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R-matrix theory of charge transfer

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The *R*-matrix theory of Wigner is applied to the description of charge exchange. By making use of the correct coordinates for each arrangement, the boundary conditions are properly satisfied. Unphysical long-range couplings do not appear, and the use of "electronic traveling factors" is avoided. The wave functions for different arrangements are nonorthogonal, and are essentially equivalent to the "intersecting waves" of Delos [Phys. Rev. A 23, 2301 (1981)]. It is shown under appropriate simplifying assumptions that the *R*-matrix formalism reduces to the high-energy two-state approximation of Kramers and Brinkman. The main task of the *R*-matrix theory is the determination of the matrix elements of the Hamiltonian between basis functions belonging to different arrangements. This is achieved by methods of functional transfer combined with appropriate simplifications arising from the smallness of m/M. This leads to the central result that the transformation of a highly oscillating nuclear radial function from one arrangement to another brings with it a highly oscillating function of the electronic coordinates of the new arrangement. This causes off-diagonal elements of the Hamiltonian matrix to decrease rapidly as the energy increases. Consequently the cross section for charge transfer also decreases with increasing energy.

I. INTRODUCTION

The process whereby an atom A during a collision with another atom B transfers one or more electrons to B has for long presented a problem of fundamental theoretical importance. More recently this process has also assumed great technological significance in the performance of nuclear fusion devices. The stripping of electrons in tokamaks from the hydrogen atom fuel by highly charged ions already present is the chief energy-loss process that occurs in these devices. The reliable determination of total cross sections for such encounters over a collision energy range of, say, 0—5 keV is therefore a vital piece of information needed for the design of new machines that will one day produce more power than they consume.

The first calculations of charge-transfer effect were carried out by Oppenheimer[1] and by Kramers and Brinkman[2] using essentially the Born approximation—but with additional simplifications. They employed atomic eigenfunctions as a basis set, these being suitable for high-energy (i.e., energy above ~10 keV) encounters. After an interval of some 20 years, this work was continued by Bates and Dalgarno[3] and by Jackson and Schiff,[4] who carried out the first full numerical applications within this first-order theory.

At collision energies below ~1 keV (i.e., at low energies), it is useful to proceed by expanding the total wave function in terms of molecular electronic eigenfunctions, rather than to use eigenfunctions of the individual atoms. This approach is the basis of the "perturbed stationary state" (PSS) approximation, first proposed by Mott[5] (see also Mott and Massey[6]), and later significantly modified by Bates and his school.[17] The whole of this early work, both at high and low energies, has been reviewed with great lucidity by Bates and McCarroll.[8]

These studies served to point out certain fundamental inconsistencies in the formulation of the theory, both in terms of atomic eigenfunctions and in terms of molecular wave functions. Much effort has since been expended—largely at low collision energies—in attempts to remove these difficulties, and this has given rise to a considerable literature on the subject. Amongst more recent works one should mention those of Crothers and Hughes,[9] Thorson and Delos,[10] Schmalz, Stechel, and Light,[11] Crothers and Todd,[12] and Delos.[13] The most extensive calculations of charge transfer to date are by Heil, Butler, and Dalgarno,[14] and by Bienstock, Heil, Bottcher, and Dalgarno[15] (see also Bienstock, Heil, and Dalgarno[16]). The field has recently been very thoroughly reviewed by Delos[17] (see, in addition, Garratt and Truhlar[18]).

The physical phenomenon of the transfer of an electron from one atom to another is brought about by the motion of the atomic nuclei relative to one another. It is clear therefore that this cannot be represented by a picture in which the electronic and nuclear motions are separated, i.e., in which the nuclei see only the average positions of the electrons. Thus as shown by Bates and McCarroll[7] the pss approximation which precisely does attempt such a separation is not normally viable unless the electronic eigenfunctions are multiplied by factors expressing the translational motion of the nuclei.

Closely tied to these considerations is the formal difficulty that the total Hamiltonian for the system is most conveniently expressed in particle-to-particle coordinates. However, the proper asymptotic form of the wave function when atoms A and B separate requires the appearance of a center-of-mass—to—center-of-mass coordinate connecting A and B. Furthermore, this coordinate is different if the separating species are instead A^+ and B^-, say, i.e., different coordinates are required for each arrangement. This may be regarded as the source of the difficulties in the theoretical description of charge transfer.

For unless the boundary conditions for the different asymptotic states are imposed using the correct center-of-mass—to—center-of-mass coordinate, all manner of troubles manifest themselves: coupling matrix elements become origin dependent and do not become zero as the interatomic separations increase. In favorable circumstances where one of the collision partners is much heavier than the other, these effects can be minimized—but not eliminated—by placing the origin at the heavy nucleus (see, e.g., Heil *et al.*[14] and Bienstock *et al.*[15,16]).

In order to avoid these difficulties it is necessary to employ distinct coordinates for each arrangement—including in each case the relevant center-of-mass—to-center-of-mass separation—and to develop an expansion of the total wave function in terms of these same coordinates.

This was first proposed by Delos.[13] His "intersecting waves" theory removes most of the inconsistencies of the earlier descriptions. Substitution of this form of the wave function into the Schrödinger equation leads directly to a set of coupled integro-differential equations for the nuclear radial functions: The coupling which actually causes the charge transfer appears here under an integral sign. Approximations suitable for low-energy collisions reduce these equations to a set of ordinary coupled differential equations.

The purpose of this present paper is to put forward an alternative procedure, based upon the Wigner R-matrix theory.[19] R-matrix theory has already been applied with good success[20,21] to the scattering of electrons from atoms and molecules, and in this paper it is shown that the formalism also possesses advantages for the description of charge transfer. The fundamental characteristic of R-matrix theory is that the physical system is surrounded by a surface Σ which encloses the "strong-interaction" region. Very general boundary conditions are imposed at Σ, and the Schrödinger equation is separately solved subject to these conditions both within and outside Σ. The effect of the boundary conditions is to produce quantized ("particle-in-a-box") solutions within the strong-interaction region. These are matched to the solutions outside Σ by means of the R matrix (see Sec. II), the matching process yielding the relationship between waves which are asymptotically incoming and outgoing, and consequently the S matrix is determined. Charge transfer corresponds to significant interaction between different arrangements and can occur only within the strong interaction region. Hence the propagation of the solutions in the region outside Σ is more or less trivial: The major task is the solution of the Schrödinger equation within the region surrounded by Σ. The determination of the eigenfunctions ω_λ and associated eigenvalues ϵ_λ within Σ proceeds by expanding the ω_λ in a suitable basis set of functions. It is here that the power of the R-matrix formalism manifests itself, for we are free to choose any functions which conform as closely as possible to the physical situation. In the present case, we select functions that describe atoms A and B and their motion relative to one another, using a coordinate system which would enable the asymptotic boundary conditions for that arrangement to be properly satisfied. In addition to these, we select functions which describe the ions A^+ and B^-, say, and their relative motion, again using coordinates appropriate to this arrangement. In other words, we use the same expansion of the wave function as Delos[13] in terms of basis functions that are expressed in different coordinates for different arrangements. The fact that the (AB) set of basis functions is not orthogonal to the (A^+B^-) set makes not the slightest complication to the R-matrix formalism. The task is a technical—but not a trivial—one of evaluating the necessary matrix elements of the Hamiltonian between basis functions belonging to different arrangements. The resulting "multiarrangement integrals" are not unlike their counterparts in quantum chemistry—the multicenter integrals—and indeed are calculated by similar techniques of functional transfer.

We begin by describing the participating atoms and ions by means of isolated atomic eigenfunctions. Such a basis set, which might be termed a "valence-bond" basis, is obviously suitable for the description of high-energy collisions in which the colliding partners do not have enough time to deform significantly.

At lower energies it is necessary to allow for some deformation of the atomic-channel functions and this leads to the use of spin-coupled orbitals. These have precisely the shape of deformed atomic states, the amount of deformation varying with the separation between the atoms or ions in a particular arrangement. Spin-coupled wave functions have been recently used very successfully by Gerratt and Raimondi[22] in compact descriptions of both ground and low-lying excited molecular electronic states.

A feature of R-matrix theory which should be emphasized is that the energy dependence occurs in an extremely simple form. The eigenfunctions ω_λ and associated eigenvalues ϵ_λ are independent of energy and consequently may be reused for many energies, the span covered being defined by the nature and number of basis functions used. Thus having determined the R matrix for an initial energy E, the S matrix and cross sections may be obtained over a whole range of other energies at very little extra cost in computation time.

A second important characteristic of the R matrix is the fact that it is real and symmetric, and this alone ensures that the S matrix is unitary and symmetric. This means that if the R matrix is approximated in some way—as is inevitably the case in almost all applications—the fundamental properties of the S matrix are preserved.

In Sec. II the R-matrix theory for a fairly general rearrangement encounter is developed and applied in Sec. III to the case of charge transfer in one-electron systems. In Sec. IV it is shown how the present formalism reduces in a two-state approximation to essentially the same expressions as those obtained by Oppenheimer[1] and by Brinkman and Kramers[2] using the Born approximation. In Sec. V it is shown how the various integrals arising in the calculation of the matrix elements of the Hamiltonian are determined by methods of functional transfer. Finally, in Sec. VI the theory is extended to many-electron systems. The central result of this paper as brought out in Secs. V and VI is that the transformation of a highly oscillating nuclear radial function from one arrangement to another brings with it a highly oscillating function of the electronic coordinates of the new arrangement. Since other electronic functions are smooth, this causes off-diagonal elements of the Hamiltonian matrix to decrease rapidly to zero as the energy increases. Consequently the cross section for charge transfer should decrease rapidly with increasing energy.

Since, for reasons described above, we make no direct use of the Born-Oppenheimer separation[23] to determine molecular electronic eigenfunctions, it is pointless to employ body-fixed coordinates: Consequently space-fixed coordinate frames are used throughout. This also makes the imposition of the asymptotic boundary conditions easier to impose: We would in any case have to carry out a transformation from body-fixed to space-fixed frames at the surface Σ.

Nevertheless the electronic wave functions and associated potential-energy curves do play a role in the present theory, though in a somewhat surprising way: For each arrangement, AB or A^+B^-, say, the eigenfunctions of the corresponding potential-energy curves are determined, and used as basis functions for the nuclear radial motion in the R-matrix calculation. Similarly the orbitals from the same valence-bond (VB) or spin-coupled VB calculation are used to construct the deformed atomic-channel states.

II. *R*-MATRIX THEORY OF REARRANGEMENT COLLISIONS

A. Channel functions

We consider a collision process in which an atom or ion A strikes a composite particle (BC) and as a result produces a new composite particle (AB) and an atom or ion C:

$$A+BC\rightarrow AB+C \ . \tag{2.1}$$

Particle B may be either another heavy particle or—as is relevant to the present situation—an electron. The two sides of Eq. (2.1) constitute two distinct *arrangements* which we label α and β, respectively. There may of course be a third arrangement $AC+B$, but for the sake of clarity this is not included in the discussion. The index γ will be used to denote either arrangement, α or β.

An appropriate partial-wave function for arrangement α $(A+BC)$ is

$$\Phi^J_{\alpha c}\sim\psi_{n_A}\psi_{n_{BC}}\chi^J_{\alpha c}(R_\alpha)\mathcal{Y}_{JM}\{(j_A,j_{BC})j_\alpha;L_\alpha;\Omega_A,\Omega_{BC},\Omega_\alpha\} \ . \tag{2.2}$$

In this expression, ψ_{n_A} and $\psi_{n_{BC}}$ are wave functions for the internal states of particles A and BC, respectively, the set of internal coordinates for both particles being denoted collectively by i_α. Function $\chi^J_{\alpha c}(R_\alpha)$ describes the relative radial motion of A and BC, the coordinate R_α measuring the distance from the center of mass of A to the center of mass of BC. The angular coordinates of R_α in space-fixed axes are denoted by Ω_α, and those pertaining to A and BC by Ω_A and Ω_{BC}, respectively. The function $\mathcal{Y}_{JM}\{\cdots\}$ in (2.2) is an angular function in which the angular momenta associated with A and with BC, j_A and j_{BC}, are coupled to give a resultant j_α. This in turn is coupled with the angular momentum L_α of relative motion of A about BC to give an overall resultant J:

$$\mathcal{Y}_{JM}\{(j_A,j_{BC})j_\alpha;L_\alpha;\Omega_A,\Omega_{BC},\Omega_\alpha\}\equiv|(J_A,j_{BC})j_\alpha;L_\alpha;J,M\rangle \ . \tag{2.3}$$

The quantum numbers $\{(j_A,j_{BC})j_\alpha;L\}$ together with the quantum numbers n_A,n_{BC} for the internal states of A and BC, define a *channel index c for arrangement α:*

$$c\equiv\{n_A,n_{BC}(j_A,j_{BC})j_\alpha;L_\alpha\} \ . \tag{2.4}$$

Corresponding to this we define a channel function $\phi^J_{\alpha c}$ which is a function of all the coordinates except the scattering coordinate R_α:

$$\phi^J_{\alpha c}=\psi_{n_A}\psi_{n_{BC}}\mathcal{Y}_{JM}\{(j_A,j_{BC})j_\alpha,L_\alpha;\Omega_A,\Omega_{BC},\Omega_\alpha\} \ . \tag{2.5}$$

A similar treatment goes through for arrangement β $(AB+C)$, the relevant coordinates now being $\{i_\beta,R_\beta,\Omega_{AB},\Omega_C,\Omega_\beta\}$ in an obvious notation. A channel function $\phi^J_{\beta c'}$ is also similarly defined:

$$\phi^J_{\beta c'}=\psi_{n_{AB}}\psi_{n_C}\mathcal{Y}_{JM}\{(j_{AB},j_C)j_\beta,L_\beta;\Omega_{AB},\Omega_C,\Omega_\beta\} \ , \tag{2.6}$$

the index c' now referring to the set of quantum numbers on the right-hand side of (2.6).

The radial functions $\chi^J_{\alpha c}(R_\alpha)$ [and similarly the $\chi^J_{\beta c'}(R_\beta)$] are subject to the following boundary conditions (assuming that the potential in a given channel decays more rapidly than R_α^{-1}):

$$\lim_{R_\alpha\to 0}\chi^J_{\alpha c}(R_\alpha)<\infty \quad (\text{for } k_{\alpha c}\geq 0) \ ;$$

$$\chi^J_{\alpha c}(R_\alpha)\sim-\frac{1}{2ik_{\alpha c}^{1/2}}\left[\frac{\delta_{cc_0}}{R_\alpha}\exp[-i(k_{\alpha c}R_\alpha-\tfrac{1}{2}L_\alpha\pi)]-S^J_{cc_0}\frac{1}{R_\alpha}\exp[i(k_{\alpha c}R_\alpha-\tfrac{1}{2}L_\alpha\pi)]\right] \quad \text{as } R_\alpha\to\infty \tag{2.7a}$$

$$=\frac{1}{k_{\alpha c}^{1/2}}\frac{\delta_{cc_0}}{R_\alpha}\sin(k_{\alpha c}R_\alpha-\tfrac{1}{2}L_\alpha\pi)+K^J_{cc_0}\frac{1}{R_\alpha}\cos(k_{\alpha c}R_\alpha-\tfrac{1}{2}L_\alpha\pi) \quad (\text{for } k_{\alpha c}\geq 0) \ ; \tag{2.7b}$$

$$\lim_{R_\alpha\to\infty}\chi^J_{\alpha c}(R_\alpha)=0 \quad (\text{for } k_{\alpha c}<0) \ . \tag{2.8}$$

The wave vector $k_{\alpha c}$ is defined by

$$\frac{\hbar^2 k_{\alpha c}^2}{2\mu_\alpha} = E - \epsilon_{n_A} - \epsilon_{n_{BC}} , \tag{2.9}$$

where E is the total energy of the system (measured relative to particles A and BC at rest in their ground states), ϵ_{n_A} and $\epsilon_{n_{BC}}$ are, respectively, the energies of the isolated systems A and BC in states ψ_{n_A} and $\psi_{n_{BC}}$; $E - E_{n_A} - E_{n_{BC}}$ is therefore just the collision energy of A and BC. The quantity μ_α is the reduced mass of A and BC, and c_0 designates the initial channel of the system before collision.

Equations (2.7)—together with the parallel relations for arrangement β—define the partial $\underline{S}^J$ and $\underline{K}^J$ matrices which are related by

$$\underline{S}^J = (\underline{1} + i\underline{K}^J)(\underline{1} - i\underline{K}^J) . \tag{2.10}$$

B. Derivation of the R matrix

According to the Wigner theory (see, e.g., Lane and Thomas,[24] Breit,[25] and Gerratt and Wilson[26]), the interacting ABC system is surrounded by a hypersurface Σ defined by *channel radii* $R_\alpha = d_\alpha$ and $R_\beta = d_\beta$. The radii are chosen large enough so that on Σ we have for the channel functions

$$(\phi^J_{\gamma c} \mid \phi^{J'}_{\gamma' c'}) = \delta_{JJ'}\delta_{\gamma\gamma'}\delta_{cc'} . \tag{2.11}$$

The integral is evaluated either in the coordinates pertaining to $\phi^{J'}_{\gamma' c'}$ with $R_{\gamma'}$ fixed at $d_{\gamma'}$, or in ϕ^J_γ coordinates (if different from those of $\phi^{J'}_{\gamma' c'}$) with R_γ fixed at d_γ.

It turns out that, due to unwanted surface terms, the Hamiltonian operator when restricted to the region within Σ is no longer Hermitian. This deficiency is overcome by adding to H an operator L_b due to Bloch[27] and given by

$$L_b = \sum_J \sum_{\gamma,c} \mid \phi^J_{\gamma c}) \frac{\hbar^2}{2\mu_\gamma} \delta(R_\gamma - d_\gamma) \times \left[\frac{1}{R_\gamma} \frac{\partial}{\partial R_\gamma} R_\gamma - b^J_{\gamma c} \right] (\phi^J_{\gamma c} \mid . \tag{2.12}$$

In this expression, the sums are over all partial waves and all channels in all arrangements. The quantities R_γ, d_γ, and μ_γ are, respectively, the relevant nuclear radial coordinate, channel radius, and reduced mass for arrangement γ. The round brackets $\mid \phi^J_{\gamma c})$ and $(\phi^J_{\gamma c} \mid$ denote eventual integration over all coordinates except R_γ. The angular bra or ket brackets will be reserved for complete integration over all coordinates. The Bloch operator contains the arbitrary real parameters $b^J_{\gamma c}$ whose role will become clear shortly. This operator is clearly a surface operator as can be seen by the presence of the δ function, whose purpose is to cancel out the surface contributions when radial integrations are restricted to $0 \le R_\gamma \le d_\gamma$.

The Schrödinger equation to be solved within Σ may therefore be written as

$$(H + L_b - E) = L_b \Psi . \tag{2.13}$$

Since $H + L_b$ is now Hermitian, the operator $H + L_b - E$ may be inverted to give

$$\Psi = (H + L_b - E)^{-1} L_b \Psi .$$

From this equation we project out the radial component of Ψ at Σ for a particular channel:

$$\begin{aligned}
(\phi^J_{\alpha c} \mid \Psi\rangle_{d_\alpha} &= (\phi^J_{\alpha c} \mid (H + L_b - E)^{-1} L_b \Psi\rangle_{d_\alpha} \\
&= \sum_{\gamma, c'} (\phi^J_{\alpha c} \mid (H + L_b - E)^{-1} \mid \phi^J_{\gamma c'}) \\
&\qquad \times (\phi^J_{\gamma c'} \mid L_b \Psi\rangle \\
&= \sum_{\gamma, c'} R^J_{\alpha c;\gamma c'} \frac{\hbar^2}{2\mu_\gamma} \left[\frac{1}{R_\gamma} \frac{\partial}{\partial R_\gamma} \{ R_\gamma (\phi_{\gamma c'} \mid \Psi\rangle \} \right. \\
&\qquad \left. - b^J_{\gamma c'} (\phi^J_{\gamma c'} \mid \Psi\rangle \right]_{d_\gamma} .
\end{aligned} \tag{2.14}$$

This equation defines the R matrix as

$$R^J_{\alpha c;\gamma c'} = (\phi^J_{\alpha c} \mid (H + L_b - E)^{-1} \mid \phi^J_{\gamma c'}) . \tag{2.15}$$

In (2.14) it can be seen that the R matrix yields the relationship between the radial components and their derivatives at the surface Σ. Once determined, this relationship is all that is required to continue the propagation of Ψ in the outer region from Σ to the asymptotic limit.

In order to obtain the R matrix in more tractable form, it is necessary to solve the eigenvalue equation

$$(H + L_b - \epsilon_\lambda)\omega_\lambda = 0 . \tag{2.16}$$

This equation is equivalent to the solution of

$$(H - \epsilon_\lambda)\omega_\lambda = 0$$

subject to the boundary conditions

$$\left[\frac{\partial}{\partial R_\gamma} \{ R_\gamma (\phi^J_{\gamma c} \mid \omega_\lambda\rangle \} - b^J_{\gamma c} (\phi^J_{\gamma c} \mid \omega_\lambda\rangle \right]_{d_\gamma} = 0 \tag{2.17}$$

for all arrangements γ and channels c. From this it can be see that the parameters $b^J_{\gamma c}$ of the Bloch operator play the role of fixed logarithmic derivatives of the radial components of ω_λ at the boundary surface.

Having solved (2.16), we may represent the inverse $(H + L_b - E)^{-1}$ as

$$(H + L_b - E)^{-1} = \sum_\lambda \frac{\mid \omega_\lambda\rangle\langle\omega_\lambda \mid}{\epsilon_\lambda - E} ,$$

and so

$$R^J_{\alpha c;\gamma c'} = \sum_\lambda \frac{(\phi^J_{\alpha c} \mid \omega_\lambda\rangle_{d_\alpha} \langle\omega_\lambda \mid \phi^J_{\gamma c'})_{d_\gamma}}{\epsilon_\lambda - E} . \tag{2.18}$$

[In the nuclear physics literature it is common to define $g^J_{\alpha c\lambda} = (\hbar^2/2\mu_\alpha)^{1/2}(\phi^J_{\alpha c} \mid \omega_\lambda\rangle_{d_\alpha}$ and the R matrix as $\sum_\lambda g^J_{\alpha c\lambda} g^J_{\gamma c'\lambda}/(\epsilon_\lambda - E)$. Equation (2.14) then becomes a relationship between $g^J_{\gamma c} = (\hbar^2/2\mu_\gamma)^{1/2}(\phi^J_{\gamma c} \mid \Psi\rangle_{d_\gamma}$ but *without* the factor $(\hbar^2/2\mu_\gamma)$ on the right-hand side.] Thus having solved (2.16), the R matrix is constructed using (2.18). This is then used in (2.14) to continue the solution of the Schrödinger equation in the outer region. This is accomplished as follows. Outside Σ we may write the partial-wave function in the form of an expansion in channel functions:

$$\Psi^J_{\gamma^0 c^0} = \sum_{\gamma, c} \frac{1}{R_\gamma} U^J_{\gamma^0 c^0;\gamma c}(R_\gamma)\phi^J_{\gamma c} , \tag{2.19}$$

in which $(\gamma^0 c^0)$ designates the state of the system before collision. It should be recalled from (2.11) that the $\phi^J_{\gamma c}$ constitute an orthonormal set in this region. When $R_\gamma = d_\gamma$ it is clear that $R_\gamma^{-1} U^J_{\gamma^0 c^0;\gamma c}(R_\gamma)$ is just the radial component $\sim (\phi^J_{\gamma c} \mid \Psi\rangle_{d_\gamma}$. The Hamiltonian is given by

$$H = -\frac{\hbar^2}{2\mu_\gamma}\frac{1}{R_\gamma^2}\frac{\partial}{\partial R_\gamma}\left[R_\gamma^2 \frac{\partial}{\partial R_\gamma}\right] + \frac{\hbar^2 \hat{L}_\gamma^2}{2\mu_\gamma R_\gamma^2} + H_\gamma + V \tag{2.20}$$

in which the H_γ is the Hamiltonian for the internal motions of the two relevant isolated particles in that arrangement. The form of H is the same for all arrangements. Substituting (2.19) and (2.20) into the Schrödinger equation $(H - E)\Psi = 0$, multiplying through by $(\phi^J_{ac} \mid$ and integrating, we obtain the following set of coupled differential equations:

$$\begin{aligned}\left[\frac{d^2}{dR_\alpha^2} - \frac{L_\alpha(L_\alpha+1)}{R_\alpha^2} - V^J_{ac;ac}(R_\alpha) + k^2_{ac}\right] U^J_{\gamma^0 c^0;ac}(R_\alpha) \\ = \sum_{c'\,(\neq c)} V^J_{ac;ac'}(R_\alpha) U_{\gamma^0 c^0;ac'}(R_\alpha) \\ (d_\alpha \le R_\alpha \le \infty)\end{aligned} \tag{2.21}$$

in which

$$V^J_{ac;ac'}(R_\alpha) = \frac{-2\mu_\alpha}{\hbar^2}(\phi^J_{ac} \mid V \mid \phi^J_{ac'}) . \tag{2.22}$$

It is important to note that these equations only involve channels within a given arrangement. This is a direct consequence of our choice of a channel radius d_α such that the orthogonality conditions (2.11) hold, and the fact that

$$(\phi^J_{\alpha c} \mid V \mid \phi^J_{\gamma c'}) = 0$$

for $\gamma \neq \alpha$ outside Σ. Equations (2.21) thus represent no more than elastic and inelastic scattering within a given arrangement, and can be integrated from $R_\alpha = d_\alpha$ to the asymptotic region using standard procedures such as the Gordon algorithm[28] or the R-matrix propagator method.[29]

III. R-MATRIX THEORY OF CHARGE TRANSFER: ONE-ELECTRON SYSTEMS

In this section we apply the foregoing theory to the process

$$A + B^+ \rightarrow A^+ + B , \tag{3.1}$$

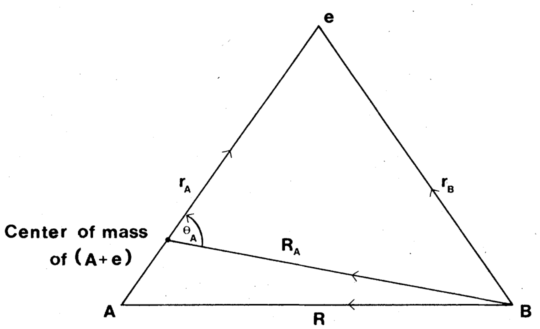

FIG. 1. Coordinate system for $A + B^+$. Arrangement α.

where A and B are both one-electron atoms. We define arrangement α when the electron is associated with nucleus A, and arrangement β when the electron is associated with B. The coordinate systems corresponding to the two arrangements are shown in Figs. 1 and 2, respectively. The Hamiltonian in space-fixed coordinates, with the center of mass of the whole system separated out, is given in α coordinates by

$$H = \frac{-\hbar^2}{2m_A}\nabla^2_{r_A} - \frac{\hbar^2}{2\mu_A}\nabla^2_{R_A} + V , \tag{3.2}$$

where

$$m_A = \frac{mM_A}{m + M_A} , \tag{3.3}$$

the reduced mass of the electron for arrangement α, m being the mass of the isolated electron and M_A that of nucleus A;

$$\mu_A = \frac{M_B(m + M_A)}{M_B + M_A + m} \tag{3.4}$$

is the reduced mass of B^+ and $(A + e)$. The potential V is given by

$$\begin{aligned} V &= \frac{e^2}{4\pi\epsilon_0}\left[\frac{-Z_A}{r_A} - \frac{Z_B}{r_B} + \frac{Z_A Z_B}{R}\right] \\ &= \frac{e^2}{4\pi\epsilon_0}\left[\frac{-Z_A}{r_A} - \frac{Z_B}{|\vec{\mathrm{R}}_A - a\vec{\mathrm{r}}_A|} + \frac{Z_A Z_B}{|\vec{\mathrm{R}}_A + \gamma_A \vec{\mathrm{r}}_A|}\right] \end{aligned} \tag{3.5}$$

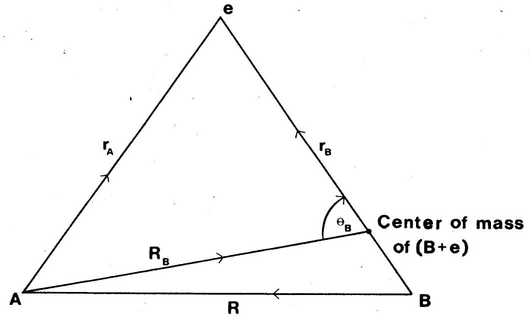

FIG. 2. Coordinate system for $A^+ + B$. Arrangement β.

in the $(\vec{r}_A,\vec{R}_A)$ coordinates pertinent to this arrangement. In this last equation,

$$a=\left[1-\frac{m}{M_A+m}\right]=1-\gamma_A \tag{3.6}$$

so that

$$\gamma_A=m/(M_A+m). \tag{3.7}$$

Similar definitions go through for arrangement β.

We begin by utilizing as channel functions the eigenfunctions of the isolated atoms: $\phi_{Anlm}(\vec{r}_A)$ and $\phi_{Bn'l'm'}(\vec{r}_B)$. This we shall term a "valence-bond basis" and is obviously suitable for high-energy collisions. Later in this paper we extend the energy range of the theory by employing more general atomic functions which are allowed to deform during collisions.

The central task is to select a basis set in terms of which the R-matrix eigenfunctions ω_λ, Eq. (2.16), may be expanded, to calculate the resulting matrix elements of the Hamiltonian, form the secular equation in the basis, and determine the corresponding eigenvalues and eigenfunctions.

For this purpose we choose the following set of basis functions:

$$\xi_A^{JM}(n,l,L_A,p_A;\vec{r}_A,\vec{R}_A)=\frac{1}{R_A}f_{p_A}^{(nlL_A)}(R_A)\phi^J_{AnlL_A}(r_A,\Omega_A,\omega_A) \tag{3.8}$$

and

$$\xi_B^{JM}(n',l',L_B,q_B;\vec{r}_B,\vec{R}_B)=\frac{1}{R_B}f_{q_B}^{(n'l'L_B)}(R_B)\phi^J_{Bn'l'L_B}(r_B,\Omega_B,\omega_B)\;.$$

The functions $R_A^{-1}f_{p_A}^{(nlL_A)}(R_A)$ and $R_B^{-1}f_{q_B}^{(n'l'L_B)}(R_B)$ are nuclear radial basis functions. The channel functions $\phi^J_A\cdots$ and $\phi^J_B\cdots$ are given by

$$\begin{aligned}\phi^J_{AnlL_A}(r_A,\Omega_A,\omega_A)&=R_{Anl}(r_A)\mathscr{Y}_{JM}\{(L_A,l)J;\Omega_A,\omega_A\}\;,\\ \phi^J_{Bn'l'L_B}(r_B,\Omega_B,\omega_B)&=R_{Bn'l'}(r_B)\mathscr{Y}_{JM}\{(L_B,l')J;\Omega_B,\omega_B\}\;.\end{aligned} \tag{3.9}$$

Here the $R_{Anl}(r_A)$ and $R_{Bn'l'}(r_B)$ are the radial parts of the relevant atomic orbitals, the angular parts of which are coupled together with the angular parts of the nuclear factors by the functions $\mathscr{Y}_{JM}\{\cdots\}$ to form the overall resultant J: $(L_A,l)J$ in the one case, $(L_B,l')J$ in the other. The two channel radii for the R matrix, d_A and d_B, are taken large enough so that for $R_A\ge d_A$ or $R_B\ge d_B$, the channel functions are orthogonal and noninteracting,

$$\begin{aligned}(\phi^J_{Ac}\,|\,\phi^J_{Bc'})&=0\;,\\ (\phi^J_{Ac}\,|\,V_I\,|\,\phi^J_{Bc'})&=0\;,\end{aligned} \tag{3.10}$$

for all c and c', where these stand for the quantum numbers (nlL_A) and $(n'l'L_B)$, respectively. The integrations are carried out, either in $(\vec{r}_A,\vec{R}_A)$ coordinates with $R_A=d_A$, or in $(\vec{r}_B,\vec{R}_B)$ coordinates with $R_B=d_B$. The interaction potential V_I for arrangement α is given by

$$V_I=\frac{e^2}{4\pi\epsilon_0}\left[\frac{-Z_B}{|\vec{R}_A-a\vec{r}_A|}+\frac{Z_AZ_B}{|\vec{R}_A+\gamma_A\vec{r}_A|}\right] \tag{3.11}$$

with a similar definition for arrangement β. [The practical evaluation of integrals such as those in (3.10) within Σ is described in Sec. V.]

In order to ensure good convergence for the R-matrix eigenfunctions, the f_p and f_q basis functions should approximate as closely as possible the actual eigenfunctions in the given energy range. For this purpose we consider the electronic potential-energy curves determined by the atomic orbitals $\phi_{Anlm}(\vec{r}_A)$ and $\phi_{Bn'l'm'}(\vec{r}_B)$ occurring in (3.9), $W_{Anl}(R_A)$ and $W_{Bn'l'}(R_B)$, respectively, and determine the corresponding eigenfunctions in the interval $(0,d_A)$ or $(0,d_B)$ in the appropriate range of energies. The distinction between the internuclear distance R and nucleus—to—center-of-mass distances R_A and R_B can be dropped for this purpose. Thus the f_p's and f_q's are determined as eigenfunctions of the following equations:

$$\left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dR^2}+W_{Anl}(R)-\frac{\hbar^2L_A^*(L_A^*+1)}{2\mu R^2}+L_R-\epsilon_{p_A}\right]\times f_{p_A}^{(nlL_A^*)}(R)=0\quad(0\le R\le d_A) \tag{3.12}$$

with a parallel definition for the f_q's. The radial Bloch operator is given by

$$L_R=\frac{\hbar^2}{2\mu}\delta(R-d_A)\left[\frac{d}{dR}-b\right]\;, \tag{3.13}$$

and serves to impose the boundary condition

$$\left[\frac{df_{p_A}^{(nlL_A^*)}}{dR}-bf_{p_A}^{(nlL_A^*)}\right]_{d_A}=0 \tag{3.14}$$

upon the radial eigenfunctions. The $f_{p_A}^{(nlL_A^*)}$ and $f_{q_B}^{(n'l'L_B^*)}$ basis functions may thus be regarded as suitably "distorted waves" for the R-matrix calculation.

The presence of the centrifugal term $\hbar^2L_A^*(L_A^*+1)/2\mu R$ in (3.12) should be noted. The inclusion of a term of this type is essential if the distorted-wave basis functions are to display the correct behavior, particularly at large values of the angular momentum L_A. However, the solution of (3.12) for every value of L_A would be too time consuming, so instead the parameter L_A^* is used where this is fixed at some suitable value. In actual practice one sets $L_A^*=J$, for it can be argued that since for a given channel, L_A may assume all values between $|J-l|$ and $J+l$, the most commonly occurring value of L_A is J.[26]

Equation (3.12) is itself solved by expanding the f_p's in a set of "primitive sine functions":

$$f_{p_A}^{(nlL_A^*)}(R_A)=\sum_{m=m_0}^{M} C_{p_A m}^{(nlL_A^*)}\sin\left[(m+\tfrac{1}{2})\pi\frac{R}{d_A}\right]. \tag{3.15}$$

This choice of sine functions corresponds to setting $b=0$ in (3.14)—i.e., to imposing a zero derivative on the eigenfunctions of (3.12) at $R_A=d_A$. This particular set has been used very successfully in R-matrix calculations of atom-molecule scattering.[26,30] [An alternative set of primitive sine functions with an arbitrary (nonzero) value for the derivative at $R_A=d_A$ is $(bd_A/2m\pi)\sin(2mR_A/d_A)$.] The sine functions form an orthonormal set in the interval $(0,d_A)$. The minimum value of m, m_0, is chosen so that the resulting eigenfunctions all possess the minimum number of nodes to cover the required energy range. Thus for a reduced mass μ equivalent to the mass of a proton confined within a channel radius $d_A=10$ bohr=5.3 Å, $m_0 \simeq 1100$ at 1 keV, and ~200 such sine functions would span another 1 keV of energy. The situation is illustrated in Fig. 3.

The R-matrix eigenfunctions for each partial wave J are expanded in the basis set (3.8):

$$\omega_\lambda^J=\sum_{n,l,L_A}\sum_{p_A} C_{p_A\lambda}^{(nlL_A)}\xi_A^{JM}(n,l,L_A,p_A;\vec{r}_A,\vec{R}_A)+\sum_{n',l',L_B}\sum_{q_B} C_{q_B\lambda}^{(n'l'L_B)}\xi_B^{JM}(n',l',L_B,q_B;\vec{r}_B,\vec{R}_B), \tag{3.16}$$

the expansion including basis functions from both arrangements. The two sets of terms in (3.16) are of course nonorthogonal, but this feature is essential for fast convergence of the series and causes no particular additional complication. The remaining task is the determination of the $C_{p_A\lambda}^{(\dots)}$ and $C_{q_B\lambda}^{(\dots)}$ coefficients and the associated eigenvalues ϵ_λ. This is achieved by substituting (3.16) into the Schrödinger equation (2.16), multiplying through by one of the basis functions, and integrating. This yields a secular equation of the form

$$\sum_{\rho}\langle \xi_\sigma^{JM}|(H+L_b-\epsilon_\lambda)|\xi_\rho^{JM}\rangle C_{\rho\lambda}=0, \tag{3.17}$$

in which the indices ρ and σ stand for the set (n,l,L_A,p_A) or (n',l',L_B,q_B). It is therefore necessary to calculate the matrix elements

$$\langle \xi_\sigma^{JM}|H|\xi_\rho^{JM}\rangle,\quad \langle \xi_\sigma^{JM}|\xi_\rho^{JM}\rangle$$

between the basis functions (3.8). When ρ and σ both refer to the same arrangement this task is more or less trivial. Consequently the central issue is the determination of such matrix elements between different arrangements—and this is the subject of Sec. V.

The R matrix is given by expression (2.18), the quantities $(\phi_{\alpha c}^J|\omega_\lambda^J\rangle_{d_\alpha}$ occurring in it now being given simply by

$$(\phi_{\alpha nlL_A}^J|\omega_\lambda^J\rangle=\sum_{p_A} C_{p_A\lambda}^{(nlL_A)}\frac{1}{d_A}f_{p_A}^{(nlL_A)}(d_A) \tag{3.18}$$

and similarly for $(\phi_{\beta n'l'L_B}^J|\omega_\lambda^J\rangle$. The rate of convergence of the sum over λ—which is now finite—in (2.18) is crucial for the reliability of the theory. In earlier applications it has been found that this summation usually does not in fact converge well, and that it is necessary to add to (2.18) a correction due to Buttle.[31] While this correction frequently improves matters considerably,[26] the essential reason for the slow convergence of the λ summation in the R matrix is due to the imposition of the boundary condition (3.14): Since the number of basis functions is finite, any linear combination of them will also satisfy the same condition at d_A or d_B, i.e., possess zero derivative. The true wave function almost certainly does not have a zero derivative at these points, and hence the R matrix converges slowly.

This problem is overcome as follows.[30] The radial eigenfunctions of Eq. (3.12) are determined in an interval $(0,d_A+\delta_A)$, where $\delta_A=10^{-1}-10^{-2}$ Å. These functions are then utilized in the correct range $(0,d_A)$, but now possess arbitrary derivatives at the boundary and are consequently very slightly nonorthogonal. This small injection of nonorthogonality into the radial basis functions has been found immediately to lead to rapid convergence of the R matrix, and a Buttle correction is no longer necessary. The calculations now remain stable in all regions: both far from and close to resonances. The extent of the nonorthogonality thus introduced is strictly controllable: If δ_A is set equal to zero, the basis set becomes orthogonal once more.

The final form of the R matrix is displayed in Fig. 4, where it is divided into four blocks which might be

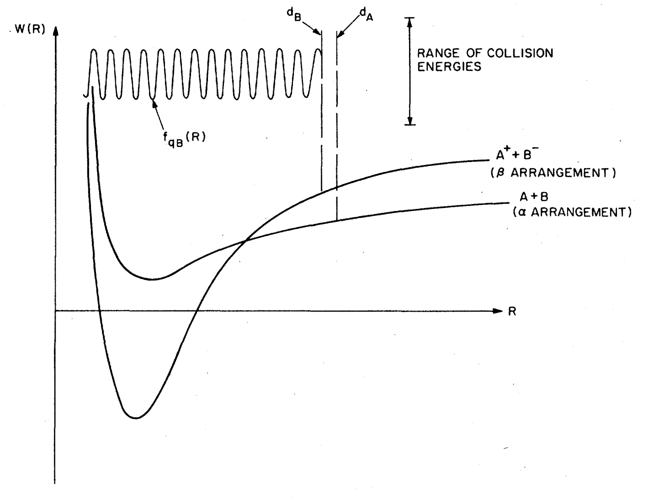

FIG. 3. Illustration of radial basis functions.

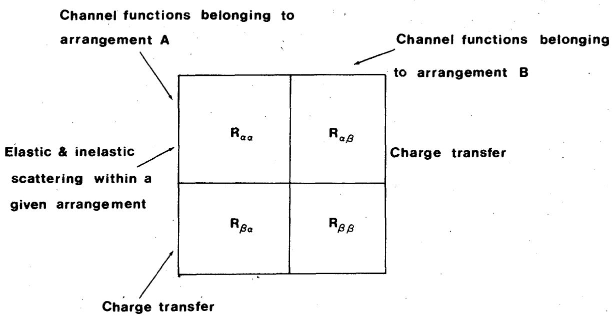

FIG. 4. Form of the R-matrix for charge transfer.

termed $(\alpha\alpha)$, $(\alpha\beta)$, $(\beta\alpha)$, and $(\beta\beta)$. The $(\alpha\alpha)$ and $(\beta\beta)$ blocks give rise to elastic and inelastic scattering within a given arrangement, while the $(\alpha\beta)$ and $(\beta\alpha)$ blocks are responsible for charge transfer.

In the region outside Σ the partial-wave function may be written as an expansion in channel functions in the form

$$\Psi^J_{\gamma^0c^0}=\sum_c \frac{1}{R_A}U^J_{\gamma^0c^0;Ac}(R_A)\phi^J_{Ac}(r_A,\Omega_A,\omega_A)$$
$$+\sum_{c'}\frac{1}{R_B}U^J_{\gamma^0c^0;Bc'}(R_B)\phi^J_{Bc'}(r_B,\Omega_B,\omega_B) \quad (3.19)$$

in which γ^0 is the initial arrangement (α or β), and c^0 stands for the initial channel quantum numbers pertaining to that arrangement. Substituting this expression into the basic R-matrix relation (2.14) and taking into account the orthogonality relations (3.10), we obtain

$$U^J_{\gamma^0c^0;Ac}(d_A)$$
$$=\sum_{\gamma,c''}\frac{\hbar^2}{2\mu_\gamma}R^J_{Ac;\gamma c''}$$
$$\times\left[\frac{\partial}{\partial R_\gamma}U^J_{\gamma^0c^0;\gamma c''}-b^J_{\gamma c''}U^J_{\gamma^0c^0;\gamma c''}\right]_{d_\gamma}, \quad (3.20)$$

and similarly for $U^J_{\gamma^0c^0;Bc'}(d_B)$. This equation relates all the radial amplitudes U^J in all arrangements to their derivatives at Σ. These relationships can be used to initiate the integration of the coupled differential equations satisfied by the U^J's:

$$\left[\frac{d^2}{dR_A^2}-\frac{L_A(L_A+1)}{R_A^2}-V_I(Ac;Ac)+k_{Ac}^2\right]U^J_{\gamma^0c^0;Ac}(R_A)$$
$$=\sum_{c''\,(\neq c)}V_I(Ac;Ac'')U^J_{\gamma^0c^0;Ac''}(R_A)$$
$$(d_A\le R_A\le\infty) \quad (3.21)$$

with a parallel set for the $U^J_{\gamma^0c^0;Bc''}$. The potential matrix elements are defined as

$$V_I(Ac;Ac'')=\frac{-2\mu_A}{\hbar^2}(\phi^J_{Ac}\mid V_I\mid\phi^J_{Ac''}) \quad (3.22)$$

[cf. Eq. (3.11)], and similarly for arrangement β. Thus the solutions in the outer region involve functions belonging to one arrangement or the other. Charge transfer—or the transmission of flux from one arrangement to another—can only occur within Σ and is then transported to the asymptotic region by means of Eqs. (3.20) and the solutions of (3.21).

The absolute amplitudes of these solutions are not determined by the R-matrix relations (3.20), but are fixed by the boundary conditions imposed:

$$U^J_{\gamma^0c^0;Ac}(R_A)\sim-\frac{1}{2ik_{Ac}^{1/2}}\left(e^{-i(k_{Ac}R_A-L_A\pi/2)}\delta_{\gamma^0A}\delta_{c^0c}-S^J_{Ac;\gamma^0c^0}e^{i(k_{Ac}R_A-L_A\pi/2)}\right) \quad (3.23a)$$
$$\simeq\frac{1}{k_{Ac}^{1/2}}[\sin(k_{Ac}R_A-\tfrac{1}{2}L_A\pi)+K^J_{Ac;\gamma^0c^0}\cos(k_{Ac}R_A-\tfrac{1}{2}L_A\pi)]\ \text{ as } R_A\rightarrow\infty\ \ (\text{for } k_{Ac}\ge 0)\,. \quad (3.23b)$$

The wave vector k_{Ac} is defined by the relation

$$\frac{\hbar^2k_{Ac}^2}{2\mu_A}=E-\epsilon_{Anl}\,, \quad (3.24)$$

where ϵ_{Anl} is the energy of the isolated atom A. The final cross section is given by

$$\sigma_{\gamma^0n^0l^0\rightarrow Anl}=\frac{\pi}{k_{Anl}^2(2l+1)}\sum_{J=0}^{\infty}(2J+1)\sum_{L_A=|J-l|}^{J+l}\sum_{L^0=|J-l^0|}^{J+l^0}|\delta_{\gamma^0A}\delta_{n^0l^0;nl}-S^J_{AnlL_A;\gamma^0n^0l^0L^0}|^2\,, \quad (3.25)$$

in which the full designation of arrangements and channels has been used.

In the keV energy range, $\sim10^4$ partial waves are required in (3.25) to attain convergence. However, the variation of the cross section with J is smooth and it is unnecessary to calculate every term. For $J\geq 100$, it is sufficient to calculate every 100th contribution, say, and to interpolate in between.[16,32]

However, it should be pointed out that for high J, the diagonal elements of the matrix in (3.17) dominate. The eigenvalues ϵ_λ and eigenvectors ω_λ can therefore be obtained by means of first-, second-, etc., order perturbation theory. Complete diagonalization of $H+L_b$ becomes unnecessary. Several alternative schemes are possible, of which one is pursued in Sec. IV. This topic will be taken up in more detail in subsequent publications.

Equations (3.21) involve only a single arrangement and consequently include few coupled channels. They therefore remain reasonably tractable at all J.

IV. CONNECTION WITH OTHER WORK: THE TWO-STATE APPROXIMATION AT HIGH ENERGIES

The purpose of the present section is to show how the R-matrix formalism for charge transfer reduces to a form which is essentially that obtained by Oppenheimer[1] and by Brinkman and Kramers.[2] This derivation serves also to highlight the essential mechanism by which charge transfer occurs.

We begin by assuming that the channel radii d_A and d_B are sufficiently large so that the interaction potential V_I is zero outside Σ in both arrangements. The partial-wave function in the outer region is now that corresponding to a free wave and is given—except for an amplitude factor—by

$$U_{\gamma^0c^0;\gamma c''}\simeq\frac{i}{2}(I_{\gamma c''}\delta_{\gamma^0\gamma}\delta_{c^0c''}-O_{\gamma c''}S_{\gamma c'';\gamma^0c^0}) , \tag{4.1}$$

in which $I_{\gamma c''}$ is an incoming wave

$$I_{\gamma c''}=k_{\gamma c''}^{-1/2}e^{-i(k_{\gamma c''}R_\gamma-l_\gamma\pi/2)} ,$$

$O_{\gamma c''}$ is a similar outgoing wave

$$O_{\gamma c''}=k_{\gamma c''}^{-1/2}e^{i(k_{\gamma c''}R_\gamma-l_\gamma\pi/2)} ,$$

and $S_{\gamma c'';\gamma^0c^0}$ is an element of the S matrix. Substituting (4.1) into the R-matrix relationship (3.20) we obtain for the S matrix

$$\underline{S}=\underline{O}^{-1}(\mathbb{1}-\underline{R}\underline{L})^{-1}(\mathbb{1}-\underline{R}\underline{L}^*)\underline{I} . \tag{4.2}$$

In this expression $\underline{O}$ and $\underline{I}$ are diagonal matrices composed, respectively, of the outgoing and incoming waves $\underline{O}_{\gamma c'}$ and $\underline{I}_{\gamma c''}$. $\underline{L}$ is given by

$$\underline{L}=\underline{O}'\underline{O}^{-1}-\underline{B} ,$$

where the prime on $\underline{O}$ indicates differentiation with respect to the scattering coordinate R_γ taken at the channel radius $R_\gamma=d_\gamma$, and $\underline{B}$ is a diagonal matrix formed from the Bloch parameters $b_{\gamma c}$. The R matrix is here given by [see parenthetical note following Eq. (2.18)]

$$R_{\alpha c;\gamma c'}=\frac{\hbar^2}{2\mu}\sum_\lambda\frac{(\phi_{\alpha c}\,|\,\omega_\lambda\rangle_{d_\alpha}\langle\omega_\lambda\,|\,\phi_{\gamma c'})_{d_\gamma}}{\epsilon_\lambda-E} , \tag{4.3}$$

where for simplicity we ignore the dependence of the reduced masses upon the arrangement.

We now consider the simplest case of hydrogen-to-proton charge transfer at high energies:

$$\mathrm{H}+\mathrm{H}^+\rightarrow\mathrm{H}^++\mathrm{H} ,$$

and take into account just a single channel within each arrangement α and β, i.e., we consider just the channels associated with the $1s_A$ or $1s_B$ states on each H atom. The R and S matrices now reduce to 2×2 matrices, labeled simply by the arrangement, α or β. Equation (4.2) may be evaluated explicitly to give

$$S_{\alpha\beta}=2i^{(l_\alpha+l_\beta+1)}(k_\alpha k_\beta)^{1/2}\frac{1}{D}R_{\alpha\beta}e^{i(k_\alpha d_A+k_\beta d_B)} , \tag{4.4}$$

where D is the determinant of the matrix $(\underline{\mathbb{1}}-\underline{R}\underline{L})$:

$$D=(1-R_{\alpha\alpha}L_\alpha)(1-R_{\beta\beta}L_\beta)-R_{\alpha\beta}^2L_\alpha L_\beta . \tag{4.5}$$

The element $S_{\alpha\beta}$ of $\underline{S}$ is thus directly proportional to $R_{\alpha\beta}$, and consequently we may concentrate attention upon this latter quantity.

The R-matrix basis functions are of the form

$$\xi_{\lambda A}=\psi_{1s_A}(r_A)\chi_{\lambda A}(\vec{R}_A)$$

and

$$\xi_{\mu B}=\psi_{1s_B}(r_B)\chi_{\mu B}(\vec{R}_B) ,$$

which we expand in partial-wave form as follows:

$$\begin{aligned}\xi_{\lambda A}&=\psi_{1s_A}(r_A)\sum_{l_\alpha}\chi_{\lambda A}^{(l_\alpha)}(R_A)P_{l_\alpha}(\cos\bar{\theta}_A) ,\\ \xi_{\mu B}&=\psi_{1s_B}(r_B)\sum_{l_\beta}\chi_{\lambda B}^{(l_\beta)}(R_B)P_{l_\beta}(\cos\bar{\theta}_B) ,\end{aligned} \tag{4.6}$$

where $\bar{\theta}_A$ is the angle between $\vec{R}_A$ and the space-fixed Z axis, and similarly for $\vec{R}_B$ and $\bar{\theta}_B$.

For each pair of partial waves

$$\begin{aligned}\xi_{\lambda A}^{(l_\alpha)}&=\psi_{1s_A}(r_A)\chi_{\lambda A}^{(l_\alpha)}(R_A)P_{l_\alpha}(\cos\bar{\theta}_A) ,\\ \xi_{\mu B}^{(l_\beta)}&=\psi_{1s_B}(r_B)\chi_{\mu B}^{(l_\beta)}(R_B)P_{l_\beta}(\cos\bar{\theta}_B) ,\end{aligned} \tag{4.7}$$

it is necessary to form the Hamiltonian matrix

$$(V_{AB})_{\lambda l_\alpha;\mu l_\beta}=\langle\xi_{\lambda A}^{(l_\alpha)}\,|H\,|\,\xi_{\mu B}^{(l_\beta)}\rangle \tag{4.8}$$

within Σ, and to diagonalize it in order to obtain the eigenfunctions and associated eigenvalues. For this purpose we assume that the radial functions $\chi_{\lambda A}^{(l_\alpha)}(R_A)$ already satisfy the equation

$$\left[\frac{1}{R_A^2}\frac{d}{dR_A}\left[R_A^2\frac{d\chi_{\lambda A}^{(l_\alpha)}}{dR_A}\right]-\left[\frac{l_\alpha(l_\alpha+1)}{R_A^2}+V_I(1s_A;1s_A)\right.\right.$$
$$\left.\left.-\,\epsilon_{AA}^{(l_\alpha)}\right]\right]\chi_{\lambda A}^{(l_\alpha)}(R_A)=0 \tag{4.9}$$

with boundary condition

$$\left[\frac{d\chi_{\lambda A}^{(l_\alpha)}}{dR_A}\right]_{d_A}=0 , \tag{4.10}$$

i.e., with Bloch parameter b equal to zero. The potential $V_I(1s_A;1s_A)$ occurring in (4.9) is the interaction potential for this arrangement. Similar considerations apply for arrangement β. This means that the parts

$$(V_{AA})_{\lambda l_\alpha;\lambda' l'_\alpha} \quad\text{and}\quad (V_{BB})_{\mu l_\beta;\mu' l'_\beta}$$

of the Hamiltonian matrix are already diagonal with elements $\epsilon_{\lambda A}^{(l_\alpha)}$ and $\epsilon_{\mu B}^{(l_\beta)}$, respectively.

The remainder of the Hamiltonian matrix is diagonalized by means of first-order perturbation theory. This procedure yields two sets of functions:

$$\omega_{\lambda A}^{(l_\alpha)}=\xi_{\lambda A}^{(l_\alpha)}+\sum_{\mu,l_\beta}\frac{(V_{BA})_{\mu l_\beta;\lambda l_\alpha}}{\epsilon_{\lambda A}^{(l_\alpha)}-\epsilon_{\mu B}^{(l_\beta)}}\xi_{\mu B}^{(l_\beta)}$$

and

$$\omega_{\mu B}^{(l_\beta)}=\xi_{\mu B}^{(l_\beta)}+\sum_{\lambda,l_\alpha}\frac{(V_{AB})_{\lambda l_\alpha;\mu l_\beta}}{\epsilon_{\mu B}^{(l_\beta)}-\epsilon_{\lambda A}^{(l_\alpha)}}\xi_{\lambda A}^{(l_\alpha)} . \tag{4.11}$$

The nonorthogonality between the two sets of basis functions $\xi_{\lambda A}^{(l_\alpha)}$ and $\xi_{\mu B}^{(l_\beta)}$ has been neglected although even if it had not, there would be no material difference in the result beyond an increase in complexity. To this order of perturbation, the eigenvalues $\epsilon_{\lambda A}^{(l_\alpha)},\epsilon_{\mu B}^{(l_\beta)}$ remain unchanged. Substituting (4.11) into (4.3) we obtain after a little manipulation

$$R_{\alpha\beta}^{(l_\alpha l_\beta)}=-4[(2l_\alpha+1)(2l_\beta+1)]^{-1}$$
$$\times\sum_{\lambda,\mu}\frac{\chi_{\lambda A}^{(l_\alpha)}(d_A)(V_{AB})_{\lambda l_\alpha;\mu l_\beta}\chi_{\mu B}^{(l_\beta)}(d_B)}{(\epsilon_{\lambda A}^{(l_\alpha)}-E)(\epsilon_{\mu B}^{(l_\beta)}-E)} . \tag{4.12}$$

In order to evaluate this expression explicitly, we introduce the partial-wave Green's function corresponding to Eq. (4.9). In terms of the eigenfunctions $\chi_{\lambda A}^{(l_\alpha)}$ it is given by

$$G_E^{(l_\alpha)}(R'_A,R_A)=\sum_{\lambda}\frac{\chi_{\lambda A}^{(l_\alpha)}(R'_A)\chi_{\lambda A}^{(l_\alpha)}(R_A)}{\epsilon_{\lambda A}^{(l_\alpha)}-E} \tag{4.13}$$

and similarly for arrangement β. Consequently $R_{\alpha\beta}^{(l_\alpha l_\beta)}$ may be written in the form

$$R_{\alpha\beta}^{(l_\alpha l_\beta)}=-4[(2l_\alpha+\lambda)(2l_\beta+\lambda)]^{-1}$$
$$\times\int d\vec{r}_A\,d\Omega_A\int_0^{d_A}dR_A\,R_A^2[G_E^{(l_\alpha)}(R_A,d_A)P_{l_\alpha}(\cos\bar{\theta}_A)\psi_{1s_A}(r_A)H\psi_{1s_B}(r_B)P_{l_\beta}(\cos\bar{\theta}_B)G_E^{(l_\beta)}(R_B,d_B)] . \tag{4.14}$$

In keeping with the assumption of high-energy collisions, we can obtain approximate expressions for the Green's functions by neglecting the interaction potential $V_I(1s_A;1s_A)$ in (4.9). The details are given in the Appendix, but using this approximation, together with similar ones for D [Eq. (4.5)] and summing over l_α and l_β, we obtain

$$S_{\alpha\beta}=(2\mu/\hbar)id_Ad_B\langle e^{i\vec{\mathrm{k}}_\alpha\cdot\vec{\mathrm{R}}_A}\psi_{1s_A}|H|e^{i\vec{\mathrm{k}}_\beta\cdot\vec{\mathrm{R}}_B}\psi_{1s_B}\rangle \tag{4.15}$$

(neglecting the unimportant phase factor $\exp[i(k_\alpha d_A+k_\beta d_B)]$).

If we replace H by V_I in (4.15)—which is consistent with our earlier neglect of overlap between basis functions belonging to different arrangements—the matrix element in this equation is precisely the same as that obtained in earlier works[1,2] from the Born approximation. It should be noted that this result is obtained here by use of first-order perturbation theory which mixes basis functions stemming from different arrangements in the region of strong interaction. Evaluation of (4.15) is known to yield a cross section for charge transfer which varies with energy as E^{-6}. This dramatic fall in $\sigma_{\alpha\beta}$ with increasing energy is due to the interference between the waves $\exp(i\vec{\mathrm{k}}_\alpha\cdot\vec{\mathrm{R}}_A)$ and $\exp(i\vec{\mathrm{k}}_\beta\cdot\vec{\mathrm{R}}_B)$. By using the correct arrangement coordinates throughout, the R-matrix theory incorporates this essential feature of the physical process.

From Figs. 1 and 2, we see that $\vec{\mathrm{R}}_A=\vec{\mathrm{R}}+\gamma_A\vec{\mathrm{r}}_A$ and $\vec{\mathrm{R}}_B=\gamma_B\vec{\mathrm{r}}_B-\vec{\mathrm{R}}$. Substituting these expressions into (4.15) it is seen that if one uses the separation $\vec{\mathrm{R}}$ as a coordinate, the electronic wave functions ψ_{1s_A},ψ_{1s_B} acquire the "traveling factors" $\exp(i\gamma_A\vec{\mathrm{k}}_\alpha\cdot\vec{\mathrm{r}}_A)$, $\exp(i\gamma_B\vec{\mathrm{k}}_\beta\cdot\vec{\mathrm{r}}_B)$ which feature so prominently in other formulations of charge-transfer theory.[8-10] There are therefore considerable advantages in using arrangement coordinates and thereby avoiding the many difficulties associated with these factors. However, in order to carry through this program one has to evaluate integrals of the kind appearing in (4.15) for quite general atomic and nuclear wave functions. This is the task to which we now turn.

V. CALCULATION OF MULTIARRANGEMENT INTEGRALS

We begin with the overlap integral between basis functions (3.8) belonging to two different arrangements. This example will serve to illustrate the general techniques for evaluating such integrals. Let

$$I=\langle\xi_A^{JM}(n_A,l_A,L_A,p_A;\vec{\mathrm{r}}_A,\vec{\mathrm{R}}_A)\,|\,\xi_B^{JM}(n_B,l_B,L_B,q_B;\vec{\mathrm{r}}_B,\vec{\mathrm{R}}_B)\rangle , \tag{5.1}$$

the brackets implying integration over coordinates $(\vec{r}_A,\vec{R}_A)$ or $(\vec{r}_B,\vec{R}_B)$ within the R-matrix boundary. In order to evaluate this integral it is necessary to transform all functions to a common set of coordinates, $(\vec{r}_B,\vec{R}_B)$ say.

The electronic radial factor of ξ_A^{JM} is $R_{An_Al_A}(r_A)$ and this is represented as a linear combination of Slater-type functions

$$r_A^{n_A-1}e^{-\eta_A r_A}$$

with known coefficients. From Fig. 2 we have that

$$\vec{r}_A=\vec{R}_B+b\vec{r}_B\ ,$$

where $b=1-m/(M_B+m)$, and corresponding to this construction we may write

$$r_A^{n-1}e^{-\eta r_A}=\left[\frac{1}{br_BR_B}\right]^{1/2}\sum_{r=0}^{\infty}(2r+1)\zeta_{n,r}(\eta;br_B;R_B)\times P_l(\cos\theta_B)\ . \qquad (5.2)$$

This is the Barnett-Coulson zeta-function[33] expansion which is well-known in quantum chemistry for the calculation of multicenter integrals. The computations of the $\zeta_{n,r}(\eta,br_B;R_B)$ functions is straightforward and is incorporated in several multicenter integral packages.[34] The only modification here is the occurrence of the scaled distance br_B.

As described in Sec. III, the nuclear radial functions are expanded in terms of primitive sine functions:

$$\frac{1}{R_A}f_{p_A}^{(nlL_A)}(R_A)=\sum_{m=m_0}^{M}C_{p_Am}^{(nlL_A)}\frac{1}{R_A}\sin(k_mR_A)\ , \qquad (5.3)$$

where $k_m=(m+\frac{1}{2})\pi/d_A$. Now from Figs. 1 and 2, we find

$$\vec{R}_A=(1-ab)\vec{r}_B-a\vec{R}_B$$
$$=\vec{\rho}_B-\vec{S}_B\ . \qquad (5.4)$$

The factor $(1-ab)$ is given by

$$(1-ab)=1-(1-\gamma_A)(1-\gamma_B)$$
$$\simeq(\gamma_A+\gamma_B) \qquad (5.5)$$

and corresponding to construction (5.4) we write[35]

$$\frac{\sin(k_mR_A)}{R_A}=\frac{\pi}{2}\sum_{s=0}^{\infty}(2s+1)\frac{J_{s+1/2}(k_m\rho_B)}{\sqrt{\rho_B}}\times\frac{J_{s+1/2}(k_mS_B)}{\sqrt{S_B}}P_s(\cos\theta_B)\ . \qquad (5.6)$$

Now for a proton with kinetic energy of 1 keV, $k_m\simeq7\times10^{10}\ \mathrm{cm}^{-1}$ and even $k_m\gamma_A\simeq4\times10^{7}\ \mathrm{cm}^{-1}$. We may therefore derive a useful high-energy approximation to (5.6) by replacing the Bessel functions by their asymptotic forms. In any case they appear in integrands with other factors which become zero as r_B or R_B become zero, so that the contribution of (5.6) in regions where ρ_B or S_B are small is not significant. Substituting

$$\left[\frac{2}{\pi k_m\rho_B}\right]^{1/2}\cos[k_m\rho_B-\tfrac{1}{2}(s+\tfrac{1}{2})-\tfrac{1}{4}\pi]$$

for the $J_{s+1/2}(k_m\rho_B)$, and similarly for the second Bessel function in (5.6), we derive

$$\frac{\sin(k_mR_A)}{R_A}=\frac{1}{2k_m\rho_BS_B}\left[\cos(k_m\rho_B-k_mS_B)\sum_s(2s+1)P_s(\cos\theta_B)-\cos(k_m\rho_B+k_mS_B)\sum_s(2s+1)(-1)^sP_s(\cos\theta_B)\right]\ .$$

However,

$$\tfrac{1}{2}\sum_s(2s+1)P_s(\cos\theta_B)=\delta(\theta_B)\ ,$$

and

$$\tfrac{1}{2}\sum_s(2s+1)(-1)^sP_s(\cos\theta_B)=\delta(\pi-\theta_B)$$

so that we have as the final formula

$$\frac{\sin(k_mR_A)}{R_A}=\frac{1}{k_m\rho_BS_B}\{\cos[k_m(\rho_B-S_B)]\delta(\theta_B)-\cos[k_m(\rho_B+S_B)]\delta(\pi-\theta_B)\}\ . \qquad (5.7)$$

It should be noted that this expression correctly preserves the oscillating structure in both $k_m\rho_B$ and k_mS_B as is required by the simple relation

$$\exp(\vec{k}_m\cdot\vec{R}_A)=\exp(\vec{k}_m\cdot\vec{\rho}_B)\exp(-\vec{k}_m\cdot\vec{S}_B)\ .$$

The complete transformation of the nuclear radial basis functions now takes the form

$$\frac{1}{R_A}f_{p_A}^{(nlL_A)}(R_A)=\frac{1}{\rho_BS_B}[Q_-^{(nlL_Ap_A)}(\rho_B,S_B)\delta(\theta_B)-Q_+^{(nlL_Ap_A)}(\rho_B,S_B)\delta(\pi-\theta_B)]\ , \qquad (5.8)$$

where

$$Q_\pm^{(nlL_Ap_A)}(\rho_B,S_B)=\sum_{m=m_0}^{M}C_{p_Am}^{(nlL_A)}\frac{1}{k_m}\cos[k_m(\rho_B\pm S_B)]\ . \qquad (5.9)$$

[It is perhaps worthwhile mentioning a *low*-energy approximation to the transformation (5.6). If k_m is very small, the Bessel function $J_{s+1/2}(k_m\rho_B)$ can be replaced by its asymptotic value as $\rho_B\rightarrow0$. Neglecting second and higher powers of $(\gamma_A+\gamma_B)$, we obtain

$$\frac{\sin(k_m R_A)}{R_A}=\frac{\sin(k_m S_B)}{S_B}+\rho_B\cos\theta_B\left[\frac{\sin(k_m\rho_B)}{S_B^2}\right.$$
$$\left.-k_m\frac{\cos(k_m S_B)}{S_B}\right]$$

which is just a Taylor expansion in the "small" parameter ρ_B.]

The transformation of the angular functions is carried out by adapting a procedure due to Schulten and Gordon[36] (SG) for heavy particle rearrangement collisions. Since the electronic angular momentum is never large, it is convenient to transform the solid spherical harmonic $r_A^l Y_{lm}(\omega_A)$. Adapting formula (85b) of SG we obtain

$$r_A^l Y_{lm}(\omega_A)=\sqrt{4\pi}r_B^l\sum_{\lambda=0}^{l}G(l,\lambda)\left[\frac{-R_B}{ar_B}\right]^{\lambda}$$
$$\times\mathcal{Y}_{lm}(\lambda,l-\lambda;\Omega_B,\omega_B)\,, \tag{5.10}$$

where

$$G(l,\lambda)=(2\lambda+1)^{-1/2}\left[\begin{matrix}2l+1\\2\lambda\end{matrix}\right]^{1/2}, \tag{5.11}$$

and a is given by (3.6).

The transformation of the nuclear angular momentum is accomplished as follows [cf. SG, Eq. (72a)]:

$$Y_{LM_L}(\Omega_A)=(-1)^L Y_{LM_L}(\Omega_B)$$
$$+\frac{m}{\mu_A}\frac{r_<}{R_>}\sqrt{4\pi}(-1)^L$$
$$\times\sum_{L'=L\pm1}F(L,L')\mathcal{Y}_{LM_L}(L',1;\Omega_B,\omega_B)\,. \tag{5.12}$$

In this expression $r_<$ and $R_>$ are, respectively, the lesser of, and the greater of, r_B and R_B. The coefficients $F(L,L')$ are given by

$$F(L,L+1)=\frac{L}{\sqrt{3}}\left[\frac{L+1}{2L+1}\right]^{1/2},$$
$$F(L,L-1)=\frac{L+1}{\sqrt{3}}\left[\frac{L}{2L+1}\right]^{1/2}. \tag{5.13}$$

Expression (5.12) is correct to first order in m/μ_A. Neglected terms are of order $(m/\mu_A)^2\simeq10^{-6}$ at the largest. For most purposes the first line of (5.12) is sufficient, the error involved in ignoring the second term is $\sim10^{-3}$. In this case the transformation is trivial. It should be recalled that in any event such approximations do not affect the unitarity or symmetry of the final S matrix as long as the Hamiltonian matrix—and hence the R matrix—remains symmetric.

Expression (5.12) is obtained from the very much more complicated expression of SG by replacing the hypergeometric function there by unity and neglecting higher powers of (m/μ_A) than the first.

Equations (5.10) and (5.12) can be combined to give a single formula. After carrying out the necessary recoupling of angular momenta we arrive at the final equation:

$$r_A^l\mathcal{Y}_{JM_J}(L,l;\Omega_A,\omega_A)$$
$$=\sum_{\lambda=0}^{l}\sum_{L'}(R_B^{\lambda}r_B^{l-\lambda})C_{l\lambda;LL'}^{J}\mathcal{Y}_{JM}(L',l-\lambda;\Omega_B,\omega_B)$$
$$+\frac{m}{\mu_A}\frac{r_<}{R_>}\sum_{\lambda',L''}D_{l\lambda';LL''}^{J}\mathcal{Y}_{JM}(L'',\lambda';\Omega_B,\omega_B) \tag{5.14}$$

in which

$$C_{l,\lambda;LL'}^{J}=(-1)^J\sqrt{4\pi}\left[\frac{-1}{a}\right]^{\lambda}G(l,\lambda)$$
$$\times[(2l+1)(2L'+1)]^{1/2}\begin{Bmatrix}l-\lambda&\lambda&l\\L&J&L'\end{Bmatrix} \tag{5.15}$$

and

$$D_{l\lambda';LL''}^{J}=(-1)^{l+L}\sqrt{4\pi}\sum_{l'=0}^{l}\sum_{L'=L\pm1}G(l,l')F(L,L')[(2L''+1)(2\lambda'+1)(2l+1)(2L+1)]\begin{Bmatrix}l'&L'&L''\\l-l'&1&\lambda'\\l&L&J\end{Bmatrix}. \tag{5.16}$$

The large curly brackets appearing in these expressions are the 6-j and 9-j symbols. In view of its small size and greatly increased complexity, it is almost certainly worth neglecting the second line of Eq. (5.14). However, it should be emphasized that the methods used here are capable of arbitrary precision if higher accuracy is indeed required.

We now employ these techniques in the evaluation of the overlap integral (5.1). We assume that the electronic radial functions are represented by a single Slater function each. Transferring all functions in $(\vec{r}_A,\vec{R}_A)$ coordinates to $(\vec{r}_B,\vec{R}_B)$ coordinates, we have from (5.2), (5.8), and (5.14)

$$I=I^{(-)}-I^{(+)}\,, \tag{5.17}$$

where

$$I^{(\pm)}=\frac{N_{n_A}N_{n_B}}{ag_{AB}}\left[\frac{1}{b}\right]^{1/2}C_{l_A,l_A-l_B;L_AL_B}^{J}$$
$$\times\sum_{r=0}^{\infty}(2r+1)[\omega_r(\pm)]$$
$$\times O_r^{(\pm)}(n_A,l_A,L_A,p_A;n_B,l_B,L_B,q_B)\,. \tag{5.18}$$

In this last expression N_{n_A},N_{n_B} are the normalization integrals for the Slater orbitals,

$$g_{AB}=(\gamma_A+\gamma_B)\ , \tag{5.19}$$

$$\omega_r(+)=(-1)^r,\ \ \omega_r(-)=1\ , \tag{5.20}$$

$$O_r^{(\pm)}(n_A,l_A,L_A,p_A;n_B,l_B,L_B,q_B)=\int_0^{d_B} dR_B[R_B^{l_A-l_B-1/2}f_{q_B}^{(n_Bl_BL_B)}(R_B)V_r^{(\pm)}(n_A,l_A,L_A,p_A;n_B,l_B;\eta_A,\eta_B;R_B)] \tag{5.21}$$

and

$$V_r^{(\pm)}(n_A,l_A,L_A,p_A;n_B,l_B;\eta_A,\eta_B;R_B)=\int_0^{\infty} dr_B[e^{-\eta_Br_B}r_B^{n_B+l_B+1/2}\zeta_{n_A-l_A,r}(\eta_A,br_B;R_B)Q_{\pm}^{(n_Al_AL_Ap_A)}(\rho_B,S_B)]\ . \tag{5.22}$$

The second term of (5.14) has been neglected in the integral (5.17). The $I^{(-)}$ and $I^{(+)}$ contributions arise from the two terms of Eq. (5.8). The delta functions in (5.8) have the following effect upon the angular integrals. The relevant integral of $I^{(-)}$ is of the form

$$\int d\omega_B \int d\Omega_B[\mathcal{Y}_{JM}(L',\omega_A-\lambda;\Omega_B,\omega_B)\times\mathcal{Y}_{JM}(L_B,l_B,\Omega_B,\omega_B)P_r(\cos\theta_B)\delta(\theta_B)]\ .$$

The angle θ_B is the angle between the vectors $\vec{r}_B$ and $\vec{R}_B$, and the effect of $\delta(\theta_B)$ is to ensure that they both lie in the same direction, i.e., that both $\vec{r}_B$ and $\vec{R}_B$ possess the same angular coordinates in space-fixed axes. Consequently the distinction between Ω_B and ω_B disappears, and the integral is simply

$$\int d\Omega[\mathcal{Y}_{JM}(L',l_A-\lambda;\Omega,\Omega)\mathcal{Y}_{JM}(L_B,l_B;\Omega,\Omega)] =\delta_{L'L_B}\delta_{l_A-\lambda,l_B}\ .$$

In the case of $I^{(+)}$, the delta function is now $\delta(\pi-\theta_B)$. This introduces a factor $(-1)^r$ into the angular integration and leads to the introduction of the factor $\omega_r(\pm)$, Eq. (5.20).

The kinetic energy terms in the Hamiltonian give rise simply to a linear combination of overlap integrals of the kind discussed here. This is because in $(\vec{r}_B,\vec{R}_B)$ coordinates, the $\nabla^2_{r_B}$ operator affects only the electronic terms and $\nabla^2_{R_B}$ only the nuclear factors: There are no cross terms. Such cross terms *will* arise from the nuclear kinetic energy term if the orbitals are of deformed atomic or spin-coupled form. For in such a case, the electronic basis functions will possess two-center character, i.e., must be considered functions of r_B and R_B. This situation is discussed in more detail in Sec. VII.

The potential-energy integrals are evaluated by expanding the relevant operators as follows [cf. Eq. (3.5)]: In $(\vec{r}_B,\vec{R}_B)$ coordinates (Fig. 2),

$$\frac{Z_AZ_B}{R}=\frac{Z_AZ_B}{|\vec{R}_B-\gamma_B\vec{r}_B|} =\frac{Z_AZ_B}{R_B}\sum_{t=0}^{\infty}\left[\gamma_B\frac{r_B}{R_B}\right]^tP_t(\cos\theta_B)\ , \tag{5.23}$$

$$\frac{-Z_A}{r_A}=\frac{-Z_A}{|\vec{R}_B+b\vec{r}_B|} =\frac{-Z_A}{r_{A'}}\sum_{t=0}^{\infty}\left[\gamma_B\frac{r_B}{r_{A'}}\right]^tP_t(\cos\theta_{A'B})\ . \tag{5.24}$$

In this last equation

$$\vec{r}_A{}'=\vec{R}_B+\vec{r}_B \tag{5.25}$$

and $\theta_{A'B}$ is the angle between $\vec{r}_B$ and $\vec{r}_{A'}$, Fig. 5. It is clear that at the very most only the first two terms, $t=0$ and 1, will be needed from expansions (5.23) and (5.24), and in most cases the $t=0$ contribution will be sufficient.

Considering just the $t=0$ and 1 terms, we may write for V in the $(\vec{r}_B,\vec{R}_B)$ system

$$V=\frac{e^2}{4\pi\epsilon_0}\left[-\frac{Z_A}{r_{A'}}-\frac{Z_B}{r_B}+\frac{Z_AZ_B}{R_B}\right] +\frac{e^2}{4\pi\epsilon_0}\gamma_B\left[\frac{Z_AZ_B}{R_B^2}r_B\cos\theta_B +Z_A\left[\frac{r_B\cos\theta_B\cos\theta_{A'}}{r_{A'}^2} -\frac{r_B\sin\theta_B\sin\theta_{A'}}{r_{A'}^2}\right]\right]\ . \tag{5.26}$$

The first line of this equation gives rise to integrals known in quantum chemistry, and presents no new problems. Indeed this part of V is *independent* of arrangement and may be evaluated in either $(\vec{r}_A,\vec{R}_A)$ or $(\vec{r}_B,\vec{R}_B)$ coordinates. The operators occurring in the remainder are of "nonstandard" form (i.e., do not normally occur in calculations of electronic structure and properties), but whose integrals are quite straightforward to evaluate using the techniques described in this section.

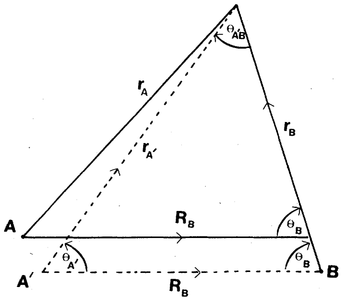

FIG. 5. Coordinate system for evaluation of nuclear attraction integrals.

The methods described in this section are extensions of procedures originally used for the evaluation of multicenter integrals and incorporated in program packages that have long become "standard." The new features here occur particularly in the $V_r^{(\pm)}(R_B)$ integrals, Eq. (5.22). The integrand involves the $Q_\pm$ functions which oscillate exceedingly rapidly. Since the rest of the integrand is smooth, this means that the $V_r^{(\pm)}(R_B)$ functions will be very small; in order to obtain accurate values of these integrals as a function of R_B it is necessary to employ quadrature techniques—such as that due to Filon[37]—which explicitly take into account the oscillating nature of the integrand. These and similar technical matters will be treated in more detail in succeeding publications with numerical applications.

The presence of the $Q_\pm$ functions in the integrand of an integration over electronic coordinates arises from the transformation of a nuclear wave function in another arrangement. The highly oscillating nature of these functions means that the off-diagonal matrix elements of the Hamiltonian are small and decrease rapidly with energy; in other words the cross section for charge transfer will fall steeply as the energy increases, which is precisely what is observed.

From this we conclude that the approximation in the transformation of electronic radial factors and all angular factors obtained by neglecting terms of order (m/μ_A) are perfectly acceptable; errors no greater than $\sim 10^{-3}$ are thereby introduced. But the transformation of the nuclear radial functions is critical, and no approximations of this kind are allowable. It is essential to maintain the oscillatory nature of these functions in the new coordinates. The "high-energy" approximation (5.7) is therefore central to this development.

VI. EXTENSION TO MANY-ELECTRON SYSTEMS

The purpose of this section is to show fairly briefly how the techniques of Secs. III and V extend to many-electron systems. We consider the charge-transfer process

$$A+B^+\rightarrow A^+ +B\ , \tag{6.1}$$

where the participating atoms and ions now involve several electrons. We begin by defining an arrangement as the assignment of N_A electrons to atom A, and N_B to atom B, where $N_A+N_B=N$, the total number of electrons in the system. The two sides of Eq. (6.1) differ in such assignments, the left-hand side corresponding to (N_A,N_B) say, while the right-hand side corresponds to (N_A-1,N_B+1). We denote such differing arrangements by $\alpha\equiv(N_A,N_B)$, $\beta\equiv(N_A^-,N_B^+)$, $\gamma\equiv(N_A^+,N_B^-)$, etc., where N_A^+, and N_A^- stand for N_A+1 or N_A-1 in an obvious notation. For simplicity of presentation we only consider one-electron transfers, i.e., just two arrangements, α and β.

Corresponding to each arrangement there is a definite coordinate system and a particular form of the Hamiltonian. In every case, we define N_A electron-nuclear coordinates $\vec{r}_{\mu A}$ $(\mu=1,\ldots,N_A)$ and similarly N_B coordinates $\vec{r}_{\nu B}$ $(\nu=N_A+1,\ldots,N_A+N_B)$. The coordinate $R_{N_AN_B}$ joins the center of mass of atom A to the center of mass of atom B, and passes through the center of mass of the entire system. The situation is illustrated in Fig. 6 for the case of a collision between, say, $\mathrm{Li}(^2S)+\mathrm{Li}(^2S)$ which might result in $\mathrm{Li}^+(^1S)+\mathrm{Li}^-(^1S)$.

The Hamiltonian for arrangement $\alpha\equiv(N_A,N_B)$ in this coordinate system, with motion of the center of mass of the whole system separated out, is given by

$$H=-\frac{\hbar^2}{2m_A}\sum_{\mu=1}^{N_A}\nabla^2_{\mu A}-\frac{\hbar^2}{2m_B}\sum_{\nu=1}^{N_B}\nabla^2_{\nu_B}-\frac{\hbar^2}{2\mu_{AB}}\nabla^2_{R_{AB}}+V\ . \tag{6.2}$$

The indices $\mu,\lambda,\ldots$ will be used for coordinates joining electron positions to nucleus A, and $\nu,\sigma,\ldots$ for coordinates connecting electrons and nucleus B. The reduced masses in (6.2) are given by

$$m_A=\frac{mM_A}{m+m_A},\quad m_B=\frac{mM_B}{m+M_B}\ , \tag{6.3}$$

these being the reduced masses of an electron with respect to atom A or atom B, and

$$\mu_{AB}\equiv\mu_{N_AN_B}=\frac{M_A^TM_B^T}{M_A^T+M_B^T}\ , \tag{6.4}$$

where M_A^T is the total mass of atom A:

$$M_A^T=M_A+N_Am\ , \tag{6.5}$$

and similarly for B. Equation (6.4) defines the reduced mass of atoms A and B. The value of μ_{AB} depends upon the arrangement and is more properly specified as $\mu_{N_AN_B}$. Similar remarks apply to $\vec{R}_{AB}$, which is short for $\vec{R}_{N_AN_B}$.

Mass-polarization contributions, of the form

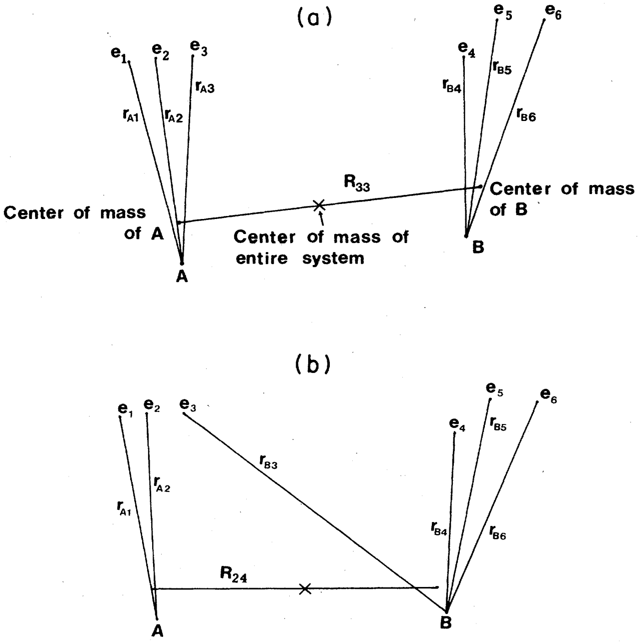

FIG. 6. (a) Coordinate system for a six-electron system in arrangement $\alpha\equiv(3,3)$. (b) Arrangement $\beta\equiv(2,4)$.

$$-\frac{\hbar^2}{2M_A}\sum_{\substack{\mu,\lambda\\ \mu\neq\lambda}}\vec{\nabla}_{\mu A}\cdot\vec{\nabla}_{\lambda A} \text{ and } -\frac{\hbar^2}{2M_B}\sum_{\substack{\nu,\sigma\\ \nu\neq\sigma}}\vec{\nabla}_{\nu B}\cdot\vec{\nabla}_{\sigma B}$$

have been neglected in (6.2) since these play no role in the physical processes of interest here. Otherwise Hamiltonian (6.2) is complete. The potential energy is given by

$$\begin{aligned}V=&\frac{e^2}{4\pi\epsilon_0}\sum_{\mu=1}^{N_A}\left[-\frac{Z_A}{r_{\mu A}}-\frac{Z_B}{r_{\mu B}}\right]\\&+\frac{e^2}{4\pi\epsilon_0}\sum_{\nu=N_A+1}^{N}\left[-\frac{Z_A}{r_{\nu A}}-\frac{Z_B}{r_{\nu B}}\right]\\&+\frac{e^2}{4\pi\epsilon_0}\left[\sum_{\substack{i,j=1\\ i<j}}^{N}\frac{1}{r_{ij}}+\frac{Z_AZ_B}{R}\right]. \qquad (6.6)\end{aligned}$$

In arrangement (N_A,N_B) the distances $r_{\mu B}$, $r_{\nu A}$, and R are given, respectively, by

$$r_{\mu B}=|\vec{r}_{\mu A}-\vec{R}_{AB}-\vec{\delta}_A+\vec{\delta}_B| , \qquad (6.7a)$$

$$r_{\nu A}=|\vec{r}_{\nu B}+\vec{R}_{AB}+\vec{\delta}_A-\vec{\delta}_B| , \qquad (6.7b)$$

and

$$R=|\vec{R}_{AB}+\vec{\delta}_A-\vec{\delta}_B| , \qquad (6.7c)$$

where

$$\vec{\delta}_A\equiv\vec{\delta}_{N_A}=\gamma_{N_A}\sum_{\lambda=1}^{N_A}\vec{r}_{A\lambda} , \qquad (6.8)$$

$$\vec{\delta}_B\equiv\vec{\delta}_{N_B}=\gamma_{N_B}\sum_{\sigma=N_A+1}^{N}\vec{r}_{B\sigma} ,$$

and

$$\gamma_{N_A}=m/M_A^T,\ \ \gamma_{N_B}=m/M_B^T . \qquad (6.9)$$

The vector $\vec{\delta}_{N_A}$ joins the nucleus of atom A to the center of mass of the atom in arrangement (N_A,N_B), and similarly for $\vec{\delta}_{N_B}$.

In order to construct suitable basis functions for charge transfer, we begin with electronic wave functions for atoms A and B in arrangement (N_A,N_B):

$$\Phi_A(\alpha_A,L_A,S_A,M_{L_A},M_{S_A}),\ \ \Phi_B(\alpha_B,L_B,S_B,M_{L_B},M_{S_B})$$

in which α_A,α_B denote the electronic configurations of the two atoms, and the other quantum numbers L_A, S_A, etc., have their usual meanings as the net electronic orbital and spin angular momenta. From Φ_A,Φ_B we form antisymmetrized products in which the spins S_A,S_B are coupled to form a resultant S_{AB} and the orbital angular momenta to a resultant L_{AB}:

$$\begin{aligned}&\Phi_{AB}[\alpha_A,\alpha_B(S_A,S_B)S_{AB},M_{S_{AB}};(L_A,L_B)L_{AB},M_{L_{AB}}]\\&\quad=\sum_{M_{S_A},M_{S_B}}\ \sum_{M_{L_A},M_{L_B}}\mathscr{A}[\Phi_A(\alpha_A,L_A,S_A,M_{L_A},M_{S_A})\Phi_B(\alpha_B,L_B,S_B,M_{L_B},M_{S_B})]\\&\qquad\times\langle S_A,S_B,M_{S_A},M_{S_B}\,|\,S_{AB},M_{S_{AB}}\rangle\langle L_A,L_B,M_{L_B}\,|\,L_{AB},M_{L_{AB}}\rangle , \qquad (6.10)\end{aligned}$$

in which $\mathscr{A}$ is the usual antisymmetrizing operator. The "channel angular momentum" L_{AB} is in turn coupled to the nuclear orbital angular momentum l_{AB} to form an overall resultant N_J:

$$\sum_{M_{L_{AB}}}\sum_{m_{l_{AB}}}\Phi_{AB}(\ldots,L_{AB},M_{L_{AB}})Y_{l_{AB},M_{l_{AB}}}\langle L_{AB},l_{AB},M_{L_{AB}},m_{l_{AB}}\,|\,N_J,M_J\rangle=\phi_{c_{AB}}^{N_J}(r_A,r_B;\omega_A,\omega_B;\Omega_{AB}) . \qquad (6.11)$$

The $\phi_{c_{AB}}^{N_J}$ are the channel functions of arrangement (N_A,N_B), the index c_{AB} standing for

$$c_{AB}\equiv\{\alpha_A,\alpha_B(S_A,S_B)S_{AB};[(L_A,L_B)L_{AB};l_{AB}]\} . \qquad (6.12)$$

All angular functions are in space-fixed coordinates, ω_A,ω_B collectively denoting the angles $\omega_{A1},\ldots,\omega_{AN_A}$ and $\omega_{BN_A+1},\ldots,\omega_{BN}$ of the electrons. Similarly, r_A,r_B stand for the collective electronic radial coordinates of the two atoms, and Ω_{AB} denotes the angular coordinates of the vector $\vec{R}_{AB}$. The net spin angular momentum S_{AB} and N_J are not coupled since the Hamiltonian (6.2) does not contain any terms corresponding to spin-orbit interaction. The final basis functions are then formed as

$$\begin{aligned}&\xi_{c_{AB};p_{AB}}^{N_J}(\vec{r}_A,\vec{r}_B;R_{AB})\\&\quad=\frac{1}{R_{AB}}f_{c_{AB};p_{AB}}(R_{AB})\phi_{c_{AB}}^{N_J}(r_A,r_B;\omega_A,\omega_B;\Omega_{AB}) , \qquad (6.13)\end{aligned}$$

where $R_{AB}^{-1}f_{c_{AB};p_{AB}}(R_{AB})$ is the nuclear radial basis function.

Similar considerations go through for arrangement (N_{A^+},N_{B^-}), only that A and B are everywhere replaced by A^+ and B^-, respectively.

The R-matrix eigenfunctions are represented as linear combinations of basis functions drawn from both arrangements:

$$\omega_A^{N_J}=\sum_{c_{AB}}\sum_{p_{AB}} C(c_{AB},p_{AB};\lambda)\xi^{N_J}_{c_{AB},p_{AB}}(\vec{r}_A,\vec{r}_B;\vec{R}_{AB})$$
$$+\sum_{c_{A^+B^-}}\sum_{q_{A^+B^-}} C(c_{A^+B^-},q_{A^+B^-};\lambda)$$
$$\times\xi^{N_J}_{c_{A^+B^-};q_{A^+B^-}}(\vec{r}_{A^+},\vec{r}_{B^-};\vec{R}_{A^+B^-}). \tag{6.14}$$

In order to determine the $C(\ldots;\lambda)$ coefficients occurring here, it is necessary to form the Hamiltonian matrix over the basis functions and to diagonalize it. Matrix elements between basis functions stemming from the same arrangement are straightforward to evaluate. The essential task—as in the one-electron case—is to evaluate matrix elements between different arrangements. The Hamiltonian matrix will however remain diagonal in S_{AB}. In the remaining part of this section we indicate how the techniques of Sec. V are extended to the many-electron case.

Referring to Fig. 6 we see that for each arrangement we may write

$$\vec{R}=\vec{R}_{AB}+\vec{\delta}_{N_A}-\vec{\delta}_{N_B}\quad\text{for } (N_A,N_B)$$
$$=\vec{R}_{A^+B^-}+\vec{\delta}_{N_{A^+}}-\vec{\delta}_{N_{B^-}}\quad\text{for } (N_{A^+},N_{B^-}) .$$

Hence

$$\vec{R}_{A^+B^-}=\vec{R}_{AB}+\vec{\delta}_{N_A}-\vec{\delta}_{N_B}-\vec{\delta}_{N_{A^+}}+\vec{\delta}_{N_{B^-}} . \tag{6.15}$$

We assume that the charge transfer occurs by the transference of electron N_A from nucleus A to nuclear B, and this corresponds to the difference in the configurations $(\alpha_A\alpha_B)$ and $(\alpha_{A^+}\alpha_{B^-})$. In other words the coordinates of the channel functions $\phi^{N_J}_{c_{AB}}$ and $\phi^{N_J}_{c_{A^+B^-}}$ differ in just one electron only. Corresponding to this we have from (6.15)

$$\vec{\delta}_{N_{B^-}}=\gamma_{N_{B^-}}\sum_{\nu=N_A}^{N}\vec{r}_{B\nu}$$
$$=\gamma_{N_{B^-}}\vec{r}_{BN_A}+\gamma_{N_{B^-}}\sum_{\nu=N_A+1}^{N}\vec{r}_{B\nu}$$
$$=\gamma_{N_{B^-}}\vec{r}_{BN_A}+\vec{\delta}_{N_B}+O(m/M_B)^2 .$$

In addition,

$$\vec{r}_{BN_A}=\vec{r}_{AN_A}-\vec{R}_{AB}+O(m/M_A) .$$

Substituting these relations into (6.15) we find

$$\vec{R}_{A^+B^-}=\vec{R}_{AB}(1-\gamma_{N_{B^-}})+(\vec{\delta}_{N_A}-\vec{\delta}_{N_{A^+}})+\gamma_{N_{B^-}}\vec{r}_{AN_A}$$
$$=\vec{R}_{AB}(1-\gamma_{N_{B^-}})+(\gamma_{N_A}+\gamma_{N_{B^-}})\vec{r}_{AN_A}$$
$$+O((m/M_A)^2,(m/M_B)^2) . \tag{6.16}$$

This equation, which relates the center-of-mass—to—center-of-mass vectors in two different arrangements should be compared with Eqs. (5.4) and (5.5) in the one-electron case. From triangle construction (6.16) we immediately derive the transformation for the nuclear radial basis functions [cf. Eq. (5.7)]:

$$\frac{\sin(k_m R_{A^+B^-})}{R_{A^+B^-}}$$
$$=\frac{1}{k_m\rho_{AB}S_{AB}}\{\cos[k_m(\rho_{AB}-S_{AB})]\delta(\theta_{N_A})$$
$$-\cos[k_m(\rho_{AB}+S_{AB})]\delta(\pi-\theta_{N_A})\} , \tag{6.17}$$

where

$$\vec{S}_{AB}=(1-\gamma_{N_{B^-}})\vec{R}_{AB} ,$$
$$\vec{\rho}_{AB}=(\gamma_{N_A}+\gamma_{N_{B^-}})\vec{r}_{AN_A} , \tag{6.18}$$

and θ_{N_A} is the angle between R_{AB} and r_{AN_A}.

Expression (6.17) is central to this development: It shows that on transforming nuclear radial basis functions from arrangement (A^+,B^-) to (A,B), a part of the highly oscillating nature of this function is also transfered to the *coordinate of the electron which is shifted.* From this conclusions reached earlier also now apply: The higher the energy, the more violent the oscillations and the more effectively all off-diagonal matrix elements are averaged to zero—and hence the smaller the cross section for charge transfer.

The angular transformations go through as in Sec. V. One may use the individual formulas (5.10) and (5.12) and recouple the result. In any case it is not useful at this stage to derive a general formula, since the amount of recoupling is prodigous. It is more transparent to consider individual cases on their merits. However, the fundamental point should be emphasized that this transformation involves functions which are "smooth," and that the neglect of terms of order m/M_A or m/M_B causes little error. This is not so in (6.17) where it is essential to maintain a distinction between center-of-mass—to—center-of-mass coordinates in the different arrangements.

Similar remarks apply to the transference of the electronic radial factors which are of course smoothly varying functions. Corresponding to transformation (6.16) we also have

$$\vec{r}_{BN_A}=\vec{r}_{AN_A}-\vec{R}_{AB}-\vec{\delta}_{N_A}+\vec{\delta}_{N_B}$$
$$=(1-\gamma_{N_A})\vec{r}_{AN_A}-\vec{R}_{AB}-\gamma_{N_A}\sum_{\mu=1}^{N_A-1}\vec{r}_{A\mu}$$
$$+\gamma_{N_B}\sum_{\nu=N_A+1}^{N}\vec{r}_{B\nu}$$
$$\simeq(1-N_A\gamma_{N_A})\vec{r}_{AN_A}-\vec{R}_{AB}+N_B\gamma_{N_B}\vec{r}_{BN_A} ,$$

or,

$$(1-N_B\gamma_{N_B})\vec{r}_{BN_B}=(1-N_A\gamma_{N_A})\vec{r}_{AN_A}-\vec{R}_{AB} . \tag{6.19}$$

This equation should be compared to the triangle relationship immediately preceding Eq. (5.2)—and to which (6.19) correctly reduces in the case of a single electron. The two arrangements are then characterized by (0,1) and (1,0). From (6.19) there immediately follows a zeta-function expansion similar to (5.2) involving the scaled distances

$$s_B=(1-N_B\gamma_{N_B})r_{BN_A}$$

and (6.20)

$$s_A=(1-N_A\gamma_{N_A})r_{AN_A}\ .$$

The single orbital involved in the charge-transfer process may then be transformed by Eq. (5.2).

The off-diagonal elements of the Hamiltonian matrix may now be evaluated by the techniques described here and in Sec. V. The details of these one- and two-electron multiarrangement integrals will be described in subsequent publications together with numerical applications.

VII. FINAL REMARKS

The electronic part of the basis functions described in this paper consists of products of undeformed atomic states—antisymmetrized when appropriate. This valence bond basis is suitable for high-energy collisions ($\gtrsim 1$ keV) when the interacting systems have no time to distort. In order to extend the range of the theory to lower energies it is necessary either to use a much larger basis set of atomic target functions or to allow for some deformation of the atomic states.

As described in Sec. I this can be done by using spin-coupled orbitals.[22] In the simplest case of a H(1s) state interacting with some other ion, the 1s orbital is replaced by the linear combination

$$\phi_A \sim \psi_{1s_A}+\lambda\psi_{1s_B}\ . \tag{7.1}$$

The coefficient λ is determined by a spin-coupled calculation of the molecular electronic state involved: the same calculation providing the potential $W(R_A)$ from which the nuclear distorted-wave basis functions are determined. The parameter λ is a function of the relevant center-of-mass—to—center-of-mass separation R_A, and becomes zero as R_A becomes large.

In the R-matrix calculation of charge transfer, the use of a deformed atomic state (7.1) amounts to the addition to the set (3.9) of channel functions of the type

$$R_{Bnl}(r_B)\mathscr{Y}_{JM}[(L_A,l)J;\Omega_A,\omega_B]\ . \tag{7.2}$$

It should be noted that this is now a function of R_A and will be affected by the nuclear kinetic energy term $(-\hbar^2/2\mu_A)\nabla^2_{R_A}$ in the Hamiltonian giving rise to radial and angular coupling matrix elements similar to those encountered in studies of the crossing of potential energy curves.[14,15]

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APPENDIX: DETERMINATION OF APPROXIMATE R-MATRIX GREEN'S FUNCTION

In order to obtain an approximate expression for the Green's function

$$G_E^{(l)}(R,R')=\sum_\lambda \frac{\chi_\lambda^{(l)}(R)\chi_\lambda^{(l)}(R')}{\epsilon_\lambda^{(l)}-E} \tag{A1}$$

[cf. Eq. (4.12)], we consider solutions of the "field-free" equation

$$\frac{1}{R^2}\frac{d}{dR}\left[R^2\frac{d\chi}{dR}\right]+\left[k^2-\frac{l(l+1)}{R^2}\right]\chi(R)=0 \tag{A2}$$

which satisfy the R-matrix boundary conditions

$$\begin{aligned}&\chi(R)<\infty \quad \text{as } R\to 0\\ &\left[\frac{d\chi}{dR}\right]_d=0\ .\end{aligned} \qquad \text{(A3}$$

In general the two linearly independent solutions of (A2) are $j_l(kR)$, which is a spherical Bessel function of the first kind, and $n_l(kR)$, a spherical Bessel function of the second kind. The function $j_l(kR)$ satisfies the boundary conditions at $R=0$, but for $R=d$ the combination

$$p_l(kR)=n_l(kR)j_l'(kd)-n_l'(kd)j_l(kR) \tag{A4}$$

satisfies the boundary condition at $R=d$. In this, the prime denotes differentiation with respect to R. From $j_l(kR)$ and $p_l(kR)$ we construct the Green's function in the form

$$G_E^{(l)}(R,R')=\begin{cases}\dfrac{j_l'(kR)p_l(kR')}{kj_l'(kd)}, & R\le R'\\[2ex] \dfrac{p_l(kR)j_l(kR')}{kj_l'(kd)}, & R>R'\ .\end{cases} \tag{A5}$$

In particular we find that

$$G_E^{(l)}(R,d)=\frac{-j_l(kR)}{k^2d^2j_l'(kd)}\ . \tag{A6}$$

Substituting this expression into Eq. (4.14) and replacing the upper limit of the integration over R_A by ∞, we obtain

$$\begin{aligned}R_{\alpha\beta}^{(l_\alpha l_\beta)}&=4[(2l_\alpha+1)(2l_\beta+1)k_\alpha^2k_\beta^2d_A^2d_B^2j_{l_\alpha}'(k_\alpha d_A)j_{l_\beta}'(k_\beta d_B)]^{-1}\\ &\quad\times\langle\psi_{1s_A}j_{l_\alpha}(k_\alpha R_A)P_{l_\alpha}(\cos\bar\theta_A)\,|\,H\,|\,\psi_{1s_B}j_{l_\infty}(k_\beta R_B)P_{l_\infty}(\cos\bar\theta_B)\rangle\ .\end{aligned} \tag{A7}$$

In order to evaluate the $(l_\alpha l_\beta)$ contribution to the S matrix (4.4), it is necessary to evaluate D. This is given approximately by

$$D = R_{\alpha\alpha} R_{\beta\beta} L_\alpha L_\beta = -R_{\alpha\alpha} R_{\beta\beta} k_\alpha k_\beta \,. \tag{A8}$$

The $(l_\alpha l_\beta)$ contribution to this is given by

$$D^{(l_\alpha l_\beta)} = -G_E^{(l_\alpha)}(d_A, d_A) G_E^{(l_\beta)}(d_B, D_B) \tag{A9}$$

$$= \left[\frac{\hbar^2}{2\mu} \right]^2 \frac{16}{[(2l_\alpha+1)(2l_\beta+1)]^2} \times \frac{j_{l_\alpha}(k_\alpha d_A) j_{l_\beta}(k_\beta d_B)}{k_\alpha k_\beta d_A^2 d_B^2 j'_{l_\alpha}(k_\alpha d_A) j'_{l_\beta}(k_\beta d_B)} \,, \tag{A10}$$

and hence

$$\frac{R_{\alpha\beta}^{(l_\alpha l_\beta)}}{D^{(l_\alpha l_\beta)}} = \frac{2\mu}{\hbar^2} \frac{(2l_\alpha+1)(2_{l_\beta}+1)}{4 j_{l_\alpha}(k_\alpha d_A) j_{l_\beta}(k_\beta d_B)} \frac{1}{k_\alpha k_\beta} \langle \cdots | H | \cdots \rangle .$$

Replacing $j_{l_\alpha}(\cdots) j_{l_\beta}(\cdots)$ by the average values of their asymptotic expressions, $1/2k_\alpha k_\beta$, and summing over all l_α and l_β we find

$$\begin{aligned} S_{\alpha\beta} &\simeq \frac{2\mu}{\hbar^2} i (k_\alpha k_\beta)^{1/2} d_A d_B \\ &\quad \times \sum_{l_\alpha, l_\beta} (2l_\alpha+1) i^{l_\alpha} (2l_\beta+1) i^{l_\beta} \langle \cdots | H | \cdots \rangle \\ &= \frac{2\mu}{\hbar^2} i (k_\alpha k_\beta)^{1/2} d_A d_B \\ &\quad \times \langle e^{i \vec{k}_\alpha \cdot \vec{R}_A} \psi_{1s_A} | H | e^{i \vec{k}_\beta \cdot \vec{R}_B} \psi_{1s_B} \rangle \,, \end{aligned} \tag{A11}$$

or

$$S_{\alpha\beta} = \frac{2\mu}{\hbar^2} i d_A d_B \langle e^{i \vec{k}_\alpha \cdot \vec{R}_A} \psi_{1s_A} | H | e^{i \vec{k}_\beta \cdot \vec{R}_B} \psi_{1s_B} \rangle \tag{A12}$$

for plane-wave functions normalized to a flux of $\mu/\hbar$ as before.

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