PHYSICAL REVIEW VOLUME 179, NUMBER 1 5 MARCH 1969

Diabatic and Adiabatic Representations for Atomic Collision Problems*

Felix T. Smith
Stanford Research Institute, Menlo Park, California 94025

(Received 31 July 1968)

The equations of the general Born-Oppenheimer separation into electronic and heavy-particle coordinates are re-examined, and the coupled equations that result for the heavy-particle motion are expressed in a particularly simple form. This is accomplished by introducing a generalized matrix operator for the effective momentum associated with the heavy particles; the matrix portion of this operator represents a coupling of the nuclear momentum with the electronic motion. The commutator between the momentum and potential matrices is a force matrix, which provides an alternative means of evaluating the momentum matrix. The momentum coupling has both radial and angular parts; the angular momentum coupling agrees with Thorson's expression. In the usual adiabatic molecular representation, the potential energy matrix is diagonalized, and all the coupling is thrown into the radial and angular momentum matrices. For collision problems it is often more important to diagonalize the radial momentum matrix, putting the radial off-diagonal coupling into the potential matrix; this generates a family of diabatic representations, the most important of which dissociates to unique separated atom states. This standard diabatic representation has the properties called for by Lichten, is uniquely defined even with the inclusion of configuration interaction, and leads immediately to the Landau-Zener-Stueckelberg limiting case under appropriate conditions.

A. INTRODUCTION

1. Background of the Problem

In atomic and molecular collisions, inelastic processes are exceedingly common and important, but the formulation of their theory in general terms remains a vexatious problem. Two points of view appear to be perpetually in conflict. On the one hand, the viewpoint of molecular theory leads to an adiabatic representation of the process in terms of molecular potential curves obeying the noncrossing rule. On the other, a dynamic view closer to the experimental situation emphasizes the importance of elastic scattering from smooth potentials violating the noncrossing rule and of inelastic processes connected with the very crossings that are missing in the adiabatic picture. Formally, the adiabatic representation is solidly established; to develop a similar formal basis for the dynamic view is one of the principal aims of this paper.

Following the model of Born and Oppenheimer[1] for molecular problems, it is usual to take advantage of the extreme difference in masses between electrons and nuclei to separate the electronic and nuclear coordinates. For an enormous range of problems the nuclear motion can be taken as slow compared with the electronic motion, and it has appeared natural to base a description of the collision process on the representation of adiabatic molecular states. This representation is all the more attractive because it is now relatively convenient to make numerical computations of electronic wave functions and energy levels as a function of the internuclear coordinates, which are treated as fixed (or adiabatically varying) parameters. Particularly appealing from a theoretical point of view is the fact that a unique and rigorous prescription exists for this adiabatic representation, namely the variational theorem applied in the domain of the electronic coordinates for each fixed internuclear configuration.

In itself the adiabatic representation gives no obvious indication of the parameter governing inelastic transition probabilities. Indeed, from the adiabatic point of view all such inelastic transitions result from a breakdown of the Born-Oppenheimer separation of coordinates. Formally the correction terms representing this breakdown can be given rigorous definition, and the resulting equations have been set down by a number of authors including Massey and Smith,[2] Kronig,[3] Born,[4] and others.[5] Unfortunately, the important matrices appearing have all too seldom been evaluated.

In practice, the adiabatic representation has never really proved to be a satisfactory basis for calculating most inelastic effects or even elastic scattering. This is due simply to the fact that the correction terms may become exceedingly large, so that simplifying expansion procedures fail.

It was observed quite early by Landau,[6] Zener,[7] and Stueckelberg[8] that one of the most important sources of inelastic transitions lies in the situation where two adiabatic molecular states approach each other closely. Ordinarily in such a circumstance the problem is more naturally (if less rigorously) defined in a representation based not on states that are strict eigenfunctions of the electronic Hamiltonian for each nuclear configuration, but rather in terms of states each of which has a simple molecular orbital structure and out of which the correct adiabatic solutions can be constructed (at least approximately) as a linear combination. When the states are of the same over-all symmetry there is no inhibition preventing the approximate molecular orbital states from crossing, but the strict adiabatic states avoid each other and obey the noncrossing rule. In the adiabatic representation such a close approach of two states is referred to as an avoided crossing (or a "pseudocrossing").

Even though the representation in terms of approximate molecular orbitals appears to be less unique and rigorous than the adiabatic representation, it was observed by Landau, Zener, and Stueckelberg that the collision equations in such a situation lend themselves to a well-behaved expansion treatment in which the unperturbed, crossing states could be considered as governing the elastic scattering in the system, and the interaction between the states could be treated in the high-energy limit as a comparatively small perturbation causing the inelastic transition. This procedure turns out to be valid for the most important range of the collision parameters in a great many physical situations, and the resulting Landau-Zener formula has had very wide applicability and success even though it does not cover all the range of physically interesting situations.

In a version of the Landau-Zener treatment used by many authors, including Bates[9] and Nikitin,[10] the adiabatic representation is taken as a starting point but modified immediately by making a particular linear combination of two of the adiabatic states in the neighborhood of the avoided crossing. This method is satisfactory for its purpose but aesthetically somewhat unsatisfying because it is not clear how to construct the basic linear combinations in more general situations where several states may be interacting and not merely two. Lichten[11] has, however, boldly gone ahead and suggested abandoning the representation in adiabatic states for collision problems and proposed that a better starting point would be a set of states to which he gives the name "diabatic," which have the property of running smoothly through the crossings. In a number of specific cases Lichten has shown how these states can be described approximately by using simple molecular orbital considerations. By using a combination of one-electron orbitals it is indeed possible, as Lichten points out, to define such a diabatic basis set at all values of the internuclear parameters. The price paid for this representation, namely the omission of configuration interaction, is a high one. Lichten's definition, therefore, is very valuable for intuitive and semiquantitative arguments, but perhaps less effective for practical calculations than the rather *ad hoc* method of combining selected adiabatic states.

The technique of projection operators[12] can be made as accurate as desired, and leads to a unique scattering matrix, but there still remains in it the arbitrariness inherent in the choice of projections. It has seemed to me desirable to seek an alternative definition of diabatic states which might be formalized as uniquely and generally as the definition of adiabatic states and yet would be closer in spirit to the adiabatic definitions than Lichten's version based on one-electron orbitals. One of the evidences that such a definition might be found is the fact that the adiabatic representation has the peculiarity that when the interactions between the states are small the states approach extremely closely and their potential curves have very sharp bends, corresponding to a rather sharp and sudden switch from one molecular orbital structure to the other. Necessarily these bends become sharper as the interactions between the states become smaller. Intuitively it seems obvious that the underlying smooth curves that can be drawn through these avoided crossings must have some physical reality and be definable in equally unique terms as adiabatic ones.

This hope has been given further support by the empirical observation of numerous regularities in elastic scattering even in situations where many avoided crossings are to be expected adiabatically. The empirical observations in elastic scattering often show an underlying regularity, suggesting that the basic elastic scattering is determined by one or more smoothly varying potential curves.[13] Perturbations are, of course, seen arising from the interactions that also are responsible for inelastic transitions, but on the whole these appear in the elastic scattering as rather small and local deviations from an otherwise very smooth and regular behavior. These regularities apply not only to the elastic scattering predominantly governed by a single potential, but also to the elastic scattering patterns in situations like $He^+ + He$ where interference patterns involving two or more molecular states can be seen.[14] In such cases the interference patterns also show extraordinary regularity over very wide ranges of the relevant parameters of the scattering.

It has not been clear that these regularities in themselves demonstrated the existence of pure potential scattering involving smooth potential curves. It was indeed conceivable that a smooth dependence might also result if there were slowly varying velocity-dependent terms in the interaction. Fortunately, it can be shown that such a velocity dependence is not involved.

In what follows I shall show that there exists a definition of diabatic states as rigorous and satisfying as that for adiabatic ones. Diabatic and adiabatic representations have equal uniqueness and validity and a translation between one and the other is always possible. Some past conflicts in terminology now turn out to depend on the point of view: for example, what is diabatically a perfectly respectable crossing may adiabatically be only an avoided crossing.

2. Method of Treatment

In this paper, the problem of atomic collisions is formulated once again in terms of the Born-Oppenheimer separation. The non-Born-Oppenheimer terms will be carefully examined and the coupled equations representing the inelastic collision problem will be formulated in a particularly simple way. Through this formal development it will be shown that the collision problem depends fundamentally upon three matrices that express properties of the electronic state as a function of the internuclear parameters. Only one of these matrices, the electronic energy or potential matrix, appears in the adiabatic representation, in which this matrix is diagonalized everywhere. Of equal importance to the collision problem, however, are two other matrices, one of which can be called the radial momentum matrix, and the other an angular momentum matrix. Together with some of their derivatives, these matrices fully define the collision problem.

An important by-product arises from the careful examination of the coupling terms in the collision problem. The commutator between the potential and momentum matrices involves a force matrix, which will often be easier to compute than the momentum matrix itself; if the force matrix and the potential matrix are found, the evaluation of the momentum matrix is easy. This has considerable value for the computation of the matrices of the collision problem, an effort which should more frequently be undertaken in the course of molecular structure calculations.

The distinction between adiabatic and diabatic states is clarified when one examines the radial momentum matrix as well as the electronic energy matrix. The adiabatic representation is defined by diagonalizing the electronic energy, but if this is done the off-diagonal terms in the radial momentum matrix become large. On the other hand, the radial momentum matrix may itself be diagonalized, in which case the electronic energy matrix is no longer diagonal. It will be shown that it is possible to diagonalize the radial momentum matrix everywhere, and this seems to be the basis for a satisfactory diabatic representation.

The principal aim of this paper is to make precise the distinction between diabatic and adiabatic representations and their connection with the coupling of states at crossings and elsewhere. The discussion is most conveniently carried on in the framework of a molecular coordinate system, where the important heavy-particle coordinate is the internuclear vector, and the electron positions are measured from the internuclear center of mass. Unfortunately, this coordinate frame is not suited to describing properly the initial and final states of a collision problem, which obviously involve separated atoms and demand a coordinate frame in which the heavy-particle coordinate is the vector between the atomic centers of mass. This well-known aspect of the problem is quite distinct from the question of defining diabatic and adiabatic representations, which can be done either in the molecular or the interatomic frame, but it is essential to their use in scattering problems. I therefore hope to devote some attention to the question of coordinate frames and the dissociation limit in a subsequent paper.

For the most part, attention will be concentrated on the collision of two atoms. However, possible generalizations to polyatomic systems will also be given some attention.

B. FORMAL DEVELOPMENT

1. The Equations in General Form

If $\vec{R}$ represents the relative internuclear coordinates, and $\vec{r}$ the coordinates of all the electrons (in a nonrotating frame), and the Hamiltonian is

$$H = T^{nu} + H' , \quad 2MT^{nu} = \vec{p}^{\,nu} \cdot \vec{p}^{\,nu} ,$$

$$H' = T^{el} + V(\vec{R},\vec{r}) , \tag{1}$$

where T^{nu} is the nuclear kinetic energy, $\vec{p}^{\,nu}$ is the momentum of relative nuclear motion, T^{el} is the electronic kinetic energy, and V is the entire interaction potential including internuclear repulsion, the wave function can be written formally as

$$\Omega(\vec{R},\vec{r}) = \sum_k \psi_k^{nu}(\vec{R})\chi_k^{el}(\vec{R},\vec{r}) . \tag{2}$$

The Schrödinger equation can be integrated, if the χ_k are known, becoming

$$\int \chi_j^*(\vec{R},\vec{r})(H-E)\Omega(\vec{R},\vec{r})d\vec{r} = 0 . \tag{3}$$

In the electronic functions χ_k the coordinates $\vec{R}$ are to be considered parameters, at each value of which the χ_k are assumed to form an orthonormal and complete set with respect to the variables $\vec{r}$:

$$\langle j|k\rangle = \int \chi_j^*(\vec{R},\vec{r})\chi_k(\vec{R},\vec{r})d\vec{r} = \delta_{jk} . \tag{4}$$

The electronic Hamiltonian H' is usually real; if so, the functions χ_k can be taken as real also. Using the same bracket notation for integration over $\vec{r}$ alone, the following matrices are needed in Eq. (3):

$$U_{jk}(\vec{R}) = \langle j|H'|k\rangle , \tag{5}$$

$$\vec{\mathrm{P}}_{jk}(\vec{\mathrm{R}}) = \langle j | \vec{\mathrm{p}}^{\,\mathrm{nu}} | k \rangle \, . \tag{6}$$

These matrices are Hermitian [for $\vec{\underline{\mathrm{P}}}$ this can be shown by applying $\vec{\mathrm{p}}^{\,\mathrm{nu}}$ to Eq. (4)]. Since $\vec{\mathrm{p}}^{\,\mathrm{nu}}$ is imaginary, if the χ_k are real, the diagonal elements of $\vec{\underline{\mathrm{P}}}$ vanish. A third matrix is often introduced, but it can be shown to depend exclusively on $\vec{\underline{\mathrm{P}}}$; the proof involves only the orthogonality and completeness of the functions χ_k:

$$\underline{\mathrm{B}}(R) = 2M\langle | T^{\mathrm{nu}} | \rangle = \vec{\underline{\mathrm{P}}} \cdot \vec{\underline{\mathrm{P}}} + \vec{\mathrm{p}}^{\,\mathrm{nu}} \cdot \vec{\underline{\mathrm{P}}} \tag{7}$$

The matrix $\vec{\underline{\mathrm{P}}}$ can be thought of as a part of a matrix operator representing the generalized momentum of the heavy-particle problem,

$$\vec{\underline{\mathcal{P}}} = \vec{\underline{\mathrm{P}}}(R) + \underline{1}\,\vec{\mathrm{p}}^{\,\mathrm{nu}} \, . \tag{8}$$

If we then form the generalized kinetic energy operator

$$\underline{\mathcal{T}} = (2M)^{-1} \vec{\underline{\mathcal{P}}} \cdot \vec{\underline{\mathcal{P}}}$$

$$= \underline{1}\, T^{\mathrm{nu}} + (2M)^{-1}(\vec{\underline{\mathrm{P}}} \cdot \vec{\underline{\mathrm{P}}} + \vec{\mathrm{p}}^{\,\mathrm{nu}} \cdot \vec{\underline{\mathrm{P}}}) + M^{-1} \vec{\underline{\mathrm{P}}} \cdot \vec{\mathrm{p}}^{\,\mathrm{nu}} \tag{9}$$

the coupled equations resulting from (3) can be written in matrix form as

$$(\underline{\mathcal{T}} + \underline{\mathrm{U}}(\vec{\mathrm{R}}) - \underline{1}\, E)\underline{\Psi}(\vec{\mathrm{R}}) = 0 \, . \tag{10}$$

Thus to set up the full coupled equations we need to know the matrices $\underline{\mathrm{U}}(\vec{\mathrm{R}})$ and $\vec{\underline{\mathrm{P}}}(\vec{\mathrm{R}})$, and no others.

We can evaluate the commutator

$$[\vec{\underline{\mathcal{P}}}, \underline{\mathrm{U}}] = [\vec{\underline{\mathrm{P}}}, \underline{\mathrm{U}}] + (\vec{\mathrm{p}}^{\,\mathrm{nu}}\underline{\mathrm{U}}) = (\hbar/i)\,\vec{\underline{\mathrm{F}}}(R) \, , \tag{11}$$

where $\vec{\mathrm{F}}_{jk}(\vec{\mathrm{R}}) = \frac{i}{\hbar}\langle j | (\vec{\mathrm{p}}^{\,\mathrm{nu}} V(\vec{\mathrm{R}}, \vec{\mathrm{r}})) | k \rangle \, .$ (12)

(The operator $\vec{\mathrm{p}}^{\,\mathrm{nu}}$ is not considered to operate beyond the close of a parenthesis.) The force matrix $\vec{\underline{\mathrm{F}}}(\vec{\mathrm{R}})$ may be easier to compute than $\vec{\underline{\mathrm{P}}}(\vec{\mathrm{R}})$ itself [Eq. (6)], and Eq. (11) can then be used to evaluate $\vec{\underline{\mathrm{P}}}$.

Under a unitary transformation $C(\vec{\mathrm{R}})$ such that

$$\underline{\Psi}(\vec{\mathrm{R}}) = \underline{\mathrm{C}}(\vec{\mathrm{R}})\underline{\Psi}'(\vec{\mathrm{R}}) \, , \tag{13}$$

where $\underline{\Psi}$ is the column matrix of all the nuclear wave functions $\psi_k^{\mathrm{nu}}(\vec{\mathrm{R}})$, the important matrices transform as follows:

$$\underline{\mathrm{U}}'(R) = \underline{\mathrm{C}}^{-1}(\vec{\mathrm{R}})\underline{\mathrm{U}}(\vec{\mathrm{R}})\underline{\mathrm{C}}(\vec{\mathrm{R}}) \, , \tag{14}$$

$$\vec{\underline{\mathrm{F}}}'(R) = \underline{\mathrm{C}}^{-1}(\vec{\mathrm{R}})\vec{\underline{\mathrm{F}}}(\vec{\mathrm{R}})\underline{\mathrm{C}}(\vec{\mathrm{R}}) \, , \tag{15}$$

$$\vec{\underline{\mathcal{P}}}' = \underline{\mathrm{C}}^{-1}(\vec{\mathrm{R}})\vec{\underline{\mathcal{P}}}\underline{\mathrm{C}}(\vec{\mathrm{R}}) \, , \tag{16}$$

$$\vec{\underline{\mathrm{P}}}'(\vec{\mathrm{R}}) = \underline{\mathrm{C}}^{-1}(\vec{\mathrm{R}})\vec{\underline{\mathrm{P}}}(\vec{\mathrm{R}})\underline{\mathrm{C}}(\vec{\mathrm{R}}) + \underline{\mathrm{C}}^{-1}(\vec{\mathrm{R}})(\vec{\mathrm{p}}^{\,\mathrm{nu}}\underline{\mathrm{C}}(\vec{\mathrm{R}})). \tag{17}$$

2. Molecular Representations

Let us now consider a molecular representation, where the electron coordinates are converted from the stationary frame of reference to one rotating with the internuclear vector $\vec{\mathrm{R}} = (R, \Theta, \Phi)$:

$$\vec{\mathrm{r}}_i = (r_i, \theta_i, \varphi_i) \rightarrow \vec{\mathrm{r}}_i{}' = (r_i, \theta_i{}', \varphi_i{}') \, , \tag{18}$$

where the relationship

$$\theta_i{}' = \theta_i{}'(\theta_i, \varphi_i, \Theta, \Phi), \quad \varphi_i{}' = \varphi_i{}'(\theta_i, \varphi_i, \Theta, \Phi) \, , \tag{19}$$

is given explicitly by

$$\begin{aligned} \cos\theta_i{}' \cos\varphi_i{}' &= \cos\Theta \cos\theta_i \cos(\varphi_i + \Phi) \\ &\qquad - \sin\Theta \sin\theta_i \, , \\ \cos\theta_i{}' \sin\varphi_i{}' &= \cos\theta_i \sin(\varphi_i + \Phi) \, , \\ \sin\theta_i{}' &= \sin\Theta \cos\theta_i \cos(\varphi_i + \Phi) + \cos\Theta \sin\theta_i \, . \end{aligned} \tag{20}$$

Consequently we have the partial derivatives

$$\begin{aligned} &\frac{\partial\theta_i{}'}{\partial\Theta} = \cos\varphi_i{}', \quad \frac{\partial\varphi_i{}'}{\partial\Theta} = \tan\theta_i{}' \sin\varphi_i{}' \, , \\ &\frac{1}{\sin\Theta}\frac{\partial\theta_i{}'}{\partial\Phi} = -\sin\varphi_i{}' \, , \\ &\frac{1}{\sin\Theta}\frac{\partial\varphi_i{}'}{\partial\Phi} = \tan\theta_i{}' \cos\varphi_i{}' + \cot\Theta. \end{aligned} \tag{21}$$

In the molecular representation the wave functions $\chi_k(\vec{\mathrm{R}}, \vec{\mathrm{r}})$, the potential $V(\vec{\mathrm{R}}, \vec{\mathrm{r}})$, and any related functions $f(\vec{\mathrm{R}}, \vec{\mathrm{r}})$, depend on Θ and Φ only implicitly through the angles $\theta_i{}'$ and $\varphi_i{}'$:

$$f(R, \Theta, \Phi; r_i, \theta_i, \varphi_i) = f^{\mathrm{m}}(R; r_i, \theta_i{}', \varphi_i{}') \, . \tag{22}$$

Thus in constructing the partial derivatives $\partial f/\partial\Theta$, $\partial f/\partial\Phi$ one can use the operators

$$\begin{aligned} D_1 &= \sum_i \left(\cos\varphi_i{}' \frac{\partial}{\partial\theta_i{}'} + \tan\theta_i{}' \sin\varphi_i{}' \frac{\partial}{\partial\theta_i{}'} \right) \\ &= (i/\hbar) L_y \, , \\ D_2 &= \sum_i \left(\sin\varphi_i{}' \frac{\partial}{\partial\theta_i{}'} - \tan\theta_i{}' \cos\varphi_i{}' \frac{\partial}{\partial\varphi_i{}'} \right) \\ &= -(i/\hbar) L_x \, , \\ D_3 &= \textstyle\sum_i \partial/\partial\varphi_i{}' = (i/\hbar) L_z \, , \end{aligned} \tag{23}$$

where $\vec{\mathrm{L}} = (L_x, L_y, L_z)$ is the total orbital angular momentum operator for the electrons in the molecular frame.

The vector matrices $\vec{\underline{\mathrm{P}}}$ and $\vec{\underline{\mathrm{F}}}$ arise from $\vec{\mathrm{p}}^{\,\mathrm{nu}}$

operating as a gradient on the scalar functions $\chi_k(\vec{\mathrm{R}},\vec{\mathrm{r}})$ and $V(\vec{\mathrm{R}},\vec{\mathrm{r}})$. When the vectors are written in their spherical polar components and a molecular representation is used, we have

$$\begin{aligned} p_R^{\mathrm{grad}} &= \frac{\hbar}{i}\frac{\partial}{\partial R}, \\ p_\Theta^{\mathrm{grad}} &= \frac{\hbar}{iR}\frac{\partial}{\partial\Theta} = \frac{\hbar}{iR}D_1 = \frac{L_y}{R} \\ p_\Phi^{\mathrm{grad}} &= \frac{\hbar}{iR\sin\Theta}\frac{\partial}{\partial\Phi} = \frac{\hbar}{iR}(-D_2+\cot\Theta D_3) \\ &= \frac{(L_x+\cot\Theta L_z)}{R}\,. \end{aligned} \tag{24}$$

It is easy to see that the important matrices $\underline{\mathrm{U}}^{\mathrm{m}}(R)$, $\underline{\mathrm{P}}_R{}^{\mathrm{m}}(R)$, $\underline{\mathrm{P}}_\Theta{}^{\mathrm{m}}(R)$, $\underline{\mathrm{F}}_R{}^{\mathrm{m}}(R)$, $\underline{\mathrm{F}}_\Theta{}^{\mathrm{m}}(R)$ (where the superscript m refers specifically to the matrices expressed in the rotating molecular frame) are all independent of Θ and Φ, and that we may write also

$$\begin{aligned} \underline{\mathrm{P}}_\Phi{}^{\mathrm{m}}(R,\Theta) &= \underline{\mathrm{Q}}_x{}^{\mathrm{m}}(R)+\cot\Theta\,\underline{\mathrm{Q}}_z{}^{\mathrm{m}}(R), \\ \underline{\mathrm{P}}_\Theta{}^{\mathrm{m}}(R) &= \underline{\mathrm{Q}}_y{}^{\mathrm{m}}(R), \end{aligned} \tag{25}$$

$$\begin{aligned} \underline{\mathrm{F}}_\Phi{}^{\mathrm{m}}(R,\Theta) &= \underline{\mathrm{G}}_x{}^{\mathrm{m}}(R)+\cot\Theta\,\underline{\mathrm{G}}_z{}^{\mathrm{m}}(R), \\ \underline{\mathrm{F}}_\Theta{}^{\mathrm{m}}(R) &= \underline{\mathrm{G}}_y{}^{\mathrm{m}}(R), \end{aligned} \tag{26}$$

where $$\underline{\mathrm{Q}}_i{}^{\mathrm{m}}(R) = R^{-1}\underline{\mathrm{L}}_i = R^{-1}\langle|L_i|\rangle, \tag{27}$$

$$\underline{\mathrm{G}}_i{}^{\mathrm{m}}(R) = R^{-1}\langle|(L_i V^{\mathrm{m}}(R,\vec{\mathrm{r}}_i'))|\rangle. \tag{28}$$

Finally, in forming the generalized kinetic energy operator $\underline{\mathcal{T}}^{\mathrm{m}}$ (Eq. 8) we need the divergence,

$$\vec{\mathrm{p}}^{\,\mathrm{div}} = \frac{\hbar}{i}\left[\frac{2}{R}+\frac{\partial}{\partial R},\ \frac{1}{R}\left(\cot\Theta+\frac{\partial}{\partial\Theta}\right),\ \frac{1}{R\sin\Theta}\frac{\partial}{\partial\Phi}\right], \tag{29}$$

which operates on $\underline{\vec{\mathrm{P}}}$ to give

$$\begin{aligned} \vec{\mathrm{p}}^{\,\mathrm{nu}}\cdot\underline{\vec{\mathrm{P}}} &= \vec{\mathrm{p}}^{\,\mathrm{div}}\cdot\underline{\vec{\mathrm{P}}}^{\mathrm{m}} \\ &= \frac{\hbar}{i}\left(\frac{2}{R}\underline{\mathrm{P}}_R{}^{\mathrm{m}}(R)+\frac{\partial\underline{\mathrm{P}}_R{}^{\mathrm{m}}(R)}{\partial R}+\cot\Theta\,\underline{\mathrm{P}}_\Theta{}^{\mathrm{m}}(R)\right). \end{aligned} \tag{30}$$

We can now evaluate the expressions of Eq. (9), writing

$$\underline{\mathcal{T}} = \underline{1}\,T^{\mathrm{nu}}+(2M)^{-1}\underline{\mathrm{S}}_R+(2MR^2)^{-1}\underline{\mathrm{S}}_\Omega, \tag{31}$$

$$\underline{\mathrm{S}}_R = \underline{\mathrm{P}}_R{}^2(R)$$

$$+\frac{\hbar}{i}\left(\frac{2}{R}\underline{\mathrm{P}}_R(R)+\frac{\partial\underline{\mathrm{P}}_R(R)}{\partial R}+2\underline{\mathrm{P}}_R(R)\frac{\partial}{\partial R}\right), \tag{32}$$

$$\begin{aligned} \underline{\mathrm{S}}_\Omega &= \underline{\mathrm{L}}_x{}^2(R)+\underline{\mathrm{L}}_y{}^2(R)+\underline{\mathrm{L}}_z{}^2(R)\cot^2\Theta \\ &\quad -\frac{2\hbar}{i}\frac{\cos\Theta}{\sin^2\Theta}\underline{\mathrm{L}}_z(R)\frac{\partial}{\partial\Phi}-\underline{\mathrm{X}}, \end{aligned} \tag{33}$$

$$\begin{aligned} \underline{\mathrm{X}} &= \cot\Theta\,[\underline{\mathrm{L}}_x(R)\underline{\mathrm{L}}_z(R)+\underline{\mathrm{L}}_z(R)\underline{\mathrm{L}}_x(R) \\ &\quad -i\hbar\underline{\mathrm{L}}_y(R)]-\frac{2\hbar\underline{\mathrm{L}}_x(R)}{\sin\Theta}\frac{\partial}{\partial\Phi}+\frac{2\hbar\underline{\mathrm{L}}_y(R)}{i}\frac{\partial}{\partial\Theta}. \end{aligned} \tag{34}$$

$\underline{\mathrm{S}}_\Omega$ contains all the angular momentum coupling terms. These have also been evaluated by Thorson,[5] whose expression for the equivalent of $\underline{\mathrm{X}}$, obtained from (34) by using the angular momentum commutation law, is

$$\tfrac{1}{2}\underline{\mathrm{X}} = \cot\Theta\,\underline{\mathrm{L}}_x\underline{\mathrm{L}}_z-\frac{\hbar\underline{\mathrm{L}}_x}{\sin\Theta}\frac{d}{d\Phi}+\frac{\hbar\underline{\mathrm{L}}_y}{i}\frac{d}{d\Theta}. \tag{35}$$

The most general transformation between molecular representations involves a unitary matrix $\underline{\mathrm{C}}(R)$; the matrix $\underline{\mathrm{P}}_R{}^{\mathrm{m}}(R)$ then transforms to

$$\underline{\mathrm{P}}_R{}^{\mathrm{m}\prime}(R) = \underline{\mathrm{C}}^{-1}(R)\left[\left(\underline{\mathrm{P}}_R{}^{\mathrm{m}}(R)+\frac{\hbar}{i}\frac{\partial}{\partial R}\right)\underline{\mathrm{C}}(R)\right], \tag{36}$$

and all the other matrices $\underline{\mathrm{U}}$, $\underline{\mathrm{P}}_\Theta$, $\underline{\mathrm{P}}_\Phi$, and $\underline{\vec{\mathrm{F}}}$ (denoted in general by $\underline{\mathrm{M}}$) transform in the simple fashion

$$\underline{\mathrm{M}}'(R) = \underline{\mathrm{C}}^{-1}(R)\underline{\mathrm{M}}(R)\underline{\mathrm{C}}(R). \tag{37}$$

3. The Adiabatic Representation

The adiabatic representation (denoted by the superscript a) is defined by the requirement that the potential matrix $\underline{\mathrm{U}}^{\mathrm{a}}(R)$ be diagonal at all R. Consequently the commutation relation (10) reduces to

$$\begin{aligned} &\vec{\mathrm{P}}_{jk}{}^{\mathrm{a}}(R)[U_{jj}{}^{\mathrm{a}}(R)-U_{kk}{}^{\mathrm{a}}(R)] \\ &\quad = \delta_{jk}[\vec{\mathrm{p}}^{\,\mathrm{nu}}U_{jj}{}^{\mathrm{a}}(R)]-(\hbar/i)\vec{\mathrm{F}}_{jk}{}^{\mathrm{a}}(R). \end{aligned} \tag{38}$$

When $j=k$ this becomes a case of the Hellman-Feynman theorem,

$$\frac{\partial}{\partial R}U_{jj}{}^{\mathrm{a}}(R) = F_{R,jj}{}^{\mathrm{a}}(R), \tag{39}$$

and when $j\neq k$ it gives a prescription for computing $\underline{\mathrm{P}}_R{}^{\mathrm{a}}$ and $\underline{\mathrm{P}}_\Theta{}^{\mathrm{a}}$,

$$\begin{aligned} \vec{\mathrm{P}}_{jk}{}^{\mathrm{a}}(R) &= (\hbar/i)[U_{kk}{}^{\mathrm{a}}(R)-U_{jj}{}^{\mathrm{a}}(R)]^{-1} \\ &\quad \times\vec{\mathrm{F}}_{jk}{}^{\mathrm{a}}(R),\quad (j\neq k). \end{aligned} \tag{40}$$

This shows an expected peaking near avoided crossings in $\underline{\mathrm{U}}^{\mathrm{a}}(R)$. The wave functions $\chi_k{}^{\mathrm{a}}$ can be taken as real, and the diagonal elements of $\underline{\vec{\mathrm{P}}}^{\mathrm{a}}$ then vanish identically.

When the generalized nuclear kinetic energy operator $\underline{\mathcal{T}}^{\mathrm{a}}$ [Eq. (8)] is evaluated, one of the terms needed in the divergence (30) is the derivative $(\partial/\partial R)\ \underline{\mathrm{P}}_R{}^{\mathrm{a}}(R)$. We can convert it into easily evaluated integrals by using (40), (39), and the identity

$$\frac{\hbar}{i}\frac{\partial}{\partial R}\,\underline{\mathrm{F}}_R{}^{\mathrm{a}}(R)=[\,\underline{\mathrm{F}}_R{}^{\mathrm{a}}(R),\ \underline{\mathrm{P}}_R{}^{\mathrm{a}}(R)]+\frac{\hbar}{i}\,\underline{\mathrm{K}}^{\mathrm{a}}(R)\,, \quad (41)$$

where $K_{jk}{}^{\mathrm{a}}(R)=\left\langle j\left|\frac{\partial^2 V}{\partial R^2}\right|k\right\rangle$. (42)

4. Diabatic Representations

These considerations show how to construct the full coupled equations in the adiabatic representation, but it is useful to look at other representations. The most important of these can be obtained by diagonalizing the matrix operator $\underline{\mathcal{P}}_R$. The transformation matrix $\underline{\mathrm{C}}^{\mathrm{d}}(R)$, converting the adiabatic representation into one in which $\underline{\mathcal{P}}_R{}^{\mathrm{d}}$ is diagonal [and $\underline{\mathrm{U}}^{\mathrm{d}}(R)$ is nondiagonal], satisfies an equation like (29) in which the new matrix $\underline{\mathrm{P}}_R{}^{\mathrm{d}}(R)$ is diagonal; it is in fact always possible to find a transformation from any molecular representation to a particular one in which $\underline{\mathrm{P}}_R{}^{\mathrm{d}}$ vanishes everywhere:

$$\underline{\mathrm{P}}_R{}^{\mathrm{m}}(R)\underline{\mathrm{C}}^{\mathrm{md}}(R)+\frac{\hbar}{i}\frac{\partial}{\partial R}\underline{\mathrm{C}}^{\mathrm{md}}(R)$$

$$=\underline{\mathrm{C}}^{\mathrm{md}}(R)\underline{\mathrm{P}}_R{}^{\mathrm{d}}(R)=0\,. \quad (43)$$

At infinity we take a boundary condition such that the new representation becomes identical with the adiabatic one. This can be done because the commutator between $\underline{\mathrm{P}}_R$ and $\underline{\mathrm{U}}$, Eq. (11), vanishes as $R\to\infty$. $\underline{\mathrm{C}}^{\mathrm{d}}(R)$ is then the solution of the integral equation

$$\underline{\mathrm{C}}^{\mathrm{md}}(R)=\underline{1}+(i/\hbar)\int_R^\infty \underline{\mathrm{P}}_R{}^{\mathrm{m}}(R')\underline{\mathrm{C}}^{\mathrm{md}}(R')\,dR'\,, \quad (44)$$

which can formally be solved by iteration,

$$\underline{\mathrm{C}}^{\mathrm{md}}(R)=\underline{1}+(i/\hbar)\int_R^\infty \underline{\mathrm{P}}_R{}^{\mathrm{m}}(R')\,dR'$$

$$+(i/\hbar)^2\int_R^\infty \underline{\mathrm{P}}_R{}^{\mathrm{m}}(R')\int_{R'}^\infty \underline{\mathrm{P}}_R{}^{\mathrm{m}}(R'')$$

$$\times\, dR''dR'+\cdots\,. \quad (45)$$

In the new representation the potential matrix $\underline{\mathrm{U}}^{\mathrm{d}}(R)$ is no longer diagonal, and avoided crossings become real crossings. For this reason, following Lichten's terminology,[11] we can call this a diabatic representation. In this representation the operator $\underline{\mathcal{T}}$ is given simply by

$$2M\underline{\mathcal{T}}=2MT^{\mathrm{nu}}\,\underline{1}+\underline{\mathrm{S}}_\Omega\left(R,\Theta,\frac{\partial}{\partial\Theta},\frac{\partial}{\partial\Phi}\right), \quad (46)$$

where $\underline{\mathrm{S}}_\Omega$ is given by Eqs. (33) and (34). The diabatic representation forms the natural starting point for the treatment of interactions depending on the radial motion near crossings.

The most important condition defining the diabatic representation is the vanishing of the matrix $\underline{\mathrm{P}}_R{}^{\mathrm{d}}(R)$. This condition defines only a family of representations, and any constant unitary transformation (independent of R) is still permitted. The standard diabatic representation, which is of most direct use for collision problems, is obtained if we require also that the potential matrix at infinity $\underline{\mathrm{U}}^{\mathrm{d}}(\infty)$ be diagonal. This means that the standard diabatic representation becomes identical with the adiabatic representation in the limit of large R, and that both dissociate to the same states; ordinarily these are assumed to be products of unique atomic states. Another diabatic representation of special importance is the one that goes to unique united atom states at $R=0$, thus diagonalizing $\underline{\mathrm{U}}(0)$. If we identify this representation by u, and the standard one by d, and observe that the adiabatic representation goes correctly to both limits, we have the pair of defining equations for the transformation matrices,

$$\underline{\mathrm{C}}^{\mathrm{d}}(R)=\underline{1}+(i/\hbar)\int_R^\infty \underline{\mathrm{P}}_R{}^{\mathrm{a}}(R')\underline{\mathrm{C}}^{\mathrm{d}}(R')\,dR'\,, \quad (47)$$

$$\underline{\mathrm{C}}^{\mathrm{u}}(R)=\underline{1}-(i/\hbar)\int_0^R \underline{\mathrm{P}}_R{}^{\mathrm{a}}(R')\underline{\mathrm{C}}^{\mathrm{a}}(R')\,dR'\,. \quad (48)$$

In the diabatic picture an important question is, how do standard diabatic states (based on separated atoms) correlate with the united atom limit? Instead of the familiar adiabatic correlation diagram, the answer is furnished by the diabatic correlation matrix $\underline{\mathrm{N}}$. It is not hard to see that it can be connected with the transformation matrices of (47) and (48) by the equation.

$$\underline{\mathrm{N}}=\underline{\mathrm{C}}^{\mathrm{u}}(R)\underline{\mathrm{C}}^{\mathrm{d}}(R)=\underline{\mathrm{C}}^{\mathrm{d}}(0)=\underline{\mathrm{C}}^{\mathrm{u}}(\infty)\,. \quad (49)$$

The expressions (47) to (49) are formally identical with the basic equations of time-dependent scattering theory if we identify $\underline{\mathrm{C}}^{\mathrm{d}}$ and $\underline{\mathrm{C}}^{\mathrm{u}}$ with the time-development operators $U_\pm(t)$, $\underline{\mathrm{P}}_R{}^{\mathrm{a}}(R)$ with the interaction operator $H_{\mathrm{int}}(t)$, and $\underline{\mathrm{N}}$ with the scattering matrix $\underline{\mathrm{S}}$. It follows that formally the Lippman-Schwinger variational procedures[15] can be carried over virtually without change.

Molecular wave functions are now usually calculated in the adiabatic representation which is particularly adapted to the situation where the nuclear motion is small. The diabatic representation is better adapted to the collision problem;

it can be obtained from the adiabatic representation if the required matrix elements, especially $\underline{\vec{P}}^{a}$, are available. In practice adiabatic solutions are only available for a few of the lowest states of a given system, and they become harder and harder to generate at smaller internuclear distances. However, there is no real need to pass through the adiabatic representation in order to reach the diabatic one.

A diabatic representation can be obtained from any molecular representation in which the functions are orthonormal and complete if one solves Eqs. (43) to (45). As Lichten in particular has pointed out,[11] a representation based on a combination of one-electron molecular orbitals without configuration interaction usually provides an approximate diabatic representation that is a better starting point for the collision problem than the adiabatic one. In any such representation the matrices $\underline{U}$ and $\underline{\vec{P}}$ should be constructed; using them one can either set up the full coupled equations immediately in that representation or solve Eq. (43) and find the exact diabatic representation.

In going from Eq. (43) to Eq. (44), I assumed that the initial molecular representation had the correct dissociation properties at infinity, separating to the proper states of the separated atoms. If that is not the case the representation that is obtained from Eq. (44) or (45) will have the proper diabatic properties but will not dissociate correctly. However, as we have seen this can be easily corrected by making a second unitary transformation whose coefficients are independent of R, and which is chosen to restore the proper conditions at infinity by diagonalizing $\underline{U}(\infty)$.

In the practical treatment of collision problems it may sometimes be desirable to change representations in different parts of the problem, for instance by using the diabatic representation near a crossing and the adiabatic one in other regions, or perhaps by forming a partial diabatic combination from a small subset of the adiabatic states which are expected to interact especially strongly with each other.

5. Angular Diabatic Representations

A third representation can be achieved by diagonalizing $\underline{P}_{\Theta}(R)$, using the transformation equation (30) and performing a diagonalization of the usual type. The same procedure can be applied to diagonalize any other of three matrices $\underline{Q}_i(R)$ [Eq. (25)] together with the matrix

$$\underline{Q}^2(R) = \sum_i \underline{Q}_i^{\,2}(R)\,, \tag{50}$$

which clearly commutes with all of them. Obviously, none of these matrices commutes with $\underline{P}_R$:

$$[\underline{P}_R^{\,m}\,, \underline{Q}_i^{\,m}] = \frac{\hbar}{i}\,\frac{\partial}{\partial R}\,\underline{Q}_i^{\,m}(R)\,. \tag{51}$$

Furthermore, none of these matrices except

$$\underline{L}_z(R) = R\underline{Q}_z(R) = \langle\,|\,L_z\,|\,\rangle \tag{52}$$

commutes with $\underline{U}(R)$. Representations based on these matrix diagonalizations may be useful for dealing with crossings between states of different symmetry where angular coupling is important; they lead to what can be called angular diabatic representations, in distinction to the simple (or radial) diabatic one.[16]

6. An Example: Radial Coupling

Consider a two-state diabatic interaction with the real potential matrix

$$\underline{U}^{d}(R) = \begin{pmatrix} U_{11}^{\,d}(R) & U_{12}^{\,d}(R) \\ U_{12}^{\,d}(R) & U_{22}^{\,d}(R) \end{pmatrix}\,. \tag{53}$$

The matrix that diagonalizes $\underline{U}^{d}$ can be written

$$\begin{gathered} \underline{C}(R) = \begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix}\,, \quad \alpha = \alpha(R)\,, \\ \tan 2\alpha = 2U_{12}^{\,d}(R)/[U_{22}^{\,d}(R) - U_{11}^{\,d}(R)]\,. \end{gathered} \tag{54}$$

The adiabatic potential matrix is then

$$\underline{U}^{a}(R) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \bar{U}(R) + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} u(R)\,, \tag{55}$$

$$\begin{aligned} \text{where}\quad \bar{U}(R) &= \tfrac{1}{2}[U_{11}^{\,d}(R) + U_{22}^{\,d}(R)]\,, \\ U_d(R) &= \tfrac{1}{2}[U_{11}^{\,d}(R) - U_{22}^{\,d}(R)]\,, \\ u^2(R) &= U_d^{\,2}(R) + [U_{12}^{\,d}(R)]^2\,. \end{aligned} \tag{56}$$

The adiabatic radial momentum matrix is

$$\underline{P}_R^{\,a}(R) = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \hbar\,\alpha'(R)\,, \tag{57}$$

$$\begin{aligned} \alpha'(R) = \frac{\partial\alpha}{\partial R} &= \frac{1}{2u^2(R)} \\ &\times [U_{12}^{\,d}(R)U_d'(R) - U_d(R)U_{12}'(R)]\,\cdot \end{aligned} \tag{58}$$

In the matrix $\underline{B}$ we encounter both

$$(\underline{P}_R^{\,a})^2 = \underline{1}\,\hbar^2[\alpha'(R)]^2\,, \tag{59}$$

which is diagonal and provides no coupling, and the divergence term

$$p_R^{\text{div}}\,\underline{\mathrm{P}}_R^{\mathrm{a}}(R) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \hbar^2 [\alpha''(R) + \frac{2}{R}\,\alpha'(R)] , \tag{60}$$

which is seen to be anti-Hermitian. The only Hermitian coupling term occurring in $\underline{\mathrm{S}}_R$ is

$$\underline{\mathrm{P}}_R^{\mathrm{a}}(R) p_R = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \hbar^2 \alpha'(R) \frac{\partial}{\partial R} , \tag{61}$$

which is indeed Hermitian in its operation on the nuclear wave function.

The case of a curve crossing, there is a point R_{x} where the difference potential $U_d(R_{\mathrm{x}})$ vanishes. At that point we have

$$\alpha'(R_{\mathrm{x}}) = U_d'(R_{\mathrm{x}})/2U_{12}^{\mathrm{d}}(R_{\mathrm{x}}) = 1/\Delta R_{\mathrm{x}} . \tag{62}$$

In the Landau-Zener model both U_d' and U_{12}^{d} are assumed to be constants in the region around R_{x}. α' is then also constant, and its reciprocal ΔR_{x} is a length characterizing the effective width of the crossing region.

In the collision problem there is no advantage in diagonalizing the matrix $\underline{\mathrm{U}}$, unless the new off-diagonal element introduced in the matrix $\underline{\mathrm{P}}_R$ is smaller than the original $U_{12}(R)$ that was transformed away. This gives a criterion that can be used to decide when such a transformation is advantageous, and when not. The matrix $\underline{\mathrm{P}}_R$ appears in (61) in a product with the radial component of the nuclear momentum, which we can incorporate in the dimensionless ratios

$$\lambda_i(R) = \hbar\alpha'(R) v_{Ri}(R)/2U_{12}^{\mathrm{d}}(R) , \tag{63}$$

where the radial velocity v_R strictly varies with state,

$$\tfrac{1}{2} M v_{Ri}^2(R) = E - U_{ii}(R) - l(l+1)\hbar^2/2MR^2 . \tag{64}$$

When evaluated at R_{x} these reduce to the single constant

$$\lambda(R_{\mathrm{x}}) = \frac{\hbar v_R(R_{\mathrm{x}})}{2U_{12}(R_{\mathrm{x}})\Delta R_{\mathrm{x}}} = \frac{v_R(R_{\mathrm{x}})}{v_{\mathrm{x}}} , \tag{65}$$

where v_{x} is a characteristic velocity that appears also in the Landau-Zener transition probability.

In (63) the numerator represents the adiabatic coupling and the denominator the diabatic coupling. Thus we see from (65) that there is always some velocity below which the diabatic coupling exceeds the adiabatic even at the crossing point, so that the diabatic representation loses its advantage at low velocity.

Next we may look at the behavior of (63) in the limit of large R. In that case we must expect the limits

$$U_{12}(\infty) = 0 , \quad U_{12}'(\infty) = 0 , \quad U_d'(\infty) = 0, \quad U_d(\infty) = \text{const} , \tag{66}$$

while we may expect the logarithmic derivative of $U_{12}(R)$ to go to a finite limit,

$$- U_{12}(R)/U_{12}'(R) = s_{12}(R) \rightarrow s_{12}(\infty) . \tag{67}$$

The ratios λ_i of (63) then all go to the common limit,

$$\lambda(\infty) = \hbar v_\infty / 4U_d(\infty) s_{12}(\infty) , \tag{68}$$

which again suggests that the diabatic representation is preferable at higher velocities and the adiabatic one at lower. It is easy now to see from the form of (63) that the diabatic representation is preferable at all R at high velocities. We can expect the same thing to hold for the many-state as well as the two-state situation. A sketch comparing the magnitudes of the diabatic and adiabatic terms is given in Fig. 1.

A second contribution to the adiabatic coupling comes from the anti-Hermitian divergence term (60); this term involves the second derivative

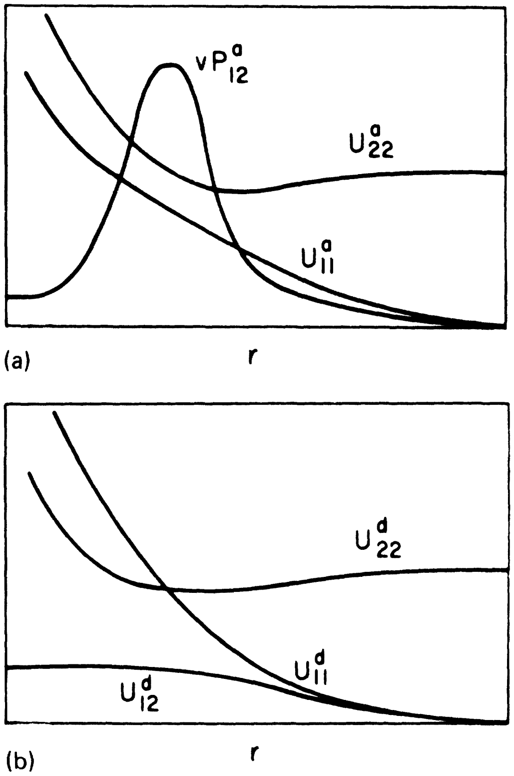

FIG. 1. Potentials and coupling matrix elements for a two-state crossing (qualitative behavior). (a) Adiabatic potentials $U_{11}^{\mathrm{a}}(R)$ and $U_{22}^{\mathrm{a}}(R)$ and the product of the velocity and the momentum coupling element, $vP_{12}^{\mathrm{a}}(R)$. (b) The elements of the diabatic potential matrix $U_{ij}^{\mathrm{d}}(R)$.

$$\begin{aligned}\alpha''(R) = &-[2\alpha'(R)/u^2(R)] \\ &\times[U_d(R)U_d'(R) + U_{12}(R)U_{12}'(R)] \\ &+[1/2u^2(R)] \\ &\times[U_{12}(R)U_d''(R) - U_d(R)U_{12}''(R)]\ , \end{aligned} \tag{69}$$

which gives

$$\alpha''(R_{\mathrm{x}}) = -\frac{U_d'(R_{\mathrm{x}})U_{12}'(R_{\mathrm{x}})}{U_{12}^2(R_{\mathrm{x}})} + \frac{U_d''(R_{\mathrm{x}})}{2U_{12}(R_{\mathrm{x}})}\ . \tag{70}$$

A comparison between the magnitudes of the diabatic potential interaction and the adiabatic divergence term (60) leads to a second dimensionless ratio,

$$\mu(R) = \frac{\hbar^2[\alpha''(R) + 2R^{-1}\alpha'(R)]}{2MU_{12}(R)}\ ; \tag{71}$$

this quantity is independent of the velocity. In the Landau-Zener (LZ) special case we have $\alpha_{\mathrm{LZ}}''(R_{\mathrm{x}}) = 0$ and therefore

$$\begin{aligned}\mu_{\mathrm{LZ}}(R_{\mathrm{x}}) &= \frac{\hbar^2 U_d'(R_{\mathrm{x}})}{2MR_{\mathrm{x}}U_{12}^2(R_{\mathrm{x}})} \\ &= \frac{\hbar^2}{MU_{12}(R_{\mathrm{x}})R_{\mathrm{x}}\Delta R_{\mathrm{x}}} \\ &= \frac{2\hbar}{Mv_{\mathrm{x}}R_{\mathrm{x}}}\ . \end{aligned} \tag{72}$$

In general the adiabatic coupling will be a sum of the velocity coupling (61) and the static divergence coupling (60), so that we must really consider the sum $\lambda(R) + \mu(R)$. As an example, in the Landau-Zener case and looking at the crossing point only, we have [combining (65) and (72)]

$$\lambda(R_{\mathrm{x}}) + \mu_{\mathrm{LZ}}(R_{\mathrm{x}}) = \lambda(R_{\mathrm{x}})\left(1 + \frac{2\hbar}{MR_{\mathrm{x}}v_R(R_{\mathrm{x}})}\right)\ . \tag{73}$$

As would be expected, the velocity coupling dominates at high velocities, and the diabatic representation is preferable in that limit. The divergence coupling may dominate only when the velocities are so low that the deBroglie wavelength at the crossing point exceeds the distance R_{x} itself.

7. Another Example: Angular Coupling

In both diabatic and adiabatic representation, the angular coupling of Eqs. (33) and (34) may be important, and it should be considered along with the radial coupling. Since $\underline{\mathrm{L}}_z$ and $\underline{\mathrm{L}}_x^2 + \underline{\mathrm{L}}_y^2$) are diagonal, the angular coupling is confined to the terms in (34). For the present illustration let us assume that the nuclear motion is in the plane $\Phi = 0$ (or $Y = 0$) and ignore the out-of-plane momentum term in $\partial/\partial\Phi$. Then $-i\hbar\,\partial/\partial\Theta$ can be identified semiclassically with the nuclear angular momentum component $J_Y = Mv_\infty b$, where b is the impact parameter. The coupling terms remaining in (34) are then a static one $\underline{\mathrm{X}}_{\mathrm{s}}$ and a dynamic one $\underline{\mathrm{X}}_{\mathrm{d}}$,

$$\begin{aligned}\underline{\mathrm{X}}_{\mathrm{s}} = \cot\Theta\,[&\underline{\mathrm{L}}_x(R)\underline{\mathrm{L}}_z(R) + \underline{\mathrm{L}}_z(R)\underline{\mathrm{L}}_x(R) \\ &- i\hbar\,\underline{\mathrm{L}}_y(R)]\ ,\quad \underline{\mathrm{X}}_{\mathrm{d}} = 2\underline{\mathrm{L}}_y(R)J_Y\ . \end{aligned} \tag{74}$$

The static coupling terms are of no special interest, behaving much like the potential coupling. The dynamic term is more interesting, because its magnitude increases with the velocity so that it may become a dominant coupling term. This may happen especially at crossings which persist even in the adiabatic representation, particularly crossings between states of differing molecular symmetry. In that case the potential coupling $U_{12}(R)$ in the ordinary (radial) diabatic representation vanishes, and the dynamic angular coupling takes over. We now may wish to decide whether to use an ordinary radial diabatic representation, or an angular one.

The dynamic coupling term in the radial diabatic representation depends on the off-diagonal element of $\underline{\mathrm{L}}_Y$,

$$W(R) = \frac{L_{Y,12}(R)J_Y}{2MR^2} = \frac{L_{Y,12}(R)v_\infty b}{2R^2}\ , \tag{75}$$

We can now change to an angular diabatic representation, diagonalizing the matrix

$$\begin{pmatrix} U_{11}{}^{\mathrm{d}}(R) & W(R) \\ W(R) & U_{22}{}^{\mathrm{d}}(R) \end{pmatrix} \tag{76}$$

by equations precisely similar to (54) *ff*. The transformation is a rotation matrix like (54), but with the angle $\beta(R)$ defined by

$$\tan 2\beta = -W(R)/U_d(R)\ . \tag{77}$$

In the angular representation the most important coupling at high velocity is a dynamic one like (61). We therefore form the dimensionless ratio between the coupling $W(R)$ and $|P_R{}^{\mathrm{ang}}|v_R(R)$, where the superscript "ang" denotes the angular diabatic representation:

$$\begin{aligned}\nu(R) &= \frac{W(R)}{v_R P_R{}^{\mathrm{ang}}(R)} = \frac{W(R)}{\hbar\beta'(R)v_R(R)} \\ &= \frac{2W(R)[U_d^2(R) + W^2(R)]}{\hbar v_R(R)[W(R)U_d'(R) - U_d(R)W'(R)]}\ . \end{aligned} \tag{78}$$

Referring to (75), and assuming fixed impact parameter b, we see that the numerator contains a higher power of v than the denominator. At high velocities, then, the angular diabatic representation may be preferable to the radial one.

8. Generalized Adiabatic Representations

We have seen that it is important in the coupled equations (10) to give separate consideration to the dynamic coupling terms $\vec{\underline{P}} \cdot \vec{p}^{\,\mathrm{nu}}$ and to the non-Hermitian divergence terms $\vec{p}^{\,\mathrm{div}} \cdot \vec{\underline{P}}$. However, the static Hermitian term $(1/2M)^{-} \vec{\underline{P}} \cdot \vec{\underline{P}}$ can be added to $\underline{U}$ to form an augmented potential matrix $\underline{W}$, so that the matrix Hamiltonian can be written

$$\underline{\mathcal{H}} = \underline{\mathcal{T}} + \underline{U} = T^{\mathrm{nu}} + \underline{W}(R, \Theta)$$

$$+ (2M)^{-1}(\vec{p}^{\,\mathrm{div}} \cdot \vec{\underline{P}} + 2\vec{\underline{P}} \cdot \vec{p}^{\,\mathrm{nu}}). \qquad (79)$$

The augmented potential can in turn be split into two portions,

$$\underline{W}(R, \Theta) = \underline{U} + (2M)^{-1} \vec{\underline{P}} \cdot \vec{\underline{P}} = \underline{W}_R(R) + \underline{W}_\Theta(R, \Theta), \qquad (80)$$

where

$$\underline{W}_R(R) = \underline{U}(R) + (2M)^{-1} \underline{P}_R{}^2(R)$$

$$+ (2MR^2)^{-1}[\underline{L}_x{}^2(R) + \underline{L}_y{}^2(R)], \qquad (81)$$

and

$$\underline{W}_\Theta(R, \Theta) = (2MR^2)^{-1} \cot\Theta [\underline{L}_x(R) \underline{L}_z(R)$$

$$+ \underline{L}_z(R) \underline{L}_x(R) + \underline{L}_z{}^2(R) \cot\Theta]. \qquad (82)$$

We can now obtain two generalized adiabatic representations, depending on whether we diagonalize only the R-dependent portion $\underline{W}_R(R)$ or the whole augmented potential $\underline{W}(R, \Theta)$. The second alternative obviously involves more labor, because of the Θ dependence. In general, I expect these representations to be of far less value than the diabatic ones, but they may have some usefulness in occasional situations at low energy.

9. Hermiticity of the Equations

Equation (60) reveals an awkward feature of the coupled equations (10), the non-Hermiticity of $\underline{B}$, Eq. (7), and therefore of $\underline{\mathcal{T}}$ also. In fact it can be shown that

$$\underline{B} + \underline{B}^{\dagger} = 2\vec{\underline{P}} \cdot \vec{\underline{P}}, \qquad (83)$$

and $\underline{B} - \underline{B}^{\dagger} = 2\vec{p}^{\,\mathrm{div}} \cdot \vec{\underline{P}}$; $\qquad (84)$

the latter, obviously, is the non-Hermitian term. Though it would be easy to restore Hermiticity by omitting the divergence term, the solutions $\psi_k(R)$ of the resulting equations, when combined with the χ_k to form Ω [Eq. (2)], would not give a proper solution of the original Schrödinger equation. The non-Hermitian divergence term must therefore be included in the coupled equations. Evidently this is a reflection of the fact that if Eq. (2) is looked upon as a transformation connecting the functions Ω and ψ_k, it is not necessarily a unitary transformation.

10. United Atom Representations

At small internuclear distances it is convenient to use a united-atom representation using as a basis the unperturbed wave functions $\chi_k{}^{\mathrm{w}}(\vec{r})$ for the united atom, with the electron coordinates $\vec{r}$ measured in a nonrotating frame. In that case the potential matrix $\underline{U}^{\mathrm{w}}$ will depend on R, and all components of the vector matrix $\underline{P}^{\mathrm{w}}$ will vanish identically. The latter property makes the coupled equations particularly simple, and this representation has the diabatic property for both the radial and angular parts of $\vec{\underline{P}}^{\mathrm{w}}$. However, as R becomes large one must pay for this simplicity by coupling together a large number of states, because many off-diagonal terms in $\underline{U}^{\mathrm{w}}(R)$ become large.

A rotating united-atom representation is also possible, where we can use as a basis the united-atom functions $\chi_k{}^{\mathrm{r}}(\vec{r}\,')$ with the electron coordinates $\vec{r}\,'$ rotating with $\vec{R}$. In this representation $\underline{P}_R{}^{\mathrm{r}}$ vanishes, but $\underline{P}_\Theta{}^{\mathrm{r}}$ and $\underline{P}_\Phi{}^{\mathrm{r}}$ do not. However, the latter matrices will be constant, independent of R.

11. The Molecular Scattering Matrix

The development thus far has been devoted to formulating the complete set of matrix elements needed for the atomic collisions problem based on a set of molecular electronic wave functions computed in the usual way at fixed values of the internuclear distance R. The various representations obtained by diagonalizing one or another of the matrix elements are all connected with each other, and any one of them could be used for setting up the coupled equations for the heavy-particle motion that must ultimately be solved. If these equations could be solved in full, any representation would be as good as another; differences come in only when approximations are used or a truncated set of states is employed – as always must be done in practice.

The computational problem of solving the coupled equations will not be discussed in this paper. The aim of such a computation is usually to obtain the scattering matrix, from which cross sections can be deduced by simple procedures.

It is, however, of some importance to look more closely at the content of the scattering matrix in the molecular coordinate frame. First, let us note that the force matrix $\underline{\vec{F}}$ [Eq. (11)] vanishes as $R \to \infty$, and the matrix $\underline{U}$ commutes with $\underline{\vec{P}}$ in the limit; the asymptotic form of the molecular electronic wave functions can therefore be taken so as to diagonalize $\underline{U}$ even in a diabatic representation. Accordingly, the scattering matrix is indeed independent of the representation being used.

The molecular wave functions and matrix elements we have been discussing are defined in a molecular frame where $\vec{R}$ is the internuclear vector and the electronic coordinates $\vec{r}_i$ (space fixed) or $\vec{r}_i{}'$ (rotating with $\vec{R}$) are measured from the internuclear center of mass. In this frame the asymptotic form of an incoming (−) or outgoing (+) spherical wave of angular momentum $l\hbar$ in the molecular state j can be written

$$\Omega^{\pm}_{jlm}(E,\vec{R},\vec{r}) = R^{-1} v_j^{-1/2} F_l^{\pm}(K_j R) \times Y_{lm}(\Theta,\Phi)\chi_j(R,\vec{r}\,') , \qquad (85)$$

where Y_{lm} is a standard spherical harmonic, v_j is the velocity, and K_j the wave number, and the functions F are given by

$$\begin{aligned} F_0(x) &= e^{-ix} \\ F_l^{-}(x) &= [F_l^{+}(x)]^* = x^l \frac{d}{dx}[x^{-l}F_{l-1}(x)] \\ &= i^{-l}e^{-ix}[1 - i\,l(l+1)/2x + \cdots] . \end{aligned} \qquad (86)$$

The velocity and wave number are obviously related to the total energy E by

$$\{2M[E - U_{jj}(\infty)]\}^{1/2} = Mv_j = \hbar K_j . \qquad (87)$$

The natural boundary condition to take in the molecular frame is a single incoming state j connected by the molecular scattering matrix $\underline{S}^{\mathrm{m}}$ with a number of outgoing states k, so that the full solution has the limiting form given by

$$\Omega^{\mathrm{m}}_{jlm}(E,\vec{R},\vec{r}) \to \Omega^{-}_{jlm}(E,\vec{R},\vec{r}) - \textstyle\sum_{k,l',m'} \underline{S}^{\mathrm{m}}_{jk}(E;lm,l'm')\Omega^{+}_{kl'm'}(E,\vec{R},\vec{r}) . \qquad (88)$$

It is important to recognize that the expression (88) represents the asymptotic form of a complete solution to the collision problem, in the sense that no terms have been omitted from the Hamiltonian H and that the family of solutions of this form make up a complete set, so that any other solutions can be expressed in terms of these functions. It is also very important to note that the molecular boundary condition used here does not accurately represent the physical situation of two atoms colliding or separating with their respective electron clouds in motion along with the nuclei; this situation, which was emphasized by Bates and McCarroll,[17] is especially important at high energies. This physical situation must be dealt with by applying atomic instead of molecular boundary conditions; I hope to discuss it further in a separate publication.

12. Ionizing States

In principle, states with one or more electrons liberated into the continuum can be handled in a molecular representation without any formal difficulty, since these states remain orthogonal to the bound states. In practice metastable autoionizing states are often especially important, and it is frequently desirable to treat them as if they were bound states rather than as parts of the continuum. If the continuum is also included, special care must be taken to insure that all the states represented are properly orthogonal, or to insure that any lack of orthogonality is represented where necessary by additional terms in the equations.

13. Polyatomic Systems

This development has been carried out with diatomic systems exclusively in mind. However, it can formally be generalized to polyatomic systems, including the collision of atoms with diatomic molecules as one of the simplest cases. Formally the vector $\vec{R}$ must then be treated as six dimensional (or larger). A greater number of representations is then possible, including ones where the molecular binding is changed, as in the three systems $A + BC$, $C + AB$, and $B + CA$, with the fourth possibility of three free particles $A + B + C$. One way of treating such a system would be to introduce the generalized distance coordinates[18] appropriate to three-body (or many-body) problems and define a radial diabatic representation using that generalized distance in the definition of $\underline{P}_R$.

Polyatomic systems are particularly important because of the necessity for treating chemical reaction problems by a well-based collision theory. The prevalence of curve crossings even in diatomic systems that has recently been revealed by both theory and experiment suggests that such crossings will be even more important in triatomic and larger systems. For that reason the development of a theoretical basis for treating such problems is becoming urgent.

At the present moment much effort is going into the computerized study of chemically reactive collisions using an assumption of adiabatic potential surfaces. The importance of nonadiabatic terms in the collision equations must also be recognized.

I believe that calculations based on a single-potential energy surface will be of very limited usefulness in the real world of chemically reacting systems, and that electronic transitions between a multiplicity of states are likely to play a very large role in such events.[19,20,21] Even where adiabatic calculations with a single potential surface are valid, it is desirable to demonstrate their validity, and this can only be done in the framework of a theory which takes proper account of all the couplings between states that may exist, so that they can be evaluated and proved to be small. If these couplings are strong, quantum effects associated with such nonadiabatic behavior may prove to be one of the most important features of many chemical reaction processes. Probably such quantum effects will turn out to be more important than the quantum effects associated with barrier leakage and vibrational zero-point energy that are often discussed in connection with the movement of systems over adiabatic surfaces.

C. SUMMARY

This paper has two principal aims:
(1) To recapitulate concisely the coupled equations for the general inelastic atomic scattering, including the expressions available for the calculation of the necessary matrix elements from molecular wave functions, and (2) to establish a general definition of a diabatic representation suitable to the dynamical collision problem just as rigorous as the definition of the adiabatic representation.

Using a molecular coordinate system, the complete collision problem is transformed into a frame rotating with the internuclear axis and a Born-Oppenheimer separation of nuclear and electronic wave functions is introduced. At each value of R the electronic wave functions must form a complete and orthogonal set, but otherwise they may be chosen freely in a variety of representations. All the terms in the coupled equations for the nuclear motion are then examined. The matrices needed for this dynamical problem are of three types: a potential matrix $\underline{U}$, the angular momentum matrices $\underline{L}_x$, $\underline{L}_y$, and $\underline{L}_z$, and the radial momentum matrix $\underline{P}_R$. Related to these are some force matrices, which provide an alternative route for the calculation of the momentum matrices.

Special representations can be generated by diagonalizing one or another of the above matrices. The well-known adiabatic representation is obtained by diagonalizing $\underline{U}$. In this paper I propose to define the diabatic representation as one that diagonalizes the momentum matrix $\underline{P}_R$ at all values of R. The transformation leading to this representation from any other can be expressed as either a differential or an integral equation, provided that the radial momentum matrix is known in the initial representation. Simple molecular orbital representations that neglect the configuration interaction are often, as Lichten has observed. good approximations to the diabatic representation, and therefore form a better starting point for arriving at the diabatic representation than does the adiabatic representation. The formal parallel between the integral equation for the diabatic representation and the integral equation of the Lippmann-Schwinger theory for the scattering matrix can be used to introduce a variational principle, although its practical utility is not yet clear.

After an examination of some schematic examples involving coupling of two states only, several other possible representations are briefly discussed, each of them being generated by diagonalizing one of the matrices of the full coupled equations. The structure of the scattering matrix in the molecular coordinate frame is briefly examined. Finally, the possibility of extending these procedures to molecular collisions, three-body processes, and chemically reactive collisions is pointed out.

---

*Supported in part by National Aeronautics and Space Administration, Goddard Space Flight Center, and in part by Stanford Research Institute.

[1] M. Born and J. R. Oppenheimer, Ann. Physik 84, 457 (1927).

[2] H. S. W. Massey and R. A. Smith, Proc. Roy. Soc. (London) A142, 142 (1933).

[3] R. deL. Kronig, *Band Spectra and Molecular Structure* (Cambridge University Press, New York, 1930).

[4] M. Born, Nachr. Akad. Wiss. Göttingen, II Math-Physik. Kl. 1951, Nr. 6; M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), Appendix VIII.

[5] W. R. Thorson, J. Chem. Phys. 34, 1744 (1961); 42, 3878 (1965).

[6] L. D. Landau, Physik. Z. Sowjetunion 2, 46 (1932).

[7] C. Zener, Proc. Roy. Soc. (London) A137, 696 (1932).

[8] E. C. G. Stueckelberg, Helv. Phys. Acta 5, 369 (1932).

[9] D. R. Bates, Proc. Roy. Soc (London) A257, 22 (1960); Atomic and Molecular Processes, edited by D. R. Bates (Academic Press, Inc., New York, 1962), p. 608.

[10] E. E. Nikitin, in Chemische Elementarprozesse, edited by H. Hartmann (Springer-Verlag, Berlin, 1968).

[11] W. Lichten, Phys. Rev. 131, 229 (1963); 139, A27 (1965); 164, 131 (1967).

[12] T. F. O'Malley, Phys. Rev. 162, 98 (1967).

[13] F. T. Smith, R. P. Marchi, W. Aberth, D. C. Lorents, and O. Heinz, Phys. Rev. 161, 31 (1967).

[14] E. Everhart, Phys. Rev. 132, 2083 (1963); D. C. Lorents and W. Aberth, Phys. Rev. 139, A1017 (1965).

[15] B. A. Lippmann and J. Schwinger, Phys. Rev. 79, 469 (1950).

[16] W. Lichten, Bull. Am. Phys. Soc. 13, 596 (1968).

[17] D. R. Bates and R. McCarroll, Proc. Roy. Soc. (London) A245, 175 (1958).

[18] F. T. Smith, Phys. Rev. 120, 1058 (1960); J. Math. Phys. 3, 735 (1962).

[19] B. A. Thrush, Ann. Rev. Phys. Chem. 19, 371 (1968).

[20] J. L. Magee, J. Chem. Phys. 8, 687 (1940).

[21] D. R. Herschbach, in Molecular Beams, edited by J. Ross (Interscience Publishers, New York, 1966), p. 319.