

The Coupling of Electronically Adiabatic States in Atomic and Molecular Collisions

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I. Introduction

Spectroscopic information on the bound states of molecular systems is usually analyzed with the aid of Born–Oppenheimer electronically adiabatic potential energy curves or surfaces. For collision problems attention is divided more evenly between electronically adiabatic and electronically diabatic representations. Adiabatic basis sets diagonalize the electronic Hamiltonian; they have the advantages that they often provide the most uncoupled available representation for low-energy collisions, that adiabatic potential energies may be defined and calculated accurately by the variational principle, and that one can accurately include the important effects of molecular charge relaxation in adiabatic basis sets. Adiabatic representations have the disadvantage that the coupling operators are derivative operators in the coordinate representation and are somewhat inconvenient for calculations.

Diabatic representations are those in which the electronic Hamiltonian is not diagonal. Suitably chosen diabatic basis sets have the advantage that they provide representations that are more uncoupled for high-energy collisions and cases of narrowly avoided crossings, and that their dominant coupling may be provided by potential terms. For processes of interest in chemistry, the advantages of the adiabatic representation are often more important. This article is primarily concerned with the coupling between states in electronically adiabatic representations. The advantages of adiabatic and diabatic basis sets may often be combined by defining diabatic basis sets in terms of adiabatic basis sets. This article is also concerned with the ways in which this can be done.

Section II begins with a discussion of the different forms that the non-adiabatic coupling operators and the coupled scattering equations take when different coordinate systems are used to describe the electronic degrees of freedom. We show that the correct scattering boundary conditions cannot be enforced naturally in coordinate systems that are convenient for obtaining and expressing Born–Oppenheimer electronically adiabatic wave functions. This can lead to nonvanishing coupling even at infinite distances between atomic and molecular subsystems. The lack of a clear-cut basis for choosing a coordinate system can also lead to ambiguity in the coupling when the subsystems are close together. Various approaches to resolving these problems are discussed. One approach is to pick a coordinate system, use it consistently to calculate an approximate wave function with some finite basis set, and extract scattering amplitudes from the calculation by imposing scattering boundary conditions on the wave functions as well as possible within the chosen basis set. This procedure is fool-proof in principle, but may be slowly convergent as the size of the basis set is increased. It is necessary to have procedures for such rigorous calculations to serve as foundations and

benchmarks, and a large part of this article (especially Sections II,E; II,G; III,A; and IV,B) is concerned with such procedures. Less rigorous procedures are often more convenient and appropriate for obtaining meaningful results for particular physical processes. A large variety of such procedures have been suggested and we review them briefly in Section II,H. An example of this approach is discussed in more detail in Section III,B, and some useful numerical methods are discussed in Section IV,A.

Section III discusses transformations between diabatic and adiabatic coordinate systems. One important aspect of such transformations concerns attempts to find diabatic representations in which the derivative coupling is negligible. Another aspect concerns the possibility of using the non-uniqueness of diabatic representations to constrain the matrix elements to have simple or desirable properties. We discuss these questions with examples.

Sections II and III leave us with coupled differential equations to be solved, and Section IV discusses an approach to the numerical solution of these equations. In particular, Section IV is concerned with the use of approximately adiabatic representations that are independent of internuclear distance over finite-length sectors. In such representations the states are coupled by transformations at the boundaries of sectors rather than by derivative coupling operators. We show how the *R*-matrix propagation method with adiabatic basis function allows the use of derivative coupling operators to be replaced by overlap integrals, which, in turn, we evaluate in terms of standard nuclear-derivative matrix elements.

The physical effects and mathematical formalisms discussed in this article are of interest for atom-atom, atom-molecule, and molecule-molecule collisions. To emphasize certain important aspects of adiabatic representations with the fewest extraneous complications, we restrict most of the detailed development to atom-atom collisions, but the subjects discussed are motivated by the whole field of molecular collisions at chemical energies, not just by atom-atom collisions. Some aspects of nonadiabatic effects in atom-molecule collisions are treated in the article by Reberstrost in volume 6B of this serial publication.

The treatment and the references of the present article are not intended to be exhaustive, but rather to give a perspective on selected aspects of the problem. Although semiclassical methods are often applied to electronically inelastic collisions, the present article deals for the most part only with time-independent quantum mechanical scattering theory; the reader is referred to the introduction of Thorson's 1965 paper for a discussion of the foundations of the subject. A more general overview of the theory of electronically non-adiabatic collisions in chemistry has been given by Tully (1976).

This article is partly a review and partly new work. The most important new work is in Sections II,E; III,B; and IV,C.

II. The Scattering Problem in a Born–Oppenheimer Electronically Adiabatic Basis

A. COORDINATES, HAMILTONIANS, AND ANGULAR MOMENTA

As an example, we explicitly consider in Section II a system of two nuclei A and B of masses m_A and m_B , respectively, and one electron of mass m_e , with the center of mass of the three-particle system at rest. We neglect spin and we assume the charges of A and B are different. We exclude processes in which an electron becomes detached (ionization). This example is representative of a system of two atomic cores and one active electron and more broadly of a general diatomic system; however, it allows us to dispense with the complications associated with antisymmetrization, homonuclear symmetry, and final states with three separated subsystems. A set of relative coordinates convenient for the description of the molecule are the relative internuclear coordinate \mathbf{R}' (distance from A to B) and the location \mathbf{r}' of the electron relative to the center of mass of the nuclei. The prime indicates the coordinates are a space-fixed system. The components of \mathbf{R}' are

$$\mathbf{R}' = R' \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix} \quad (1)$$

where R' is the magnitude of \mathbf{R}' . The Hamiltonian in the space-fixed coordinate system is

$$H = -\frac{\hbar^2}{2\mu_{AB}} \nabla_{\mathbf{R}'}^2 - \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}'}^2 - \frac{\hbar^2}{2(m_A + m_B)} \nabla_{\mathbf{r}'}^2 + V(\mathbf{r}', \mathbf{R}') \quad (2)$$

where

$$\mu_{AB} = m_A m_B / (m_A + m_B) \quad (3)$$

The body-fixed molecular coordinate system is taken to have the z axis along the internuclear vector and will be denoted without the prime. The space-fixed and body-fixed coordinates are related by a rotation

$$\mathbf{R} = \mathcal{R}(\phi, \theta, 0)\mathbf{R}' \quad (4)$$

$$\mathbf{r} = \mathcal{R}(\phi, \theta, 0)\mathbf{r}' \quad (5)$$

where†

$$\mathcal{R}(\phi, \theta, 0) = \begin{bmatrix} \cos \theta \cos \phi & \cos \theta \sin \phi & -\sin \theta \\ -\sin \phi & \cos \phi & 0 \\ \sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta \end{bmatrix} \quad (6)$$

In the body-fixed coordinate system the Hamiltonian can be written (Kolos and Wolniewicz, 1963; Pack and Hirschfelder, 1968)

$$H = -\frac{\hbar^2}{2\mu_{AB}} \nabla_R^2 - \frac{\hbar^2}{2m_e} \nabla_r^2 - \frac{\hbar^2}{2(m_A + m_B)} \nabla_r^2 + V(\mathbf{r}, R) \quad (7)$$

where

$$\hbar^2 \nabla_R^2 = \frac{\hbar^2}{R} \frac{\partial^2}{\partial R^2} R - \frac{L^2}{R^2} \quad (8)$$

$$\hbar^2 \nabla_r^2 = \frac{\hbar^2}{r} \frac{\partial^2}{\partial r^2} r - \frac{J_e^2}{r^2} \quad (9)$$

L is the angular momentum operator of the motion of A relative to B, and J_e is the electronic angular momentum operator relative to the center of mass of the nuclei in the body-fixed coordinate system. The total angular momentum is given by

$$\mathbf{J}_{\text{tot}} = \mathbf{L} + \mathbf{J}_e \quad (10)$$

The eigenvalue of L^2 will be called $l(l+1)\hbar^2$ and the eigenvalue of the component J_{ez} on the body-fixed axis will be called $\Omega\hbar$. Notice that L^2 is not diagonal in the body-frame representation used in conjunction with Eq. (7). One could simplify Eq. (7) by writing

$$\mu_e^{-1} = m_e^{-1} + (m_A + m_B)^{-1} \quad (11)$$

but we do not do this because the second electronic kinetic energy term contains cross terms in many-electron systems and is often neglected. This is the mass polarization term for our one-electron system.

It is also possible to use coordinates in which the electronic coordinate is not referred to the center of mass of the nuclei as origin. We define the

† We use the same rotation matrices and representations of the rotation group as used by Pack and Hirschfelder (1968). These differ from those of Rose (1957).

space-fixed electronic coordinate with respect to an arbitrary point on a line between the two nuclei as

$$\mathbf{r}'_a = \mathbf{r}'_A - a\mathbf{R}' \quad (12)$$

where a is a number between 0 and 1 and \mathbf{r}'_A is the electronic coordinate measured from nucleus A. The Hamiltonian can then be rewritten as

$$\begin{aligned} H = & -\frac{\hbar^2}{2\mu_{AB}} \nabla_{\mathbf{R}'_a}^2 - \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}'_a}^2 - \hbar^2 \left[\frac{1-a}{m_A} - \frac{a}{m_B} \right] \nabla_{\mathbf{R}'_a} \cdot \nabla_{\mathbf{r}'_a} \\ & - \frac{\hbar^2}{2} \left[\frac{(1-a)^2}{m_A} + \frac{a^2}{m_B} \right] \nabla_{\mathbf{r}'_a}^2 + V(\mathbf{r}'_a, \mathbf{R}'_a) \end{aligned} \quad (13)$$

where \mathbf{R}'_a is the same as \mathbf{R}' , but $\nabla_{\mathbf{R}'_a}$ implies $(\nabla_{\mathbf{R}'})_{\mathbf{r}'_a}$, i.e., \mathbf{r}'_a fixed, whereas $\nabla_{\mathbf{R}'}$ implies $(\nabla_{\mathbf{R}'})_{\mathbf{r}'}$. The coordinate \mathbf{r}' is the same as $\mathbf{r}'_{a\text{CMN}}$ where CMN denotes center of mass of the nuclei and

$$a_{\text{CMN}} = m_B/(m_A + m_B) \quad (14)$$

The choice of Eq. (14) is particularly convenient because it removes the $\nabla_{\mathbf{R}'_a} \cdot \nabla_{\mathbf{r}'_a}$ cross term. Another special choice of the $(\mathbf{r}'_a, \mathbf{R}'_a)$ coordinate system that is sometimes useful is to let \mathbf{r}'_a be the vector to the electron from the geometric center of the nuclei (see, e.g., Kolos and Wolniewicz, 1963; Kolos, 1970).

The body-fixed electronic coordinate with arbitrary origin is defined analogously, i.e.,

$$\mathbf{r}_a = \mathbf{r}_A - a\mathbf{R} \quad (15)$$

$$= \mathcal{R}(\phi, \theta, 0)\mathbf{r}'_a \quad (16)$$

The Hamiltonian in the body-fixed $(\mathbf{r}_a, \mathbf{R}_a)$ coordinate system is

$$\begin{aligned} H = & -\frac{\hbar^2}{2\mu_{AB}} \frac{1}{R_a} \frac{\partial^2}{\partial R_a^2} R_a + \frac{L_a^2}{2\mu_{AB} R_a^2} \\ & + \frac{\hbar}{R_a} \left[\frac{1-a}{m_A} - \frac{a}{m_B} \right] \left\{ -i \frac{\partial}{\partial x_a} L_{ay} + i \frac{\partial}{\partial y_a} L_{ax} - \hbar \frac{\partial}{\partial z_a} \frac{\partial}{\partial R_a} R_a \right\} \\ & - \frac{\hbar^2}{2} \left[\frac{1}{m_e} + \frac{(1-a)^2}{m_A} + \frac{a^2}{m_B} \right] \nabla_{\mathbf{r}_a}^2 + V(\mathbf{r}_a, R_a) \end{aligned} \quad (17)$$

where \mathbf{L}_a is the nuclear angular momentum in the $(\mathbf{r}_a, \mathbf{R}_a)$ coordinate system, L_{ax} and L_{ay} are the body-fixed components of \mathbf{L}_a , and $\mathbf{r}_a = (x_a, y_a, z_a)$. This can be rewritten as

$$\begin{aligned}
 H = & -\frac{\hbar^2}{2\mu_{AB}} \frac{1}{R_a} \frac{\partial^2}{\partial R_a^2} R_a + \frac{1}{2\mu_{AB} R_a^2} [J_{\text{tot}}^2 - 2J_z^2 + J_{ea}^2 - J_{ea-} J_+ - J_{ea+} J_-] \\
 & + \frac{\hbar}{2R_a} \left[\frac{1-a}{m_A} - \frac{a}{m_B} \right] \left[-\left(\frac{\partial}{\partial x_a} - i \frac{\partial}{\partial y_a} \right) (J_+ - J_{ea+}) \right. \\
 & \left. + \left(\frac{\partial}{\partial x_a} + i \frac{\partial}{\partial y_a} \right) (J_- - J_{ea-}) \right. \\
 & \left. - 2\hbar \frac{\partial}{\partial z_a} \left(\frac{\partial}{\partial R_a} \right) R_a \right] - \frac{\hbar^2}{2} \left[\frac{1}{m_e} + \frac{(1-a)^2}{m_A} + \frac{a^2}{m_B} \right] \nabla_{r_a}^2 + V(\mathbf{r}_a, R_a) \quad (18)
 \end{aligned}$$

where J_{ea} is the electronic angular momentum relative to the origin specified by a ,

$$J_{ea\pm} = J_{eax} \pm iJ_{eay} \quad (19)$$

$$J_{\pm} = J_{\text{tot},x} \pm iJ_{\text{tot},y} \quad (20)$$

and J_{eax} , J_{eay} and $J_{\text{tot},x}$, $J_{\text{tot},y}$ are the x and y components of \mathbf{J}_{ea} and \mathbf{J}_{tot} , respectively. We have used the fact that the total angular momentum is the sum of \mathbf{J}_{ea} and \mathbf{L}_a in obtaining Eq. (18). Notice that although H given by Eq. (18) is Hermitian, Eq. (18) is not term-by-term Hermitian. This will be especially important for Eqs. (65) and (66) later.

To describe the system with infinitely separated nuclei it is convenient to use the space-fixed atomic Jacobi coordinates \mathbf{r}'_{α} and \mathbf{R}'_{α} where \mathbf{r}'_{α} is the location of the electron relative to nucleus α and \mathbf{R}'_{α} is the location of the other nucleus α' with respect to the center of mass of nucleus α and the electron. These coordinates are related to the molecular coordinate system by

$$\mathbf{R}'_{\alpha} = \frac{m_{\alpha}(m_A + m_B + m_e)}{(m_{\alpha} + m_e)(m_A + m_B)} \mathbf{R}' - \frac{f_{\alpha} m_e}{m_{\alpha} + m_e} \mathbf{r}' \quad (21)$$

$$\mathbf{r}'_{\alpha} = \frac{f_{\alpha} m_{\alpha'}}{m_A + m_B} \mathbf{R}' + \mathbf{r}' \quad (22)$$

where $\alpha' = A, B$ with $\alpha = B, A$, respectively, and where

$$f_{\alpha} = \begin{cases} +1, & \alpha = A \\ -1, & \alpha = B \end{cases} \quad (23)$$

In the space-fixed Jacobi coordinates the Hamiltonian is

$$H = -(\hbar^2/2\mu_{AB}^\alpha)\nabla_{R_\alpha}^2 - (\hbar^2/2\mu_e^\alpha)\nabla_{r_\alpha}^2 + V(\mathbf{r}'_\alpha, \mathbf{R}'_\alpha) \quad (24)$$

where

$$\mu_{AB}^\alpha = [(m_\alpha + m_e)m_{\alpha'}]/(m_\alpha + m_e + m_{\alpha'}) \quad (25)$$

$$\mu_e^\alpha = m_\alpha m_e / (m_\alpha + m_e) \quad (26)$$

$$\hbar^2 \nabla_{R_\alpha}^2 = \frac{\hbar^2}{R'_\alpha} \frac{\partial^2}{\partial R'^2_\alpha} R'_\alpha - \frac{L'^2_\alpha}{R'^2_\alpha} \quad (27)$$

$$\hbar^2 \nabla_{r_\alpha}^2 = \frac{\hbar^2}{r'_\alpha} \frac{\partial^2}{\partial r'^2_\alpha} r'_\alpha - \frac{J'^2_{e\alpha}}{r'^2_\alpha} \quad (28)$$

L'_α is the angular momentum operator of the motion of nucleus α' relative to the center of mass of the α -electron pair, and $J'_{e\alpha}$ is the electronic angular momentum operator relative to the nucleus α . The total angular momentum in these coordinates is given by

$$\mathbf{J}_{\text{tot}} = \mathbf{L}'_\alpha + \mathbf{J}'_{e\alpha} \quad (29)$$

The eigenvalues of L'^2_α and the component $L'_{z\alpha}$ will be called $l_\alpha(l_\alpha + 1)\hbar^2$ and $m_\alpha\hbar$, respectively. The eigenvalues of $J'^2_{e\alpha}$ and the component $J'_{e\alpha z}$ will be called $j(j + 1)\hbar^2$ and $m_j\hbar$, respectively. The transformations of Eqs. (21) and (22) can be rewritten as

$$\mathbf{R}'_\alpha = (\mu_{AB}/\mu_{AB}^\alpha)\mathbf{R} - [(f_\alpha\mu_e^\alpha)/m_\alpha]\mathbf{r}' \quad (30)$$

$$\mathbf{r}'_\alpha = [(f_\alpha\mu_{AB})/m_\alpha]\mathbf{R} + \mathbf{r}' \quad (31)$$

This transformation can be inverted to give

$$\mathbf{R} = \mathbf{R}'_\alpha + f_\alpha(\mu_e^\alpha/m_\alpha)\mathbf{r}'_\alpha \quad (32)$$

$$\mathbf{r}' = (\mu_{AB}/\mu_{AB}^\alpha)\mathbf{r}'_\alpha - f_\alpha(\mu_{AB}/m_\alpha)\mathbf{R}'_\alpha \quad (33)$$

B. ELECTRONIC BASES AND COUPLED CHANNEL EQUATIONS

Born–Oppenheimer electronically adiabatic states are eigenfunctions of the molecular electronic Hamiltonian in the body-fixed frame with R fixed:

$$[-(\hbar^2/2m_e)\nabla_r^2 + V(\mathbf{r}, R)]\phi_{an\Omega}^a(\mathbf{r}, R) = \varepsilon_{an\Omega}^a(R)\phi_{an\Omega}^a(\mathbf{r}, R) \quad (34)$$

The first subscript on $\phi_{an\Omega}^a$ denotes the center to which the electron is bound as R goes to infinity, and n denotes the molecular principal quantum number for the electronic state. The basis functions $\phi_{an\Omega}^a$ are defined relative to the

body-fixed axes and are functions of R , but independent of \hat{R} . A caret denotes a unit vector. The superscripts in Eq. (34) denote adiabatic.

In the space-fixed frame we explicitly indicate the dependence of the basis functions upon angular components of \mathbf{R}' , however, the eigenvalues $\varepsilon_{\alpha n \Omega}^a(R)$ will still be simply functions of the magnitude of \mathbf{R}' .

The total wave function for a collisional event may be written†

$$\Psi_{\alpha_0 n_0 \Omega_0}(\mathbf{r}', \mathbf{R}') = \sum_{\alpha n \Omega} \phi_{\alpha n \Omega}^a(\mathbf{r}', \mathbf{R}') f_{\alpha n \Omega \alpha_0 n_0 \Omega_0}(\mathbf{R}') \tag{35}$$

where $\alpha_0, n_0,$ and Ω_0 specify initial conditions and the wave function satisfies

$$(H - E)\Psi_{\alpha_0 n_0 \Omega_0} = 0 \tag{36}$$

We note the important orthogonality property

$$\langle \phi_{\gamma n_1 \Omega_1}^a(\mathbf{r}', \mathbf{R}') | \phi_{\alpha n \Omega}^a(\mathbf{r}', \mathbf{R}') \rangle_{\mathbf{r}'} = \delta_{\gamma \alpha} \delta_{n_1 n} \delta_{\Omega_1 \Omega} \tag{37}$$

where a subscript on a matrix element denotes the variables integrated over. Using Eqs. (2), (34), (35), and (37), and requiring

$$\langle \phi_{\gamma n_1 \Omega_1}^a(\mathbf{r}', \mathbf{R}') | H - E | \Psi_{\alpha_0 n_0 \Omega_0} \rangle_{\mathbf{r}'} = 0 \tag{38}$$

for a set of γ, n_1, Ω_1 yields

$$\begin{aligned} & \left[-\frac{\hbar^2}{2\mu_{AB}} \nabla_{R'}^2 + \varepsilon_{\gamma n_1 \Omega_1}^a(R) - E \right] f_{\gamma n_1 \Omega_1 \alpha_0 n_0 \Omega_0}(\mathbf{R}') \\ & - \sum_{\alpha n \Omega} \left\{ \frac{\hbar^2}{2(m_A + m_B)} \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{r}'}^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'} + \frac{\hbar^2}{2\mu_{AB}} \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{R'}^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'} \right. \\ & \left. + \frac{\hbar^2}{\mu_{AB}} \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{R'} | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'} \cdot \nabla_{R'} \right\} f_{\alpha n \Omega \alpha_0 n_0 \Omega_0}(\mathbf{R}') = 0 \end{aligned} \tag{39}$$

We use the convention that a derivative or gradient operator in a matrix element does not operate outside the matrix element.

Another expansion of the total wave function is given by

$$\Psi_{\alpha_0 n_0 \Omega_0}(\mathbf{r}', \mathbf{R}') = \sum_{JM} \Psi_{\alpha_0 n_0 \Omega_0}^{JM}(\mathbf{r}', \mathbf{R}') \tag{40}$$

$\Psi_{\alpha_0 n_0 \Omega_0}^{JM}(\mathbf{r}', \mathbf{R}')$ is the component corresponding to conserved values J and M of the quantum numbers for total angular momentum and its component on a

† When we use the same function name with different arguments we mean the same quantity rewritten in terms of the new arguments. Thus the functional form is different.

space-fixed axis; α_0 , n_0 , and Ω_0 specify initial conditions; and the wave functions satisfy

$$(H - E)\Psi_{\alpha_0 n_0 \Omega_0}^{JM} = 0 \quad (41)$$

$$J_{\text{tot}}^2 \Psi_{\alpha_0 n_0 \Omega_0}^{JM} = J(J + 1)\hbar^2 \Psi_{\alpha_0 n_0 \Omega_0}^{JM} \quad (42)$$

$$J_{\text{tot}, z'} \Psi_{\alpha_0 n_0 \Omega_0}^{JM} = M\hbar \Psi_{\alpha_0 n_0 \Omega_0}^{JM} \quad (43)$$

Specifying the initial conditions by Ω_0 is convenient for using body-fixed coordinates (see, e.g., Pack 1974; Walker and Light, 1975; initial conditions are discussed in more detail in Section II,C). $\Psi_{\alpha_0 n_0 \Omega_0}^{JM}(\mathbf{r}', \mathbf{R}')$ can be rotated into body-fixed coordinates by expanding in coefficients $D_{\Omega M}^J$ of the irreducible representations of the rotation group (Pack and Hirschfelder, 1968), i.e.,

$$\Psi_{\alpha_0 n_0 \Omega_0}^{JM}(\mathbf{r}', \mathbf{R}') = \sum_{\Omega=-J}^J D_{\Omega M}^J(\phi, \theta, 0) \Psi_{\Omega \alpha_0 n_0 \Omega_0}^J(\mathbf{r}, R) \quad (44)$$

in which

$$J_{\text{tot}, z} \Psi_{\Omega \alpha_0 n_0 \Omega_0}^J = \Omega \hbar \Psi_{\Omega \alpha_0 n_0 \Omega_0}^J \quad (45)$$

The expansion coefficients can then be further expanded in the Born-Oppenheimer basis set

$$\Psi_{\Omega \alpha_0 n_0 \Omega_0}^J(\mathbf{r}, R) = R^{-1} \sum_{an} \phi_{an}^a(\mathbf{r}, R) g_{an \Omega \alpha_0 n_0 \Omega_0}^J(R) \quad (46)$$

Substituting Eqs. (7) and (44) into (41) yields the coupled equations (Pack and Hirschfelder, 1968)

$$H_{\Omega, \Omega-1} \Psi_{\Omega-1, \alpha_0 n_0 \Omega_0}^J(\mathbf{r}, R) + (H_{\Omega\Omega} - E) \Psi_{\Omega \alpha_0 n_0 \Omega_0}^J(\mathbf{r}, R) + H_{\Omega, \Omega+1} \Psi_{\Omega+1, \alpha_0 n_0 \Omega_0}^J(\mathbf{r}, R) = 0 \quad (47)$$

where

$$H_{\Omega\Omega} = -\frac{\hbar^2}{2\mu_{AB}R} \frac{\partial^2}{\partial R^2} R + \frac{1}{2\mu_{AB}R^2} [\hbar^2 J(J+1) - 2\hbar^2 \Omega^2 + J_e^2] - \frac{\hbar^2}{2m_e} \nabla_r^2 - \frac{\hbar^2}{2(m_A + m_B)} \nabla_r^2 + V(\mathbf{r}, R) \quad (48)$$

$$H_{\Omega, \Omega \pm 1} = -\frac{\hbar[(J \pm \Omega + 1)(J \mp \Omega)]^{1/2} J_{e\mp}}{2\mu_{AB}R^2} \quad (49)$$

and

$$J_{e\pm} = J_{ex} \pm iJ_{ey} \quad (50)$$

Substituting Eq. (46), using orthogonality,

$$\langle \phi_{\gamma n_1 \Omega_1}^a(\mathbf{r}, R) | \phi_{\alpha n \Omega}^a(\mathbf{r}, R) \rangle_{\mathbf{r}} = \delta_{\gamma\alpha} \delta_{n_1 n} \delta_{\Omega_1 \Omega} \quad (51)$$

[which is consistent with Eq. (37)], and requiring

$$\langle \phi_{\gamma n_1 \Omega_1}^a(\mathbf{r}, R) | \text{Eq. (47)} \rangle_{\mathbf{r}} = 0 \quad (52)$$

for a set of γ , n_1 , and Ω_1 leads to coupled radial equations

$$\begin{aligned} & \left\{ -\frac{\hbar^2}{2\mu_{AB}} \frac{d^2}{dR^2} + \varepsilon_{\gamma n_1 \Omega}^a(R) - E + \frac{\hbar^2}{2\mu_{AB} R^2} [J(J+1) - 2\Omega^2] \right\} g_{\gamma n_1 \Omega \alpha n \Omega_0}^J(R) \\ & + \sum_{\alpha n} \left[\frac{1}{2\mu_{AB} R^2} \langle \phi_{\gamma n_1 \Omega}^a | J_e^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}} - \frac{\hbar^2}{2(m_A + m_B)} \langle \phi_{\gamma n_1 \Omega}^a | \nabla_{\mathbf{r}}^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}} \right. \\ & - \frac{\hbar^2}{2\mu_{AB}} \left(2 \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial}{\partial R} \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}} \frac{d}{dR} \right. \\ & \left. \left. + \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial^2}{\partial R^2} \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}} \right) \right] g_{\alpha n \Omega \alpha n \Omega_0}^J(R) = \sum_{\alpha n} \frac{\hbar}{2\mu_{AB} R^2} \\ & \times \left\{ [(J - \Omega + 1)(J + \Omega)]^{1/2} \langle \phi_{\gamma n_1, \Omega}^a | J_{e+} | \phi_{\alpha n, \Omega-1}^a \rangle_{\mathbf{r}} g_{\alpha n, \Omega-1, \alpha n \Omega_0}^J \right. \\ & + [(J + \Omega + 1)(J - \Omega)]^{1/2} \langle \phi_{\gamma n_1, \Omega}^a | J_{e-} | \phi_{\alpha n, \Omega+1}^a \rangle_{\mathbf{r}} \\ & \left. \times g_{\alpha n, \Omega+1, \alpha n \Omega_0}^J(R) \right\} \quad (53) \end{aligned}$$

The diagonal part ($\gamma = \alpha$, $n_1 = n$, $\Omega_1 = \Omega$) of this equation agrees with the equation for the adiabatic approximation originally derived by Van Vleck (1936).

The electronic wave functions can also be considered functions of the space-fixed coordinates (\mathbf{r}'_a , \mathbf{R}'_a) and the total wave function $\Psi_{\alpha_0 n_0 \Omega_0}$ can be expanded in this coordinate system to yield

$$\Psi_{\alpha_0 n_0 \Omega_0}(\mathbf{r}'_a, \mathbf{R}'_a) = \sum_{\alpha n \Omega} \phi_{\alpha n \Omega}^a(\mathbf{r}'_a, \mathbf{R}'_a) f_{\alpha n \Omega \alpha_0 n_0 \Omega_0}(\mathbf{R}'_a) \quad (54)$$

The orthogonality condition now reads

$$\langle \phi_{\gamma n_1 \Omega_1}^a(\mathbf{r}'_a, \mathbf{R}'_a) | \phi_{\alpha n \Omega}^a(\mathbf{r}'_a, \mathbf{R}'_a) \rangle_{\mathbf{r}'_a} = \delta_{\gamma\alpha} \delta_{n_1 n} \delta_{\Omega_1 \Omega} \quad (55)$$

which follows from $\mathbf{R}'_a = \mathbf{R}'$ and Eq. (51). We require that

$$\langle \phi_{\gamma n_1 \Omega_1}^a(\mathbf{r}'_a, \mathbf{R}'_a) | H - E | \Psi_{\alpha_0 n_0 \Omega_0} \rangle_{\mathbf{r}'_a} = 0 \quad (56)$$

for a set of γ, n_1, Ω_1 . This yields the set of coupled equations

$$\begin{aligned} & \left[-\frac{\hbar^2}{2\mu_{AB}} \nabla_{R'_a}^2 + \varepsilon_{\gamma n_1 \Omega_1}^a(R'_a) - E \right] f_{\gamma n_1 \Omega_1 \alpha_0 n_0 \Omega_0}(\mathbf{R}'_a) \\ & + \sum_{\alpha n \Omega} \left\{ -\frac{\hbar^2}{2\mu_{AB}} \left[\langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{R'_a}^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} + 2 \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{R'_a} | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} \cdot \nabla_{R'_a} \right] \right. \\ & - \hbar^2 \left[\frac{1-a}{m_A} - \frac{a}{m_B} \right] \left[\langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{r}'_a} \cdot \nabla_{R'_a} | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} \right. \\ & \left. \left. + \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{r}'_a} | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} \cdot \nabla_{R'_a} \right] - \frac{\hbar^2}{2} \left[\frac{(1-a)^2}{m_A} + \frac{a^2}{m_B} \right] \right\} \\ & \times \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{r}'_a}^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} \left\} f_{\alpha n \Omega \alpha_0 n_0 \Omega_0}(\mathbf{R}'_a) = 0 \quad (57) \end{aligned}$$

Notice that these coupled equations can be obtained directly from the coupled equations (39) in the $(\mathbf{r}', \mathbf{R}')$ coordinates by use of the transformation

$$\mathbf{r}'_a = \mathbf{r}' + (a_{CMN} - a)\mathbf{R}' \quad (58)$$

$$\mathbf{R}'_a = \mathbf{R}' \quad (59)$$

and the relationships between the derivative coupling matrices

$$\begin{aligned} & \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{R}'} | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'} \\ & = \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{R}'_a} | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} + (a_{CMN} - a) \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{r}'_a} | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} \\ & = \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{R}'_a} | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} + (a_{CMN} - a) \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{r}'_a} | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} \quad (60) \end{aligned}$$

$$\begin{aligned} & \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{R}'}^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'} \\ & = \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{R}'_a}^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} + 2(a_{CMN} - a) \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{r}'_a} \cdot \nabla_{\mathbf{R}'_a} | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} \\ & \quad + (a_{CMN} - a)^2 \langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{\mathbf{r}'_a}^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}'_a} \quad (61) \end{aligned}$$

Thus the derivative coupling matrices appearing in Eq. (39) are affected by changing the electronic origin. Thus one is not free to use an arbitrary origin for the derivative coupling matrices and still use Eq. (39).

Coupled radial equations analogous to Eqs. (47)–(53) can be obtained in the body-fixed $(\mathbf{r}_a, \mathbf{R}_a)$ coordinates. The wave function $\Psi_{\alpha_0 n_0 \Omega_0}^{JM}(\mathbf{r}'_a, \mathbf{R}'_a)$ satisfies Eqs. (41)–(43) and can be rotated to the body-fixed coordinates as in Eq. (44):

$$\Psi_{\alpha_0 n_0 \Omega_0}^{JM}(\mathbf{r}'_a, \mathbf{R}'_a) = \sum_{\Omega=-J}^J D_{\Omega M}^J(\phi, \theta, 0) \Psi_{\Omega \alpha_0 n_0 \Omega_0}^J(\mathbf{r}_a, R_a) \quad (62)$$

Then we expand $\Psi_{\Omega \alpha_0 n_0 \Omega_0}^J$ in the Born–Oppenheimer basis set

$$\Psi_{\Omega \alpha_0 n_0 \Omega_0}^J = R_a^{-1} \sum_{an} \phi_{an\Omega}^a(\mathbf{r}_a, R_a) g_{an\Omega \alpha_0 n_0 \Omega_0}^J(R_a) \quad (63)$$

The coupled equations for $\Psi_{\Omega \alpha_0 n_0 \Omega_0}^J(\mathbf{r}_a, R_a)$ are obtained (see, e.g., Pack and Hirschfelder, 1968) by use of the Hamiltonian of Eq. (18):

$$H_{a\Omega, \Omega-1} \Psi_{\Omega-1, \alpha_0 n_0 \Omega_0}^J(\mathbf{r}_a, R_a) + (H_{a\Omega\Omega} - E) \Psi_{\Omega \alpha_0 n_0 \Omega_0}^J(\mathbf{r}_a, R_a) + H_{a\Omega, \Omega+1} \Psi_{\Omega+1, \alpha_0 n_0 \Omega_0}^J(\mathbf{r}_a, R_a) = 0 \quad (64)$$

where

$$H_{a\Omega\Omega} = -\frac{\hbar^2}{2\mu_{AB} R_a} \frac{\partial^2}{\partial R_a^2} R_a + \frac{1}{2\mu_{AB} R_a^2} [\hbar^2 J(J+1) - 2\hbar^2 \Omega^2 + J_{ea}^2] + \frac{\hbar}{2R_a} \left(\frac{1-a}{m_A} - \frac{a}{m_B} \right) \left[\left(\frac{\partial}{\partial x_a} - i \frac{\partial}{\partial y_a} \right) J_{ea+} - \left(\frac{\partial}{\partial x_a} + i \frac{\partial}{\partial y_a} \right) J_{ea-} - 2\hbar \frac{\partial}{\partial z_a} \frac{\partial}{\partial R_a} R_a \right] - \frac{\hbar^2}{2} \left[\frac{1}{m_e} + \frac{(1-a)^2}{m_A} + \frac{a^2}{m_B} \right] \nabla_{r_a}^2 + V(\mathbf{r}_a, R_a) \quad (65)$$

$$H_{a\Omega, \Omega \pm 1} = -\hbar[(J \pm \Omega + 1)(J \mp \Omega)]^{1/2} \times \left[\frac{J_{ea\mp}}{2\mu_{AB} R_a^2} \pm \frac{\hbar}{2R_a} \left(\frac{1-a}{m_A} - \frac{a}{m_B} \right) \left(\frac{\partial}{\partial x_a} \mp i \frac{\partial}{\partial y_a} \right) \right] \quad (66)$$

The Born–Oppenheimer basis states remain orthogonal in this coordinate system

$$\langle \phi_{\gamma n_1 \Omega_1}^a(\mathbf{r}_a, R_a) | \phi_{\alpha n \Omega}^a(\mathbf{r}_a, R_a) \rangle_{r_a} = \delta_{\gamma\alpha} \delta_{n_1 n} \delta_{\Omega_1 \Omega} \quad (67)$$

and we require that

$$\langle \phi_{\gamma n_1 \Omega_1}^a(\mathbf{r}_a, R_a) | \text{Eq. (64)} \rangle = 0 \quad (68)$$

for a set of γ , n_1 , and Ω_1 . Substitution of Eq. (63) gives the coupled radial equations for a set of γ , n_1 , and Ω_1 :

$$\begin{aligned}
& \left\{ -\frac{\hbar^2}{2\mu_{AB}} \frac{d^2}{dR_a^2} + \varepsilon_{\gamma n_1 \Omega}^a(R_a) - E + \frac{\hbar^2}{2\mu_{AB} R_a^2} [J(J+1) - 2\Omega^2] \right\} g_{\gamma n_1 \Omega a_0 n_0 \Omega_0}^J(R_a) \\
& + \sum_{an} \left\{ -\frac{\hbar^2}{2\mu_{AB}} \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial^2}{\partial R_a^2} \right| \phi_{an\Omega}^a \right\rangle_{r_a} - \frac{\hbar^2}{\mu_{AB}} \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial}{\partial R_a} \right| \phi_{an\Omega}^a \right\rangle_{r_a} \frac{d}{dR_a} \right. \\
& + \frac{1}{2\mu_{AB} R_a^2} \langle \phi_{\gamma n_1 \Omega}^a | J_{ea}^2 | \phi_{an\Omega}^a \rangle_{r_a} + \frac{\hbar}{2R_a} \left(\frac{1-a}{m_A} - \frac{a}{m_B} \right) \\
& \times \left[\left\langle \phi_{\gamma n_1 \Omega}^a \left| \left(\frac{\partial}{\partial x_a} - i \frac{\partial}{\partial y_a} \right) J_{ea+} \right| \phi_{an\Omega}^a \right\rangle_{r_a} \right. \\
& - \left. \left\langle \phi_{\gamma n_1 \Omega}^a \left| \left(\frac{\partial}{\partial x_a} + i \frac{\partial}{\partial y_a} \right) J_{ea-} \right| \phi_{an\Omega}^a \right\rangle_{r_a} \right. \\
& - 2\hbar R_a \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial}{\partial z_a} \frac{\partial}{\partial R_a} \right| \phi_{an\Omega}^a \right\rangle_{r_a} - 2\hbar R_a \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial}{\partial z_a} \right| \phi_{an\Omega}^a \right\rangle_{r_a} \frac{d}{dR_a} \left. \right] \\
& - \frac{\hbar^2}{2} \left[\frac{(1-a)^2}{m_A} + \frac{a^2}{m_B} \right] \langle \phi_{\gamma n_1 \Omega}^a | \nabla_{r_a}^2 | \phi_{an\Omega}^a \rangle_{r_a} \left. \right\} g_{an\Omega a_0 n_0 \Omega_0}^J(R_a) \\
& = \sum_{an} \left\{ \hbar [(J + \Omega + 1)(J - \Omega)]^{1/2} \left[\frac{1}{2\mu_{AB} R_a^2} \langle \phi_{\gamma n_1 \Omega}^a | J_{ea-} | \phi_{an, \Omega+1}^a \rangle_{r_a} \right. \right. \\
& + \frac{\hbar}{2R_a} \left(\frac{1-a}{m_A} - \frac{a}{m_B} \right) \left\langle \phi_{\gamma n_1, \Omega}^a \left| \frac{\partial}{\partial x_a} - i \frac{\partial}{\partial y_a} \right| \phi_{an, \Omega+1}^a \right\rangle_{r_a} \left. \right] g_{an, \Omega+1, a_0 n_0 \Omega_0}^J(R_a) \\
& + \hbar [(J - \Omega + 1)(J + \Omega)]^{1/2} \left[\frac{1}{2\mu_{AB} R_a^2} \langle \phi_{\gamma n_1 \Omega}^a | J_{ea+} | \phi_{an, \Omega+1}^a \rangle_{r_a} \right. \\
& - \frac{\hbar}{2R_a} \left(\frac{1-a}{m_A} - \frac{a}{m_B} \right) \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial}{\partial x_a} + i \frac{\partial}{\partial y_a} \right| \phi_{an, \Omega-1}^a \right\rangle_{r_a} \left. \right] \\
& \times g_{an, \Omega-1, a_0 n_0 \Omega_0}^J(R_a) \tag{69}
\end{aligned}$$

The derivative coupling matrices in the (\mathbf{r}, \mathbf{R}) and $(\mathbf{r}_a, \mathbf{R}_a)$ coordinate systems are related by the transformations

$$\begin{aligned}
& \left\langle \phi_{\gamma n_1 \Omega_1}^a \left| \frac{\partial}{\partial R} \right| \phi_{an\Omega}^a \right\rangle_{\mathbf{r}} \\
& = \left\langle \phi_{\gamma n_1 \Omega_1}^a \left| \frac{\partial}{\partial R_a} \right| \phi_{an\Omega}^a \right\rangle_{\mathbf{r}} + (a_{CMN} - a) \left\langle \phi_{\gamma n_1 \Omega_1}^a \left| \frac{\partial}{\partial z_a} \right| \phi_{an\Omega}^a \right\rangle_{\mathbf{r}} \\
& = \left\langle \phi_{\gamma n_1 \Omega_1}^a \left| \frac{\partial}{\partial R_a} \right| \phi_{an\Omega}^a \right\rangle_{\mathbf{r}_a} + (a_{CMN} - a) \left\langle \phi_{\gamma n_1 \Omega_1}^a \left| \frac{\partial}{\partial z_a} \right| \phi_{an\Omega}^a \right\rangle_{\mathbf{r}_a} \tag{70}
\end{aligned}$$

$$\begin{aligned}
& \left\langle \phi_{\gamma n_1 \Omega_1}^a \left| \frac{\partial^2}{\partial R^2} \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}} \\
&= \left\langle \phi_{\gamma n_1 \Omega_1}^a \left| \frac{\partial^2}{\partial R_a^2} \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}_a} + 2(a_{\text{CMN}} - a) \left\langle \phi_{\gamma n_1 \Omega_1}^a \left| \frac{\partial}{\partial R_a} \frac{\partial}{\partial z_a} \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}_a} \\
&+ (a_{\text{CMN}} - a)^2 \left\langle \phi_{\gamma n_1 \Omega_1}^a \left| \frac{\partial^2}{\partial z_a^2} \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}_a} \quad (71)
\end{aligned}$$

However, in transforming the coupled equations from the (\mathbf{r}, \mathbf{R}) coordinates to the $(\mathbf{r}_a, \mathbf{R}_a)$ coordinates, it is also necessary to transform the angular momentum matrix elements. The necessary relationships for such a transformation are

$$\begin{aligned}
J_e^2 &= J_{e_a}^2 + (a_{\text{CMN}} - a) \hbar R_a \left[\left(\frac{\partial}{\partial x_a} - i \frac{\partial}{\partial y_a} \right) J_{e_a+} - \left(\frac{\partial}{\partial x_a} + i \frac{\partial}{\partial y_a} \right) J_{e_a-} \right] \\
&- (a_{\text{CMN}} - a)^2 \hbar^2 R_a^2 \left[\nabla_{\mathbf{r}_a}^2 - \frac{\partial^2}{\partial z_a^2} \right] \quad (72)
\end{aligned}$$

$$J_{e_{\pm}} = J_{e_a \pm} \mp (a_{\text{CMN}} - a) \hbar R_a \left[\frac{\partial}{\partial x_a} \pm i \frac{\partial}{\partial y_a} \right] \quad (73)$$

Using Eqs. (70)–(73), the coupled equations (69) can be obtained from the coupled equation (53) in the (\mathbf{r}, \mathbf{R}) coordinate system; therefore the radial functions $g_{\alpha n \Omega \alpha n_0 \Omega_0}^J$ are actually the same in both sets of coupled equations. In considering the whole set of equations, Eqs. (53) or (69), we emphasize that the origin used in defining the derivative-coupling and angular-momentum-coupling matrices must be consistent with the origin used in defining the coupled equations.

Another useful expansion of the wave function $\Psi_{\alpha_0 n_0 \Omega_0}^{JM}$ is

$$\Psi_{\alpha_0 n_0 \Omega_0}^{JM} = \sum_{\alpha=A, B} \sum_{\Omega=-J}^J D_{\Omega M}^J(\phi, \theta, 0) \Psi_{\alpha \Omega \alpha_0 n_0 \Omega_0}^J(\mathbf{r}_{a(\alpha)}, R_{a(\alpha)}) \quad (74)$$

where $\mathbf{r}_{a(\alpha)}$ and $\mathbf{R}_{a(\alpha)}$ are defined in the body-fixed frame of reference and $a(\alpha) = 0$ or 1 for $\alpha = A$ or B , respectively; i.e., the electronic origin is at nucleus α for the states for which the electron is attached to atom α at large R . Substitution in Eq. (41) gives the coupled equations

$$\begin{aligned}
& \sum_{\alpha=A, B} [H_{a(\alpha)\Omega, \Omega-1} \Psi_{\alpha, \Omega-1, \alpha_0 n_0 \Omega_0}^J(\mathbf{r}_{a(\alpha)}, R_{a(\alpha)}) \\
&+ (H_{a(\alpha)\Omega\Omega} - E) \Psi_{\alpha \Omega \alpha_0 n_0 \Omega_0}^J(\mathbf{r}_{a(\alpha)}, R_{a(\alpha)}) \\
&+ H_{a(\alpha)\Omega, \Omega+1} \Psi_{\alpha, \Omega+1, \alpha_0 n_0 \Omega_0}^J(\mathbf{r}_{a(\alpha)}, R_{a(\alpha)})] = 0 \quad (75)
\end{aligned}$$

where $H_{a(x)\Omega\Omega}$ and $H_{a(x)\Omega, \Omega \pm 1}$ are given by Eqs. (65) and (66). The wave function $\Psi_{\alpha\Omega\alpha_0n_0\Omega_0}^J(\mathbf{r}_{a(x)}, \mathbf{R}_{a(x)})$ can be expanded in the adiabatic basis set

$$\Psi_{\alpha\Omega\alpha_0n_0\Omega_0}^J(\mathbf{r}_{a(x)}, \mathbf{R}_{a(x)}) = R_{a(x)}^{-1} \sum_n \phi_{\alpha n \Omega}^a(\mathbf{r}_{a(x)}, \mathbf{R}_{a(x)}) g_{\alpha n \Omega \alpha_0 n_0 \Omega_0}^J(R_{a(x)}) \quad (76)$$

Substituting Eq. (76) into Eq. (75) and closing from the left with

$$\int d\mathbf{r}_{a\gamma} \phi_{\gamma n_1 \Omega_1}^{a*}(\mathbf{r}_{a(\gamma)}, \mathbf{R}_{a(\gamma)})$$

for a set of γ , n_1 , and Ω_1 leads to the coupled equations

$$\begin{aligned} \sum_{\alpha n} \left\{ \left[\left(-\frac{\hbar^2}{2\mu_{AB}} \frac{d^2}{dR_{a(x)}^2} + \varepsilon_{\alpha n \Omega}^a(R_{a(x)}) - E + \frac{\hbar^2}{2\mu_{AB} R_{a(x)}^2} [(J+1) - 2\Omega^2] \right) \delta_{\gamma\alpha} \delta_{n_1 n} \right. \right. \\ - \frac{\hbar^2}{2\mu_{AB}} \left(\left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial^2}{\partial R_{a(x)}^2} \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}_{a(x)}} + \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial}{\partial R_{a(x)}} \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}_{a(x)}} \frac{d}{dR_{a(x)}} \right) \\ + (2\mu_{AB} R_{a(x)}^2)^{-1} \langle \phi_{\gamma n_1 \Omega}^a | J_{ea(x)}^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}_{a(x)}} \\ + \frac{\hbar}{2R_{a(x)} m_x} \left[\left\langle \phi_{\gamma n_1 \Omega}^a \left| \left(\frac{\partial}{\partial x_{a(x)}} - i \frac{\partial}{\partial y_{a(x)}} \right) J_{ea(x)} + \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}_{a(x)}} \right. \\ - \left. \left\langle \phi_{\gamma n_1 \Omega}^a \left| \left(\frac{\partial}{\partial x_{a(x)}} + i \frac{\partial}{\partial y_{a(x)}} \right) J_{ea(x)} - \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}_{a(x)}} \right. \\ - 2\hbar R_{a(x)} \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial}{\partial z_{a(x)}} \frac{\partial}{\partial R_{a(x)}} \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}_{a(x)}} \\ - 2\hbar R_{a(x)} \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial}{\partial z_{a(x)}} \right| \phi_{\alpha n \Omega}^a \right\rangle_{\mathbf{r}_{a(x)}} \frac{d}{dR_{a(x)}} \Big] \\ - \frac{\hbar^2}{2m_x} \langle \phi_{\gamma n_1 \Omega}^a | \nabla_{\mathbf{r}_{a(x)}}^2 | \phi_{\alpha n \Omega}^a \rangle_{\mathbf{r}_{a(x)}} \Big] g_{\alpha n \Omega \alpha_0 n_0 \Omega_0}^J(R_{a(x)}) \\ - \hbar [(J + \Omega + 1)(J - \Omega)]^{1/2} \left((2\mu_{AB} R_{a(x)}^2)^{-1} \langle \phi_{\gamma n_1 \Omega}^a | J_{ea(x)} - | \phi_{\alpha n, \Omega+1}^a \rangle_{\mathbf{r}_{a(x)}} \right. \\ + \left. \frac{\hbar f_x}{2m_x R_{a(x)}} \left\langle \phi_{\gamma n, \Omega}^2 \left| \frac{\partial}{\partial x_{a(x)}} - i \frac{\partial}{\partial y_{a(x)}} \right| \phi_{\alpha n, \Omega+1}^a \right\rangle_{\mathbf{r}_{a(x)}} \right) g_{\alpha n, \Omega+1, \alpha_0 n_0 \Omega_0}^J(R_{a(x)}) \\ - \hbar [(J - \Omega + 1)(J + \Omega)]^{1/2} \left((2\mu_{AB} R_{a(x)}^2)^{-1} \langle \phi_{\gamma n_1 \Omega}^a | J_{ea(x)} + | \phi_{\alpha n, \Omega-1}^a \rangle_{\mathbf{r}_{a(x)}} \right. \\ - \left. \frac{\hbar f_x}{2m_x R_{a(x)}} \left\langle \phi_{\gamma n_1 \Omega}^a \left| \frac{\partial}{\partial x_{a(x)}} + i \frac{\partial}{\partial y_{a(x)}} \right| \phi_{\alpha n, \Omega-1}^a \right\rangle_{\mathbf{r}_{a(x)}} \right) \\ \left. \times g_{\alpha n, \Omega-1, \alpha_0 n_0 \Omega_0}^J(R_{a(x)}) \right\} = 0 \quad (77) \end{aligned}$$

Alternatively, using the transformations in Eqs. (70)–(73) and the fact that $R = R_a = R_{a(\alpha)}$, the coupled equations given above can be derived directly from those given in Eq. (69). Since the transformation involves no approximations, the radial wave functions in each set of equations are equivalent. The advantage of using the coupled equations (77) is that they are more uncoupled at large R .

It will be useful later to have defined electronic basis functions that are centered on one nucleus and translate with that nucleus, but do not rotate with the \hat{R}' axis and have no explicit dependence upon the internuclear distance. These functions do have an implicit dependence upon \mathbf{R}' because they translate with the nuclei. They are eigenfunctions of the atomic electronic Hamiltonian

$$[-(\hbar^2/2\mu_e^2)\nabla_{r'_\alpha}^2 + V_\alpha(r'_\alpha)]\phi_{pjm_j}^\alpha(r'_\alpha) = \epsilon_{pj}^\alpha \phi_{pjm_j}^\alpha(r'_\alpha) \quad (78)$$

and are therefore called atomic states. $V_\alpha(r'_\alpha)$ is the limit of $V(r'_\alpha, \mathbf{R}'_\alpha)$ as R'_α and (R'_α/r'_α) tend to infinity. The label p denotes the atomic principal quantum number and the label j denotes the electronic angular momentum quantum number. The total wave function can be expanded in these (overcomplete) atomic basis states to give

$$\Psi_{\alpha_0 p_0 j_0 m_{j_0}} = \sum_{\alpha p j m_j} \phi_{pjm_j}^\alpha(r'_\alpha) \tilde{f}_{\alpha p j m_j \alpha_0 p_0 j_0 m_{j_0}}(\mathbf{R}'_\alpha) \quad (79)$$

The wave function $\Psi_{\alpha_0 p_0 j_0 m_{j_0}}$ satisfies the Schroedinger equation with the Hamiltonian given most conveniently by Eq. (24). Requiring

$$\langle \phi_{p_1 j_1 m_{j_1}}^\gamma(r'_\gamma, \mathbf{R}'_\gamma) | H - E | \Psi_{\alpha_0 p_0 j_0} \rangle_{r'_\gamma} = 0 \quad (80)$$

for a set of γ , p_1 , j_1 , and m_{j_1} yields the equation

$$\sum_{\alpha p j m_j} \langle \phi_{p_1 j_1 m_{j_1}}^\gamma(r'_\gamma) | -(\hbar^2/2\mu_{AB}^2)\nabla_{R'_\alpha}^2 + H_{e\alpha} - E | \phi_{pjm_j}^\alpha(r'_\alpha) \tilde{f}_{\alpha p j m_j \alpha_0 p_0 j_0 m_{j_0}}(\mathbf{R}'_\alpha) \rangle_{r'_\gamma} = 0 \quad (81)$$

where

$$H_{e\alpha} = -(\hbar^2/2\mu_e^2)\nabla_{r'_\alpha}^2 + V(r'_\alpha, \mathbf{R}'_\alpha) \quad (82)$$

The wave functions $\tilde{f}_{\alpha p j m_j \alpha_0 p_0 j_0 m_{j_0}}(\mathbf{R}'_\alpha)$ are explicitly included in this integration because \mathbf{R}'_α is a function of r'_γ for $\alpha \neq \gamma$. This leads to coupled integro-differential equations that are much more difficult to solve than the differential equations (39). The coupled equations are

$$\begin{aligned} & [-(\hbar^2/2\mu_{AB}^2)\nabla_{R'_\gamma}^2 - E] \tilde{f}_{\gamma p_1 j_1 m_{j_1} \alpha_0 p_0 j_0 m_{j_0}}(\mathbf{R}'_\gamma) \\ & + \sum_{p j m_j} \langle \phi_{p_1 j_1 m_{j_1}}^\gamma | H_{e\alpha} | \phi_{pjm_j}^\alpha \rangle_{r'_\gamma} \tilde{f}_{\gamma p j m_j \alpha_0 p_0 j_0 m_{j_0}}(\mathbf{R}'_\gamma) \\ & + \sum_{\alpha \neq \gamma} \sum_{p j m_j} \langle \phi_{p_1 j_1 m_{j_1}}^\gamma(r'_\gamma) | H - E | \phi_{pjm_j}^\alpha[r'_\alpha(r'_\gamma, \mathbf{R}'_\gamma)] \\ & \times \tilde{f}_{\alpha p j m_j \alpha_0 p_0 j_0 m_{j_0}}[\mathbf{R}'_\alpha(r'_\gamma, \mathbf{R}'_\gamma)] \rangle_{r'_\gamma} = 0 \end{aligned} \quad (83)$$

The last term in Eq. (83) contains the rearrangement kernel that describes the exchange of an electron between the nuclei during the collision.

A convenient method for coupling the angular momenta to obtain scattering wave functions obeying Eqs. (42) and (43) has been given by Percival and Seaton (1957) and Arthurs and Dalgarno (1960) (see also Blatt and Biedenharn, 1952; Truhlar *et al.*, 1975). The total wave function $\Psi_{\alpha_0 p_0 j_0 m_j 0}$ is expanded in scattering states that are eigenfunctions of J_{tot} and $J_{\text{tot}, z'}$

$$\Psi_{\alpha_0 p_0 j_0 m_j 0} = \sum_{JM} \Psi_{\alpha_0 p_0 j_0 m_j 0}^{JM} \quad (84)$$

and each JM component has the expansion

$$\Psi_{\alpha_0 p_0 j_0 m_j 0}^{JM} = \sum_{l_{\alpha 0}} \tilde{A}_{\alpha_0 p_0 j_0 m_j 0 l_{\alpha 0}}^{JM} \Psi_{\alpha_0 p_0 j_0 l_{\alpha 0}}^{JM} \quad (85)$$

The atomic states are expanded in spherical harmonics

$$\phi_{p j m_j}^{\alpha}(\mathbf{r}'_{\alpha}) = P_{p j}^{\alpha}(\mathbf{r}'_{\alpha}) Y_{j m_j}(\hat{\mathbf{r}}'_{\alpha}) \quad (86)$$

and we expand $\Psi_{\alpha_0 n_0 l_{\alpha 0}}^{JM}$ as

$$\Psi_{\alpha_0 p_0 j_0 l_{\alpha 0}}^{JM} = \sum_{\alpha p j l_{\alpha}} P_{p j}^{\alpha}(\mathbf{r}'_{\alpha}) \mathcal{Y}_{j l_{\alpha}}^{JM}(\hat{\mathbf{r}}'_{\alpha}, \hat{\mathbf{R}}'_{\alpha})(R'_{\alpha})^{-1} \tilde{g}_{\alpha p j l_{\alpha} p_0 j_0 l_{\alpha 0}}^J(R'_{\alpha}) \quad (87)$$

The functions $\mathcal{Y}_{j l_{\alpha}}^{JM}(\hat{\mathbf{r}}'_{\alpha}, \hat{\mathbf{R}}'_{\alpha})$ are eigenfunctions of J_{tot}^2 , $J_{\text{tot}, z'}$, L_{α}^2 , and $J_{\alpha z}^2$ and are given by

$$\mathcal{Y}_{j l_{\alpha}}^{JM}(\hat{\mathbf{r}}'_{\alpha}, \hat{\mathbf{R}}'_{\alpha}) = \sum_{m_j = -j}^j \sum_{m_{\alpha} = -l_{\alpha}}^{l_{\alpha}} C(j l_{\alpha} J; m_j m_{\alpha} M) Y_{j m_j}(\hat{\mathbf{r}}'_{\alpha}) Y_{l_{\alpha} m_{\alpha}}(\hat{\mathbf{R}}'_{\alpha}) \quad (88)$$

where $C(j l_{\alpha} J; m_j m_{\alpha} M)$ is a Clebsch-Gordan coefficient. Coupled equations for the radial functions $\tilde{g}_{\alpha p j l_{\alpha} p_0 j_0 l_{\alpha 0}}^J(R'_{\alpha})$ can be obtained by substituting Eq. (87) into the equation

$$\int d\hat{\mathbf{R}}'_{\gamma} \int d\mathbf{r}'_{\gamma} P_{p_1 j_1}^{\gamma*}(\mathbf{r}'_{\gamma}) \mathcal{Y}_{j_1 l_{\gamma 1}}^{JM*}(\hat{\mathbf{r}}'_{\gamma}, \hat{\mathbf{R}}'_{\gamma})(H - E) \Psi_{\alpha_0 p_0 j_0 l_{\alpha 0}}^{JM} = 0 \quad (89)$$

where the Hamiltonian is given in Eq. (24). The resulting coupled equations for a set of γ , p_1 , j_1 , and l_{γ} , are

$$\begin{aligned} & \left[-\frac{\hbar^2}{2\mu_{\text{AB}}^{\gamma}} \frac{d^2}{dR_{\gamma}^{\prime 2}} + \frac{\hbar^2 l_{\gamma 1} (l_{\gamma 1} + 1)}{2\mu_{\text{AB}}^{\gamma} R_{\gamma}^{\prime 2}} - E \right] \tilde{g}_{\gamma p_1 j_1 l_{\gamma 1} p_0 j_0 l_{\alpha 0}}^J(R'_{\gamma}) \\ & + \sum_{p_1 j_1} \left\{ \int d\hat{\mathbf{R}}'_{\gamma} \int d\mathbf{r}'_{\gamma} \mathcal{Y}_{j_1 l_{\gamma 1}}^{JM*}(\hat{\mathbf{r}}'_{\gamma}, \hat{\mathbf{R}}'_{\gamma}) P_{p_1 j_1}^{\gamma*}(\mathbf{r}'_{\gamma}) [H_{\alpha} P_{p j}^{\gamma}(\mathbf{r}'_{\gamma}) \mathcal{Y}_{j l_{\gamma}}^{JM}(\hat{\mathbf{r}}'_{\gamma}, \hat{\mathbf{R}}'_{\gamma})] \right\} \\ & \times \tilde{g}_{\gamma p j l_{\gamma} p_0 j_0 l_{\alpha 0}}^J(R'_{\gamma}) + \sum_{\alpha \neq \gamma} \sum_{p j l_{\alpha}} \int d\hat{\mathbf{R}}'_{\alpha} \int d\mathbf{r}'_{\alpha} P_{p j}^{\alpha*}(\mathbf{r}'_{\alpha}) \mathcal{Y}_{j l_{\alpha}}^{JM*}(\hat{\mathbf{r}}'_{\alpha}, \hat{\mathbf{R}}'_{\alpha}) \\ & \times (H - E) P_{p j}^{\alpha}(\mathbf{r}'_{\alpha}, R'_{\alpha}) \mathcal{Y}_{j l_{\alpha}}^{JM}(\hat{\mathbf{r}}'_{\alpha}, \hat{\mathbf{R}}'_{\alpha})(\mathbf{r}'_{\alpha}, \mathbf{R}'_{\alpha}) \\ & \times \tilde{g}_{\alpha p j l_{\alpha} p_0 j_0 l_{\alpha 0}}^J(R'_{\alpha})(\mathbf{r}'_{\alpha}, \mathbf{R}'_{\alpha}) = 0. \end{aligned} \quad (90)$$

7. ASYMPTOTIC BOUNDARY CONDITIONS

Proper scattering boundary conditions can be imposed upon the total wave function $\Psi_{\alpha_0 n_0 \Omega_0}$ or $\Psi_{\alpha_0 p_0 j_0 m_{j_0}}$ only in the (r'_α, R'_α) coordinate system. The coordinates $(\mathbf{r}', \mathbf{R}')$ or (\mathbf{r}, \mathbf{R}) are not appropriate at large R because neither \mathbf{r}' nor \mathbf{r} remains finite as R becomes large. In these coordinate systems the electron is referenced to the center of mass of the nuclei, and it is translating with respect to this origin. Because of this, the derivative-coupling matrices do not vanish at large R . Consider the matrix element $\langle \phi_{\gamma n_1 \Omega_1}^a | \nabla_{R'} | \phi_{\alpha n \Omega}^a \rangle_{r'}$ for $\gamma = \alpha = A$ and $n_1 \neq n$. From Eq. (60) we obtain

$$\langle \phi_{A n_1 \Omega_1}^a | \nabla_{R'} | \phi_{A n \Omega}^a \rangle_{r'} = \langle \phi_{A n_1 \Omega_1}^a | \nabla_{R'_A} | \phi_{A n \Omega}^a \rangle_{r'_A} + a_{CMN} \langle \phi_{A n_1 \Omega_1}^a | \nabla_{r'_A} | \phi_{A n \Omega}^a \rangle_{r'_A} \quad (91)$$

For large R the first term in this equation vanishes; however, the second term does not. Since these derivative couplings between the electronic states persist at large R in Eq. (39), the channel functions $f_{\alpha n \Omega \alpha_0 n_0 \Omega_0}(\mathbf{R}')$ do not satisfy the usual scattering boundary conditions (Mott and Massey, 1965, p. 429). Similar considerations apply to Eqs. (53) and (69) and to the functions $g_{\alpha n \Omega \alpha_0 n_0 \Omega_0}^J(R)$. A formal analysis of the asymptotic behavior of $\Psi_{\alpha_0 n_0 \Omega}(\mathbf{r}, R)$ has been given by Kouri and Curtiss (1971).

In the space-fixed (r'_α, R'_α) coordinate system, the correct scattering boundary conditions for the total wave function $\Psi_{\alpha_0 p_0 j_0 m_{j_0}}$ are†

$$\Psi_{\alpha_0 p_0 j_0 m_{j_0}}(\mathbf{r}'_{\alpha_0}, \mathbf{R}'_{\alpha_0}) \underset{R \rightarrow \infty}{\sim} \exp(i\mathbf{k}_{p_0 j_0}^{\alpha_0} \cdot \mathbf{R}'_{\alpha_0}) \phi_{p_0 j_0 m_{j_0}}^{\alpha_0}(\mathbf{r}'_{\alpha_0}) + \sum_{\alpha p j m_j} R'_\alpha^{-1} \mathcal{F}_{\alpha p j m_j \alpha_0 p_0 j_0 m_{j_0}}(\hat{R}'_\alpha) \exp(i\mathbf{k}_{p j}^\alpha R'_\alpha) \phi_{p j m_j}^\alpha(\mathbf{r}'_\alpha) \quad (92)$$

where $\mathcal{F}_{\alpha p j m_j \alpha_0 p_0 j_0 m_{j_0}}(\hat{R}'_\alpha)$ is the amplitude for scattering from state $\alpha_0 p_0 j_0 m_{j_0}$ to state $\alpha p j m_j$, and the initial and final wave vectors are $\mathbf{k}_{p_0 j_0}^{\alpha_0}$ and $\mathbf{k}_{p j}^\alpha$, respectively. The magnitude of the wave vector is

$$k_{p j}^\alpha = [(2\mu_{AB}^\alpha / \hbar^2)(E - \epsilon_{p j}^\alpha)]^{1/2} \quad (93)$$

It is also possible to impose the scattering boundary conditions directly upon the wave functions $\tilde{f}_{\alpha p j m_j \alpha_0 p_0 j_0 m_{j_0}}(\mathbf{R}'_\alpha)$ and $\tilde{g}_{\alpha p j l \alpha_0 p_0 j_0 l \alpha_0}(\mathbf{R}'_\alpha)$. Comparing Eqs. (79) and (92) show that

$$\tilde{f}_{\alpha p j m_j \alpha_0 p_0 j_0 m_{j_0}}(\mathbf{R}'_\alpha) \underset{R \rightarrow \infty}{\sim} \exp(i\mathbf{k}_{p_0 j_0}^{\alpha_0} \cdot \mathbf{R}'_\alpha) \delta_{\alpha \alpha_0} \delta_{p p_0} \delta_{j j_0} \delta_{m_j m_{j_0}} + R'_\alpha^{-1} \mathcal{F}_{\alpha p j m_j \alpha_0 p_0 j_0 m_{j_0}}(\hat{R}'_\alpha) \exp(i\mathbf{k}_{p j}^\alpha R'_\alpha) \quad (94)$$

† Throughout this article the asymptotic boundary conditions are given for the case where the long-range potentials decay more rapidly than Coulomb potentials. The extension to include Coulomb boundary conditions in some or all channels is straightforward (see, e.g., Messiah, 1965, p. 421; Faist, 1975).

Equations (92)–(94) may be derived from the asymptotic limit of the coupled equations (83). As R'_γ becomes large with r'_γ finite, the matrix elements of the electronic Hamiltonian become diagonal with the atomic energies $\epsilon_{p_j}^\gamma$ on the diagonal, and the rearrangement kernel vanishes as the overlap between the electronic wave functions on the different nuclei goes to zero. Therefore, the limit of Eq. (83) as R'_γ and (R'_γ/r'_γ) tend to infinity is

$$\begin{aligned} & \left[-(\hbar^2/2\mu_{AB}^\gamma) \nabla_{R'_\gamma}^2 - (\hbar^2/2\mu_{AB}^\gamma) k_{p_{1j_1}}^{\gamma 2} \right] \tilde{f}_{\gamma p_{1j_1} m_{j_1} \alpha_0 p_0 j_0 m_{j_0}}(R'_\gamma) = 0 \\ & \text{for large } R'_\gamma \end{aligned} \quad (95)$$

Similarly, the coupled equations (90) for the radial wave functions $\tilde{g}_{\gamma p_{1j_1} \alpha_0 p_0 j_0 l_{\alpha_0}}^J(R'_\gamma)$ decouple at large R'_γ and finite r'_γ . The expression in braces involving the electronic energy reduces to $\epsilon_{p_j}^\gamma \delta_{p_1 p} \delta_{j_1 j} \delta_{l_{\gamma 1} l_\gamma}$, the rearrangement kernel vanishes, and Eq. (90) becomes

$$\begin{aligned} & \frac{\hbar^2}{2\mu_{AB}^\gamma} \left[-\frac{d^2}{dR_\gamma'^2} + \frac{l_{\gamma 1}(l_{\gamma 1} + 1)}{R_\gamma'^2} - (k_{p_{1j_1}}^\gamma)^2 \right] \tilde{g}_{\gamma p_{1j_1} l_{\gamma 1} \alpha_0 p_0 j_0 l_{\alpha_0}}^J(R'_\gamma) = 0 \\ & \text{for large } R'_\gamma \end{aligned} \quad (96)$$

The asymptotic behavior of the radial wave functions is given by

$$\begin{aligned} & \tilde{g}_{\alpha p_{1j_1} \alpha_0 p_0 j_0 l_{\alpha_0}}^J(R'_\alpha) \underset{R'_\alpha \rightarrow \infty}{\sim} \delta_{\alpha \alpha_0} \delta_{p p_0} \delta_{j j_0} \delta_{l_{\alpha} l_{\alpha_0}} \exp[-i(k_{p_j}^\alpha R'_\alpha - l_\alpha \pi/2)] \\ & - (k_{p_0 j_0}^{\alpha_0}/k_{p_j}^\alpha)^{1/2} S_{\alpha p_{1j_1} \alpha_0 p_0 j_0 l_{\alpha_0}}^J \exp[i(k_{p_j}^\alpha R'_\alpha - l_\alpha \pi/2)] \end{aligned} \quad (97)$$

where $S_{\alpha p_{1j_1} \alpha_0 p_0 j_0 l_{\alpha_0}}^J$ is an element of the scattering matrix (S matrix). The expansion coefficients $\tilde{A}_{\alpha_0 p_0 j_0 m_{j_0} l_{\alpha_0}}^{JM}$ of Eq. (85) can be identified by using the asymptotic limit (97) in combination with Eqs. (84), (85), and (87) to obtain the asymptotic limit of the total wave functions $\Psi_{\alpha_0 p_0 j_0 m_{j_0}}$. Comparison of this asymptotic behavior to Eq. (92) gives (see, e.g., Child, 1974, p. 102)

$$\tilde{A}_{\alpha_0 p_0 j_0 m_{j_0} l_{\alpha_0}}^{JM} = [(2l_{\alpha_0} + 1)\pi]^{1/2} i^{l_{\alpha_0} + 1} (k_{p_0 j_0}^{\alpha_0})^{-1} C^*(j_0 l_{\alpha_0} J; m_{j_0} 0 M) \quad (98)$$

and the scattering amplitude is given by

$$\begin{aligned} & \mathcal{F}_{\alpha p_{1j_1} \alpha_0 p_0 j_0 m_{j_0}}(\hat{R}'_\alpha) \\ & = \sum_{J l_{\alpha_0} l_{\alpha} m_{l_\alpha}} \left[\frac{(2l_{\alpha_0} + 1)}{k_{p_0 j_0}^{\alpha_0} k_{p_j}^\alpha} \right] i^{l_{\alpha_0} - l_\alpha + 1} C^*(j_0 l_{\alpha_0} J; m_{j_0} 0 m_{j_0}) \\ & \quad \times [S_{\alpha p_{1j_1} \alpha_0 p_0 j_0 l_{\alpha_0}}^J - \delta_{\alpha \alpha_0} \delta_{p p_0} \delta_{j j_0} \delta_{l_{\alpha} l_{\alpha_0}}] C(j l_\alpha J; m_j m_{l_\alpha} m_{j_0}) Y_{l_\alpha m_{l_\alpha}}(\hat{R}'_\alpha) \end{aligned} \quad (99)$$

In Section II,B we considered several basis sets and coordinate systems for expanding the total scattering wave function. The most convenient from the point of view of solving the coupled equations is the Born–Oppenheimer basis set in the body-fixed coordinate system (\mathbf{r}, R) . However, we have just

known that these coordinates are not appropriate for imposing scattering boundary conditions. Although we can easily impose scattering boundary conditions by using atomic basis states expressed in the space-fixed coordinates, the coupled equations for the radial wave functions $\tilde{g}_{\alpha p j \mu_{\alpha} \rho_0 j_0 l_{\alpha 0}}^j(R'_\alpha)$ are very complicated in this coordinate system. Further, the expansion of the molecular electronic wave functions in terms of pure atomic states is slowly convergent. Many procedures for circumventing these problems have been proposed in the literature and we shall discuss some of them in Sections II,D; II,E; II,G; and II,H.

D. ELECTRON TRANSLATION FACTORS

Bates and McCarroll (1958) suggested removing the defect of the molecular coordinate system by employing electronic basis functions that include electron translation factors (ETFs), and there is a large literature concerned with the further development of this approach (see, e.g., Hahn and Russek, 1968; Schneiderman and Russek, 1969; Riley and Green, 1971; Taulbjerg *et al.*, 1975; Dahler *et al.*, 1977; Crothers and Hughes, 1978; Basu *et al.*, 1978; Thorson and Delos, 1978a; and references cited in these articles). Most of this work has been formulated in a semiclassical framework, the classical path method (Bates, 1962, p. 549; Mott and Massey, 1965, p. 802; Bates and Holt, 1966; Delos *et al.*, 1972; Riley, 1973; Tully, 1976) in which internuclear motion is treated classically. The most common version of this is the time-dependent straight-line impact parameter method. The classical path approximation is not always valid at chemical energies. We shall continue to use the time-independent quantal formalism already presented in Sections II,B and II,C. In this section we derive the coupled channel equations for the case that ETFs are included in the basis set.

ETFs can be motivated by manipulating the asymptotic boundary conditions of Eq. (92) for the total wave function in the space-fixed coordinates ($\mathbf{r}'_\alpha, \mathbf{R}'_\alpha$). Substitution of Eq. (30) for $\mathbf{R}'_\alpha(\mathbf{r}', \mathbf{R}')$ into Eq. (92) gives

$$\begin{aligned} \Psi_{\alpha_0 \rho_0 j_0 m_j_0} \underset{R' \rightarrow \infty}{\sim} & \sum_{\alpha p j m_j} \phi_{p j m_j}^\alpha(\mathbf{r}'_\alpha) \exp[-i(f_\alpha \mu_e^\alpha / m_\alpha) \mathbf{k}_{p j}^\alpha \cdot \mathbf{r}'] \\ & \times \{ \delta_{\alpha \alpha_0} \delta_{p p_0} \delta_{j j_0} \delta_{m_j m_j_0} \exp[i(\mu_{AB} / \mu_{AB}^\alpha) \mathbf{k}_{p j}^\alpha \cdot \mathbf{R}'] \\ & + R_\alpha^{-1} \mathcal{F}_{\alpha p j m_j \alpha_0 \rho_0 j_0 m_j_0}(\hat{\mathbf{R}}'_\alpha) \exp[ik_{p j}^\alpha R'_\alpha + i(f_\alpha \mu_e^\alpha / m_\alpha) \mathbf{k}_{p j}^\alpha \cdot \mathbf{r}'] \} \quad (100) \end{aligned}$$

From Eq. (30) we note that

$$\mathbf{R}'_\alpha = \frac{\mu_{AB}}{\mu_{AB}^\alpha} \mathbf{R}' - \frac{f_\alpha \mu_e^\alpha}{m_\alpha} \frac{\mathbf{r}' \cdot \mathbf{R}'}{R'} + O\left[\left(\frac{\mu_e^\alpha}{m_\alpha}\right)^2\right] \quad (101)$$

where $O(x)$ denotes a quantity of order of smallness of x . This simplifies the last exponent in Eq. (100) to

$$\begin{aligned} ik_{pj}^\alpha R'_\alpha + i \frac{f_\alpha \mu_e}{m_\alpha} \mathbf{k}_{pj}^\alpha \cdot \mathbf{r}' \\ = i \frac{\mu_{AB}}{\mu_{AB}^\alpha} k_{pj}^\alpha R' + i \frac{f_\alpha \mu_e}{m_\alpha} (\mathbf{k}_{pj}^\alpha \cdot \mathbf{r}' - k_{pj}^\alpha \hat{R}' \cdot \mathbf{r}') + O\left[\left(\frac{\mu_e^\alpha}{m_\alpha}\right)^2\right] \end{aligned} \quad (102)$$

The second term on the right-hand side of Eq. (102) vanishes at large R' because

$$k_{pj}^\alpha \hat{R}' \underset{(R'/r'_\alpha) \rightarrow \infty}{\sim} k_{pj}^\alpha \quad (103)$$

We can use Eqs. (30) and (31) to obtain \mathbf{R}'_α as a function of \mathbf{R}' and \mathbf{r}'_α . This yields

$$\mathbf{R}'_\alpha = \mathbf{R}' - (f_\alpha \mu_e / m_\alpha) \mathbf{r}'_\alpha \quad (104)$$

and the limits

$$R'_\alpha \underset{(R'/r'_\alpha) \rightarrow \infty}{\sim} R' - (f_\alpha \mu_e / m_\alpha) [(r'_\alpha \cdot \mathbf{R}') / R'] \quad (105)$$

$$R'^{-1} \underset{(R'/r'_\alpha) \rightarrow \infty}{\sim} R'^{-1} + O(R'^{-2}) \quad (106)$$

$$\hat{R}'_\alpha \underset{(R'/r'_\alpha) \rightarrow \infty}{\sim} \hat{R}' + O(R'^{-2}) \quad (107)$$

Substituting Eqs. (102), (103), (106), and (107) into Eq. (100) yields

$$\begin{aligned} \Psi_{\alpha_0 p_0 j_0 m_j_0} \underset{R' \rightarrow \infty}{\sim} \sum_{\alpha p j m_j} \phi_{p j m_j}^\alpha(\mathbf{r}'_\alpha) \exp[-i(f_\alpha \mu_e^\alpha / m_\alpha) \mathbf{k}_{pj}^\alpha \cdot \mathbf{r}'] \\ \times \{\delta_{\alpha \alpha_0} \delta_{p p_0} \delta_{j j_0} \delta_{m_j m_{j_0}} \exp[i(\mu_{AB} / \mu_{AB}^\alpha) \mathbf{k}_{pj}^\alpha \cdot \mathbf{R}'] \\ + R'^{-1} \mathcal{F}_{\alpha p j m_j \alpha_0 p_0 j_0 m_{j_0}}(\hat{R}') \exp[i(\mu_{AB} / \mu_{AB}^\alpha) k_{pj}^\alpha R']\} \\ + O(R'^{-2}) + O[(\mu_e / m_\alpha)^2] \end{aligned} \quad (108)$$

The first exponential in Eq. (108) is the ETF. This equation shows that if we multiply each electronic basis function by an ETF we may impose the usual scattering boundary conditions on the \mathbf{R}' coordinate. The ETF in Eq. (108) depends on α and the energy of the atomic state but not on m_j . Other choices are possible.

To motivate the choice of ETFs in a molecular basis, we must first consider the large- R limit of the molecular basis functions. Every molecular state tends to either one atomic state or a linear combination of degenerate atomic states; however, there are some subtleties. First, the equations

Defining the molecular and atomic states, Eqs. (34) and (78), respectively, contain different masses. These masses are related by

$$\mu_e^a = m_e[1 - (m_e/m_a)] + O[(m_e/m_a)^2] \quad (109)$$

Because of this the electronic eigenvalues in the two basis sets differ even asymptotically, and it can be shown (Delos and Thorson, 1979) that

$$\varepsilon_{an\Omega}^a(R') \underset{R' \rightarrow \infty}{\sim} \varepsilon_{pj}^a + O(m_e/m_a) \quad (110)$$

A second difference is that the molecular states rotate with the body-fixed z axis, whereas the atomic states do not. If we consider atomic states that rotate with the internuclear axis and we assume that the atomic states are $(2j + 1)$ -fold degenerate, then we can write the limit of $\phi_{an\Omega}^a$ as follows (Pack and Hirschfelder, 1970):

$$\phi_{an\Omega}^a(\mathbf{r}, R) \underset{R \rightarrow \infty}{\sim} \sum_{m_j} D_{\Omega m_j}^j(\phi, \theta, 0) \phi_{pj(n\Omega)m_j}^a(\mathbf{r}') + O(m_e/m_a) \quad (111)$$

where $pj(n\Omega)$ denotes the values of p and j for the atomic level to which $\phi_{an\Omega}^a$ tends. Let

$$k_{an\Omega} = \lim_{R \rightarrow \infty} \{2\mu_{AB}[E - \varepsilon_{an\Omega}^a(R)]/\hbar^2\}^{1/2} \quad (112)$$

Then, Eqs. (93) and (110) yield

$$k_{an\Omega} = k_{pj(n\Omega)}^a + O(m_e/m_a) \quad (113)$$

Motivated by Eqs. (108), (111), and (113), the total wave function may be expanded in basis functions $\phi_{an\Omega}^a(\mathbf{r}', \mathbf{R}')$ that include ETFs and involve the adiabatic states instead of the atomic states. Thus,

$$\Psi_{\alpha_0 n_0 \Omega_0} = \sum_{an\Omega} \phi_{an\Omega}^a(\mathbf{r}', \mathbf{R}') \tilde{f}_{an\Omega \alpha_0 n_0 \Omega_0}^c(\mathbf{R}') \quad (114)$$

where

$$\phi_{an\Omega}^a(\mathbf{r}', \mathbf{R}') = \phi_{an\Omega}^a(\mathbf{r}', \mathbf{R}') \exp[-(f_a \mu_e^a/m_a) \mathbf{k}_{pj(n\Omega)} \cdot \mathbf{r}'] \quad (115)$$

Coupled equations are obtained by requiring

$$\langle \phi_{\gamma n_1 \Omega_1}^c | H - E | \Psi_{\alpha_0 n_0 \Omega_0} \rangle_{\mathbf{r}'} = 0 \quad (116)$$

for a set of γ , n_1 , and Ω_1 . We note that although the $\{\phi_{an\Omega}^a\}$ functions form an orthonormal basis set the functions $\phi_{an\Omega}^c$ do not; we will denote their overlap integrals by

$$S_{\gamma n_1 \Omega_1 an\Omega}^c(\mathbf{R}') = \langle \phi_{\gamma n_1 \Omega_1}^c | \phi_{an\Omega}^c \rangle_{\mathbf{r}'} \quad (117)$$

By use of the Hamiltonian of Eq. (2), we obtain the coupled equations

$$\begin{aligned} \sum_{an\Omega} \{ S_{\gamma n_1 \Omega_1 an\Omega}^c(\mathbf{R}') [-(\hbar^2/2\mu_{AB}) \nabla_{R'}^2 - E] + 2\mathbf{F}_{\gamma n_1 \Omega_1 an\Omega}^c(\mathbf{R}') \cdot \nabla_{R'} \\ + G_{\gamma n_1 \Omega_1 an\Omega}^c(\mathbf{R}') + H_{\gamma n_1 \Omega_1 an\Omega}^c(\mathbf{R}') \} \tilde{f}_{an\Omega \alpha_0 n_0 \Omega_0}^c(\mathbf{R}') = 0 \end{aligned} \quad (118)$$

in which

$$\mathbf{F}_{\gamma n_1 \Omega_1 \alpha n \Omega}^e(\mathbf{R}') = -(\hbar^2/2\mu_{AB}) \langle \phi_{\gamma n_1 \Omega_1}^e | \nabla_{\mathbf{R}'} | \phi_{\alpha n \Omega}^e \rangle_{\mathbf{r}'} \quad (119)$$

$$G_{\gamma n_1 \Omega_1 \alpha n \Omega}^e(\mathbf{R}') = -(\hbar^2/2\mu_{AB}) \langle \phi_{\gamma n_1 \Omega_1}^e | \nabla_{\mathbf{R}'}^2 | \phi_{\alpha n \Omega}^e \rangle_{\mathbf{r}'} \quad (120)$$

$$H_{\gamma n_1 \Omega_1 \alpha n \Omega}^e(\mathbf{R}') = \langle \phi_{\gamma n_1 \Omega_1}^e | -(\hbar^2/2m_c) \nabla_{\mathbf{r}'}^2 + V(\mathbf{r}', \mathbf{R}') | \phi_{\alpha n \Omega}^e \rangle_{\mathbf{r}'} \\ - \hbar^2/[2(m_A + m_B)] \langle \phi_{\gamma n_1 \Omega_1}^e | \nabla_{\mathbf{r}'}^2 | \phi_{\alpha n \Omega}^e \rangle_{\mathbf{r}'} \quad (121)$$

We now wish to show that in the large- R' limit, the couplings arising from the terms $\mathbf{F}_{\gamma n_1 \Omega_1 \alpha n \Omega}^e(\mathbf{R}')$ and $G_{\gamma n_1 \Omega_1 \alpha n \Omega}^e(\mathbf{R}')$ are canceled by terms arising from the ETFs.

We can replace all derivative operators in the $(\mathbf{r}', \mathbf{R}')$ coordinate system with those in the $(\mathbf{r}'_\alpha, \mathbf{R}'_\alpha)$ coordinate system by using the transformation given in Eqs. (30) and (31). This yields

$$\nabla_{\mathbf{R}'} = (\mu_{AB}/\mu_{AB}^2) \nabla_{\mathbf{R}'_\alpha} + (f_\alpha \mu_{AB}/m_\alpha) \nabla_{\mathbf{r}'_\alpha} \quad (122)$$

$$\nabla_{\mathbf{r}'} = \nabla_{\mathbf{r}'_\alpha} - (f_\alpha \mu_c/m_\alpha) \nabla_{\mathbf{R}'_\alpha} \quad (123)$$

If the adiabatic states tended asymptotically to linear combinations of the nonrotating atomic states, then $\nabla_{\mathbf{R}'_\alpha}$ operating on these asymptotic states would be strictly zero. However, because of the relationship in Eq. (111), the situation is more complicated. To illustrate the essential feature of ETFs we continue the present development with the approximation

$$\lim_{\substack{R' \rightarrow \infty \\ R'/r' \rightarrow \infty}} \nabla_{\mathbf{R}'_\alpha} \phi_{\alpha n \Omega}^a(\mathbf{r}', \mathbf{R}') \cong 0 \quad (124)$$

which is equivalent to the approximation

$$\lim_{\substack{R' \rightarrow \infty \\ R'/r' \rightarrow \infty}} \phi_{\alpha n \Omega}^a(\mathbf{r}', \mathbf{R}') \cong \sum_{m_j} d_{\alpha n \Omega m_j} \phi_{p_j(n \Omega) m_j}^\alpha(\mathbf{r}'_\alpha) \quad (125)$$

where the $d_{\alpha n \Omega m_j}$ are some constants.

Actually, this is not an approximation if one limits the state expansion to Σ states that tend to atomic states of S symmetry. (The more complicated situation is discussed further in Section II.F.) With these approximations we can write the asymptotic limits of the coupling matrices and Hamiltonian matrix

$$\mathbf{F}_{\gamma n_1 \Omega_1 \alpha n \Omega}^e(\mathbf{R}') \underset{\substack{R' \rightarrow \infty \\ \text{approx Eq. (125)}}}{\sim} -(\hbar^2 f_\alpha / 2m_\alpha) \sum_{m_j} d_{\gamma n_1 \Omega_1 m_j}^* d_{\alpha n \Omega m_j} \\ \times \int d\mathbf{r}' \phi_{p_1 j_1(n_1 \Omega_1) m_j}^{\gamma*}(\mathbf{r}'_\alpha) e_{\gamma n_1 \Omega_1}^*(\mathbf{r}') e_{\alpha n \Omega}(\mathbf{r}') \nabla_{\mathbf{r}'_\alpha} \phi_{p_j(n \Omega) m_j}^\alpha(\mathbf{r}'_\alpha) \quad (126)$$

$$G_{\gamma n_1 \Omega_1 \alpha n \Omega}^e(\mathbf{R}') \underset{\text{approx Eq. (1 25)}}{\widetilde{R' \rightarrow \infty}} - (\hbar^2 \mu_{AB} / 2m_\alpha^2) \sum_{m_j, m_j} d_{\gamma n_1 \Omega_1 m_j}^* d_{\alpha n \Omega m_j} \\ \times \int d\mathbf{r}' \phi_{p_1 j_1(n_1 \Omega_1) m_j}^{\gamma*}(\mathbf{r}'_\gamma) e_{\gamma n_1 \Omega_1}^*(\mathbf{r}') e_{\alpha n \Omega}(\mathbf{r}') \nabla_{\mathbf{r}'_\alpha}^2 \phi_{p_j(n \Omega) m_j}^\alpha(\mathbf{r}'_\alpha) \quad (127)$$

$$H_{\gamma n_1 \Omega_1 n \Omega}^e(\mathbf{R}') \underset{\text{approx Eq. (1 25)}}{\widetilde{R' \rightarrow \infty}} \sum_{m_j, m_j} d_{\gamma n_1 \Omega_1 m_j}^* d_{\alpha n \Omega m_j} \\ \times \int d\mathbf{r}' \phi_{p_1 j_1(n_1 \Omega_1) m_j}^{\gamma*}(\mathbf{r}'_\gamma) e_{\gamma n_1 \Omega_1}^*(\mathbf{r}') e_{\alpha n \Omega}(\mathbf{r}') \left\{ - \frac{\hbar^2}{2\mu_e} \left[- \left(\frac{\mu_e^\alpha}{m_\alpha} k_{p_j(n \Omega)}^\alpha \right)^2 \right. \right. \\ \left. \left. - 2i \frac{f_\alpha \mu_e^\alpha}{m_\alpha} \mathbf{k}_{p_j(n \Omega)}^\alpha \cdot \nabla_{\mathbf{r}'_\alpha} + \nabla_{\mathbf{r}'_\alpha}^2 \right] + V(\mathbf{r}', \mathbf{R}') \right\} \phi_{p_j(n \Omega) m_j}^\alpha(\mathbf{r}'_\alpha) \quad (128)$$

where the electron translation factors are given by

$$e_{\alpha n \Omega}(\mathbf{r}') = \exp[-i(f_\alpha \mu_e^\alpha / m_\alpha) \mathbf{k}_{p_j(n \Omega)}^\alpha \cdot \mathbf{r}'] \quad (129)$$

For sufficiently large R' , $\tilde{f}_{\alpha n \Omega \alpha n_0 \Omega_0}^e(\mathbf{R}')$ behaves as a free translational state,

$$\tilde{f}_{\alpha n \Omega \alpha n_0 \Omega_0}^e(\mathbf{R}') \underset{R' \rightarrow \infty}{\widetilde{\exp}} [i(\mu_{AB} / \mu_{AB}^\alpha) \mathbf{k}_{p_j(n \Omega)}^\alpha \cdot \mathbf{R}'] \quad (130)$$

and

$$\nabla_{\mathbf{R}'} \tilde{f}_{\alpha n \Omega \alpha n_0 \Omega_0}^e(\mathbf{R}') \underset{R' \rightarrow \infty}{\widetilde{\exp}} i(\mu_{AB} / \mu_{AB}^\alpha) \mathbf{k}_{p_j(n \Omega)}^\alpha \tilde{f}_{\alpha n \Omega \alpha n_0 \Omega_0}^e(\mathbf{R}') \quad (131)$$

Combining Eqs. (126)–(128) and using Eq. (131), we obtain

$$[2\mathbf{F}_{\gamma n_1 \Omega_1 \alpha n \Omega}^e(\mathbf{R}') \cdot \nabla_{\mathbf{R}'} + G_{\gamma n_1 \Omega_1 \alpha n \Omega}^e(\mathbf{R}') + H_{\gamma n_1 \Omega_1 \alpha n \Omega}^e(\mathbf{R}') - E] \tilde{f}_{\alpha n_1 \Omega_1 \alpha n_0 \Omega_0}^e(\mathbf{R}') \\ \underset{R' \rightarrow \infty}{\widetilde{\sum}} \sum_{m_j, m_j} d_{\gamma n_1 \Omega_1 m_j}^* d_{\alpha n \Omega m_j} \left\{ \int d\mathbf{r}' \phi_{p_1 j_1(n_1 \Omega_1) m_j}^{\gamma*}(\mathbf{r}'_\gamma) e_{\gamma n_1 \Omega_1}^*(\mathbf{r}') \right. \\ \times e_{\alpha n \Omega}(\mathbf{r}') \left[- \frac{\hbar^2}{2} \left(\frac{1}{\mu_e} + \frac{\mu_{AB}}{m_\alpha^2} \right) \nabla_{\mathbf{r}'_\alpha}^2 + \hbar^2 \left(i \frac{f_\alpha \mu_e^\alpha}{m_\alpha \mu_e} - i \frac{f_\alpha \mu_{AB}}{m_\alpha \mu_{AB}^\alpha} \right) \mathbf{k}_{p_j(n \Omega)}^\alpha \cdot \nabla_{\mathbf{r}'_\alpha} \right. \\ \left. \left. + \frac{\hbar^2 \mu_e^{\alpha 2}}{2\mu_e m_\alpha^2} k_{p_j(n \Omega)}^{\alpha 2} + V - E \right] \phi_{p_j(n \Omega) m_j}^\alpha(\mathbf{r}'_\alpha) \right\} \tilde{f}_{\alpha n \Omega \alpha n_0 \Omega_0}^e(\mathbf{R}') \quad (132)$$

$$= \sum_{m_j, m_j} d_{\gamma n_1 \Omega_1 m_j}^* d_{\alpha n \Omega m_j} \left[\int d\mathbf{r}' \phi_{p_1 j_1(n_1 \Omega_1) m_j}^{\gamma*}(\mathbf{r}'_\gamma) e_{\gamma n_1 \Omega_1}^*(\mathbf{r}') e_{\alpha n \Omega}(\mathbf{r}') \right. \\ \times \left(- \frac{\hbar^2}{2\mu_e} \nabla_{\mathbf{r}'_\alpha}^2 + V - E + \frac{\hbar^2 \mu_e^{\alpha 2}}{2\mu_e m_\alpha^2} k_{p_j(n \Omega)}^{\alpha 2} \right) \phi_{p_j(n \Omega) m_j}^\alpha(\mathbf{r}'_\alpha) \left. \right] \tilde{f}_{\alpha n \Omega \alpha n_0 \Omega_0}^e(\mathbf{R}') \quad (133)$$

$$= - \frac{\hbar^2}{2\mu_{AB}} \left(\frac{\mu_{AB}}{\mu_{AB}^\alpha} k_{p_j(n \Omega)}^\alpha \right)^2 \sum_{m_j, m_j} d_{\gamma n_1 \Omega_1 m_j}^* d_{\alpha n \Omega m_j} \int d\mathbf{r}' \phi_{p_1 j_1(n_1 \Omega_1) m_j}^{\gamma*}(\mathbf{r}'_\gamma) \\ \times e_{\gamma n_1 \Omega_1}^*(\mathbf{r}') e_{\alpha n \Omega}(\mathbf{r}') \phi_{p_j(n \Omega) m_j}^\alpha(\mathbf{r}'_\alpha) \tilde{f}_{\alpha n \Omega \alpha n_0 \Omega_0}^e(\mathbf{R}') \quad (134)$$

We used Eqs. (3), (11), and (12) and the fact that the terms containing $\nabla_{\mathbf{R}'}$ cancel to obtain Eq. (133), and we used Eqs. (78) and (93) to obtain Eq. (134). Therefore, in the asymptotic limit, the coupled equations (118) simplify to

$$\sum_{a n \Omega} S_{\gamma n_1 \Omega_1 a n \Omega}^c(\mathbf{R}') \left[-\frac{\hbar^2}{2\mu_{AB}} \nabla_{\mathbf{R}'}^2 - \frac{\hbar^2}{2\mu_{AB}} \left(\frac{\mu_{AB}}{\mu_{AB}^\alpha} k_{p j(n\Omega)}^\alpha \right)^2 \right] \tilde{f}_{a n \Omega z_0 n_0 \Omega_0}^c(\mathbf{R}') = 0 \quad \text{for large } R' \quad (135)$$

where

$$S_{\gamma n_1 \Omega_1 a n \Omega}^c(\mathbf{R}') \underset{R' \rightarrow \infty}{\sim} \sum_{m_j n_j} d_{\gamma n_1 \Omega_1 m_j}^* d_{a n \Omega m_j} \times \langle \phi_{p_1 j_1(n_1 \Omega_1) m_j}^\gamma | \exp\{i[(f_\gamma \mu_e^\gamma / m_\gamma) \mathbf{k}_{p_1 j_1(n_1 \Omega_1)}^\gamma - (f_a \mu_e^a / m_a) \mathbf{k}_{p j(n\Omega)}^\alpha] \cdot \mathbf{r}'\} | \phi_{p j(n\Omega) m_j}^\alpha \rangle_{R'} \quad (136)$$

Notice in Eq. (135) that all derivative coupling vanishes; however, there still remains a trivial coupling due to the nondiagonal overlap matrix $S_{\gamma n_1 \Omega_1 a n \Omega}^c$. This can be removed by multiplying the matrix equation (135) from the left by the inverse of the overlap matrix. The transformed coupled equations decouple asymptotically with the correct speeds $\hbar k_{p j}^\alpha / \mu_{AB}^\alpha$.

Although the previous development, Eqs. (100)–(136), has been based on the $(\mathbf{r}', \mathbf{R}')$ coordinate system and ETFs of the form

$$\exp[-i(f_a \mu_e^a / m_a) \mathbf{k}_{p j(n\Omega)}^\alpha \cdot \mathbf{r}']$$

a similar development could be carried out using the $(\mathbf{r}'_a, \mathbf{R}'_a)$ coordinate system and ETFs of the form

$$\exp(-i\lambda_{za} \mathbf{k}_{p j(n\Omega)}^\alpha \cdot \mathbf{r}'_a) \quad \text{or} \quad \exp(-i\lambda_{za} \mathbf{k}_{p j(n\Omega)}^\alpha \cdot \mathbf{r}'_{a(\alpha)})$$

In addition one could consider an expansion in basis functions that tend to

$$\phi_{a n \Omega}^a \exp(-i\lambda_{za} \mathbf{k}_{p j}^\alpha \cdot \mathbf{r}'_a)$$

at large R' but have arbitrary modifications in the ETF at small R' . The arbitrariness of a and of the ETFs at small R' is a serious drawback of the ETF approach. Another, even more serious, drawback of ETFs is that the required input to the coupled equations includes the electronic matrix elements (121), which are much more difficult to compute and much less readily available than the Born–Oppenheimer electronic potential curves $\epsilon_{a n \Omega}^a(R)$, which are required in the coupled equations (39) or (53). In Section II,E we discuss a method for solving the more convenient coupled equations (53) obtained without using ETFs in the expansion, but nevertheless applying correct boundary conditions to the scattering wave functions. The relative merits of the two approaches are compared briefly in Section II,H.

REARRANGEMENT-ANALYSIS METHOD

Another approach to computing the scattering amplitude is suggested by considering the collision from the point of view of rearrangement scattering theory. Recall that the difficulty is associated with the fact that the most convenient coordinate systems, the (\mathbf{r}, R) or $(\mathbf{r}', \mathbf{R}')$ coordinates, for computing the scattering wave function are not natural coordinate systems for applying scattering boundary conditions. The same problem also occurs in chemical reactions, which are a special case of rearrangement scattering. The connection of the present problem to rearrangement scattering can be seen even more directly by considering the $(\mathbf{r}_a, \mathbf{R}'_a)$ coordinate system. In this coordinate system the infinite-range coupling between states in which the active electron resides on A at $R = \infty$ (A states) can be eliminated by choosing $a = 0$, and the infinite-range coupling between B states can be eliminated by choosing $a = 1$. (The coupling of A states to B states has a finite range in any coordinate system because of overlap effects.) But if A and B states are important for the same problem, then no one choice of a (i.e., no one choice of origin for the electronic coordinates) can eliminate all the infinite-range coupling. The presence of both A and B states means that rearrangement scattering is possible. Thus the possibility of rearrangement scattering is intrinsically tied to the difficulties.

One approach to rearrangement scattering is to use "natural collision coordinates"; these are coordinates defined in such a way that as each possible combination of ratios of interparticle distances approaches an asymptotic limit, the coordinates tend to the natural coordinates for applying scattering boundary conditions for that arrangement of particles (see, e.g., Marcus, 1968). In the present problem one would require a single set of coordinates that becomes equivalent to $(\mathbf{r}'_A, \mathbf{R}'_A)$ as R' , (R'_A/r'_A) , and r'_B tend to infinity, but becomes equivalent to $(\mathbf{r}'_B, \mathbf{R}'_B)$ as R' , (R'_B/r'_B) , and r'_A tend to infinity. Approaches to the present problem based on natural collision coordinates have been published recently by Mittleman and Tai (1973) (see also Mittleman, 1975) and Thorson and Delos (1978b). The disadvantage of natural collision coordinates is that they are very complicated and are often difficult to deal with. In addition the mass ratios involved make them less appropriate for electron transfer than for chemical reactions.

Another method for electronic-state coupling based on recognizing that electron transfer is a rearrangement collision has been presented by Stechel *et al.* (1979). Their method uses nonorthogonal coordinates and non-orthogonal (tending to overcomplete) basis sets. Various aspects of their methods are discussed later in this section in Section II,H, and in Section IV.

Another approach to calculations on systems involving more than one arrangement channel is to obtain a set of linearly independent solutions

to the Schrodinger equation in any convenient coordinate system, and then take linear combinations of these solutions that satisfy the correct rearrangement-scattering boundary conditions (Diestler and McKoy, 1968; see also Truhlar and Kuppermann, 1972). In practice one obtains a set of linearly independent *approximate* solutions because one truncates the coupled equations by retaining only a finite number of terms in the expansion of the wave function. The last step in the procedure just outlined is called the asymptotic analysis and we will call it the rearrangement-analysis method. A particularly close analogy to the present problem is provided by Diestler's (1971) method for treating the collinear reaction $A + BC$ by solving coupled equations in the coordinate R_{AC} (the A-to-C distance) and imposing correct scattering boundary conditions involving both the $(R_{AB}, R_{AB,C})$ and $(R_{BC}, R_{A,BC})$ coordinates, where, e.g., $R_{AB,C}$ is the distance from the center of mass of AB to C. This is analogous in the present problem to solving coupled equations in the coordinates (\mathbf{r}, R) or $(\mathbf{r}', \mathbf{R}')$ and imposing correct scattering boundary conditions involving both the $(\mathbf{r}'_A, \mathbf{R}'_A)$ coordinates and the $(\mathbf{r}'_B, \mathbf{R}'_B)$ coordinates. This approach is worked out in the rest of this section.

The most convenient way to obtain a set of linearly independent approximate wave functions is to propagate the radial wave functions $g_{\alpha n \Omega_0 n_0 \Omega_0}^J(R)$ in the body-fixed (\mathbf{r}, R) or (\mathbf{r}_a, R_a) coordinate system into the asymptotic region. Using Eqs. (44) and (46), the component of the total wave function with a particular J and M and initial conditions i_0 is constructed from the radial functions as follows:

$$\Psi_{i_0}^{JM}(\mathbf{r}', \mathbf{R}') = \sum_{\alpha n \Omega} D_{\Omega M}^J(\phi, \theta, 0) \phi_{\alpha n \Omega}^a(\mathbf{r}, R) R^{-1} g_{\alpha n \Omega i_0}^J(R) \quad (137)$$

where we have replaced the indices $\alpha_0 n_0 \Omega_0$ by i_0 because we here choose arbitrary initial conditions in the solution of the equations (53) or (69). One possible choice of initial conditions is

$$g_{\alpha n \Omega i_0}(R)|_{R=0} = 0 \quad (138)$$

$$(d/dR) g_{\alpha n \Omega i_0}(R)|_{R=0} = \delta_{ii_0} \quad (139)$$

where i is a linear index denoting the i th combination of α , n , and Ω . Given $\Psi_{i_0}^{JM}(\mathbf{r}', \mathbf{R}')$, one could use the fact that \hat{R}' is (θ, ϕ) to project out the radial functions at $R = R_2$ as follows

$$g_{\gamma n_1 \Omega_1 i_0}^J(R_2) = R_2 \int d\hat{R}' \int d\mathbf{r}' \phi_{\gamma n_1 \Omega_1}^{a*}(\mathbf{r}', R_2) \times [(2J + 1)/4\pi]^{1/2} D_{\Omega_1 M}^{J*}(\phi, \theta, 0) \Psi_{i_0}^{JM}(\mathbf{r}', R_2, \hat{R}') \quad (140)$$

Equation (140) shows that we obtain the same radial function for each choice of M in $\Psi_{i_0}^{JM}(\mathbf{r}', \mathbf{R}')$; one could use this feature to simplify the subsequent

algebra by using the fact that for the convention used by Pack and Hirschfelder (1968) and here,

$$D_{\Omega_0}^{J*}(\phi, \theta, 0) = (-1)^{\Omega} [4\pi/(2J + 1)]^{1/2} Y_{J\Omega}(\theta, \phi)$$

In the space-fixed ($\mathbf{r}'_\alpha, \mathbf{R}'_\alpha$) coordinate system $\Psi_{i_0}^{JM}$ has the asymptotic form

$$\begin{aligned} \Psi_{i_0}^{JM} \underset{R \rightarrow \infty}{\sim} \sum_{\alpha p j l_\alpha} \mathcal{Y}_{j l_\alpha}^{JM}(\hat{r}'_\alpha, \hat{R}'_\alpha) P_{pj}^\alpha(r'_\alpha) R_\alpha'^{-1} \{ \Gamma_{\alpha p j l_\alpha i_0}^J \exp[-i(k_{pj}^\alpha R'_\alpha - l_\alpha \pi/2)] \\ + \Delta_{\alpha p j l_\alpha i_0}^J \exp[+i(k_{pj}^\alpha R'_\alpha - l_\alpha \pi/2)] \} \end{aligned} \quad (141)$$

Substituting Eq. (141) into Eq. (140) and using the asymptotic forms for R'_α and \hat{R}'_α given in Eqs. (105) and (107), we obtain

$$\begin{aligned} g_{\gamma n_1 \Omega_1 i_0}^J(R_2) \underset{R_2 \rightarrow \infty}{\sim} \sum_{\alpha p j l_\alpha} \{ \mathcal{S}_{\gamma n_1 \Omega_1 \alpha p j l_\alpha}^{J+}(R_2) \exp[-i(k_{pj}^\alpha R_2 - l_\alpha \pi/2)] \Gamma_{\alpha p j l_\alpha i_0}^J \\ + \mathcal{S}_{\gamma n_1 \Omega_1 \alpha p j l_\alpha}^{J-}(R_2) \exp[i(k_{pj}^\alpha R_2 - l_\alpha \pi/2)] \Delta_{\alpha p j l_\alpha i_0}^J \} \end{aligned} \quad (142)$$

where

$$\begin{aligned} \mathcal{S}_{\gamma n_1 \Omega_1 \alpha p j l_\alpha}^{J\pm}(R_2) = [(2J + 1)/4\pi]^{1/2} \int d\hat{R}' \int d\mathbf{r}' \phi_{\gamma n_1 \Omega}^{a*}(\mathbf{r}', R_2) D_{\Omega M}^{J*}(\phi, \theta, 0) \\ \times \exp[\pm i f_\alpha(\mu_e^\alpha/m_e) k_{pj}^\alpha \mathbf{r}'_\alpha(\mathbf{r}', R_2, \hat{R}') \cdot \hat{R}'] \\ \times \mathcal{Y}_{j l_\alpha}^{JM}[\hat{r}'_\alpha(\mathbf{r}', R_2, \hat{R}'), \hat{R}'] P_{pj}^\alpha[r'_\alpha(\mathbf{r}', R_2, \hat{R}')] \end{aligned} \quad (143)$$

Although the \mathcal{S} -matrix elements depend on R_2 , they do go asymptotically to a constant limit $\tilde{\mathcal{S}}_{\gamma n_1 \Omega_1 \alpha p j l_\alpha}^{J\pm}$. Using Eq. (111) for the limit of the molecular states at large R and replacing the integration variable \mathbf{r}' by \mathbf{r}'_α , we obtain

$$\begin{aligned} \tilde{\mathcal{S}}_{\gamma n_1 \Omega_1 \alpha p j l_\alpha}^{J\pm} = \delta_{\gamma\alpha} [(2J + 1)/4\pi]^{1/2} \sum_{m_{j1}} \int d\hat{R}' \int d\mathbf{r}'_\alpha D_{\Omega_1 m_{j1}}^{j_1*}(\phi, \theta, 0) \phi_{p_1 j_1 (n_1 \Omega_1) m_{j_1}}^{a*}(\mathbf{r}'_\alpha) \\ \times D_{\Omega_1 M}^{J*}(\phi, \theta, 0) \exp[\pm i f_\alpha(\mu_e^\alpha/m_e) k_{pj}^\alpha \mathbf{r}'_\alpha \cdot \hat{R}'] \mathcal{Y}_{j l_\alpha}^{JM}(\hat{r}'_\alpha, \hat{R}') P_{pj}^\alpha(r'_\alpha) \end{aligned} \quad (144)$$

The Kronecker delta $\delta_{\gamma\alpha}$ arises because at large R the overlap of the atomic basis functions on different nuclei is negligible.

The derivative of Eq. (142) gives a second set of equations

$$\begin{aligned} \frac{d}{dR} g_{\gamma n_1 \Omega_1 i_0}^J(R_2) \underset{R_2 \rightarrow \infty}{\sim} \sum_{\alpha p j l_\alpha} \{ -i k_{pj}^\alpha \mathcal{S}_{\gamma n_1 \Omega_1 \alpha p j l_\alpha}^{J+}(R_2) \\ \times \exp[-i(k_{pj}^\alpha R_2 - l_\alpha \pi/2)] \Gamma_{\alpha p j l_\alpha i_0}^J + i k_{pj}^\alpha \mathcal{S}_{\gamma n_1 \Omega_1 \alpha p j l_\alpha}^{J-}(R_2) \\ \times \exp[i(k_{pj}^\alpha R_2 - l_\alpha \pi/2)] \Delta_{\alpha p j l_\alpha i_0}^J \} \end{aligned} \quad (145)$$

The derivatives of the \mathcal{S} -matrix elements are set equal to zero in Eq. (145) because these matrix elements approach constant asymptotically. The

procedure is now clear. One retains N terms in the expansion of Eq. (46) and solves the N coupled differential equations (53) with arbitrary initial conditions [e.g., those in Eqs. (138) and (139)] over an interval of R from the origin to some R_2 . Then one calculates the integrals in Eq. (143) or their limits [Eq. (144)] and solves the $2N$ simultaneous equations (142) and (145), or their analogs with $\tilde{\mathcal{I}}$ matrices substituted for \mathcal{I} matrices, for $\{\Gamma_{\alpha p j l_{\alpha} i_0}^J\}$ and $\{\Delta_{\alpha p j l_{\alpha} i_0}^J\}$ for N sets of α , p , j , and l_{α} . Notice that if the N terms retained in Eq. (46) could be expanded in N atomic states, then one would at this point have the same information as if one had: (1) retained N terms in the expansion of Eq. (87); (2) solved the coupled equations (90) with N sets of arbitrary initial conditions for N sets of N radial functions $\tilde{g}_{\alpha p j l_{\alpha} i_0}^J$ over the interval of R_{α} and R_{γ} from 0 to about R_2 ; and (3) analyzed the N linearly independent radial functions for their asymptotic form. One would then take linear combinations of the $\tilde{g}_{\alpha p j l_{\alpha} i_0}^J(R_{\alpha})$ to form a set of scattering states $\tilde{g}_{\alpha p j l_{\alpha} i_0}^J(R_{\alpha})$ using one of the standard methods (e.g., Gordon, 1971, or Lester, 1971) appropriate to nonrearrangement scattering. The same linear combinations procedure can be applied in the present case as follows. The correct scattering states are linear combinations of the functions $\Psi_{i_0}^{JM}$ whose asymptotic form is given in Eq. (141):

$$\Psi_{\alpha p j l_{\alpha}}^{JM} = \sum_{i_0} B_{\alpha p j l_{\alpha} i_0}^J \Psi_{i_0}^{JM} \quad (146)$$

The coefficients in Eq. (146) are determined so that the linear combinations have the asymptotic form obtained by substituting Eq. (97) in Eq. (87):

$$\sum_{i_0} B_{\gamma p_1 j_1 l_{\gamma} i_0}^J \Gamma_{\alpha p j l_{\alpha} i_0}^J = \delta_{\gamma \alpha} \delta_{p_1 p} \delta_{j_1 j} \delta_{l_{\gamma} l_{\alpha}} \quad (147)$$

$$\sum_{i_0} B_{\gamma p_1 j_1 l_{\gamma} i_0}^J \Delta_{\alpha p j l_{\alpha} i_0}^J = (k_{p_1 j_1}^{\gamma} / k_{p j}^{\alpha})^{1/2} S_{\gamma p_1 j_1 l_{\gamma} i_0}^J \quad (148)$$

Equation (147) for N sets of γ , p_1 , j_1 , and l_{γ} , is a set of N equations that is to be solved for the B matrix for N sets of α , p , j , and l_{α} . The results are to be substituted into Eq. (148) to yield the S matrix. The scattering amplitude is then given by Eq. (99). In principle, the results should then be converged with respect to increasing both R_2 and N .

The procedure just described has the advantage that the propagation step (solution of the truncated coupled equations over an interval from 0 to R_2) is carried out using the convenient body-fixed expansion basis, but correct scattering boundary conditions are applied at large R_{α} and R_{γ} . The body-fixed expansion basis is convenient because the required input is that which is most readily available from ab initio electronic structure calculations, and because the coupled equations are simpler than those for the atomic basis.

In addition, in the energy range of interest for chemistry, one would generally expect more accurate results by retaining N adiabatic electronic states in the expansion at small R than would be obtained by retaining N states in an atomic basis.

There are many possible variations of the previous procedure that may be useful in practice. For example, it may be advantageous to propagate the coupled equations in the form of Eq. (53) only out to some intermediate distance $R = R_1 < R_2$. Then one could transform to some other representation that is more convenient at large R and propagate to convergence in the new representation. For example, one could transform to the representation of Eqs. (74) and (76) and propagate the solutions to the coupled equations (77). This involves the coordinates $(\mathbf{r}_{a(x)}, R)$ and is equivalent to using both (\mathbf{r}_A, R) and (\mathbf{r}_B, R) . This provides a link to the asymptotic analysis involving boundary conditions expressed most naturally in terms of $(\mathbf{r}'_A, \mathbf{R}'_A)$ and $(\mathbf{r}'_B, \mathbf{R}'_B)$. It also provides a closer analogy to the propagation step Diestler employed in his treatment of the $A + BC$ chemical reaction. The modification of Eqs. (137)–(148) when Eqs. (74) and (76) are used instead of Eqs. (44) and (46) is straightforward.

Another interesting possibility is to transform at large distance to the atomic representation. The main disadvantage of using atomic basis states in the $(\mathbf{r}', \mathbf{R}'_x)$ coordinate system is the difficulty of solving the integrodifferential equations (90). However, at large R the rearrangement kernel vanishes and the two arrangements decouple. Thus it might be convenient to propagate the radial wave functions $g_{\alpha n \Omega \alpha_0 n_0 \Omega_0}^J(R)$ in the interaction region $R < R_1$ and use these to calculate values of the radial wave functions $\tilde{g}_{\alpha p j l \alpha_0 p_0 j_0 l \alpha_0}^J(R'_x)$ at large R . Once these are obtained they can be propagated and analyzed for the scattering information.

To accomplish the transformation described in the previous paragraph, we first note that the component of the wave function with specified J and M and arbitrary initial conditions has the expansion

$$\Psi_{i_0}^{JM} = \sum_{\alpha p j l \alpha} \mathcal{Y}_{j l \alpha}^{JM}(\hat{r}'_{\alpha}, \hat{R}'_{\alpha}) P_{p j}^{\alpha}(r'_{\alpha}) R_x'^{-1} \tilde{g}_{\alpha p j l \alpha i_0}^J(R'_x) \quad (149)$$

Thus the radial wavefunctions at $R'_x = R'_{x1}$ are projected out of the wave function $\Psi_{i_0}^{JM}$ by

$$\tilde{g}_{\alpha p j l \alpha i_0}^J(R'_{x1}) = R'_{x1} \int d\hat{R}'_{\alpha} \int d\mathbf{r}'_{\alpha} \mathcal{Y}_{j l \alpha}^{JM*}(\hat{r}'_{\alpha}, \hat{R}'_{\alpha}) P_{p j}^{\alpha}(r'_{\alpha}) \Psi_{i_0}^{JM} \quad (150)$$

The wave function $\Psi_{i_0}^{JM}$ required in Eq. (150) may be constructed from Eq. (137) and the functions $g_{\alpha n \Omega \alpha i_0}^J$ obtained by solving the body-fixed coupled

equations. Doing this yields

$$\begin{aligned} \tilde{g}_{\alpha p j l \alpha i o}^J(R'_{\alpha 1}) = & \sum_{\gamma n \Omega} \int d\hat{R}'_{\alpha} \int d\mathbf{r}'_{\alpha} \mathcal{Y}_{j l \alpha}^{JM*}(\hat{r}'_{\alpha}, \hat{R}'_{\alpha}) P_p^{\alpha*}(r'_{\alpha}) D_{\Omega M}^J(\phi, \theta, 0) \\ & \times \phi_{\gamma n \Omega}^{\alpha}[\mathbf{r}'_{\alpha}, R'_{\alpha 1}, \hat{R}'_{\alpha}], R(\mathbf{r}'_{\alpha}, R'_{\alpha 1}, \hat{R}'_{\alpha}) \\ & \times R'_{\alpha 1} R^{-1}(\mathbf{r}'_{\alpha}, R'_{\alpha 1}, \hat{R}'_{\alpha}) g'_{\gamma n \Omega i o}^J[R(\mathbf{r}'_{\alpha}, R'_{\alpha 1}, \hat{R}'_{\alpha})] \quad (151) \end{aligned}$$

Computing $\tilde{g}_{\alpha p j l \alpha i o}^J(R'_{\alpha})$ and its derivative at $R'_{\alpha} = R'_{\alpha 1}$ or the function at two values of R'_{α} will give sufficient information to initialize the integration of Eq. (90). The value of $R'_{\alpha 1}$ should be taken large enough that the rearrangement kernel vanishes and the equations can be propagated separately in each arrangement, i.e., the channels with $\alpha = A$ decouple from those with $\alpha = B$. The transformation step (151) replaces the rearrangement-analysis step. The calculation can be completed by analyzing for the Γ and Δ matrices as in nonrearrangement scattering and by applying Eqs. (146)–(148).

Another transformation procedure is incorporated in the method of Stechel *et al.* (1979). They suggest performing special propagation steps to convert information about the derivative matrix (i.e., the Wigner R matrix, defined in Section IV) from a constant- R surface in $(\mathbf{r}'_{a(\alpha)}, \mathbf{R}')$ coordinates to constant- R_{α} surfaces in both of the $(\mathbf{r}'_{\alpha}, \mathbf{R}'_{\alpha})$ Jacobi coordinate systems. These special propagation steps are very complicated, and they were not implemented in the computations of Schmalz *et al.* (1979).

One of the main goals of this section has been to provide a formally correct method for handling the infinite-range coupling in scattering calculations involving several electronic states and body-fixed coordinates. In particular, we have sought and presented a method that (1) uses as input the electronically adiabatic potential curves and derivative coupling matrices that are available from state-of-the-art *ab initio* calculations in the (\mathbf{r}, R) coordinate system; (2) makes no restriction on the kind of basis sets used to calculate these quantities and in particular does not require a basis of atomic states; and (3) provides a formally correct and computationally oriented way to eliminate spurious infinite-range coupling even when the important electronic states include states differing by an electron transfer at large R and when more than one electronic state is important for each of the separated collision partners.

F. BODY-FRAME RADIAL EQUATIONS FOR Σ STATES

In many applications of the theory, the coupling between states with quantum numbers Ω and $\Omega \pm 1$ can be neglected. This is true for scattering governed by Σ potential energy curves when the coupling to Π states may be neglected at all R . Consider, for example, a scattering problem involving only

Σ states that tend at large R to atomic states of S symmetry. For this case, the matrix elements of J_c^2 vanish asymptotically. Neglecting them and the mass polarization terms, we obtain the following from Eqs. (47) and (48) for this case:

$$\left[-\frac{\hbar^2}{2\mu_{AB}R} \frac{\partial^2}{\partial R^2} R + \frac{\hbar^2}{2\mu_{AB}R^2} l(l+1) - \frac{\hbar^2}{2m_e} \nabla_r^2 + V(\mathbf{r}, R) - E \right] \Psi_{0\alpha_0 n_0}^l(\mathbf{r}, R) = 0 \quad (152)$$

For this special case we introduce a simplified notation in which the superscript $J = l$ is not shown, q is a collective index replacing α, n , and Ω , and q_1 is a collective index used to replace γ, n_1 , and Ω_1 . Then $\Psi_{0\alpha_0 n_0}(\mathbf{r}, R)$ is renamed and expanded in the adiabatic basis as follows:

$$\Psi_{q_0}(\mathbf{r}, R) = R^{-1} \sum_q \phi_q^a(\mathbf{r}, R) \chi_{qq_0}^a(R) \quad (153)$$

where the superscript on the radial function is a reminder that this expansion, like all other expansions considered in Section II, involves electronically adiabatic basis functions. The expansion (153) leads to the coupled equations

$$\left[-\frac{\hbar^2}{2\mu_{AB}} \frac{d^2}{dR^2} + \frac{\hbar^2 l(l+1)}{2\mu_{AB}R^2} - E \right] \chi_{qq_0}^a(R) + \sum_{q_1} \left[H_{qq_1}^a(R) + 2F_{q_1 q}^a(R) \frac{d}{dR} + G_{q_1 q}^a(R) \right] \chi_{qq_0}^a(R) = 0 \quad (154)$$

in which

$$H_{q_1 q}^a(R) = \langle \phi_{q_1}^a | -(\hbar^2/2m_e) \nabla_r^2 + V(\mathbf{r}, R) | \phi_q^a \rangle_r = \varepsilon_q^a(R) \delta_{\gamma_2} \delta_{n_1 n} \quad (155)$$

$$F_{q_1 q}^a(R) = -(\hbar^2/2\mu_{AB}) \langle \phi_{q_1}^a | \partial/\partial R | \phi_q^a \rangle_r \quad (156)$$

$$G_{q_1 q}^a(R) = -(\hbar^2/2\mu_{AB}) \langle \phi_{q_1}^a | \partial^2/\partial R^2 | \phi_q^a \rangle_r \quad (157)$$

At this point it is instructive to examine the projection method for imposing scattering boundary conditions for this simplified example. We will assume that the projection is being carried out at large enough R that \mathcal{J} -matrix elements nondiagonal in the arrangement index α may be neglected, and the others have assumed their asymptotic form $\tilde{\mathcal{J}}$. For this example, Eq. (142) simplifies to

$$\chi_{q_1 i_0}^a = \sum_p \{ \tilde{\mathcal{J}}_{q_1 \gamma p 0 l}^+ \Gamma_{\gamma p 0 l i_0} \exp[-i(k_{p_0}^\gamma R - l\pi/2)] + \tilde{\mathcal{J}}_{q_1 \gamma p 0 l}^- \Delta_{\gamma p 0 l i_0} \exp[i(k_{p_0}^\gamma R - l\pi/2)] \}, \quad \text{for large } R \quad (158)$$

where, writing q_1 explicitly as $\gamma n_1 0$,

$$\begin{aligned} \tilde{\mathcal{J}}_{\gamma n_1 0 \gamma p 0 l}^{\pm} = & [(2l + 1)^{1/2} / (4\pi)^{3/2}] \int d\hat{R}' \int d\mathbf{r}'_y P_{p_1 0(n_1 0)}^{\gamma}(\mathbf{r}'_y) D_{0M}^l(\phi, \theta, 0) \\ & \times \exp[\pm i k_{p_0}^{\gamma} (f_{\gamma} \mu_e^{\gamma} / m_{\gamma}) \mathbf{r}'_y \cdot \mathbf{R}'] Y_{l0}(\hat{R}') P_{p_0}^{\gamma}(r'_y) \end{aligned} \quad (159)$$

This integral may be reduced to a finite sum of one-dimensional integrals.

This short section has illustrated the great simplifications that occur when only Σ potential curves and S atomic states are involved. Other cases rapidly become more complicated. For example, consider a state involving only Σ - Σ coupling at small R but where one of the Σ states dissociates to an atom in a P state. In such a case, body-fixed adiabatic states at large R are linear combinations of states defined in the space-fixed frame, and the uncoupled space-fixed states at large R are linear combinations of both Σ and Π body-frame adiabatic states. This means that one cannot replace $J(J + 1) - 2\Omega^2 + J_c^2$ by $l(l + 1)$ in Eq. (48) and that the transformation to an uncoupled representation at large R is more complicated. Not only is it more complicated to remove the infinite-range couplings, but also one must consider an appropriate basis for treating efficiently (e.g., transforming away or diagonalizing) the long-range couplings that decay as R^{-1} and R^{-2} . Various aspects of these problems have been discussed in the literature (see, e.g., Bates, 1957a,b; Thorson, 1965, 1969; Knudson and Thorson, 1970; Pack and Hirschfelder, 1970; Rosenthal, 1971; Mies, 1973; Thorson and Delos, 1978a).

G. DIAGONALIZATION METHOD

In Section II,E we discussed the imposition of scattering boundary conditions by projecting the basis states onto the uncoupled states of the atomic Jacobi coordinate system. This allows the scattering boundary conditions to be satisfied as well as possible within the finite basis set used. Clearly, the same objective can be achieved by diagonalizing the asymptotic coupling matrix in the chosen basis set, and that is the subject of the present section.

In the semiclassical formalism (see references cited in the first paragraph of Section II,D), one can remove the infinite-range coupling without using electron translation factors by a diagonalization technique that has been presented in various versions by Knudson and Thorson (1970), Rosenthal (1971), Albat *et al.* (1975), Albat and Gruen (1976), and Albat and Wirsam (1977). One advantage of a diagonalization technique over the method of Section II,E is that a diagonalization is easier than the computation of the \mathcal{J} or $\tilde{\mathcal{J}}$ integrals. Since the classical path assumption of the semiclassical formalism is often invalid at chemical energies it is useful to have an analog of this diagonalization technique for the time-independent second-order

quantal equations. Such an analog was worked out in the Wentzel-Kramers-Brillouin (WKB) approximation by Knudson and Thorson (1970). For the purely quantal case a Hermitian equivalent of the second-order equations that can be diagonalized has been obtained by M. E. Riley (personal communication, 1979), and the rest of this section is based on his development.

We consider the Σ -state equations given in Eq. (154) and rewrite them in matrix notation as

$$\left[\frac{d^2}{dR^2} \mathbf{I} - \frac{4\mu_{AB}}{\hbar^2} \mathbf{F}^a(R) \frac{d}{dR} + \mathbf{Y}(R) \right] \chi^a(R) = 0 \quad (160)$$

in which \mathbf{I} is the $N \times N$ unit matrix and

$$\mathbf{Y}(R) = -[l(l+1)/R^2] - (2\mu_{AB}/\hbar^2)[\mathbf{H}^a(R) + \mathbf{G}^a(R) - E] \quad (161)$$

is an $N \times N$ matrix that is a generalization of the square of the local wave number. The matrices \mathbf{F}^a , \mathbf{G}^a , and \mathbf{H}^a are given by

$$F_{qq_0}^a(R) = -(\hbar^2/2\mu_{AB}) \langle \phi_q^a | d/dR | \phi_{q_0}^a \rangle \quad (162)$$

$$G_{qq_0}^a(R) = -(\hbar^2/2\mu_{AB}) \langle \phi_q^a | d^2/dR^2 | \phi_{q_0}^a \rangle \quad (163)$$

$$H_{qq_0}^a(R) = \delta_{qq_0} \epsilon_q^a(R) \quad (164)$$

We wish to deal with Eq. (161) for $R = \infty$ and so we note that $\mathbf{G}^a(R)$ becomes Hermitian in this limit. Therefore $\mathbf{Y}(\infty)$ may be diagonalized by a unitary transformation \mathbf{U}^{pa} , i.e.,

$$\mathbf{U}^{pa} \mathbf{Y}(\infty) \mathbf{U}^{pa\dagger} = (\mathbf{K}^p)^2 \quad (165)$$

where \dagger denotes the Hermitian adjoint and \mathbf{K}^p is a diagonal matrix. We then transform the solution vector, first-derivative coupling matrix, and coupled equations as follows:

$$\chi^a(R) = \mathbf{U}^{pa\dagger} \chi^p(R) \quad (166)$$

$$\mathbf{F}^p(R) = \mathbf{U}^{pa} \mathbf{F}^a(R) \mathbf{U}^{pa\dagger} \quad (167)$$

$$\left[\frac{d^2}{dR^2} \mathbf{I} - \frac{4\mu_{AB}}{\hbar^2} \mathbf{F}^p(R) \frac{d}{dR} + (\mathbf{K}^p)^2 \right] \chi^p(R) = 0 \quad (168)$$

Next we must convert these equations to an equivalent first-order system. To do this we define π^p by

$$\frac{d}{dR} \chi^p = i\mathbf{K}^p \pi^p(R) + \frac{4\mu_{AB}}{\hbar^2} \mathbf{F}^p(R) \chi^p(R) \quad (169)$$

Equations (168) and (169) and the fact that $\mathbf{F}^p(R)$ becomes constant at large R imply

$$\frac{d}{dR} \pi^p = i\mathbf{K}^p \chi^p(R) \quad (170)$$

Equations (169) and (170) are together equivalent to the coupled equations (168) and we write them in a supermatrix notation as

$$\frac{d}{dR} \bar{\chi}^p = i\bar{\mathbf{Y}}(R)\bar{\chi}^p(R) \quad (171)$$

where

$$\bar{\chi}^p(R) = \begin{pmatrix} \chi^p(R) \\ \pi^p(R) \end{pmatrix} \quad (172)$$

and

$$\bar{\mathbf{Y}}(R) = \begin{pmatrix} -(4\mu_{AB}i/\hbar^2)\mathbf{F}^p(R) & \mathbf{K}^p \\ \mathbf{K}^p & \mathbf{0} \end{pmatrix} \quad (173)$$

It is interesting that Eqs. (171) are the same in form as those treated in the semiclassical framework by Albat and Gruen (1976) at $R = \infty$. We could now use their procedures. They made an R -dependent transformation designed to minimize the long-range coupling. Here we make a simpler single transformation based on one large- R value or on $R = \infty$. A single transformation can eliminate the infinite-range coupling between states of the same Ω and the R^{-1} coupling between states of different Ω , but an R -dependent transformation is generally required to eliminate the R^{-2} coupling.

Since \mathbf{K}^p is diagonal and $\mathbf{F}^p(R)$ is skew-Hermitian, $\bar{\mathbf{Y}}(R)$ is Hermitian. Therefore it can be diagonalized by a unitary transformation; we do so at $R = \infty$

$$\bar{\mathbf{K}}(R) = \bar{\mathbf{U}}^{fp} \bar{\mathbf{Y}}(R) \bar{\mathbf{U}}^{fp\dagger} \quad (174)$$

in which all quantities are $2N \times 2N$ matrices and $\bar{\mathbf{U}}^{fp}$ is chosen so that $\bar{\mathbf{K}}(\infty)$ is diagonal. This yields

$$\bar{\chi}^p(R) = \bar{\mathbf{U}}^{fp\dagger} \bar{\chi}^f(R) \quad (175)$$

and

$$\frac{d}{dR} \bar{\chi}^f = i\bar{\mathbf{K}}(R)\bar{\chi}^f(R) \quad (176)$$

Since $\bar{\mathbf{K}}(\infty)$ is diagonal, Eq. (176) shows that the scattering equations have been decoupled at $R = \infty$. The decoupled equations imply a new electronic basis that is as uncoupled as possible at large R . One can then obtain solutions to the coupled equations in any convenient representation, transform to the new one at large R , and apply uncoupled scattering boundary conditions in the new representation. The electronic basis functions in the first new representation are given by

$$\phi^p = U^{pa} \phi^a \quad (177)$$

but those defined implicitly by Eq. (175) are more complicated.

Riera and Salin (1977) have questioned the physical relevance of the transformed states obtained by a diagonalization scheme. The physical relevance is that they take into account the electron translational effect as well as possible within the finite basis used. The assumption of a finite basis is practically unavoidable. Notice that even adiabatic basis sets are in practice strictly adiabatic only within a finite basis.

H. DISCUSSION

We have seen in Section II,B that different coordinate systems lead to different sets of nonadiabatic coupling terms in the time-independent quantum mechanical formulation of scattering problems involving more than one electronic state. In Section II,C we saw that no choice of origin for the electronic coordinates makes the radial part of the nonadiabatic coupling between all electronically adiabatic states vanish for infinite separation of the subsystems. This may also be an indication that adiabatic basis sets do not account properly for the physics of nonadiabatic coupling at small R and that small expansion sets will be inaccurate. General practical techniques for overcoming these difficulties have not yet been demonstrated in the literature, but several possibilities have been suggested or suggest themselves. Some of these have been discussed in Sections II,D, II,E, and II,G, and further discussion is presented in this section.

The most common approach to this problem in the chemical literature is to ignore it. One assumes that all coupling due to nuclear derivative operators vanishes in some diabatic representation.† Then one diagonalizes the electronic Hamiltonian in that representation to compute an adiabatic basis. The radial part of the nuclear-derivative coupling in the adiabatic basis is then given entirely by derivatives of the matrix elements of the diagonalizing transformation; these are independent of origin and vanish at

† Any basis that is not adiabatic (i.e., in which the matrix of H_e is not diagonal) will be called diabatic.

infinity. Although this approach is quite common, the assumptions are usually only implicit, and the dangers and nonuniqueness of neglecting the nuclear-derivative coupling in any particular diabatic basis are often not mentioned. This approach, however, is sometimes made explicitly, and it need not be a bad approximation in all cases. For example, Preston and Tully (1971) and Tully (1973) use this procedure in their approximation of nonadiabatic coupling terms by the diatomics-in-molecules method. In that method the diabatic basis is a generalized valence-bond basis. Tully (1973) argues that in many cases of interest, the nonadiabatic coupling between two diabatic states is important only in fairly localized regions in which two diabatic states cross and the adiabatic states avoid crossing. In this case the derivatives of the transformation matrix elements from the diabatic basis are indeed much larger than the transformation of the nuclear-derivative coupling of the diabatic basis. There also exist, however, very many interesting transitions where the coupling is not so strong and localized and the above approximation is poor (see, e.g., Oppenheimer, 1972). The nonuniqueness of this approach is also ill-suited to the present state-of-the-art of quantum chemistry. Accurate adiabatic potential energy curves are independent of the basis set and coordinate system used to calculate them, and ideally one desires the same kind of independence for the nonadiabatic coupling terms. This is especially important for highly accurate calculations employing large basis sets chosen for their ability to span a space in a computationally convenient way rather than on the basis of physically motivated diabatic models.

The danger of assuming that the nuclear-derivative coupling is zero in physically motivated diabatic cases is illustrated by considering the nature of a complete diabatic basis in which the radial nuclear-derivative coupling does vanish. In such a diabatic representation (Smith, 1969),[†] the basis functions are totally independent of R (Andresen and Nielsen, 1971; Gabriel and Taulbjerg, 1974). Such a basis would consist, for example, of sets of Slater-type orbitals centered at two points a distance R_0 apart. This basis would have to be able to describe the electronic states not only when $R = R_0$, but also for all other R values. Clearly, it would take many such basis functions to represent the adiabatic states, and the diagonal Hamiltonian matrix elements as a function of R in this basis would not be expected to resemble the usual diabatic potential curves. Truncated basis sets within which all the radial first-derivative coupling vanishes may be useful from a computational point of view because they allow a treatment of truncated adiabatic spaces,

[†] Smith's treatment of diabatic states has been generalized to include atom-molecule collisions by Baer (1975, 1976) (see also Top and Baer, 1977).

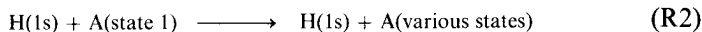
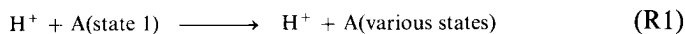
including all derivative coupling, by a transformation to a representation with no derivative coupling. This kind of incomplete diabatic basis is discussed further in Sections III and IV.

To obtain only the physically meaningful part of the nonadiabatic coupling, one might consider a basis set that depends as little as possible on R , but still allows a description of the molecular states in a reasonably small basis set. The minimum R dependence in such a basis set would be that due to configurations constructed with fixed linear combinations of frozen atomic orbitals that translate with the nuclei. Numrich and one of the authors (Numrich and Truhlar, 1975) suggested that a molecular adiabatic representation be constructed using such a basis and that the nonadiabatic coupling be obtained by retaining the action of the nuclear-momentum operators on the transformation coefficients from this basis to the adiabatic basis. These contributions are independent of origin and vanish at infinity. In this approach one neglects the action of the nuclear momentum operators on the translating frozen atomic functions but keeps all other contributions. The retained contributions correspond physically to polarization of the atomic charge distributions, covalent bonding, and charge transfer. In the language of Delos and Thorson (1979), a basis of state functions that translate with the nuclei but do not change in any other way is called " F diabatic" where F stands for fixed one-center orbitals. Such a basis is also called a valence-bond basis, and a separated-atom basis is a special case. Notice, however, that a generalized valence-bond calculation (Goddard *et al.*, 1973) or a diatomics-in-molecules calculation with semiempirical adjustment of integrals (Tully, 1977) does not correspond to frozen atomic orbitals as the original valence-bond scheme does. The assumption that the nuclear momentum coupling vanishes in an F -diabatic representation provides a consistent scheme for obtaining physically reasonable nonadiabatic terms at chemical energies (Numrich and Truhlar, 1975; Delos and Thorson, 1979). However, its usefulness is limited by the necessity to do the calculation in an F -diabatic basis, which is not computationally the most efficient one, or to reexpress an adiabatic representation obtained some other way in an F -diabatic basis. Delos and Thorson (1979) have suggested that a nearly optimal definition of nonadiabatic coupling in a general molecular basis can be obtained by using a "special switching function" defined so that the results are equivalent to neglecting the nuclear momentum coupling in an F -diabatic basis. The implicit assumption in this and related approaches is that redefining the nonadiabatic coupling terms compensates for lack of ETFs in the basis and speeds convergence for truncated expansions. Results obtained with basis sets of fixed atomic orbitals will be discussed further in Section III.

Redmon and Micha (1974; Redmon, 1973) also used a valence-bond basis. They performed the transformation to the adiabatic basis in two steps, a Schmidt orthogonalization and diagonalization of H_e , and retained the derivative coupling caused by the latter but not that caused by the former. This procedure means that their results are not independent of the method of orthogonalization and are not equivalent to neglecting derivative coupling in an F -diabatic basis. Numrich and Truhlar (1975) used symmetric orthogonalization that makes the orthogonal basis as similar as possible to the valence-bond basis. Furthermore, they retained the action of the derivative operators on the orthogonalizing transformation so that their derivative couplings in the adiabatic basis are independent of the method of orthogonalization (the adiabatic potential curves are independent of the method of orthogonalization in either case). In unpublished work Redmon and Micha showed that the derivative coupling caused by the orthogonalizing transformation did not make a large difference for the case they studied (M. J. Redmon, personal communication, 1979). This need not always be true.

A procedure for redefining nonadiabatic coupling terms that removes the nonzero coupling at infinity has been derived by Chen *et al.* (1973; Hatton *et al.*, 1975). The net result of their manipulations is that one calculates the nonadiabatic coupling with the origin at the center of mass of the nuclei and then subtracts from each nonadiabatic coupling matrix element at every R the value calculated for it with this origin for $R = \infty$. This approach has been criticized for not addressing the correct physics of the nonadiabatic coupling at small R (SethuRaman *et al.*, 1973; Thorson and Delos, 1978a).

For some problems, one of the subsystems is in the same asymptotic electronic state for all channels of interest. Examples are



We have pointed out already that in cases like the above, the nonadiabatic coupling can be made to vanish at infinity by putting the origin at the center of mass of A. This approach has recently been discussed and used in a semi-classical framework by Riera and Salin (1976). If, however, we must also consider electron transfer to H(1s) and H(2s) in Eq. (R1) or if we must also consider excitation of H(2s) in Eq. (R2), then no single choice of origin will make all the nonadiabatic couplings vanish at infinity. Thus the method is not general. Another defect of the method is its lack of uniqueness for the nonadiabatic coupling at small subsystem separations. For example, we could consider letting the origin be a function of internuclear distance R in an atom-atom collision. The Riera-Salin prescription corresponds to putting the origin at A for all R . But any other choice for which the origin tends to

A as R tends to infinity will also eliminate the nonzero couplings between channels differing only in the electronic state of A . One requires a prescription for the choice of origin at small R .

Piacentini and Salin (1974, 1977) have proposed an extension of the above scheme in the context of the semiclassical formalism. With the electronic origin on center A the coupling between states with $\alpha = A$ vanishes at large R , and they calculate state-to-state cross sections among these states in a standard fashion. Since their method conserves flux they then calculate the sum of all cross sections for transitions involving an electron transfer from A to B by subtracting the sum of the A -to- A transition probabilities (including the elastic one) from unity. This shows that one can calculate the total cross section for charge transfer even in the presence of the infinite-range coupling but that state-to-state cross sections for charge transfer are more difficult.

It is appropriate here to recall that any choice of electronic origin other than the center of mass of the nuclei introduces an electronic-nuclear cross term into the kinetic energy. This term need not be considered in the semiclassical treatments for the following reason. The choice of electronic origin at the center of mass of the nuclei implies a unique factorization of the nuclear motion in the semiclassical treatment (Riley, 1973). A change of origin implies a new factorization and introduces a new electronic derivative and cross term. One can, however, make the cross term vanish by multiplying by a coordinate-dependent phase factor; this yields the same form of equation for any choice of electronic origin (Riley, 1973; see also Thorson and Delos, 1978b). One need deal with this change of factorization only if the phase of the wave function is used. The same simplification cannot be achieved in the purely quantal formalism employed here. In the quantal formulation, if the electronic-nuclear derivative cross term is not included, then one should choose the origin at the center of mass of the nuclei for a consistent calculation (however, one presumably might leave the cross term out if one is trying to introduce purposeful inconsistencies to compensate for the lack of ETFs).†

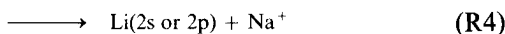
Melius and Goddard (1972, 1974) have proposed a scheme for fixing the origin in the semiclassical formalism for collisions with only one active electron, i.e., for calculations in which all electrons except one may be considered to be frozen cores. Let the orbital of the active electron be $\phi_i(\mathbf{r}, R)$ in state i . Based on considering the atomic cores as potentials moving in the

† Another simplification that occurs in the semiclassical framework is that in the semiclassical limit the second-derivative coupling does not occur. The first-derivative coupling, which is multiplied by the internuclear velocity, becomes for this reason relatively more important than the second-derivative coupling as the velocity increases, and the second-derivative coupling need not be considered in the semiclassical limit. This does not, however, mean that the second-derivative coupling is unimportant in the low-energy quantal case; on the contrary it is sometimes quite important.

reference frame of the electron, they propose calculating the nonadiabatic coupling at R between states i and j with the electronic origin at

$$z_{ij}(R) = \frac{\langle |\phi_i(\mathbf{r}, R)| |z| |\phi_j(\mathbf{r}, R)| \rangle_{\mathbf{r}}}{\langle |\phi_i(\mathbf{r}, R)| |1| |\phi_j(\mathbf{r}, R)| \rangle_{\mathbf{r}}} \quad (178)$$

This scheme makes all nonadiabatic couplings vanish at infinity, even when electronic excitation is allowed on both centers as in



Furthermore, it corresponds to a physically motivated choice of origin for small R , e.g., for $i = j$ it corresponds to putting the origin at the center of mass of the electron when the system is in that state. One should keep in mind, however, that it is mathematically inconsistent to use a different origin for the different elements of the coupling matrix at one R . Notice the relationship of this method to that embodied by Eqs. (74)–(77). Those equations involve a different electronic origin for different derivative coupling matrix elements but in a completely consistent way.

Taulbjerg and Briggs (1975b) have also suggested a scheme that involves different origins for different matrix elements. In their scheme each coupling is evaluated using the origin that makes it vanish at infinity. The exchange couplings that vanish at infinity for any origin are evaluated using the CMN origin. Like the modifications suggested by Melius and Goddard (1972, 1974) and Thorson and Delos (1978a), their suggestion is motivated by trying to compensate for missing ETFs.

Other approaches to correcting the deficiencies of the Born–Oppenheimer electronically adiabatic representation involve expanding the total wavefunction in modified electronic states. One possibility is to include electron translation factors. In this approach one actually replaces the Born–Oppenheimer electronically adiabatic basis by another one modified so as to satisfy the correct scattering boundary conditions. This approach has been discussed in detail in Section II.D. Other approaches involve expanding in atomic bases. Poppe and Wolken (1977) have suggested expanding the wave function in an atomic basis in orthogonal Jacobi coordinates and expressing the Hamiltonian and coupled equations in the standard body-fixed coordinates. Stechel *et al.* (1979; see also Schmalz *et al.*, 1979) have suggested expanding the wave function in an atomic basis and expressing the Hamiltonian and coupled equations in nonorthogonal coordinates. They suggest a special R -matrix-propagation step for transforming the Wigner derivative matrix at large R from a surface of constant R to a constant- R_x surface at which one can apply scattering boundary conditions.

There is no guarantee that electron translation factors, despite the additional difficulties and complexities they introduce, will speed up convergence of the state expansion at small R ,[†] and one expects a separated-atom basis to lead to even slower convergence than either the adiabatic basis or the ETF-modified basis. For these reasons we prefer to expand the total wave function in the standard Born–Oppenheimer basis set. It should be noted that the expansion of Eq. (46) in adiabatic basis functions in the (\mathbf{r}, R) coordinates can always be made sufficiently exact by adding more terms. However, it is possible that it is slowly convergent in some cases and may require many terms. Inclusion of basis functions containing electron translation factors might provide a more rapidly convergent expansion in at least some cases, but these factors are difficult to handle in practice and involve choices in computational strategy that have not been well studied. The advantage of an optimal basis is that one gets convergence with less functions. An advantage of a simple basis is that one can apply a rigorous formalism without extra approximations (aside from truncation to a finite basis). Then one is at least assured that the calculations will converge (and will converge to the correct answer) when the basis gets large enough to span the necessary space. It is sometimes stated as a disadvantage of the Born–Oppenheimer (BO) basis that the expansion of state functions involving ETFs in a BO basis will require contributions from continuum functions of the BO basis. This need not be a serious obstacle to the use of a BO basis because (1) the expansion needs to be reasonably converged but not complete, and (2) expansion of continuum contributions in a square integrable basis is now a well-established technique in practical scattering calculations (see, e.g., Gallaher and Wilets, 1968; Geltman, 1972; Heller *et al.*, 1973; see also the discussion in Riley and Green, 1971). If one uses the standard BO basis though, one requires special techniques to impose the scattering boundary conditions as well as possible within the chosen basis. Such special techniques have been presented in Sections II,E and II,G. The method of Section II,E employs a straightforward expansion in the standard body-fixed Born–Oppenheimer basis functions at small R in conjunction with a rearrangement-analysis and application of correct scattering boundary conditions at large R . The method of Section II,G involves an asymptotic diagonalization of the coupling instead of a rearrangement analysis.

[†] Inclusion of electron translation factors is known to improve the basis at such high energies that internuclear velocities are not negligible with respect to electronic orbital velocities, but there is not much computational experience for energies of chemical interest [e.g., for $\text{He}^{2+} + \text{H} \rightarrow \text{He}^+ + \text{H}^+$, it appears that the standard electronically adiabatic basis is adequate for relative kinetic energies up to a few hundred eV, but that electron translation factors speed convergence at higher energies (Winter and Lane, 1978; Vaaben and Taulbjerg, 1979)].

The use of standard BO basis sets and the methods of Sections II,E and II,G has a number of advantages. Such combinations of procedures do not involve inconsistencies or extra assumptions to remove the infinite-range coupling, do not involve the extra labor of solving coupled differential equations containing complicated terms from electron translation factors, and do not require using an atomic basis in the small- R strong-interaction region. The use of the standard Born–Oppenheimer basis set means that these approaches can take advantage of state-of-the-art techniques (see, e.g., Browne, 1971; Green *et al.*, 1976; Albat and Wirsam, 1977; Olson *et al.*, 1975, 1976, 1978; Shipsey *et al.*, 1978; Stern *et al.*, 1978; Winter and Lane, 1978; Macía and Riera, 1978a, and references therein) for calculating adiabatic electronic energies and derivative-coupling matrix elements.

Additional practical considerations related to two of the approaches discussed in this section form the basis of the rest of this article. Sections III,A and IV,C are concerned with further aspects of the rigorous approach involving a BO adiabatic basis as discussed in the previous two paragraphs. Sections III,B and IV,B discuss some practical techniques for implementing the approach of physically motivated diabatic basis sets.

III. Transformation to Diabatic Representations

A. P -DIABATIC BASIS SETS

In this section we consider some practical aspects of transformations between diabatic and adiabatic representations. We will illustrate the discussion by considering an N_e -electron generalization of the radial equations (154) of Section II. Let \mathbf{r}'_i be a vector from the center of mass of the nuclei to electron i in the space-fixed frame of reference, and let \mathbf{x} denote the collection $\{\mathbf{r}'_i\}_{i=1}^{N_e}$. The Hamiltonian for the system of N_e electrons and 2 nuclei may be written (Hirschfelder and Meath, 1967)

$$H = -(\hbar^2/2\mu_{AB}) \nabla_{\mathbf{R}'}^2 + H_e - [\hbar^2/2(m_A + m_B)] \sum_{ij} \nabla_{\mathbf{r}'_i} \cdot \nabla_{\mathbf{r}'_j} \quad (\text{A1})$$

in which the electronic Hamiltonian is

$$H_e = -(\hbar^2/2m_e) \sum_i \nabla_{\mathbf{r}'_i}^2 + V(\mathbf{x}', \mathbf{R}') \quad (\text{A2})$$

and the term containing the double sum in Eq. (A1) is the mass polarization term. As in Section II we rotate to a coordinate system $(\mathbf{x}, \mathbf{R}) = (\{\mathbf{r}'_i\}_{i=1}^{N_e}, \mathbf{R})$

such that \mathbf{R} lies on the z axis. In these body-fixed coordinates the total Hamiltonian is

$$H = -\frac{\hbar^2}{2\mu_{AB}} \frac{1}{R} \frac{\partial^2}{\partial R^2} R + \frac{L^2}{2\mu_{AB}R^2} + H_e - \frac{\hbar^2}{2(m_A + m_B)} \sum_{ij} \nabla_{r_i} \cdot \nabla_{r_j} \quad (\text{A3})$$

and the electronic Hamiltonian is

$$H_e = -(\hbar^2/2m_e) \sum_i \nabla_{r_i}^2 + V(\mathbf{x}, R) \quad (\text{A4})$$

The approximate radial equations (154) are generalized to a many-electron system by noting that the electronic Hamiltonian in the matrix element $H_{q_1q}^a(R)$ is now given by Eq. (A4). The mass polarization term of Eq. (A3) and Σ - Π coupling are neglected in the approximate radial equations, which can be rewritten in matrix notation as

$$\left\{ -\frac{\hbar^2}{2\mu_{AB}} \left[\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} + \mathbf{K}^2 \right] \mathbf{I} + \mathbf{V}^a(R) + 2\mathbf{F}^a(R) \frac{d}{dR} + \mathbf{G}^a(R) \right\} \boldsymbol{\chi}^a(R) = 0 \quad (\text{A5})$$

in which \mathbf{I} is the unit matrix,

$$K_{q_1q} = \delta_{q_1q} k_q \quad (\text{A6})$$

$$k_q = [2\mu_{AB}(E - \varepsilon_q)]^{1/2}/\hbar \quad (\text{A7})$$

$$\varepsilon_q = \lim_{R \rightarrow \infty} \varepsilon_q^a(R) \quad (\text{A8})$$

$$V_{q_1q}^a(R) = \delta_{q_1q} [\varepsilon_q^a(R) - \varepsilon_q] \quad (\text{A9})$$

$$F_{q_1q}^a(R) = -(\hbar^2/2\mu_{AB}) \langle \phi_{q_1}^a(\mathbf{x}, R) | d/dR | \phi_q^a(\mathbf{x}, R) \rangle_{\mathbf{x}} \quad (\text{A10})$$

$$G_{q_1q}^a(R) = -(\hbar^2/2\mu_{AB}) \langle \phi_{q_1}^a(\mathbf{x}, R) | d^2/dR^2 | \phi_q^a(\mathbf{x}, R) \rangle_{\mathbf{x}} \quad (\text{A11})$$

and $\varepsilon_q^a(R)$ is an adiabatic potential curve given by

$$\varepsilon_q^a(R) = \langle \phi_q^a(\mathbf{x}, R) | H_e | \phi_q^a(\mathbf{x}, R) \rangle_{\mathbf{x}} \quad (\text{A12})$$

In matrix notation, Eq. (153) for a set of initial conditions q_0 is summarized as

$$\boldsymbol{\Psi} = R^{-1} [\boldsymbol{\phi}^a(\mathbf{x}, R)]^T \boldsymbol{\chi}^a(R) \quad (\text{A13})$$

where $\boldsymbol{\Psi}$ is a row vector of elements Ψ_{q_0} , $\boldsymbol{\phi}^a$ is a column vector of elements ϕ_q^a , superscript T denotes a transpose, each column of $\boldsymbol{\chi}^a(R)$ corresponds to a different linearly independent solution of Eq. (154), and the different rows of $\boldsymbol{\chi}^a(R)$ correspond to different channels.

We will assume in Sections III and IV that the electronic basis functions are chosen as real. It follows that \mathbf{F}^a is a skew-symmetric matrix, i.e.,

$$[\mathbf{F}^a(R)]^T = -\mathbf{F}^a(R) \quad (\text{A14})$$

A consequence of Eq. (A14) is that the diagonal elements of $\mathbf{F}^a(R)$ are zero. If the electronic basis is complete, then it can be shown (Smith, 1969; Sidis and Lefebvre-Brion, 1971; Andresen and Nielsen, 1971; Babamov, 1978) that

$$\mathbf{G}^a(R) = \frac{d}{dR} \mathbf{F}^a(R) - \frac{2\mu_{AB}}{\hbar^2} [\mathbf{F}^a(R)]^2 \quad (\text{A15})$$

A disadvantage of using the Born–Oppenheimer adiabatic basis is that the derivative coupling terms complicate the numerical solution. It is interesting to examine a transformation to a representation in which the first-derivative coupling vanishes; for a truncated basis, Delos and Thorson (1979) have called this a *P*-diabatic representation. Any basis that is not adiabatic (i.e., in which the matrix of H_e is not diagonal) will be called diabatic. First we consider the transformation to a general orthogonal diabatic representation

$$\phi^a(\mathbf{x}, R) = [\mathbf{U}^{oa}(R)]^T \phi^o(\mathbf{x}, R) \quad (\text{A16})$$

in which

$$[\mathbf{U}^{oa}(R)]^{-1} = [\mathbf{U}^{oa}(R)]^T \quad (\text{A17})$$

In terms of this basis the total wave function may be written

$$\Psi = R^{-1} [\phi^o(R)]^T \chi^o(R) \quad (\text{A18})$$

From Eqs. (A13), (A16), and (A18) and the fact that $\mathbf{U}^{oa}(R)$ is unitary, we obtain

$$\chi^a(R) = [\mathbf{U}^{oa}(R)]^T \chi^o(R) \quad (\text{A19})$$

Under a unitary transformation the derivative coupling matrices transform as

$$\mathbf{F}^o(R) = -(\hbar^2/2\mu_{AB}) \langle \phi^o(\mathbf{x}, R) | d/dR | [\phi^o(\mathbf{x}, R)]^T \rangle_{\mathbf{x}} \quad (\text{A20})$$

$$= \mathbf{U}^{oa}(R) \mathbf{F}^a(R) [\mathbf{U}^{oa}(R)]^{-1} - (\hbar^2/2\mu_{AB}) \mathbf{U}^{oa}(R) (d/dR) [\mathbf{U}^{oa}(R)]^{-1} \quad (\text{A21})$$

and

$$\mathbf{G}^o(R) = -(\hbar^2/2\mu_{AB}) \langle \phi^o(\mathbf{x}, R) | d^2/dR^2 | [\phi^o(\mathbf{x}, R)]^T \rangle_{\mathbf{x}} \quad (\text{A22})$$

$$= \mathbf{U}^{oa}(R) \mathbf{G}^a(R) [\mathbf{U}^{oa}(R)]^{-1} + 2\mathbf{U}^{oa}(R) \mathbf{F}^a(R) (d/dR) [\mathbf{U}^{oa}(R)]^{-1} - (\hbar^2/2\mu_{AB}) \mathbf{U}^{oa}(R) (d^2/dR^2) [\mathbf{U}^{oa}(R)]^{-1} \quad (\text{A23})$$

Now we consider a basis $\{\phi^d(\mathbf{x}, R)\}$ for which the first derivative coupling $\mathbf{F}^d(R)$ vanishes. The unitary transformation $\mathbf{U}^{da}(R)$ that generates this basis must satisfy the differential equation obtained by setting the right-hand side of Eq. (A21) to zero:

$$(\hbar^2/2\mu_{AB})(d/dR)[\mathbf{U}^{da}(R)]^{-1} = \mathbf{F}^a(R)[\mathbf{U}^{da}(R)]^{-1} \quad (\text{A24})$$

Notice that the solution to this differential equation is automatically unitary if $\mathbf{F}^a(R)$ is a real skew-symmetric matrix. In this case the coupled equations (A5) of the adiabatic representation transform to

$$\left\{ -\frac{\hbar^2}{2\mu_{AB}} \left[\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} + \frac{2\mu_{AB}E}{\hbar^2} \right] \mathbf{I} + \mathbf{H}^d(R) + \mathbf{G}^d(R) \right\} \chi^d(R) = 0 \quad (\text{A25})$$

in which

$$\mathbf{H}^d(R) = \mathbf{U}^{da}(R) \langle \phi^a(\mathbf{x}, R) | H_e | [\phi^a(\mathbf{x}, R)]^T \rangle_{\mathbf{x}} [\mathbf{U}^{da}(R)]^{-1} \quad (\text{A26})$$

$$\mathbf{G}^d(R) = \mathbf{U}^{da}(R) \{ \mathbf{G}^a(R) - (d\mathbf{F}^a/dR) + (2\mu_{AB}/\hbar^2)[\mathbf{F}^a(R)]^2 \} [\mathbf{U}^{da}(R)]^{-1} \quad (\text{A27})$$

Although $\mathbf{G}^d(R)$ does not vanish for a finite basis, Eqs. (A15) and (A27) show that for a complete set, $\mathbf{G}^d(R)$ vanishes if $\mathbf{F}^d(R)$ vanishes.

It has been noted in Section II, G (and originally by Andresen and Nielsen, 1971; and Gabriel and Tjaulberg, 1974) that in the limit of a complete electronic basis, the diabatic basis functions defined by Eqs. (A15) and (A24) are, apart from possible phase factors, independent of internuclear separation. It would be impractical to perform accurate electronic structure calculations in such a basis in which the functions do not move with the nuclei. One possible use of the transformation just defined is for numerical work with truncated (i.e., finite or incomplete) basis sets (see, e.g., Heil and Dalgarno, 1979). In truncating a basis one should ideally first transform to the representation in which the expansion is expected to be most rapidly convergent, then truncate, then transform within the truncated manifold to the representation that makes the coupled equations most convenient. This is the rationale for using *P*-diabatic bases, i.e., one truncates the adiabatic representation, then for convenience one transforms away the coupling caused by the first derivative in the truncated manifold.†

There are an infinite number of *P*-diabatic transformations corresponding to different boundary conditions on the differential equation (A24). If $\mathbf{F}^a(R)$

†A similar idea has been used by Johnson (1974) and is called the diabatic decoupling approximation.

vanishes at large R , a convenient boundary condition for Eq. (A24) is

$$\lim_{R \rightarrow \infty} \mathbf{U}^{\text{da}}(R) = \mathbf{I} \quad (\text{A28})$$

B. APPROXIMATELY P -DIABATIC BASIS SETS

Equations (A24) and (A28) give a well-defined procedure for obtaining a P -diabatic basis from an adiabatic basis in which the derivative coupling matrices are known. However, in many studies of electronic excitation problems, reasonable approximations to the adiabatic potential energy curves are known but the derivative coupling terms have not been computed. Faist and Levine (1976) have developed a method that does not require knowing the derivative couplings for obtaining the P -diabatic transformation approximately for two-state models in which the adiabatic curves show an avoided crossing. Another procedure is to use physical arguments to approximate the diabatic basis, i.e., to define a basis in which the basis functions in some sense vary slowly with R . One might then assume that all the coupling in the adiabatic basis arises from the transformation from the slowly varying basis to the adiabatic basis; this is equivalent to assuming that the slowly varying basis is the P -diabatic basis. Some examples of this approach (using valence bond bases and F -diabatic bases) are mentioned in Section II, H and there are many other examples in the literature (see, e.g., O'Malley, 1971; Sidis and Lefebvre-Brion, 1971; Evans *et al.*, 1971; Evans and Lane, 1973; Taulbjerg and Briggs, 1975a; Aubert and Le Sech, 1976; Cohen, 1976; Kubach and Sidis, 1976; Stern *et al.*, 1977; Sidis and Kubach, 1978; Gauyacq, 1978). Macías and Riera (1978b) have proposed a method for constructing diabatic states that is based on a formal analysis of the variation of expectation values in the vicinity of an avoided crossing and employs special orbital models designed to eliminate or considerably reduce the derivative coupling within a limited manifold. A special case of common occurrence concerns fine-structure transitions. In many cases the adiabatic states computed without spin-orbit coupling form a good diabatic basis when spin-orbit coupling is included, i.e., the nuclear-derivative operators cause much less coupling than the spin-orbit interaction does (see, e.g., Mies, 1973; Cohen *et al.*, 1978; Becker *et al.*, 1979). In the present section we consider methods of approximating the diabatic bases that are based on assuming some knowledge of the diabatic Hamiltonian matrix $\mathbf{H}^{\text{d}}(R)$. The goal is to obtain diabatic bases that are slowly varying and thus have only small derivative coupling.

One procedure for obtaining diabatic bases is to model the off-diagonal elements of $\mathbf{H}^{\text{d}}(R)$ and then solve for the diagonal elements that give the correct adiabatic energies. For a two-state curve crossing problem this

amounts to solving the following set of bilinear equations for H_{11}^d and H_{22}^d at each R :

$$\det[\mathbf{H}^d(R) - \varepsilon_q^a(R)\mathbf{I}] = 0, \quad q = 1, 2 \quad (\text{A29})$$

These two equations have two roots, one of which is obtained from the other by interchanging H_{11}^d and H_{22}^d ,

$$H_{qq}^d(R) = \frac{1}{2}[\varepsilon_1^a(R) + \varepsilon_2^a(R)] \pm (\{\frac{1}{2}[\varepsilon_2^a(R) - \varepsilon_1^a(R)]\}^2 - [H_{12}^d(R)]^2)^{1/2} \quad (\text{A30})$$

Curve crossings occur in the diabatic representation whenever the radicand in (A30) is zero. However, for real roots, $H_{12}^d(R)$ is restricted to be no greater than the adiabatic energy splitting. Thus $H_{12}^d(R)$ must equal but not cross $\frac{1}{2}[\varepsilon_2^a(R) - \varepsilon_1^a(R)]$ at the curve crossing, and one must be very careful in constructing diabatic curves that cross but remain real.

For systems with more than two states the problem becomes more complicated. Since the off-diagonal elements of the diabatic Hamiltonian matrix tend to zero at $R = \infty$, its eigenvectors all have only one component at infinity. But for an N -state problem, the matrix of eigenvectors may tend to any one of $N!$ possible permutations of the unit matrix. For the physical root the eigenvector matrix tends to the identity matrix as $R \rightarrow \infty$; this ensures that

$$H_{qq}^a(R) \xrightarrow{R \rightarrow \infty} \varepsilon_q^a(R) \quad (\text{A31})$$

for all q . A numerical solution for the $H_{qq}^a(R)$ that reproduces a set of $\varepsilon_q^a(R)$ will not necessarily yield the physical root.

One particular way to model the off-diagonal elements of the diabatic Hamiltonian matrix is to calculate them with physically motivated, slowly varying basis functions, e.g., with F -diabatic basis functions. Such basis functions do not form an orthogonal set at finite R so we must generalize the formulation of Eqs. (A16)–(A27), which applies only for an orthogonal diabatic basis. Consider an expansion of the total wave function in a non-orthogonal diabatic basis:

$$\Psi = R^{-1}[\Phi^n(\mathbf{x}, R)]^T \chi^n(R) \quad (\text{A32})$$

This expansion yields the following coupled equations:

$$\left\{ -\frac{\hbar^2}{2\mu_{AB}} \mathbf{S}(R) \left[\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} + \frac{2\mu_{AB}E}{\hbar^2} \right] + \mathbf{H}^n(R) + 2\mathbf{F}^n(R) \frac{d}{dR} + \mathbf{G}^n(R) \right\} \chi^n(R) = 0 \quad (\text{A33})$$

in which

$$S_{q_1q}(R) = \langle \phi_{q_1}^n(\mathbf{x}, R) | \phi_q^n(\mathbf{x}, R) \rangle_{\mathbf{x}} \quad (\text{A34})$$

$$H_{q_1q}^n(R) = \langle \phi_{q_1}^n(\mathbf{x}, R) | H_\epsilon | \phi_q^n(\mathbf{x}, R) \rangle_{\mathbf{x}} \quad (\text{A35})$$

$$F_{q_1q}^n(R) = -(\hbar^2/2\mu_{AB}) \langle \phi_{q_1}^n(\mathbf{x}, R) | d/dR | \phi_q^n(\mathbf{x}, R) \rangle \quad (\text{A36})$$

$$G_{q_1q}^n(R) = -(\hbar^2/2\mu_{AB}) \langle \phi_{q_1}^n(\mathbf{x}, R) | d^2/dR^2 | \phi_q^n(\mathbf{x}, R) \rangle_{\mathbf{x}} \quad (\text{A37})$$

Notice that Eq. (A33) contains the derivative coupling matrices $\mathbf{F}^n(R)$ and $\mathbf{G}^n(R)$. In Section IV,B we shall discuss the solution of these coupled equations when $\mathbf{F}^n(R)$ and $\mathbf{G}^n(R)$ are neglected. The nonorthogonal basis of Eqs. (A32)–(A37) can be transformed to an orthogonal basis by

$$\phi^o(\mathbf{x}, R) = [\mathbf{A}^o(R)]^T \phi^n(\mathbf{x}, R) \quad (\text{A38})$$

in which

$$\mathbf{A}^o(R) = \mathbf{C}(R)\mathbf{U}^{so}(R) \quad (\text{A39})$$

$$\mathbf{C}(R) = \mathbf{S}^{-1/2}(R) \quad (\text{A40})$$

and where $\mathbf{U}^{so}(R)$ is an arbitrary unitary matrix. In this general orthogonal coordinate system the wave-function expansion and coupled equations are

$$\Psi = [\phi^o(\mathbf{x}, R)]^T \chi^o(R) \quad (\text{A41})$$

and

$$\left\{ \left[-\frac{\hbar^2}{2\mu_{AB}} \frac{d^2}{dR^2} + \frac{\hbar^2 l(l+1)}{2\mu_{AB} R^2} - E \right] \mathbf{I} + \mathbf{H}^o(R) + \mathbf{G}^o(R) + 2\mathbf{F}^o(R) \frac{d}{dR} \right\} \chi^o(R) = 0 \quad (\text{A42})$$

where $\mathbf{H}^o(R)$, $\mathbf{G}^o(R)$, and $\mathbf{F}^o(R)$ are defined analogously to the quantities in Eqs. (A34)–(A36), but with $\phi_{q_1}^o(\mathbf{x}, R)$ and $\phi_q^o(\mathbf{x}, R)$ replacing $\phi_{q_1}^n(\mathbf{x}, R)$ and $\phi_q^n(\mathbf{x}, R)$, respectively.

A particularly useful orthogonal diabatic basis set $\phi^s(\mathbf{x}, R)$ is defined by taking $\mathbf{U}^{so}(R)$ as the identity matrix; in this case the transformation (A38) is called symmetric orthogonalization (Löwdin, 1970). The total wave function can be expanded in this basis by

$$\Psi = [\phi^s(\mathbf{x}, R)]^T \chi^s(R) \quad (\text{A43})$$

$$= [\phi^n(\mathbf{x}, R)]^T \mathbf{C}(R) \chi^s(R) \quad (\text{A44})$$

$$= [\phi^n(\mathbf{x}, R)]^T \chi^n(R) \quad (\text{A45})$$

In deriving (A45) we used

$$\chi^s(R) = \mathbf{C}^{-1}(R) \chi^n(R) \quad (\text{A46})$$

which follows from Eqs. (A32), (A38)–(A40), (A43), and $\mathbf{U}^{s0} = \mathbf{I}$. The coupled equations transform to

$$\left\{ \left[-\frac{\hbar^2}{2\mu_{AB}} \frac{d^2}{dR^2} + \frac{\hbar^2 l(l+1)}{2\mu_{AB} R^2} - E \right] \mathbf{I} + \mathbf{H}^s(R) + \mathbf{G}^s(R) + 2\mathbf{F}^s(R) \frac{d}{dR} \right\} \chi^s(R) = 0 \quad (\text{A47})$$

in which

$$\mathbf{H}^s(R) = \mathbf{C}(R)\mathbf{H}^n(R)\mathbf{C}(R) \quad (\text{A48})$$

$$\mathbf{F}^s(R) = -(\hbar^2/2\mu_{AB})\mathbf{C}^{-1}(R)(d\mathbf{C}/dR) + \mathbf{C}(R)\mathbf{F}^n(R)\mathbf{C}(R) \quad (\text{A49})$$

$$\mathbf{G}^s(R) = -(\hbar^2/2\mu_{AB})\mathbf{C}^{-1}(R)(d^2\mathbf{C}/dR^2) + [\mathbf{C}(R)\mathbf{G}^n(R)\mathbf{C}(R) + 2\mathbf{C}(R)\mathbf{F}^n(R)(d\mathbf{C}/dR)] \quad (\text{A50})$$

Another possible choice of $\mathbf{U}^{s0}(R)$ is the transformation $\mathbf{U}^{sa}(R)$ that diagonalizes $\mathbf{H}^s(R)$. This yields the adiabatic basis

$$\phi^a(\mathbf{x}, R) = [\mathbf{U}^{sa}(R)]^T \phi^s(\mathbf{x}, R) \quad (\text{A51})$$

$$= \mathbf{T}^T(R) \phi^n(\mathbf{x}, R) \quad (\text{A52})$$

where

$$\mathbf{T}(R) = \mathbf{C}(R)\mathbf{U}^{sa}(R) \quad (\text{A53})$$

From Eqs. (A43), (A51), and (A52) we obtain

$$\Psi = [\phi^a(\mathbf{x}, R)]^T \chi^a(R) \quad (\text{A54})$$

where

$$\chi^a(R) = [\mathbf{U}^{sa}(R)]^{-1} \chi^s(R) \quad (\text{A55})$$

$$= [\mathbf{T}(R)]^{-1} \chi^n(S) \quad (\text{A56})$$

The coupled equations transform to those given in Eqs. (A5)–(A12). We note the relationships between the matrix elements in the diabatic bases ϕ^s and ϕ^n and the adiabatic basis:

$$\varepsilon_q^a(R) = \sum_{q_1 q_2} [\mathbf{U}^{sa}(R)]_{q_1}^{-1} H_{q_1 q_2}^s(R) U_{q_2 q}^{sa}(R) \quad (\text{A57})$$

$$\mathbf{F}^a(R) = -(\hbar^2/2\mu_{AB})[\mathbf{U}^{sa}(R)]^{-1}(d\mathbf{U}^{sa}/dR) + [\mathbf{U}^{sa}(R)]^{-1}\mathbf{F}^s(R)\mathbf{U}^{sa}(R) \quad (\text{A58})$$

$$= -(\hbar^2/2\mu_{AB})[\mathbf{T}(R)]^{-1}(d\mathbf{T}/dR) + [\mathbf{T}(R)]^T\mathbf{F}^n\mathbf{T}(R) \quad (\text{A59})$$

$$\mathbf{G}^a(R) = -(\hbar^2/2\mu_{AB})[\mathbf{U}^{sa}(R)]^{-1}(d^2\mathbf{U}^{sa}/dR^2) + 2[\mathbf{U}^{sa}(R)]^{-1}\mathbf{F}^s(R)(d\mathbf{U}^{sa}/dR) + [\mathbf{U}^{sa}(R)]^{-1}\mathbf{G}^s(R)\mathbf{U}^{sa}(R) \quad (\text{A60})$$

$$= -(\hbar^2/2\mu_{AB})\mathbf{T}^{-1}(R)(d^2\mathbf{T}/dR^2) + \{2[\mathbf{T}(R)]^T\mathbf{F}^n(R)(d\mathbf{T}/dR) + [\mathbf{T}(R)]^T\mathbf{G}^n(R)\mathbf{T}(R)\}. \quad (\text{A61})$$

As an example of the above procedure we shall attempt to model $1^1\Sigma^+$ states of $K + H$ by using as input some electronic structure calculations (Numrich and Truhlar, 1975, 1978) that employed an F -diabatic valence-bond basis. We neglect spin-orbit coupling. The calculated nonorthogonal diabatic Hamiltonian matrix will be called $\mathbf{H}^n(R)$ and the calculated overlap matrix will be called $\mathbf{S}(R)$. Retaining three valence-bond F -diabatic basis functions, the predicted adiabatic energies are in only qualitative agreement with experiment. This is illustrated in Fig. 1a. We tested several procedures for obtaining a new 3×3 diabatic Hamiltonian matrix [also called $\mathbf{H}^n(R)$] that, combined with the 3×3 part of the valence-bond $\mathbf{S}(R)$, yields adiabatic energies for the two lowest $1^1\Sigma^+$ states in agreement with experiment. (The more common but less realistic procedure of modeling the curve crossings in this system by two-state models will not be considered here.) The three lowest adiabatic $1^1\Sigma^+$ states will hence forth be called X, A, and B'. These three states correlate in the separated-atom limit with $K(4s) + H(1s)$, $K(4p) + H(1s)$, and $K(5s) + H(1s)$. However this correlation of the B' state results from an avoided crossing at $R > 20a_0$ with a state correlating with $K^+ + H^-$. Here we are interested in $R < 15a_0$ so we may consider the third asymptote to be the ionic one. The diabatic states will be labeled 1, 2, and 3 corresponding to asymptotic correlations with K^+ , $K(4s)$, and $K(4p)$, respectively. In each case considered below, $H_{11}^n(R)$ and one or more additional $H_{ij}^n(R)$ were adjusted so that the experimental values of $\epsilon_X^a(R)$ and $\epsilon_A^a(R)$ are reproduced.

Figure 1b shows the resulting $H_{11}^n(R)$ and $H_{22}^n(R)$ when they are readjusted to reproduce $\epsilon_X^a(R)$ and $\epsilon_A^a(R)$ over the range where the values are known from a Rydberg-Klein-Rees (RKR) analysis of spectroscopic measurements. The procedure is more complicated than Eqs. (A29) and (A30) because it is based on a 3-state formalism including overlap. $H_{11}^n(R)$ and $H_{22}^n(R)$ must be obtained from

$$\det[\mathbf{H}^n(R) - \epsilon_i^a(R)\mathbf{S}(R)] = 0, \quad i = X, A \quad (\text{A62})$$

The solution is

$$H_{11}^n(R) = \omega_1 - (\omega_1^2 - 4\omega_2)^{1/2} \quad (\text{A63})$$

$$H_{22}^n(R) = (a_{X23}H_{11}^n - b_X)/(c_{X33}H_{11}^n - a_{X13}) \quad (\text{A64})$$

where

$$\omega_1 = (a_{X13}a_{A23} - a_{A13}a_{X23} + c_{X33}b_A - c_{A33}b_X)/2(c_{X33}a_{A23} - c_{A33}a_{X23}) \quad (\text{A65})$$

$$\omega_2 = (a_{X13}b_A - a_{A13}b_X)/(c_{X33}a_{A23} - c_{A33}a_{X23}) \quad (\text{A66})$$

$$a_{ijk} = [H_{jk}^n(R) - \epsilon_i^a(R)S_{jk}(R)]^2 + c_{i33}\epsilon_i^a(R) \quad (\text{A67})$$

$$b_i = 2c_{i12}c_{i13}c_{i23} - c_{i13}^2\epsilon_i^a(R) + a_{i23}\epsilon_i^a(R) - c_{i33}c_{i12}^2 \quad (\text{A68})$$

$$c_{ijk} = H_{jk}^n(R) - \epsilon_i^a(R)S_{jk}(R) \quad (\text{A69})$$

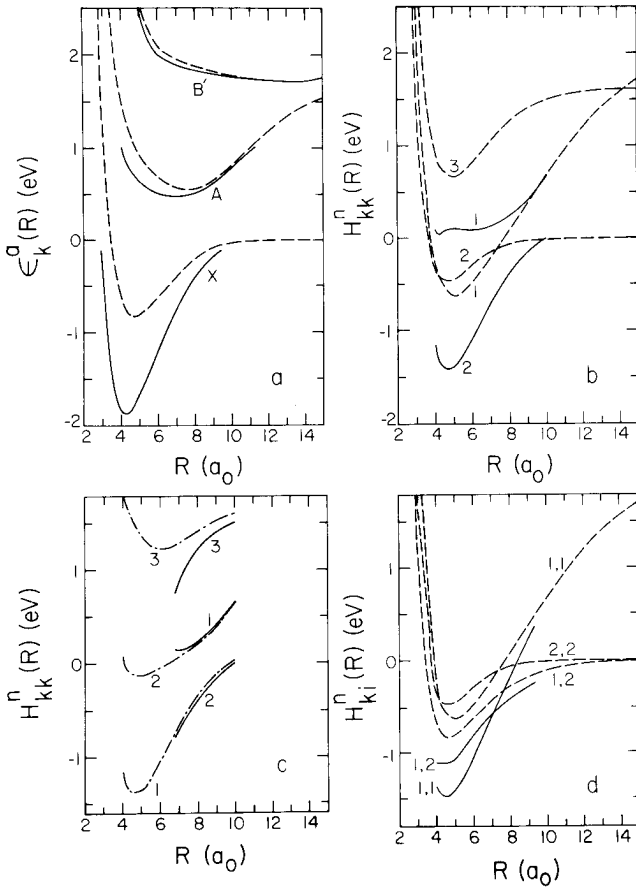


Fig. 1. Adiabatic potential curves and diabatic potential curves and couplings for KH as functions of internuclear distance as discussed in Section III. (a) Adiabatic potential curves: solid curves are RKR values (Numrich and Truhlar, 1975) for X and A states and 4-state valence-bond calculations (Numrich and Truhlar, 1975) for the B' state; dashed curves are 3-state valence-bond calculations for X, A, and B' states. (b) Diabatic potential curves: solid curves are adjusted so that solid X and A adiabatic potential curves of (a) are reproduced in a 3-state calculation; dashed curves are valence-bond calculations. (c) Diabatic potential curves: solid curves are adjusted so that solid X, A, and B' adiabatic potential curves of (a) are reproduced in a 3-state calculation; dot-dashed curves are a false root. (d) Diabatic potential curves and couplings: solid curves are adjusted so that solid X and A adiabatic potential curves of (a) are reproduced in a 3-state calculation; dashed curves are valence-bond calculations.

A second root can be obtained by changing the sign before the square root in Eq. (A63); however, this root has the undesirable behavior that $H_{11}^n(R)$ and $H_{22}^n(R)$ tend to $\epsilon_X^a(R)$ and $\epsilon_A^a(R)$ at large R . Equations (A63)–(A69) were evaluated as a function of R , and the results are shown in Fig. 1b. The most interesting aspect of the results is that $H_{11}^n(R)$ and $H_{22}^n(R)$ do not cross as they did in the valence-bond calculation. [For comparison, the values calculated by the valence-bond method are also shown in Fig. 1b.]

Another way to adjust the diabatic curves is to solve for $H_{ii}^n(R)$, $i = 1, 2, 3$, subject to the constraint that the 3-state calculation [again using the $S_{ij}(R)$ and the other $H_{ij}^n(R)$ unchanged from the valence-bond calculation] reproduce the RKR values for the adiabatic X and A states and the 4-state calculations for the B' state (the latter being the most accurate result available for the B' state). This corresponds to solving Eq. (A62) with $i = X, A$, and B' for $H_{11}^n(R)$, $H_{22}^n(R)$, and $H_{33}^n(R)$. There are six sets of roots to these equations, and we solved for some of them numerically. Two of these roots are shown in Fig. 1c. The root that goes to the correct asymptotic values is indicated as a solid curve. This root could not be found for $R < 6.8a_0$, presumably because it is not a real root in this region. However, for the region where these curves exist they do not cross. A second root in which the $H_{11}^n(R)$ and $H_{22}^n(R)$ curves have their correct asymptotic value interchanged is shown as a dot-dashed curve. The existence of this root shows that physically meaningless diabatic curves can be obtained that reproduce the experimental adiabatic potential curves. If one found such a root numerically at small R , one might be tempted to join it smoothly to the correct asymptotes; this would of course lead to incorrect conclusions. It is important to establish that any numerically determined root is a physically meaningful one.

Another way to adjust the diabatic curves is by a "least-squares" procedure. We tried this by adjusting all six $H_{ij}^n(R)$ such that the RKR values were exactly reproduced for the X and A states, the 4-state calculations were exactly reproduced for the B' state, and subject to these constraints the sum of the squares of the deviations from the original six $H_{ij}^n(R)$ were minimized. The results are shown in Figs. 2a and b. Notice that $H_{11}^n(R)$ and $H_{22}^n(R)$ now cross in a physically realistic way. Comparing these results to those in Figs. 1b and c illustrates the wide diversity of diabatic Hamiltonian matrices that can reproduce the experimental X and A adiabatic potential curves. Figure 2b shows the original $H_{ij}^n(R)$ for comparison to the new ones. It is encouraging that the differences are small. The present treatment would appear to be more realistic than requiring $H_{ij}^n(R)$ be locally constant so that the minimum splitting of the adiabatic potential curves coincides with the diabatic crossing (see, e.g., Stine and Muckerman, 1976).

Two problems with the least-squares procedures are the numerical difficulty of finding the solutions and the possibility to find local minima in the

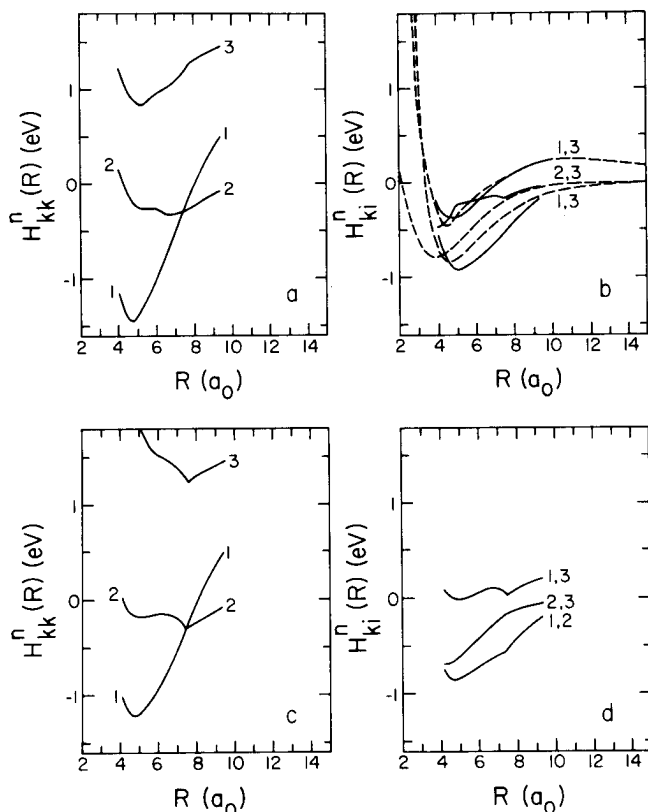


Fig. 2. Diabatic potential curves and couplings for KH as functions of internuclear distance as determined by least-squares procedure discussed in Section III. The solid curves are: (a) Potential curves for root 1; (b) couplings for root 1; (c) potential curves for root 2; (d) couplings for root 2. The dashed curves in (b) are the valence-bond results.

sum of squares. Such a local minimum was found for $R < 7.5a_0$ and is illustrated in Figs. 2c and 2d. The diabatic Hamiltonian matrix is quite different for this root, but it correctly reproduces the adiabatic energies at all R and it can be connected continuously to the correct asymptotes.

One difficulty with all the procedures explained so far is that they lead to more long-range attraction in $H_{22}^n(R)$ than seems physically reasonable. So we performed a final calculation in which $H_{22}^n(R)$ was constrained to its original value. We varied $H_{11}^n(R)$ and $H_{12}^n(R)$ to obtain the RKR values for $\epsilon_X^A(R)$ and $\epsilon_A^A(R)$. These results are shown in Fig. 1d where they are compared to the original values. The diabatic potential curves $H_{11}^n(R)$ and $H_{22}^n(R)$ do exhibit a curve crossing. Further, the modified $H_{11}^n(R)$ and $H_{12}^n(R)$ show

qualitatively the same character as the originally calculated matrix elements. Since the original calculation employed an F -diabatic basis, one would probably be safe to use the modified $\mathbf{H}^n(R)$ with the assumption that derivative coupling is negligible. Notice that we have not obtained a unique or rigorous diabatic basis set but rather one that should give physically meaningful results in practical calculations. This completes our illustration of model calculations of diabatic representations. The KH system has illustrated some of the practical ambiguities and pitfalls in such calculations.

C. RECAPITULATION

Diabatic bases, i.e., bases that do not diagonalize the electronic Hamiltonian, may be used in two quite distinct ways. One use is to provide a representation equivalent to some adiabatic basis, but in which the first-derivative coupling has been transformed away. In the limit of an infinite basis it is possible to simultaneously transform away the second-derivative coupling; however, the diabatic basis becomes quite unphysical in this limit. Diabatic basis sets defined so that the first derivative coupling vanishes within the finite set are called P diabatic.

The second kind of diabatic basis set does not really correspond to no derivative coupling. Compared to the mathematical transformations used to obtain P -diabatic basis sets, the second kind of diabatic basis is generally obtained by physical arguments. This kind of basis set is called approximately P diabatic. The justification for approximately P -diabatic basis sets is that for many problems it should be possible to write down basis sets that have strong potential couplings but only weak derivative couplings. Then it is a reasonable approximation to neglect the derivative couplings in such a basis, i.e., to assume that the basis really is P diabatic.

One particularly useful way to define approximately P -diabatic basis sets is to build them from functions that are adiabatic in different subspaces. Thus approximate electronic wave functions corresponding to various configurations may be optimized using the variational principle by diagonalizing the electronic Hamiltonian in appropriately restricted subspaces. When these approximate electronic wave functions are then considered together the electronic Hamiltonian need not be diagonal and may in fact show strong interactions. If the original subspaces were suitably restricted these potential couplings will dominate the derivative couplings. Several references for this approach are given in the first paragraph of Section III,B. Notice that this approach allows one to incorporate important effects of electronic relaxation as a function of R into a convenient diabatic framework. These electronic

Relaxation effects are very important for collisions at chemical energies. Only at much higher energies can quantitative results be obtained with small diabatic basis sets composed of atomic orbitals without molecular charge polarization. Nevertheless, the latter basis sets provide a useful limit in that the derivative coupling is as small as possible, consistent with the potential curves and couplings still behaving in a chemically intuitive and physically reasonable way. Thus it is useful to have a name for diabatic basis sets of this type and they are called *F* diabatic.

IV. Solution of the Coupled Channel Equations by *R*-Matrix Propagation

In this section we show how the *R*-matrix propagation method of Light and Walker (1976) can be implemented to solve the coupled channel equations in the various representations considered in the previous sections. Section IV,A considers the coupled equations (A42) in a general orthogonal basis and shows how to obtain a solution when the derivative coupling matrices $F^{\circ}(R)$ and $G^{\circ}(R)$ are neglected. In that case, the close-coupling equations reduce to the standard form for inelastic collisions of distinguishable particles when no rearrangement is possible. These equations could be solved by many standard techniques (e.g., the Numerov method), and we use this standard case to illustrate the *R*-matrix propagation method. The coupled equations (A47) are a special case of (A42) and their solution when $F^{\circ}(R)$ and $G^{\circ}(R)$ are neglected can also be obtained by the method of Section IV,A. In Section IV,B we consider the more general coupled equations (A33) that hold in a general nonorthogonal basis and we present the equations developed by Stechel *et al.* (1979) for solving these equations when the derivative coupling matrices $F^{\circ}(R)$ and $G^{\circ}(R)$ are neglected. The approach in Section IV,C is for calculations in an adiabatic representation where the input information is the set of electronically adiabatic potential energy curves and the nonadiabatic derivative coupling matrices, and no derivative coupling matrices are assumed negligible.

The reader is referred to the literature for an introduction to the *R*-matrix propagation method and for other ways of applying it (Light and Walker, 1976; Stechel *et al.*, 1978; Mullaney and Truhlar, 1979; Truhlar *et al.*, 1979; Light *et al.*, 1979). The only other application of the *R*-matrix propagation method to electronically inelastic scattering is the work of Stechel *et al.* (1979) (see also Schmalz *et al.*, 1979; Light *et al.*, 1979). That work is discussed in Sections IV,B and D. Johnson and Levine (1972) have also proposed a method, not involving *R*-matrix propagation, which is similar to our method of Section IV,C. A comparison is made in Section IV,D.

A. INPUT IN AN ORTHOGONAL DIABATIC REPRESENTATION

We subdivide the radial coordinate into sectors labeled (*i*). Within each sector, the wave functions $\Psi_{q_0}(\mathbf{x}, R)$ are expanded in a primitive electronic basis that is independent of R within the sector. For example, within sector (*i*) we may expand in a general orthogonal basis $\phi^o(\mathbf{x}; i)$

$$\Psi_{q_0}^{(i)}(\mathbf{x}, R) = \sum_q \phi_q^o(\mathbf{x}; i) \chi_{q_0}^o(R; i) \quad (\text{B1})$$

where $\phi_q^o(\mathbf{x}; i)$ is the value of $\phi_q^o(\mathbf{x}, R)$ at the center of sector (*i*). We assume all $\phi_q^o(\mathbf{x}, R)$ are real. Since the $\phi_q^o(\mathbf{x}; i)$ are unchanged within a sector, substitution of Eq. (B1) into the Schrodinger equation leads, using the approximations of Section II,F, to coupled equations in each sector with no derivative coupling. For example, in sector (*i*) one obtains

$$(d^2/dR^2)\chi^o(R; i) = \mathbf{D}^o(R; i)\chi^o(R; i) \quad (\text{B2})$$

where

$$\mathbf{D}^o(R; i) = \frac{2\mu_{AB}}{\hbar^2} \left\{ \mathbf{H}^o(R; i) + \left[\frac{\hbar^2 l(l+1)}{2\mu_{AB}R^2} - E \right] \mathbf{I} \right\} \quad (\text{B3})$$

R_C^i is the center of sector (*i*), and

$$H_{sq}^o(R; i) = \langle \phi_s^o(\mathbf{x}; R_C^i) | H_e(R) | \phi_q^o(\mathbf{x}; R_C^i) \rangle_{\mathbf{x}} \quad (\text{B4})$$

Thus $H_{sq}^o(R; i)$ involves using basis functions that would usually be used only for calculations at $R = R_C^i$ to calculate the Hamiltonian matrix at a general R in sector (*i*). We shall see that the algorithm we derive will require $\mathbf{H}^o(R; i)$ only for $R = R_C^i$.

The first step is to diagonalize $\mathbf{D}^o(i)$ defined by

$$\mathbf{D}^o(i) = \mathbf{D}^o(R_C^i; i) = \mathbf{D}^o(R_C^i) \quad (\text{B5})$$

This yields a diagonal matrix $\lambda^2(i)$ that is related to the quantities appearing above by

$$\lambda^2(i) = [\mathbf{U}^{oa}(i)]^T \mathbf{D}^o(i) \mathbf{U}^{oa}(i) \quad (\text{B6})$$

$$= (2\mu_{AB}/\hbar^2) ([\mathbf{U}^{oa}(i)]^T \mathbf{H}^o(i) \mathbf{U}^{oa}(i) + \{[\hbar^2 l(l+1)/2\mu_{AB}R^2] - E\} \mathbf{I}) \quad (\text{B7})$$

$$= (2\mu_{AB}/\hbar^2) (\mathbf{H}^a(R_C^i) + \{[\hbar^2 l(l+1)/2\mu_{AB}R^2] - E\} \mathbf{I}) \quad (\text{B8})$$

where

$$H_{sq}^a(R) = \delta_{sq} \langle \phi_s^a(\mathbf{x}, R) | H_e(R) | \phi_q^a(\mathbf{x}, R) \rangle_{\mathbf{x}} \quad (\text{B9})$$

Notice that the transformation \mathbf{U}^{oa} is the same as defined in Eq. (A16) and can be related to those of Eqs. (A39) and (A51) by

$$\mathbf{U}^{oa}(i) = [\mathbf{U}^{so}(R_C^i)]^T \mathbf{U}^{sa}(R_C^i) \quad (\text{B10})$$

$\mathbf{U}^{so}(R)$ and $\mathbf{U}^{sa}(R)$ are defined by Eqs. (A39) and (A51), respectively. The diagonalization defines the transformation to the general orthogonal adiabatic basis $\phi^a(\mathbf{x}; i)$ where

$$\phi^a(\mathbf{x}; i) = \phi^a(\mathbf{x}, R_C^i) \quad (\text{B11})$$

$$\Psi^{(i)}(\mathbf{x}, R) = [\phi^a(\mathbf{x}; i)]^T \chi^a(R; i) \quad (\text{B12})$$

$$\phi^a(\mathbf{x}; i) = [\mathbf{U}^{oa}(i)]^T \phi^o(\mathbf{x}; i) \quad (\text{B13})$$

$$\chi^a(R; i) = [\mathbf{U}^{oa}(i)]^T \chi^o(R; i) \quad (\text{B14})$$

These equations are analogous to (A51), (A54), and (A55). In this convention, the columns of Ψ and $\chi^a(R; i)$ correspond to linearly independent wave functions, i.e., solutions to the coupled equations with different initial conditions or boundary conditions. In the adiabatic representation, the coupled equations (B2) become

$$(d^2/dR^2)\chi^a(R; i) = \lambda^2(R; i)\chi^a(R; i) \quad (\text{B15})$$

where

$$\lambda^2(R; i) = [\mathbf{U}^{oa}(i)]^{-1} \mathbf{D}^o(R; i) \mathbf{U}^{oa}(i) \quad (\text{B16})$$

Notice that $\lambda(R; i)$ is diagonal only at $R = R_C^i$. We rewrite Eq. (B15) as

$$\frac{d}{dR} \begin{bmatrix} \chi^a(R; i) \\ (d/dR)\chi^a(R; i) \end{bmatrix} = \begin{bmatrix} \mathbf{0} & \mathbf{I} \\ \lambda(i)^2 & \mathbf{0} \end{bmatrix} \begin{bmatrix} \chi^a(R; i) \\ (d/dR)\chi^a(R; i) \end{bmatrix} \quad (\text{B17})$$

where $\mathbf{0}$ is the null matrix. This has the solution by the Magnus method (Light 1971):

$$\begin{bmatrix} \chi^a[R_C^i - \frac{1}{2}h^i; i] \\ (d/dR)\chi^a[R_C^i - \frac{1}{2}h^i; i] \end{bmatrix} = \exp\{\mathbf{B}[R_C^i - \frac{1}{2}h^i, R_C^i + \frac{1}{2}h^i]\} \\ \times \begin{bmatrix} \chi^a[R_C^i + \frac{1}{2}h^i; i] \\ (d/dR)\chi^a[R_C^i + \frac{1}{2}h^i; i] \end{bmatrix} \quad (\text{B18})$$

in which

$$\mathbf{B}[R_C^i - \frac{1}{2}h^i, R_C^i + \frac{1}{2}h^i] = -h^i \begin{bmatrix} \mathbf{0} & \mathbf{I} \\ \lambda(i)^2 & \mathbf{0} \end{bmatrix} + \mathbf{0}[(h^i)^3] \quad (\text{B19})$$

and h^i is the length of sector (i). The final results of the calculations should be converged with respect to decreasing the set of $\{h^i\}$. The radial wave function in the adiabatic basis can be propagated across the sector (i) by retaining only the leading term in Eq. (B19). This yields

$$\begin{bmatrix} \chi^a(R_L^i; i) \\ (d\chi^a/dR)(R_L^i; i) \end{bmatrix} = \begin{bmatrix} \mathbf{P}_1^{(i)} & \mathbf{P}_2^{(i)} \\ \mathbf{P}_3^{(i)} & \mathbf{P}_4^{(i)} \end{bmatrix} \begin{bmatrix} \chi^a(R_R^i; i) \\ (d\chi^a/dR)(R_R^i; i) \end{bmatrix} \quad (\text{B20})$$

where R_L^i , R_R^i are the value of the radial coordinate at the left and right boundaries of sector (i). The sector propagators $\mathbf{P}_j^{(i)}$ are expressed in terms of the diagonal matrix $\lambda^2(i)$ as follows:

$$[\mathbf{P}_1^{(i)}]_{jk} = [\mathbf{P}_4^{(i)}]_{jk} = \begin{cases} \delta_{jk} \cosh[-h^i |\lambda_{jj}(i)|], & \lambda_{jj}^2(i) > 0 \\ \delta_{jk} \cos[-h^i |\lambda_{jj}(i)|], & \lambda_{jj}^2(i) < 0 \end{cases} \quad (\text{B21})$$

$$[\mathbf{P}_2^{(i)}]_{jk} = \begin{cases} \delta_{jk} |\lambda_{jj}(i)|^{-1} \sinh[-h^i |\lambda_{jj}(i)|], & \lambda_{jj}^2(i) > 0 \\ \delta_{jk} |\lambda_{jj}(i)|^{-1} \sin[-h^i |\lambda_{jj}(i)|], & \lambda_{jj}^2(i) < 0 \end{cases} \quad (\text{B22})$$

$$[\mathbf{P}_3^{(i)}]_{jk} = \begin{cases} \delta_{jk} |\lambda_{jj}(i)| \sinh[-h^i |\lambda_{jj}(i)|], & \lambda_{jj}^2(i) > 0 \\ -\delta_{jk} |\lambda_{jj}(i)| \sin[-h^i |\lambda_{jj}(i)|], & \lambda_{jj}^2(i) < 0 \end{cases} \quad (\text{B23})$$

To obtain a solution that is continuous and has continuous first derivatives between sectors it is required that

$$\Psi_{q_0}^{(i-1)}(\mathbf{x}, R_R^{i-1}) = \Psi_{q_0}^{(i)}(\mathbf{x}, R_L^i) \quad (\text{B24})$$

and

$$\frac{d}{dR} \Psi_j^{(i-1)}(\mathbf{x}, R_R^{i-1}) = \frac{d}{dR} \Psi_j^{(i)}(\mathbf{x}, R_L^i) \quad (\text{B25})$$

Substituting Eq. (B12) gives

$$[\Phi^a(\mathbf{x}; i-1)]^T \chi^a(R_R^{i-1}; i-1) = [\Phi^a(\mathbf{x}; i)]^T \chi^a(R_L^i; i) \quad (\text{B26})$$

$$[\Phi^a(\mathbf{x}; i-1)]^T \frac{d}{dR} \chi^a(R_R^{i-1}; i-1) = [\Phi^a(\mathbf{x}; i)]^T \frac{d}{dR} \chi^a(R_L^i; i) \quad (\text{B27})$$

Defining

$$\mathcal{O}_{sq}^0(i-1; i) = \langle \phi_s^0(\mathbf{x}; i-1) | \phi_q^0(\mathbf{x}; i) \rangle_{\mathbf{x}} \quad (\text{B28})$$

$$\mathcal{F}(i-1; i) = [\mathbf{U}^{oa}(i-1)]^T \mathcal{O}^0(i-1; i) \mathbf{U}^{oa}(i) \quad (\text{B29})$$

and using

$$\langle \phi_s^a(\mathbf{x}; i-1) | \phi_q^a(\mathbf{x}; i-1) \rangle_{\mathbf{x}} = \delta_{sq} \quad (\text{B30})$$

$$\begin{aligned} \langle \phi_s^a(\mathbf{x}; i-1) | \phi_q^a(\mathbf{x}; i) \rangle_{\mathbf{x}} &= \sum_{s_1 q_1} U_{s_1 s}^{oa}(i-1) \langle \phi_{s_1}^0(\mathbf{x}; i-1) | \phi_{q_1}^0(\mathbf{x}; i) \rangle_{\mathbf{x}} \\ &\quad \times U_{q_1 q}^{oa}(i) \\ &= \{[\mathbf{U}^{oa}(i-1)]^T \mathcal{O}^0(i-1; i) \mathbf{U}^{oa}(i)\}_{sq} \quad (\text{B31}) \end{aligned}$$

we obtain

$$\begin{bmatrix} \chi^a(R_R^{i-1}; i-1) \\ (d\chi^a/dR)(R_R^{i-1}; i-1) \end{bmatrix} = \begin{bmatrix} \mathcal{F}(i-1; i) & \mathbf{0} \\ \mathbf{0} & \mathcal{F}(i-1; i) \end{bmatrix} \begin{bmatrix} \chi^a(R_L^i; i) \\ (d\chi^a/dR)(R_L^i; i) \end{bmatrix} \quad (\text{B32})$$

Combining Eqs. (B20) and (B32) and the result to be derived below for $\mathcal{O}(i-1; i)$ allows the wave function to be propagated over many sectors.

In the method of Light and Walker (1976), the Wigner derivative matrix, called the R matrix, is propagated instead of the wave function. The sector R matrices $\mathbf{r}_j^{(i)}$ relate the wave function at the right-hand sides of sectors $(i+1)$ and (i) to their derivatives,

$$\begin{bmatrix} \chi^a(R_R^{i-1}; i-1) \\ \chi^a(R_R^i; i) \end{bmatrix} = \begin{bmatrix} \mathbf{r}_1^{(i)} & \mathbf{r}_2^{(i)} \\ \mathbf{r}_3^{(i)} & \mathbf{r}_4^{(i)} \end{bmatrix} \begin{bmatrix} (d/dR)\chi^a(R_R^{i-1}; i-1) \\ -(d/dR)\chi^a(R_R^i; i) \end{bmatrix} \quad (\text{B33})$$

The sector R matrices are determined by combining Eqs. (B20) and (B32) to relate the wave functions and derivatives at the right-hand side of sector $(i-1)$ to the wave functions and derivatives at the right-hand side of sector (i) . The resulting equations are then rearranged to the form of Eq. (B33) and the sector R matrices are identified as

$$\mathbf{r}_1^{(i)} = \mathcal{F}(i-1; i) \mathbf{P}_1^{(i)} [\mathcal{F}(i-1; i) \mathbf{P}_3^{(i)}]^{-1} \quad (\text{B34})$$

$$\mathbf{r}_2^{(i)} = \mathcal{F}(i-1; i) \mathbf{P}_3^{(i)-1} \quad (\text{B35})$$

$$\mathbf{r}_3^{(i)} = [\mathcal{F}(i-1; i) \mathbf{P}_3^{(i)}]^{-1} \quad (\text{B36})$$

$$\mathbf{r}_4^{(i)} = \mathbf{P}_3^{(i)-1} \mathbf{P}_4^{(i)} \quad (\text{B37})$$

For regular solutions, the global R matrix $\mathbf{R}_4^{(i)}$ is the Wigner derivative matrix, i.e., it relates the radial wave functions at the right-hand side of sector (i) to their derivatives (see Stechel *et al.*, 1978; Harvey, 1979; Truhlar *et al.*, 1979):

$$\chi^a(R_R^i; i) = -\mathbf{R}_4^{(i)} \frac{d}{dR} \chi^a(R_R^i; i) \quad (\text{B38})$$

The global R matrix is obtained by combining the sector R -matrix equations (B33) for sector (i) with the global R -matrix equation (B38) for sector (i) to give the R -matrix propagation equation (Zvijac and Light 1976)

$$\mathbf{R}_4^{(i)} = \mathbf{r}_4^{(i)} - \mathbf{r}_3^{(i)} [\mathbf{R}_4^{(i-1)} + \mathbf{r}_1^{(i)}]^{-1} \mathbf{r}_2^{(i)} \quad (\text{B39})$$

Thus the global R matrix is obtained by applying Eq. (B39) recursively with the global R matrix for the first sector given by

$$\mathbf{R}_4^{(1)} = \mathbf{r}_4^{(1)} \quad (\text{B40})$$

in which $\mathbf{r}_4^{(1)}$ is determined from the behavior of regular solutions for small R .

For the rearrangement analysis presented in Eqs. (137)–(148) of Section II,C, it is necessary to obtain N linearly independent regular radial wavefunctions and their derivatives at $R = R_2$, where R_2 is some large value. This is easily accomplished by using Eq. (B38) with $R_2 = R_R^1$ and letting $\chi^a(R_2; i) = \mathbf{I}$. Alternatively, since \mathbf{F}^0 and \mathbf{G}^0 are being neglected one might wish to apply scattering boundary conditions directly in the body-fixed coordinates. In this case a scattering matrix can be calculated directly from \mathbf{R}_4^1 with large R_R^1 using standard techniques (see, e.g., Harvey, 1979; Truhlar *et al.*, 1979).

The R -matrix propagation method has the important practical advantage that channels can easily be deleted as the propagation proceeds from the strongly coupled small- R region to the weakly coupled large- R region. This advantage is not unique to R matrix propagation, but the channel-reduction procedure can be carried out particularly easily in this method (Harvey, 1979; Truhlar *et al.*, 1979).

The R -matrix propagation method does not require explicit knowledge of the internal (i.e., electronic) wave function. However, the derivation just given shows that it is equivalent to propagation in an adiabatic representation. Although we chose to expand in an orthogonal diabatic primitive basis, we immediately made a transformation to the adiabatic representation. Consider using the adiabatic representation as the primitive basis for expansion

$$\Psi_{q_0}^{(i)}(\mathbf{x}, R) = \sum_q \phi_q^a(\mathbf{x}; i) \chi_{q_0}^a(R; i) \quad (\text{B41})$$

This leads to the coupled equations

$$\frac{d^2}{dR^2} \chi^a(R; i) = \mathbf{D}^a(R; i) \chi^a(R; i) \quad (\text{B42})$$

in which

$$\mathbf{D}^a(R; i) = (2\mu_{AB}/\hbar^2)(\mathbf{H}^a(R; i) + \{[\hbar^2 l(l+1)/2\mu_{AB} R^2] - E\} \mathbf{I}) \quad (\text{B43})$$

and

$$H_{sq}^a(R; i) = \delta_{sq} \langle \phi_s^a(\mathbf{x}, R_C^i) | H_e(R) | \phi_q^a(\mathbf{x}, R_C^i) \rangle_{\mathbf{x}} \quad (\text{B44})$$

Comparison of Eqs. (B43) and (B44) to Eqs. (B3), (B4), (B10), and (B16) shows that

$$\mathbf{D}^a(R; i) = \lambda^2(R; i) \quad (\text{B45})$$

Comparison of Eqs. (B42) and (B45) to Eq. (B15) shows that the coupled equations in a given sector are independent of representation. Since the matching is already done in the adiabatic representation, the R -matrix propagation is independent of basis set.

To complete the algorithm we must show how to obtain the overlap matrix $\mathcal{O}^0(i-1; i)$ of Eq. (B28). In principle, it could be evaluated by performing the integration

$$\mathcal{O}_{sq}^0(i-1; i) = \int d\mathbf{x} \phi_s^{0*}(\mathbf{x}, R_C^{i-1}) \phi_q^0(\mathbf{x}, R_C^i) \quad (\text{B46})$$

However, in this section we wish to obtain $\mathcal{O}^\circ(i-1; i)$ in a manner consistent with neglecting all derivative coupling in the orthogonal diabatic basis, i.e., consistent with the solution to Eq. (A42) of Section III with \mathbf{F}° and \mathbf{G}° set to zero. We do this by comparing the solution to the coupled equations as obtained by the method described earlier in this section to a direct solution to the coupled equations (A42) with these derivative coupling matrices neglected.

A method for solving the coupled channel equations (A42) directly is the Magnus-Light method (Light, 1971). This method is similar to the Light-Walker R -matrix propagation method and is outlined below. Equations (A42) may be rewritten

$$\left(\frac{d^2}{dR^2} \mathbf{I} - \frac{2\mu_{AB}}{\hbar^2} \mathbf{H}^\circ(R) - \frac{l(l+1)}{R^2} \mathbf{I} + \frac{2\mu_{AB}E}{\hbar^2} \mathbf{I} \right) \chi^\circ(R) - \eta \left[\mathbf{g}^\circ(R) + 2\mathbf{f}^\circ(R) \frac{d}{dR} \right] \chi^\circ(R) = 0 \quad (\text{B47})$$

where

$$\mathbf{g}^\circ(R) = (2\mu_{AB}/\hbar^2) \mathbf{G}^\circ(R) = -(\Phi^\circ | d^2/dR^2 | \Phi^\circ) \quad (\text{B48})$$

$$\mathbf{f}^\circ(R) = (2\mu_{AB}/\hbar^2) \mathbf{F}^\circ(R) = -(\Phi^\circ | d/dR | \Phi^\circ) \quad (\text{B49})$$

and we have introduced a parameter η in front of the derivative coupling matrices so that we can neglect \mathbf{F}° and \mathbf{G}° by setting $\eta = 0$. Equation (B47) can be written in a matrix notation as

$$\frac{d}{dR} \begin{bmatrix} \chi^\circ(R) \\ \frac{d}{dR} \chi^\circ(R) \end{bmatrix} = \mathbf{A}^\eta(R) \begin{bmatrix} \chi^\circ(R) \\ \frac{d}{dR} \chi^\circ(R) \end{bmatrix} \quad (\text{B50})$$

where $\mathbf{A}^\eta(R)$ is a $2N \times 2N$ matrix given by

$$\mathbf{A}^\eta(R) = \begin{bmatrix} \mathbf{0} & \mathbf{I} \\ \mathbf{D}^\circ(R) + \eta \mathbf{g}^\circ(R) & 2\eta \mathbf{f}^\circ(R) \end{bmatrix} \quad (\text{B51})$$

in which

$$\mathbf{D}^\circ(R) = \frac{2\mu_{AB}}{\hbar^2} \mathbf{H}^\circ(R) + \left[\frac{l(l+1)}{R^2} - \frac{2\mu_{AB}E}{\hbar^2} \right] \mathbf{I} \quad (\text{B52})$$

The solution to Eq. (B50) may be written (Light, 1971)

$$\begin{bmatrix} \chi^\circ(R_0 - h) \\ \frac{d}{dR} \chi^\circ(R_0 - h) \end{bmatrix} = \exp[\mathbf{C}^\eta(R_0 - h, R_0)] \begin{bmatrix} \chi^\circ(R_0) \\ \frac{d}{dR} \chi^\circ(R_0) \end{bmatrix} \quad (\text{B53})$$

where

$$\begin{aligned} C^n(R_0 - h, R_0) = & - \int_{R_0-h}^{R_0} dR A^n(R) + \frac{1}{2} \int_{R_0-h}^{R_0} dR \int_{R_0-h}^{R_0} dR' [A^n(R), A^n(R')] \\ & + O(h^3) \end{aligned} \quad (\text{B54})$$

and $[\dots]$ is the quantum mechanical commutator. We divide the R coordinate into sectors of length h^i from R_L^i to R_R^i and approximate the matrix $A^n(R)$ within each sector as linear in R

$$A^n(R) \cong A^n(i) + (R - R_L^i) \frac{dA^n}{dR}(R_L^i) \quad \text{for } R_L^i \leq R \leq R_R^i \quad (\text{B55})$$

Substituting this in Eq. (B54) yields

$$C^n(R_L^i, R_R^i) \cong -h^i A^n(i) + O[(h^i)^3] \quad \text{for } R_L^i \leq R \leq R_R^i \quad (\text{B56})$$

Through terms of order $(h^i)^2$, Eqs. (B53) and (B56) yield

$$\begin{aligned} \left[\begin{array}{c} \chi^o(R_R^1) \\ \frac{d}{dR} \chi^o(R_R^1) \end{array} \right] = & \exp[-h^2 A^n(2)] \exp[-h^3 A^n(3)] \dots \\ & \times \exp[-h^i A^n(i)] \left[\begin{array}{c} \chi^o(R_R^i) \\ \frac{d}{dR} \chi^o(R_R^i) \end{array} \right] \end{aligned} \quad (\text{B57})$$

This solution to the coupled channel equations is particularly useful for comparison with the result of the R -matrix propagation method since both use the idea of dividing the R coordinate into sectors.

We now wish to cast the solution to the coupled equations by the R -matrix propagation method into a form similar to Eq. (B57). The adiabatic radial wave functions can be propagated across many sectors by using Eqs. (B20) and (B32).

$$\begin{aligned} & \left[\begin{array}{c} \chi^a(R_R^1; 1) \\ \frac{d}{dR} \chi^a(R_R^1; 1) \end{array} \right] \\ & = \left[\begin{array}{cc} \mathcal{F}(1, 2) & \mathbf{0} \\ \mathbf{0} & \mathcal{F}(1, 2) \end{array} \right] \left[\begin{array}{cc} \mathbf{P}_1^{(2)} & \mathbf{P}_2^{(2)} \\ \mathbf{P}_3^{(2)} & \mathbf{P}_4^{(2)} \end{array} \right] \left[\begin{array}{cc} \mathcal{F}(2, 3) & \mathbf{0} \\ \mathbf{0} & \mathcal{F}(2, 3) \end{array} \right] \left[\begin{array}{cc} \mathbf{P}_1^{(3)} & \mathbf{P}_2^{(3)} \\ \mathbf{P}_3^{(3)} & \mathbf{P}_4^{(3)} \end{array} \right] \\ & \times \dots \times \left[\begin{array}{cc} \mathcal{F}(i-1; i) & \mathbf{0} \\ \mathbf{0} & \mathcal{F}(i-1; i) \end{array} \right] \left[\begin{array}{cc} \mathbf{P}_1^{(i)} & \mathbf{P}_2^{(i)} \\ \mathbf{P}_3^{(i)} & \mathbf{P}_4^{(i)} \end{array} \right] \left[\begin{array}{c} \chi^a(R_R^i; i) \\ \frac{d}{dR} \chi^a(R_R^i; i) \end{array} \right] \end{aligned} \quad (\text{B58})$$

From Eqs. (B6) and (B18)–(B20) we can show that

$$\begin{bmatrix} \mathbf{P}_1^{(i)} & \mathbf{P}_2^{(i)} \\ \mathbf{P}_3^{(i)} & \mathbf{P}_4^{(i)} \end{bmatrix} = \exp \left\{ -h^i \begin{bmatrix} \mathbf{0} & \mathbf{I} \\ \lambda^2(i) & \mathbf{0} \end{bmatrix} \right\} \quad (\text{B59})$$

$$= \begin{bmatrix} [\mathbf{U}^{\text{oa}}(i)]^T & \mathbf{0} \\ \mathbf{0} & [\mathbf{U}^{\text{oa}}(i)]^T \end{bmatrix} \exp \left\{ -h^i \begin{bmatrix} \mathbf{0} & \mathbf{I} \\ \mathbf{D}^{\text{o}}(i) & \mathbf{0} \end{bmatrix} \right\} \begin{bmatrix} \mathbf{U}^{\text{oa}}(i) & \mathbf{0} \\ \mathbf{0} & \mathbf{U}^{\text{oa}}(i) \end{bmatrix} \quad (\text{B60})$$

$$= \begin{bmatrix} [\mathbf{U}^{\text{oa}}(i)]^T & \mathbf{0} \\ \mathbf{0} & [\mathbf{U}^{\text{oa}}(i)]^T \end{bmatrix} \exp[-h^i A^{\eta=0}(i)] \begin{bmatrix} \mathbf{U}^{\text{oa}}(i) & \mathbf{0} \\ \mathbf{0} & \mathbf{U}^{\text{oa}}(i) \end{bmatrix} \quad (\text{B61})$$

Using Eq. (B14) to transform Eq. (B58) to the nonorthogonal diabatic representation and using Eq. (B29) for $\mathcal{F}(i-1; i)$ and Eq. (B61) for the sector propagation yields

$$\begin{aligned} & \begin{bmatrix} \chi^{\text{o}}(R_{\mathbf{R}}^1; 1) \\ \frac{d}{dR} \chi^{\text{o}}(R_{\mathbf{R}}^1; 1) \end{bmatrix} \\ &= \begin{bmatrix} \mathcal{O}^{\text{o}}(1; 2) & \mathbf{0} \\ \mathbf{0} & \mathcal{O}^{\text{o}}(1; 2) \end{bmatrix} \exp[-h^2 A^{\eta=0}(2)] \begin{bmatrix} \mathcal{O}^{\text{o}}(2; 3) & \mathbf{0} \\ \mathbf{0} & \mathcal{O}^{\text{o}}(2; 3) \end{bmatrix} \\ & \times \exp[h^3 A^{\eta=0}(3)] \times \cdots \times \begin{bmatrix} \mathcal{O}^{\text{o}}(i-1; i) & \mathbf{0} \\ \mathbf{0} & \mathcal{O}^{\text{o}}(i-1; i) \end{bmatrix} \\ & \times \exp[h^i A^{\eta=0}(i)] \begin{bmatrix} \chi^{\text{o}}(R_{\mathbf{R}}^i; i) \\ \frac{d}{dR} \chi^{\text{o}}(R_{\mathbf{R}}^i; i) \end{bmatrix} \quad (\text{B62}) \end{aligned}$$

Although Eq. (A62) is not written explicitly as a propagation of an R matrix, it is equivalent to the R -matrix propagation method presented earlier. Comparing it to Eq. (B57) with $\eta = 0$ shows that the overlap matrix consistent with setting η equal to zero is

$$\mathcal{O}(i-1; i) = \mathbf{I} \quad (\text{B63})$$

This completes the method of propagation when the input information is in an orthogonal representation and derivative coupling is neglected (or negligible) in that representation.

B. INPUT IN A NONORTHOGONAL DIABATIC REPRESENTATION

In this section we consider the coupled equations (A33) corresponding to a nonorthogonal basis, and we discuss the solution for the case that the derivative coupling matrices \mathbf{F}^n and \mathbf{G}^n are neglected (or negligible). One could attempt to find the solution by the methods of Section IV,A, but Stechel *et al.* (1979) have pointed out that such an approach leads to questions about the proper definitions of Hermitian operators and transformations in Hilbert spaces defined by nonorthogonal basis sets. In order to derive the correct solution, they developed the algebra of nonorthogonal basis sets in a given Hilbert space and of transformations between Hilbert spaces, each defined by nonorthogonal, incomplete bases. In this section we summarize their solution. The radial coordinate is again divided into sectors labeled (i) and within each sector the total wave function is expanded in a general non-orthogonal basis $\phi^n(\mathbf{x}; i)$ that is independent of R within the sector.

$$\Psi_{q_0}^{(i)}(\mathbf{x}, R) = \sum_q \phi_q^n(\mathbf{x}; i) \chi_{q_0}^n(R; i) \quad (\text{B64})$$

Substitution into the Schrodinger equations gives

$$\frac{d^2}{dR^2} \chi^n(R; i) = \mathbf{D}^n(R) \chi^n(R; i) \quad (\text{B65})$$

where

$$\mathbf{D}^n(R; i) = \frac{2\mu_{AB}}{\hbar^2} \left\{ \mathbf{S}^{-1}(i) \mathbf{H}^n(R; i) + \left[\frac{\hbar^2 l(l+1)}{2\mu_{AB} R^2} - E \right] \mathbf{I} \right\} \quad (\text{B66})$$

$$\mathbf{S}(i) = \mathbf{S}(R_C^i) \quad (\text{B67})$$

$$H_{sq}^n(R; i) = \langle \phi_s^n(\mathbf{x}; R_C^i) | H_e(R) | \phi_q^n(\mathbf{x}; R_C^i) \rangle_x \quad (\text{B68})$$

The matrix $\mathbf{D}^n(R; i)$ is diagonalized to yield

$$\lambda^2(R; i) = \mathbf{T}^{-1}(i) \mathbf{D}^n(R; i) \mathbf{T}(i) \quad (\text{B69})$$

where

$$\mathbf{T}(i) = \mathbf{S}^{-1/2}(i) \mathbf{U}^{\text{sa}}(R_C^i) \quad (\text{B70})$$

The transformation from the nonorthogonal basis to the adiabatic, diagonal basis is given by

$$\phi^a(\mathbf{x}; i) = \mathbf{T}^T(i) \phi^n(\mathbf{x}; i) \quad (\text{B71})$$

$$\chi^a(\mathbf{x}; i) = \mathbf{T}^{-1}(i) \chi^n(\mathbf{x}; i) \quad (\text{B72})$$

The sector R matrices are again defined in the adiabatic representation by Eq. (B33) and are given by Eqs. (B34)–(B37). However, the recursion formula for the global R matrix is now given by

$$\mathbf{R}_4^{(i)} = \mathbf{r}_4^{(i)} - \mathbf{r}_3^{(i)}[\mathbf{r}_1^{(i)} + \mathcal{F}(i-1; i)\mathcal{F}^T(i-1; i)\mathbf{R}^{(i-1)}]^{-1}\mathbf{r}_2^{(i)} \quad (\text{B73})$$

where

$$\mathcal{F}(i-1; i) = \mathbf{T}^{-1}(i-1)\mathbf{T}(i) \quad (\text{B74})$$

Notice that the extra matrix product in Eq. (B73) vanishes in the case $\mathbf{S} = \mathbf{I}$. T. G. Schmalz, J. C. Light, and E. B. Stechel (personal communication) tried substituting \mathcal{F}^{-1} for \mathcal{F}^T in Eq. (B73) for problems with $\mathbf{S} \neq \mathbf{I}$, and they found that conservation of probability was often violated by several orders of magnitude. Only the transpose form preserves the unitarity of the scattering matrix. Since \mathcal{F}^{-1} equals \mathcal{F}^T for orthogonal basis sets, a careful analysis of the correct treatment of mappings between nonorthogonal Hilbert spaces is required to derive the correct equation (Stechel *et al.*, 1979).

C. INPUT IN AN ADIABATIC REPRESENTATION

Another approach to electronic state coupling problems is to assume that one has the adiabatic potential energy curves and nonadiabatic derivative coupling matrices from electronic structure calculations carried out in a Born–Oppenheimer framework.

There has been little work on the direct integration of the coupled differential equations that arise when the adiabatic representation is chosen. Evans *et al.* (1971) have solved these equations by a finite difference method including deferred corrections through sixth order. Their method has the disadvantage that it requires more than one pass through the integration region. Zimmerman and George (1975a,b) have rewritten the N coupled second-order differential equations as $2N$ coupled first-order differential equations and solved them by a predictor–corrector method. Babamov (1978) has developed a method that involves first solving the coupled equations with the nonadiabatic couplings set equal to zero, then using these solutions to construct the solutions with nonadiabatic coupling present; the uncoupled equations were solved by a piecewise analytic method and the integration for the inelastic problem was carried out with a predictor–corrector algorithm. Thus all these cases involved finite difference approximations at some stage. In the examples considered it was assumed that the derivative coupling in the adiabatic representation arises entirely from the transformation from another basis set that was assumed to have no derivative coupling. This simplifies the adiabatic–diabatic transformation and makes it convenient

to test the solution in the adiabatic representation by comparison to a solution obtained in the more standard diabatic representation.

In this section we present a method that is very convenient when the starting information consists of electronically adiabatic potential curves and nonadiabatic derivative coupling matrix elements. The method includes the full coupling caused by both first-derivative and second-derivative couplings, and it does not require finite difference approximations, prior solution of the uncoupled equations, or an explicit transformation to a diabatic basis. It is based on the R -matrix propagation method. We believe that it shares some of the advantages of the R -matrix propagation technique of Stechel *et al.* (1979). However, their method involves an expansion in atomic states and nonorthogonal coordinates. Thus the two methods are quite different. In particular, the present method has the characteristic, which should be a distinct advantage at chemical energies, that it allows for input in the form of standard Born–Oppenheimer potential energy curves and nonadiabatic coupling matrices, and it involves the usual body-fixed coordinate system. Again, we use the R -matrix propagation method. The primitive electronic basis is taken to be the adiabatic basis $\phi^a(\mathbf{x}; R)$, and $\phi^a(\mathbf{x}, R_C^i)$ is used as an R -independent basis function in all of sector (i). The propagation matrices $\mathbf{P}_j^{(i)}$ are given by Eqs. (B8) and Eqs. (B21)–(B23). The only difference for this case from the method of Section IV,A is the determination of the matrices $\mathcal{T}(i-1; i)$ that give the correct matching conditions. These are now to be determined in such a way as to include the effect of all the derivative coupling terms.

From Eqs. (B29) and (B31) we see that

$$\mathcal{T}_{sq}(i; i+1) = \langle \phi_s^a(\mathbf{x}; i) | \phi_q^a(\mathbf{x}; i+1) \rangle_{\mathbf{x}} \quad (\text{B75})$$

Define

$$M_{sq}(R_C^i, y) = \langle \phi_s^a(\mathbf{x}, R_C^i) | \phi_q^a(\mathbf{x}, R_C^i + y) \rangle_{\mathbf{x}} \quad (\text{B76})$$

so that

$$\mathcal{T}_{sq}(i; i+1) = M_{sq}[R_C^i, \frac{1}{2}(h^i + h^{i+1})] \quad (\text{B77})$$

Differentiating $\mathbf{M}(R_C^i, y)$ with respect to y we obtain

$$\frac{d}{dy} M_{sq}(R_C^i, y) = \left\langle \phi_s^a(\mathbf{x}, R_C^i) \left| \frac{d}{dy} \phi_q^a(\mathbf{x}, R_C^i + y) \right. \right\rangle_{\mathbf{x}} \quad (\text{B78})$$

$$= -(2\mu_{AB}/\hbar^2) \sum_{s_1} M_{ss_1}(R_C^i, y) F_{s_1q}^a(R_C^i + y) \quad (\text{B79})$$

where $\mathbf{F}^a(R)$ is the nonadiabatic derivative coupling matrix of Eq. (A10). Equation (B79) can be solved for $\mathbf{M}(R_C^i, y)$ by the Magnus method; the result is

$$\mathbf{M}(R_C^i, y) = \mathbf{M}(R_C^i, 0) \exp[\mathbf{N}(R_C^i, y)] \quad (\text{B80})$$

where

$$\begin{aligned} \mathbf{N}(R_C^i, y) = & -(2\mu_{AB}/\hbar^2) \int_0^y dy' \mathbf{F}^a(R_C^i + y') \\ & + 2(\mu_{AB}/\hbar^2)^2 \int_0^y dy' \int_0^{y'} dy'' [\mathbf{F}^a(R_C^i + y'), \mathbf{F}^a(R_C^i + y'')] + \dots \end{aligned} \quad (\text{B81})$$

and

$$\mathbf{M}(R_C^i, 0) = \mathbf{I} \quad (\text{B82})$$

We expand the coupling matrix in a Taylor series around the midpoint R_M^i between two sector centers

$$\mathbf{F}^a(R_C^i + y) \cong \mathbf{F}^a(R_M^i) + (y + R_C^i - R_M^i) \frac{d\mathbf{F}^a}{dR}(R_M^i) \quad (\text{B83})$$

where

$$R_M^i = \frac{1}{2}(R_C^i + R_C^{i+1}) \quad (\text{B84})$$

Substitution of Eq. (B83) into Eq. (B81), retaining terms through order $(h^i + h^{i+1})^2$, yields

$$\mathbf{N}[R_C^i, \frac{1}{2}(h^i + h^{i+1})] = -(2\mu_{AB}/\hbar^2) [\frac{1}{2}(h^i + h^{i+1})] \mathbf{F}^a(R_M^i) + O[(h^i + h^{i+1})^3] \quad (\text{B85})$$

and

$$\mathcal{T}(i; i+1) = \exp[-(2\mu_{AB}/\hbar^2) [\frac{1}{2}(h^i + h^{i+1})] \mathbf{F}^a(R_M^i)] + O[(h^i + h^{i+1})^3] \quad (\text{B86})$$

The exponential of $\mathbf{F}^a(R_M^i)$ can be evaluated in the usual way by diagonalizing $\mathbf{F}^a(R_M^i)$. Since \mathbf{F}^a is skew symmetric, it can be diagonalized by a unitary transformation. If it is more convenient one could approximate $\mathbf{F}^a(R_M^i)$ by $\frac{1}{2}[\mathbf{F}^a(R_C^i) + \mathbf{F}^a(R_C^{i+1})]$. This completes the method of propagation when the input information is in the adiabatic approximation and derivative coupling is included.

D. COMPARISON OF APPROACHES

Notice the similarity between Eqs. (B79) and (A24). Taking a transpose of Eq. (A24) and using Eqs. (A14) and (A17), we obtain

$$d\mathbf{U}^{\text{da}}/dR = -(2\mu_{AB}/\hbar^2) \mathbf{U}^{\text{da}}(R) \mathbf{F}^a(R) \quad (\text{B87})$$

Comparison to Eq. (B79) shows that $\mathbf{U}^{\text{da}}(R)$ and $\mathbf{M}(R_C^i, y)$ obey the same differential equation. However, the boundary conditions are different. In

practice, if the last sector is sector (i_{\max}), the boundary condition (A28) that is applied to $\mathbf{U}^{\text{da}}(R)$ when the derivative coupling vanishes at large R becomes

$$\mathbf{U}^{\text{da}}(R_C^{i_{\max}}) = \mathbf{I} \quad (\text{B88})$$

whereas Eq. (B82) shows that \mathbf{M} gets re-initialized to \mathbf{I} at the center of every sector. Therefore,

$$\begin{aligned} \mathbf{U}^{\text{da}}(R_C^i) = & \{\mathbf{M}[R_C^{i_{\max}-1}, \frac{1}{2}(h^{i_{\max}-1} + h^{i_{\max}})]\}^T \\ & \times \{\mathbf{M}[R_C^{i_{\max}-2}, \frac{1}{2}(h^{i_{\max}-2} + h^{i_{\max}-1})]\}^T \\ & \times \cdots \times \{\mathbf{M}[R_C^i, \frac{1}{2}(h^i + h^{i+1})]\}^T \end{aligned} \quad (\text{B89})$$

Using Eq. (B77) we can write Eq. (B89) as

$$\begin{aligned} \mathbf{U}^{\text{da}}(R_C^i) = & [\mathcal{T}(i_{\max} - 1; i_{\max})]^T [\mathcal{T}(i_{\max} - 2; i_{\max} - 1)]^T \cdots \\ & \times [\mathcal{T}(i; i + 1)]^T \end{aligned} \quad (\text{B90})$$

This shows that when the derivative coupling vanishes at large R , and is included in the R -matrix propagation method, the transformation matrices $\mathcal{T}(i; i + 1)$ can be used to construct the transformation from the adiabatic representation to the P -diabatic representation in which all first-derivative coupling vanishes. Furthermore, using Eq. (B75) for $\mathcal{T}(i; i + 1)$ and assuming that the electronic basis is complete, Eq. (B90) shows that

$$U_{sq}^{\text{da}}(R_C^i) = \langle \phi_s^a(\mathbf{x}; i_{\max}) | \phi_q^a(\mathbf{x}; i) \rangle_{\mathbf{x}} \quad (\text{B91})$$

The diabatic basis is given by

$$\phi^{\text{d}}(\mathbf{x}, R) = \mathbf{U}^{\text{da}}(R) \phi^{\text{a}}(\mathbf{x}, R) \quad (\text{B92})$$

which follows from Eq. (A16) when $\phi^{\text{a}}(\mathbf{x}, R)$ is real. Substituting Eq. (B91) into Eq. (B92) yields

$$\phi_q^{\text{d}}(\mathbf{x}; i) = \sum_s \langle \phi_q^{\text{a}}(\mathbf{x}; i_{\max}) | \phi_s^{\text{a}}(\mathbf{x}; i) \rangle_{\mathbf{x}} \phi_s^{\text{a}}(\mathbf{x}; i) \quad (\text{B93})$$

If and only if the electronic basis is complete, this becomes

$$\phi_q^{\text{d}}(\mathbf{x}; R_C^i) = \phi_q^{\text{a}}(\mathbf{x}; R_C^{i_{\max}}) \quad (\text{B94})$$

Thus, if the electronic basis is complete, the diabatic basis becomes independent of R , as has been noticed previously.

In this section we have considered two ways in which the R -matrix propagation method can be applied to multi-electronic-state scattering problems. In the first version, Sections IV,A and IV,B, one identifies some diabatic basis in which the derivative coupling terms are all assumed to vanish. This diabatic basis may be a general nonorthogonal basis in section IV,B, but it is restricted to be orthogonal in Section IV,A. Then one solves the scattering problem

by transforming within each sector to the adiabatic basis obtained by diagonalizing the local electronic Hamiltonian in the chosen diabatic basis at the center of the sector. This method allows for the use of physically motivated approximations such as discussed in Sections II and III, e.g., the diatomics-in-molecules method or the assumption that derivative coupling vanishes in F -diabatic or single-configuration bases.

The second method, Section IV,C, is appropriate when the input information consists of Born–Oppenheimer adiabatic potentials and nonadiabatic coupling matrices calculated in a Born–Oppenheimer adiabatic basis. Thus this method is suitable for state-of-the-art ab initio calculations (although this kind of input may also be obtained from more approximate calculations when accurate ones are not available). The calculation is carried out using the adiabatic basis at the center of each sector as a primitive basis throughout the whole sector. The overlap matrix required to transform from the primitive basis in one sector to the primitive basis in the next is expressed in terms of the input nonadiabatic coupling information. After propagating to large R , it is necessary to apply the correct scattering boundary conditions and this can be done using the projection technique discussed in Section II.

It is useful to compare our approach to that proposed by Stechel *et al.* (1979) (see also Light *et al.*, 1979; Schmalz *et al.*, 1979). They proposed a propagation scheme using the coordinates R , \mathbf{r}_A , and \mathbf{r}_B in nonorthogonal basis sets of functions centered at A and B. No derivative coupling is neglected, and a special, more complicated R -matrix propagation step is proposed to convert to \mathbf{R}'_α , \mathbf{r}'_α coordinates at large subsystem separations. The method discussed in Sections IV,A and B involves the coordinates \mathbf{R} and \mathbf{r} , general nonorthogonal basis sets, and the assumption that derivative coupling may be neglected in some diabatic basis. This method is suitable for model calculations or for accurate calculations on systems with curve crossings where the neglect of derivative coupling in a well-chosen diabatic basis set need not be a serious error. The method of Section IV,C is appropriate for cases where the ab initio calculations are available for the adiabatic potential energy curves and nonadiabatic derivative coupling matrices. There is no restriction on the kind of basis functions that can be used to obtain these. No derivative coupling is neglected. Instead of a special R -matrix propagation step at large R , one may apply one of the methods of Section II,E or II,G.

Finally, we compare our approach to the method of Johnson and Levine (1972). These workers also employ the expansion of Eq. (B1) and the diagonalization of Eqs. (B6)–(B8). They propose that the wave function be propagated similarly to Eqs. (B20)–(B23) and that Eqs. (B24) and (B25) be used to match at sector boundaries. They assume that the primitive basis is orthogonal and that the matching procedure involves integrals similar to

those in Eq. (B46). In the present work we have eliminated the need to calculate these integrals by writing the matching procedure in terms of the standard derivative coupling matrices. In addition, the propagation of the R matrix rather than the wave function has important advantages. An important practical advantage is that it is stable even in the presence of closed channels (Light and Walker, 1976). There are also important formal advantages (Stechel *et al.*, 1979; Light *et al.*, 1979), e.g., the ability to develop a propagation scheme that ensures conservation of particle flux even in a nonorthogonal basis.

V. Summary

In Sections II,A–II,D and Section III we derived the coupled scattering equations that describe electronically inelastic collisions in various representations and coordinate systems; in Sections IV,A, IV,B, and IV,C we discussed numerical methods for the solution of these coupled equations; and in Sections II,E and II,G we discussed the calculation of scattering amplitudes by imposing the correct scattering boundary conditions on the solutions. Application of these ideas to various physical systems also involves choosing an electronic basis and obtaining the matrix elements required as input for the coupled equations. We have discussed some aspects of that part of the theory briefly; a review of other aspects is given elsewhere (Browne, 1971).

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References

- Albat, R., and Gruen, N. (1976). *J. Phys. B* **9**, L463.
- Albat, R., and Wirsam, B. (1977). *J. Phys. B* **10**, 81.
- Albat, R., Gruen, N., and Wirsam, B. (1975). *J. Phys. B* **8**, 2520.
- Andresen, B., and Nielsen, S. E. (1971). *Mol. Phys.* **21**, 523.
- Arthurs, A. M., and Dalgarno, A. (1960). *Proc. R. Soc. London, Ser. A* **256**, 540.
- Aubert, M., and Le Sech, C. (1976). *Phys. Rev A* **13**, 632.
- Babamov, V. K. (1978). *J. Chem. Phys.* **69**, 3414.
- Baer, M. (1975). *Chem. Phys. Lett.* **35**, 112.
- Baer, M. (1976). *Chem. Phys.* **15**, 49.

- Basu, D., Mukherjee, S. C., and Sural, D. P. (1978). *Phys. Rep.* **42**, 145.
- Bates, D. R. (1957a). *Proc. R. Soc. London Ser. A* **240**, 437.
- Bates, D. R. (1957b). *Proc. R. Soc. London, Ser. A* **243**, 15.
- Bates, D. R., ed. (1962). "Atomic and Molecular Processes." Academic Press, New York.
- Bates, D. R., and Holt, A. R. (1966). *Proc. R. Soc. London Ser. A* **292**, 168.
- Bates, D. R., and McCarroll, R. (1958). *Proc. R. Soc. London, Ser. A* **245**, 175.
- Becker, C. H., Casavecchia, P., Lee, Y. T., Olson, R. E., and Lester, W. A., Jr. (1979). *J. Chem. Phys.* **70**, 5477.
- Blatt, J. M., and Biedenharn, L. C. (1952). *Rev. Mod. Phys.* **24**, 249.
- Browne, J. C. (1971). *Adv. At. Mol. Phys.* **7**, 47.
- Chen, J. C. Y., Ponce, V. H., and Watson, K. M. (1973). *J. Phys. B* **6**, 965.
- Child, M. S. (1974). "Molecular Collision Theory." Academic Press, New York.
- Cohen, J. S. (1976). *Phys. Rev. A* **13**, 86.
- Cohen, J. S., Collins, L. A., and Lane, N. F. (1978). *Phys. Rev. A* **17**, 1343.
- Crothers, D. S. F., and Hughes, J. G. (1978). *Proc. R. Soc. London, Ser. A* **359**, 345.
- Dahler, J. S., Nielson, S. E., and Numrich, R. W. (1977). *J. Phys. B* **10**, L257.
- Delos, J. B., and Thorson, W. R. (1979). *J. Chem. Phys.* **70**, 1774.
- Delos, J. B., Thorson, W. R., and Knudson, S. K. (1972). *Phys. Rev. A* **6**, 709.
- Diestler, D. J. (1971). *J. Chem. Phys.* **54**, 4547.
- Diestler, D. J., and McKoy, V. (1968). *J. Chem. Phys.* **48**, 2951.
- Evans, S. A., and Lane, N. F. (1973). *Phys. Rev. A* **8**, 1385.
- Evans, S. A., Cohen, J. S., and Lane, N. F. (1971). *Phys. Rev. A* **4**, 2235.
- Faist, M. B. (1975). Ph.D. Thesis, Ohio State University, Columbus.
- Faist, M. B., and Levine, R. D. (1976). *J. Chem. Phys.* **64**, 2953.
- Gabriel, H., and Taulbjerg, K. (1974). *Phys. Rev. A* **10**, 741.
- Gallaher, D. F., and Wilets, L. (1968). *Phys. Rev.* **169**, 139.
- Gauyacq, J. P. (1978). *J. Phys. B* **11**, L217.
- Geltman, S. (1972). *Phys. Electron. At. Collisions, Invited Pap. Prog. Rep. Int. Conf.*, 7th, 1971, 216.
- Goddard, W. A., III, Dunning, T. H., Jr., Hunt, W. J., and Hay, P. J. (1973). *Acc. Chem. Res.* **6**, 368.
- Gordon, R. G. (1971). *Methods Comput. Phys.* **10**, 81.
- Green, T. A., Michels, H. H., and Browne, J. C. (1976). *J. Chem. Phys.* **64**, 3951.
- Hahn, Y., and Russek, A. (1968). *Phys. Rev.* **168**, 78.
- Harvey, N. M. (1979). Ph.D. Thesis, University of Minnesota, Minneapolis.
- Hatton, G. J., Chen, J. C. Y., Isihara, T., and Watson, K. M. (1975). *Phys. Rev. A* **12**, 1281.
- Heil, T. G., and Dalgarno, A. (1979). *J. Phys. B* **12**, L557.
- Heller, E. J., Rescigno, T. N., and Reinhardt, W. P. (1973). *Phys. Rev. A* **8**, 2946.
- Hirschfelder, J. O., and Meath, W. J. (1967). *Adv. Chem. Phys.* **12**, 3.
- Johnson, B. R. (1974). *Chem. Phys. Lett.* **27**, 289.
- Johnson, B. R., and Levine, R. D. (1972). *Chem. Phys. Lett.* **13**, 168.
- Knudson, S. K., and Thorson, W. R. (1970). *Can. J. Phys.* **48**, 313.
- Kolos, W. (1970). *Adv. Quantum Chem.* **5**, 99.
- Kolos, W., and Wolniewicz, L. (1963). *Rev. Mod. Phys.* **35**, 473.
- Kouri, D. J., and Curtiss, C. F. (1971). *Mol. Phys.* **21**, 609.
- Kubach, C., and Sidis, V. (1976). *Phys. Rev. A* **14**, 152.
- Lester, W. A., Jr. (1971). *Methods Comput. Phys.* **10**, 211.
- Light, J. C. (1971). *Methods Comput. Phys.* **10**, 111.
- Light, J. C., and Walker, R. B. (1976). *J. Chem. Phys.* **65**, 4272.
- Light, J. C., Walker, R. B., Stechel, E. B., and Schmalz, T. G. (1979). *Comput. Phys. Commun.* **17**, 89.

- Löwdin, P. O. (1970). *Adv. Quantum Chem.* **5**, 185.
- Macías, A., and Riera, A. (1978a). *J. Phys. B* **11**, 1077.
- Macías, A., and Riera, A. (1978b). *J. Phys. B* **11**, L489.
- Marcus, R. A. (1968). *Discuss. Faraday Soc.* **44**, 7.
- Melius, C. F., and Goddard, W. A., III (1972). *Chem. Phys. Lett.* **15**, 524.
- Melius, C. F., and Goddard, W. A., III (1974). *Phys. Rev. A* **10**, 1541.
- Messiah, A. (1965). "Quantum Mechanics," Vol. I. Wiley, New York.
- Mies, F. H. (1973). *Phys. Rev. A* **7**, 942.
- Mittleman, M. H. (1975). *J. Chem. Phys.* **62**, 4450.
- Mittleman, M. H., and Tai, H. (1973). *Phys. Rev. A* **8**, 1880.
- Mott, N. F., and Massey, H. S. W. (1965). "The Theory of Atomic Collisions," 3rd ed. Oxford Univ. Press, London and New York.
- Mullaney, N. A., and Truhlar, D. G. (1979). *Chem. Phys.* **39**, 91.
- Numrich, R. W., and Truhlar, D. G. (1975). *J. Chem. Phys.* **79**, 2745.
- Numrich, R. W., and Truhlar, D. G. (1978). *J. Phys. Chem.* **82**, 68.
- Olson, R. E., Shipsey, E. J., and Browne, J. C. (1975). *J. Phys. B* **8**, 905.
- Olson, R. E., Shipsey, E. J., and Browne, J. C. (1976). *Phys. Rev. A* **13**, 180.
- Olson, R. E., Shipsey, E. J., and Browne, J. C. (1978). *J. Phys. B* **11**, 699.
- O'Malley, T. F. (1971). *Adv. At. Mol. Phys.* **7**, 223.
- Oppenheimer, M. (1972). *J. Chem. Phys.* **57**, 3899.
- Pack, R. T. (1974). *J. Chem. Phys.* **60**, 633.
- Pack, R. T., and Hirschfelder, J. O. (1968). *J. Chem. Phys.* **49**, 4009.
- Pack, R. T., and Hirschfelder, J. O. (1970). *J. Chem. Phys.* **52**, 4198.
- Percival, I. C., and Seaton, M. J. (1957). *Proc. Cambridge Philos. Soc.* **53**, 654.
- Piacentini, R. D., and Salin, A. (1974). *J. Phys. B* **7**, 1666.
- Piacentini, R. D., and Salin, A. (1977). *J. Phys. B* **10**, 1515.
- Poppe, D., and Wolken, G., Jr. (1977). *Chem. Phys. Lett.* **25**, 131.
- Preston, R. K., and Tully, J. C. (1971). *J. Chem. Phys.* **54**, 4297.
- Redmon, M. J. (1973). Ph.D. Thesis, University of Florida, Gainesville.
- Redmon, M. J., and Micha, D. A. (1974). *Int. J. Quantum Chem., Symp.* **8**, 253.
- Riera, A., and Salin, A. (1976). *J. Phys. B* **9**, 2877.
- Riera, A., and Salin, A. (1977). *J. Phys. B* **10**, L515.
- Riley, M. E. (1973). *Phys. Rev. A* **7**, 626.
- Riley, M. E., and Green, T. A. (1971). *Phys. Rev. A* **4**, 619.
- Rose, M. E. (1957). "Elementary Theory of Angular Momentum." Wiley, New York.
- Rosenthal, H. (1971). *Phys. Rev. Lett.* **27**, 635.
- Schmalz, T. G., Stechel, E. B., and Light, J. C. (1979). *J. Chem. Phys.* **70**, 5660.
- Schneiderman, S. B., and Russek, A. (1969). *Phys. Rev.* **181**, 311.
- SethuRaman, V., Thorson, W. R., and Lebeda, C. F. (1973). *Phys. Rev. A* **8**, 1316.
- Shipsey, E. J., Redmon, L. T., Browne, J. C., and Olson, R. E. (1978). *Phys. Rev. A* **18**, 1961.
- Sidis, V., and Kubach, C. (1978). *J. Phys. B* **11**, 2687.
- Sidis, V., and Lefebvre-Brion, H. (1971). *J. Phys. B* **4**, 1040.
- Smith, F. T. (1969). *Phys. Rev.* **179**, 111.
- Stechel, E. B., Walker, R. B., and Light, J. C. (1978). *J. Chem. Phys.* **69**, 3518.
- Stechel, E. B., Schmalz, T. G., and Light, J. C. (1979). *J. Chem. Phys.* **70**, 5640.
- Stern, B., Baudon, J., Lefebvre, P., Rahmat, G., and Vassilev, G. (1977). *J. Phys. B* **10**, 2165.
- Stern, B., Gauyacq, J. P., and Sidis, V. (1978). *J. Phys. B* **11**, 653.
- Stine, J. R., and Muckerman, J. T. (1976). *J. Chem. Phys.* **65**, 3975.
- Taulbjerg, K., and Briggs, J. S. (1975a). *J. Phys. B* **8**, 1895.
- Taulbjerg, K., and Briggs, J. S. (1975b). *J. Phys. B* **8**, 1909.
- Taulbjerg, K., Vaaben, J., and Fastrup, B. (1975). *Phys. Rev. A* **12**, 2325.

- Thorson, W. R. (1965). *J. Chem. Phys.* **42**, 3878.
- Thorson, W. R. (1969). *J. Chem. Phys.* **50**, 1702.
- Thorson, W. R., and Delos, J. B. (1978a). *Phys. Rev. A* **18**, 117.
- Thorson, W. R., and Delos, J. B. (1978b). *Phys. Rev. A* **18**, 135.
- Top, Z. H., and Baer, M. (1977). *Chem. Phys.* **25**, 1.
- Truhlar, D. G., and Kuppermann, A. (1972). *J. Chem. Phys.* **56**, 2232.
- Truhlar, D. G., Mead, C. A., and Brandt, M. A. (1975). *Adv. Chem. Phys.* **33**, 295.
- Truhlar, D. G., Harvey, N. M., Onda, K., and Brandt, M. A. (1979). In "Proceedings of the NRCC Workshop on Algorithms and Computer Codes for Atomic and Molecular Quantum Scattering Theory" (L. D. Thomas, ed.), p. 220. Lawrence Berkeley Laboratory, Berkeley, California.
- Tully, J. C. (1973). *J. Chem. Phys.* **59**, 5122.
- Tully, J. C. (1976). In "Dynamics of Molecular Collisions" (W. H. Miller, ed.), Part B, p. 217. Plenum, New York.
- Tully, J. C. (1977). In "Semiempirical Methods of Electronic Structure Calculation" (G. A. Segal, ed.), Part A, p. 173. Plenum, New York.
- Vaaben, J., and Taulbjerg, K. (1979). *Abstr. Pap., Int. Conf. Phys. Electron. At. Collisions, 11th, 1979*, 566.
- Van Vleck, J. H. (1936). *J. Chem. Phys.* **4**, 327.
- Walker, R. B., and Light, J. C. (1975). *Chem. Phys.* **7**, 84.
- Winter, T. G., and Lane, N. F. (1978). *Phys. Rev. A* **17**, 66.
- Zimmerman, I. H., and George, T. F. (1975a). *Chem. Phys.* **7**, 323.
- Zimmerman, I. H., and George, T. F. (1975b). *J. Chem. Phys.* **63**, 2109.
- Zvijac, D. J., and Light, J. C. (1976). *Chem. Phys.* **12**, 237.