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Slow Heavy-Particle Collision Theory Based on a Quasiadiabatic Representation of the Electronic States of Molecules*

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Collisions between heavy particles which entail a change in electronic state (such as changes in ionization or excitation) are considered in the low-velocity ($v \ll 1$ a.u.) region. The electronic part of the problem is treated in a way which is both exact and at the same time lends itself most directly to the solution of the collision problem. This is done by introducing a representation of the electronic Hamiltonian H_{el} for the molecular system which is *exact but nondiagonal*. The basis states, which are a generalization of the resonant and potential scattering states of resonance theory, are not constrained by the noncrossing rule. Using these states as an expansion basis, the full Schrödinger equation for the collision is reduced to an effectively finite set of coupled two-body equations for the heavy-particle motion. The only approximation made, aside from small velocity, is the Born-Oppenheimer approximation. Therefore, both the electronic problem and the resultant problem of coupled heavy-particle motions may be treated with an accuracy that should be comparable with that of the corresponding molecular-stationary-state calculations.

I. INTRODUCTION

THE present paper is concerned with slow ($v \ll 1$ a.u.) reactive collisions between atoms or ions, $A^m + B^n \rightarrow A^o + B^p$, where the superscripts indicate the state of ionization or excitation of the atom. These reactions comprise certain charge-exchange and mutual neutralization collisions as well as collisional excitation and deexcitation of atoms (including elastic scattering), and have a bearing on some noncollisional processes resulting in dissociation such as predissociation and photon-induced dissociation.

Since this class of reactions involves a change of electronic state, Bates and Massey[1] have been able to describe them with some success using the Landau-Zener two-state theory.[2] This theory starts with two "zeroth-order" electronic states whose potential energy curves cross (or pseudocross), and then calculates semiclassically the probability of a transition from one zeroth-order state to the other. This approach can in principle be improved on in two independent ways. First, it has been pointed out that the semiclassical solution of the nuclear-motion problem may sometimes leave something to be desired,[3] so that there is need for both refinement and generalization of the nuclear problem. Secondly, the electronic part of the problem in the Landau-Zener approach has never been well formulated. The situation is so bad that the so-called zeroth-order electronic states, which are the starting point of the theory, are simply not defined (for states of the same symmetry) except that they must be "sufficiently inaccurate" that they violate the noncrossing rule of von Neumann and Wigner.[4]

It is the purpose of the present paper to put *the electronic part* of the problem on a better footing. In particular, we require the treatment of the electronic Hamiltonian H_{el} to have the following two properties: (1) It must be *exact* and explicitly defined, in contrast with the zeroth-order states mentioned above, so that among other things one may be able to take full advantage of the progress which has been made in recent years in the art of calculating the discrete electronic states of molecular systems. (2) The electronic problem should be treated in such a way that if possible the very valuable Born-Oppenheimer approximation remains fully valid to the same extent that it is valid for the stationary states of molecules. Requirement (1) differentiates the present treatment from the Landau-Zener approach, while requirement (2) rules out the use of the conventional adiabatic states as will be shown.

To satisfy these two conditions, it has been found necessary to introduce a new *quasiadiabatic representation* of H_{el}. In contrast with the conventional adiabatic representation used exclusively by chemists and spectroscopists, which is diagonal, the new representation is *nondiagonal*, with the off-diagonal matrix elements furnishing the coupling for the electronic transitions. An interesting consequence of the nondiagonality is that the potential curves in this representation are not constrained by the noncrossing rule[4] so that they freely cross one another.

Section II of the paper is devoted to the derivation and analysis of this nondiagonal representation of N_{el}. In Sec. III, the solution of the full collision problem is expanded in the states of the quasiadiabatic representation, and the exact coupled equations for the heavy-particle motion are derived in a form which it is believed should be immediately useful. Section IV is a summary.

II. QUASIADIABATIC REPRESENTATION OF H_{el}

In order to introduce the representation of the electronic Hamiltonian H_{el} on which the solution of the

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[1] D. R. Bates and H. S. W. Massey, Phil. Mag. **45**, 112 (1954).

[2] L. Landau, Physik. Z. Sowjetunion **2**, 46 (1932); C. Zener, Proc. Roy. Soc. (London) **A137**, 696 (1932); E. C. G. Stueckelberg, Helv. Phys. Acta **5**, 370 (1932).

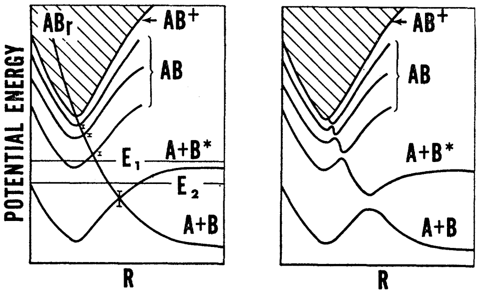
[3] D. R. Bates, Proc. Roy. Soc. (London) **A257**, 22 (1960).

[4] J. von Neumann and E. P. Wigner, Physik Z. **30**, 467 (1929).

collision problem in Sec. III depends, the reader's indulgence is asked while we consider a physical process which is not included in the direct subject matter of the present paper but which leads us most directly into this new representation, namely, dissociative recombination ($e+AB^+\rightarrow AB_r\rightarrow A+B$). This process is universally described in terms of a set of potential energy curves such as those of Fig. 1(a), which depicts schematically all the electronic "states" (for a particular symmetry) of the molecular system AB, including the electronic continuum (shaded region), a dissociating state AB_r, and a Rydberg series of discrete states.

According to this picture, recombination occurs through an electronic transition from the electronic continuum to the discrete state AB_r which crosses it, and this latter state then dissociates directly to the products $A+B$. While this picture seems natural, if we ask critically what these states are and how they are defined, it becomes clear that they are *not* the eigenstates of H_{el}, i.e., the conventional adiabatic states which diagonalize this operator. This is seen most directly when we remember that the adiabatic states are strictly bound by the noncrossing rule,[4] whereas the state AB_r in Fig. 1(a) flagrantly violates this rule, by first crossing the entire Rydberg series, and even worse by cutting through the continuum[5] as well. By contrast, the way that the *adiabatic* states would look for the same system is indicated schematically in Fig. 1(b), which one can see renders the dissociative attachment process quite incomprehensible.

Since the curves of Fig. 1(a) which are necessary to explain dissociative attachment do not belong to the conventional adiabatic states, we must ask *what are they*? From the discrete region alone, this would present quite a serious puzzle, which might defy solution. However, when we consider the region where the curve AB_r crosses the continuum, the proper interpretation of these crossing states soon becomes clear, for a discrete state like AB_r which is degenerate with (crosses) a continuum is a familiar situation in theoretical physics and has been dealt with exhaustively.[6] Such a discrete state is, of course, a *resonance*. It is not an actual eigenstate of the Hamiltonian (H_{el} here) but requires an artificial constraint for its definition as described below, and hence is often called a "quasistationary state." It was by the use of such states and a special decomposition or representation of the Hamiltonian based on them, that the problem of dissociative attachment ($e+AB\rightarrow AB_r^-\rightarrow A^-+B$, closely related to dissociative recombination) has recently been successfully treated in a fully quantitative way.[7,8] It is the purpose of this paper to define a similar representation of H_{el} in the discrete as well as the continuous region of Fig. 1(a), in order to put the problem of slow heavy-particle collisions on a similar firm footing, so that it may be discussed as simply as possible and with a minimum of approximations.



(a) (b)

FIG. 1. Potential-energy curves for a typical molecular system AB, exhibiting schematically the electronic states of single symmetry, including the electronic continuum (shaded region), a discrete Rydberg series, and a dissociating state AB_r. In (a) the states belong to the quasiadiabatic representation of H_{el}, exhibited in Eq. (5). Note that AB_r in (a) cuts across all the other states. The vertical markers at each crossing indicate twice the magnitude of the coupling terms V_i. (E_1 and E_2 are merely typical energies.) The curves in (b) belong to the conventional adiabatic or diagonal representation of H_{el} for the same system. They are characterized by their strict adherence to the noncrossing rule, so that the former AB_r curve is now fragmented and prevented from either reaching or entering the continuum.

The definition of the resonance or quasistationary state for the auto-ionizing electronic states of molecules is discussed in some detail in Ref. 7 as well as elsewhere.[9] For the present purpose, the main features are as follows: The electronic wave function ϕ_r of the resonant state is artificially restricted in some way to a portion of Hilbert space by a projection operator Q^0, while its energy eigenvalue

$$\langle\phi_r Q^0 \mid H_{el} \mid Q^0\phi_r\rangle=\epsilon_r(R) \qquad (1)$$

is made stationary. (As in any adiabatic definition, the internuclear distance R appears parametrically in all quantities.)

Having defined ϕ_r, a new projection operator Q onto

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[5] The prohibition against crossing a continuum is rarely discussed, possibly because it turns out to be a trivial statement. If we remember that a particular adiabatic eigenstate of H_{el} is defined as the nth lowest-energy level of this operator ($n=1, 2, 3 \cdots$), then if we follow any such nth level from right to left, it is clear that, since it is the nth level for all R, it can never penetrate a finite distance into the continuum, but can at most become coincident with its lower limit [the AB^+ curve in Fig. 1(b)]. In a different context, this is discussed for the H_2^- system by E. R. Davison [J. Chem. Phys. **36**, 1080 (1962)].

[6] H. Feshbach, Ann. Phys. (N.Y.) **5**, 357 (1958); **19**, 287 (1962); and references to previous work therein contained.

[7] T. F. O'Malley, Phys. Rev. **150**, 14 (1966).

[8] The same approach is also in large part implicit in the earlier treatment of J. N. Bardsley, A. Herzenberg, and F. Mandl, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 415. However, the explicit approach of these authors does not lend itself to generalization in this direction.

[9] See for example, J. C. Y. Chen, J. Chem. Phys. **40**, 3513 (1964).

this state, together with its orthogonal complement P, are now constructed by

$$Q=|\phi_r\rangle\langle\phi_r|,\qquad P=1-Q. \tag{2}$$

These new operators P and Q may be used to exhibit the electronic Hamiltonian in the form of a nondiagonal matrix[7] (which will form the basis of the remaining discussion of this section) as follows:

$$H_{\mathrm{el}}=\begin{bmatrix} QH_{\mathrm{el}}Q & QH_{\mathrm{el}}P \\ PH_{\mathrm{el}}Q & PH_{\mathrm{el}}P \end{bmatrix}. \tag{3}$$

(The wave function operated on by H_{el} then becomes formally a vectorlike quantity with components $Q\phi=\phi_r$ and $P\phi$.) The eigenstates of the operator $PH_{\mathrm{el}}P$, with wave functions $\phi_{p,i}$ ($i=1, 2, \cdots$), satisfy the equation

$$PH_{\mathrm{el}}P\phi_{p,i}=\epsilon_{p,i}(R)\phi_{p,i}, \tag{4}$$

which may also be written in the same form as (1) for the eigenvalues of QHQ. These states are usually called potential scattering states, since they normally comprise the electronic continuum (scattering) states, with, however, the constraint imposed by P of orthogonality to the state ϕ_r. However, for the purpose of the present paper an important and necessary generalization must be made. The definitions (1) through (4) are here applied consistently *for all R*, even in the discrete region outside the shaded area of Fig. 1(a). As a result, the spectrum of $PH_{\mathrm{el}}P$, i.e., the so-called "potential scattering states," now includes not only the electronic continuum but also all of the discrete Rydberg states which are crossed by the curve AB_r to whose wave function ϕ_r they are constrained to be orthogonal.[10]

The eigenstates $\phi_{p,i}$ of the operator $PH_{\mathrm{el}}P$ from Eq. (4) may now be used to write the representation Eq. (3) of H_{el} in the more explicit form

$$H_{\mathrm{el}}=\begin{bmatrix} \epsilon_r & V_1 & V_2 & V_3 & \cdots \\ V_1 & \epsilon_{p1} & 0 & 0 & \cdots \\ V_2 & 0 & \epsilon_{p2} & 0 & \cdots \\ V_3 & 0 & 0 & \epsilon_{p3} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix}, \tag{5}$$

where

$$V_i(R)=(\phi_r,\ H_{\mathrm{el}}\phi_{p,i}). \tag{6}$$

The V_i which are the close analogs of $V_{\bar{a}}$ of Ref. 7 couple all states only to ϕ_r, the orthogonal state or states whose potential curve crosses theirs.[11,11a]

Consider Eq. (5) which plays a central role in the theory developed in this paper. It exhibits *an exact nondiagonal representation of* H_{el}, the electronic Hamiltonian. Since the representation (5) is adiabatic (as is any representation of H_{el}) but is based on the quasistationary states of this operator, it is called the *quasi-adiabatic representation* to distinguish it from the adiabatic representation used by the chemists, which is the exact *diagonal* representation.

Now since H_{el} is only a part of the full Hamiltonian H for the molecular system, there is now law of physics which says that it must be diagonal.[12] The analysis of the H_{el} problem simply furnishes us with *the raw material* for solving the total physical problem (in which the motion of the nuclei is always important). We may therefore prepare this raw material either in the form of a diagonal or nondiagonal representation, whichever best lends itself to solving the physical problem.

As was mentioned above, the nondiagonal quasi-adiabatic representation (3) as used in Ref. 7 had the remarkable effect of rendering the dissociative attachment problem not only tractable but even fairly simple. Upon reflection it is clear why the representation (3) lends itself so well to the analysis of this reaction while the diagonal adiabatic representation would not. The reason is that electron attachment involves a change in electronic state. As it turned out, it was precisely the off-diagonal matrix elements $PH_{\mathrm{el}}Q$ which gave the probability amplitude for the essential electronic transition.[13] It is for just this reason, namely, the presence of the off-diagonal matrix elements V_i connecting the different electronic states, that the presently defined

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[10] Note that it is just this constraint of orthogonality which allows these states to cross the curve AB_r. Since the derivation of the noncrossing rule assumes that the states discussed belong to the *same* Hamiltonian, it therefore does not hold between the states of $PH_{\mathrm{el}}P$ and those of $QH_{\mathrm{el}}Q$.

[11] It has been assumed that with the removal of ϕ_r none of the states left in P space tend to cross as did ϕ_r in Fig. 1(b). In order to be perfectly general, if this situation should develop in an unusual case, then a second ϕ_r would have to be defined in P space and the above procedure repeated, etc.

[11a] Y. Demkov [Dolk. Akad. Nauk SSSR **166**, 1076 (1966) (English transl.: Soviet Phys.—Doklady **11**, 138 (1966))] has represented the ionic and covalent molecular states in a form identical to Eq. (5).

[12] This important fact regarding molecular states seems to have been overlooked generally. For an exception, see W. Lichten, Phys. Rev. **131**, 229 (1963). Lichten's nondiagonal representation was an approximate one, based on single configuration molecular orbitals, but had a number of qualitative features in common with the present exact one. Quantitatively, however, even if one considers these single orbital states as the beginning of a full representation, the large magnitude of their off-diagonal matrix elements V_i, which are sometimes as great as several eV, would unfortunately rule out their use in a practical way for the purpose of the present paper. In a very recent paper, R. D. Levine [J. Chem. Phys. **46**, 331 (1967)] seems also to have employed this single configuration representation for a purpose similar to that of this paper.

[13] Conversely, it is clear why the *permanent* states of molecules, which involve no electronic transition (as opposed to collisions or reactions), are best described by the adiabatic representation, just because it *is* diagonal. It is presumably for this reason that the adiabatic representation has found such a favor among the spectroscopists and chemists, while being mainly a source of embarrassment to collision theorists.

nondiagonal representation (5) is chosen in the next section to describe the collision problem, which by definition is concerned with transitions between electronic states.

Since the quasiadiabatic representation of H_{el}, defined by Eqs. (1)–(5) applied for all R, is determined by the projection operator Q^0, this operator deserves further consideration before passing on to Sec. III. The Q^0 which we have assumed and which was used in defining the curves of Fig. 1(a) was that of Feshbach[14] or preferably some simplified version[15] of this projection operator, which describes a state in which an electron is bound to an *excited core*.[16] A good example in the literature of empirically determined molecular states which clearly correspond to ϕ_r as determined by Feshbach's Q^0, rather than to states of the adiabatic representation, are the states of He_2 known as B core states.[17] These have been interpreted as composed of an electron bound to the excited B state of the He_2^+ core, so that as pointed out in Ref. 7 they directly satisfy Feshbach's definition. Just as the AB_r curve of Fig. 1(a), these B core curves are entirely unaffected by the noncrossing rule in that they cut through the electronic continuum[5] at small R and then cross a complete Rydberg series.[18]

Of course there is a certain amount of flexibility in the choice of Q^0, and in fact *any artificial constraint* on the wave function which leads to a physically meaningful and useful state may legitimately be used. In addition to the core-excited states of Feshbach, there is at least one other obvious choice of the operator Q^0 which will sometimes be needed, namely, one which would explicitly define *an ionic state* for all R.[19] A set of potential curves for a representation based on such an ionic state is shown schematically in Fig. 2. To complicate matters a little, this representation might arise within the P space described by Fig. 1(a) (see Ref. 11). Finally, wherever there is a choice between Q^0's which differ only in complexity, perhaps the same criterion should be used as for resonant states, namely that Q^0 should be as simple as possible without, however, allowing the V_i to become large.

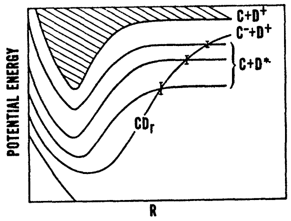

FIG. 2. Potential-energy curves shown schematically for the quasiadiabatic electronic states of the fictitious molecular system *CD*. These states (all of a particular symmetry) belong to a nondiagonal representation of H_{el} based on the quasistationary *ionic state* denoted CD_r. As in Fig. 1(a), the vertical markers are drawn equal to twice the off-diagonal coupling terms V_i at the crossings.

III. SOLUTION OF THE COLLISION PROBLEM

Given the nondiagonal quasiadiabatic representation of H_{el}, defined in the last section, it is now relatively straightforward to expand the total wave function ψ in the complete set of electronic wave functions ϕ_r and $\phi_{p,i}$ which are the basis of this representation; thus

$$\psi = Q\psi + P\psi = \phi_r \zeta_r(\mathbf{R}) + \sum_i \phi_{p,i}\zeta_{p,i}(\mathbf{R}), \tag{7}$$

where the sum over i includes integration over the electronic continuum as well. Substituting (7) into the Schrödinger equation for the full Hamiltonian $H = H_{\text{el}} + T_R$ (T_R is the nuclear kinetic-energy operator), the resulting equations may first be written without approximation in the familiar symbolic form

$$\begin{aligned} P(H-E)P\psi &= -PHQ\psi, \\ Q(H-E)Q\psi &= -QHP\psi, \end{aligned} \tag{8}$$

just as in Ref. 7.

We now make just one approximation, *the Born-Oppenheimer approximation*, by neglecting T_R operating on all the electronic functions ϕ_j. This is equivalent to the principal approximations made in Sec. 5 of Ref. 7 for the dissociative attachment problem. It is also equivalent to the approximations normally made in studying the stationary states of molecules, neither more nor less approximate. With this one approximation then we get in place of Eq. (8) the coupled equations

$$\begin{aligned} (T_R + \epsilon_r - E)\zeta_r &= -\sum_i V_i \zeta_{p,i}, \\ (T_R + \epsilon_{p,i} - E)\zeta_{p,i} &= -V_i \zeta_r, \end{aligned} \tag{9}$$

where $i = 1, 2, \cdots$ and the V_i are given by Eq. (6).

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[14] See Ref. 6. For an application of this operator to a simple system (H^- and He) see T. F. O'Malley and S. Geltman, Phys. Rev. **137**, A1344 (1965). H. S. Taylor and J. K. Williams [J. Chem. Phys. **42**, 4063 (1965)] effectively use it for a more complex system (H_2^-).

[15] See for example L. Lipsky and A. Russek, Phys. Rev. **142**, 59 (1966).

[16] It should be mentioned that the more general Kapur-Peierls definition of a resonance as used in Ref. 8 has been deliberately excluded. The main reason for this is that the Kapur-Peierls states can easily be shown to reduce, in the discrete region of Fig. 1, to ordinary bound states of the adiabatic or diagonal representation to H_{el}, and so are not interesting in the present context.

[17] R. S. Mulliken, Phys. Rev. **136**, A962 (1964).

[18] This behavior as portrayed in Ref. 17 is not completely one hundred percent consistent. As drawn there, each of the curves mentioned avoids crossing the lowest state in the Rydberg series, although they cross all higher ones. It should be pointed out here that an apparent discrepancy between Ref. 17 and the experimental result of W. W. Robertson [J. Chem. Phys. **42**, 2064 (1965)] disappears when one recognizes that B core states properly belong to a nondiagonal representation of H_{el} and therefore need not avoid crossing even the lowest Rydberg states of the same symmetry.

[19] The atomic orbital approximation for such a projection operator has been in use for a long time. See for example, L. Pauling, J. Am. Chem. Soc. **54**, 988 (1932).

The coupled equations (9) for the nuclear wave functions ζ_j are the desired result of the present paper. They couple only those states whose quasiadiabatic potential curves cross. In their derivation they involve only those approximations which are customarily made in analyzing the stationary states of molecules, namely the Born-Oppenheimer approximation, and also the related assumption of small internuclear velocities ($v \ll 1$ a.u.) in that the effects of the Coriolis force[20,21] and of electron momentum transfer (where it is appropriate) have not been considered. As a result of this, an accuracy is expected for the solutions of (9) which is comparable to that for the molecular-stationary-state problem.[22]

It might be instructive to compare the present results, Eq. (9), with those that have occasionally been obtained when the states of the diagonal adiabatic representation have been used as an expansion basis in place of Eq. (7). In that case a set of formal coupled equations is obtained which are equivalent to the exact Eqs. (8). The trouble with the equations coupling the adiabatic states comes when one looks for some good approximation to render the equations tractable. If the minimal Born-Oppenheimer approximation is made as was done to derive (9), the equations become completely uncoupled because of the absence of off-diagonal matrix elements in H_{el}, and one then loses all the physics. It is for this reason that the coupled equations for the adiabatic states have always remained merely formal relations which have never been of any use in actual collision problems. The present result therefore differs from that obtained with adiabatic states precisely in the explicit appearance in Eqs. (9) of the electronic coupling terms V_i which link any two crossing electronic states. [Incidentally, if one should ever wish to drop the Born-Oppenheimer approximation in using the present formalism it would be a straightforward matter to go back to the exact Eq. (8) and include all the nonadiabatic coupling.]

As in Ref. 7, *the formal solution* of the collision equations (9) may be written by examining the asymptotic behavior of the wave functions. (The same normalization is assumed for all continuum functions as in Ref. 7.) If r is the incident channel, the transition matrix element $T_{i,r}$ may be expressed as

$$T_{i,r} = \langle \zeta_i^{h-} \,|\, V_i \,|\, \zeta_r^{+} \rangle, \tag{10}$$

where the ζ^h are the homogeneous solutions of Eq. (9) (neglecting the V_i's), and the superscript $+(-)$ means a plane plus outgoing (incoming) wave. The equation satisfied by ζ_r^+ may be written by using the standard expansion for the Green's functions $[g_i = (E - T - \epsilon_i + i\delta)^{-1}$ as $\delta \to 0]$, in a form closely analogous to Eq. (4.15) of Ref. 7 with a complex potential as

$$(T_R + \epsilon_r + \Delta - \tfrac{1}{2} i\Gamma - E)\zeta_r^+ = 0, \tag{11}$$

where

$$\Delta = \sum_j \sum_v \,|\, V_j \zeta_{j,v}^h \rangle (E - E_{j,v})^{-1} \langle \zeta_{j,v}^h V_j \,| \tag{12}$$

and

$$\Gamma = 2\pi \sum_{j\ \mathrm{open}} \,|\, V_j \zeta_j^h \rangle \langle \zeta_j^h V_j \,|. \tag{13}$$

Δ and Γ are the level shift and width operators, analogous to but different in detail (especially Γ) from those of Ref. 7. The difference results from the fact that the electron channel was open there while here it is considered closed. The subscript v means vibrational state (both discrete and continuous). The ζ_j^h in Eq. (13) have no subscript v because this nuclear state is necessarily in the continuum since Γ has contributions only from open channels. By using the semiclassical nature of the ζ's, Δ and Γ may be further simplified of course, but this will not be developed here.

It is interesting to contemplate the complex, energy-dependent, nonlocal optical potential operating on the wave function ζ_r in Eq. (11). The real part, $\epsilon_r + \Delta$, is an effective energy-dependent potential energy curve for motion in the state r when coupled to the states j. It has sometimes been said that finding such an energy-dependent potential curve would be one desirable alternative to the adiabatic potential curves. For those who see the problem that way, this is the desired energy-dependent curve. The imaginary part $-\frac{1}{2} i\Gamma$ is, of course, a measure of the transition probability from r to each of the states j. Although a full analysis of this term would require the exact solution of Eq. (11) or (9), its first-order matrix element, $\langle \zeta_r^h \,|\, \Gamma \,|\, \zeta_r^h \rangle$ is easily evaluated for a single partial wave. It is equal, to within a normalization factor, to $\sum_j p_{LZ}(j)$, where $P_{LZ}(j) = 4\pi V_j^2/\hbar v \Delta F$ is the first-order probability, from the Landau-Zener theory,[2] of a transition from the curve r to j.

For completeness, a transition from the state i to j in P space may also be expressed in a form similar in appearance to Eq. (10) as

$$T_{j,i} = \langle \zeta_j^{h-} \,|\, V_j \,|\, \zeta_r^{+} \rangle, \tag{14}$$

where now, however, ζ_r^+ satisfies the *inhomogeneous* equation, coupling it to the incident channel i,

$$(T_R + \epsilon_r + \Delta - \tfrac{1}{2} i\Gamma - E)\zeta_r^+ = -V_i \zeta_i^{h+}. \tag{15}$$

Equations (14) and (15) are analogous to Eq. (5.9a) of Ref. 7, which described vibrational excitation.

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[20] W. R. Thorson, J. Chem. Phys. **39**, 1431 (1963).

[21] The neglect of the Coriolis force shows up in the fact that the $V_i = V_i(R)$ are scalars, exactly as in the molecular-structure problem. Note that the corresponding (but more complicated) quantities V_a of Eq. (5.3) of Ref. 7 were also said (improperly in that case) to be scalars, resulting in a prediction of isotropic cross sections for the attachment problem. This is presently being corrected.

[22] Note also that the electronic quantities ϵ_j and V_j in (9) may be calculated by essentially the same methods as are used for the adiabatic potential curves. An interesting practical consequence of this is that the computation of these quantities may reasonably be left to those who are expert at such calculations leaving collision theorists free to devote their efforts to the coupled Eqs. (9), a proper collision problem.

An important practical consideration in using Eq. (9) or the equivalent formal expressions (11), (15), etc. is the ***number*** of states which are effectively coupled. Although the number of equations in (9) is infinite, it is a known consequence of the semiclassical nature of the wave functions that actual *transitions* can only occur between states whose curves cross either below or very near the energy E. This follows from two facts: (a) that a nuclear wave function (say ζ_r) vanishes quite rapidly in the classically inaccessible region beyond its turning point, and (b) a consequence of the Frank-Condon principle which makes transitions probable only in the immediate vicinity of a crossing point (formerly called "pseudocrossing point"). So if the crossing point is well above E then both of the wave functions will be vanishingly small there, and so therefore will be the transition probability.

However, while transitions to these higher states have a vanishingly small probability, the situation is somewhat different for the *level shift* Δ of Eq. (12) induced by these states. This vanishes more slowly as the difference in energy increases. Although the magnitude of V_i should normally be such as to make the contribution of the higher states negligible anyway, the following procedure allows it to be considered explicitly in the simplest way.

In order to take advantage of the effective finiteness of the number of coupled equations in (9), let J be the number of the states $AB_{p,i}$ whose curves cross that of AB_r[11] either below or very near the energy E. It is then trivial to eliminate the remaining states formally from Eqs. (9) in favor of ζ_r by writing

$$\zeta_{p,j}=(E-T-\epsilon_j)^{-1}V_j\zeta_r \quad \text{for} \quad j>J.$$

Substituting this into (9) gives the finite set of coupled equations

$$(T+\epsilon_r+\Delta'-E)\zeta_r=-\sum_{j=1}^{J}V_j\zeta_{p,j},$$

$$(T+\epsilon_{p,j}-E)\zeta_{p,j}=-V_j\zeta_r, \qquad (j=1,2,\cdots J), \tag{16}$$

where

$$\Delta'=\sum_{j>J}V_j(E-T-\epsilon_{p,j})^{-1}V_j.$$

Equations (16) are fully equivalent to the infinite set (9), but emphasize the practical aspect that only $J+1$ states are effectively coupled while the higher states cause at most a level shift. Δ' may be simplified. Remembering that the Green's functions in Δ' act on $V_j\zeta_r$, we make a standard semiclassical approximation, related to the Born–Oppenheimer approximation, that V_j varies slowly compared to ζ_r. Then using Eq. (11) satisfied by ζ_r, the partial level shift Δ' becomes

$$\Delta'=-\mathrm{Re}\sum_{j>J}V_j(\epsilon_{p,j}-\tilde{\epsilon}_r)^{-1}V_j, \tag{17}$$

where $\tilde{\epsilon}_r=\epsilon_r+\Delta-\frac{1}{2}i\Gamma$. Experience has shown[23] that the magnitude of level shifts for higher Rydberg states falls off very rapidly (apparently as j^{-3} if j is the principal Rydberg quantum number). Accordingly, we expect that Δ' will normally be negligible since the lowest one or more states are not included in it. In addition, in evaluating (17) it is expected that the approximation $\tilde{\epsilon}_r\simeq\epsilon_r$ should be satisfactory. If it is not, the state in question should probably also be included in the set of coupled equations (16).

Two-State Problem

Equations (16) (the final result of the present paper) represent the heavy-particle collision problem effectively as a finite set of coupled two-body equations, with the *number* determined by the number of curve crossings which occur below or very near to the energy E. The simplest and most immediately interesting special case of Eqs. (16) corresponds to E_1 of Fig. 1(a). This determines a *two-state problem* ($J=1$) and Eqs. (16) reduce to two coupled equations

$$(T_R+\epsilon_r+\Delta'-E)\zeta_r=-V_1\zeta_p,$$

$$(T_R+\epsilon_p-E)\zeta_p=-V_1\zeta_r. \tag{18}$$

These are identical in form with the coupled equations which form the basis of the Landau–Zener theory.[2] The only difference is that now the electronic part of the problem has been treated honestly and without approximation, so that instead of undefined "zeroth-order" states or crude atomic-orbital approximations, there appear instead the electronic quantities ϵ_r, $\epsilon_{p,1}$, V_1, and Δ', defined by the exact quasiadiabatic representation (5) of H_{el}. Work presently being done on the two-state problem should therefore rest on a firmer foundation than heretofore when viewed as the solution of Eq. (18).

The energy E_2 of Fig. 1(a) corresponds to a different kind of two-state problem in which one of the two channels is closed. Depending on where one starts, the physical problem is either that of predissociation or resonant elastic scattering. In the latter case, it should be pointed out that each one of the vibrational levels ζ_1^h of the closed channel state $AB_{p,1}$ [the one marked $A+B^*$ in Fig. 1(a)] constitutes a separate resonance level, so that the present problem, Eq. (18), then becomes simply a particular realization, for each partial wave, of the multilevel resonant scattering problem which has been worked out in detail in the literature.[24] This is most readily exhibited by considering the appropriate two-state form of Eq. (11), which becomes,

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[23] P. G. Burke and D. D. McVicar, Proc. Phys. Soc. (London) **86**, 989 (1965).

[24] See for example, U. Fano [Phys. Rev. **124**, 1866 (1961)], where this problem is worked out in Sec. V. The undefined quantities ϕ_n, ψ_E, V_{En} of that paper are readily identified with the quantities appearing in the homogeneous solutions of the present Eqs. (18), and the matrix elements of V_1 taken between these homogeneous states.

using (17) with $J=1$,

$$[T_R+\epsilon_r+\Delta'+\sum_v | V_1\zeta_{1,v}{}^h\rangle(E-E_{1,v})^{-1} \times\langle\zeta_{1,v}{}^h V_1 | -E]\zeta_r{}^+=0. \quad (19)$$

Equation (19) exhibits the multilevel resonance structure of the problem perhaps most clearly.

One-State Problem

If the energy is reduced still further so that it goes well below the lowest crossing point in Fig. 1(a), an interesting limiting case, *the one-state problem*, occurs. In this case, it is still legitimate to start from Eqs. (18) [Eq. (9) would do as well]. From (18), we derive this time the equation for ζ_p (which now describes a low-lying vibrational state), with the same considerations used above, and find

$$[T_R+\epsilon_p-V_1(\tilde{\epsilon}_r-\epsilon_p)^{-1}V_1-E]\zeta_p=0. \quad (20)$$

With Eq. (20) for the one-state problem, we have now recovered the standard equation for the low-lying vibrational states of a molecular level! The potential in (20) is just a roundabout way of writing the lowest potential energy curve in the usual diagonal representation. The present formalism, therefore, as embodied in Eqs. (16), is powerful enough to include as a special case the equations resulting from the diagonal representation of H_{el} whenever the physics is such (i.e., a one-state situation), that this representation is the appropriate one, in addition to describing electronic transitions in the simplest way.

Finally, the 3-, 4-, and n-state problems generated by Eq. (16) in the appropriate energy ranges may be handled by a direct extension of the methods used for the two-state problem, either by direct numerical integration,[25] which is a possible although perhaps clumsy procedure, or by an extension of the semiclassical methods of Landau, Zener, and Stueckelberg,[2] which is being actively pursued by a number of workers.[26]

IV. SUMMARY

In the present paper, a large class of slow atomic-collision processes, those involving a change in molecular electronic state and resulting in excitation, de-excitation, scattering, or various kinds of electron transfer, has been reduced to a set of two or more coupled two-body equations (16). The approximation made in reducing the electronic part of the problem was simply the Born-Oppenheimer approximation together with that of small velocities ($v\ll 1$ a.u.).

In order to effect this reduction to coupled equations, it was necessary to introduce an exact nondiagonal representation, the quasiadiabatic representation, of the electronic Hamiltonian H_{el}, whose states among other things are not subject to the noncrossing rule. This representation is determined by the quasistationary state AB_r (or $AB_r{}^+$, etc.) defined with the help of a projection operator Q^0. This latter might be either Feshbach's projection onto the excited states of the target molecule, or else one that somehow specifies a particular distribution of charges so that for example $AB_r{}^+\rightarrow A+B^+$ or $AB_r\rightarrow A^-+B^+$.

Since such a nondiagonal representation of H_{el} seems to be required in order to treat collision processes, it is believed that it is just as important and as basic in its own right as is the more familiar diagonal adiabatic representation. Further, since its computation is more or less equivalent to that of the adiabatic electronic states, an attractive division of labor suggests itself when the present formulation of the problem is employed, with the electronic quantities of Eq. (5) being calculated most appropriately by molecular structure specialists while the resulting coupled equations (16) are analyzed and solved by collision theorists.

Quantitative application of this approach to certain charge-changing collisions is presently being studied.

Note added in proof. An interesting observation has been made about the large R behavior of quasistationary states (such as AB_r of Fig. 1) for molecular systems. It has been pointed out [M. Mittleman and J. C. Y. Chen (private communication)] that, for certain choices of Q^0, the asymptotic value of the energy $\epsilon_r(R)$ may not be precisely equal to the "physical" energy of the two separated atoms.

Because this observation might be interpreted as an objection to the present theory, in which such states may play a prominent role, it is important to point out that this energy difference, where it occurs, is simply the familiar level shift Δ, as defined in Eq. (12) [see also Eqs. (16) and (17)]. The occurrence of level shifts is inseparable in general from the use of quasistationary states, and since in the present case their numerical values follow as a direct by-product of solving the coupled equations (16), it should be emphasized that the existence of level shifts presents no special difficulty for the present theory, either in principle or in practice.

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[25] See D. R. Bates, H. C. Johnston, and I. Stewart, Proc. Phys. Soc. (London) **84**, 517 (1964); also W. D. Ellison and S. Borowitz, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 790.

[26] See, for example, W. R. Thorson and S. A. Boorstein in *Proceedings of the Fourth International Atomic Collisions Conference* (Science Bookcrafters, Inc., Hastings, New York, 1965), p. 218; also V. K. Bykovskii, E. E. Nikitin, and M. Ya Ovchinnikova, Zh. Eksperim. i Teor. Fiz. **47**, 750 (1964) [English transl.: Soviet Phys.—JETP. **20**, 500 (1965)].