{ij}h\right)\left(\frac{\partial g}{\partial r_i}R_k+\frac{\partial h}{\partial r_i}r_k+\delta_{ik}h\right)\\ &+\frac{1}{(M_A+M_B)}\left(\frac{m}{M}\right)^2\left(\frac{\partial g}{\partial r_i}R_j+\frac{\partial h}{\partial r_i}r_j+\delta_{ij}h\right)\left(\frac{\partial g}{\partial r_i}R_k+\frac{\partial h}{\partial r_i}r_k+\delta_{ik}h\right).\end{aligned}\qquad(6)$$

The relative importance of the various terms can be estimated by noting that $\partial/\partial\xi_k$ acting on a scattering function is of order $Mv/\hbar$, where v is the relative heavy-particle speed. Thus, coming from the first of the three terms in Eq. (6) are contributions of order $Mv^2/\hbar^2$, $mv^2/\hbar^2$, and $(m/M)mv^2/\hbar^2$. The second term in Eq. (6) is of order $mv^2/\hbar^2$ and the third term is of order $(m/M)mv^2/\hbar^2$. The largest term is the heavy-particle kinetic energy computed with the reduced mass of the nuclei. The kinetic correction terms $mv^2/\hbar^2$ are very small at thermal velocities but comparable to the electronic energies when $v\sim 1$ atomic unit (a.u.). The terms of order $(m/M)mv^2/\hbar^2$ should frequently be negligible in practice. When the parameters are constant,

$$A_{kj}=\delta_{kj}\left[\frac{(1+mg/M)^2}{M}+\frac{1}{m}\left(\frac{m}{M}\right)^2h^2+\frac{1}{(M_A+M_B)}\left(\frac{m}{M}\right)^2h^2\right].\qquad(7)$$

The terms in brackets in Eq. (7) can be used to define the reciprocal of a system-reduced mass in

Eq. (5). In the special case of Eq. (3) it is of course equal to $1/(M_A+m)+1/M_B$. Dropping the smallest terms in Eq. (6) or (7) amounts, as far as reduced-mass effects are concerned, to making an error of order $(m/M)^2$. Such terms will ultimately be neglected.

The $\partial/\partial\xi_j$ operators also act on the electronic eigenfunctions. Acting on an electronic eigenfunction $\partial/\partial\xi_j$ can be estimated to be of order $(1/a_0)$ where a_0 is the atomic unit of length. Thus the A_{ij} terms also give rise to contributions to Eq. (5) of order $v/(\hbar a_0)$, $(m/M)v/(\hbar a_0)$, and $(m/M)^2 v/(\hbar a_0)$. The largest terms correspond to the regular nonadiabatic coupling terms of the pss method. It should be sufficient for most purposes to neglect the higher order terms in (m/M). Finally, when both derivative terms operate on an electronic eigenfunction the contributions from terms in Eq. (6) to Eq. (5) are $(1/M)a_0^{-2}$, $(1/M)(m/M)a_0^{-2}$, and $(1/M)(m/M)^2 a_0^{-2}$. The first of these contributions corresponds to regular small terms (e.g., adiabatic correction terms) of the pss method.

Next, let us consider the cross-derivative terms in Eq. (5). Their coefficient B_{jk} is given by

$$\begin{aligned}B_{jk}=&\frac{2}{M}\left[\left(1+\frac{m}{M}g\right)\delta_{ij}+\frac{m}{M}\frac{\partial g}{\partial R_i}R_j+\frac{m}{M}\frac{\partial h}{\partial R_i}r_j\right]\left(\gamma\delta_{ik}+\frac{\partial\gamma}{\partial R_i}R_k+\frac{m}{M}\frac{\partial f}{\partial R_i}r_k\right)\\&+\frac{2}{M}\left(\frac{\partial g}{\partial r_i}R_j+\frac{\partial h}{\partial r_i}r_j+\delta_{ij}h\right)\left[\left(1+\frac{m}{M}f\right)\delta_{ik}+\left(\frac{m}{M}\right)\frac{\partial f}{\partial r_i}r_k+\frac{\partial\gamma}{\partial r_i}R_k\right]\\&+\frac{2}{(M_A+M_B)}\left(\frac{m}{M}\right)\left(\frac{\partial g}{\partial r_i}R_j+\frac{\partial h}{\partial r_i}r_j+\delta_{ij}h\right)\left[\left(1+\frac{m}{M}f\right)\delta_{ik}+\left(\frac{m}{M}\right)\frac{\partial f}{\partial r_i}r_k+\frac{\partial\gamma}{\partial r_i}R_k\right].\end{aligned}\tag{8}$$

The size of the cross-derivative contribution to Eq. (5) can be estimated with $\partial/\partial\xi_j\sim Mv/\hbar$ and $\partial/\partial\eta_k\sim a_0^{-1}$. Thus the first two terms of B_{jk} contain the largest contributions which are $\sim v/a_0\hbar$. The rest of the terms are $\sim(m/M)v/a_0\hbar$. When $\partial/\partial\xi_j$ operates on an electronic eigenfunction the largest terms are $\sim(1/M)a_0^{-2}$.

For constant parameters,

$$\begin{aligned}B_{jk}=\frac{2}{M}\delta_{jk}\bigg[&\left(1+\frac{m}{M}g\right)\gamma+\left(1+\frac{m}{M}f\right)h\\&+\frac{m}{(M_A+M_B)}\left(1+\frac{m}{M}f\right)h\bigg].\end{aligned}\tag{9}$$

The cross-derivative coefficient (9) vanishes for transformation (3) as well as for the identical transformation with g, γ, h, and $f=0$.

The term $D_j(\partial/\partial\xi_j)$ contributes terms of the same order of magnitude to Eq. (5) as the cross-derivative term. We have

$$\begin{aligned}D_j=&\frac{1}{M}\left(\frac{m}{M}\right)\left(2\frac{\partial g}{\partial R_j}+\frac{\partial^2 g}{\partial R_i\partial R_i}R_j+\frac{\partial^2 h}{\partial R_i\partial R_i}r_j\right)\\&+\frac{1}{m}\left(\frac{m}{M}\right)\frac{\partial}{\partial r_i}\left(\frac{\partial g}{\partial r_i}R_j+\frac{\partial h}{\partial r_i}r_j+\delta_{ij}h\right)\\&+\frac{1}{(M_A+M_B)}\left(\frac{m}{M}\right)\left(\frac{\partial^2 g}{\partial r_i\partial r_i}R_j+\frac{\partial^2 h}{\partial r_i\partial r_i}r_j+\frac{\partial h}{\partial r_j}+\frac{\partial h}{\partial r_j}\right).\end{aligned}\tag{10}$$

As before, when $\partial/\partial\xi_j$ operates on a scattering function the result is $\sim Mv/\hbar$. Thus, the largest velocity-dependent contributions from Eq. (10) to Eq. (5) come from the second term in Eq. (10) and are $\sim v/(\hbar a_0)$. The remaining terms of this type are $\sim(m/M)v(\hbar a_0)$. When $\partial/\partial\xi_j$ operates on an electronic function, the largest contribution to Eq. (5) from Eq. (10) is a_0^{-2}/M. For constant parameters $D_j=0$. At this point all the terms in Eq. (5) which differentiate the scattering functions have been defined. The discussion of the remaining terms will be postponed.

Further restrictions on the transformation defined by Eqs. (1) and (4) will now be introduced. To guarantee that the exact scattering equations decouple in the asymptotic region it is sufficient that the above transformations tend toward transformation (3) if, in molecular state G, the electron ends up on atom A, or to the analogous transform if it ends up on atom B. Then T as given by (5) will be separable in the proper variables with vanishing B_{jk}, D_j, and E_j. In the united-atom limit we elect to restrict the transformation (1) so as to keep $(\vec{\xi}-\vec{R})/R$ of order m/M. Otherwise ξ loses a desirably close relationship to the physical variable R. Subject to the above conditions, any transformation is acceptable.

In most scattering applications, adiabatic correction terms, terms of the mass-polarization type, and electron-reduced-mass terms are omitted from the kinetic energy. The approximate atomic functions used to define the S matrix are then taken to be those from the separated-atom limit of the fixed-nucleus molecular eigenfunctions. Correspondingly, the parameters in the transformation (1) are chosen to guarantee separability of the truncated form of Eq. (5). The omission of terms of order a_0^{-2}/M compared to retained terms of order $v/\hbar a_0$ requires $Mva_0/\hbar$

$\gg 1$.[43]

We impose our first specific condition on the parameters by requiring that the leading term in D_j from Eq. (5) vanish for all R. This type of term does not appear in the kinetic energy operator of the regular pss theory. From Eq. (10), it can be shown that the necessary conditions on the parameters are

$$\frac{\partial g}{\partial r_i} = k(R) R_i\,, \qquad g = k(R)(\vec{\mathrm{R}} \cdot \vec{\mathrm{r}}) + j(R)\,, \tag{11}$$

where j, k, h are arbitrary functions of R.[44] With Eqs. (11) satisfied, the contributions of D_j of Eq. (5) are at most of order $(m/Mv/\hbar a_0)$ or $(m/M)a_0^{-2}/M$ and can eventually be omitted. Now consider the separability requirement that the leading term of B_{jk} vanish as $R \to \infty$. In this limit the parameters are constant, and from Eq. (9) we require $\gamma(\infty) = -h(\infty)$. Instead of this boundary condition, we impose the stronger condition

$$h(R) = -\gamma(R)\,. \tag{12}$$

This guarantees that the leading term of B_{jk} vanishes in any region where the transformation parameters are constant. Then B_{jk} takes the form

$$B_{jk} = \frac{2}{M}\left(\frac{1}{R}\frac{d\gamma}{dR} + k(R)\right) R_j R_k + O\left(\frac{m}{M^2}\right), \tag{13}$$

where $O(m/M^2)$ stands for all the remaining terms in Eq. (8). The requirement that the leading term of B_{jk} vanish in the separated-atom limit now becomes

$$k(R)R^2 \to 0\,. \tag{14}$$

as $R \to \infty$.

Evidently, the leading term of B_{jk} could be made to vanish identically by choosing $k = -R^{-1}(d\gamma/dR)$. This possibility will be discussed below Eq. (18). At this point it is convenient to set

$$f \equiv 0 \tag{15}$$

in Eq. (4), so $\delta = 1$ in Eq. (1). Inspection shows that f appears only in the higher-order terms of B_{jk}. Moreover, it can be verified that f contributes only terms of order $(m/M)v/\hbar a$, $(m/M)a_0^2/M$, and smaller to the rest of the terms in Eq. (5). Setting $f = 0$ thus simplifies the theory without altering its content to the order retained. The last requirement to be introduced has to do with the Jacobian of the transformation (1) for constant parameters. In this case $k(R)$ must vanish because of Eq. (11) and the Jacobian J becomes

$$J = \left(1 + \frac{m}{M} j(R) - \frac{m}{M}\gamma h\right)^3\,. \tag{16}$$

This shows that the condition

$$j(R) = \gamma(R) h(R) \tag{17}$$

is sufficient to make J exactly unity in the separated-atom limit and to guarantee for all R that J departs from unity only because the transformation coefficients in Eq. (1) are changing with R. The final transformation is

$$\begin{aligned} \vec{\xi} &= \alpha \vec{\mathrm{R}} + \frac{m}{M} h \vec{\mathrm{r}}\,, \\ \vec{\eta} &= \gamma(R)\vec{\mathrm{R}} + \vec{\mathrm{r}}\,, \\ \alpha &= 1 + \frac{m}{M}[k(R)(\vec{\mathrm{R}} \cdot \vec{\mathrm{r}}) + \gamma h]\,, \\ h &= -\gamma\,, \end{aligned} \tag{18}$$

where $\gamma(R)$ and $k(R)$ are arbitrary, subject to Eq. (14). Transformation (18) involves two functions, $\gamma(R)$ and $k(R)$. In the semiclassical limit, they provide enough flexibility for independent variation of the angular and radial components of a vector translational factor in the scattering plane. Had the first term in Eq. (13) been set equal to zero, only one independent function would have been available. In the author's opinion, this is not enough, because the molecular properties parallel or perpendicular to the internuclear line are too dissimilar to warrent such an assumption *a priori*.

It is instructive to compare Eq. (18) with Eq. (3) for the separated atoms. We identify γ with p so that $\vec{\eta} = \vec{\mathrm{r}}_A$. Then, from Eq. (18) with $k = 0$,

$$\begin{aligned} \vec{\xi} &= \vec{\mathrm{R}} - \frac{m}{M}\gamma(\vec{\mathrm{r}} + \gamma\vec{\mathrm{R}}) \\ &= \vec{\mathrm{R}} - \frac{m}{M_A}(\vec{\mathrm{r}} + p\vec{\mathrm{R}})\,. \end{aligned} \tag{19}$$

Transformation (19) agrees with the exact transformation (3) except for terms of order $(m/M)^2$ in $\vec{\xi}$.[45]

To apply Eqs. (18) one needs the corresponding simplified expression for A_{jk} from Eqs. (5) and (6). The result is

$$A_{kj}\frac{\partial}{\partial \xi_k}\frac{\partial}{\partial \xi_j} = \frac{1}{M}\frac{\partial}{\partial \xi_i}\frac{\partial}{\partial \xi_i} + \left(\frac{m}{M^2}\right)t + O\left(\frac{m^2}{M^3}\frac{\partial}{\partial \xi_j}\frac{\partial}{\partial \xi_k}\right), \tag{20}$$

where the $O((m^2/M^3)\cdots)$ terms can be retained by using Eq. (6), and

$$\begin{aligned} t = {} & [2k(\vec{\mathrm{R}} \cdot \vec{\mathrm{r}}) - (\gamma)^2]\Delta_{\vec{\xi}} + 2\left(k - \frac{1}{R}\frac{d\gamma}{dR}\right)(\vec{\mathrm{R}} \cdot \vec{\nabla}_{\xi})(\vec{\eta} \cdot \vec{\nabla}_{\xi}) \\ & + \left(\frac{2}{R}\frac{dk}{dR}(\vec{\mathrm{R}} \cdot \vec{\mathrm{r}}) - \frac{2}{R}\gamma\frac{d\gamma}{dR} - 4\gamma k + (kr)^2\right) R_k R_j \frac{\partial}{\partial \xi_k}\frac{\partial}{\partial \xi_j}\,. \end{aligned} \tag{21}$$

To the same order, the analogous formula for

B_{jk} is Eq. (13). That for D_j is Eq. (10) without the second term, which vanishes for Eq. (18).

To complete expression (5) for the kinetic energy resulting from transformation (18), the formulas for the coefficients of the η derivatives are needed. Rather than reproduce the lengthy general formulas for Eq. (1), we give just the complete results for Eq. (18). Then

$$\begin{aligned} E_j &= \frac{1}{M}\left(2\frac{\partial\gamma}{\partial R_j} + R_j \Delta_{\vec{R}}\gamma\right) , \\ C_{jk} &= \frac{1}{M}\left(\gamma\delta_{ij} + \frac{\partial\gamma}{\partial R_i}R_j\right)\left(\gamma\delta_{ik} + \frac{\partial\gamma}{\partial R_i}R_k\right) \\ &\quad + \frac{1}{m}\delta_{jk} + \frac{1}{(M_A+M_B)}\delta_{jk} . \end{aligned} \tag{22}$$

For constant γ, E_j is zero and the first term of C_{jk} is equivalent to a modification of the electron reduced-mass term.

Equation (5) can now be written

$$\begin{aligned} \frac{-2}{\hbar^2}T &= \frac{1}{M}\Delta_{\vec{\xi}} + \frac{m}{M^2}t + \frac{2}{M}\left(k + \frac{1}{R}\frac{d\gamma}{dR}\right)R_j R_k \frac{\partial}{\partial\xi_j}\frac{\partial}{\partial\eta_k} \\ &\quad + \frac{1}{m}\frac{\partial}{\partial\eta_i}\frac{\partial}{\partial\eta_i} + C_1 + C_2 . \end{aligned} \tag{23}$$

Here t is defined by Eq. (21), C_1 represents the $O(a_0^{-2}/M)$ terms from Eq. (22), and C_2 represents the $O(m a_0^{-2}/M^2)$ and $O(mv/\hbar a_0 M)$ and smaller terms from Eqs. (6), (8), and (10). Equation (23) is still exact. It shows that the error introduced in scattering amplitudes by dropping the terms C_1 and C_2 should be of the order of the effects on level separations and matrix elements of electron reduced-mass or adiabatic correction effects. The term t is also very small at low-impact velocities. Indeed, for sufficiently low velocities, it is of the same size as the adiabatic correction terms.

Equation (23) shows how to express the kinetic energy operator in terms of whatever variables appear in the expansion term to which the Hamiltonian operator in the Langrangian is being applied. We turn next to the discussion of angular momentum conservation.

III. ANGULAR MOMENTUM CONSERVATION: THE CHOICE OF BODY-FIXED REFERENCE FRAMES

An important feature of the pss method for atom-atom collisions is that by going over to molecule-fixed electron coordinates for the electronic basis functions, which then depend only on R and not on $\hat{R}$, the conservation of the total orbital angular momentum allows a block diagonalization and substantial simplification of the scattering equations. Because of Eq. (2), the same use of angular momentum conservation is also rigorously possible in terms of the coordinates defined in Eqs. (1) and (18). However, in this case the coordinate that is analogous to the polar axis for the heavy particles is $\hat{\xi}$, not $\hat{R}$. This difference is of order (m/M). From Eq. (18), the sine of the angle δ between $\hat{\xi}$ and $\hat{R}$ is given by

$$|\sin\delta| = \frac{|\vec{\xi}\times\vec{R}|}{\xi R} = \left|\frac{m}{M}\frac{\hat{R}\times\gamma\vec{r}}{\xi}\right| . \tag{24}$$

For bound electronic states, the numerator is uniformly bounded for all R and, unless ξ becomes too small, $|\sin\delta|$ is of order m/M. Evidently as $\xi\rightarrow 0$, δ can become very large. In order to always maintain a close correspondence between $\vec{R}$ and $\vec{\xi}$, it will be required that as $R\rightarrow 0$

$$k\rightarrow 0, \quad \gamma/R\rightarrow 0 . \tag{25}$$

Equations (25) and (18) guarantee that as $R\rightarrow 0$, $\xi/R\rightarrow 1$ and $|\sin\delta|\rightarrow 0$. In addition, it also intended that $\gamma(R)$ should be such that $|\sin\delta|$ is $O(m/M)$ for all R In practice we will reject a solution $\gamma(R)$ which violates this condition.

The use of $\hat{\xi}$ instead of $\hat{R}$ as the polar axis for the description of the total orbital angular momentum suggests the use of electronic basis functions for which the rotation-reflection symmetry axis is also $\hat{\xi}$ rather than the internuclear line.[46] Then the Kronig formulation of angular momentum conservation can be taken over. Consider a particular state G whose fixed-nucleus electronic eigenfunction is $\psi_G(\rho, z, \phi; R)$ where ρ, z, ϕ are body-fixed cylindrical coordinates for $\vec{r}$ with $\hat{z}=\hat{R}$. By Eq. (18) with the state dependence made explicit, $\vec{\eta}_G = \vec{r} + \gamma_G(R)\vec{R}$. We now define a variable $\vec{r}_G$ to be the analog of $\vec{r}$ in the $\vec{\xi}, \vec{\eta}$ system. We take

$$\vec{r}_G = \vec{\eta}_G - \gamma_G(\xi_G)\vec{\xi}_G . \tag{26}$$

The variables $\rho_G z_G \phi_G$ are then defined as the body-fixed cylindrical coordinates for $\vec{r}_G$ based on $\vec{\xi}_G$ with $\hat{z}_G = \hat{\xi}_G$. The Gth basis function is then taken to be $\psi_G(\rho_G, z_G, \phi_G; \xi_G)$. Its relation to $\psi_G(\rho, z, \phi; R)$ is given by Eqs. (18) and (26) using Taylor's expansion to first order in m/M. By construction

$$\left(-\frac{\hbar^2}{2m}\frac{\vec{\partial}}{\partial\eta_G}\cdot\frac{\vec{\partial}}{\partial\eta_G} + V(\rho_G, z_G, \phi_G; \xi_G)\right)\psi_G(\rho_G, z_G, \phi_G; \xi_G) = \mathcal{E}_G(\xi_G)\psi_G(\rho_G, z_G, \phi_G; \xi_G), \tag{27}$$

where $V(\rho, z, \phi, R)$ is the electron's potential energy and $\mathcal{E}_G$ includes the nuclear repulsion. The difference ΔV between the two potentials is taken into account to first order in (m/M) using

$$\Delta V \equiv V(\rho_G, z_G, \phi_G, \xi_G) - V(\rho, z, \phi, R) + \left(\frac{\partial V}{\partial \rho}(\rho_G - \rho) + \frac{\partial V}{\partial z}(z_G - z) + \frac{\partial V}{\partial \phi}(\phi_G - \phi)\right) + \frac{\partial V}{\partial R}(\xi_G - R)\,. \qquad (28)$$

Since all the coordinate differences in Eq. (28) are of order m/M, ΔV is of the order of the electron reduced-mass terms. When the Hamiltonian H is applied to $\psi_G(\vec{\eta};\xi)$, using Eq. (23), the quantity $(\mathcal{E}_G - \Delta V)\psi_G$ will appear along with the other terms from Eqs. (23). The influence of ΔV on transition probabilities, phase shifts, etc., will be of order m/M and, therefore, negligible for most scattering applications.

One point about the use of an expansion based on $\hat{\xi}$ as polar axis rather than $\hat{R}$ is worth emphasizing. If the actual scalar potential $V(\rho, z, \phi, R)$ is expressed in terms of $\vec{\xi}$ and $\vec{\eta}$, it is independent of the polar angles θ_ξ, ψ_ξ of $\vec{\xi}$ relative to an arbitrary nonrotating frame and independent of the azimuthal angle of $\vec{\eta}$ when it is referred to the body-fixed axes $\hat{\theta}_\xi, \hat{\phi}_\xi, \hat{\xi}$. This means that the actual V does not preclude the use of the polar axis $\vec{\xi}$ in connection with an exact treatment of angular momentum conservation.

We are now ready to formulate the scattering expansion and derive the system Lagrangian. This is done in Sec. IV.

IV. THE CONSTRUCTION OF TRIAL SOLUTIONS FOR A ONE-ELECTRON HETEROPOLAR SYSTEM

In this section the Lagrangian functional is derived for one-electron heteropolar systems. In the one-electron case the electron spin can be factored out once and for all and omitted from the electronic basis functions. These may be written in the form

$$\chi_G = (2\pi)^{-1/2} A_{p\Lambda}(\rho_G, \zeta_G; \xi_G)\exp(i\Lambda\phi_G)\,, \qquad (29)$$

where G stands for the number pair $p\Lambda$, $\Lambda = 0, \pm 1, \pm 2, \ldots$, and p numbers the states with the same Λ. States with $\Lambda = 0$ are Σ states, etc. As discussed in Sec. III, the variables ρ_G, ϕ_G, ζ_G are the body-fixed cylindrical coordinates of $\vec{\eta}_G$, taking $\vec{\xi}_G$ as the axis of rotation symmetry. The subscripts G on $\vec{\xi}_G$ and $\vec{\eta}_G$ are required because each state G has its own transformation (18). The states $p\Lambda$ and $p - \Lambda$ are degenerate and $A_{p-\Lambda} = (-1)^\Lambda A_{p\Lambda}$. The $A_{p\Lambda}$ are real and normalized. The functions γ_G and k_G in Eq. (18) are arbitrary except that they depend only on $|\Lambda|$.

A trial solution can now be written down. Let the quantum numbers for the system's space-fixed angular momentum be K, M_K and let the initial beam direction be the space-fixed quantization axis. In a typical situation, only one value of M_K will occur, namely that of the component of the total initial electronic angular momentum along the initial beam direction. The trial solution is then written in the form

$$\phi_{G'} = \sum_K \sum_{M_K} \phi_{G'}^{KM_K}\,, \qquad (30)$$

where

$$\phi_{G'}^{KM_K} = (4\pi)^{1/2}(2K+1)^{1/2} \times \sum_{n\Lambda} A_{n\Lambda}(\rho_G, \zeta_G; \xi_G)(-1)^\Lambda[(2K+1)/(8\pi^2)]^{1/2} \times D^K_{\Lambda M_K}(\phi_G, \theta_G, \psi_G) R^K_{n\Lambda;G'}(\xi_G)/\xi_G\,. \qquad (31)$$

In Eqs. (30) and (31) the subscript G' denotes an initial state for the scattering.[47] The rotation matrix and the spherical harmonics in the hydrogenic functions are defined using the conventions discussed in Ref. 48. The angles θ_G and ψ_G are the polar angles of $\vec{\xi}_G$ with respect to the space-fixed frame.

The individual terms of Eq. (31) are not parity eigenfunctions for the system and do not lead to the simplest possible form for the scattering equations. Therefore, following Kronig, we replace the products $A_{n\Lambda}D^K_{\Lambda M_K}$, $\Lambda = 0, \pm 1, \pm 2, \ldots$, by the functions $Q^{KM_K}_{n\Lambda\epsilon}$ where now $\Lambda \geqslant 0$ and $\epsilon = \pm 1$. By definition,

$$Q^{KM_K}_{n\Lambda\epsilon} = \delta_{\epsilon 1}\delta_{\Lambda 0} A_{n0} D^K_{0M_K} + (1 - \delta_{\Lambda 0})\frac{1}{\sqrt{2}}\,(A_{n\Lambda}D^K_{\Lambda M_K} + \epsilon A_{n-\Lambda}D^K_{-\Lambda M_K})\,. \qquad (32)$$

In place of Eq. (31) we write

$$\Phi_{G'}^{KM_K} = (4\pi)^{1/2}(2K+1)^{1/2} \sum_{n\Lambda\epsilon} (-1)^\Lambda[(2K+1)/(8\pi^2)]^{1/2} \times Q^{KM_K}_{n\Lambda\epsilon} R^K_{n\Lambda\epsilon;G'}(\xi_G)/\xi_G\,, \qquad (33)$$

where G stands for $\eta\Lambda\epsilon$ and G' is analogously defined. The coordinates ξ_G and $\vec{\eta}_G$ and the parameters γ_G and k_G now depend on the new G.

The radial scattering functions $R^K_{G;G'}$, the γ_G, and the k_G are to be determined variationally from the functional

$$\mathcal{L}(\psi_1, \psi_2) = \int d\vec{R} \int d\vec{r}\, \psi_1(H - E)\psi_2\,, \qquad (34)$$

where ψ_1 and ψ_2 are trial solutions.[12] $\mathcal{L}$ is equal to $-(\hbar^2/2M)$ times the functional I of Ref. 12. The Lagrangian is defined in terms of the original variables. The coupled equations for the radial scattering functions used in this paper always make $\mathfrak{L}(\psi_1,\psi_2)$, $\mathfrak{L}(\psi_2,\psi_1)$, $\mathfrak{L}(\psi_1^*,\psi_2)$, and $\mathfrak{L}(\psi_2,\psi_1^*)$ all vanish. As a result, unitarity and detailed balancing are satisfied by the solutions, if all terms in $H-E$ are kept in the coupled equations.[49] When terms of order m/M are omitted, as is proposed here, and done in paper II, a separate investigation is required to determine the extent to which their neglect influences the above relations.

Let us now write down $\mathfrak{L}(\psi_1,\psi_2)$ for the one-electron case, using overbars to keep track of the distinct sums and variables in ψ_1 and ψ_2. The result can be written as

$$\mathfrak{L}(\psi_1,\psi_2)=\sum_{\overline{K}\overline{M}_K}\sum_{KM_K}\mathfrak{L}(\Phi_{\overline{G}'}^{\overline{K}\overline{M}_K},\Phi_{G'}^{KM_K})\,, \tag{35}$$

$$\mathfrak{L}(\phi_{\overline{G}'}^{\overline{K}\overline{M}_K},\phi_{G'}^{KM_K})=\frac{(2K+1)(2\overline{K}+1)}{2\pi}\sum_{\bar n\overline{\Lambda}\bar\epsilon}\sum_{n\Lambda\epsilon}(-1)^{\Lambda+\overline{\Lambda}}\int d\vec{\bar\xi}_{\overline{G}}\int d\vec{\bar\eta}_{\overline{G}}J_{\overline{G}}^{-1}R_{\overline{G};\overline{G}'}^{\overline{K}}(\bar\xi_{\overline{G}})\bar\xi_{\overline{G}}^{-1}Q_{\bar n\overline{\Lambda}\bar\epsilon}^{\overline{K}\overline{M}_K}(H-E)[Q_{n\Lambda\epsilon}^{KM_K}R_{G;G'}^{K}(\xi_G)\xi_G^{-1}]\,. \tag{36}$$

In each term of the sum over $\overline{n\Lambda\epsilon}$, the original volume element $d\vec{R}d\vec{r}$ has been expressed in terms of the volume element $d\vec{\xi}_{\overline{G}}d\vec{\eta}_{\overline{G}}$ using the Jacobian $J_{\overline{G}}$ of the transformation (18). The coupled equations for the $R_{G,G'}^{K}(\xi_G)$ can be obtained by setting the variation of Eq. (36) with respect to $R_{\overline{G},\overline{G}'}^{\overline{K}}(\xi_{\overline{G}})$ equal to zero. This will guarantee that $\mathfrak{L}$ vanishes whenever its right-hand trial function is a solution of the coupled equations. However, it is preferable to first simplify the equations by carrying out the angle integrations. This requires a bit of manipulation since the rotation matrices contained in Eq. (36) are functions of different arguments.

The first step is to express the $Q_{n\Lambda\epsilon}^{KM_K}$ in terms of rotation matrices using Eq. (32) and to write the kinetic energy T in terms of $\vec{\xi}_G,\vec{\eta}_G$ using Eq. (23). It can then be shown that

$$(H-E)A_{n\Lambda}D_{\Lambda M_K}^{K}R_{n|\Lambda|\epsilon;G'}^{K}=\sum_{\tau=-1}^{1}D_{\Lambda+\tau,M_K}^{K}C_{n\Lambda,\tau}^{K}\,. \tag{37}$$

In Eq. (37) Λ may be either positive or negative as is required for use in connection with Eq. (32). The $C_{n\Lambda,\tau}^{K}$ are written out in Eq. (40). For the present all that need be stated is that they are independent of the variables ϕ_G,θ_G,ψ_G which appear in $D_{\Lambda+\tau,M_K}^{K}$. We next express the $D_{\Lambda+\tau,M_K}^{K}(\phi_G,\theta_G,\psi_G)$ in terms of the $D_{\Sigma M_K}^{K}(\bar\phi_{\overline{G}},\bar\theta_{\overline{G}},\bar\psi_{\overline{G}})$ which appear in the trial function ψ_1. The required relation is worked out in Ref. 40. It is

$$D_{\Lambda M_K}^{K}(\phi_G,\theta_G,\psi_G)=\sum_{\Sigma}d_{\Lambda\Sigma}^{K}(\theta_{1,0}-\bar\theta_{1,0})D_{\Sigma M_K}^{K}(\bar\phi_{\overline{G}},\bar\theta_{\overline{G}},\bar\psi_{\overline{G}})\,,$$

$$\theta_{1,0}=-\sin^{-1}\left(\frac{m}{M}\,\frac{\gamma_G\rho_G}{\xi_G}\right),$$

$$\bar\theta_{1,0}=-\sin^{-1}\left(\frac{m}{M}\,\frac{\bar\gamma_{\overline{G}}\bar\rho_{\overline{G}}}{\xi_{\overline{G}}}\right). \tag{38}$$

Note that the expressions for $\theta_{1,0}$ and $\bar\theta_{1,0}$ contain γ_G from transformation (18). Equation (38) exhibits the important point that the argument of $d_{\Lambda\tau}^{K}$ is of order m/M. Since the total angular momentum K is ~M, the argument of $d_{\Lambda\tau}^{K}$ cannot be set equal to zero (which would give $\delta_{\Lambda\tau}$). However, one can expect to be able to evaluate the multipliers of m/M in the argument of $D_{\Lambda\tau}^{K}$ to lowest order in m/M. Then only the difference between γ_G and $\bar\gamma_{\overline{G}}$ need be accounted for.

Using Eqs. (38), (37), (36), and the orthogonality properties of the rotation matrices,

$$\begin{aligned}\mathfrak{L}(\Phi_{\overline{G}'}^{\overline{K},\overline{M}_K},\Phi_{G'}^{KM_K})={}&(4\pi)(2K+1)\delta_{\overline{K}K}\delta_{-\overline{M}_KM_K}\sum_{\bar n\overline{\Lambda}\bar\epsilon}\sum_{n\Lambda\epsilon}(-1)^{\Lambda+\overline{\Lambda}+\overline{M}_K}\int\bar\xi_{\overline{G}}d\bar\xi_{\overline{G}}R_{\overline{G};\overline{G}'}^{K}(\bar\xi_{\overline{G}})\int\bar\rho_{\overline{G}}d\bar\rho_{\overline{G}}d\bar\zeta_{\overline{G}}J_{\overline{G}}^{-1}A_{\bar n\overline{\Lambda}}(\bar\rho_{\overline{G}}\bar\zeta_{\overline{G}};\xi_{\overline{G}})\\&\times\Bigg[\delta_{\epsilon1}\delta_{\bar\epsilon1}\Big(\delta_{\overline{\Lambda}0}\delta_{\Lambda0}\sum_{\tau}d_{\tau0}^{K}C_{n0,\tau}^{K}+\delta_{\overline{\Lambda}0}(1-\delta_{\Lambda0})2^{1/2}\sum_{\tau}d_{\Lambda+\tau0}^{K}C_{n\Lambda,\tau}^{K}+\delta_{\Lambda0}(1-\delta_{\overline{\Lambda}0})2^{1/2}\sum_{\tau}d_{\tau\overline{\Lambda}}^{K}C_{n0,\tau}^{K}\Big)\\&+\bar\epsilon(\delta_{\epsilon1}\delta_{\bar\epsilon1}+\delta_{\epsilon-1}\delta_{\bar\epsilon-1})(1-\delta_{\overline{\Lambda}0})(1-\delta_{\Lambda0})\Big(\sum_{\tau}d_{\Lambda+\tau\overline{\Lambda}}^{K}C_{n\Lambda,\tau}^{K}+\epsilon\sum_{\tau}d_{-\Lambda+\tau\overline{\Lambda}}^{K}C_{n-\Lambda,\tau}^{K}\Big)\Bigg]\,.\end{aligned} \tag{39}$$

The Lagrangian is diagonal in the angular momentum K. The Kroneker delta symbols $\delta_{\epsilon1}$, etc., in Eq. (39) exhibit the fact that states with different values of ϵ (i.e., different scattering-plane reflection symmetries) do not mix. The symbols $\delta_{\overline{\Lambda}0}$, $(1-\delta_{\overline{\Lambda}0})$, etc., distinguish sigma states from the other states. The $C_{n\Lambda,\tau}^{K}$ are defined by Eq. (37). In practice, calculations are most likely to be based on the neglect of the terms of order m/M, $(m/M)v$, etc., discussed in Secs. II and III. Therefore the $C_{n\Lambda,\tau}^{K}$ are given neglecting C_1 and C_2 in Eq. (46) as well as ΔV from Eq. (28).[50] We have

$$\frac{-2M\xi_G}{\hbar^2}C^K_{n\Lambda,0}=\Biggl\{\left(\frac{\partial}{\partial\xi_G}\right)^2-\frac{[K(K+1)-\Lambda^2]}{\xi_G^2}+\frac{2M}{\hbar^2}[E-\mathcal{E}_G(\xi_G)]-\frac{\vec{\mathrm{L}}_G^2-\hbar^2\Lambda^2}{\hbar^2\xi_G^2}+2\left(\frac{d\gamma_G}{dR}+Rk_G\right)R\frac{\partial}{\partial\zeta_G}\left(\frac{\partial}{\partial\xi_G}-\frac{1}{\xi_G}\right)$$

$$+\frac{m}{M}[-\gamma_G^2+2k_GR(\zeta_G-R\gamma_G)]\left[\left(\frac{\partial}{\partial\xi_G}\right)^2-\frac{K(K+1)-\Lambda^2}{\xi_G^2}\right]$$

$$+\frac{m}{M}\Biggl[2R^2\frac{dk_G}{dR}(\zeta_G-\gamma_GR)-2R\gamma_G\frac{d\gamma_G}{dR}-4R^2\gamma_Gk_G+R^4k_G^2$$

$$+2\left(k_GR-\frac{d\gamma_G}{dR}\right)\zeta_G\Biggr]\left(\frac{\partial}{\partial\xi_G}\right)^2\Biggr\}A_{n\Lambda}(\rho_G,\zeta_G;\xi_G)R^K_{n|\Lambda|\epsilon;G'}(\xi_G)\,,$$

$$\frac{-2M\xi_G}{\hbar^2}C^K_{n\Lambda,\pm1}=\pm[(K\pm\Lambda+1)(K\mp\Lambda)]^{1/2}\left[\frac{1}{\xi_G^2}\left(\frac{\partial}{\partial\theta_G}\mp\Lambda\cot\theta_G\right)+\frac{m}{M}\left(\frac{d\gamma_G}{dR}-k_GR\right)\frac{\rho_G}{\xi_G}\frac{\partial}{\partial\xi_G}\right]A_{n\Lambda}(\rho_G,\zeta_G;\xi_G)R^K_{n|\Lambda|\epsilon;G'}(\xi_G). \quad (40)$$

In these equations, which hold for both positive and negative values of Λ, G stands for $n|\Lambda|\epsilon$. In Eq. (40) L_G is the electron orbital angular momentum defined in terms of $\vec{\eta}_G$, and θ_G is the polar angle of $\vec{\eta}_G$ in body-fixed, spherical coordinates, η_G, θ_G, ϕ_G. All the m/M terms in Eq. (40) come from the term t in Eqs. (21) and (23). These terms are at most of order mv^2 as discussed in Sec. II. In them, derivatives of $A_{n\Lambda}$ with respect to ξ_G are to be dropped. Aside from the variables used and the accompanying term t, the operators in $C^K_{n\Lambda,\tau}$ are just those of the pss method.

Variation of the Lagrangian (39) with respect to $R^K_{\overline{G};\overline{G}'}(\xi_{\overline{G}})$ yields a set of coupled integro-differential equations. One has to express the G variables in terms of the $\overline{G}$ variables, so $R^K_{n\Lambda\epsilon;G'}(\xi_G)$ has to remain under the $\overline{G}$ integral sign. However, approximations are available which convert the equations to simpler ordinary differential equations. At low velocities a Taylor's expansion of $R^K_{n\Lambda;G'_{AB}}(\xi_G)$ about $\xi_{\overline{G}}$ can be used.[40] In the semiclassical limit, an analogous treatment of the slowly varying coefficients of the in and out waves can be carried out. In both cases, ordinary differential equations result. If desired, the terms omitted from Eq. (40) can be retained for special applications. For example, one may want to take adiabatic correction terms into account.

V. DISCUSSION

Equations (39) and (40) provide a new, more flexible description of low-energy atom-atom collisions for one-electron heteronuclear systems. The equations are more flexible because they allow for the variational determination of the transformation parameters $\gamma_G(R)$ and $k_G(R)$ at all energies for which a molecular basis approach should be fruitful. These state and R-dependent parameters represent a simple generalization of the constant vector translation factors of Bates and McCarroll. The generalization of the theory to homopolar and many-electron systems is worked out in some detail but not completely in Ref. 40.

The integro-differential form of Eq. (39) probably prohibits its direct use for calculations. Our philosophy is to use the Lagrangian (39) as the basis for accurate semiclassical or low-velocity quantal approximations which lead to Lagrangian functionals of simpler form and to ordinary differential equations for the scattering functions and transformation parameters. Both approximations are worked out in Ref. 40. The semiclassical approximation is the subject of paper II.[51]

In order to decouple the variationally determined equations for the transformation parameters, γ_G and k_G, from the coupled scattering equations for $R^K_{G,G'}$, a weak coupling approximation is used. This is done by defining suitable more weakly-coupled diabatic states to replace certain strongly coupled molecular electronic eigenstates at high energies. The diabatic states are therefore essential to our high-energy approximation. These diabatic states are defined in terms of linear combinations of electronic eigenfunctions. The Appendix provides a definition of the diabatic states and exhibits the required modification of the terms in Eq. (40).

The semiclassical approximation of paper II has recently been applied in both adiabatic and diabatic versions to C^{6+}-H collisions for H-atom energies up to 30 keV.[52] The results are encouraging.

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APPENDIX: BASIS FUNCTIONS MADE FROM LINEAR COMBINATIONS OF ELECTRONIC EIGENFUNCTIONS. INTERPOLATING OR DIABATIC STATES

The basis functions of Sec. IV were taken to be fixed-nucleus electronic eigenfunctions. One may refer to this trial solution as an adiabatic trial solution. It is well known that as a function of internuclear separation, R, a fixed-nucleus electronic eigenfunction can undergo a large change in its character (its electron charge distribution) in a localized region $[R_0,R_1]$ around a point R_C of "avoided crossing" with another electronic eigenfunction of the same symmetry. In the simplest example, the eigenfunctions exchange their character as R traverses the region $[R_0,R_1]$. In the avoided-crossing region it is convenient to say loosely that the pair of states "interact," while outside the region there is no particular indication that they are interacting more strongly with each other than with other states. Usually, plots of the potential energy curves, the radial coupling, and the dipole matrix elements allow one to identify the points R_0, R_C, and R_1 with reasonable precision. The smaller the interval R_1-R_0, the larger the radial coupling matrix element, and the less arbitrary the choice. However, a completely unambiguous choice of $[R_0,R_1]$ is probably not possible in general, particularly when R_1-R_0 is of the order of an atomic unit or larger. The conceptual problem is to define when a state is no longer interacting with one or more of its neighbors. The remarks just made apply equally well to avoided crossings of several states of the same symmetry over a region $[R_0,R_1]$.

In general, it is advantageous in treating collisions numerically to have expansion basis functions which are as slowly varying with internuclear separation as possible. In an adiabatic expansion, problems of coupling strength, numerical accuracy, storage, and interpolation are all aggravated by narrow avoided crossings which frequently are of little importance to the scattering phenomena of primary interest. For this reason it is useful to consider scattering expansions defined in terms of more slowly varying basis functions which interpolate between the electronic eigenfunctions across the region $[R_0,R_1]$. The functions we shall introduce below are so similar in their behavior to diabatic states that we shall refer to them as such. However, they can be called interpolating states if a distinction appears desirable.[53,54]

By definition, in this paper and in paper II, diabatic or interpolating states are R-dependent linear combinations of molecular eigenfunctions of the same symmetry generated by an orthogonal transformation with the following properties:

(1) The transformation is the identity at $R=R_0$ and, with possible sign changes, renumbers the eigenfunctions at $R=R_1$.

(2) The first and second derivatives of the transformation vanish at R_0 and R_1.

(3) In the transformed basis the radial coupling matrix element has values for $R_0 \leq R \leq R_1$ which are of the same size as the original radial coupling outside this interval. In practice this means a substantial reduction in the radial coupling on $[R_0,R_1]$.

(4) The transformed radial coupling and its derivatives are continuous at R_0 and R_1.

Conditions (2) and (4) are minimal continuity conditions. Stronger ones are possible and might be desirable. Condition (3) is the one which makes the use of the term diabatic appropriate. In fact, the equation of Smith[37] is used in slightly modified form to generate an approximate transform. In its original form, but for a finite number of interacting states, the transform obtained by solving Smith's equations makes the new radial coupling zero on $[R_0,R_1]$. This new coupling is not continuous with the old at R_0 and R_1. For this reason an antisymmetric correction matrix is added to the original antisymmetric radial coupling matrix and chosen in such a way that when Smith's equations are now solved, the transformed coupling is continuous in value and slope with the original coupling at both R_0 and R_1. The correction matrix elements are required to vary as little as possible on $[R_0,R_1]$ and to be small compared to the original radial coupling where this coupling is large. They are otherwise arbitrary. With a correction matrix chosen, Smith's equations yield a transform which satisfies all the above conditions except that if it is the identity at R_0 it will not quite be a renumbering matrix at R_1. If the scheme described here is working, at R_1, each column of the transform matrix will have just one element whose absolute value is close to one. All other elements in the column will be small in absolute value. This preliminary transform is converted into a final one, satisfying all the conditions, by multiplying it by an orthogonal normalizing matrix which is the identity at R_0 and whose value at R_1 is chosen to make the final transform a renumbering transform at $R=R_1$. The first and second derivatives of the normalizing matrix need to vanish at R_0 and R_1. The normalizing matrix is also somewhat arbitrary, but it should be kept as close to the identity and as slowly varying as possible. We have parametrized this matrix as a product of elementary rotations. Preliminary tests of this scheme have been made on the states of HeH^+, considering up to four interacting states. So long as $R_1 - R_0$ does not exceed one or two atomic units, the corrections to the basic Smith transform are small, and their inherent arbitrariness should have little influence on a computed cross section. Also, the precise choice of R_1 and R_0 is not critical. It should not be forgotten, of course, that in the case of an isolated, reasonably narrow avoided crossing, the potential curves and the Landau-Zener-Stueckelberg theory can provide a suitable transform.

The radial coupling in Smith's equation is $\langle(\partial/\partial R)_{\vec{r}}\rangle_{\bar{G}G}$ where $\vec{r}$ locates the electron with respect to the nuclear center of mass. Since this term does not always vanish in the separated-atom limit, it is advantageous to base the transform on an antisymmetric radial coupling matrix which does vanish. We use the low-velocity limit of the radial coupling matrix which appears in our scattering equations. Since it depends on the transformation parameters, these parameters and the diabatic transform are determined simultaneously by iteration. The specific equations are given in paper II and in Ref. 40.

In summary, let $\{\psi_H\}$ be a set of electronic eigenfunctions of the same symmetry. Then a more slowly varying set $\{\chi_G\}$ of the same symmetry can be constructed from

$$\chi_G = \sum_H \psi_H \Omega_{HG}(R), \tag{A1}$$

where $\Omega_{HG}(R)$ is the orthogonal matrix which represents the net result of all the interpolating transforms one has elected to introduce.

A change in notation will allow the formalism of Sec. IV to be used with electronic functions other than molecular eigenfunctions; for example, the linear combination of eigenfunctions just described. Assume that this function, still called χ_G, has the form given by Eq. (29). Also assume that, as $R \to \infty$, χ_G becomes one of the eigenfunctions ψ_G so that the S matrix need not be redefined. Now in Sec. IV the assumption that χ_G is an electronic eigenfunction was used only to obtain $(2M/\hbar^2)\mathcal{E}_G A_{n\Lambda}$ in Eq. (40), using Eq. (27). Therefore, defining an operator h_Λ by

$$\left(-\frac{\hbar^2}{2m}\Delta_{\eta G} + V\right) A_{p\Lambda}(2\pi)^{-1/2} e^{i\Lambda\Phi_G} = (2\pi)^{1/2} e^{i\Lambda\Phi_G}(h_\Lambda) A_{p\Lambda}, \tag{A2}$$

the use of function χ_G which is an eigenfunction only as $R \to \infty$ results in the replacement of $(2M/\hbar^2)\mathcal{E}_G A_{n\Lambda}$ in Eq. (40) by $(2M/\hbar^2) h_\Lambda A_{n\Lambda}$. The operator h_Λ is readily applied to Eq. (A1) because the Ω_{HG} depend only on R.

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[41] The undesired coupling is sometimes called "spurious" coupling. However, it is easy to show that at large R the effect of this coupling is to generate the best approximation to translational factors which can be manufactured from the available basis states.

[42] Compare with the mass scaling approach used in Ref. 8.

[43] The adiabatic correction terms, etc., are taken into account in the low-velocity quantal approximation presented in Ref. 40.

[44] The necessary equations (11) are obtained by setting the second term of D_j equal to zero and expressing this equation in terms of the scalars R, r^k, and $\vec{r}^k \cdot \vec{R}$. It is easy to see that conditions (11) are sufficient.

[45] A modification of Eq. (18) is possible which makes the agreement exact. Equations (11), (15), and (17) are retained and used to simplify Eq. (9). The relation $B_{jk}=0$ provides a linear equation for $k(R)$ in terms of the $\gamma(R)$. To first order in m/M, $h(R)=-\gamma(R)$, as in Eqs. (12) and (18).

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