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MODIFIED METHOD OF PERTURBED STATIONARY STATES. I

T. A. Green

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MODIFIED METHOD OF PERTURBED STATIONARY STATES

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ABSTRACT

The reaction coordinate approach of Mittleman is used to generalize the method of Perturbed Stationary States. A reaction coordinate is defined for each state in the scattering expansion in terms of parameters which depend on the internuclear separation. These are to be determined from a variational principle described by Senkyu. The variational result agrees with that of Bates and McCarroll in the limit of separated atoms but is generally different elsewhere. The theory is formulated for many-electron systems, and the construction of the scattered expansion is discussed for simple one-, two-, and three-electron systems. The scattering expansion and the Lagrangian for the radial scattering functions are given in detail for a heteronuclear one-electron system.

Abstract

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MODIFIED METHOD OF PERTURBED STATIONARY STATES I.

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 and for applications to the interstellar medium. Currently, charge exchange between highly stripped ions and hydrogen atoms is of some significance to the operation of magnetic fusion energy devices. In the latter case, H-atom energies from a few keV 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 (p.s.s.). 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. The author has found Refs. 1-6 instructive for physical insight, technical formalism, or both. In particular, the paragraph starting on p. 440 of the paper by Bates, Massey and Stewart¹ 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.

This paper proposes a new wave-theoretic modification of the p.s.s. method for diatomic systems. It was most directly influenced by the work of Bates and McCarroll² on the one hand and by that of Mittleman⁷ on the other. Although it was developed independently, the theory reported here is also closely related in some aspects to the work of Thorson and Delos.⁸ The theory is similar to References 7 and 8 in

that reaction coordinates are introduced in place of the internuclear separation in such a way that the individual terms in the modified p.s.s. expansion can become solutions of the time-independent Schroedinger 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. 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 factors² included.

This work seeks to improve on the original theory of Bates and McCarroll² 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 center-of-mass variables to a new set, one of which is the reaction coordinate.^{7,8,29} This approach guarantees that the conservation laws are obeyed and resolves all questions related to Galilean invariance automatically.³⁰ Second, the transformation parameters introduced into the scattering expansion can be determined from the variational principle for inelastic collisions described by Demkov.³¹ This procedure avoids an a priori choice of parameters, and leads to values for the parameters at all

internuclear separations. Our work shows that in the semiclassical approximation the parameters appear in translational factors of the Bates-McCarroll 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. Others do not appear to acknowledge the importance of such considerations at all. 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 non-orthogonality of the basis and despite the need to compute new coupling matrix elements for each energy and impact parameter.⁹⁻¹⁵ 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.¹¹⁻¹² 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 any supporting calculations, it is hard to believe that the approaches based on a single reaction coordinate or upon an overall translational factor can yield the correct energy dependence for charge exchange at the upper end of this energy region.^{16,17} By contrast, in the two 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.¹⁸⁻²⁰

3. At low energies, 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 energies²¹⁻²³ the results have agreed closely with those obtained¹⁷ through the use of an overall translational factor of the type defined by Schneiderman and Russek²⁴ or by Levy and Thorson.²⁵

The first statement above is in contradiction to the conclusions of some researchers^{8,17} who seem to regard the use of non-orthogonal expansions as undesirable at low energies. We disagree with this point of view. In the case of the rotational transition considered in Refs. 17 and 21-23, it was shown some time ago that if terms up to first order in velocity were retained in the matrix elements, unitary coupled equations with a diagonal overlap could be obtained for the Bates-Williams theory²¹ in a simple way.²⁸ In addition, it will be shown in this work that, to the same order in velocity, the coupled radial equations of the present theory have the same formal structure for both radial and rotational coupling as those based on orthogonal expansions. 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 17. 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 at low energies are not compelling.

The use of the variational principle is central to this work and therefore merits discussion here. A variational trial function is limited by the forms used to define it. As in Refs. 7 and 8, we rely primarily on the potency of the molecular electronic eigenfunctions. The modifications introduced by the 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 in the form of the transformation that this work differs from that in Refs. 7 and 8. The quite reasonable physical arguments behind the approach of Refs. 7, 8, 24, and 17 are well documented and will not be repeated here. However, we note again that no calculations or experiments rule out the Bates-McCarroll approach. We will introduce a reaction 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. This is complicated in general; but at the level of typical two- and three-state calculations, it simplifies considerably.

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 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 what is the best way to formulate such a problem. One approach⁷ 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 two other approaches which yield reasonable results but which could stand further investigation. The first approach would average the high frequencies out of the Euler-Lagrange equations for the transformation parameters. The second would consider adiabatic or diabatic formulations for which the coupling between basis states is weak. Both procedures decouple the determination of the parameters from that of the radial scattering functions. The resulting parameters then depend primarily on electronic structure.

There is another new aspect of this work which merits discussion. An attempt has been made here to formulate the theory for multi-electron systems, not just in a conceptual way, but operationally. This is difficult and tedious, but important.⁷ The generalization involves having a pair of parameters for each orbital in an approximate orbital product function. Only inequivalent orbitals have distinct parameters. In this way, inner electrons which remain attached to one nucleus throughout a collision can be treated differently from electrons in outer orbitals. Such a product corresponds to a state based on a single configuration.³² Now, single configuration functions are not always good approximations to electronic eigenfunctions. If they are then

used in a scattering expansion, one either has to calculate the result of the Hamiltonian operator applied to these functions directly or relate them to known energy eigenfunctions. The direct calculation becomes a problem when translational factors are introduced at high energies, because the direct calculation of the two-center exchange terms with translational factors is very time consuming.³³ For this reason, the orbital "products" in this theory are always defined in terms of linear combinations of spin-free, fixed-nucleus electronic eigenfunctions for different values of the total spin.^{34,35} The application of the Hamiltonian to the linear combinations of eigenfunctions is then straightforward. The required combinations are found to a sufficient approximation, starting from the completeness relation for the irreducible representations of the symmetric group.³⁶

The use of spin-free electronic eigenfunctions, as well as the related formalism for the treatment of the electron spin and the Pauli exclusion principle are well known in quantum chemistry.^{34,35} The use of the formalism to derive atom-atom scattering equations is straightforward if, as in this work, relativistic effects are neglected.

As will be seen, our formulation of a scattering expansion for a many-electron system is not particularly simple and requires a detailed knowledge of the system's molecular structure. For this reason, we have confined the discussion of scattering expansions to systems with three or fewer electrons. However, the transformation theory and the exact elimination of the external angle variables, using angular momentum conservation, are worked out for any number of electrons. This step makes it possible to obtain radial scattering equations without introducing, for example, an Eikonal approximation with its restriction to small-angle scattering.³⁷

The construction of scattering expansions for many-electron systems, makes use of the concept of diabatic states. In this paper, diabatic states 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 close to that proposed by Smith, but using a finite set of electronic states.^{38,39} The details are presented in Section VI-B in order to set down the prescription used in computations. The discussion is not intended to add to the conceptual foundation of diabatic states.

The results of this work are divided into two papers. In this paper, Sections II and III summarize the many-electron spin formalism, introduce the usual scattering boundary conditions, and establish notation. In Section IV, the transformation which defines the new scattering variables of the theory is developed. Section V lays the groundwork for the exact treatment of angular momentum conservation through a special choice of electronic basis functions.

Section VI concerns one-electron systems. In Section VI-A the construction of the scattering expansion and the derivation of the Lagrangian are carried out in detail for one-electron heteropolar systems. Section VI-B is concerned with diabatic states, and Section VI-C considers one-electron homopolar systems. The theory is not as completely developed for homopolar systems as for heteropolar ones. For the former, the expansion involves an additional parameter to be optimized. This is the amount of mixing of asymptotically degenerate gerade and ungerade states as a function of internuclear separation. In the original formulation of Bates and McCarroll,² expansion terms are formed by combining these pairs of states in equal amounts at all internuclear separations. We would like to relax this requirement and determine the amount of mixing variationally. There is no problem in formulating the required equations for H_2^+ . However, the research on the simultaneous optimization of all the parameters for H_2^+ has not been carried to a definite conclusion. For this

reason, the discussion of homonuclear systems is restricted to the construction of the scattering expansion terms for H_2^+ and H_2 .

Section VII presents the discussions of scattering expansions for two- and three-electron systems. The heteropolar molecule HeH^+ is considered in some detail. Then, briefer discussions of expansions for H_2 and HeH -like systems are given. The case of HeH leads to a somewhat startling consequence of the theory. Finally, some important ways to simplify the many-electron equations are discussed.

The second paper⁴⁰ is devoted to one-electron heteropolar systems and starts with the Lagrangian of Section VI-A. Its purpose is to reduce the integro-differential equations of the present paper to approximate ordinary differential equations which are amenable to computation. In the first half of the paper, 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 formulae for the transformation parameters are also derived. The second half of Paper II⁴⁰ presents a low-velocity, quantal approximation to the Lagrangian of Section VI-A. From this, equations of the same formal structure as those of Reference 8 are then derived. Finally, a one-state optimization of the transformation parameters is given.

II. REVIEW OF MANY-ELECTRON SPACE AND SPIN FORMALISM AND DEFINITION OF NOTATION.

Since the theory is to be developed for a spin-independent Hamiltonian, it is convenient to eliminate the N -electron spin eigenfunctions from the calculation at an early stage. Consider an N -electron system, and let the total spin and space-fixed spin projection quantum numbers be S and M , respectively. For each N , S , and M , there is a complete orthonormal set of N -electron spin functions $\phi(N, S, M; r)$, where r labels the members of the set. The number of functions r is equal to the dimension g_S of a particular irreducible representation $\alpha(S)$ of the symmetric group of permutations of N objects.^{41,42} We have

$$\langle \phi(N, S', M'; r') | \phi(N, S, M; r) \rangle = \delta_{S'S} \delta_{M'M} \delta_{r'r} \quad (1)$$

where $\langle A | B \rangle$ designates the inner product of A and B .

An arbitrary N -electron space-spin function, ψ , which is a total spin eigenfunction of given S and M and which satisfies the Pauli exclusion principle can be written in terms of arbitrary space functions $F_k(\vec{r}_1, \dots, \vec{r}_N)$

as

$$\psi = (N!)^{-1} \sum_R \epsilon_R P_R Q_R \sum_{k=1}^{g_S} F_k(\vec{r}_1, \dots, \vec{r}_N) \theta(N, S, M; k) \quad (2)$$

In Eq. (2) the sum is over all $N!$ permutations R , Q_R is the spin-space permutation operator and P_R is the coordinate-space permutation operator. The function ϵ_R is $+1$ for even permutations and -1 for odd ones. Using the group property of the spin eigenfunctions⁴¹

$$Q_R \theta(N, S, M; k) = \sum_{\lambda=1}^{g_S} A^{(S)}(R)_{\lambda k}^* \theta(N, S, M; \lambda), \quad (3)$$

ψ can be expressed in the form

$$\psi = \sum_{\lambda=1}^{g_S} \phi_{\lambda}^{(S)} \theta(N, S, M; \lambda), \quad (4)$$

where

$$\phi_{\lambda}^{(S)} = \frac{1}{g_S} \sum_{k=1}^{g_S} \bar{\phi}_{\lambda k}^{(S)} F_k \quad (5)$$

By definition

$$\bar{e}_{\lambda k}^{(S)} = (g_S/N!) \sum_R e_R A^{(S)}(R)_{\lambda k}^* P_R \quad (6a)$$

As a result of (6a),

$$(\bar{e}_{\lambda k}^{(S)})^\dagger = \bar{e}_{k\lambda}^{(S)} \quad (6b)$$

$$\bar{e}_{\lambda'k'}^{(S')} \bar{e}_{\lambda k}^{(S)} = \delta_{S'S} \delta_{k'\lambda} \bar{e}_{\lambda'k}^{(S)} \quad (6c)$$

Here $\dagger$ signifies the adjoint permutation operator. The $\bar{e}_{\lambda k}^{(S)}$ are convenient because, as is indicated in Eq. (5), for any k , and any arbitrary space function F_k , $\bar{e}_{\lambda k}^{(S)} F_k$ defines a set of functions f_λ such that $\sum_\lambda f_\lambda \phi(N, S, M, \lambda)$ satisfies the Pauli exclusion principle.^{41,43} Thus any time we have constructed the spatial part of a scattering expansion term to our satisfaction, the Pauli principle can be satisfied in a straightforward way, using the $\bar{e}_{\lambda k}^{(S)}$. The $\bar{e}_{\lambda k}^{(S)}$ are called projectors in Refs. 35 and 43.

Equation (4), by projection onto the spin functions, allows the Schroedinger equation for the bound and continuum states of a diatomic molecule to be expressed in terms of the unknown space functions $F_k(\vec{r}_1, \dots, \vec{r}_N)$. Let the nuclear masses be M_A, M_B and the nuclear charges be Z_A, Z_B ; let the vector $\vec{R}$ go from nucleus A to nucleus B, and let the electrons be located with respect to the center of mass of the nuclei by coordinate vectors $\vec{r}_i, i=1, N$. Let M be the reduced mass of the two nuclei, let $p = M_B/(M_A + M_B)$ and let $q = M_A/(M_A + M_B)$. Then, neglecting relativistic effects, the center of mass Hamiltonian $H = T + V$ for the system is⁵

$$H = -\frac{\hbar^2}{2M} \Delta_R - \frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_{\vec{r}_i} - \frac{\hbar^2}{2(M_A + M_B)} \sum_i \sum_j \vec{\nabla}_{\vec{r}_i} \cdot \vec{\nabla}_{\vec{r}_j} + V, \quad (7)$$

where the potential energy V is given by

$$V = \frac{Z_A Z_B e^2}{R} - \sum_i \left\{ \frac{Z_A e^2}{|\vec{r}_i - \vec{p}_R|} + \frac{Z_B e^2}{|\vec{r}_i - \vec{q}_R|} \right\} + \sum_i \sum_{j < i} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}. \quad (8)$$

In Eqs. (7) and (8) m and e are the electron mass and charge. If the nuclear-kinetic-energy term and mass-polarization term are dropped from H , the remainder is the fixed-nucleus electronic Hamiltonian H_e . Both Hamiltonians naturally commute with all the electron spin operators, with all the $N!$ electron coordinate permutation operators, and therefore with all the projectors of Eqs. (6).

From Eqs. (4) and (7)

$$\langle \psi | H \psi \rangle = \sum_{\lambda} \langle \phi_{\lambda}^{(S)} | H \phi_{\lambda}^{(S)} \rangle, \quad (9)$$

$$\langle \psi | \psi \rangle = \sum_{\lambda} \langle \phi_{\lambda}^{(S)} | \phi_{\lambda}^{(S)} \rangle. \quad (10)$$

The insertion of the expression (5) into Eqs. (9) and (10) yields

$$\langle \psi | H \psi \rangle = \frac{1}{g_S} \sum_k \sum_{k'} \langle F_{k'} | H \bar{\phi}_{k'k}^{(S)} F_k \rangle, \quad (11)$$

$$\langle \psi | \psi \rangle = \frac{1}{g_S} \sum_k \sum_{k'} \langle F_{k'} | \bar{\phi}_{k'k}^{(S)} F_k \rangle. \quad (12)$$

upon the use of Eqs. (6b) and (6c). With H replaced by He and each F_k given as a sum of products of one-electron space orbitals, Eqs. (11) and (12) are a well-known starting point for the calculation of fixed-nucleus electronic wavefunctions.^{14,15} Equations (1)-(12) show how the space-spin structure required by the Pauli principle is impressed, through the projectors, on the space functions.

Before proceeding to the scattering problem, we pursue one further development. From Eqs. (5) and (6c)

$$\phi_{\kappa}^{(S)} = \frac{1}{g_S} \sum_{k=1}^{g_S} \bar{e}_{\kappa k}^{(S)} F_k \quad , \quad (13)$$

$$\begin{aligned} \bar{e}_{\lambda \kappa}^{(S)} \phi_{\kappa}^{(S)} &= \frac{1}{g_S} \sum_{k=1}^{g_S} \bar{e}_{\lambda \kappa}^{(S)} \bar{e}_{\kappa k}^{(S)} F_k \\ &= \frac{1}{g_S} \sum_{k=1}^{g_S} \bar{e}_{\lambda k}^{(S)} F_k = \phi_{\lambda}^{(S)} \quad . \end{aligned} \quad (14)$$

Equation (14) shows that from one $\phi_{\kappa}^{(S)}$, the whole g_S -dimensional set of $\phi_{\lambda}^{(S)}$ can be constructed. Moreover, Eqs. (9) and (10) can be transformed into

$$\begin{aligned} \langle \psi | H \psi \rangle &= \sum_{\lambda} \langle \phi_{\kappa}^{(S)} | H \bar{e}_{\kappa \lambda}^{(S)} \phi_{\lambda}^{(S)} \rangle \\ &= g_S \langle \phi_{\kappa}^{(S)} | H \phi_{\kappa}^{(S)} \rangle \quad , \end{aligned} \quad (15)$$

$$\langle \psi | \psi \rangle = g_S \langle \phi_{\kappa}^{(S)} | \phi_{\kappa}^{(S)} \rangle \quad . \quad (16)$$

In Eqs. (15) and (16) there is no sum over κ . Also, using Eq. (14) and the commutativity of H with the projectors it follows that if one $\phi_{\kappa}^{(S)}$ is an eigenfunction of H , so are all the $\phi_{\lambda}^{(S)}$. The use of Eq. (5) in Eqs. (15) and (16) again leads to Eqs. (11) and (12). In summary, one representative of the set of ϕ_{λ} is all that is needed.

III. BOUNDARY CONDITIONS FOR ATOM-ATOM SCATTERING, NEGLECTING IONIZATION. DEFINITION OF THE SCATTERING AMPLITUDE.

In this paper ionization is neglected. At large internuclear separations the approximate solutions of the Schroedinger equation should describe atoms or ions interacting at long range. Let G_A stand for the set of parameters $(N_A, \Gamma_A, L_A, \mu_A, S_A, \bar{M}_A)$. These are the number N_A of electrons bound to A, the total orbital angular momentum quantum numbers L_A, μ_A , and total spin quantum numbers $S_A, \bar{M}_A$ of the atomic state on A. The rest of the state's necessary quantum numbers are designated by Γ_A . Let G_B be defined analogously and let G_{AB} be the set $G_A + G_B$. The basic unsymmetrized product function $\bar{\psi}_{G_{AB}}$ for a channel consisting of an atom-pair AB is then

$$\bar{\psi}_{G_{AB}} = F_{G_{AB}}(\vec{R}_{AB}) \psi_{G_A}(\vec{r}_{1A}, \dots, \vec{r}_{N_A A}) \psi_{G_B}(\vec{r}_{(N_A+1)B}, \dots, \vec{r}_{N_B B}). \quad (18)$$

In Eq. (18) ψ_{G_A} is a normalized approximate space-spin atomic eigenfunction, whose spin-dependence is not shown explicitly. In Eq. (18) each electron on A(B) is referred to nucleus A(B), and $\vec{R}_{AB}$ goes from the center of mass of atom A to that of atom B. In these coordinates the Schroedinger equation becomes separable as the internuclear separation R becomes infinite.⁵ From the product function

$\bar{\psi}_{G_{AB}}$ an antisymmetric function $\psi_{G_{AB}}$ can be constructed. Let

$$\psi_{G_{AB}} = \frac{1}{\sqrt{\binom{N}{N_A}}} \sum_P c_P P Q_P \bar{\psi}_{G_{AB}} \quad (19)$$

The sum is over the $\binom{N}{N_A}$ distinct exchanges of electrons between the atoms. Each permutation in Eq. (19) changes $\vec{R}_{AB}$ relative to $\vec{R}$. Since as $R \rightarrow \infty$, the A and B functions do not overlap each other, $\psi_{G_{AB}}$ can be normalized with respect to the electron coordinates in that limit. If the ψ_{G_B} and ψ_{G_A} of Eq. (18) are atomic eigenfunctions they jointly form an orthonormal set as $R \rightarrow \infty$. However, since exact eigenfunctions are usually not available, it will be assumed that the ψ_{G_A} are orthonormal and diagonalize the Hamiltonian for atom A, etc. This requirement can be satisfied, for example, by computing all the approximate ψ_{G_A} in one configuration-interaction calculation for atom A.

From the function $\psi_{G_{AB}}$, the corresponding spin-free functions $\phi_{\lambda G_{AB}}^{(S)}$ are computed by projection onto the complete set of N-electron spin functions $\phi(N, S, M, \lambda)$ according to Eq. (4). We can write

$$\psi_{G_{AB}} = \sum_S \sum_{\lambda} \phi_{\lambda G_{AB}}^{(S)} \phi(N, S, M_A + M_B; \lambda) \quad (19a)$$

Equation (19a) determines how the functions $F_{G_{AB}}(\vec{R}_{AB})$ are related to the spin-free functions $\phi_{\lambda G_{AB}}^{(S)}$ in the asymptotic region.

The amplitude for scattering into the final channel G_{AB} from an initial channel $G_{A'B'}$ is defined in terms of the behavior of $F_{G_{AB}}(\vec{R}_{AB})$ of Eq. (18) as $R \rightarrow \infty$. In this limit $\vec{R}_{AB} \rightarrow \vec{R}$ for all permutations in Eq. (19). Therefore, adding $G_{A'B'}$ to designate the initial channel,

$$\begin{aligned}
f_{G_{AB}G_{A'B'}}(\hat{R}_{AB}) \rightarrow f_{G_{AB}G_{A'B'}} \exp \left\{ i k_{A'B'} Z_{A'B'} \right. \\
+ i \alpha_{A'B'} \ln (k_{A'B'} (R_{A'B'} - Z_{A'B'})) \left. \right\} \\
+ (R_{AB})^{-1} f_{G_{AB}G_{A'B'}}(\hat{R}) \exp \left\{ i k_{AB} R_{AB} \right. \\
- i \alpha_{AB} \ln (2k_{AB} R_{AB}) \left. \right\} . \quad (20)
\end{aligned}$$

In Eq. (20) $\alpha_{AB} = Z_A Z_B e^2 / \hbar v_{AB}$ and the laboratory frame Z-axis has been taken along the incident beam direction.

The differential cross section for scattering in the direction $\hat{R}$ into the G_{AB} channel is given by

$$\frac{d\sigma}{d\Omega} = \frac{v_{AB}}{v_{A'B'}} \left| f_{G_{AB}G_{A'B'}}(\hat{R}) \right|^2 . \quad (21a)$$

In Eqs. (20), (21a),

$$\hbar k_{AB} = M_{AB} v_{AB} ,$$

$$\frac{\hbar^2 k_{AB}^2}{2M_{AB}} = E - E_{G_A} - E_{G_B} ,$$

$$M_{AB} = \frac{(N_A + N_A m)(N_B + N_B m)}{(N_A + N_B + (N_A + N_B)m)} , \quad (21b)$$

where E_{G_A} and E_{G_B} are the approximate atomic eigenvalues, and E is the system total energy in the c.m. frame. In Section VI-A a partial-wave expression for the scattering amplitude will be given.

IV. THE CONSTRUCTION OF A LOW-ENERGY SCATTERING EXPANSION IN SUCH A WAY THAT THE EQUATIONS FOR THE SCATTERING FUNCTIONS DECOUPLE IN THE ASYMPTOTIC REGION. THE USE OF A STATE-DEPENDENT REACTION COORDINATE AND THE TRANSFORMATION OF THE SYSTEM KINETIC ENERGY.

In order to compute the scattering amplitudes $f_{G_{AB}, G_{A'B'}}(\hat{R})$, for some initial channel $G_{A'B'}$, an approximate solution $\psi_{G_{A'B'}}$ of

$$(H - E) \psi_{G_{A'B'}} = 0 \quad (22)$$

must be found for which as $R \rightarrow \infty$

$$\psi_{G_{A'B'}} \rightarrow \sum_{G_{AB}} \psi_{G_{AB} G_{A'B'}} \quad (23)$$

On the right-hand side of Eq. (23) the subscript $G_{A'B'}$ has been appended to the functions defined in Eqs. (18)-(20). The sum is always over a finite number of channels. One possible method for solving Eq. (22) approximately is to choose a set of G_{AB} and to use for all R

$$\psi_{G_{A'B'}} = \sum_{G_{AB}} \psi_{G_{AB} G_{A'B'}} \quad (24)$$

Evidently Eq. (24) describes an atomic basis expansion. The scattering functions $F_{G_{AB}G_{A'B'}}(\vec{R}_{AB})$ from Eq. (18) are determined by projecting Eq. (22) onto the electronic functions which appear in Eq. (18). These are

$$\bar{\chi}_{G_{AB}} = \psi_{G_A}(\vec{r}_{1A}, \dots, \vec{r}_{N_A A'}) \psi_{G_B}(\vec{r}_{(N_A+1)B}, \dots, \vec{r}_{N_B}) \quad (25)$$

The projection is carried out with $\vec{R}_{AB}$ for $\bar{\chi}_{G_{AB}}$ held fixed. The result is a set of integro-differential equations.⁴⁶ Reference 46 gives a one-electron example. The scattering functions cannot be removed from the electron coordinate integrals because they depend on the channel-dependent variable $\vec{R}_{AB}$. The equations decouple as $R \rightarrow \infty$.

The equations described above have not been popular for computations. However, in weak-coupling approximations they lead directly to well-known results. One could apply in-out decoupling and semi-classical approximations to the equations and deduce a set of coupled ordinary differential equations.⁴⁷ The matrix elements would contain plane-wave translational factors of the Bates-McCarroll type, in a many-electron form.³³

As is well known, atomic-basis expansions are normally created with the internuclear separation $\vec{R}$ as the scattering variable. This approach yields differential-scattering equations directly. In order to get the equations to decouple as $R \rightarrow \infty$, translational factors are multiplied into the electronic basis functions. This approach has been widely used with considerable success.⁴⁸

Consider now the creation of an electronic basis for slow collisions.

The logical functions to use are those of the p.s.s. method, i.e., the fixed-nucleus electronic eigenfunctions for the AB molecule. One well-known difficulty with this method is that with a scattering function $F_{G_{AB}}(\vec{R})$ of the internuclear separation $\vec{R}$ instead of $\vec{R}_{AB}$, the individual terms in the expansion do not become exact solutions of the Schroedinger equation as $R \rightarrow \infty$. The differential equations obtained for the $F_{G_{AB}}(\vec{R})$ have non-zero coupling for all R amongst all channels which are connected by dipole-allowed transitions. Bates and McCarroll² 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.

In this paper a molecular analogue of Eq. (24) is explored as an alternative to the direct introduction of translational factors. Each term in the scattering expansion is based on an approximate orbital product Ξ , which is an R -dependent linear combination of spin-free eigenfunctions. Associated with Ξ are a reaction coordinate $\vec{\zeta}(\vec{R}, \vec{r}^k)$ and a set of electron coordinates $\vec{r}^n(\vec{R}, \vec{r}^k)$. The expansion term then takes the form, projector $\times \Xi \times F(\vec{\zeta})$, where F is the scattering function, and the projector from Section II is used to satisfy the Pauli exclusion principle. The linear combinations which make up Ξ are defined in Section VII.

Once the terms in an expansion have been constructed, the next step is to apply $H - E$ to them as in Eq. (22). Since H is symmetric with respect to exchange, it can be moved inside the projector directly onto the product $F(\vec{\zeta}) \Xi(\vec{r}^1, \vec{r}^k)$. At this point, it becomes necessary to express H in terms of $\vec{\zeta}, \vec{r}^1$ so that the actual equations for the unknown $F(\vec{\zeta})$ for each term can be deduced. The rest of this section will therefore be concerned

with the transformation defined below in Eq. (26) and with its influence on the form of the kinetic energy operator of Eq. (7). The discussion is essential, but tedious, and leads to Eqs. (41) and (46).

In order to define the electron coordinates $\vec{r}_n$ and the reaction coordinate $\vec{\xi}$ for a particular term in a scattering expansion the coordinate transformation

$$\vec{\xi} = \alpha \vec{R} + \sum_{k=1}^N \beta^k \vec{r}^k,$$

$$\vec{r}_n = \gamma^n \vec{R} + \delta^n \vec{r}^n, \quad n = 1, N \quad (26)$$

is introduced. 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^i , γ^i and δ^i were called transformation parameters in the Introduction. The parameters are scalar functions of R , r^k and $s^k_{\vec{R} \cdot \vec{r}^k}$.

Only scalar functions are introduced so the expression for the total orbital angular momentum,

$$-i\hbar \left[\vec{R} \times \frac{\partial}{\partial \vec{R}} + \sum_k \vec{r}^k \times \frac{\partial}{\partial \vec{r}^k} \right] = -i\hbar \left[\vec{\xi} \times \frac{\partial}{\partial \vec{\xi}} + \sum_k \vec{r}_n^k \times \frac{\partial}{\partial \vec{r}_n^k} \right] \quad (27)$$

is form invariant. The model for the transformation finally used in this paper is suggested by the transformation to separated-atom, center-of-mass variables.⁴⁹ This transformation will now be discussed. Suppose that electrons

(1,...,N_A) are attached to nucleus A and electrons (N_A+1,...,N) are attached to nucleus B. Let

$$\vec{r}_i^1 = \vec{r}^1 + p\vec{R}, \quad i = 1, N_A$$

$$\vec{r}_i^1 = \vec{r}^1 - q\vec{R}, \quad i = N_A + 1, N$$

$$\begin{aligned} \vec{r} &= \vec{R} + \frac{m}{N_B + N_B m} \sum_{i=N_A+1}^N (\vec{r}_i^1 - q\vec{R}) - \frac{m}{N_A + N_A m} \sum_{i=1}^{N_A} (\vec{r}_i^1 + p\vec{R}) \\ &= \vec{R}_{AB}, \end{aligned} \quad (28)$$

where $N_B = N - N_A$, and the rest of the notation is defined above Eq. (7). The definitions of p and q are such that $\vec{r}_i^1 + p\vec{R}$ is the vector from nucleus A to electron i, etc. The reaction coordinate $\vec{r}$ is just $\vec{R}_{AB}$ of Eq. (18), the vector from the center of mass of fragment A to that of fragment B. The Jacobian of the transformation (28) is unity. The special thing about transformation (28) is that the transformed system kinetic energy is separable with respect to $\vec{R}_{AB}$ and the other variables.¹² That is, the kinetic energy contains

terms $\frac{\partial^2}{\partial \xi^2} \cdot \frac{\partial^2}{\partial \eta^2}$ in the kinetic energy. Thus, when the kinetic energy operator

is applied to separated-atom functions of the form (18), the partial derivatives with respect to $\vec{R}_{AB}$ (at fixed $\vec{r}^1$) produce a non-zero result only on $F_{G_{AB}}$. By contrast, in the original variables $\vec{R}, \vec{r}^1$ the kinetic energy is given by Eq. (7), and $\frac{\partial^2}{\partial \vec{R}^2}$ at fixed $\vec{r}^1$ does not vanish when applied to

$\psi_{G_A} \psi_{G_B}$ in Eq. (18). Now the fixed-nucleus electronic eigenfunctions of the p.s.s. method actually tend toward sums of the products $\psi_{G_A} \psi_{G_B}$. Consequently, the p.s.s. equations based on scattering functions $F_{G_{AB}}(\vec{R})$ do not decouple.

Using Eq. (28) as a model we seek transformations of the form (26) 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 can be introduced so that no large distortions of the volume element are allowed. We require that the Jacobian of the transformation (26) be unity to at least first order in m/M .

This condition is imposed by assuming that

$$\begin{aligned}\alpha &= 1 + (m/M)g \quad , \\ \beta^k &= (m/M) h^k \quad , \\ \epsilon^k &= 1 + (m/M) f^k \quad .\end{aligned}\tag{29}$$

In Eqs. (26) and (29) γ^k , g , h^k and f^k are all $O(1)$ or smaller as (m/M) approaches zero.

The result of Eqs. (29) is that through transformation (26) $\vec{\xi} = \vec{R}$ up to terms of order m/M and $\vec{\eta}^n = \gamma^n \vec{R} + \vec{r}$ up to terms of order m/M . Thus the reaction coordinate is kept close to $\vec{R}$, and the n 'th

electron is nearly located with respect to a point shifted by $-\gamma \vec{R}$ along the internuclear line from the center of mass of the nuclei. As Bates and McCarroll² showed, the first-order change from $\vec{R}$ to $\vec{\xi}$ is important because in the scattering functions, $\vec{\xi}$ or $\vec{R}$ is multiplied by the heavy-particle momentum.

The next step in the program is to express the kinetic energy T of Eq. (7) in terms of the new variables defined in Eqs. (26) and (29).

The result is

$$\begin{aligned} \frac{-2}{\hbar^2} T = & A_{kj} \frac{\partial}{\partial \xi_k} \frac{\partial}{\partial \xi_j} + \sum_n B_{jk}^n \frac{\partial}{\partial \xi_j} \frac{\partial}{\partial \eta_k^n} \\ & + \sum_n \sum_m C_{jk}^{nm} \frac{\partial}{\partial \eta_j^n} \frac{\partial}{\partial \eta_k^m} + D_j \frac{\partial}{\partial \xi_j} + \sum_n E_j^n \frac{\partial}{\partial \eta_j^n} . \end{aligned} \quad (30)$$

In Eq. (30) the subscripts represent space-fixed vector components and the Einstein summation convention is used. The superscripts number the electrons from 1 to N . The coefficient A_{kj} is

$$\begin{aligned}
A_{kj} = & \frac{1}{M} \left(\left(1 + \frac{m}{M}g\right) \delta_{ij} + \frac{m}{M} \frac{\partial g}{\partial R_i} R_j + \sum_n \frac{m}{M} \frac{\partial h^n}{\partial R_i} r_j^n \right) \\
& \times \left(\left(1 + \frac{m}{M}g\right) \delta_{ik} + \frac{m}{M} \frac{\partial g}{\partial R_i} R_k + \sum_p \frac{m}{M} \frac{\partial h^p}{\partial R_i} r_k^p \right) \\
& + \frac{1}{m} \left(\frac{m}{M}\right)^2 \sum_i \left(\frac{\partial g}{\partial r_i^i} R_j + \sum_n \frac{\partial h^n}{\partial r_i^i} r_j^n + \epsilon_{ij} h^i \right) \left(\frac{\partial g}{\partial r_i^i} R_k + \sum_m \frac{\partial h^m}{\partial r_i^i} r_k^m + \epsilon_{ik} h^i \right) \\
& + \frac{1}{(M_A + M_B)} \left(\frac{m}{M}\right)^2 \sum_{i,p} \left(\frac{\partial g}{\partial r_i^i} R_j + \sum_n \frac{\partial h^n}{\partial r_i^i} r_j^n + \epsilon_{ij} h^i \right) \\
& \times \left(\frac{\partial g}{\partial r_i^p} R_k + \sum_m \frac{\partial h^m}{\partial r_i^p} r_k^m + \epsilon_{ik} h^p \right) . \tag{31}
\end{aligned}$$

The relative importance of the various terms can be estimated by noting that $\partial/\partial \epsilon_k$ 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. (31) are contributions of order $Mv^2/\hbar^2$, $mv^2/\hbar^2$, and $(m/M)mv^2/\hbar^2$. The second term in Eq. (32) 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 be negligible. When the parameters are constant

$$A_{kj} = A_{kj} \left\{ \frac{(1 + \frac{m}{M})^2}{M} + \frac{1}{m} \left(\frac{m}{M} \right)^2 \sum_l (h^l)^2 + \frac{1}{(M_A + M_B)} \left(\frac{m}{M} \right)^2 \sum_l \sum_p h^l h^p \right\}. \quad (32)$$

The terms in {} of Eq. (32) can then be used to define the reciprocal of a system-reduced mass in Eq. (30). In the special case of Eq. (28) it is equal to $1/(M_A + N_A m) + 1/(M_B + N_B m)$, the reduced mass of the system, atom A + atom B. From this it is seen that dropping the smallest terms in Eq. (31) 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 $\partial/\partial \epsilon_{ij}$ operators also act on the electronic eigenfunctions. Acting on an electronic eigenfunction $\partial/\partial \epsilon_{ij}$ 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. (30) 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 non-adiabatic coupling terms of the p.s.s. 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. (31) to Eq. (30) are $\frac{1}{M} a_0^{-2}$, $\frac{1}{M} \left(\frac{m}{M} \right) a_0^{-2}$, and $\frac{1}{M} \left(\frac{m}{M} \right)^2 a_0^{-2}$. The first of these contributions corresponds to regular terms (e.g. adiabatic correction terms) of the p.s.s. method.

Next, let us consider the cross-derivative terms in Eq. (30). Their coefficient B_{jk}^n is given by

$$\begin{aligned}
B_{jk}^n = & \frac{2}{M} \left(\left(1 + \frac{m}{M} g \right) \varepsilon_{ij} + \frac{m}{M} \frac{\partial g}{\partial R_i} R_j + \frac{m}{M} \sum_p \frac{\partial h^p}{\partial R_i} r_j^p \right) \\
& \times \left(\gamma^n \varepsilon_{ik} + \frac{\partial \gamma^n}{\partial R_i} R_k + \frac{m}{M} \frac{\partial f^n}{\partial R_i} r_k^n \right) \\
& + \frac{2}{M} \sum_j \left(\frac{\partial g}{\partial r_i^j} R_j + \sum_p \frac{\partial h^p}{\partial r_i^j} r_j^p + \varepsilon_{ij} h^m \right) \\
& \times \left(\left(1 + \frac{m}{M} f^n \right) \varepsilon_{nk} \varepsilon_{ik} + \left(\frac{m}{M} \right) \frac{\partial f^n}{\partial r_i^k} r_k^n + \frac{\partial \gamma^n}{\partial r_i^k} R_k \right) \\
& + \frac{2}{(M_A + M_B)} \left(\frac{m}{M} \right) \sum_j \sum_m \left(\frac{\partial g}{\partial r_i^j} R_j + \sum_p \frac{\partial h^p}{\partial r_i^j} r_j^p + \varepsilon_{ij} h^m \right) \\
& \times \left(\left(1 + \frac{m}{M} f^n \right) \varepsilon_{nk} \varepsilon_{ik} + \left(\frac{m}{M} \right) \frac{\partial f^n}{\partial r_i^k} r_k^n + \frac{\partial \gamma^n}{\partial r_i^k} R_k \right). \quad (33)
\end{aligned}$$

The size of the cross-derivative contribution to Eq. (30) can be estimated with $\partial/\partial \varepsilon_j \sim Mv/\hbar$ and $\partial/\partial r_k^n \sim a_0^{-1}$. Thus the first two terms of B_{jk}^n 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 $\partial/\partial \varepsilon_j$ operates on an electronic eigenfunction the largest terms are $\sim \frac{1}{M} a_0^{-2}$.

For constant parameters,

$$B_{jk}^n = \frac{2}{M} \varepsilon_{jk} \left\{ \left(1 + \frac{m}{M} g \right) \gamma^n + \left(1 + \frac{m}{M} f^n \right) h^n + \frac{m}{(M_A + M_B)} \left(1 + \frac{m}{M} f^n \right) \sum_p h^p \right\}. \quad (34)$$

The cross-derivative coefficient (34) vanishes for transformation (28), as well as for the identical transformation with g , γ^n , h^n , and $f^n = 0$. The term $D_j(\partial/\partial \epsilon_j)$ contributes terms of the same order of magnitude to Eq. (30) as the cross-derivative term. We have

$$\begin{aligned}
 D_j = & \frac{1}{M} \left(\frac{m}{M} \right) \left(2 \frac{\partial g}{\partial R_j} + \frac{\partial^2 g}{\partial R_j^2 \partial R_i} R_j + \sum_n \frac{\partial^2 h^n}{\partial R_j^2 \partial R_i} r_j^n \right) \\
 & + \frac{1}{m} \left(\frac{m}{M} \right) \sum_i \frac{\partial}{\partial r_i^2} \left(\frac{\partial g}{\partial r_i^2} R_j + \sum_n \frac{\partial h^n}{\partial r_i^2} r_j^n + \gamma_{ij} h^2 \right) \\
 & + \frac{1}{(M_A + M_B)} \left(\frac{m}{M} \right) \sum_i \sum_p \left(\frac{\partial^2 g}{\partial r_i^2 \partial r_i^p} R_j + \sum_n \frac{\partial^2 h^n}{\partial r_i^2 \partial r_i^p} r_j^n + \frac{\partial h^2}{\partial r_i^p} + \frac{\partial h^p}{\partial r_i^2} \right). \quad (35)
 \end{aligned}$$

As before, when $\partial/\partial \epsilon_j$ operates on a scattering function the result is $\sim v/\hbar$. Thus the largest velocity-dependent contributions from Eq. (35) to Eq. (30) come from the second term in Eq. (35) and are $\sim v/(\hbar a_0)$. The remaining terms of this type are $\sim (m/M)v/(\hbar a_0)$. When $\partial/\partial \epsilon_j$ operates on an electronic function, the largest contribution to Eq. (30) from Eq. (35) is a_0^{-2}/M . For constant parameters $D_j = 0$. At this point all the terms in Eq. (30) 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. (26) and (29) will now be introduced. To guarantee that the exact equations decouple in the asymptotic region it is sufficient that the above trans-

formation tend toward that transformation (28) which is appropriate to the function of form (18) to which the operator (30) is being applied in the scattering expansion. Then T as given by (30) will be separable in the proper variables with vanishing B_{jk}^n , D_j , and E_j^n . In the united-atom limit we elect to restrict the transformation (26) so as to keep $(\xi-R)/R$ 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 general, one would like to use coordinates adapted to the scattering expansion in such a way that it converges as rapidly as possible. In addition, simplicity of formulation and relative ease of computation need to be considered. The latter consideration recommends the search for a single transformation which can be used for all terms of the expansion. This philosophy is inherent in the work of References 7, 8 and 24. As explained in the Introduction, in this work, there will be a transformation for each term in the scattering expansion. Each transformation will be relatively simple, and in the semiclassical limit the parameters of the transformation will appear in translational factors of the type introduced by Bates and McCarroll. In order to adapt the transformations to the expansion as well as possible, the parameters will eventually be determined variationally. Hopefully this will influence the expansion convergence in a beneficial way.

We now take up specific additional restrictions on the transformation. In most scattering applications, adiabatic correction terms, terms of the mass-polarization type, and electron-reduced-mass terms are omitted from Eq. (30). The approximate atomic functions in Eq. (18) are then those from the separated-atom limit of the fixed-nucleus molecular eigenfunctions. Correspondingly, the parameters in the transformations are chosen to guarantee separability of the truncated form of Eq. (30). The omission of

terms of order a_0^{-2}/M compared to retained terms of order $v/\hbar a_0$ requires $Mva_0/\hbar \gg 1$.⁵⁰

In Eq. (30) the $\partial/\partial \xi_j^2$ is taken at fixed π_j^2 . Since the relation of π^2 to R changes with R , $\partial/\partial \xi_j^2$ can be written as the sum of a term analogous to $\partial/\partial R$ and terms proportional to $\partial/\partial \pi_j^2$. Thus, some terms from $A_{kj}(\partial/\partial \xi_k)(\partial/\partial \xi_j)$ involve the same operators as those from $B_{jk}^n(\partial/\partial \xi_j)(\partial/\partial \pi_k^n)$. For this reason, we will require that B_{jk}^n vanish only in the separated-atom limit. On the other hand, we shall require that the leading term in D_j from Eq. (30) vanish for all R . From Eq. (35), the necessary conditions on the parameters are

$$h^k = h^k(R)$$

$$\frac{\partial g}{\partial r_i^k} = k^k(R) R_i$$

$$g = \sum_k k^k(R) (\vec{R} \cdot \vec{r}^k) + j(R) \quad (36a)$$

where j, k^k, h^k are arbitrary functions of R .⁵¹ With Eqs. (36a) satisfied, the contributions of D_j to Eq. (30) are at most $(m/M)v/(\hbar a_0)$ or $(m/M)a_0^{-2}/M$ and can eventually be omitted. Now consider the requirement that the leading term of B_{jk}^n vanish as $R \rightarrow \infty$. In this limit the parameters are constant, and from Eq. (34) we require $\gamma^n(\infty) = -h^{(n)}(\infty)$. Instead of this boundary condition, we impose the stronger condition

$$h^n(R) = -\gamma^n(R) \quad (36b)$$

Then B_{jk}^n takes the form

$$B_{jk}^n = \frac{2}{M} \left(\frac{1}{R} \frac{d\gamma^n}{dR} + k^n(R) \right) R_j R_k + O(m/M^2), \quad (37)$$

where $O(m/M^2)$ stands for all the remaining terms in Eq. (33). The requirement that the leading term of B_{jk}^n vanish in the separated-atom limit now becomes

$$k^n(R) R^2 \rightarrow 0, \quad (38)$$

as $R \rightarrow \infty$.

Evidently, the leading term of B_{jk}^n could be made to vanish identically by choosing $k^n = -R^{-1}(d\gamma^n/dR)$. This possibility will be discussed below Eq. (41). At this point it is convenient to set

$$f^n = 0 \quad (39)$$

in Eq. (29), so $\delta^n = 1$ in Eq. (26). Inspection shows that f^n appears only in the higher-order terms of B_{jk}^n . Moreover, it can be verified that f^n contributes only terms of order $(m/M)v/\hbar a_0, (m/Ma_0^{-2})$ and smaller to the rest of the terms in Eq. (30). Setting $f^n = 0$ 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 (26) for constant parameters. In this case $k^k(R)$ must vanish and the Jacobian J becomes

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

This shows that the condition,

$$j(R) = \sum_k \gamma^k(R) h^k(R) \quad (40)$$

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. (26) are changing with R . The final transformation is

$$\vec{r} = \alpha \vec{R} + \frac{m}{M} \sum_n h^n \vec{r}^n ,$$

$$\alpha^n = \gamma^n(R) \vec{R} + \vec{r}^n ,$$

$$\alpha = 1 + \frac{m}{M} \sum_n (k^n(R) (\vec{R} \cdot \vec{r}^n) + \gamma^n h^n)$$

$$h^n = - \gamma^n , \quad (41)$$

where $\gamma^n(R)$ and $k^n(R)$ are arbitrary, subject to Eq. (38). Transformation (41) involves two functions, $\gamma^n(R)$ and $k^n(R)$. 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. (37) been set equal to zero, only one independent function would have been available. This is not enough, because the molecular properties parallel or perpendicular to the internuclear line are too dissimilar.

It is instructive to compare Eq. (41) with Eq. (28) for the separated atoms. We identify $\gamma^i = p$, $i = 1, N_A$, and $\gamma^i = -q$, $i = N_A + 1, N$. Then from Eq. (41) with $k^n = 0$.

$$\begin{aligned}\vec{\zeta} &= \vec{R} - \frac{m}{M} \sum_n \gamma^n (\vec{r}^n + \gamma^n \vec{R}) \\ &= \vec{R} - \frac{m}{M_A} \sum_{n=1}^{N_A} (\vec{r}^n + p \vec{R}) \\ &\quad + \frac{m}{M_B} \sum_{n=N_A+1}^N (\vec{r}^n - q \vec{R}) .\end{aligned}\quad (42)$$

Transformation (42) agrees with the exact transformation (28) except for terms of order $(m/M)^2$ in $\vec{\zeta}$.⁵²

To apply Eqs. (41) one needs the corresponding simplified expression for A_{jk} from Eqs. (30) and (31). The result is

$$\begin{aligned}A_{kj} \frac{\partial}{\partial \zeta_k} \frac{\partial}{\partial \zeta_j} &= \frac{1}{M} \frac{\partial}{\partial \zeta_j} \frac{\partial}{\partial \zeta_k} + (m/M^2) \sum_n \gamma^n \\ &\quad + 0 \left(m^2/M^3 \frac{\partial}{\partial \zeta_j} \frac{\partial}{\partial \zeta_k} \right) ,\end{aligned}\quad (43)$$

where the $O(m^2/M^2 \dots)$ terms can be retained by using Eq. (31), and

$$\begin{aligned} T^n = & \left[2k^n (\vec{R} \cdot \vec{r}^n) - \langle \gamma^n \rangle^2 \right]_{\Delta_{\vec{r}}} + 2 \left(k^n - \frac{1}{R} \frac{d\gamma^n}{dR} \right) (\vec{R} \cdot \vec{v}_{\vec{r}}) (\vec{r}^n \cdot \vec{v}_{\vec{r}}) \\ & + \left(\frac{2}{R} \frac{dk^n}{dR} (\vec{R} \cdot \vec{r}^n) - \frac{2}{R} \gamma^n \frac{d\gamma^n}{dR} - 4\gamma^n k^n + (k^n R)^2 \right) R_k R_j \frac{\partial}{\partial \epsilon_k} \frac{\partial}{\partial \epsilon_j} . \quad (44) \end{aligned}$$

To the same order, the analogous formula for B_{jk}^n is Eq. (37). That for D_j is Eq. (35). Without the second term which vanishes for Eq. (41).

To complete the expression (30) for the kinetic energy resulting from transformation (41), the formulae for the coefficients of the n^k derivatives are needed. Rather than reproduce the lengthy general formulae for Eq. (26), we give just the complete results for Eq. (41). Then

$$\begin{aligned} E_j^n &= \frac{1}{M} \left(2 \frac{\partial \gamma^n}{\partial R_j} + R_j \Delta_R \gamma^n \right) , \\ C_{jk}^{nm} &= \frac{1}{M} \left(\gamma^n \delta_{jk} + \frac{\partial \gamma^n}{\partial R_j} R_j \right) \left(\gamma^m \delta_{jk} + \frac{\partial \gamma^m}{\partial R_j} R_k \right) \\ &+ \frac{1}{m} \delta_{nm} \epsilon_{jk} + \frac{1}{(M_A + M_B)} \epsilon_{jk} . \quad (45) \end{aligned}$$

The last two terms of C_{jk}^{nm} are the same as the original terms in Eq. (7). For constant γ^n , E_j^n is zero and the first term of C_{jk}^{nm} is equivalent to a modification of the electron-mass and the mass-polarization terms.

Equation (30) can now be written

$$\begin{aligned} \frac{-2}{\hbar^2} T = & \frac{1}{M} \Delta_{\vec{r}} + \frac{m}{M} \sum_n T^n + \frac{2}{M} \sum_n \left(k^n + \frac{1}{R} \frac{dy^n}{dR} \right) R_{ij} R_{jk} \frac{\partial}{\partial F_j} \frac{\partial}{\partial \eta_k} \\ & + \frac{1}{m} \sum_n \frac{\partial}{\partial \eta_i^n} \frac{\partial}{\partial \eta_j^n} + C_1 + C_2 \end{aligned} \quad (46)$$

Here T^n is defined by Eq. (44), C_1 represents the $O(a_0^{-2}/M)$ terms from Eq. (45), and C_2 represents the $O(ma_0^{-2}/M^2)$ and $O(mv/\hbar a_0 M)$ and smaller terms from Eqs. (31), (33), and (35). Eq. (46) 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 and mass-polarization effects. The terms T^n are also very small at low-impact velocities. Indeed, for sufficiently low velocities, they are of the same size as the mass-polarization terms.

Equation (46) 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 Lagrangian is being applied. Note that in this formulation we are working directly with the original Hamiltonian rather than introducing a new adiabatic Hamiltonian as in Ref. 7. We turn next to the discussion of angular momentum.

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

An important feature of the p.s.s. 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 diagonalization and substantial simplification of the scattering equations. Because of Eq. (27), the same use of angular momentum conservation is also rigorously possible in terms of the coordinates defined in Eqs. (26) and (41). 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. (41), the sine of the angle δ between $\hat{\xi}$ and $\hat{R}$ is given by

$$|\sin \delta| = \frac{|\vec{\xi} \times \vec{R}|}{\xi R} = \left| \frac{m}{M} \frac{\hat{R} \cdot \sum \gamma^n \vec{r}^n}{\xi} \right|. \quad (47)$$

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 $R \rightarrow 0$

$$k^n \rightarrow 0, \quad \frac{\gamma^n}{R} \rightarrow 0. \quad (48)$$

Equations (48) and (41) guarantee that as $R \rightarrow 0$, $\hat{z}_i/R \rightarrow 1$ and $|\sin \delta| \rightarrow 0$. In addition, it is intended that for all R the $\gamma^n(R)$ should be such that $|\sin \delta|$ is $O(m/M)$.

The use of $\hat{z}_i$ 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 $\hat{z}_i$ rather than the internuclear line.⁵³ Then the Kronig formulation of angular momentum conservation can be taken over. Consider a particular state G whose fixed-nucleus eigenfunction is $\psi_G(\rho^n, z^n, \phi^n; R)$ where (ρ^n, z^n, ϕ^n) are body-fixed cylindrical coordinates for $\vec{r}^n$ based $\hat{R}$ with $\hat{z} = \hat{R}$. By Eq. (41) with the state dependence made explicit, $\vec{r}_G^n = \vec{r}^n + \gamma_G^n(R) \hat{R}$. We now define a variable $\vec{r}_G^n$ to be the analog of $\vec{r}^n$ in the $\hat{z}_i, \tau_i^n$ system. We take

$$\vec{r}_G^n = \vec{r}_G^n - \gamma_G^n(\hat{z}_i) \hat{z}_G \quad (49)$$

The variables $(\rho_G^n, z_G^n, \phi_G^n)$ are then defined as the body-fixed cylindrical coordinates for $\vec{r}_G^n$ based on $\hat{z}_G$ with $\hat{z}_G = \hat{z}_G$. The G -th basis function is then taken to be $\psi_G(\rho_G^n, z_G^n, \phi_G^n, \xi_G)$. Its relation to $\psi_G(\rho^n, z^n, \phi^n, R)$ is given by Eqs. (41) and (49) using Taylor's expansion to first order in m/M . By construction

$$\left(-\frac{\hbar^2}{2m} \sum_{n=1}^N \frac{\partial}{\partial \mathbf{r}_G^n} \frac{\partial}{\partial \mathbf{r}_G^n} + V(\rho_G^n, \mathbf{z}_G^n, \phi_G^n; \varepsilon_G) \right) \psi_G(\rho_G^n, \mathbf{z}_G^n, \phi_G^n; \varepsilon_G) \\ = \varepsilon_G(\varepsilon_G) \psi_G(\rho_G^n, \mathbf{z}_G^n, \phi_G^n; \varepsilon_G) \quad , \quad (50)$$

where $V(\rho^n, \mathbf{z}^n, \phi^n, R)$ is the potential energy from Eqs. (7) and (8) and ε_G includes the nuclear repulsion. The difference between the two potentials is taken into account to first order in (m/M) using

$$\Delta V \equiv V(\rho_G^n, \mathbf{z}_G^n, \phi_G^n; \varepsilon_G) - V(\rho^n, \mathbf{z}^n, \phi^n; R) \\ = \sum_n \left\{ \frac{\partial V}{\partial \rho^n} (\rho_G^n - \rho^n) + \frac{\partial V}{\partial \mathbf{z}^n} (\mathbf{z}_G^n - \mathbf{z}^n) + \frac{\partial V}{\partial \phi^n} (\phi_G^n - \phi^n) \right\} + \frac{\partial V}{\partial R} (\varepsilon_G - R). \quad (51)$$

Since all the coordinate differences in Eq. (51) are of order m/M , ΔV is of the order of the mass-polarization and electron-reduced-mass terms. When H of Eq. (7) is applied to $\psi_G(\mathbf{r}^n; \varepsilon)$, using Eq. (46), the quantity $(\mathcal{H}_G - \Delta V)\psi_G$ will appear along with the other terms from Eqs. (46) and (7). 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 R is worth emphasizing. If $V(\rho^n, z^n, \phi^n, R)$ is expressed in terms of $\hat{\xi}$ and $\hat{n}$, it is independent of the polar angles θ_{ξ}, ψ_{ξ} of $\hat{\xi}$ relative to an arbitrary non-rotating frame and depends only on the differences of the azimuthal angles of the $\hat{n}$ when these are referred to the body-fixed axes $\theta_{\xi}, \phi_{\xi}, \hat{\xi}$. This means that the original V does not preclude the use of the polar axis $\hat{\xi}$ in connection with angular momentum conservation.

VI. CONSTRUCTION OF TRIAL SOLUTIONS FOR ONE-ELECTRON SYSTEMS

The construction of trial solutions to use in the variational principle is complicated by the need to satisfy the Pauli exclusion principle and by the inherent complexity possible for a many-electron diatomic molecule. For this reason, the discussion will proceed by stages of increasing complexity. One-electron systems are discussed in this section; two- and three-electron systems in the next. In Subsection A, heteronuclear molecules are treated in detail using electronic molecular eigenfunctions as the basis. In Subsection B, interpolating or diabatic states are introduced. In Subsection C, expansions for homonuclear systems are outlined.

A. Heteronuclear molecules using an eigenfunction basis.

This is the basic Subsection. Subsections B and C will utilize its results. In the one-electron case the electron spin can be factored out once and for all and omitted from the electronic eigenfunctions. These may then be written in the form

$$\chi_G = (2\pi)^{-1/2} A_{p_i}(\nu_G, \zeta_G; \zeta_G) \exp(i\Delta\phi_G), \quad (52)$$

where G stands for the number pair $p\Lambda$; $\Lambda=0, \pm 1, \pm 2, \dots$, and p numbers the states with the same Λ . States with $\Lambda=0$ are I states, etc. The variables ρ_G, ϕ_G, r_G are the body-fixed cylindrical coordinates of $\vec{n}_G^1 \equiv \vec{n}_G$ taking $\vec{e}_G$ as the axis of rotation symmetry. The subscripts G on $\vec{e}_G$ and $\vec{n}_G$ are required because each state G has its own transformation (41). 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 $\gamma_G^1 = \gamma_G$ and $k_G^1 = k_G$ in Eq. (41) are arbitrary except that they depend only on $|\Lambda|$. The states are labeled in such a way that each eigenvalue $\epsilon(p\Lambda)$ has a continuous derivative with respect to internuclear separation.

The 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

$$\phi_{G'AB}^1 = \sum_K \sum_{M_K} \phi_{G'AB}^{KM_K}, \quad (53)$$

where

$$\begin{aligned}
t_{GAB}^{KM_K} &= (4\pi)^{\frac{1}{2}} (2K+1)^{\frac{1}{2}} \sum_{n'l} A_{n'l}(\phi_G, \psi_G; \epsilon_G) (-1)^l [(2K+1)/(8\pi^2)]^{\frac{1}{2}} \\
&\times D_{lM_K}^K(\phi_G, \psi_G; \psi_G) R_{n'l; GAB}^K(\epsilon_G)/\epsilon_G. \quad (54)
\end{aligned}$$

In Eqs. (53) and (54) the subscript G_{AB}^i denotes an initial state for the scattering. The asymptotic behavior of ψ_{GAB}^i is discussed following Eq. (75).⁵⁴ The rotation matrix and the spherical harmonics in the hydrogenic wave functions are defined using the conventions discussed in Ref. 34. The angles ϕ_G and ψ_G are the polar angles of $\vec{\epsilon}_G$ with respect to the space-fixed frame. The radial scattering functions $R_{n'l; n'l'}^K$, the ψ_G , and the k_G are to be determined variationally from the functional

$$\mathcal{V}(\psi_1, \psi_2) = \int dR \int dr \psi_1 (H - E) \psi_2, \quad (55)$$

where ψ_1 , and ψ_2 are trial solutions.³¹ $\mathcal{V}$ is equal to $-(\hbar^2/2M)$ times the functional I of Ref. 31. The Lagrangian is defined in terms of the original variables. The coupled equations for the radial scattering functions used in this paper always make $\mathcal{V}(\psi_1, \psi_2)$, $\mathcal{V}(\psi_2, \psi_1)$, $\mathcal{V}(\psi_1^*, \psi_2)$, and $\mathcal{V}(\psi_2, \psi_1^*)$ 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.⁵⁵ When terms of order m/M are omitted, as is proposed here, and done in paper II,⁴⁰ a separate investigation is required to determine the extent to which their neglect influences the above relations.

Let us now write down $\mathcal{V}(\psi_1, \psi_2)$ for the one-electron case, using bars to keep track of the distinct sums in ψ_1 and ψ_2 . We transform the expression (54) for ψ_1 slightly to introduce D^* in place of D , using Eq. (24.7) of Ref. 34. Then

$$\mathcal{V}(\psi_1, \psi_2) = \sum_{\bar{R}\bar{A}} \sum_{\bar{K}\bar{M}} \mathcal{V} \left(\begin{pmatrix} \bar{R}\bar{A} \\ \bar{G}_{AB}^{\bar{A}} \end{pmatrix}, \begin{pmatrix} \bar{K}\bar{M} \\ \bar{G}_{AB}^{\bar{M}} \end{pmatrix} \right), \quad (56)$$

$$\mathcal{V} \left(\begin{pmatrix} \bar{R}\bar{M}_K \\ \bar{G}_{AB}^{\bar{A}} \end{pmatrix}, \begin{pmatrix} \bar{K}\bar{M}_K \\ \bar{G}_{AB}^{\bar{M}} \end{pmatrix} \right) = \frac{(2\bar{K}+1)(2\bar{K}+1)}{2^{\bar{K}}} \sum_{\bar{n}, \bar{A}} \sum_{\bar{n}, \bar{A}} (-1)^{\bar{A} + \bar{A} + \bar{M}_K}$$

$$\times \int d\vec{r}_G \int d\vec{r}_G U^{-1} R_{\bar{G}\bar{G}}^{\bar{K}} \begin{pmatrix} \bar{r}_G \\ \bar{n}, \bar{A}; \bar{G}_{AB}^{\bar{A}} \end{pmatrix} \epsilon_G^{-1} R_{\bar{G}\bar{G}}^{\bar{K}} \begin{pmatrix} \bar{r}_G \\ \bar{n}, \bar{A}; \bar{G}_{AB}^{\bar{M}} \end{pmatrix}^* A_{\bar{n}, \bar{A}} \begin{pmatrix} \bar{r}_G \\ \bar{G} \end{pmatrix} \begin{pmatrix} \bar{r}_G \\ \bar{G} \end{pmatrix} \\ \times (H-E) \left\{ A_{\bar{n}, \bar{A}} \begin{pmatrix} \bar{r}_G \\ \bar{G} \end{pmatrix} \begin{pmatrix} \bar{r}_G \\ \bar{G} \end{pmatrix} D_{\bar{A}\bar{M}_K}^{\bar{K}} \begin{pmatrix} \bar{r}_G \\ \bar{G} \end{pmatrix} \begin{pmatrix} \bar{r}_G \\ \bar{G} \end{pmatrix} R_{\bar{n}, \bar{A}; \bar{G}_{AB}^{\bar{A}}}^{\bar{K}} \begin{pmatrix} \bar{r}_G \\ \bar{G} \end{pmatrix} \epsilon_G^{-1} \right\}. \quad (57)$$

In each term of the sum over $\bar{n}, \bar{A}$, the original volume element $d\vec{r}_G d\vec{r}_G^*$ has been expressed in terms of the volume element $d\vec{r}_G d\vec{r}_G^*$ using the Jacobian $J_{\bar{G}}$ of the transformation (41). The coupled equations for the $R_{\bar{n}, \bar{A}; \bar{G}_{AB}^{\bar{A}}}^{\bar{K}}(\epsilon_G)$ can be obtained by setting the variation of Eq. (57) with respect to $R_{\bar{n}, \bar{A}; \bar{G}_{AB}^{\bar{A}}}^{\bar{K}}(\epsilon_G)$ equal to zero. This will guarantee that $\mathcal{V}$ 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 are functions of different arguments.

First, the kinetic energy T is expressed in terms of $\vec{\xi}_G, \vec{n}_G$ using Eq. (46). It can then be shown that the results of $(H-E)\{ \}$ in Eq. (57) can be written in the form

$$(H - E)\{ \} = \sum_{\tau=-1}^1 D_{\Lambda+\tau, M_K}^K(\phi_G, \theta_G, \psi_G) C_{G\tau}^K \quad (58)$$

where the $C_{G\tau}^K$, which are given later in Eq. (71), are independent of the variables in $D_{\Lambda+\tau, M_K}^K$. The next step is to express the $D_{\Lambda+\tau, M_K}^K(\phi_G, \theta_G, \psi_G)$ in terms of $D_{\Lambda+\tau, M_K}^K(\phi_-, \theta_-, \psi_-)$. The orthogonality relations for the rotation matrices will then simplify Eqs. (56) and (57).

It is convenient to give just one derivation, valid for the N -electron system. The final results are Eqs. (66) and (68). In the N -electron case the electron azimuthal angle ϕ in the rotation matrices is replaced by

$$\phi \equiv \frac{1}{N} \sum_{n=1}^N \phi^n \quad (59)$$

Consider the first of Eqs. (41) and let

$$\begin{aligned} \vec{\xi}_0 &= \alpha \vec{R} \quad , \\ \vec{\xi}_n &\equiv \vec{\xi}_{n-1} + \beta \vec{r}^n \quad , \quad n = 1, N \\ \vec{\xi} &\equiv \vec{\xi}_N \quad . \end{aligned} \quad (60)$$

With $\vec{R}$, and the $\vec{r}^L$ fixed, a sequence of vectors $\vec{z}_n$ is defined by Eq. (60). The first is parallel to $\vec{R}$ and the last is $\vec{z}$. Let the space-fixed spherical coordinates of $\vec{z}_n$ be designated by $\xi_n, \theta_n, \varphi_n$. For each n a set of axes based on $\xi_n, \theta_n, \varphi_n$ can be set up. If the p -th electron coordinate vector $\vec{r}^p$ is projected onto $\xi_n, \theta_n, \varphi_n$, its cylindrical coordinates are designated as $\rho_n^p, \phi_n^p, z_n^p$. The relation between $\hat{e}_n, \hat{\theta}_n, \hat{\varphi}_n, \hat{e}_{n-1}$, and $\vec{r}^n$ is illustrated in Fig. 1. The fact that $\hat{e}_n, \hat{e}_{n-1}$, and $\vec{r}^n$ lie in the same plane is important, and follows from Eq. (60). Now let R_n^n be the rotation $\{\phi_n^n, \theta_n^n, \varphi_n^n\}$ which first carries the space-fixed axes $\hat{Z}, \hat{X}, \hat{Y}$ into $\hat{e}_n, \hat{\theta}_n, \hat{\varphi}_n$ and follows this by the rotation ϕ_n^n about $\hat{e}_n$ so that the final axes $\hat{z}_f, \hat{x}_f, \hat{y}_f$ are as shown in Fig 1. Also let R_{n-1}^n be the rotation $\{\phi_{n-1}^n, \theta_{n-1}^n, \varphi_{n-1}^n\}$. These rotations are related by

$$R_n^n = \{0, \theta_{n,n-1}, 0\} R_{n-1}^n, \quad (61)$$

where $\theta_{n,n-1}$ is the angle between ξ_n and ξ_{n-1} . From Eq. (60)

$$\theta_{n,n-1} = \sin^{-1}(\beta^n \rho_{n-1}^n / \xi_n). \quad (62)$$

Figure 1. Relation of adjacent body-fixed frames. The space-fixed axes are XYZ.

From Eq. (61) and the group property of the rotation matrices

$$\begin{aligned}
 D_{\Lambda M_K}^K(R_n^n) &= \sum_{\Sigma} D_{\Lambda \Sigma}^K(\{0, \theta_{n,n-1}, 0\}) D_{\Sigma M_K}^K(R_{n-1}^n) \\
 &= \sum_{\Sigma} D_{\Lambda \Sigma}^K(\{0, \theta_{n,n-1}, \phi_{n-1}^n - \phi_{n-1}^{n-1}\}) D_{\Sigma M_K}^K(R_{n-1}^{n-1}) \\
 &= \sum_{\Sigma} D_{\Lambda \Sigma}^K(\mathcal{R}_{n,n-1}) D_{\Sigma M_K}^K(R_{n-1}^{n-1}), \quad n > 1 \\
 &= \sum_{\Sigma} d_{\Lambda \Sigma}^K(\theta_{1,0}) D_{\Sigma M_K}^K(\phi_0^1, \theta_0, \psi_0), \quad n = 1 \quad (63)
 \end{aligned}$$

where $\mathcal{R}_{n,n-1} = \{0, \theta_{n,n-1}, \phi_{n-1}^n - \phi_{n-1}^{n-1}\}$ for $n > 1$.

The repeated use of Eq. (63) shows that

$$\begin{aligned}
 D_{\Lambda M_K}^K(R_N^N) &= \sum_{\Sigma} D_{\Lambda \Sigma}^K(\mathcal{R}) D_{\Sigma M_K}^K(\phi_0^1, \theta_0, \psi_0) \\
 \mathcal{R} &= \mathcal{R}_{N,N-1} \mathcal{R}_{N-1,N-2} \cdots \mathcal{R}_{2,1} \mathcal{R}_{1,0} \quad (64)
 \end{aligned}$$

where $R_{1,0}$ is defined to be $\{0, \theta_{1,0}, 0\}$. A second transformation (41) defined by $\bar{\alpha}, \bar{\beta}^L, \bar{\gamma}^L$ can be related to the one above by inverting Eq. (64). Thus,

$$D_{\Lambda M_K}^K(R_N^N) = \sum_{\tau} D_{\Lambda \tau}^K(\mathcal{R} \cdot \mathcal{R}^{-1}) D_{\tau M_K}^K(R_N^N). \quad (65)$$

The last step is to replace $\exp(i\Lambda\phi_N^N)$ by $\exp(i\Lambda/N) \sum_P \phi_N^P$ in $D_{\Lambda M_K}^K(R_N^N)$ of Eq. (65). The analogous substitution is made in $D_{\Lambda M_K}^K(R_N^N)$. With ϕ and $\bar{\phi}$ defined by Eq. (59) and taking note that $\bar{\xi}_N \equiv \bar{\xi}$

$$D_{\Lambda M_K}^K(\phi, \theta_\xi, \psi_\xi) = \sum_{\tau} \left[e^{-i\Lambda(\phi_N^N - \phi_N^1 + \phi_N^N - \phi_N^2 + \dots + \phi_N^N - \phi_N^N)/N} \right. \\ \left. \times D_{\Lambda, \tau}^K(\mathcal{R}, \bar{\mathcal{R}}^{-1}) e^{i\tau(\bar{\phi}_N^N - \bar{\phi}_N^1 + \dots + \bar{\phi}_N^N - \bar{\phi}_N^N)/N} \right] \\ \times D_{\tau M_K}^K(\bar{\phi}, \bar{\theta}_\xi, \bar{\psi}_\xi). \quad (66)$$

In Eq. (66) $\xi, \theta_\xi, \psi_\xi$ are the spherical coordinates of $\vec{\xi}$, etc. Equation (66) is the final result, with $\mathcal{R}$ and $\bar{\mathcal{R}}$ given by Eq. (64). The important thing about Eq. (66) is that the function in the square bracket, when expressed in terms of the variables defined by the barred transformation, is independent of all three angles which appear in $D_{\tau M_K}^K(\bar{\phi}, \bar{\theta}_\xi, \bar{\psi}_\xi)$. It depends only on $\bar{\xi}, \bar{\xi}_N^k, \bar{\phi}_N^k$ and the differences $\bar{\phi}_N^k - \bar{\phi}_N^0$. This can be verified by first expressing the quantities in the bracket in terms of scalar products of the vectors $\vec{\xi}_n$ and $\vec{n}$. Leaving off the bars,

$$\xi_n^2 = \vec{\xi}_n \cdot \vec{\xi}_n, \\ \xi_n^k = \vec{\xi}_n \cdot \vec{n}^k / \xi_n, \\ \phi_n^k = (\vec{n}^k \cdot \vec{n}^k - (\xi_n^k)^2)^{1/2} \quad (67)$$

$$\vec{\eta}^k \cdot \vec{\eta}^m = z_{n,n}^{k,m} + \rho_{n,n}^k \cos(\phi_n^k - \phi_n^m) .$$

Next use Eq. (60) and Eqs. (41) to express $\vec{\xi}_n$ in terms of $\vec{\xi} = \vec{\xi}_N$, the $\vec{\eta}^k$ and the scalar parameters $\gamma^k(R)$, etc. The scalar products in Eq. (67) can then be related to the scalar products $\vec{\xi} \cdot \vec{\xi}$, $\vec{\xi} \cdot \vec{\eta}^k$, $\vec{\eta}^k \cdot \vec{\eta}^m$, and these can be expressed in terms of $\xi, \rho_N^k, \phi_N^k - \phi_N^m, z_N^k$ using Eq. (67) with $n=N$. The resulting expression still contains functions of R . However, R too can be expressed in terms of $\vec{\xi}$, $\vec{\xi} \cdot \vec{\eta}^k$, $\vec{\eta}^k \cdot \vec{\eta}^m$ using the inverse of Eqs. (41). Because no Euler angles appear in the [] in Eq. (66), Eq. (57) can be simplified using the orthogonality properties of the rotation matrices.

We return to the one-electron case. Equation (66) becomes

$$D_{\Lambda M_K}^K(\phi, \theta_{\xi}, \psi_{\xi}) = \sum_{\Sigma} d_{\Lambda \Sigma}^K(\theta_{1,0} - \bar{\theta}_{1,0}) D_{\Sigma M_K}^K(\bar{\phi}, \bar{\theta}_{\xi}, \bar{\psi}_{\xi}) .$$

$$\theta_{1,0} = \sin^{-1}(\beta^{-1} \rho_0^{-1} / \xi) = - \sin^{-1}(\frac{m}{M} \gamma^{-1} \rho_0^{-1} / \xi) ,$$

$$\bar{\theta}_{1,0} = \sin^{-1}(\bar{\beta}^{-1} \bar{\rho}_0^{-1} / \bar{\xi}) = - \sin^{-1}(\frac{\bar{m}}{\bar{M}} \bar{\gamma}^{-1} \bar{\rho}_0^{-1} / \bar{\xi}) . \quad (68)$$

The last expressions for $\theta_{1,0}$ and $\bar{\theta}_{1,0}$ are from transformation (41).

Equation (67) yields the important point that the argument of $d_{\frac{1}{2}, \frac{1}{2}}^K$ is of order m/M . Since the total angular momentum K is $\sim M$, the argument of $d_{\frac{1}{2}, \frac{1}{2}}^K$ cannot be set equal to zero (which would give $d_{\frac{1}{2}, \frac{1}{2}}^K$). However, one can expect to be able to evaluate the multipliers of m/M in the argument of $d_{\frac{1}{2}, \frac{1}{2}}^K$ to lowest order in m/M . Then only the difference between $\gamma^{\frac{1}{2}}$ and $\bar{\gamma}^{\frac{1}{2}}$ need be accounted for.

Let us identify the unbarred transform in Eq. (68) with the transform for state G in Eq. (57) and the barred transform in Eq. (68) with that for state $\bar{G}$ in Eq. (57). Using Eqs. (68), (58), (57), and the orthogonality properties of the rotation matrices,

$$\begin{aligned} \int \left(\begin{matrix} R_{K,AB}^{K,AB} \\ R_{K,AB}^{K,AB} \end{matrix} \right) &= (4\pi)^{(2K+1)/2} \sum_{\bar{K}K} \sum_{\bar{M}M_K} (-1)^{K+\bar{M}+M_K} \\ &\int_{\bar{G}} d\bar{\gamma} \int_G d\gamma \frac{R_{\bar{n}-\bar{\gamma};G_{AB}}^K(\bar{\gamma})}{\bar{n}-\bar{\gamma};G_{AB}} \int_G d\gamma \int_{\bar{G}} d\bar{\gamma} \frac{J^{-1}A_{\bar{n}-\bar{\gamma};G_{AB}}(\bar{\gamma})}{\bar{n}-\bar{\gamma};G_{AB}} \\ &\sum_{\tau} d_{\bar{n}+\tau,\tau}^K(\theta_1, \gamma, \bar{\gamma}) C_{G\tau}^K \end{aligned} \quad (69)$$

When the argument of $d_{\Lambda+\tau, \bar{\Lambda}}^K$ approaches zero, $d_{\Lambda+\tau, \bar{\Lambda}}^K$ approaches $\delta_{\Lambda+\tau, \bar{\Lambda}}$.

In this case the well-known selection rule $\Delta\Lambda = 0, \pm 1$ is seen to apply.

Its origin, of course, is Eq. (58). By setting equal to zero the variation of $\mathcal{V}$ with respect to $R_{\bar{n}-\bar{\Lambda}; B_{AB}}^K(\epsilon_G)$, we find that for each K and $\bar{n}, \bar{\Lambda}$,

$$\sum_{n\Lambda} (-1)^n \int d\zeta_G d\rho_G \frac{A}{\bar{n}\bar{\Lambda}} \left(\rho_G, \zeta_G; \zeta_G \right) \sum_{\tau} d_{\Lambda+\tau, \bar{\Lambda}}^K (\theta_{1,0} - \bar{\theta}_{1,0}) C_{G\tau}^K = 0 \quad (70)$$

Equations (57) and (58) determine the $C_{G\tau}^K$. 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 Sections IV and V. Therefore the $C_{G\tau}^K$ are given neglecting C_1 and C_2 in Eq. (46) as well as ΔV from Eq. (51).⁵⁶ We have

$$\begin{aligned} -\frac{2M\epsilon_G}{\hbar^2} C_{G0}^K &= \left\{ \left(\frac{\partial}{\partial \epsilon_G} \right)^2 - \frac{K(K+1) - \Lambda^2}{\epsilon_G^2} + \frac{2M}{\hbar^2} (E - \epsilon_G(\zeta_G)) - \frac{\epsilon_G^2 - \hbar^2 \Lambda^2}{\hbar^2 \epsilon_G^2} \right. \\ &+ 2 \left(\frac{d\gamma_G}{dR} + Rk_G \right) R \frac{\partial}{\partial \epsilon_G} \left(\frac{\partial}{\partial \epsilon_G} - \frac{1}{\epsilon_G} \right) \\ &\left. + \frac{m}{M} \left[-\gamma_G + 2k_G R (\zeta_G - R\gamma_G) \right] \left| \left(\frac{\partial}{\partial \epsilon_G} \right)^2 - \frac{K(K+1) - \Lambda^2}{\epsilon_G^2} \right| \right\} \end{aligned}$$

$$\begin{aligned}
& + \frac{m}{M} \left[2R \frac{d^2 k_G}{dR^2} (\epsilon_G - \epsilon_G R) - 2R \epsilon_G \frac{d^2 \epsilon_G}{dR^2} - 4R^2 \epsilon_G k_G + R^4 k_G^2 \right. \\
& \left. + 2 \left(k_G R - \frac{d \epsilon_G}{dR} \right) \epsilon_G \left(\frac{\partial}{\partial \epsilon_G} \right)^2 \right] A_{n\ell}(\epsilon_G, \epsilon_G; \epsilon_G) R_{n\ell; G_{AB}}^K(\epsilon_G) .
\end{aligned}$$

$$\begin{aligned}
\frac{-2M \epsilon_G}{\hbar^2} C_{G\pm}^K &= \pm \sqrt{(K \pm \ell + 1)(K \mp \ell)} \left\{ \frac{1}{\epsilon_G^2} \left(\frac{\partial}{\partial \epsilon_G} \mp \ell \cot \alpha_G \right) \right. \\
& \left. + \frac{m}{M} \left(\frac{d \epsilon_G}{dR} - k_G R \right) \frac{\epsilon_G}{\epsilon_G} \frac{\partial}{\partial \epsilon_G} \right\} A_{n\ell}(\epsilon_G, \epsilon_G; \epsilon_G) R_{n\ell; G_{AB}}^K(\epsilon_G) . \quad (71)
\end{aligned}$$

In Eq. (71) $\vec{L}_G$ is the electron orbital angular momentum defined in terms of ϵ_G and α_G is the polar angle of $\vec{n}_G$ in body-fixed spherical coordinates, $\epsilon_G, \alpha_G, \phi_G$. All the m/M terms in Eq. (71) come from the $\sum_n T^n$ term in Eqs. (44) and (46). These terms are at most of order mv^2 as discussed in Section IV. In them, derivatives of $A_{n\ell}$ with respect to ϵ_G are to be dropped.

Except for the variables used and the cross-derivative term, the terms without a factor m/M are the usual terms of the p.s.s. method without the electron-reduced mass and mass-polarization terms from Eq. (45). There are some original R variables still in Eq. (71). To order m/M , R and ϵ_G are equal. They are generally interchangeable, except in the rapidly varying radial scattering function $R_{n\ell; G_{AB}}^K(\epsilon_G)$.

Equations (70) and (71) are integro-differential equations analogous to the ones mentioned below Eq. (25). One has to express the G variables in terms of the $\bar{G}$ variables, so $R_{n\Lambda;G_{AB}}^K(\epsilon_G)$ has to remain under the $\bar{G}$ integral sign. However, approximations are available which convert the equations to simpler ordinary differential equations. At low velocities a Taylor's expansion of $R_{n\Lambda;G_{AB}}^K(\epsilon_G)$ about $\epsilon_{\bar{G}}$ can be used. 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. Both approximations have been studied for one-electron systems and are reported in Paper II.⁴⁰ In the same paper the parameters γ_G and k_G are determined variationally.

Besides being diagonal in K and independent of M , Eq. (70) possesses the other important symmetry of the p.s.s. method: that of reflection symmetry in the scattering plane. To prove this, let Eqs. (70) with the C_{GT}^K from Eq. (71) be written in the operator form

$$\sum_{n\Lambda} O_{n\Lambda;n\Lambda} R_{n\Lambda} = 0 \quad (72)$$

where the initial state dependence $n'\Lambda'$ and the K dependence of the radial function have been omitted temporarily. The operators $O_{n\Lambda;n\Lambda}$ are linear and real. Also, provided the k_G and the γ_G depend only on $|\Lambda|$ as will be assumed, it follows from the relations $d_{-m'-m}^K(\theta) = (-1)^{m'-m} d_{m'm}^K(\theta)$ and $A_{p-\Lambda} = (-1)^\Lambda A_{p\Lambda}$ that

$$O_{n-\Lambda;n-\Lambda} = O_{n\Lambda;n\Lambda} \quad (73)$$

From Eqs. (72) and (73) one readily derives for all $\bar{n}, \bar{\tau} > 0$,

$$\begin{aligned} \sum_{\bar{n}} 0_{\bar{n}0; n0}^R R_{n0} + \sum_{\bar{n}} \sum_{\tau > 0} 0_{\bar{n}0; n\tau} (R_{n\tau} + R_{n-\tau}) &= 0, \\ 2 \sum_{\bar{n}} 0_{\bar{n}\bar{\tau}; n0}^R R_{n0} + \sum_{\bar{n}} \sum_{\tau > 0} (0_{\bar{n}\bar{\tau}; n\tau} + 0_{\bar{n}\bar{\tau}; n-\tau}) (R_{n\tau} + R_{n-\tau}) &= 0, \\ \sum_{\bar{n}} \sum_{\tau > 0} (0_{\bar{n}\bar{\tau}; n\tau} - 0_{\bar{n}\bar{\tau}; n-\tau}) (R_{n\tau} - R_{n-\tau}) &= 0. \end{aligned} \quad (74)$$

The functions $(R_{n\tau} - R_{n-\tau})$ are scattering functions associated with electronic states which are antisymmetric with respect to reflection in the scattering plane. They couple only with each other. Note that the coupling of the functions $R_{n\tau} + R_{n-\tau}$ with each other is different from that of the functions $R_{n\tau} - R_{n-\tau}$. At low velocities, however, the $\Delta\Lambda = 0, \pm 1$ selection rule inherent in the rotation matrices of Eq. (70) causes the difference term to go to zero relative to the common coupling $0_{\bar{n}\bar{\tau}; n\tau}$.

To complete the discussion of one-electron asymmetric problems, the boundary conditions on the radial scattering functions must be related to the scattering amplitudes in Eq. (20). First, consider the form of Eqs. (70) and (71) as ξ_G and ξ_G approach infinity. Terms which couple states on different nuclei vanish exponentially. Also, the variational determination of γ_G will require that $\gamma_G \rightarrow p$ for all states on nucleus A and $\gamma_G \rightarrow q$ for all states on nucleus B.⁵⁷ Thus in all terms which do not vanish exponentially $\gamma_G \rightarrow \gamma_G$, the derivatives of γ_G vanish, the variables $\vec{\xi}_G, \vec{\eta}_G$ become the appropriate separated-atom variables to order $(m/M)^2$ and $d_{A+\tau, \lambda}^K$ in Eq. (70) approaches

$\delta_{\Lambda+\tau, \Lambda}$. Finally, the molecular wave functions tend toward fixed combinations of atomic wave functions quantized along $\hat{\xi}_G$.

As $\epsilon_G \rightarrow \infty$, therefore, Eqs. (70) tend toward ordinary differential equations which describe the separated-atom scattering problem. They differ from the usual p.s.s. equations because the variables $\vec{\xi}_G, \vec{\eta}_G$ replace $\vec{R}, \vec{r}$. As $\epsilon_G \rightarrow \infty$, Eqs. (70) decouple and the radial scattering functions tend toward sums of incoming and outgoing waves. Their coefficients are related to the S-matrix.

At this point it is necessary to make the notation more specific. Let $C = A(B)$ denote the nuclei and let n_{Λ} be hydrogenic quantum numbers. The hydrogenic channel states are then designated by $\psi_{Cn\Lambda}$. The molecular eigenfunctions can now be expressed in separated-atom notation as $x_{Cnr\Lambda}$. The labeling is such that as $\epsilon_G \rightarrow \infty$

$$x_{Cnr\Lambda}(\rho_G, \phi_G, \zeta_G; \xi_G) \rightarrow \sum_{\lambda=|\Lambda|}^{n-1} \psi_{Cn\lambda\Lambda}(\rho_G, \phi_G, \zeta_G) T_{\lambda r}^{Cn} \quad (75)$$

Equation (75) accounts for the Stark mixing of the degenerate hydrogenic λ sublevels in the asymptotic molecular eigenfunction. The matrix $T_{\lambda r}^{Cn\Lambda}$ is orthogonal. The index r labels different molecular eigenfunctions which belong to the same $Cn\Lambda$ manifold. The lower limit on λ can be set equal to zero by defining $T_{\lambda r}^{Cn\Lambda}$ to be zero for λ or $r < |\Lambda|$. Introducing the new notation we can write

$$\begin{aligned}
R_{Cn\Lambda; C'n'\ell'm'}^K(\epsilon_G) \rightarrow & \left\{ a(Cn\Lambda; C'n'\ell'm') e^{i(k_{Cn} \epsilon_G - a_{Cn} 2n(2k_{Cn} \epsilon_G))} \right. \\
& \left. - b(Cn\Lambda; C'n'\ell'm') e^{-i(k_{Cn} \epsilon_G - a_{Cn} 2n(2k_{Cn} \epsilon_G))} \right\} \\
& \times (2ik_{Cn}^{1/2} k_{C'n'}^{1/2})^{-1} .
\end{aligned} \quad (76)$$

In Eq. (76) k_{Cn} is the asymptotic wave number from Eqs. (70) and (71) and a_{Cn} is the appropriate Coulomb parameter. The initial state index G'_{AB} is now written $C'n'\ell'm'$. From Eqs. (52)-(54) and Eq. (75),

$$\begin{aligned}
|C'n'\ell'm'\rangle \rightarrow & \sum_K \sum_{M_K} (4\pi)^{1/2} (2K+1)^{1/2} \sum_{Cn\Lambda} \sum_2 \psi_{Cn\Lambda, 2r}^{Cn\Lambda} \\
& \times \mathcal{W}'(KM_K; 0, 0; G'_{AB}) R_{Cn\Lambda; C'n'\ell'm'}^K(\epsilon_G) / \epsilon_G ,
\end{aligned} \quad (77)$$

where

$$\mathcal{W}'(KM_K; 0, 0; G'_{AB}) = (-1)^A \sqrt{\frac{2K+1}{4\pi}} D_{AM_K}^K(0, 0; G'_{AB}) . \quad (78)$$

Equation (77) can now be expressed in terms of space-fixed coordinates using the relation⁵⁴

$$\psi_{Cn\lambda\Lambda}(\phi_G, \phi_G, \zeta_G) \mathcal{M}(K M_K \Lambda; 0 0 \psi_G) = \sum_L \sum_m (-1)^\Lambda \sqrt{\frac{2L+1}{2K+1}} C(L\lambda K; 0\Lambda) \\ \times C(L\lambda K; M_K - m, m) \psi_{Cn\lambda m}(\vec{r}_C) Y_L^{M_K - m}(\phi_G, \psi_G) \quad (79)$$

In Eq. (79) the spherical harmonic and the Clebsch-Gordan coefficient are in the notation of Rose. The hydrogenic wave function on the right is now quantized in the same space-fixed frame used to define $\phi_G \psi_G$. The insertion of (79) and (76) into (77) produces

$$\phi_{C'n'\lambda'm'} \rightarrow \sum_{Cn\lambda m} \psi_{Cn\lambda m}(\vec{r}_C) \sum_{LM_K} (4\pi)^{\frac{1}{2}} (2L+1)^{\frac{1}{2}} Y_L^{M_K - m}(\phi_C, \psi_C) \\ \times \sum_K \sum_\Lambda \sum_r (-1)^\Lambda T_{\lambda r}^{Cn\Lambda} C(L\lambda K; 0\Lambda) C(L\lambda K; M_K - m, m) \\ \times \left\{ a(Cn r \Lambda; C'n' \lambda' m') e^{i\tilde{\theta}} - b(Cn r \Lambda; C'n' \lambda' m') e^{-i\tilde{\theta}} \right\} \\ \times (2i \epsilon_C k_{Cn}^{\frac{1}{2}} k_{C'n'}^{\frac{1}{2}})^{-1} \quad (80)$$

In Eq. (80), $\tilde{\theta} = k_{Cn} \epsilon_C^{-\alpha} \lambda n(2k_{Cn} \epsilon_C)$, and $\vec{r}_G$ has been replaced by its separated-atom equivalent $\vec{r}_C$. The sums in Eq. (80) are restricted by the allowed variable ranges of the C-coefficients.

To have the proper asymptotic form, $\phi_{C'n'\lambda'm'}$ must be expressible as

$$\begin{aligned}
\gamma_{C'n', \ell, m'} \rightarrow & \sum_{Cn \lambda m} \psi_{Cn \lambda m}(\vec{r}_C) \sum_L (4\pi)^{\frac{1}{2}} (2L+1)^{\frac{1}{2}} Y_L^{m'-m}(\gamma_C, \psi_C) \\
& \times \left[S_{Cn \lambda m; C'n', \ell, m'}(L) e^{i\tilde{\gamma}} - (-1)^{L-\delta_C+\delta_{C'n'}+\delta_{\ell}+\delta_{m'm}} e^{-i\tilde{\gamma}} \right] \\
& \times (21k_{Cn}^{\frac{1}{2}} k_{C'n'}^{\frac{1}{2}} \epsilon_C)^{-1}. \quad (51)
\end{aligned}$$

If $S_{Cn \lambda m; C'n', \ell, m'}(L) = \delta_{C'n', L} e^{2i\delta_{C'n', L}}$, where $\delta_{C'n', L}$ is a real phase shift,

$$\begin{aligned}
\phi_{C'n', \ell, m'} \rightarrow & \psi_{C'n', \ell, m'}(\vec{r}_C) \sum_L (2L+1)^{\frac{1}{2}} P_L(\cos \theta_C) e^{i\delta_{C'n', L}} (21k_{C'n'} \epsilon_{C'})^{-1} \\
& \times \left[e^{i(k_{C'n'} \epsilon_{C'} - a_{C'n', \ell n}(2k_{C'n'} \epsilon_{C'}) + \delta_{C'n', L} - \frac{1}{2}L\pi)} - e^{-i(\dots)} \right]. \quad (82)
\end{aligned}$$

This function describes elastic scattering by a modified Coulomb field.

The comparison of Eqs. (80) and (81) shows that $M_K = m'$ and that

$$\begin{aligned}
S_{Cn \lambda m; C'n', \ell, m'}(L) = & \sum_K \sum_{\Lambda} \sum_r (-1)^{\Lambda} T_{2r}^{Cn \Lambda} C(L \ell K; 0 \Lambda) \\
& \times C(L \ell K; m' - m, m) a(Cn r \Lambda; C'n' \ell, m') ,
\end{aligned}$$

and

$$\begin{aligned}
(-1)^{L-\delta_C+\delta_{C'n'}+\delta_{\ell}+\delta_{m'm}} = & \sum_K \sum_{\Lambda} \sum_r (-1)^{\Lambda} T_{2r}^{Cn \Lambda} C(L \ell K; 0 \Lambda) \\
& \times C(L \ell K; m' - m, m) b(Cn r \Lambda; C'n' \ell, m') . \quad (83)
\end{aligned}$$

The first of the above equations determines the scattering matrix. To find $b(Cn\Lambda; c'n'l'm')$, we insert the inverse of Eq. (79),

$$\begin{aligned} \psi_{Cn\Lambda m}(\vec{r}_C) y_L^{m'-m}(\theta_C, \psi_C) &= \sum_{\Lambda'} \sum_K (-1)^{\Lambda'} \sqrt{\frac{2L+1}{2K+1}} C(L\Lambda K; 0\Lambda') C(L\Lambda K; m'-m, m) \\ &\times \psi_{Cn\Lambda'}(\rho_C, \phi_C, z_C) \mathcal{Y}(K, m', \Lambda'; \theta_C, \psi_C) \end{aligned} \quad (84)$$

into Eq. (81) and compare with Eqs. (77) and (76). This leads to the result that

$$b(Cn\Lambda; c'n'l'm') = (-1)^{K+l'+m'} \delta_{C'} \delta_{c'n'} \delta_{\Lambda-m'} \left(T^{C'n'\Lambda} \right)^{-1} r_{l'}. \quad (85)$$

It is straightforward to show that this value for b satisfies the second of Eqs. (83). The scattering amplitude $f_{Cn\Lambda m; c'n'l'm'}(\hat{R}_C)$ in Eq. (20) follows from Eq. (81). For other than elastic scattering

$$\begin{aligned} f_{Cn\Lambda m; c'n'l'm'}(\hat{R}_C) &= (2\pi)^{\frac{1}{2}} k_{Cn}^{\frac{1}{2}} k_{c'n}^{\frac{1}{2}})^{-1} \sum_L (4\pi)^{\frac{1}{2}} (2L+1)^{\frac{1}{2}} \\ &\times y_L^{m'-m}(\theta_C, \psi_C) S_{Cn\Lambda m; c'n'l'm'}(L) \end{aligned} \quad (86)$$

The total cross section from the integration of Eq. (21a) is

$$Q_{Cnzm;C'n'z'm'} = \frac{1}{k_{C'n'}} \sum_L (2L+1) \left| S_{Cnzm;C'n'z'm'}(L) \right|^2. \quad (87)$$

In Eq. (87) a factor consisting of the ratio of the system-initial-reduced mass to the system-final-reduced mass has been dropped. It is easy to show that

$$\sum_z \sum_m Q_{Cnzm;C'n'z'm'} = \frac{r}{k_{C'n'}} \sum_K \sum_{\ell} \sum_r (2K+1) \times \left| a(Cnr\Lambda;C'n'z'm') \right|^2, \quad (88)$$

Thus sums of Q over final degenerate sublevels can be computed directly from the $a(\)$.

This completes the discussion of an electronic eigenfunction expansion for one-electron heteropolar systems. In paper II, starting from Eqs. (69) and (71), coupled, ordinary differential equations for the radial-scattering functions will be derived and variational formulae for the parameters γ_G and k_G will be deduced. In II it will turn out to be necessary to introduce diabatic basis functions for use at high velocities. These will also be needed in connection with many-electron expansions. We therefore take up this subject next.

B. Basis Functions made from Linear Combinations of Electronic Eigenfunctions; Interpolating or Diabatic States.

The basis functions of Subsection A 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 (i.e. nodal structure, electron charge distribution, etc.) 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 $[R_0, R_1]$.

During collisions there frequently is a substantial probability for transitions in regions of avoided crossing. In these cases it is advantageous in treating the collisions numerically to have the expansion basis functions as slowly varying with internuclear separation as possible. In an adiabatic expansion, problems of 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.^{58,59}

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 derivative are continuous with the original values 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 Smith³⁸ 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. 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 in excess of $(0.9)^{1/2}$. All other elements in the column will be less than $(0.1)^{1/2}$ 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 parameterized 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. Splines or polynomials were used to define smooth interpolations. 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 $(\partial/\partial R) \sum_i \vec{r}_i \cdot \vec{G}$ where $\vec{r}_i$ locate the electrons with respect to the nuclear center of mass. Since this term does not always vanish in the separated-atom limit, there may be some advantage in basing the transforms on some anti-symmetric radial coupling matrix which does vanish. This could be done, for example, with the zero-energy limit of the radial coupling in Eq. (90) of Paper II.⁴⁰ We have not tested this point. When the region $[R_0, R_1]$ is narrow, the results should be insensitive to the choice of radial coupling.

In summary, let $\{\chi_{\alpha}\}$ 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

$$\chi_G = \sum_H U_{HG}(R) \chi_H, \quad (89)$$

where $U_{HG}(R)$ is the orthogonal matrix which represents the net result of all the interpolating transforms one has elected to introduce. There is some inherent arbitrariness in the χ_G . However, the author expects that its influence on scattering cross sections should be negligible.

A change in notation will allow the formalism of Section VI-A 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. (52). Also assume that as $R \rightarrow \infty$, χ_G becomes the old eigenfunction χ_G so that the S-matrix need not be redefined. Now the assumption that χ_G is an electronic eigenfunction was used only to obtain $(2M/\hbar^2) \epsilon_G A_{n\lambda}$ in Eq. (71), using Eq. (50). Therefore defining an operator h_{λ} by

$$\left\{ -\frac{\hbar^2}{2m} \nabla_{nG}^2 + V \right\} A_{p\lambda} (2\tau)^{-1/2} e^{i\mathbf{k} \cdot \mathbf{r}} \chi_G = (2\tau)^{1/2} e^{i\mathbf{k} \cdot \mathbf{r}} h_{\lambda} A_{p\lambda}, \quad (90)$$

the use of function χ_G which is an eigenfunction only as $R \rightarrow \infty$ results in the replacement of $(2M/\hbar^2) \epsilon_G A_{n\lambda}$ in Eq. (71) by $(2M/\hbar^2) h_{\lambda} A_{n\lambda}$.

C. Expansions for One-Electron Homopolar Systems.

In a heteropolar system the molecular eigenfunctions tend toward atomic eigenfunctions as $R \rightarrow \infty$. However, in homopolar systems the electronic fixed-nucleus Hamiltonian possesses inversion symmetry with respect to the midpoint of the internuclear line. Consequently, each eigenfunction ψ_G has an associated eigenfunction $\psi_{P(G)}$ of opposite inversion symmetry which becomes degenerate with ψ_G as $R \rightarrow \infty$. The simplest example for H_2^+ or HD^+ is the pair $1s\sigma_g, 2p\sigma_u$. As is well known, the pair of associated eigenfunctions tend toward the sum and difference of atomic eigenfunctions on the two centers as $R \rightarrow \infty$. In the large- R region where the energy difference between ψ_G and $\psi_{P(G)}$ is very small, all linear combinations of ψ_G and $\psi_{P(G)}$ must be considered equally suitable basis functions until a choice based on dynamics is found. Following Bates and McCarroll,² a way to obtain basis functions which tend toward atomic eigenfunctions as $R \rightarrow \infty$ is to introduce functions $x_G^A = 2^{-1/2}(\psi_G + \psi_{P(G)})$ and $x_G^B = 2^{-1/2}(\psi_G - \psi_{P(G)})$, where A and B designate the two nuclei. Then the product functions

$$x_G^A F_G^A(\vec{R}_A) \quad , \quad x_G^B F_G^B(\vec{R}_B) \quad (91)$$

can become exact solutions of the Schroedinger equation provided $\vec{R}_A$ goes from the center of mass of atom A to nucleus B and $\vec{R}_B$ goes from nucleus A to the center of mass of atom B. In this work, in order not to impose the separated-atom superposition at all R , the functions

$$x_G = \cos \tau_G \psi_G + \sin \tau_G \psi_{P(G)} \quad (92a)$$

$$x_{P(G)} = \cos \tau_{P(G)} \psi_{P(G)} + \sin \tau_{P(G)} \psi_G \quad (92b)$$

are introduced as basis functions with τ_G being a slowly varying, R -dependent function to be determined variationally along with the parameters γ_G and k_G from Eq. (41). Qualitatively, the author expects that as the result of the optimization x_G will go from $\pm\gamma/4$ in the separated-atom limit to small values once the energy difference between the G and $P(G)$ states grows to a significant fraction of its united-atom value. Then x_G will be approximately equal to ψ_G for small R and will be either an atomic A- or B-state at large R . It is essential for completeness that if x_G becomes an A-state, $x_{P(G)}$ becomes a B state, or conversely. If the nuclear masses are not identical the nucleus with the greater mass has the lower atomic eigenvalue. This electron-reduced-mass effect can be included in the calculation of the ψ_G and $\psi_{P(G)}$ which appear in Eqs. (92). In Eq. (92a) for example, one calculates both ψ_G and $\psi_{P(G)}$ from Eq. (70) of II,⁴⁰ using for γ_G the value from the transformation associated with x_G .

Assuming equal nuclear charges but different nuclear masses, Eqs. (92) define a set of basis functions, which, as in Section VI-B, are linear combinations of molecular eigenfunctions. These may be used to build a trial scattering function as was done in Eqs. (52)-(54) for an expansion based on eigenfunctions. The equations of the theory are formally the same as those of the heteropolar system once allowance is made for the use of the linear combinations of eigenfunctions. However, in the homonuclear case the coefficients of the linear combinations are not given in advance as in Section VI-B, but must be determined dynamically.

If the two nuclei are identical, the full Hamiltonian is invariant with respect to their interchange or, equivalently, with respect to the inversion of all the electrons through the midpoint of the internuclear line. The individual terms in the expansion based on Eqs. (92) do not possess this symmetry. Therefore, for identical nuclei the trial expansion is symmetrized. By convention let ψ_G be the gerade eigenfunction and $\psi_{p(G)}$ be the ungerade one. Then we construct the trial functions ϕ from gerade or ungerade terms of the form

$$\begin{aligned}\phi_G &= 2^{-1/2}(1 + \bar{I}) \left\{ (\cos \tau_G \psi_G + \sin \tau_G \psi_{p(G)}) F_G(\vec{r}_G) \right\}, \\ \phi_{p(G)} &= 2^{-1/2}(1 - \bar{I}) \left\{ (\cos \tau_{p(G)} \psi_{p(G)} + \sin \tau_{p(G)} \psi_G) F_{p(G)}(\vec{r}_{p(G)}) \right\},\end{aligned}\quad (93)$$

where $\bar{I}$ stands for electron inversion in the midpoint of the internuclear line. In Eq. (93) $F_G(\vec{r}_G)$ is the scattering function which is expanded in terms of angular-momentum eigenfunctions and radial-scattering functions as in Eq. (54). The symmetrization in Eq. (93) complicates the structure of the Lagrangian and the analysis carried out in Section VI-A for heteropolar systems. However, the problems are those of detail not of principle. With $\tau_G = \pi/4$ and a plane wave for $F_G(\vec{r}_G)$, the forms introduced by Bates and McCarroll for symmetric resonant systems are recovered.

In the case of identical nuclei the symmetry-adapted basis functions (93) are advantageous because gerade and ungerade functions do not couple.

When the nuclei have different masses, it is still possible to use symmetry-adapted terms of the form (93) in place of the unsymmetrized terms based on Eqs. (92). Then the gerade and ungerade terms will be coupled.

As with the Eqs. (69)-(71) for heteropolar systems, the crucial question is whether the optimization program proposed here leads to practical results. For one-electron, heteropolar systems, Ref. 40 provides computational equations of the usual form and formulae for the parameters γ_G and k_G . For homopolar systems, the author has made preliminary studies of the simultaneous optimization of γ_G, k_G, τ_G . In the separated-atom region, the optimized values agree with those of Bates and McCarroll. However, a formula for τ_G covering all internuclear separations has not yet been found.⁶⁰

VII. CONSTRUCTION OF TRIAL SOLUTIONS FOR SYSTEMS WITH MORE THAN ONE ELECTRON.

As explained in the Introduction and first part of Section IV, the electron coordinates r_G^n and reaction coordinate ξ_G for an expansion term G are introduced in conjunction with an approximate orbital product, Π_G . This approximate product is an appropriately chosen linear combination of spin-free eigenfunctions. In this section we first assume that suitable functions Π_G have been found and state how a many-electron Lagrangian is to be constructed from them. Then the task of finding the Π_G is taken up for HeH^+ , H_2 , and HeH . The most detailed discussion is given for HeH^+ in Subsection VII-A. The discussion of the other two systems is primarily qualitative, but illustrates the features of the method.

Let us now consider Π_G to be given, and, as was done in Eqs. (52) and (54), split off the overall azimuthal angle dependence from Π_G by writing

$$\Pi_G = (2\pi)^{-1/2} A_G e^{i\Lambda\phi_G}, \quad (94)$$

where ϕ is defined by Eq. (59) and the subscript indicates that ξ is taken as the rotational symmetry axis, as described in Section V. Here A_G is a sum of spin-free eigenfunctions each lacking the common term factored

out. A_G is a function of the variables $\phi_G^z, \phi_G^f, \epsilon_G$ and the differences in the ϕ_G^L defined in Section V. To construct the scattering expansion we next multiply π_G for each G by a scattering function. This can be visualized by inserting the many-electron A_G into Eq. (54) in place of A_{nA} . At this point the Pauli exclusion principle has not been satisfied. To do this, the G^{th} term of the new Eq. (54) is operated on by the sum of projectors $N_{Gk}^S \bar{E}_{rk}^S(S)$ defined in Section II. Here N_G^S is a normalization factor. The result is the r^{th} partner of the spin-free expansion term for the total spin S .⁶¹ The formulation of the many-electron Lagrangian is then straightforward using the methods outlined in Section II.

Because the projectors are sums of electron-coordinate permutations, the expansions are increased in length. However, each term still has the structure expressed for the one-electron system by Eq. (54). Consequently the application of the Hamiltonian operator in the many-electron version of Eq. (55) can be carried out for each permutation in the way described in Section VI, using the N -electron equation (6E). The permutations present in the two functions of Eq. (55) cause "exchange"-type contributions to the Lagrangian to appear.⁶²

There is evidently quite a bit of bookkeeping involved in the many-electron formulation. Fortunately most of it is of the kind already well understood from molecular structure theory and computations. The essential feature of the expansions described above is that they are electronic eigenfunction expansions. As a result the electron repulsion terms, which could cause great complications in computations, are absent. We now consider how

to find the linear combinations of spin-free eigenfunctions η_G which represent approximate orbital products.

A. The Two-Electron System HeH^+ .

Consider a pair of one-electron orbitals $\phi_1(\vec{r}_1)$ and $\phi_2(\vec{r}_2)$. Then the equation

$$\phi_1 \phi_2 = 2^{-1/2} \left\{ 2^{-1/2} (1 + P_{12}) \phi_1 \phi_2 + 2^{-1/2} (1 - P_{12}) \phi_1 \phi_2 \right\} \quad (95)$$

is evidently an identity. In Eq. (95) a standard ordering of electron coordinates 1, 2, in the product has been introduced. If ϕ_1 and ϕ_2 are normalized and $\langle \phi_1 | \phi_2 \rangle = 0$, $2^{-1/2} (1 \pm P_{12}) \phi_1 \phi_2$ is normalized. This suggests the ansatz

$$\eta_G = \phi_1 \phi_2 = 2^{-1/2} (\psi_G^{(0)} + \psi_G^{(1)}) \quad , \quad (96)$$

in which actual singlet and triplet spin-free eigenfunctions of a multiplet pair replace the symmetrized products in Eq. (95). Equation (96) defines a quantity which is supposed to be a product to a good approximation. This requires that the two states of the singlet-triplet multiplet pair be expressible to a reasonable approximation in the form (95) with $\langle \phi_1 | \phi_2 \rangle = 0$.

These assumptions are exactly satisfied in the separated-atom region whenever the electrons are on different centers. In general they should also be satisfied to a sufficient approximation at those internuclear separations where the triplet and singlet eigenfunctions of the pair are not interacting with other states of the same symmetry. The ansatz (96) represents a compromise. In the interest of having eigenfunctions as basis functions, we have somewhat blurred the correlation between the transformation parameters and orbitals, except in the separated atom limit. This does not appear to the author to be a serious limitation on the formulation.

Equation (96) is incorrect in regions where the states $\psi_G^{(S)}$ interact with other states $\psi_H^{(S)}$ of the same symmetry as discussed for one-electron systems in Section VI-B. The locations of the triplet-system avoided crossings do not coincide with those of the singlet system. Consequently, near narrow avoided crossings the triplet valence orbital is not at all equal to the singlet one. This problem can be remedied by introducing interpolating or diabatic states as in Section VI-B. In these the diabatic valence orbitals change slowly, the assumption of identical triplet and singlet orbitals is reasonably valid, and the use of Eq. (96) should be all right.

Thus instead of Eq. (96) we can take

$$\pi_G' = \phi_1'(\vec{r}^1) \phi_2'(\vec{r}^2) = 2^{-1/2} \left(\sum_H \psi_H^{(0)} \Omega_{HG}^{(0)} + \sum_H \psi_H^{(1)} \Omega_{HG}^{(1)} \right), \quad (97)$$

where $\sum_H \psi_H^{(S)} \Omega_{HG}^{(S)}$ defines the diabatic state labeled with S and G. The use of Eq. (97) generates a diabatic expansion. By applying the inverse of $\Omega_{HG}^{(0)}$ to the right-hand side of Eq. (97) one can define

$$\pi_G'' = \phi_1''(\vec{r}^1) \phi_2''(\vec{r}^2) = 2^{-1/2} \left(\psi_G^{(0)} + \sum_H \sum_K \psi_H^{(1)} \Omega_{HK}^{(1)} (\Omega_{KG}^{(0)})^{-1} \right). \quad (98)$$

Taking ϕ_1 to be the valence orbital in Eq. (98), $\phi_1''(\vec{r}^1) \sim \phi_1'(\vec{r}^1) \cdot \phi_1(\vec{r}^1)$. The orbital $\phi_2''(\vec{r}^2)$ is a singlet-state adiabatic valence orbital, which replaces that defined by Eq. (96) in the triplet and singlet-crossing regions. If the triplet and singlet transforms are nearly identical, Eqs. (98) and (96) are nearly equivalent. An adiabatic triplet-state orbital can be defined from Eq. (97) in a completely analogous way.

To form the term in the scattering expansion corresponding to $\psi_G^{(n)}$, one multiplies expression (98) by a scattering function and applies the singlet-state projector. The result is a term

$$\begin{aligned} \phi_G^{(0)} = \frac{1}{2} (1 + P_{12}) & \left\{ \left(\psi_G^{(0)} + \sum_H \sum_K \psi_H^{(1)} \Omega_{HK}^{(1)} (\Omega_{KG}^{(0)})^{-1} \right) \right. \\ & \times F \left(\alpha_G R - \frac{\pi}{R} \left(\gamma_G^1 \vec{r}^1 + \gamma_G^2 \vec{r}^2 \right) \right) \left. \right\} \quad (99) \end{aligned}$$

Here α_G is defined in Eqs. (41). The arguments of the electronic functions are ξ_G , etc. as described below Eq. (94).⁶³ If ξ_G , the argument of F , is not altered by P_{12} , for example if γ_G^n and k_G^n are zero or m/M is set equal to zero, Eq. (99) reduces to just $\psi_G^{(0)} F$ since $\frac{1}{2}(1 + P_{12})$ annihilates the triplet function. The generation of $\psi_G^{(1)}$ is completely analogous. Using Eq. (97) a diabatic expansion term can equally well be constructed from Eq. (95). Equation (99) shows how each term in the scattering expansion is expressed as a linear combination of spin-free eigenfunctions.

In the case of an isolated closed-shell-type state such as the 1Σ ground state of HeH^+ , there is no triplet state with which to make distinct orbitals. For this case the orbitals are treated as equivalent, with $\gamma^1 = \gamma^2$ and $k^1 = k^2$. Then $P_{12} \xi = \xi$ and the scattering expansion term is taken simply as the product of the spin-free eigenfunction and a scattering function $F(\xi)$.

We must now discuss how to make orbital products in the separated-atom region. As in the case of avoided crossings the procedure is complicated by interaction between near-lying states in the region of transition to separated-atom behavior. This occurs whenever the conditions for near-resonant charge exchange, as described by Demkov,^{64,65} are satisfied. The HeH^+ system provides a wealth of examples because of the near degeneracy of the atomic levels $\text{He}^+(1s) + \text{H}(n\ell)$ and $\text{He}(1s, n\ell) + \text{H}^+$. The point is that the triplet and singlet levels approach their separated-atom limits at different rates because the helium singlet and triplet level schemes do not coincide. Consequently, the molecular valence orbital is different for singlets and triplets. The core orbital is always nearly $\text{He}^+(1s)$. In addition, the singlet $\text{He}(1s, n\ell)$ level may lie above the $\text{He}^+(1s) + \text{H}(n\ell)$ level while the triplet $\text{He}(1s, n\ell)$ level lies below it. This is the case for $\text{He}(1s, 2p)$. This means that the singlet-triplet eigenfunction pair which should be added to make a product function in the molecular region is not the same pair which should be added in the

separated-atom limit. This situation is illustrated for HeH^+ π -states in Fig. 2. With increasing R , the singlet molecular eigenfunctions undergo a Demkov transition from the forms $2^{-1/2}(A \pm B)$ to the forms A , B , where A is the wave function for $\text{He}(1s, 2p\pi) + \text{H}^+$ and B is that for $\text{He}^+(1s) + \text{H}(2p\pi)$. The same thing is true of the pair of triplet states. Owing to the difference between the singlet and triplet separations at $R = \infty$, the singlet transition takes place at larger R than the triplet. As in the case of avoided crossings the interpolating transformation can be found from the radial coupling matrix elements in a manner completely analogous to that described in Section VI-B. Using L and U for lower and upper (in energy), respectively,

$$\psi_L^{(0)} = \cos\theta^{(0)} B^{(0)} + \sin\theta^{(0)} A^{(0)}$$

$$\psi_U^{(0)} = -\sin\theta^{(0)} B^{(0)} + \cos\theta^{(0)} A^{(0)}$$

$$\psi_L^{(1)} = \cos\theta^{(1)} A^{(1)} + \sin\theta^{(1)} B^{(1)}$$

$$\psi_U^{(1)} = -\sin\theta^{(1)} A^{(1)} + \cos\theta^{(1)} B^{(1)} \quad (100)$$

$\theta^{(S)}$ is defined for $R_0^{(S)} \leq R < \infty$ and characterizes the Demkov transform. As $R \rightarrow R_0^{(S)}$, $\theta^{(S)} \rightarrow 0$; as $R \rightarrow \infty$, $\theta^{(S)} \rightarrow \pi/4$. For $R < R_0^{(S)}$ the forms at $R_0^{(S)}$ are assumed to hold. However, it is possible to choose $A^{(1)}$ and $B^{(1)}$ which more naturally are too different from the separated-atom eigenfunctions if the method is to make any sense. From Eq. (100)

Figure 2. Schematic long-range behavior of lowest singlet and triplet pi-states for HeH^+

$$A^{(0)} = \sin\theta^{(0)} \psi_L^{(0)} + \cos\theta^{(0)} \psi_U^{(0)}$$

$$B^{(0)} = \cos\theta^{(0)} \psi_L^{(0)} - \sin\theta^{(0)} \psi_U^{(0)}$$

$$A^{(1)} = \cos\theta^{(1)} \psi_L^{(1)} - \sin\theta^{(1)} \psi_U^{(1)}$$

$$B^{(1)} = \sin\theta^{(1)} \psi_L^{(1)} + \cos\theta^{(1)} \psi_U^{(1)} . \quad (101)$$

We now assume that, as with the diabatic states, product functions for A and B states are given by

$$\phi_1(\vec{r}^1) \phi_A(\vec{r}^2) = 2^{-1/2} (A^{(0)} + A^{(1)})$$

$$\phi_1(\vec{r}^1) \phi_B(\vec{r}^2) = 2^{-1/2} (B^{(0)} + B^{(1)}) . \quad (102)$$

From Eqs. (100) and (102)

$$\begin{aligned} \psi_L^{(0)} &= (1 + P_{12}) \left\{ \cos\theta^{(1)} 2^{-1/2} \phi_1(\vec{r}^1) \phi_B(\vec{r}^2) + \sin\theta^{(1)} 2^{-1/2} \phi_1(\vec{r}^1) \phi_A(\vec{r}^2) \right\} , \\ &= 2^{-1/2} (1 + P_{12}) \left\{ \phi_1(\vec{r}^1) \left[\cos\theta^{(1)} \phi_B(\vec{r}^2) + \sin\theta^{(1)} \phi_A(\vec{r}^2) \right] \right\} \\ &\equiv 2^{-1/2} (1 + P_{12}) \tau_L^{(0)} . \end{aligned} \quad (103)$$

Analogous equations hold for the other eigenfunctions. Equation (104) relates $\psi_L^{(0)}$ to a symmetrized product function. The product function $\tau_L^{(0)}$ is expressed in terms of eigenfunctions by

$$\begin{aligned}
\psi_L^{(n)} &= 2^{-1/2} \cos \theta^{(0)} \left(\cos \theta^{(0)} \psi_L^{(0)} - \sin \theta^{(n)} \psi_U^{(0)} + \sin \theta^{(1)} \psi_L^{(1)} + \cos \theta^{(1)} \psi_U^{(1)} \right) \\
&+ 2^{-1/2} \sin \theta^{(0)} \left(\sin \theta^{(n)} \psi_L^{(0)} + \cos \theta^{(n)} \psi_U^{(0)} + \cos \theta^{(1)} \psi_L^{(1)} - \sin \theta^{(1)} \psi_U^{(1)} \right) \\
&= 2^{-1/2} \left(\psi_L^{(0)} + \sin(\theta^{(0)} + \theta^{(1)}) \psi_L^{(1)} + \cos(\theta^{(0)} + \theta^{(1)}) \psi_U^{(1)} \right). \quad (104)
\end{aligned}$$

This equation is analogous to Eq. (98). As $\psi_L^{(0)}$ and $\psi_U^{(1)}$ are combined to make the product function; when both $\psi_L^{(0)}$ and $\psi_U^{(1)}$ have reached $\sim 1/4$, $\psi_L^{(1)}$ and $\psi_U^{(0)}$ are combined. The term $\psi_L^{(0)}$ in the scattering expansion corresponding to $\psi_L^{(0)}$ is finally obtained by inserting () from Eq. (104) in Eq. (99).

Once again if $P_{12} F = F$, the triplet terms from Eq. (104) are annihilated and the expansion term is just $\psi_L^{(0)} F$.

To conclude the discussion, let us compare qualitatively the diabatic and adiabatic values of the transformation parameters γ_A for the valence orbitals of a pair of HeH^+ states which undergo an avoided crossing at $R=R_C$. Suppose that for $R < R_C$ the lower state is like an atomic A-state and the upper state is like an atomic B-state. There will be a diabatic $\gamma_A \sim M_B / (M_A + M_B)$ and $\gamma_B \sim -M_A / (M_A + M_B)$, each nearly constant through the whole region where the two states are isolated from other states of the same symmetry. The

adiabatic ψ_l for the lower state will switch monotonically from ψ_A to ψ_B with increasing R as the avoided crossing is traversed; the adiabatic ψ_u for the upper state will switch from ψ_B to ψ_A . During the transition the adiabatic valence orbitals relocate and pass through a region of $A + B$ character as the change from A character to B character takes place. Another general trend in HeH^+ valence orbitals is the trend with decreasing R from A or B separated-atom character through H_2^+ character, where the center of electronic charge is close to the midpoint of the internuclear line, to united-atom character where the center of electronic charge tends toward the center of nuclear charge. The core orbital is nearly a He^+ orbital for all R until the proton penetrates the $\text{He}^+(1s)$ charge cloud substantially.

B. Qualitative Discussion of Basic Construction for H_2 .

The hydrogen molecule is more complicated than HeH^+ .¹¹ First, H_2 is homopolar; second, the ionic channel greatly influences the low-lying electronic states. Since H_2 and HD are homopolar, to make a product of atomic wave functions at large R from the molecular ones, we must superimpose nearly degenerate gerade and ungerade spin-free eigenfunctions of both triplet and singlet symmetries. In the separated-atom region this is a straightforward procedure.²⁸ Also, at small internuclear separations the triplet and singlet eigenfunctions of the excited states can be well described by Eq. (96) with ϕ_1 close to $H_1^+(1s\sigma)$, and ϕ_2 an appropriate gerade or ungerade function. Thus, a term in the trial solution will be given by an equation like Eq. (99) where the first bracket () is an independent linear combination of eigenfunctions which is a linear combination of the type (96) at small R and is an appropriate separated-atom combination at large R . In addition, the gerade and ungerade projection operators are applied to Eq. (99) to generate expansion terms of gerade and ungerade symmetry. The simplest states to discuss are those of Π and Δ symmetry where for the lower states there are no avoided crossings and the triplet and singlet orbitals appear to be sufficiently similar that Eqs. (96) can be used for all R . If we want to construct an expansion term corresponding to the $C^1\Pi_u 2p$ state of H_2 for example, we insert

$$\begin{aligned} \phi_1(\vec{r}^1)\phi_2(\vec{r}^2) = \frac{1}{\sqrt{2}} & \left[\cos\tau \left(C^1\Pi_u 2p\pi + C^3\Pi_u 2p\pi \right) \right. \\ & \left. + \sin\tau \left(C^1\Pi_g 3d\pi + C^3\Pi_g 3d\pi \right) \right] \end{aligned} \quad (105)$$

in Eq. (99) and apply $2^{-1}(1-\bar{I})$ to the result. As in Section VI-C, α is to be determined variationally. It is expected to become small as the energy difference between the $2p$ - and $3d$ - states becomes large. As $P \rightarrow \infty$ must approach $\pi/4$ in order for $\psi_1(\vec{r}^1)\psi_2(\vec{r}^2)$ to approach a product of atomic eigenfunctions, one on A, the other on B. Some of the higher states can be expected to undergo avoided crossings with states of the same symmetry. These can be treated using Eqs. (97) or (98).

The sigma states are complicated by the well-known interaction of the $(2p\sigma_u)^2$ configuration with $(1s\sigma_g)^2$, $(1s\sigma_g)(2s\sigma_g)(1s\sigma_g)(3s\sigma_g)$, and other $^1\Sigma_g^+$ configurations. To find approximate orbital products we first define diabatic or interpolating states for the singlet gerade and ungerade states correlating to H^+H^- . The method used is that of Section VI-B, based on a knowledge of the radial coupling matrix elements. At large R these diabatic ionic states cross the excited non-ionic levels for principal quantum numbers two and three. Below $R \sim 6$ a.u. only the gerade state interacts further with other states, giving rise to the potential curves with double minima. Between $R=2$ and $R=6$ a.u. this gerade state interacts strongly with the adjacent $^1\Sigma_g^+$ adiabatic states. The resulting diabatic state which coincides with the ionic state at $R \sim 6$ a.u. tends toward the character $(2p\sigma_u)^2$ at smaller R . The other $^1\Sigma_g^+$ diabatic states can be labeled $(1s\sigma_g)(2s\sigma_g)$, $(1s\sigma_g)(3s\sigma_g)$, etc. Their diabatic valence orbitals are not very different from those of the corresponding $^1\Sigma_g^+$ eigenfunctions which are not involved with the ionic configurations. Also the energy expectation values of the $2s$, $3s$, etc. diabatic states have the same kind of monotonic R -behavior possessed by the corresponding triplet eigenfunctions. At this point diabatic transforms for any other avoided crossings should also be calculated.

It is now possible to superimpose the spin-free sigma eigenfunctions to make diabatic product functions in a manner analogous to that given in

Eq. (165). The ground state $X^1_{\Sigma_g^+} 1s_{\sigma_g}$ is combined with $b^3_{\Sigma_u^+} 2p_{\sigma_u}$. The diabatic state correlating to $^1_{\Sigma_u^+} (H^+H^-)$ is combined with $^1_{\Sigma_g^+} (H^+H^-)$ and with $b^3_{\Sigma_u^+} 2p_{\sigma_u}$. The diabatic state $^3_{\Sigma_g^+} (H^+H^-)$ is combined with $^1_{\Sigma_u^+} (H^+H^-)$. The $b^3_{\Sigma_u^+} 2p_{\sigma_u}$ state is combined with $B^3_{\Sigma_u^+} 2p_{\sigma_u}$ and $X^1_{\Sigma_g^+}$. It is anticipated that in slow collisions only nearly degenerate states will combine to any great extent. By applying the inverses of the diabatic transforms to the diabatic expansion terms, one can define adiabatic and mixed-expansion terms just as was done in going from Eq. (97) to Eq. (98). However in that case the core orbital was essentially not influenced by the transform, and so the result could be interpreted in terms of an adiabatic valence orbital. In general this is not the case since both orbitals may be changing.

is a closed-shell system based on a closed-shell core.

To illustrate (105), how to construct an expansion for more than two electrons we consider the simplest examples: the low-lying states of He^+ or Li^+ . In the first case the molecular states correlate to $\text{He}(1s)^2$, $^1\Pi_u$; in the second they correlate to $\text{Li}^+(1s^2) + (n;)$ and $\text{Li}(1s^2 n;)^+$. The states are all doublet states and the excited states are based on a core which is $\text{He}^+(1s)$ or $\text{Li}^{++}(1s)$, respectively. For three electrons in a spin-1 state, the analogue of Eq. (99) becomes

$$\begin{aligned} \psi_r^{(1/2)} &= N^{(1/2)} \left(\bar{e}_r^{(1/2)} + \bar{e}_r^{(1/2)} \right) \psi_r^{(1/2)} \\ &= F \left(\alpha R - (m/M) (\gamma^1 \bar{r}^1 + \gamma^2 \bar{r}^2 + \gamma^3 \bar{r}^3) \right) \Big|_r, \end{aligned} \quad (106)$$

$$\psi_r^{(1/2)} = \psi_{11} \psi_{12} \psi_{13}$$

where ψ_r is given by Eq. (41), and the projectors $\bar{e}_r^{(1/2)}$ are defined in Eq. (6).

Intuitively, the closed-shell nature of the core tells us that we should take $\psi^1 = \psi^2 = \psi^3$ in Eq. (106). The problem then is to find a sum of eigenfunctions which to a good approximation can be used to replace the orbital product $\psi_{11} \psi_{12} \psi_{13}$ in Eq. (106).

A problem presents itself at this point. There are two distinct orbitals to deal with, but there is no other nearly degenerate physical state whose spin-free eigenfunction can be combined, for example, with that of the ground state to make the required product. The source of the problem is that for three or more electrons the space spanned by the $\bar{e}^{(1/2)}$ is not

complete. For three electrons one needs in addition the subspace of totally antisymmetric space functions. Let its projection operator be $p^{(sym)}$. The missing functions are the spin-free eigenfunctions $\psi^{(sym)}$ of the electronic Hamiltonian in the subspace spanned by $p^{(sym)}$. When applied to a closed-shell product $\phi_1\phi_2\phi_3$, or any function which is exchange-symmetric in the first two electrons,

$$\begin{aligned}\bar{e}_{01}^{(1)} \phi_1\phi_2\phi_3 &= \bar{e}_{11}^{(1)} \phi_1\phi_2\phi_3 = 0, \\ \bar{e}_{22}^{(1)} \phi_1\phi_2\phi_3 &= \frac{1}{3} (2 - p_{23} - p_{13}) \phi_1\phi_2\phi_3, \\ p^{(sym)} \phi_1\phi_2\phi_3 &= \frac{1}{3} (1 + p_{23} + p_{13}) \phi_1\phi_2\phi_3.\end{aligned}\quad (107)$$

Hence,

$$\phi_1\phi_2\phi_3 = \bar{e}_{22}^{(1)} \phi_1\phi_2\phi_3 + p^{(sym)} \phi_1\phi_2\phi_3, \quad (108a)$$

$$= \eta^{(1)} \psi_{22}^{(1)} + \eta^{(sym)} \psi^{(sym)}. \quad (108b)$$

In Eq. (108) we have defined $\psi^{(1)}$ and $\psi^{(sym)}$ by assuming ϕ_1 and ϕ_2 , $\psi^{(1)}$, and $\psi^{(sym)}$ are normalized. Then

$$\left(N^{(1_2)}\right)^2 = \langle \phi_1 \phi_1 \phi_3 | \hat{O}_{22}^{(1_2)} | \phi_1 \phi_1 \phi_3 \rangle .$$

$$\left(N^{(sym)}\right)^2 = \langle \phi_1 \phi_1 \phi_3 | \hat{P}^{(sym)} | \phi_1 \phi_1 \phi_3 \rangle . \quad (109)$$

We want to use Eq. (108b) as a model for the replacement of the orbital product by a sum of spin-free eigenfunctions whose main configurations agree reasonably well with the product orbitals. Now, Eq. (109) brings the orbitals into Eq. (108b) explicitly through the overlap $\langle \phi_1 | \phi_3 \rangle$. In order not to complicate the theory at this point we assume

$$\langle \phi_1 | \phi_3 \rangle = 0 .$$

$$N^{(1_2)} = \left(\frac{2}{3}\right)^{1/2} ;$$

$$N^{(sym)} = \left(\frac{1}{3}\right)^{1/2} . \quad (110)$$

Then the basic ansatz is

$$\psi^{(1_2)} = \phi_1 \phi_1 \phi_2 = \left(\frac{2}{3}\right)^{1/2} \left(\frac{1}{2} (\psi_1^{(1_2)} + \psi_2^{(1_2)}) + 2^{-1/2} \psi^{(sym)} \right) . \quad (111)$$

Here $\psi_r^{(1_2)}$, $r=1,2$, are the orthonormal spin-free partner eigenfunctions. Michels and Harris have calculated values of the $\phi_r^{(1_2)}$ for the low-lying states of HeH.⁶⁹ The closed-shell spin coupling is indeed dominant. Not surprisingly there are no values available for $\psi^{(sym)}$.

Equation (111) for $\Psi^{(1)}$ is to be used in Eq. (106). We take $N^{(1)} = (3/2)^{1/2}$. Then if $P_{IJ}F = F$ for all IJ , $\Psi_r^{(1)}$ is equal to $\Psi_r^{(1)}F$. Again, the use of the actual spin-free eigenfunctions makes Eq. (111) an ansatz since only the main configurations are compatible with the product.⁶⁹ The use of Eq. (111) assumes similar main orbitals for $\Psi_r^{(1)}$ and $\Psi^{(sym)}$. Therefore, avoided crossings have to be treated as for two-electron systems.

The new aspect of Eq. (111) is the appearance of the space-exchange-symmetric eigenfunctions $\Psi^{(sym)}$. For their evaluation, a modification of the existing molecular structure codes would be required.

5. Approximations for Many-Electron Systems.

The preceding subsections outline a method of constructing a many-electron scattering expansion and obtaining the Lagrangian for its radial scattering functions. Because new degrees of freedom are allowed in the expansion, it contains more terms and more transformation parameters to be determined. Also, the scheme of using eigenfunction sums to represent approximate products has caused the spin-free eigenfunctions for all spin values to appear in the equations for each spin value.

Such complexity was arrived at by following the reasonable arguments presented in the foregoing sections. However, it is important to be able to reduce the complexity of practical calculations as much as possible. The author regards the method outlined above as a starting point for further approximations--one accurate enough to rely on for slow collisions in most circumstances, yet more directly amenable to straightforward approximation than the original Schroedinger equation.

The first approximation of importance is the semiclassical approximation presented in II for one-electron heteropolar systems. This approximation concerns the radial scattering functions primarily and can be applied equally well to the many-electron formulations. Indeed, one can develop the semiclassical many-electron equations directly within the time-dependent framework, including the equations for optimizing the translational factors for each orbital.

The equations of this time-dependent formulation still use spin-free eigenfunctions of all spin values to define approximate orbital products.

Equally important are low-velocity approximations, either semiclassical or quantal. These eliminate the plane-wave-Eates-McCarroll-type translational factors from the semiclassical coupling matrix elements and lead to the simple coupled ordinary differential equations used by most researchers. The low-velocity form of the Euler-Lagrange equations for the transformation parameters then become relatively simple algebraic equations.

The case of non⁴ excited states at low velocities is instructive in connection with the third important type of approximation. Because there is a core and a valence orbital there are algebraic equations for both core and valence transformation parameters. These involve mixed matrix element integrals of the form

$$I_{rp} = \int d\mathbf{r}_1 d\mathbf{r}_2 x_r^{(1)} (\alpha_1 - \alpha_2) x_p^{(0)} \quad (112)$$

where the $x^{(s)}$ are spin-free functions, the superscript designates the spin S , and α_i is a one-electron operator. The mixed matrix elements arise from the orbital-product construction and are what make a distinction between orbitals possible in terms of eigenfunctions. When the approximate core and valence orbitals of the triplet and singlet spin-free functions corresponding to a multiplet pair are nearly equal, I_{rp} can be approximated as

$$I_{rp} \sim \int d\vec{r}_1 d\vec{r}_2 x_r^{(n)} (\eta_1 + \eta_2) x_p^{(n)} . \quad (113)$$

Thus the mixed matrix elements can be approximately replaced by ordinary matrix elements. To the same approximation the roles of (1) and (0) can be reversed. These approximations can readily be tested. For HeH^+ we have used the above procedure to derive algebraic equations for the valence orbital transformation parameters in terms of ordinary two-electron matrix elements and the core parameters. If one desires, then, the core parameters can be obtained from the one-electron formulae for HeH^{++} and the valence electron parameter from the simplified two-electron matrix elements. Approximations of the type (113) open the way to substantial simplifications of the theory, which may eliminate the mixed matrix elements. In HeH^+ this method should work well at all reasonably large R , but may be subject to non-negligible errors for R less than about 3 a.u.

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52. A modification of Eq. (41) is possible which makes the agreement exact. Eqs. (36a), (39), and (40) are retained and used to simplify Eq. (34). The relation $B_{jk}^n = 0$ provides linear equations for the $k^n(R)$ in terms of the $\gamma^n(R)$. To first order in m/M $h^n(R) = -\gamma^n(R)$ as in Eqs. (36b) and (41).
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54. For information about molecular eigenfunction expansions and their asymptotic forms, the author relied heavily on Ref. 4.
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