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Theory of electronic transitions in slow atomic collisions

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This review deals with quantitative descriptions of electronic transitions in atom-atom and ion-atom collisions. In one type of description, the nuclear motion is treated classically or semiclassically, and a wave function for the electrons satisfies a time-dependent Schrödinger equation. Expansion of this wave function in a suitable basis leads to time-dependent coupled equations. The role played by electron-translation factors in this expansion is noted, and their effects upon transition amplitudes are discussed. In a fully quantum-mechanical framework there is a wave function describing the motion of electrons and nuclei. Expansion of this wave function in a basis which spans the space of electron variables leads to quantum-mechanical close-coupled equations. In the conventional formulation, known as perturbed-stationary-states theory, certain difficulties arise because scattering boundary conditions cannot be exactly satisfied within a finite basis. These difficulties are examined, and a theory is developed which surmounts them. This theory is based upon an intersecting-curved-wave picture. The use of rotating or space-fixed electronic basis sets is discussed. Various bases are classified by Hund's cases (a)–(e). For rotating basis sets, the angular motion of the nuclei is best described using symmetric-top eigenfunctions, and an example of partial-wave analysis in such functions is developed. Definitions of adiabatic and diabatic representations are given, and rules for choosing a good representation are presented. Finally, representations and excitation mechanisms for specific systems are reviewed. Processes discussed include spin-flip transitions, rotational coupling transitions, inner-shell excitations, covalent-ionic transitions, resonant and near-resonant charge exchange, fine-structure transitions, and collisional autoionization and electron detachment.

CONTENTS

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GLOSSARY OF SYMBOLS

The symbols used in this review are listed below with an indication of where they first appear in text.

$\underline{\mathbf{A}}$	Matrix representing effect of displacement	(2.61)
$\underline{A}^R,\underline{A}^\Theta,A^\Phi$	Components of $\underline{\mathbf{A}}$	(2.67)
$\underline{\mathbf{A}}_0,\underline{\mathbf{A}}_1$	Terms in $\underline{\mathbf{A}}$	(A46)
$\underline{\mathbf{A}}_M,\underline{\mathbf{A}}_F$	$\underline{\mathbf{A}}$-matrix calculated from class M or class F representation	(4,13) and below (4.26)
$\underline{B}$	Corrected second-derivative matrix	Table IV, (3.66) and (A8)
$\underline{B}_R$	Radial term in $\underline{B}$	(A11)
$\underline{B}^0$	Second-derivative matrix	(3.18), (A8)
b	Impact parameter	
CMN	Center-of-mass of the nuclei	
D_n^a		(3.48)
d_0	Range of interaction	(1.10)
$d_k(t)$	Coefficient in expansion	(2.23)
E	Total energy	
ETF	Electron-translation-factor	
F_A,F_B,F_k	Electron-translation-factors	(2.17), (2.52)
class F	Fixed one-center states	(2.46)
$f_k(\mathbf{r};R)$ or $f_k(\mathbf{r}';\mathbf{R})$	Switching functions	(2.49)
$f(\Theta,\Phi)$	Scattering amplitudes	(3.8), (A15)
g	gerade (see π)	
g		(4.18)
H	Full Hamiltonian for electrons and nuclei	(1.12)
h	Electronic Hamiltonian	(1.12)
h_{BO}	Electrostatic part of electronic Hamiltonian	(1.12)
h_{soc}	Magnetic part of electronic Hamiltonian, mainly spin-orbit coupling	(1.12)
h_A^0,h_B^0	Atomic electronic Hamiltonians	(2.15)
h_0^A,h_0^B	Atomic electronic Hamiltonian (correct electronic reduced mass)	(3.4)
h_e	Molecular electronic Hamiltonian (same as h_{BO} except possibly for electronic reduced mass)	(2.15)
h_n		(3.49)
$\mathcal{H}(v)$		(2.26b)
$\mathcal{H}(\Theta,\Phi)$	Symmetric top eigenfunction	(A1)
$\underline{I}$	Electron-reduced mass correction matrix ("Isotopic coupling")	Table IV
I		(4.16)
$\mathbf{j}$	Total electronic angular momentum, $\mathbf{j}=\mathbf{L}+\mathbf{S}$	
$\mathbf{J},J$	Total angular momentum, and its quantum number	
J	Also a label for channels, $J=A,B$	
$\mathbf{K},K$	Total angular momentum exclusive of spin, $\mathbf{K}=\mathbf{J}-\mathbf{S}$	
$\mathbf{k}_{n_A},\mathbf{k}_{n_B}$	Wave-vectors in scattering boundary conditions	(3.6)
k,k_A,k_B	General labels for molecular or atomic states	
L_x,L_y,L_z	Operators representing electronic orbital angular momentum	(2.40)

L	Electronic-angular-momentum quantum number	
L_n^x, L_n^y, L_n^z	Corrected angular-momentum operators	(A7)
$\mathcal{L}$	A Lagrangian density	(4.15)
M_A, M_B	Nuclear masses	
M	Component of electronic spin on space-fixed z' axis	
M_N, M_K, M_J	Component of N, K, J on space-fixed z axis	
m_0, m, m_A, m_B	Electronic mass and reduced masses	Table III
m_A, m_B	Labels for atomic states (like n_A, n_B or k_A, k_B)	
$\mathbf{N}, N$	Nuclear orbital angular momentum operator, and the corresponding quantum number	
n	A general label, or, for hydrogenic states, the principal quantum number	
n_A, n_B	Labels for atomic states	
n_ξ, n_η, n_ϕ	Quantum numbers for prolate spheroidal coordinates	above (4.49)
Θ		(3.41)
$\underline{P}$	Matrix of total change of electronic basis functions with R	(2.60), (3.17) Table IV
$\underline{\mathbf{p}}$	Matrix of electronic momentum operator	(2.64)
$\underline{Q}$	Quantum angular-coupling matrix	(A12a)
$\mathbf{R}_{\mathrm{CM}}^0, \mathbf{R}_{\mathrm{CMN}}^0, \mathbf{R}_A^0, \mathbf{R}_B^0$	Positions relative to laboratory origin	Fig. 3, (2.1), (2.2)
$\mathbf{R}$	Internuclear vector	(2.4)
$R = \lvert\mathbf{R}\rvert$	Internuclear distance	
$\bar{\mathbf{R}}$	Common numerical values of ξ_m's	(3.60)
R_x	Crossing point	(Sec. IV.A.4)
$\mathbf{r}'$	Vector coordinate of electron relative to center-of-mass of nuclei, with components (x', y', z') defined relative to a space-fixed frame	
$\mathbf{r}$	Same, with components (x, y, z) defined relative to rotating molecular frame	
$\mathbf{r}_A, \mathbf{r}_B$	Electron coordinate relative to nucleus A or B	(2.9)
$\mathbf{r}_g$	Electron coordinate relative to geometric center of molecule	Fig. 5
$\underline{S}$	Overlap matrix	
$\underline{S}(\mathbf{v})$	Velocity-dependent overlap matrix $\underline{S} = \underline{S}(\mathbf{v}=0)$	
S	Total electronic spin angular momentum quantum number	
$S_{nl}(r;\epsilon)$	Sturmian function	(2.33)
$\mathbf{s}_k(\mathbf{r};\mathbf{R})$	Part of exponent in electron-translation-factor, or displacement in intersecting-curved-waves theory	(2.52), (2.53) (3.37), (3.38)
s_∞	Reduced coupling strength parameter	(4.43a)
$\underline{\mathcal{S}}$	Quantum $\mathcal{S}$-matrix	(A13)
T	Kinetic energy	(3.2)
T_n	Nuclear kinetic energy	(1.12)
$T(R)$	Reduced energy-gap function	(4.35)
$\underline{U}$	Transformation matrix	(4.2)–(4.4)
u	Ungerade (see π)	
$u_n^{KM_k}(R)$	Nuclear radial wave functions	(A9)
V	Total potential energy of all electrons and nuclei	
V_0^A, V_0^B	Potential energy of interaction of electron(s) with nucleus A or B	(3.3)
$\underline{V}$	Matrix representing all "potential" couplings	(4.25)
$\mathbf{v} \equiv \mathbf{v}_{\mathrm{nuc}}$	Internuclear velocity, spherical components v^R, v^Θ, v^Φ	(1.10), (2.6)
$\mathbf{v}_A, \mathbf{v}_B$	Velocity of nucleus A or B	(2.17)
v_{el}	Typical velocity of electron in a bound state	
$\underline{W}$	Truncated transformation matrix	(4.30)
$\mathbf{w}$	Electron-transport-velocity	(4.21)
x, y, z	Components of electron position vector $\mathbf{r}(=\mathbf{r}')$ in molecular frame	
x', y', z'	Components of electron position vector $\mathbf{r}'(=\mathbf{r})$ in space-fixed frame	
X, Y, Z	Cartesian components of $\mathbf{R}$ in space-fixed frame	
$Y_{NM_N}(\Theta, \Phi)$	Spherical harmonic (phase conventions as in Edmonds's book)	
$\hat{Z}_A, \hat{Z}_B$	Charge of nuclei A, B	
α	Parameter in ETF	below (4.14)
$\alpha_{nl}(\epsilon)$	Effective nuclear charge parameter	(2.33)
β	Parameter in ETF	below (4.14)
$\Gamma_n^{ab}, \gamma_n^{ab}$		(3.45)
$\underline{\gamma}$	Momentum-transfer matrix	(2.62)
$\Delta(R)$	Energy-gap function, $V_{22}(R) - V_{11}(R)$	(4.41)
ϵ	Energy of an electronic state, usually a function of R	(1.10)
$\epsilon_{k_A}, \epsilon_{k_B}$	Energies of atomic states	below (2.17)
$\epsilon_{n_A}^0, \epsilon_{n_B}^0$	Energies of atomic states	(3.12)
ζ	Parameter (like orbital exponent) in $\phi(\mathbf{r};\boldsymbol{R})$	
$\zeta_{\mathrm{LZ}}, \zeta_{\mathrm{RZD}}$	Landau-Zener or Rosen-Zener-Demkov parameters	(4.42), (4.43)
$\underline{\eta}$	Part of $\boldsymbol{\gamma}$	(2.63)
Θ	Angle defining orientation of internuclear axis	Figs. 4, 5
κ_k		(2.46), (A5c)

Λ	Conserved component of electronic angular momentum on internuclear axis	
λ	$(M_A-M_B)/(M_A+M_B)$	
μ	Nuclear reduced mass $M_AM_B/(M_A+M_B)$	
μ_A, μ_B	Channel reduced masses	Table III
$\xi_n(\mathbf{r}';\mathbf{R})$	Coordinate in Intersecting-Curved-Waves theory	(3.37)
$\underline{\Pi}$	Corrected vector nonadiabatic coupling	Table IV
π	Electronic parity symmetry (gerade or ungerade). Symmetry of electronic state on inversion of all electrons through the geometric center of the nuclei	
ρ_A, ρ_B	Positions of nuclei relative to CMN	(2.3)
ρ	Electron density	(4.21)
Σ	Component of electron spin on internuclear axis	
$\sigma_{k_A}, \sigma_{k_B}$	Cross-section for transition to k_A or k_B state, also denoted $\sigma_{k_A \leftarrow n_B}$	(2.21), (2.22)
$\underline{\sigma}$	Correction to $\underline{S}$	(2.57)
Υ	Wave function for electrons in classical trajectory framework	(1.14)
Φ	Angle defining orientation of internuclear axis	Fig. 4
$\phi(\mathbf{r};R)$	An electronic state defined for fixed nuclei, expressed in rotating molecular frame	(1.15)
$\phi(\mathbf{r};\mathbf{R})$	Same state reexpressed in space-fixed frame	
ϕ_{k_A}, ϕ_{k_B}	An A- or B-atomic electronic state. These may be either rotating or space-fixed	(2.17) or (2.32)
$\phi^0_{k_A}, \phi^0_{k_B}$	These differ from ϕ_{k_A}, ϕ_{k_B} because of the electronic reduced mass in the Hamiltonian	(3.5)
$\hat{\phi}$	State displaced onto surface of constant ξ	
$\underline{\chi}$	Nuclear wave functions	(3.15) or (3.39)
Ψ	Full wave function for electrons and nuclei	(1.11)
Ω	Component of total electronic angular momentum on internuclear axis, $\Omega=\Lambda+\Sigma$	
ω	Angle in a 2×2 matrix $\underline{U}$	(4.34)
ω	Spin orbit precession frequency (Appendix)	
+/−	Symmetry with respect to reflection in a plane containing the nuclei	(2.28) and Fig. 6

I. INTRODUCTION

The quantum theory of atomic collisions is practically as old as quantum mechanics itself. Despite its age, however, the subject has undergone a vigorous expansion in the past decade: Many conceptual difficulties inherent in the theory have finally been resolved, and a host of calculations on specific systems has provided concrete substance to the abstract formalism. The purpose of this review is to integrate recent developments with older work to give a unified framework for the theory of slow atomic collisions.

A. Processes and energy range

Let us begin by specifying more precisely the processes of interest to us. We shall consider binary collisions involving neutral atoms or positive or negative atomic ions. We shall not generally be concerned with the additional complexities that arise in three-atom systems, as in ion-molecule reactions; although many of the methods discussed here can also be applied to such systems, we shall focus our attention on two-atom systems (which by themselves are sufficiently challenging).

Such atomic collisions may be purely elastic. The electrons may remain in (say) the ground state throughout the collision, and the atoms then bounce off each other elastically. Such collisions are now quite well understood, and they are not the primary subject of this work. We are concerned with the real and virtual inelastic processes that occur in binary collisions of atoms or atomic ions. Among them are:

1. *Resonant charge exchange.* The simplest example is

$$\mathrm{H}^+ + \mathrm{H}(1s) \rightarrow \mathrm{H}(1s) + \mathrm{H}^+ . \tag{1.1}$$

2. *Direct or exchange excitation,* in homonuclear systems, such as

$$\mathrm{H}^+ + \mathrm{H}(1s) \rightarrow \mathrm{H}^+ + \mathrm{H}(2p), \text{ direct} \tag{1.2}$$

$$\rightarrow \mathrm{H}(2p) + \mathrm{H}^+, \quad \text{exchange} \tag{1.3}$$

or in heteronuclear systems, such as

$$\mathrm{He}^+ + \mathrm{Ne}(2p^6) \rightarrow \mathrm{He}^+ + \mathrm{Ne}^*(2p^5 3s) .$$

This category also includes nonresonant charge transfer, as in

$$\mathrm{Na} + \mathrm{Cl} \rightarrow \mathrm{Na}^+ + \mathrm{Cl}^- \tag{1.4}$$

(a process that is sometimes called "chemi-ionization"), and the reverse process, neutralization, as in

$$\mathrm{H}^- + \mathrm{H}^+ \rightarrow \mathrm{H}(nl) + \mathrm{H}(n'l') . \tag{1.5}$$

The theory of processes like these is the main subject of this review.

3. *Ionization or detachment,* as in

$$\mathrm{H}^- + \mathrm{He} \rightarrow \mathrm{H} + \mathrm{He} + e^- , \quad \text{detachment} \tag{1.6}$$

$$\mathrm{He} + \mathrm{He} \rightarrow \mathrm{He}^+ + \mathrm{He} + e^- , \quad \text{ionization} \tag{1.7}$$

$$\rightarrow \mathrm{He}_2{}^+ + e^- , \quad \text{associative ionization} \tag{1.8}$$

$$\mathrm{He}(1s2s) + \mathrm{Ar} \rightarrow \mathrm{He} + \mathrm{Ar}^+ + e^- \quad \text{Penning ionization.} \tag{1.9}$$

These processes (some of which have also been called "chemi-ionization") are somewhat more complicated than processes (1.1)–(1.5). Transitions between discrete bound electronic states can usually be described by coupling within a small manifold of states, but transitions to states in which an electron is free involve the interaction of one or more bound states with a continuum. Because of this higher level of mathematical complexity, the theory of ionization and detachment is less fully developed than is the theory of discrete transitions (though it is now an active subject of research). Accordingly, our discussion of these processes will be comparatively brief.

We shall be concerned primarily with slow collisions: collisions for which the nuclear speed v is much less than typical electron speeds. For valence-shell excitations, the electron speed can be taken to be about 1 atomic unit ($\sim 2\times 10^6$ m/sec); then if the nuclear reduced mass is M times the proton mass, the nuclear velocity exceeds the electron velocity only if the relative collision energy exceeds $25M$ KeV. For inner-shell excitations, the electron velocity in atomic units is given by $\hat{Z}/n$, where $\hat{Z}$ is the nuclear charge and n the principal quantum number. Hence the nuclear velocity exceeds the inner-electron velocity only if the relative collision energy is greater than $25\ M\hat{Z}^2/n^2$ KeV. Accordingly, the theory developed here applies to collisions with energy varying from the thermal to the multi-KeV range. This energy range contains essentially all collisions of interest in chemistry, and in a broad area of atomic physics.

B. General characteristics of electronic transitions in slow atomic collisions

It is a general property of transitions in slow collisions that they are very improbable unless at some point the energies of the two electronic states are nearly degenerate. The Massey adiabatic criterion (Massey, 1949) states this more precisely: Transitions are improbable unless

$$(\Delta\epsilon d_0/\hbar v)\ll 1\,, \tag{1.10}$$

where $\Delta\epsilon$ is the spacing between the energy levels, d_0 is the range of the interaction (usually taken to be about 1 a_0), and v is again the relative velocity of the colliding atoms. The Massey criterion is a statement of the Heisenberg uncertainty principle as applied to atomic collisions. If $\Delta t = d_0/v$ is the time of interaction of the atoms, then in this time, the internal (i.e., electronic) energy is defined only to within $\Delta\epsilon \sim \hbar/\Delta t$. Transitions to states having energies within this range of the energy of the initial state may occur with a high probability, but transitions to other states will be unlikely.

In an early paper discussing this general principle, Hasted (1952) used the asymptotic atomic energies to calculate $\Delta\epsilon$. Although he successfully accounted for a number of observations this way, such a usage is not always appropriate, because the energies of electronic states can change substantially with internuclear distance, and two states that have quite different energies at infinite separations may become practically degenerate at finite R or in the limit as $R\to 0$. Accordingly, the degeneracies or near degeneracies that mediate the important transitions in slow collisions fall into three categories: (i) those associated with a symmetry of the united atom ($R\to 0$); (ii) those associated with the separated atoms ($R\to\infty$); (iii) those that occur at some finite R, as happens, for example, in curve crossings (Fig. 1). In any of these cases there is at least a local violation of the adiabatic criterion within the nearly degenerate manifold, and a strong coupling problem may then arise. However, such problems are tractable essentially because we can adequately describe the behavior of the electron system by an expansion in a small set of discrete electronic states. Except with respect to specified and limited degeneracies, the system otherwise behaves adiabatically, and transitions to states outside the limited degenerate manifold have small probability.

Thus it follows that in slow collisions the important transitions tend to be highly specific. For example, the cross section for $3p$ excitation of hydrogen by slow protons is orders of magnitude smaller than the cross section for $2p$ excitation. The latter transition is mediated by a degeneracy between $2p\sigma_u$ and $2p\pi_u$ states as the internuclear separation R goes to zero [as in Fig. 1(a)]; however, for the former, there is no mediating degeneracy.

The improbable, nonspecific processes that are not mediated by a degeneracy may be called "direct impact processes." These processes have rarely been considered in slow collisions because their cross sections are small. On the other hand, as the collision velocity increases, so that the nuclear velocity and the electron velocity become comparable, degeneracies become less important, and direct impact processes become more important. Hence, in this intermediate velocity range, transitions may occur to a broad spectrum of final states, and many channels may become strongly coupled. Despite this fact, certain calculations in this intermediate velocity range have been performed with considerable success by expanding the wave function in a small but carefully chosen basis set. Such calculations are in some ways very similar to low-velocity calculations, and we shall discuss them in Sec. II. B.

In slow collisions, the relevant finite manifold can often be spanned by the Born-Oppenheimer molecular electronic states, and an expansion in such states is the backbone of the theory. Certain complications have to be considered carefully: (i) The conventional expansion does not give a proper account of scattering boundary conditions, and (ii) frequently it is possible to find some other basis set that is more convenient than the Born-Oppenheimer set. (Some such basis sets have

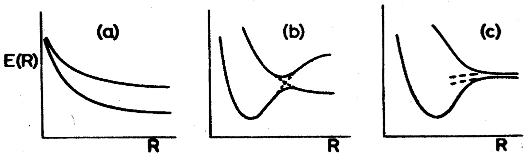

FIG. 1. Electronic energies, here denoted $E(R)$, as a function of internuclear distance R, illustrating three types of degeneracy that mediate transitions in a slow atomic collision. Degeneracy or near-degeneracy occurs (a) in the limit as $R\to 0$, (b) at finite R, and (c) in the limit as $R\to\infty$.

been called "diabatic," to suggest that they do not have the "adiabatic" behavior of the Born-Oppenheimer electronic states. The problem is to give precise definition to these states and to show when they may be useful). After these two problems are resolved, the problem is reduced to that of solving a set of coupled equations. If we are concerned only about the specific transitions that are mediated by degeneracies, and if we can ignore the much less probable nonspecific direct impact processes, then we commonly find that the system can be described by a small set of coupled equations. The formulation and solution of such finite sets of coupled equations are the main subject of this work.

C. Quantum and classical descriptions

There are two different theoretical descriptions of atomic collisions, both of which will be discussed in detail later. In the most rigorous description, the electronic and the nuclear degrees of freedom are both described by quantum mechanics; the system is described by the full stationary Schrödinger equation,

$$H(\mathbf{R},\mathbf{r}')\Psi(\mathbf{R},\mathbf{r}')=E\Psi(\mathbf{R},\mathbf{r}') \tag{1.11}$$

subject to the usual scattering boundary conditions. The full Hamiltonian is

$$H(\mathbf{R},\mathbf{r}')=T_n+h(\mathbf{r}';\mathbf{R})\,, \tag{1.12}$$

where

$$T_n=(-\hbar^2/2\mu)\nabla_R^2 \tag{1.13a}$$

and, for a one-electron system,

$$\begin{aligned} h(\mathbf{r}';\mathbf{R}) &= (-\hbar^2/2m)\nabla_{r'}^2+V(\mathbf{r}';\mathbf{R})+h_{\mathrm{soc}} \\ &= h_{\mathrm{BO}}+h_{\mathrm{soc}}\,, \end{aligned} \tag{1.13b}$$

with $V(\mathbf{r}';\mathbf{R})$ being the total potential energy of interaction of the electron and both nuclei, and h_{soc} being the "magnetic" Hamiltonian, which includes spin-orbit coupling and other smaller magnetic effects.

A much simpler description of atomic collisions (the classical trajectory description) is obtained if the nuclei are assumed to move classically along some path; then the electrons feel an intrinsically time-dependent force field because of the motion of the nuclei, and the electronic wave function $\Upsilon(\mathbf{r}',t)$ must satisfy a time-dependent Schrödinger equation,

$$h(\mathbf{r}';\mathbf{R}(t))\Upsilon(\mathbf{r}',t)=i\hbar\frac{\partial}{\partial t}\Upsilon(\mathbf{r}',t)\,. \tag{1.14}$$

If the classical path is taken to be rectilinear, with constant velocity, this approach is known as the "impact parameter method."

D. Outline of complete quantum treatment

We now wish to outline the conceptual framework within which the full Schrödinger equation is reduced to a tractable form, solved, and finally compared with experiments.

1. Expansion in a discrete basis

The process begins with the expansion of the wave function Ψ in a discrete basis that spans the electronic space. The basis which is most commonly used is the set of Born-Oppenheimer functions, which are solutions to the electronic part of the Schrödinger equation with the nuclei held fixed:

$$h_{\mathrm{BO}}(\mathbf{r}';\mathbf{R})\phi_n(\mathbf{r}';\mathbf{R})=\epsilon_n(R)\phi_n(\mathbf{r}';\mathbf{R}) \tag{1.15}$$

and the expansion of Ψ has the form

$$\Psi(\mathbf{R},\mathbf{r}')=\sum_n \chi_n(\mathbf{R})\phi_n(\mathbf{r}';\mathbf{R})\,. \tag{1.16}$$

This yields "close-coupled" equations for the nuclear wave functions $\{\chi_n(R)\}$, and those equations constitute the original quantum-mechanical form of "perturbed-stationary-states" (PSS) theory.

For many years it has been known that this approach has a number of deficiencies. All of them are related to the fact that individual terms in the expansion (1.16) do not describe the motion of the electrons as they are carried along with the nuclei. As a consequence, the coupled equations contain several types of "fictitious" couplings, some of which are of infinite range.

In this article we shall show how the original form of the PSS theory must be modified to eliminate the fictitious couplings. We shall show that the modification leads to additional terms in the close-coupled equations, which cancel infinite-range couplings and all other couplings that really represent only the displacement of the electronic basis functions with the moving atomic nuclei. We shall also define diabatic and adiabatic representations, and show their relationship to the Born-Oppenheimer representation. A properly formulated set of close-coupled equations is the essential result of this article.

The present article stops at this point, but there is much more to the theory. Perhaps someday another article will be written to review the further development of the theory, as briefly sketched below.

2. Semiclassical approximations and the relationship between quantum and classical descriptions

Although in the present article the quantum and classical trajectory descriptions are developed as separate frameworks, the relationship between the two approaches has been studied in detail. The quantum-mechanical form of the coupled equations can be reduced to the classical trajectory form by the systematic use of semiclassical approximations. These approximations define the strength and the limitations of the classical trajectory method.

3. Models and approximation methods for solving the classical trajectory equations

If there is only a small number of interacting states, the classical trajectory equations can be numerically integrated without difficulty. Nevertheless, it is useful to study certain simplified models and approximation methods because they give simple, approximate formulas for the transition probability on a given trajectory.

4. Collisional spectroscopy

From the approximate formulas, or from the numerical solution to the classical trajectory equations or to

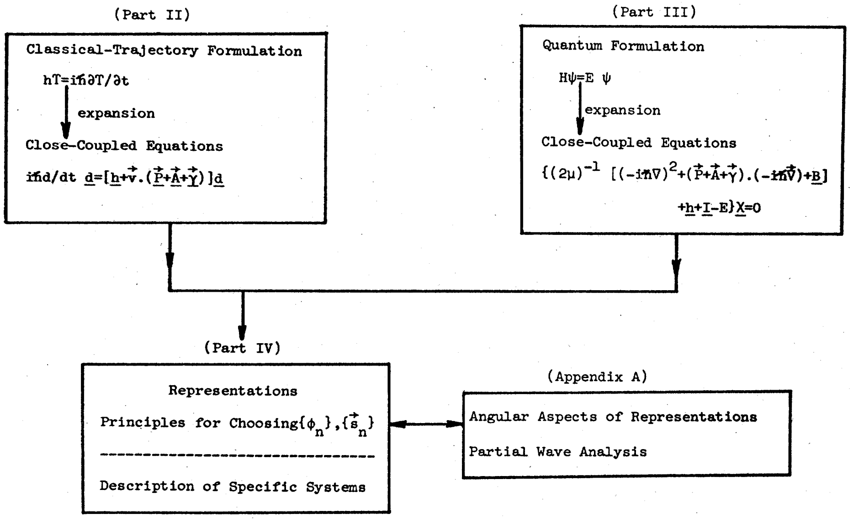

FIG. 2. Structure of this article.

the close-coupled equations in either the PSS or the corrected form, it is straightforward to obtain theoretical cross sections, either by exact numerical summation over partial waves or by using stationary phase approximations. The resulting cross sections show a great deal of interesting structure that is also found in experimental measurements. Collisional spectroscopy is the study and interpretation of these effects. This is where the theory and the experiments finally come together.

E. How to read this article

The logical structure of this article is indicated in Fig. 2. One way to read it is to start at the beginning and proceed to the end. However, there are other possibilities.

Most of Sec. II. B (intermediate-velocity collisions) is independent of the rest of the article, so it can be skipped (though II. B.2 is helpful for understanding later developments).

The reader who is not interested in the full quantum-mechanical theory can omit all of Sec. III and go directly from Sec. II to Sec. IV.

In principle, it is also possible to omit Sec. II (classical trajectory theory) and begin with the quantum-mechanical formulation in Sec. III. In a logical hierarchy, this quantum framework is the first principle, and the classical trajectory framework is an approximation that holds in a special, limiting case. However, it may be difficult to understand the quantum framework (especially the modifications to PSS theory) unless the classical trajectory theory is already understood. So although cognoscenti can begin with Sec. III, novitiates would do better to read Sec. II first.

Section III. C contains some new material. It is the final version of an approach developed by W.R. Thorson and the present author in order to correct the defects of PSS theory, and thereby to obtain an improved quantum close-coupling method. Although the derivation is not short, it leads to a very powerful formulation, which encompasses a great range of atomic collision phenomena. Readers who already know about recent developments may peruse Sec. III. C, glance through Sec. IV.A.2, and throw the rest of the article away. Finally, those who are already familiar with formal aspects of diabatics and adiabatics (Delos and Thorson, 1979) may skip most of Sec. IV.A.

It is assumed that the reader has a reasonable general background in atomic and molecular structure, and in elementary collision theory, including elastic atom-atom collisions. At various points in the text, references are given to appropriate sections of Condon and Shortley (1959), Herzberg (1950), and Slater (1963). Elastic atomic collisions are covered very adequately in the treatise by Mott and Massey (1965) and in the excellent book by Child (1974). However, since there were fundamental deficiencies in the theory of inelastic atomic collisions, we present this theory "from the beginning."[1]

II. CLASSICAL TRAJECTORY THEORY

We develop here the most general aspects of the classical trajectory description of atomic collisions. As explained earlier, in this approach the nuclei are assumed to move on a classical path, and the electrons satisfy a time-dependent Schrödinger equation. Basic definitions of coordinates, the Schrödinger equation and boundary conditions, and the development of coupled equations are presented in Sec. II.A; although there is nothing new in this section, and the ideas are quite elementary, we make a point of displaying explicitly all the assumptions that are usually hidden when the time-dependent Schrödinger equation is written down. We then review some calculations on intermediate-velocity collisions in Sec. II.B, and present simplifications applicable to slow collisions in Sec. II.C.

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[1] This article is based on lectures given mainly for advanced graduate students at William and Mary and at FOM. In connection with those lectures, the author wrote a set of exercises and problems that may be helpful for teachers and students of this subject. Some of them are scattered through the text, identified by the words "one can show . . . ." A complete set can be obtained from the author, on request.

All of the formalism developed here is applicable to an arbitrary system of two nuclei and any number of electrons. However, to keep the ideas and equations as simple as possible, we shall explicitly discuss only one-electron systems; then, in Sec. II.D, we shall show that the generalization to many-electron systems introduces no new conceptual difficulties.

A. General framework

1. Coordinate systems for describing the electron motion

There are several different frames of reference which are convenient for describing the motion of the electron(s) in a collision. They are (i) the laboratory frame, (ii) a "space-fixed" frame with origin at the center of mass of the nuclei, (iii) a rotating molecular frame, and (iv)–(vii) space-fixed and rotating frames centered on the two nuclei. The relationships among these frames of reference are important in both classical trajectory and quantum-mechanical theories of atomic collisions.

The laboratory is assumed to provide an inertial frame in which the positions of nuclei A and B and of the electron are denoted by $\mathbf{R}_A^0, \mathbf{R}_B^0, \mathbf{r}^0$ (Fig. 3). The position of the center of mass of the system is of course

$$\mathbf{R}_{\mathrm{CM}}^0 = (M_A\mathbf{R}_A^0 + M_B\mathbf{R}_B^0 + m_0\mathbf{r}^0)/(M_A + M_B + m_0)\,. \tag{2.1}$$

To describe the motion of the nuclei in the laboratory, we consider the center of mass of the nuclei (CMN):

$$\mathbf{R}_{\mathrm{CMN}}^0 = (M_A\mathbf{R}_A^0 + M_B\mathbf{R}_B^0)/(M_A + M_B) \tag{2.2}$$

and their positions relative to their center of mass

$$\rho_A = \mathbf{R}_A^0 - \mathbf{R}_{\mathrm{CMN}}^0 = \tfrac{1}{2}(-1+\lambda)\mathbf{R}\,, \tag{2.3a}$$

$$\rho_B = \mathbf{R}_B^0 - \mathbf{R}_{\mathrm{CMN}}^0 = \tfrac{1}{2}(1+\lambda)\mathbf{R}\,, \tag{2.3b}$$

$$\mathbf{R} = \mathbf{R}_B^0 - \mathbf{R}_A^0\,, \tag{2.4}$$

where

$$\lambda = (M_A - M_B)/(M_A + M_B)\,. \tag{2.5}$$

The relative nuclear velocity is

$$\mathbf{v} = d\mathbf{R}/dt \tag{2.6}$$

and, following standard convention, we take the Cartesian axes (X, Y, Z) of the laboratory frame such that the Z axis coincides with the initial direction of $\mathbf{v}$.

In principle, to fully specify the paths followed by the nuclei, we have to give the time dependence of $\mathbf{R}_{\mathrm{CMN}}(t)$ and $\mathbf{R}(t)$ [as well as $\mathbf{R}_{\mathrm{CM}}(t)$]. However, implicit in the classical trajectory framework is the idea that the nuclei are much heavier than the electrons, so the distinction between the CMN and the center of mass of the whole system is usually neglected. In that case, the CMN moves on a straight line at constant velocity relative to the laboratory, and the trajectory is specified by the time dependence of $\mathbf{R}(t)$. In the impact parameter method the nuclei themselves are assumed to move rectilinearly, and

$$\mathbf{R}(t) = \mathbf{b} + \mathbf{v}t\,, \tag{2.7}$$

where $\mathbf{v}$ is the (constant) internuclear velocity and $\mathbf{b}$ is a vector perpendicular to $\mathbf{v}$ with length equal to the impact parameter. More generally, the nuclear trajectory might be given in terms of some average potential energy of interaction of the two atoms. In any case, the vector $\mathbf{R}(t)$ is conveniently specified in terms of its length $R(t)$ and two spherical-polar angles, $\Theta(t), \Phi(t)$, that are defined relative to the orientation of the laboratory frame (Fig. 4). Since the angle $\Theta(t)$ is defined relative to the positive Z axis (the initial direction of $\mathbf{v}$), it follows that as $t \to -\infty$, $\Theta(t) \to \pi$; if the trajectory is rectilinear, then as $t \to +\infty$, $\Theta(t) \to 0$, but if it is not rectilinear, the final value of $\Theta(t)$ depends on the impact parameter, and it is called $\Theta(b)$, the deflection function. Normally the potential energy defining the nuclear trajectory is independent of Φ, the nuclear trajectory stays in a plane, the azimuthal angle $\Phi(t)$ is a constant, and it defines the collision plane. In that case, we can simplify many of the equations by taking $\Phi = 0$.

To describe the position of the electron, we may define a so-called "space-fixed frame" with origin at the CMN and orientation coinciding with the orientation of

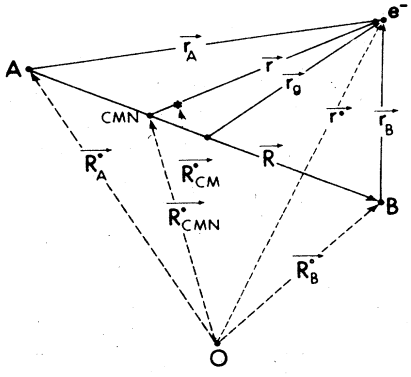

FIG. 3. Coordinates for the general molecular system A, B, e. Vectors with superscript zero are measured from an external origin O. $\mathbf{r}_g$ is the vector to e from the geometric center; CMN is the center of mass of the nuclei and is the origin for $\mathbf{r}$.

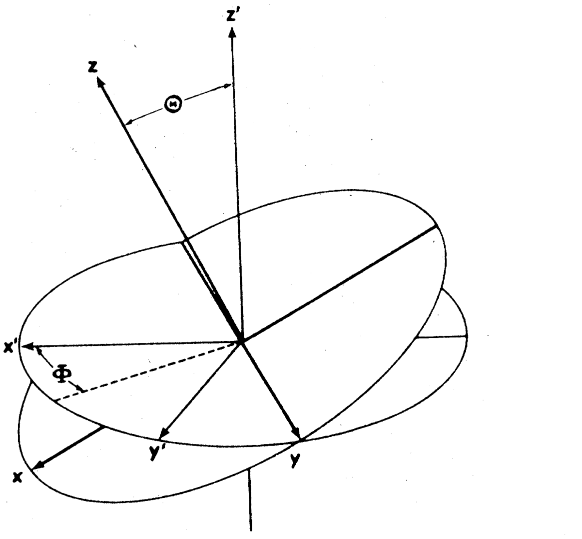

FIG. 4. Space-fixed and molecule-fixed reference frames for the molecular electron. (x', y', z') denote space-fixed axes, and (x, y, z) molecule-fixed axes. They are related via rotations by angles (θ, ϕ) as shown.

the laboratory axes. The position of the electron relative to the CMN is

$$\mathbf{r}' = \mathbf{r}^0 - \mathbf{R}_{\text{CMN}} , \tag{2.8}$$

and its components along the Cartesian axes of the space-fixed frame are denoted (x', y', z').

The electron position could also be specified relative to nucleus A or B, and we define

$$\mathbf{r}'_A = \mathbf{r}' - \rho_A = \mathbf{r}' + \tfrac{1}{2}(1 - \lambda)\mathbf{R} , \tag{2.9a}$$

$$\mathbf{r}'_B = \mathbf{r}' - \rho_B = \mathbf{r}' - \tfrac{1}{2}(1 + \lambda)\mathbf{R} . \tag{2.9b}$$

"Space-fixed atomic frames" are coordinate systems centered on nucleus A or B and translating but not rotating relative to the space-fixed frame at the CMN. The components of $\mathbf{r}'_A$ and $\mathbf{r}'_B$ in these respective frames are denoted (x'_A, y'_A, z'_A) and (x'_B, y'_B, z'_B).

The electron position can also be described by giving the components of $\mathbf{r}'$ in a "rotating molecular frame." This rotating frame is defined relative to the instantaneous position of the internuclear vector by using the polar angles $\Theta(t)$, $\Phi(t)$ as Euler angles defining two rotations: Starting from the space-fixed frame we rotate the coordinates by Φ about the z' axis, then by Θ about the new y axis (Fig. 4). Hence the components (x, y, z) of the vector $\mathbf{r}'$ in the rotating molecular frame are related to the components $(x'y'z')$ in the space-fixed frame by

$$\begin{aligned} x &= x' \cos\Theta \cos\Phi + y' \cos\Theta \sin\Phi - z' \sin\Theta , \\ y &= -x' \sin\Phi + y' \cos\Phi , \\ z &= x' \sin\Theta \cos\Phi + y' \sin\Theta \sin\Phi + z' \cos\Theta . \end{aligned} \tag{2.10}$$

The vector $\mathbf{r}$ is used to denote these collective components $(x, y, z,)$; $\mathbf{r}$ is geometrically the same vector as $\mathbf{r}'$, both being $\mathbf{r}^0 - \mathbf{R}_{\text{CMN}}$, but the prime means that components in the space-fixed frame are to be considered, while no prime means that components in the rotating molecular frame are to be considered.

Rotating atomic frames of reference may also be defined; these are centered on nuclei A or B, but oriented in the same way as the rotating molecular frame. Components of the vectors $\mathbf{r}_A, \mathbf{r}_B$, representing the position of the electron relative to the respective nuclei, are given by

$$\begin{aligned} x_A &= x_B = x , \\ y_A &= y_B = y , \\ z_A &= z + \tfrac{1}{2}(1 - \lambda)R , \\ z_B &= z - \tfrac{1}{2}(1 + \lambda)R . \end{aligned} \tag{2.11}$$

For the special case $\Phi = 0$, these coordinate systems are shown in Fig. 5.

2. Time-dependent Schrödinger equation

The wave function for the electron in the moving field of the nuclei satisfies the time-dependent Schrödinger equation

$$h\Upsilon = i\hbar \frac{\partial \Upsilon}{\partial t} . \tag{2.12}$$

As in Eq. (1.13b), the electronic Hamiltonian h contains electrostatic terms (which we like to call the "Born-Oppenheimer electronic Hamiltonian") and magnetic terms, of which the most important is spin-orbit coupling:

$$h = h_{\text{BO}} + h_{\text{soc}} . \tag{2.13}$$

One of the electrostatic terms is the electron kinetic energy, $(-\hbar^2/2m_0)\nabla^2$. This kinetic energy contains the "rest mass" m_0 of the electron, but since the nuclei are much heavier than the electron we ignore the distinction between this rest mass and the atomic or molecular reduced mass. ∇^2 contains derivatives with respect to electronic coordinates referred to *any inertial frame*; then $\partial/\partial t$ must be taken holding the electron coordinates fixed in this *same* frame of reference. One of the fundamental results of elementary quantum mechanics is that the probability density $|\Upsilon|^2$ is invariant under Galilean transformations of the reference frame (Schiff, 1955, p. 40, problem 2; Gottfried, 1966, Vol. I, p. 246 ff). In the present context, this general invariance principle implies that the coupled equations are independent of the origin of coordinates, provided that certain phase factors ("electron-translation factors") are properly included; this specific invariance will be displayed more explicitly below. If, as mentioned earlier, we neglect the difference between the center of mass of the nuclei and the center of mass of the whole system, then the space-fixed frame with origin at the CMN is an inertial frame, and we can take $\nabla^2 = \nabla^2_{r'}$, and $\partial/\partial t = (\partial/\partial t)_{r'}$.

The Born–Oppenheimer Hamiltonian also includes the full potential energy,

$$\frac{-\hat{Z}_A e^2}{r_A} - \frac{\hat{Z}_B e^2}{r_B} + \frac{\hat{Z}_A \hat{Z}_B e^2}{R} ,$$

but after the nuclear trajectory is specified, the internuclear potential energy term $\hat{Z}_A \hat{Z}_B e^2/R$ is just a (time-dependent) constant parameter in this Hamiltonian, and it can be eliminated by adjusting the phase of the wave function by the factor

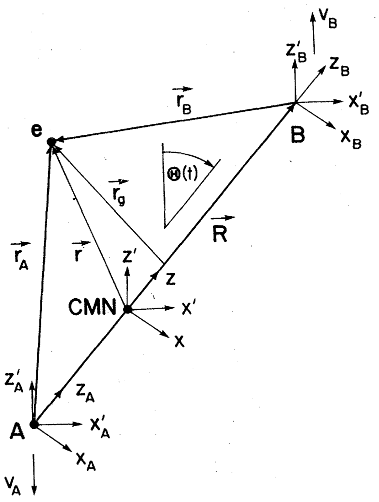

FIG. 5. Rotating and nonrotating frames of reference for electronic coordinates for the special case $\phi = 0$. The y and y' axes are into the page.

$$\exp\left(-i\int_0^t \hat{Z}_A\hat{Z}_B e^2/R(t')dt'/\hbar\right).$$

The Hamiltonian for spin-orbit coupling is given explicitly later. (Sec. IV.B.1). However, since for atoms of low $\hat{Z}$, spin-orbit coupling is small, it is frequently possible to neglect it, and we shall ignore it for now, reinstating it later when it is necessary. Hence for the purpose of this section it is sufficient to take the Hamiltonian to be

$$\begin{aligned} h=h_e &\equiv -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}'}-\frac{\hat{Z}_Ae^2}{r_A}-\frac{\hat{Z}_Be^2}{r_B}\\ &= T_e+V_0^A+V_0^B\,. \end{aligned} \tag{2.14}$$

3. Boundary conditions

a. Asymptotic form of wave function

To describe the electron wave function in the limit as $t\to\pm\infty$, when the nuclei are far apart, it is convenient to define atomic partitions of h_e:

$$h_A^0=T_e+V_0^A\,, \tag{2.15a}$$

$$h_B^0=T_e+V_0^B\,, \tag{2.15b}$$

$$h_e=h_A^0+V_0^B=h_B^0+V_0^A\,. \tag{2.15c}$$

The asymptotic states are explicitly time-dependent solutions to one of the "free" atomic Schrödinger equations,

$$h_A^0\psi_{k_A}=i\hbar\partial\psi_{k_A}/\partial t\,, \tag{2.16a}$$

$$h_B^0\psi_{k_B}=i\hbar\partial\psi_{k_B}/\partial t\,. \tag{2.16b}$$

Solutions to these equations, as expressed in the space-fixed frame, are not simply stationary atomic orbitals reexpressed in moving coordinates. The correct asymptotic states contain also an "electron-translation factor" (ETF), which represents the momentum and kinetic energy of the electron as it rides on nucleus A or B:

$$\psi_{k_A}=F_A(\mathbf{r}',t)\phi_{k_A}(\mathbf{r}'_A)\exp(-i\epsilon_{k_A}t/\hbar)\,, \tag{2.17a}$$

$$F_A(\mathbf{r}',t)=\exp[i(m\mathbf{v}_A\cdot\mathbf{r}'-mv_A^2t/2)/\hbar]\,, \tag{2.17b}$$

$$\phi_{k_A}(\mathbf{r}'_A)=\phi_{n_Al_A}(r'_A)Y_{l_Am_A}(\theta'_A,\phi'_A)\,, \tag{2.17c}$$

$$\mathbf{v}_A=d\boldsymbol{\rho}_A/dt=\tfrac{1}{2}(-1+\lambda)\mathbf{v}\,. \tag{2.17d}$$

$\phi_{k_A}(\mathbf{r}'_A)$ is an ordinary atomic orbital for atom A, and ϵ_{k_A} is its energy. Expressing the orbital as $\phi_{k_A}(\mathbf{r}'-\boldsymbol{\rho}_A(t))$, it is easy to show that Eq. (2.17) satisfies the free Schrödinger equation (2.16a) while $\phi_{k_A}(\mathbf{r}-\boldsymbol{\rho}_A(t))$ by itself does not. Similar formulas hold for ψ_{k_B}.

The proof of this assertion is straightforward . Applying Eq. (2.16a) to (2.17), we have

$$\begin{aligned}[(h_A^0-i\hbar\,\partial/\partial t)\psi_{kA}&=\exp[(i/\hbar)(-\epsilon_{kA}t+\mathrm{m}v_A\cdot\mathbf{r}'-mv_A^2t/2)]\\ &\quad\times\{[h_A^0\phi_{k_A}+\mathbf{v}_A\cdot(-i\hbar\nabla_{r'})\phi_{k_A}+(mv_A^2/2)\phi_{kA}]\\ &\quad+[-\epsilon_{kA}\phi_{kA}-(mv_A^2/2)\phi_{kA}-i\hbar\mathbf{v}_A\cdot\nabla_{\rho A}\phi_{kA}]\}, \end{aligned} \tag{2.18}$$

where the first bracket arises from h_A^0 and the second from $-i\hbar\,\partial/\partial t$). It is clear that the terms cancel exactly.

Note in particular that the last term in Eq. (2.18) represents the change with time of ϕ_{kA} that results from the displacement of this orbital with the moving nucleus. This term is canceled by a term that arises when h_A^0 acts on the ETF.

In the present context, the ETF's have never been a source of confusion. Since the earliest formulations of the theory of charge exchange (such as that of Brinkman and Kramers, 1930), ETF's have always been incorporated in calculations based on atomic representation. However, not until much later was it recognized that ETF's also have to be included in calculations based upon molecular representations, and that they also have to be incorporated somehow into quantum-mechanical formulations of collision theory.

b. Cross sections

(*i*) *Total cross sections.* Suppose for the incident beam the electronic state is the jth state of atom A; this is represented by the traveling atomic orbital $\psi_{j_A}(\mathbf{r}')$, so

$$\lim_{t\to-\infty}\langle\psi_{j_A}|\Upsilon\rangle=1\,. \tag{2.19}$$

After the collision the electron may be bound to A or B, or it may be free. As $R\to\infty$, bound states of A become orthogonal to those of B, and therefore the probability for finding the electron in the kth bound electronic state on A or B is

$$\begin{aligned} \lim_{t\to\infty}|\langle\psi_{k_A}|\Upsilon\rangle|^2&=P_{k_A}\,,\\ \lim_{t\to\infty}|\langle\psi_{k_B}|\Upsilon\rangle|^2&=P_{k_B}\,. \end{aligned} \tag{2.20}$$

The total cross section for scattering into states k_A or k_B is the integral of the transition probability over all impact parameters:

$$\begin{aligned} \sigma_{k_A}&=2\pi\int_0^\infty P_{k_A}(b)b\,db\,,\\ \sigma_{k_B}&=2\pi\int_0^\infty P_{k_B}(b)b\,db\,. \end{aligned} \tag{2.21}$$

(*ii*) *Differential cross sections.* Classical differential cross sections may be calculated by obtaining the deflection function $\Theta(b)$ and the corresponding cross section $\sigma_{cl}(\Theta,E)=b\,db/\sin\Theta\,d\Theta$, employing some reasonable effective potential for describing the nuclear motion. The differential cross section for a given transition would then be given by

$$\begin{aligned} \sigma_{k_A}(\Theta,E)&=\sigma_{cl}(\Theta,E)P_{k_A}\,,\\ \sigma_{k_B}(\Theta,E)&=\sigma_{cl}(\Theta,E)P_{k_B}\,. \end{aligned} \tag{2.22}$$

Alternately, even if the trajectories were taken to be rectilinear, differential cross sections could be calculated from an integral formula based upon an eikonal approximation (Wilets and Wallace, 1968; Glauber, 1959; see also Bransden, 1970, p. 79).

(*iii*) *Ionization cross sections.* The calculation of cross sections for ionization requires care because free particle states of A and B form an overcomplete and nonorthogonal set, even as $R\to\infty$. In spite of this formal redundance, however, it can be shown that very similar formulas to those for bound states also hold for the continuum. In particular, the existence of pronounced forward scattering peaks in the differential ionization cross section in such collisions can be simply explained by an appropriate use of the joint continua of both target and projectile atoms (Band, 1974; see also Macek, 1970)

4. Coupled equations

Since the Schrödinger equation (2.12) is an inseparable partial differential equation in at least four variables, it is practically impossible to solve directly. The standard method for solving it involves an expansion in a carefully chosen set of basis functions $\{\phi_k\}$ that span the space of the electronic coordinates. For collision problems, each basis function ϕ_k must also be multiplied by an appropriate electron-translation factor F_k. The basis functions and ETF's will be specified more fully later; for now we simply write

$$\Upsilon = \sum_k d_k(t) F_k \phi_k . \tag{2.23}$$

Operating on both sides of this equation with $(h - i\hbar\partial/\partial t)$, multiplying by $\phi_j^* F_j^*$, and integrating over electron variables leads to

$$\langle \phi_j | F_j^*(h - i\hbar\partial/\partial t) | \Upsilon \rangle = \sum_k \langle \phi_j | F_j^* F_k | \phi_k \rangle \left(-i\hbar \frac{d}{dt} d_k \right) + d_j \langle \phi_j | F_j^*(h - i\hbar\partial/\partial t) F_k | \phi_k \rangle = 0 . \tag{2.24}$$

This is a set of coupled first-order differential equations for the coefficients $d_k(t)$; in matrix notation

$$\underline{S}(v) i\hbar \frac{d}{dt} \underline{d}(t) = \underline{\mathcal{H}}(v) \underline{d}(t) \tag{2.25a}$$

or

$$i\hbar \frac{d}{dt} \underline{d}(t) = \underline{S}(v)^{-1} \underline{\mathcal{H}}(v) \underline{d}(t) , \tag{2.25b}$$

with

$$S_{jk}(v) = \langle \phi_j | F_j^* F_k | \phi_k \rangle , \tag{2.26a}$$

$$\mathcal{H}_{jk}(v) = \langle \phi_j | F_j^*(h - i\hbar\partial/\partial t) F_k | \phi_k \rangle . \tag{2.26b}$$

If the basis functions (including ETF's) formed a complete set, then the solution to these coupled differential equations would be exactly equivalent to the solution to the Schrödinger equation. Since, of course, basis sets used in actual calculations are far from complete, great care is needed in the choice of functions and ETF's.

a. Probability conservation

For a general basis set, $\underline{S}(v)$ is not diagonal and $\underline{\mathcal{H}}(v)$ is not necessarily a Hermitian matrix. Although the matrix representation of h is Hermitian (provided that the basis functions are square integrable), the matrix representing $-i\hbar\partial/\partial t$ need not be Hermitian. As a result, probability conservation is not manifest in Eqs. (2.25); in particular, $\sum_k |d_k(t)|^2$ need not be conserved. However, the total probability is not given by this expression but by $\langle \Upsilon | \Upsilon \rangle$; hence the condition for probability conservation is (Green, 1965)

$$i\hbar \frac{d}{dt} \langle \Upsilon | \Upsilon \rangle = i\hbar \frac{d}{dt} \underline{d}^\dagger \underline{S}(v) \underline{d} = \underline{d}^\dagger [\underline{\mathcal{H}} - \underline{\mathcal{H}}^\dagger + i\hbar \frac{d}{dt} \underline{S}(v)] \underline{d} = 0 ,$$

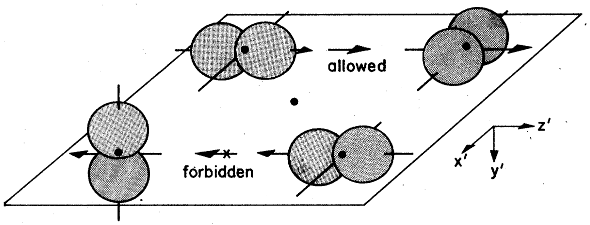

FIG. 6. Illustration of the ± symmetry selection rule. The motion of the two nuclei defines the collision plane, which is here taken to be the plane $y' = 0$. With respect to reflection through this plane, the $2p_{x'}$ and $2p_{z'}$ states have + symmetry, while the $2p_{y'}$ state has − symmetry. Hence $2p_{z'} \longleftrightarrow 2p_{x'}$, but $2p_{z'}, 2p_{x'} \not\longleftrightarrow 2p_{y'}$.

which holds if

$$\underline{\mathcal{H}} - \underline{\mathcal{H}}^\dagger + i\hbar \frac{d}{dt} \underline{S}(v) = 0 . \tag{2.27}$$

It is easy to show that this condition is satisfied for any finite discrete basis set for which the basis functions are square integrable.[2]

b. Symmetry and selection rules

Symmetry of the colliding system can be employed to reduce the number of coupled equations (Wilets and Gallaher, 1966). The electronic Hamiltonian is invariant under reflection through the collision plane, and this invariance implies a conservation law. In particular, if the initial state is symmetric or antisymmetric under this reflection, then the final state must have the same symmetry. In molecular spectroscopy this symmetry property of the electronic states is denoted ±, as in $^1\Sigma^+, {}^3\Sigma^-$, and for collisions we have the selection rule

$$+ \longleftrightarrow + ; \quad - \longleftrightarrow - ; \quad + \not\longleftrightarrow - . \tag{2.28}$$

An illustration of this rule is given in Fig. 6.

If the two nuclei have equal charge (symmetric system) then the electronic Hamiltonian is invariant under inversion through the geometric center of the molecule. This is the parity or (*gerade*-*ungerade*) symmetry of electronic states, and for such systems we have the selection rule

$$g \longleftrightarrow g ; \quad u \longleftrightarrow u ; \quad g \not\longleftrightarrow u . \tag{2.29}$$

Because of these symmetries of the Hamiltonian, the number of coupled channels can be reduced if the basis states (and ETF's) are made to have + or −, or g or u, symmetry.

For example, s, p_x, and p_z atomic states are +, while p_y states are −. Hence there are no transitions from s to p_y states so long as the nuclear trajectory is confined to a plane. Similarly, for symmetric systems, functions such as

$$F_B \phi_{kB} \pm F_A \phi_{kA} \tag{2.30}$$

have either g or u symmetry, and there will be no $\underline{\mathcal{H}}(v)$ or $\underline{S}(v)$ matrix elements connecting them.

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[2] In some early work on charge exchange (e.g., Rapp and Francis, 1962; Bates, Johnston, and Stewart, 1964; and others) the Eqs. (2.25) were symmetrized to ensure conservation of $\sum_k |d_k|^2$ instead of conservation of $\langle \Upsilon | \Upsilon \rangle$; however, Green (1965) has shown that this can lead to significant errors and that it is better to use the unsymmetrized forms.

B. Intermediate-velocity collisions

We review here some calculations dealing with collisions of protons with hydrogen atoms at velocities around one atomic unit. The purpose of this section is mainly to show the physical meaning behind the mathematical equations (2.25). In so doing, we also summarize the progress that has been made in this area, and point out some problems that still remain.

Two simplifications are important in this intermediate-velocity region. First, except for collisions at very small impact parameters, the nuclei move past each other practically on a straight line at constant velocity. Second, if the internuclear velocity is greater than the average velocity of the electron, then the electronic wave function does not have time to adjust to the changing potential field. Accordingly, Υ is best described by means of an expansion in basis states which are closely related to the states of the separated atoms. Some examples are given below.

1. Basis sets

a. Traveling atomic orbitals (TAO's)

Since the boundary conditions [Eqs. (2.17)] involve atomic eigenstates, it is natural to use these same states as the basis functions in the expansion (2.23). Thus

$$F_k\phi_k = F_A\phi_{k_A} \quad \text{and} \quad F_B\phi_{k_B}\,, \tag{2.31a}$$

where the latter are defined in (2.17). If all of the (bound and free) atomic states, ϕ_{k_A}, ϕ_{k_B} were included, then each of the sets $\{\phi_{k_A}\}, \{\phi_{k_B}\}$ would be complete, so the wave function could be expanded in *either* an A- or B-atomic basis as

$$\Upsilon = \sum_{k_A} d_{k_A} F_A \phi_{k_A}$$

$$= \sum_{k_B} d_{k_B} F_B \phi_{k_B}\,.$$

In practice, however, these expansions are rarely useful, because it is practically impossible to represent accurately a charge-exchange state (such as $F_B\phi_{k_B}$) in terms of states based on the original center ($F_A\phi_{k_A}$). A much more useful expansion is obtained by selecting a small set of both A and B states, and expanding the wave function as

$$\Upsilon = \sum_{k_A} d_{k_A} F_A \phi_{k_A} + \sum_{k_B} d_{k_B} F_B \phi_{k_B}\,. \tag{2.31b}$$

Many calculations have been performed with some success by using such an expansion. However, this expansion also leads to some difficulties. (1) The set of all ϕ_{k_A} and ϕ_{k_B} is nonorthogonal (this is a property of all the atomic bases considered) and formally overcomplete. The nonorthogonalities are not a problem in the classical trajectory method, provided that overlap integrals are explicitly included in the coupled equations (Bates, 1958). (However, in the quantum-mechanical Born approximation, these nonorthogonalities led to some confusing early results for charge exchange cross sections; see Brinkman and Kramers, 1933; Bates and Dalgarno, 1952; Jackson and Schiff, 1953; Brandsden, 1970, Chapter 8; Band, 1973; and Lin, Soong, and Tunnell, 1978). (2) Convergence of the expansion using atomic eigenfunctions may be poor, or it may converge to an incorrect result. The discrete (bound) hydrogenic states are not a complete set. Furthermore, for large n they are functions with maximum density far from the nuclei (high Rydberg states); however, important deformations of $\Upsilon(\mathbf{r}', t)$ probably occur only close to the nuclei. Similar defects of hydrogenic expansions are familiar to valence theorists. To improve convergence by explicit inclusion of continuum states would create an almost intractable problem for the coefficients and also increase the problems due to nonorthogonality and overcompleteness.

b. Rotating traveling atomic orbitals

Instead of the TAO's, which are oriented in a space-fixed frame, it may be convenient to use a set of atomic functions that follow the rotating molecular frame (Wilets and Gallaher, 1966). An example of such a rotating basis function is a $2p_z = 2p_\sigma$ state, which has its lobes aligned along the internuclear axis. Such functions can be written

$$\phi_{k_A} = \phi_{n_A l_A}(r_A) Y_{l_A m_A}(\theta_A, \phi_A)\,. \tag{2.32}$$

The states differ from those of Eq. (2.17c) in that the angles θ_A, ϕ_A specifying the electronic coordinate $\mathbf{r}_A$ are defined relative to the rotating atomic frame, while θ'_A, ϕ'_A are defined relative to a space-fixed atomic frame.

At low velocities (small $\dot{\Theta}$), the wave function Υ tends to follow the internuclear axis, so this basis is preferable. However, in the rotating frame the system experiences angular couplings which increase with increasing velocities and which can be said to decouple the electronic wave function from the internuclear axis, so, at high velocities, the wave function tends to maintain its space-fixed orientation, and the space-fixed atomic basis set is preferable.

Rotating atomic basis sets have the same orthogonality-completeness properties as do space-fixed basis sets, and the associated difficulties again arise.

c. Sturmian functions

To improve convergence of the expansion, Gallaher and Wilets (1968) suggested the use of Sturmian radial functions; these are solutions to the hydrogenic radial equation,

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{l(l+1)}{2mr^2} - \frac{\alpha_{nl}(\epsilon)}{r}\right) S_{nl}(r;\epsilon) = \epsilon S_{nl}(r;\epsilon) \tag{2.33}$$

but ϵ is an assigned (arbitrary) parameter and $\alpha_{nl}(\epsilon)$ is the eigenvalue. For what value of nuclear charge α_{nl} is the binding energy of the level equal to ϵ? The relation is (atomic units) $\alpha_{nl}(\epsilon) = n(-2\epsilon)^{1/2}$, and the Sturmian functions are thus just scaled hydrogenic functions,

$$S_{nl}(r;\epsilon) = [\alpha_{nl}(\epsilon)]^{1/2} R_{nl}(\alpha_{nl}(\epsilon) r)\,. \tag{2.34}$$

The arbitrary parameter ϵ can be selected to give useful scalings; Gallaher and Wilets used $\epsilon = -[2(l+1)^2]^{-1}$ so that $\alpha_{nl} = n/(l+1)$. The Sturmian functions form an entirely discrete complete set and have most of their density in a more compact region than do the hydrogenic states. On the other hand, because they are not eigenstates of the atomic Hamiltonians, the expansion coefficients $|d_n|$ for a Sturmian basis do not approach definite limits as $t \to \pm\infty$, but oscillate. Transition amplitudes are obtained by finding the projection of the wave function as $t \to \infty$ onto the hydrogenic TAO's. However, since the TAO's cannot be exactly reconstructed from a *finite* set of Sturmian functions, the resulting transition amplitudes also oscillate indefinitely. Gallaher and Wilets solved this problem by explicitly evaluating and neglecting the oscillatory terms.

Later Shakeshaft (1975, 1976) further developed the Sturmian function method, presenting a new way to evaluate exchange matrix elements and an alternative method for projecting the scattering amplitudes. The Gallaher and Wilets calculation made use of rotating spherical harmonics for the angular parts of the atomic orbitals, while Shakeshaft's calculation used nonrotating orbitals.

d. "Pseudostates"

Cheshire, Gallaher, and Taylor (1970) took the point of view that formal completeness of an expansion is a property whose virtue is seldom effective, since for practical reasons any expansion is truncated after (say) five to ten terms. Therefore if one is limited by computational considerations to a truncated expansion, it is important that the terms taken represent the physical wave function as closely as possible, and much less important that they be members of a formally complete set; accuracy at $N=5$ is much more important than convergence as $N \to \infty$. (This viewpoint has also prevailed for a long time in valence theory calculations, where the Rayleigh-Ritz principle provides some criterion of success).

Accordingly, these authors chose basis states as follows: (1) To avoid the problem of poor asymptotic behavior (as with the Sturmian functions), they included some unmodified hydrogenic orbitals ($1s, 2s, 2p$), one for each of the final states for which they wished to compute cross sections. (2) To this set they added some additional functions chosen to overlap well with states such as the (united-atom) wave functions of He$^+$, i.e., functions having most of their density at small r; (3) a third consideration was computational convenience, especially for the exchange (A-B) integrals. They used states of the form

$$e^{-\zeta r} W_{nl}(r) Y_{lm}(\theta, \phi)\,,$$

where orbital exponents were chosen to meet the above criteria and $W_{nl}(r)$ are polynomials such that these pseudostates are orthogonal to the hydrogenic states used. When only transitions to the hydrogenic final states are computed, no projection problems then arise.

2. Matrix elements

Important physical insight is gained by examining the matrix elements (2.26) in more detail. Following the same development as was given in Eq. (2.18), it is easy to obtain the following.

a. Direct elements.

$$S_{j_A k_A} = \langle \phi_{j_A} | \phi_{k_A} \rangle\,, \tag{2.35}$$

$$\mathcal{H}_{j_A k_A}(v) = \left\langle \phi_{j_A} \left| \left[h - i\hbar \left(\frac{\partial}{\partial t} + \mathbf{v}_A \cdot \nabla_{r'} \right) \right] \right| \phi_{k_A} \right\rangle . \tag{2.36}$$

b. Exchange elements.

$$S_{j_B k_A}(v) = \langle \phi_{j_B} | F_B^* F_A | \phi_{k_A} \rangle\,, \tag{2.37}$$

$$\mathcal{H}_{j_B k_A}(v) = \left\langle \phi_{j_B} \left| F_B^* F_A \left[h - i\hbar \left(\frac{\partial}{\partial t} + \mathbf{v}_A \cdot \nabla_{r'} \right) \right] \right| \phi_{k_A} \right\rangle . \tag{2.38}$$

Direct matrix elements for B-centered states $S_{j_B k_B}$, $\mathcal{H}_{j_B k_B}$ are obtained by replacing A by B in Eqs. (2.35) and (2.36); A-B exchange elements $S_{j_A k_B}, \mathcal{H}_{j_A k_B}$ are obtained by interchanging A and B in Eqs. (2.37) and (2.38).

The direct overlap element $S_{j_A k_A}$ is just the overlap integral between two A-centered states. In the basis sets considered above, states on the same center were taken to be orthogonal, so $S_{j_A k_A} = \delta_{jk}$. The exchange element $S_{j_B k_A}$ involves the overlap between states on two different centers. These overlaps go to zero as $R \to \infty$, but they become large at small R. This element also contains the momentum-transfer factor $F_B^* F_A$; when this factor is evaluated using Eq. (2.7) and the time derivatives of (2.3) it becomes $\exp(-im\mathbf{v} \cdot \mathbf{r}_g'/\hbar)$, where

$$\mathbf{r}_g' = \mathbf{r}' - \tfrac{1}{2}\lambda R \tag{2.39}$$

is the electron coordinate measured from the geometric center of the molecule. The same factor appears in the exchange elements $\mathcal{H}_{j_B k_A}$. At low velocities, this factor approaches unity and becomes insignificant, but at high velocities the momentum-transfer factor greatly reduces the exchange matrix elements and the probability of charge exchange.

The $\mathcal{H}$-matrix elements obviously involve the electronic Hamiltonian, which contains the changing potential fields that induce transitions from one state to another. Except in the momentum-transfer factor, these matrix elements do not involve the collision velocity, and they could be called "static" or "potential" couplings.

The other terms in $\mathcal{H}$ could be called "dynamic" or "velocity-dependent" couplings. The term $(\partial/\partial t) = (\partial/\partial t)_{\mathbf{r}}$, means the total rate of change of $|\phi_{k_A}\rangle$ as seen in the inertial frame of reference, which we took to be the space-fixed frame with origin at the center of mass of the nuclei. This total rate of change can come from several sources: (i) ϕ_{k_A} changes in the space-fixed frame because it is moving with nucleus A; (ii) functions that rotate with the molecular axis are seen to change in the space-fixed frame because of this rotation; (iii) sometimes basis functions are taken to have orbital exponents, coefficients, or other parameters that vary with internuclear separation, and $(\partial/\partial t)|\phi_{k_A}\rangle$ also involves the rate of change of such parameters.

(None of the basis functions described above contain such varying parameters, but basis functions used for slow collisions usually contain them).

The quantity $-\mathbf{v}_A\cdot\nabla_{r'}\phi_{k_A}$ represents that part of the total rate of change of $|\phi_{k_A}\rangle$ that arises from the displacement of ϕ_{k_A} with the A nucleus, and $(\partial/\partial t + \mathbf{v}_A\cdot\nabla_{r'})\phi_{k_A}$ represents the total change minus the displacement change; hence it is the net rate of change of ϕ_{k_A} as seen in the (nonrotating) A-atomic frame of reference. The formulas are telling us the intuitively obvious fact that only this net change, not including displacement, leads to velocity-dependent couplings that cause electronic transitions.

One can also verify that the same matrix elements (2.37) would be obtained, independently of the original frame of reference. (The fact that they are independent of λ is necessary and sufficient.) This is a special case of the general invariance principle mentioned in Sec. II.A.2.

a. *Angular couplings*

We have already mentioned that basis functions that rotate with the molecular frame lead to angular couplings, which we now evaluate explicitly. Consider a rotating atomic basis function $\phi_{k_A}(\mathbf{r}_A)$. Following the above discussion, we are supposed to evaluate the rate of change of this function as seen in the space-fixed A-atomic frame of reference $[\partial\phi_{k_A}(\mathbf{r}_A)/\partial t]_{r_A'}$. Now rotating *atomic* coordinates are obtained from space-fixed atomic coordinates by the same two rotations that were shown in Fig. 4, so the relationship between them is also given by Eq. (2.10), with $(x_A y_A z_A)$ appearing on the left- and $(x_A' y_A' z_A')$ on the right-hand side of this equation. Hence straightforward differentiation and a little manipulation lead directly to

$$[-i\hbar\partial\phi_{k_A}(\mathbf{r}_A)/\partial t]_{\mathbf{r}_A'} = [-\dot{\Theta}L_{y_A} + \dot{\Phi}(\sin\Theta L_{x_A} - \cos\Theta L_{z_A})]\,\phi_{k_A}$$
$$= R^{-1}[-v^{\Theta}L_{y_A} + v^{\Phi}(L_{x_A} - \cot\Theta L_{z_A})]\,\phi_{k_A}\,, \tag{2.40}$$

where v^{Θ}, v^{Φ} are the angular components of the internuclear velocity $R\dot{\Theta}$ and $R\sin\Theta\dot{\Phi}$. Usually $v^{\Phi}=0$, and the angular coupling matrix elements become

direct:

$$R^{-1}v^{\Theta}\langle\phi_{j_A}|L_{y_A}|\phi_{k_A}\rangle \tag{2.41a}$$

exchange:

$$R^{-1}v^{\Theta}\langle\phi_{j_B}|F_B^*F_A L_{y_A}|\phi_{k_A}\rangle\,. \tag{2.41b}$$

More discussion of these terms will be given in connection with slow collisions; for now we only note that since the A-atomic functions are rotating about the y_A axis (assuming $v^{\Phi}=0$) the operator that appears here is the generator of that rotation. In classical mechanics, $h-\dot{\Theta}L_{\alpha}$ is also the Hamiltonian in a frame that rotates about the α axis, and the corresponding equations of motion contain Coriolis and centrifugal "forces." Angular couplings are the quantum-mechanical analogs of these classical effects of a rotating frame of reference.

3. Some calculations on the H$^+$-H system

We now summarize some illustrative calculations on H$^+$-H(1s) collisions, using atomic representation in the region 1–100 keV.

a. *"One-state" approximation*

Because the $(\underline{g},\underline{u})$ symmetry effectively halves the number of coupled equations to be integrated, the use of an expansion consisting of one state on each atom, $F_A\phi_{1s_A}(r_A)$ and $F_B\phi_{1s_B}(r_B)$, may be called a "one-state" approximation.

Both states are spherically symmetric, so angular coupling matrix elements vanish, and there are no other velocity-dependent couplings. By combining the basis functions into states of $\underline{g}$ and $\underline{u}$ parity [as in Eq. (2.30)], two uncoupled equations are obtained, and the solution to these equations subject to the earlier-discussed boundary conditions leads directly to a simple formula for the charge exchange probability: assuming $1s_A$ is the initial state,

$$P_{1s_B} = \sin^2\int_{-\infty}^{\infty}[\mathcal{H}_{AB}(v) - S_{AB}(v)\mathcal{H}_{BB}(v)]/[1-S_{AB}^2(v)]\,dt \tag{2.42}$$

(McCarroll, 1961). Here the matrix elements involve 1s orbitals as indexed (A,B). The total charge exchange cross section is obtained by putting this into Eq. (2.21) and integrating over b. Results of McCarroll's numerical calculation are shown in Fig. 7.

So far the only approximations that have been made are (i) approximations inherent in the impact parameter method, and (ii) truncation of the expansion (2.23) to two atomic states, $1s_A, 1s_B$. Now let us consider an additional approximation, the neglect of the momentum-transfer factor $F_B^*F_A$. If the nuclear velocity v is sufficiently small, then $\exp(-imvz_g'/\hbar)$ will be slowly varying over a distance of $1a_0$, and this factor will not significantly affect the values of matrix elements. The result of setting this factor to unity is also shown in Fig. 7; at 1 keV it leads to $\lesssim$3% error, at 10 keV about 15% error, and at higher velocities it leads to poor results, greatly overestimating the charge exchange cross section. One can see that the rapid decrease in the exchange cross section at energies above 25 keV is a direct consequence of the momentum-transfer factor. A kind of first-order calculation, which approximates the sin by its argument in Eq. (2.42), is also shown in Fig. 7.

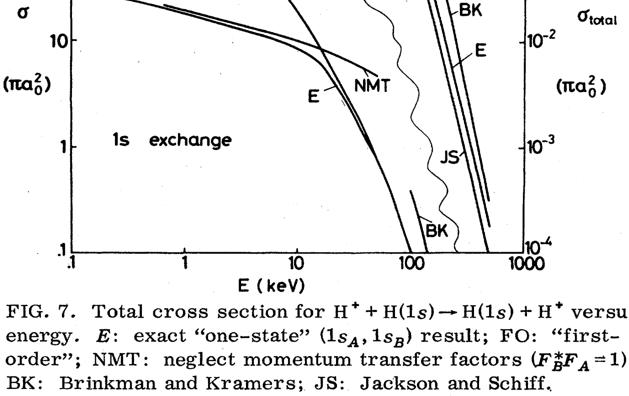

FIG. 7. Total cross section for H$^+$ + H(1s) → H(1s) + H$^+$ versus energy. E: exact "one-state" $(1s_A, 1s_B)$ result; FO: "first-order"; NMT: neglect momentum transfer factors $(F_B^*F_A=1)$; BK: Brinkman and Kramers; JS: Jackson and Schiff.

There are no experiments that directly measure the $1s_A \rightarrow 1s_B$ charge exchange cross section, but several experiments have measured the *total* exchange cross section, which primarily consists of exchange into the ground state. Bransden (1970, p. 329) compares these with calculations, and it is found that the "one-state" calculation of McCarroll is in good agreement with experimental data below 100 keV, though it may be somewhat too large at higher energies.

b. Multistate approximations[3]

Calculations on H$^+$-H collisions are summarized in Table I. We have listed only calculations that are based on the impact parameter method and atomic representations, and which obtain exact numerical solutions to the coupled equations. (There are also many calculations based on Born, eikonal, or distorted-wave methods, or upon first-order or Magnus approximations for the solution to the coupled equations, but such calculations are likely to be less accurate in general because the H$^+$-H system has strong coupling between the 1s and $2p_z$ states.) Of the listed calculations, besides the one-state calculations of McCarroll (1961), the most important are those of Rapp and Dinwiddie (1972), Cheshire, Gallaher, and Taylor (1970), and Shakeshaft (1976). (The first four listed calculations cannot give cross sections for excitations; apparently the calculations of Gallaher and Wilets contained numerical errors in the evaluation of matrix elements, and some of the results of Rapp, Dinwiddie, Storm, and Sharp were in error because of the neglect of long-range coupling between $2s$ and $2p$ states.)

First, let us consider charge transfer to the $1s$ state. On the scale of Fig. 7, differences between two-state and many-state calculations are only barely visible, so we do not reproduce them in this figure. One finds that the inclusion of additional states increases the calculated $1s \rightarrow 1s$ charge transfer cross section by a few percent over most of the energy range. The Cheshire, Gallaher, and Taylor (CGT-7) calculation gives the largest result, which is *at most* 20% above the two-state calculation (at $E = 1$ keV) and usually much closer to it.

Results for exchange excitation to the $2s$ state are shown in Fig. 8. The Rapp and Dinwiddie (RD-4) and CGT-4 calculations are based on the same atomic orbital expansion and so they are supposed to be identical; in fact, they agree to within a few percent. We have shown only the RD-4 calculation. It peaks at about 25 keV (when the proton velocity is equal to the $1s$ electron orbital velocity), has a shoulder at about 10 keV, and has a second peak at 2 keV. The RD-7 calculation is also shown, and it differs only slightly from RD-4; this suggests that the atomic orbital expansion

TABLE I. Close-coupled calculations of proton-hydrogen collisions based on atomic representations.

Symbol	Reference	Radial functions	Rotating (R) or nonrotating (NR) angular functions
M	McCarroll (1961)	$1s$ atomic	
	Cheshire (1968); McCarroll, Piacentini and Salin (1970)	$\overline{1}s$ atomic, varying orbital exponent	
	Lovell and McElroy (1965)	$1s_A 2s_A 2s_B$ and other combinations	
	Fulton and Mittleman (1965)	$1s$ atomic, including antitraveling orbitals	
	Flannery (1969)	$1s_A 2s_A 2p_{xA}\ 2p_{zA}$ (no exchange)	
	Wilets and Gallaher (1966)	$1s2s2p_x2p_z$ atomic	R
	Gallaher and Wilets (1968)	$1s2s2p_x2p_z$ Sturmian	R
	Rapp, Dinwiddie, Storm, and Sharp (1972)	$1s2s2p_x2p_z$ atomic	R
RD-4	Rapp and Dinwiddie (1972)	$1s2s2p_x2p_z$ atomic	R
RD-7		$1s2s2p_x2p_z3s3p_x3p_z$ atomic	R
CGT-4	Cheshire, Gallaher, and Taylor (1970)	$1s2s2p_x2p_z$ atomic	R
CGT-7		$1s2s2p_x2p_z\overline{3}s\overline{3}p_x\overline{3}p_z$ atomic and pseudostate	R
	Sullivan, Coleman, and Bransden (1972)	$1s_A 2s_A 2p_{x_A} 2p_{z_A}$ + closure (no exchange)	NR
S	Shakeshaft (1976)	$1s$-$\tilde{6}s$, $2p$-$\tilde{4}p$ Sturmian	NR

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[3] Results presented in this section have little direct bearing on slow collisions, so this section can be skipped without loss of continuity.

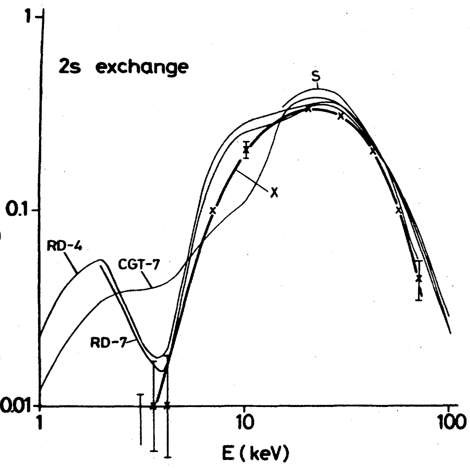

FIG. 8. Total cross section for $H^+ + H(1s) \rightarrow H(2s) + H^+$. X: experiment of Bayfield (1969).

has rapid convergence. (Whether it converges to the correct result is a separate question that we shall discuss below.)

The CGT-7 (pseudostate) and S (Sturmian) expansions involve a more compact set of functions than the atomic orbitals, so they should allow a better approximation to Υ in the important region close to the nuclei. The two calculations are in reasonable agreement with each other, both giving peaks at about 22.5 keV; both are slightly higher than the RD results, and within about 10% of each other.

At lower energies the CGT-7 calculation shows no shoulder near 10 keV, and the second peak of the RD calculation has been rounded out to a shoulder. (The S calculation was not extended to lower energies.)

Experimental data has been obtained by Bayfield (1969) and is labeled X in Fig. 8. On the whole, the shape of the experimental curve is quite similar to that of the calculations; particularly good agreement is found between all theoretical calculations and experiment above 4 keV. Near 20 keV, where the cross section is largest, the experiments lie slightly below the calculations, but the difference is less than the overall uncertainty in the experimental curves, which Bayfield estimates at 35%. At lower energies, some discrepancies appear between theory and experiment: The experimental curve has no shoulder, and shows no sign of a second peak. Despite large experimental uncertainties in this region (some of Bayfield's error bars are reproduced in Fig. 8) it appears that the CGT-7 calculation is significantly too large at $E = 4$ keV. The RD-4 and RD-7 calculations are more problematic. Certainly, for $E \gtrsim 4$ keV they are in fair agreement with the experiments, with discrepancies of generally less than 50%. Below 4 keV, while the data do not show a second peak, they do not rule it out either, there being only one published data point that clearly disagrees with the RD-7 curve. [Bayfield (1969, Fig. 5) compared his data with the then-available calculation of Gallaher and Wilets (1968), which definitely does not agree with the experiments.] It would not be surprising if the calculations were incorrect at low energies, for in that case the electrons tend to adjust adiabatically to the instantaneous positions of the nuclei, and simple atomic orbital expansions can not sufficiently allow for this. But it is also possible that the calculations are correct in this region.

In a more recent experiment, Park, Aldag, and George (1975) obtained the total cross section for direct excitation of the $n = 2$ level and compared their results with theoretical calculations. (Absolute cross sections were obtained by normalizing to the Born approximation at 200 keV.) We show the results of RD-7, CGT-7, and S calculations in Fig. 9. It is seen that the Sturmian and atomic orbital calculations are in good agreement with the experiments, but that the pseudostate calculation gives a peak that is some 40% higher than the experiment at 50 keV. This result is somewhat surprising, because it was thought that the pseudostate calculation should be quite accurate, and certainly no worse than the atomic-orbital expansion.

A possible explanation of the discrepancy was suggested by Shakeshaft. Since the pseudostates replace the complete set of hydrogenic discrete and continuum states, the calculated amplitude for transitions into pseudostates at least partly corresponds to real transitions into the continuum (i.e., ionization). Now an ionized electron quickly escapes, but electronic amplitude in a pseudostate can reappear in the real states, giving a spurious contribution to the cross section. Shakeshaft says that this is less likely to occur in the Sturmian basis, because it is somewhat less compact than the CGT pseudostates. Whatever the explanation, it is clear that there is more to be learned about ionizing transitions and their effect on the discrete transitions.

In this connection, the method of Sullivan, Coleman, and Bransden (1972) is particularly interesting (see also Bransden and Coleman, 1972, and Bransden, Coleman, and Sullivan, 1972). Instead of using pseudostates, they used a closure approximation to obtain a kind of optical potential to simulate the effects of high discrete and ionizing transitions. Though they neglected the effects of exchange, their calculation is in good agreement with the data of Park *et al.* for energies greater than 60 keV.

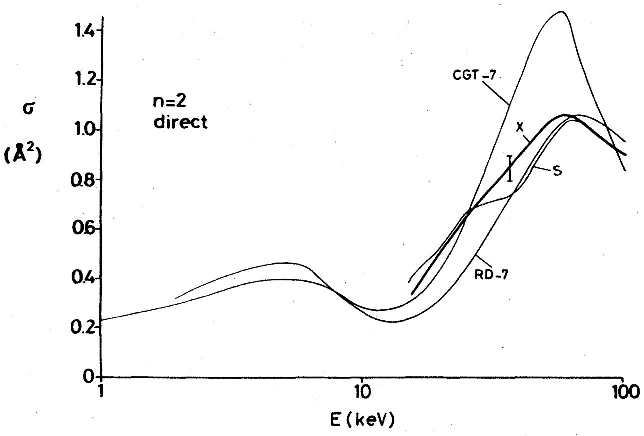

FIG. 9. Total cross section for $H^+ + H(1s) \rightarrow H^+ + H(n=2)$. X: experiment of Park *et al.* (1975).

Although this problem is interesting in itself, we do not discuss it further because, as we shall explain in the next section, it does not arise in slow collisions.[4]

4. Concluding remarks on intermediate-velocity collisions

At the beginning of this section we mentioned the two approximations that simplify the theory of intermediate-velocity collisions: rectilinear motion of the nuclei and expansion in a basis set that has atomic character (i.e., a basis in which each function is propagating with one or the other nucleus). With these simplifications, there is no ambiguity about the electron-translation factor that must be associated with each state; it can only be F_A or F_B, as defined in Eq. (2.17). However, the choice of specific basis functions is still a problem.

There are some theoretical objections to the use of an expansion in simple atomic orbitals, as in Eq. (2.31): If the basis only includes bound states, then this set is not complete, and the states of increasing n (principal quantum number) seem to be too diffuse to give a good representation of the wave function close to the nuclei. Nevertheless, this expansion gives reasonable agreement with most of the available experimental results. Pseudostates were invented to answer the theoretical objections to the atomic orbital basis, but the calculation using this basis disagrees with at least one experiment. The Sturmian basis also answers the theoretical objections to the atomic basis, and so far calculations using this basis are in good agreement with experiments on the H^+-H system.

These calculations leave open a significant conceptual problem. The essential difficulty of intermediate-velocity collisions is that many states (including also continuum states) are strongly coupled. Nevertheless, we see that it is possible to calculate cross sections for transitions among the lowest states by expansion in a small set of carefully chosen functions. On the other hand, transitions to higher discrete and continuous levels probably cannot be treated in this way because of practical limits on the size of the basis. For example, it is not yet known whether or not reliable calculations of ionization cross sections can be made using expansions in a discrete basis. New ideas and alternative calculational methods would be very interesting.

Slow collisions are somewhat simpler in this one respect. Since the electrons behave more nearly adiabatically in a slow collision, the expansion in Born-Oppenheimer eigenfunctions (or related functions) frequently leads to equations in which only a small set of states are strongly coupled. Transitions to states outside this set are improbable, and can usually be neglected (or, if necessary, their probabilities can be calculated by a form of first-order perturbation theory). In such a case, the problems associated with strong coupling of many states do not arise.

C. Slow collisions

We return to the main subject of this article, the description of slow collisions. The main physical idea that distinguishes slow collisions from the intermediate-to-fast collisions described in the preceding section is the *near-adiabatic* approximation. If the nuclei are moving slowly, then the electrons have time to adjust to the changing molecular field. For an extremely slow collision, the electrons behave adiabatically, staying always in a continuously adjusting eigenstate of the electronic Hamiltonian; in that case, no transitions take place in the collision. As the nuclear velocity increases, the electrons can only imperfectly adjust, and transitions occur that can be described by expanding Υ in terms of a small set of adiabatic eigenfunctions. However, as the collision velocity increases further, Υ is better described in terms of a "stiffer" basis set, which adjusts less completely to the changing fields. Ultimately, around $v \sim 1$, the adiabatic picture entirely fails, and the collision must be described in terms of states of atomic character, many of which are strongly coupled.

In the original form of perturbed-stationary-states (PSS) theory for slow collisions (Mott, 1933), Υ was expanded in molecular eigenfunctions, and translation factors were omitted:

$$\Upsilon=\sum_n d_n\phi_n(\mathbf{r}';\mathbf{R}(t)). \tag{2.43}$$

There are two apparently compelling arguments to justify this expansion. (1) Molecular eigenfunctions form a complete set, so any function (including Υ) has a formal expansion of this type. (2) Furthermore, as $v \to 0$, the factors $F_k \to 1$. In fact, however, coupled equations that arise from this expansion have a number of defects (listed in Sec. III.B) which make the equations unsuitable for describing general slow collisions. Bates and McCarroll (1958) were the first to point out that it is essential to retain ETF's to describe transitions even in an arbitrarily slow collision.

Therefore we continue to use the general framework and the coupled equations developed in Sec. II.A. The major questions that have to be answered are (i) What sort of basis functions best describe a collision in a given range of velocities? (ii) Given a basis function, what sort of electron-translation factor should be associated with it? (iii) What approximations can be used to put the coupled equations into the simplest possible form? In this section we give only the most general answers to these questions; specific representations for particular processes are considered later.

1. Basis states and translation factors

The wave function $\Upsilon(\mathbf{r}',t)$ is expanded in a basis as in Eq. (2.23). In many calculations, the ϕ_k's are taken to be eigenfunctions of the electronic Hamiltonian [cf. Eq. (I.15)], but frequently it is more convenient to use some other set. For now we make only the most general assumptions about the basis functions.

(1) We assume they can be written as functions $\phi_k(\mathbf{r}',\mathbf{R})$ in which the internuclear vector is a parameter. (2) We assume that these basis functions are

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[4] A much more complete listing of theoretical calculations and experimental measurements on the H^+-H system (and others) has been compiled by Takayanagi and Suzuki (1978). Theory and experiments on collisions of multiply-charged ions with hydrogen atoms are reviewed by de Heer (1979).

square integrable, representing bound electronic states, and for simplicity we take them to be real. (3) We assume that as $R \to \infty$ at least some of the basis states correspond to atomic eigenstates representing the open channels of interest. (4) We assume that these functions can be expressed in the rotating molecular frame as $\phi_k(\mathbf{r}, R)$ independent of the nuclear angles Θ, Φ, i.e., the basis consists of *rotating* atomic or molecular functions reexpressed in the space-fixed frame.

The functions $\phi_k(\mathbf{r}'; \mathbf{R})$ and $\phi_k(\mathbf{r}; R)$ are different functions of different variables, but they represent the same electronic state. Hence the two functions are equal whenever $(\mathbf{r}'; \mathbf{R})$ and $(\mathbf{r}; R)$ designate the same position of the electron relative to the nuclei, i.e.,

$$\phi_k(\mathbf{r}'; \mathbf{R}) = \phi_k(\mathbf{r}; R), \tag{2.44}$$

where the respective components of $\mathbf{r}'$ and $\mathbf{r}$ are related by Eq. (2.10). From these equations one can show that

$$-i\hbar \frac{\partial}{\partial R} \phi_k(\mathbf{r}'; \mathbf{R}) = -i\hbar \frac{\partial}{\partial R} \phi_k(\mathbf{r}; R), \tag{2.45a}$$

$$-i\hbar \frac{\partial}{\partial \Theta} \phi_k(\mathbf{r}'; \mathbf{R}) = -L_y \phi_k(\mathbf{r}; R), \tag{2.45b}$$

$$-i\hbar \frac{\partial}{\partial \Phi} \phi_k(\mathbf{r}'; \mathbf{R}) = (\sin\Theta L_x - \cos\Theta L_z) \phi_k(\mathbf{r}; R), \tag{2.45c}$$

where derivatives with respect to nuclear coordinates are evaluated holding $\mathbf{r}'$ fixed on the left-hand side of this equation, and holding $\mathbf{r}$ fixed on the right.

The expansion (2.23) also contains electron-translation factors (ETF's). The translation factor that should be associated with an atomic state is unambiguous, but translation factors for general molecular states cannot be uniquely specified *a priori*. To define the factors F_k it is convenient to define three classes of basis states (all having the very general properties listed above).

a. Fixed one-center (class F) states

A basis function $\phi_k(\mathbf{r}; R)$ is said to be in class F if there exists a constant κ_k such that $\phi_k(\mathbf{r}; R)$ depends upon R only as

$$\phi_k(\mathbf{r}; R) = \phi_k(x, y, z - \kappa_k R). \tag{2.46}$$

Class F includes all basis functions that rotate with the molecular frame and are carried along with some center (a nucleus, or the geometric center, or center of mass) but otherwise have no change whatever. We may say that they have no "intrinsic" R dependence, but only the "extrinsic" R dependence implied by Eq. (2.46). Usually only class F states centered on a nucleus are considered, and $\kappa_k = \pm \frac{1}{2}(1 \pm \lambda)$. (The rotating basis functions considered in Sec. II.B were all in class F.)

There is no ambiguity about the ETF that should be associated with a class F state. Since the whole function is moving with a definite velocity, $\mathbf{w} = \kappa \mathbf{v}$, we can take[5]

$$F_k = \exp\left[(im/\hbar)\left(\mathbf{w} \cdot \mathbf{r}' - \tfrac{1}{2} \int w^2 dt'\right)\right]. \tag{2.47}$$

b. Variable one-center (class V) states

States in class V may have additional parameters, such as orbital exponents, that are allowed to vary smoothly with R, but like the class F states these states can be associated with a specific center with which they propagate. Class V states can be written in the form

$$\phi_k(x, y, z - \kappa_k R;\ \zeta_1(R) \cdots \zeta_J(R)) \tag{2.48}$$

where $\zeta_1, \ldots, \zeta_J$ are parameters (e.g., orbital exponents) which may vary slowly with R. Since these functions also are associated with a definite center and they propagate with a definite velocity, F_k can again be taken to have the form (2.47). (A more precise mathematical definition of class V states is given in footnote 19 of Delos and Thorson, 1979.)

c. Molecular (class M) states

Class M states are distinguished from the previous two classes in that they are essentially molecular in character; the electron is shared by the two nuclei, and there is no single center with which the electron can be said to be propagating. Examples of such states are the g and u molecular orbitals for the Born–Oppenheimer states of a homonuclear diatomic system, and the valence electron orbitals for such heteronuclear systems as $(\mathrm{Li\text{-}Na})^+$, which are intrinsically molecular for $R \lesssim 10$ a.u. Class M also includes molecular states which need not be eigenstates of any particular Hamiltonian; the only essential property is their two-center character.

For such states, single-center ETF's of the form (2.47) are not appropriate because a class M orbital as a whole does not have any single velocity of propagation. Instead, the ETF for class M states is constructed using a *local* propagation velocity for an electron in such an orbital (Schneiderman and Russek, 1969). This is done by defining a switching function $f_k(\mathbf{r}; R)$, which varies smoothly as a function of electron position $\mathbf{r}$; typically it may approach -1 near nucleus A and $+1$ near nucleus B, and these limiting values must hold as $R \to \infty$. Like the basis functions, the switching function is defined in the rotating molecular frame, but can be reexpressed in space-fixed variables as in Eq. (2.44):

$$f_k(\mathbf{r}', \mathbf{R}) = f_k(\mathbf{r}; R). \tag{2.49}$$

Using the switching function, we define a local propagation velocity for an electron in orbital k:

$$\mathbf{w}_k(\mathbf{r}'; \mathbf{R}) = \tfrac{1}{2}[f_k(\mathbf{r}'; \mathbf{R}) + \lambda]\mathbf{v}. \tag{2.50}$$

Then one possible form for the ETF is

$$\exp\left[(im/\hbar)\left(\mathbf{w}_k(\mathbf{r}'; \mathbf{R}) \cdot \mathbf{r}' - \tfrac{1}{2} \int w_k^2(\mathbf{r}'; \mathbf{R}) dt'\right)\right]. \tag{2.51}$$

This is not the only possible form, however. The question of what is the best form for the ETF associated with a given molecular state does not yet have a general answer (though much progress has been made

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[5] Equation (2.18) proves that this is appropriate if $\mathbf{w}$ is constant. Schmid (1977) gives a rather formal demonstration that the above form for F_k is suitable if $\mathbf{w}$ is not constant. [His Eqs. (37) and (38) are almost the same as (2.47).]

toward an answer). However, any ETF can be written as

$$F_k = \exp[im\mathbf{v}\cdot \mathbf{s}_k(\mathbf{r}';\mathbf{R})/\hbar] \tag{2.52}$$

and this general form is sufficient for the purposes of this section.

In choosing a specific form for $\mathbf{s}_k(\mathbf{r}';\mathbf{R})$ we are guided by the following general principles. (i) For a class F basis function, if the relative velocity is constant, then F_k must be given by Eq. (2.17b), and in any case, it must reduce to such a form asymptotically. (ii) If the relative velocity is not constant, or if the basis function is not in class F, then none of the above-mentioned specific forms for $F_k\phi_k$ gives an exact solution to a Schrödinger equation; hence there is more flexibility in the choice of F_k. (iii) We prefer $\mathbf{s}_k$ to be an explicit function of $\mathbf{r}'$ (or $\mathbf{r}$) and $\mathbf{R}$ (not, for example, a function that can only be expressed as an integral). (iv) For slow collisions, the kinetic energy term, which is proportional to v^2, is less important than the momentum term, which is proportional to v. (v) The resulting coupled equations for the coefficients should be as simple as possible and should preserve as many of the molecular symmetries as possible.

From these principles, careful examination has revealed that a useful form for $\mathbf{s}_k(\mathbf{r}';\mathbf{R})$ is

$$\mathbf{s}_k(\mathbf{r}';\mathbf{R}) = \tfrac{1}{2}[f_k(\mathbf{r}';\mathbf{R})+\lambda]\mathbf{r}'_g - \tfrac{1}{8}(1-\lambda^2)\mathbf{R}. \tag{2.53}$$

The resulting ETF reduces to Eq. (2.17b) if $f_k(\mathbf{r}';\mathbf{R}) = \pm 1$ and $\mathbf{R} = \mathbf{b} + \mathbf{v}t$, and it differs from (2.51) only in the kinetic energy term. The switching function f_k is still undefined, and various ways of specifying it will be considered later.

In some cases it may be possible to use the same switching functions for all of the states in a class M basis. When this is possible, it is very convenient, because then $F_j^* F_k = 1$ for all j and k in the set. However, such an assumption is not always appropriate (for one thing, it eliminates the momentum-transfer factors that are known to be important in the atomic representation at intermediate-to-high velocities), so we shall not assume that all switching functions are necessarily the same.

We may note also that since the second term in Eq. (2.53) depends only on $\mathbf{R}$, which is a function of t, its effect is only to modify the phases of the coefficients $d_k(t)$; hence it is not really important and it can be omitted.

2. Coupled equations for slow collisions

We have already derived the general set of coupled equations (2.25) using the expansion (2.23) in the Schrödinger equation (2.12). Let us now simplify these equations by making approximations that are valid for most slow collisions. First we rewrite $\mathcal{H}_{jk}(v)$ [Eq. (2.26b)] in the form

$$\begin{aligned}\mathcal{H}_{jk}(v) = {} & \langle\phi_j | F_j^* F_k (h - i\hbar\partial/\partial t) | \phi_k\rangle \\ & + \langle \phi_j | F_j^*[h, F_k] - i\hbar \partial F_k/\partial t | \phi_k\rangle .\end{aligned} \tag{2.54}$$

Now (i) we neglect the acceleration $d\mathbf{v}/dt$ that arises from $\partial F_k/\partial t$; (ii) we expand the momentum-transfer factors $F_j^*F_k$ in powers of v, and neglect all terms of order v^2 and higher. For example, in the overlap integral $S(\mathbf{v})$, we take

$$\underline{S}(v) \simeq \underline{S} + \mathbf{v}\cdot\underline{\boldsymbol{\sigma}}, \tag{2.55}$$

where

$$S_{jk} = \langle \phi_j | \phi_k\rangle , \tag{2.56}$$

$$\sigma_{jk} = (im/\hbar)\langle\phi_j | \mathbf{s}_k - \mathbf{s}_j | \phi_k\rangle . \tag{2.57}$$

Consistent with this neglect of terms of order v^2, we take

$$[\underline{S}(\mathbf{v})]^{-1} \simeq \underline{S}^{-1} - \underline{S}^{-1}\mathbf{v}\cdot\underline{\sigma}\,\underline{S}^{-1}, \tag{2.58}$$

and by a straightforward analysis we then obtain

$$i\hbar\frac{d}{dt}\underline{d} = \underline{S}^{-1}[\underline{h} + \underline{\mathbf{v}}\cdot(\underline{\mathbf{P}} + \underline{\mathbf{A}} + \underline{\boldsymbol{\gamma}})]\underline{d}, \tag{2.59}$$

where S_{jk} and σ_{jk} are given above, and

$$\mathbf{P}_{jk} = \langle\phi_j | -i\hbar\nabla_R | \phi_k\rangle , \tag{2.60}$$

$$\mathbf{A}_{jk} = (im/\hbar)\langle\phi_j | [h, \mathbf{s}_k] | \phi_k\rangle , \tag{2.61}$$

$$\underline{\boldsymbol{\gamma}} = \underline{\boldsymbol{\eta}} - \underline{\sigma}\,\underline{S}^{-1}\underline{h}, \tag{2.62}$$

$$\boldsymbol{\eta}_{jk} = (im/\hbar)\langle\phi_j | (\mathbf{s}_k - \mathbf{s}_j)h | \phi_k\rangle . \tag{2.63}$$

Equations (2.59) are the basic coupled equations describing slow collisions in the classical trajectory framework.

3. Interpretation of terms

Each of the terms in Eq. (2.59) will be discussed more fully in connection with specific applications, and here we give only a brief explanation of the meaning of each.

(a) $\underline{S}$ is of course the ordinary overlap matrix, and it is equal to a unit matrix if the basis functions are orthonormal.

(b) $\underline{h}$ is the matrix of the electronic Hamiltonian. It can be made diagonal, and its elements are then $\epsilon_i(R)$, the electronic energy eigenvalues. In other representations its off-diagonal elements cause transitions between the states (cf. Sec. II.B).

(c) $\underline{\mathbf{P}}$ is the matrix representing the total change of the basis functions with $\mathbf{R}$. It contains rotation, distortion, polarization, and change of character of the basis functions, and all of these can lead to transitions. However $\underline{\mathbf{P}}$ also contains that part of the change of the basis functions that only represents displacement of the states with the moving nuclei. These displacement effects in $\underline{\mathbf{P}}$ have "strange" properties. Some of them are of infinite range, others decrease only as R^{-1}, all of them are origin dependent, and many lead to couplings that are not in accord with physical intuition (see Sec. III.B).

In the earlier formulations of slow collision theory, in which ETF's were entirely neglected, the only matrices to appear in the coupled equations were $\underline{S}$, $\underline{h}$, and $\underline{\mathbf{P}}$. The displacement effects contained in $\underline{\mathbf{P}}$ were responsible for the defects implicit in those theories.

(d) $\underline{\mathbf{A}}$ arises from the action of h on the electron-translation factor F_k. It is related to the term $-i\hbar\mathbf{v}_A\cdot\nabla_{r'}\phi_{k_A}$ in Eqs. (2.18) and (2.38). *Its effect is to identify and cancel that part of* $\underline{\mathbf{P}}$ *that only represents displacement.* In particular, it cancels the infinite-range and long-range couplings, cancels fictitious origin-dependent couplings, restores translational invariance, and brings the theory back into accord with physical intuition.

The effect of A can be seen more clearly by considering a special case. Assume f_k is a constant, as is suitable for a class F (or class V) basis function. Evaluation of Eq. (2.61) using (2.53) then leads directly to

$$\underline{\mathrm{A}}_{jk} = \mathrm{p}_{jk}\kappa_k \tag{2.64a}$$

or

$$\underline{\mathrm{A}} = \underline{\mathrm{p}}\underline{\mathrm{S}}^{-1}\underline{\kappa}\,, \tag{2.64b}$$

where $\underline{\mathrm{p}}$ is the matrix representing the electronic momentum,

$$\mathrm{p}_{kn} = \int \phi_k^*(\mathbf{r};R)(-i\hbar\nabla_r)\phi_n(\mathbf{r};R)d\mathbf{r}\,, \tag{2.64c}$$

and $\underline{\kappa}$ is the matrix whose elements are defined

$$\kappa_{kn} = \langle\phi_k|\kappa_n|\phi_n\rangle = S_{kn}\kappa_n\,. \tag{2.64d}$$

It follows that

$$(i\hbar)^{-1}\mathbf{v}\cdot(\underline{\mathrm{P}}+\underline{\mathrm{A}})_{jk} = \langle\phi_j|\mathbf{v}\cdot(\nabla_R+\kappa_k\nabla_{r'})|\phi_k\rangle$$

$$= \left\langle\phi_j\left|\left(\frac{\partial}{\partial t}+\kappa_k\mathbf{v}\cdot\nabla_{r'}\right)\right|\phi_k\right\rangle \tag{2.65}$$

which involves the rate of change of ϕ_k as seen in a frame of reference moving at a velocity $\kappa_k\mathbf{v}$ relative to the CMN. This now corresponds directly to Eq. (2.38).

For a more general, class M function, it would not be appropriate to take f_k constant, and neither (2.64) nor (2.65) would be correct (except in the limit as $R\to\infty$), because $\underline{\mathrm{A}}$ would also involve derivatives of f_k. Nevertheless, the more complicated $\underline{A}$ would have comparable effects and the same physical meaning.

(e) The meaning of $\underline{\sigma}$ is completely contained in Eq. (2.55). The velocity-dependent overlap matrix $\underline{S}(v)$ differs from the ordinary (zero-velocity) overlap matrix $\underline{S}$ in that the former contains the momentum-transfer factors $F_j^*F_k$; $\underline{\sigma}$ is the first-order-in-velocity correction to the overlap integral that results from this factor. σ vanishes asymptotically, since in that limit $(\mathbf{s}_k-\mathbf{s}_j)\to 0$ for states on a common center, and it vanishes identically if the same ETF is used for all states.

The matrix $\underline{\eta}$ bears the same relation to $\underline{h}$ that $\underline{\sigma}$ bears to $\underline{S}$: $\underline{\eta}$ is the first-order-in-velocity correction to the electronic Hamiltonian matrix that results from the momentum-transfer factor. Like σ it vanishes asymptotically, and it vanishes identically if the same ETF is used for all basis states. Also the combination

$$\underline{\gamma} = \underline{\eta} - \underline{\sigma}\underline{S}^{-1}\underline{h}$$

vanishes if the basis states are eigenfunctions of $\underline{h}$. Further, if the basis states are such that all but a small part of $\underline{h}$ is diagonal, then it may be possible to neglect $\underline{\gamma}$. More generally, however, it is not possible to prove that γ is negligible, and it must become more important as the velocity increases and momentum-transfer effects become significant.

At this point, we can see what is wrong with the two arguments given at the beginning of Sec. II.C to justify the neglect of translation factors. If we set $F_k=1$ at the beginning, then we retain $\underline{\mathrm{P}}$, but not $\underline{\mathrm{A}}$ or $\underline{\gamma}$. But all of these terms are multiplied by $\mathbf{v}$ to the first power. The argument that $|\mathbf{v}|$ is small does not by itself justify retaining one term but not the other. The defects of the original form of PSS theory arise from such inconsistency.

The argument that molecular eigenfunctions form a complete set is correct, but unhelpful. Equation (2.43) is formally valid, but truncation of the expansion leads to inaccuracy. Some parts of the terms retained in the PSS theory are manifestations of the error of truncation of the expansion, and not of the physics of the collision. Incorporation of ETF's changes the expansion from a formally valid ansatz to a good one: Truncation error is reduced, and all of the retained terms have physical significance.

4. Separation of radial from angular couplings, and other properties of the coupled equations

If the nuclear momentum operator in the P matrix (2.60) is expressed in spherical coordinates (R,Θ,Φ) then the angular parts of the gradient can be evaluated using Eqs. (2.45); this separates so-called "radial" from "angular" terms in the coupled equations:

$$P_{jk} = \hat{e}_R P_{jk}^R + \hat{e}_\Theta P_{jk}^\Theta + \hat{e}_\Phi P_{jk}^\Phi\,, \tag{2.66a}$$

where $\hat{e}_R, \hat{e}_\Theta, \hat{e}_\Phi$ are unit vectors for spherical coordinates and

$$P_{jk}^R = \langle\phi_j|-i\hbar\partial/\partial R|\phi_k\rangle\,, \tag{2.66b}$$

$$P_{jk}^\Theta = -R^{-1}\langle\phi_j|L_y|\phi_k\rangle\,, \tag{2.66c}$$

$$P_{jk}^\Phi = R^{-1}\langle\phi_j|L_x-\cot\Theta L_z|\phi_k\rangle\,. \tag{2.66d}$$

Corresponding components of $\underline{\mathrm{A}}$ are obtained by considering the components of s_k in the rotating molecular frame:

$$\mathrm{A}_{jk} = \hat{e}^R A_{jk}^R + \hat{e}^\Theta A_{jk}^\Theta + e^\Phi A_{jk}^\Phi\,, \tag{2.67a}$$

$$A_{jk}^R = (im/\hbar)\langle\phi_j|[h,s_k^z]|\phi_k\rangle\,, \tag{2.67b}$$

$$A_{jk}^\Theta = (im/\hbar)\langle\phi_j|[h,s_k^x]|\phi_k\rangle\,, \tag{2.67c}$$

$$A_{jk}^\Phi = (im/\hbar)\langle\phi_j|[h,s_k^y]|\phi_k\rangle\,, \tag{2.67d}$$

and a similar decomposition holds for σ, η, and γ. In most applications, the nuclear trajectory is assumed to be in a plane $\Phi=\text{constant}$, so $v^\Phi=0$, and the Φ components of these matrices can be ignored. The coupled equations, therefore, take the form

$$i\hbar\frac{d}{dt}\underline{d} = \underline{S}^{-1}[\underline{h}+v^R(\underline{P}^R+\underline{A}^R+\underline{\gamma}^R)$$

$$+v^\Theta(-\underline{L}_y/R+\underline{A}^\Theta+\underline{\gamma}^\Theta)]\underline{d}\,. \tag{2.68}$$

There are some differences between the angular couplings that appear here and those in Eq. (2.40). In the atomic representation, the basis states may be rotating about the y_A or y_B axes, which pass through one or the other nucleus; accordingly the operator L_{y_A} appears in Eq. (2.40). Molecular states, however, are assumed to rotate about the center of mass of the nuclei; hence the operator L_y appears in Eq. (2.68). However, these two descriptions must be related, and, for the special case $f_k=\pm1$, one can show that

$$-\underline{L}_y+\underline{A}^\theta R = -\underline{L}_{y_B} \text{ or } -\underline{L}_{y_A}\,. \tag{2.69}$$

This can be regarded as the angular part of Eq. (2.65). (2.65).

Two other properties of the coupled equations (2.59) may be mentioned here. One can show that they conserve probability to order v, i.e., that $i\hbar d/dt\langle\Upsilon|\Upsilon\rangle$ is comparable to terms of order v^2 which were neglected in the derivation of (2.59). Also using the closure relation for nonorthogonal states,

$$1=\sum_{jk}|\phi_j\rangle S_{jk}^{-1}\langle\phi_k|\,, \tag{2.70}$$

one can show that the coupled equations can also be written in the form

$$i\hbar\frac{d}{dt}\underline{d}=\underline{S}^{-1}[\underline{h}+\mathbf{v}\cdot(\underline{\mathbf{P}}+\underline{\mathbf{C}}_s)]\underline{d}\,, \tag{2.71}$$

where

$$\underline{\mathbf{C}}_s=(im/\hbar)(\underline{h}\,\underline{S}^{-1}\underline{\mathbf{s}}-\underline{\mathbf{s}}\,\underline{S}^{-1}\underline{h})\,, \tag{2.72}$$

$$\mathbf{s}_{jk}=\langle\phi_j|\mathbf{s}_k|\phi_k\rangle\,. \tag{2.73}$$

This form has the advantage over Eq. (2.59) that the effects of both $\underline{\mathbf{A}}$ and $\underline{\gamma}$ are contained in the one matrix $\mathbf{s}_{jk}$; however, Eqs. (2.59) and (2.71) are related only through the closure relation (2.70), so the two forms are not necessarily equivalent within a *truncated* manifold.

D. Multielectron systems

The formulas given in the above development of the theory referred to one-electron systems. However, the ideas involved can also be applied to systems having more than one electron, and most of the formulas given above can be generalized without difficulty.

Many multielectron systems can be reduced to one-electron systems by reasonable approximations. For example, if the system has one electron outside of closed shells (the Li-Na$^+$ system is a good example) then the inner electrons may be undisturbed or they may behave adiabatically in collisions at moderate velocities. They then provide only an effective potential that determines the eigenstates and energies for the outer electron. Once such an effective potential is known, the formalism developed above describes collisional transitions involving that outer electron. Not all systems can be described so simply, however.

In general, basis states suitable for intermediate-to-fast collisions can be built up from states having atomic character, i.e., centered on and propagating with nucleus A or B, as

$$\phi_{n_A}(\mathbf{r}_1\cdots\mathbf{r}_{N_A})=\phi_{n_A}(x_1,y_1,z_1-\kappa_A R;\ldots;x_{N_A}y_{N_A}z_{N_A}-\kappa_A R)\,. \tag{2.74}$$

For such states there is no ambiguity about the appropriate ETF:

$$F_A=\exp\{(im/\hbar)[\kappa_A\mathbf{v}\cdot(\mathbf{r}_1'+\cdots+\mathbf{r}_{N_A}')-\tfrac{1}{2}N_A\kappa_A^2v^2t]\}\,. \tag{2.75}$$

Then Υ can be expanded in terms of antisymmetrized products, $\mathcal{A}F_AF_B\phi_{n_A}\phi_{n_B}$, where $\mathcal{A}$ is the antisymmetrizer. All of the matrix elements involving antisymmetrized states can be reduced to matrix elements involving unsymmetrized products $F_AF_B\phi_{n_A}\phi_{n_B}$, and each of these can be reduced to a sum of terms having the same form as Eq. (2.38). Hence, although the resulting matrix elements are much more complicated than for the one-electron case, at least the ETF's present no conceptual difficulty.

On the other hand, the specific choice of basis functions (ϕ_{n_A},ϕ_{n_B}) is even more problematic than in the one-electron case. Calculations must begin with simple but reasonably accurate atomic eigenfunctions. Eventually, some sort of pseudostates might be incorporated, but this has not yet been done for multielectron systems in intermediate-velocity collisions.

For sufficiently slow collisions, Born-Oppenheimer eigenfunctions provide a well-defined basis set that is almost always a reasonable starting point. Then there are two ways to incorporate ETF's into the description. Molecular states are normally given either as an expansion in atomic states or as combinations of product states in which each electron occupies a one-particle molecular orbital. In the former case, atomic ETF's like those given in Eq. (2.75) can be appended. In the latter case, the ETF would be a product of factors like (2.52) and (2.53), with a switching function for each molecular orbital, so Υ would be expanded in terms of states of the form

$$\mathcal{A}\prod_{k=1}^{N}F_k(\mathbf{r}_k')\phi_k(\mathbf{r}_k';\,\mathbf{R}).$$

Again, the matrix elements are rather complicated, but they can all be reduced to combinations of elements like those given in Eqs. (2.55) to (2.63).

Thus it appears that multielectron systems introduce challenging problems of implementation, but problems of a type that are familiar to quantum chemists.

E. Closing

Two questions have been left unanswered relating to the theory of slow collisions. First, what should we take for the basis functions $\phi_n(\mathbf{r};R)$? Born-Oppenheimer eigenfunctions are one possibility, but other possibilities are also available. Second, assuming we take an ETF of the form (2.52), what should we take for the switching function $f_n(\mathbf{r};R)$?

These questions constitute the representation problem, and they will be considered in Sec. IV. First, however, in Sec. III we develop a fully quantum-mechanical theory of slow collisions.[6]

III. QUANTUM-MECHANICAL FORMULATION

We turn now to the quantum-mechanical formulation of slow collision theory. The classical trajectory theory developed above successfully accounts for a great variety of collision phenomena, but there are many situations in which superposition, interference, tunneling, or diffraction play a role, and for these a fully quantum-mechanical picture is needed.

In Sec. III.A below we give basic definitions, the Schrödinger equation, and boundary conditions for a collision of two atoms. Then in Sec. III.B we consider the expansion of the full wave function $\Psi(\mathbf{r};\mathbf{R})$ in terms

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[6] The reader who is not interested in the fully quantum-mechanical formulation may skip Sec. III and go directly to Sec. IV without significant loss of continuity. A very brief summary of the results of Sec. III, and thin relationship to the classical trajectory formulation is given by Delos, 1981b.

of molecular eigenfunctions. It is shown that the original form of this expansion has a number of defects, related to neglect of the motion of the electron as it is carried with a nucleus. Finally, Sec. III.C gives a fairly heavy mathematical development of a more satisfactory approach. The final result is a set of coupled equations that give a fully quantum-mechanical description of atomic collisions. Again, to keep the equations simple, we develop them explicitly only for the one-electron case, and briefly discuss the many-electron case afterwards.

A. System description

1. Coordinate systems

We consider a system having one electron of mass m_0, and two nuclei with masses M_A, M_B. Their coordinates relative to a fixed laboratory origin, $\mathbf{r}^0, \mathbf{R}_A^0, \mathbf{R}_B^0$ were indicated in Fig. 3. Now that we are considering the full dynamics of this three-body system, our description of the nuclear motion is inextricably linked to our description of the electron motion. In either quantum or classical theories of three-body systems, there are three standard Jacobi coordinate systems that are normally used (Messiah, 1965; Pars, 1965). These are shown in Fig. 10 and their relationships are given in Tables II and III.

In each case, one coordinate connects a pair of particles, and the second coordinate connects the third particle to the center of mass of the pair. Capital letters denote heavy-particle coordinates and lower case letters denote electron coordinates.

Components of the vector representing the position of the electron can be given in a space-fixed or a rotating frame. The rotating molecular frame is defined relative to the internuclear vector **R**, as in Fig. 4. Hence the molecule-fixed z axis points along the internuclear vector **R**; the x axis is perpendicular to the z axis and lies in the plane formed by **R** and the space-fixed z' axis, and the y axis is perpendicular to the x and z axes. As before, the components of the vector representing the position of the electron relative to the CMN are denoted $(x', y', z') \equiv \mathbf{r}'$ or $(x, y, z) = \mathbf{r}$ in space-fixed and rotating frames, respectively. Also we write $r_A = |\mathbf{r}_A| = |\mathbf{r}_A'|$, etc.

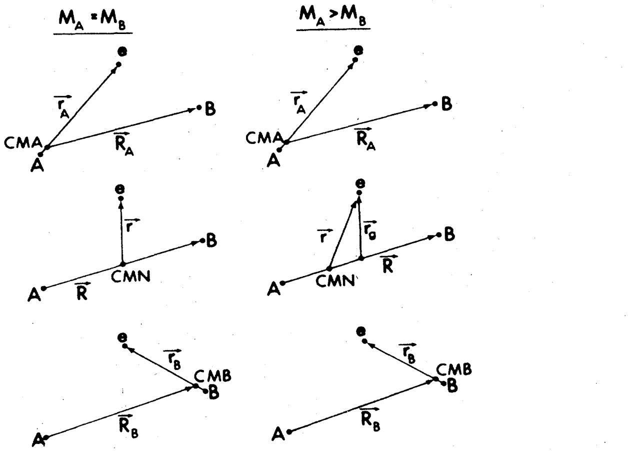

FIG. 10. Three Jacobi coordinate systems for relative coordinates of two heavy particles A, B, and an electron e, for equal masses, $M_A = M_B$, and for unequal masses, $M_A > M_B$.

TABLE II. Relations of coordinates.

$$\lambda = (M_A - M_B)/(M_A + M_B)$$

$$\tfrac{1}{2}(1+\lambda) = M_A/(M_A+M_B), \quad \tfrac{1}{2}(1-\lambda) = M_B/(M_A+M_B)$$

$$\mathbf{r} = \mathbf{r}_g + \tfrac{1}{2}\lambda \mathrm{R}$$

$$\mathbf{r}_A = \mathbf{r}_g + \tfrac{1}{2}\mathrm{R} = \mathbf{r} + \tfrac{1}{2}(1-\lambda)\mathrm{R}$$

$$\mathbf{r}_B = \mathbf{r}_g - \tfrac{1}{2}\mathrm{R} = \mathbf{r} - \tfrac{1}{2}(1+\lambda)\mathrm{R}$$

$$\begin{aligned}\mathrm{R}_A &= \frac{M_A + \frac{1}{2}m_0}{M_A + m_0}\,\mathrm{R} - \frac{m_0}{M_A + m_0}\,\mathbf{r}_g \\ &= \frac{M_A + \frac{1}{2}(1+\lambda)m_0}{M_A + m_0}\,\mathrm{R} - \frac{m_0}{M_A + m_0}\,\mathbf{r} \\ \mathrm{R}_B &= \frac{M_B + \frac{1}{2}m_0}{M_B + m_0}\,\mathrm{R} + \frac{m_0}{M_B + m_0}\,\mathbf{r}_g \\ &= \frac{M_B + \frac{1}{2}(1-\lambda)m_0}{M_B + m_0}\,\mathrm{R} + \frac{m_0}{M_B + m_0}\,\mathbf{r}\end{aligned}$$

Channels are the regions of configuration space corresponding to initial and final states of the system, when the A and B subsystems are separated: e.g., the A channel is the region in which the electron is close to nucleus A and both are far from B; obviously the system configuration is then most simply described using $(\mathbf{r}_A', \mathbf{R}_A)$ as coordinates. The molecular region is the part of configuration space in which all three particles are close together and the electron interacts with both centers; in this region the molecular coordinates $(\mathbf{r}', \mathbf{R})$ are evidently convenient. In defining these regions we do *not* wish to imply that any sharp boundary can be drawn which separates them; indeed, the channels can be regarded as asymptotic portions of the molecular region.

2. Schrödinger equation

After separation of the motion of the center of mass of the whole system, the Schrödinger equation describing relative motion is

$$H\Psi = (T + V + h_{\mathrm{soc}})\Psi = E\Psi\,. \tag{3.1}$$

In the various Jacobi coordinates, T is represented by

$$T = -\frac{\hbar^2}{2\mu_A}\nabla^2_{R_A} - \frac{\hbar^2}{2m_A}\nabla^2_{r_A'} \tag{3.2a}$$

$$= -\frac{\hbar^2}{2\mu_B}\nabla^2_{R_B} - \frac{\hbar^2}{2m_B}\nabla^2_{r_B'} \tag{3.2b}$$

$$= -\frac{\hbar^2}{2\mu}\nabla^2_{R} - \frac{\hbar^2}{2m}\nabla^2_{r'}\,. \tag{3.2c}$$

In fact, the Jacobi coordinates were defined such that the kinetic energy would contain no cross terms like $\nabla_{r'} \cdot \nabla_R$. It is possible to specify the relative positions of electron and nuclei using mixed coordinates, like $(\mathbf{r}_A', \mathbf{R})$, for example, but in that case the kinetic energy would have cross terms. V is the full potential energy of interaction of electrons and nuclei [see below Eq. (2.13)] and h_{soc} represents spin-orbit interactions and, if necessary, other magnetic effects.

TABLE III. Reduced masses corresponding to coordinates.

Coordinate	Reduced mass	
$\mathbf{r}^0$	m_0	Rest mass of electron
$\mathbf{R}_A^0$	M_A	Rest mass of A nucleus
$\mathbf{R}_B^0$	M_B	Rest mass of B nucleus
$\mathbf{R}_{\rm CM}^0$	$M_T=M_A+M_B+m_0$	Total mass of system
$\mathbf{r}_A$	$m_A=m_0M_A/(m_0+M_A)$	Electron reduced mass, channel A
$\mathbf{R}_A$	$\mu_A=(m_0+M_A)M_B/M_T$	Nuclear reduced mass, channel A
$\mathbf{r}_B$	$m_B=m_0M_B/(m_0+M_B)$	Electron reduced mass, channel B
$\mathbf{R}_B$	$\mu_B=(m_0+M_B)M_A/M_T$	Nuclear reduced mass, channel B
$\mathbf{r}$	$m=m_0(M_A+M_B)/M_T$	Molecular electron reduced mass
$\mathbf{R}$	$\mu=M_AM_B/(M_A+M_B)$	Molecular nuclear reduced mass

3. Scattering boundary conditions

The wave function Ψ satisfies the usual scattering boundary conditions (Newton, 1966; Mott and Massey, 1965): in one channel there is a plane wave with the electron in the initial electronic eigenstate and a set of outgoing spherical waves associated with the electronic states for this channel, while in the other channel there are only outgoing spherically scattered waves associated with various electronic states for that channel.

Channel eigenstates may be defined as follows. The potential V is assumed to have properties such that *in channel A* (as $R_A\to\infty$ holding r_A fixed),

$$V\to V_0^A(\mathbf{r}'_A), \tag{3.3a}$$

while in channel B (as $R_B\to\infty$ holding r_B fixed),

$$V\to V_0^B(\mathbf{r}'_B). \tag{3.3b}$$

We may then define the channel Hamiltonians,

$$h_0^A=-\frac{\hbar^2}{2m_A}\nabla^2_{r'_A}+V_0^A(\mathbf{r}'_A), \tag{3.4a}$$

$$h_0^B=-\frac{\hbar^2}{2m_B}\nabla^2_{r'_B}+V_0^B(\mathbf{r}'_B), \tag{3.4b}$$

and their electronic eigenfunctions and eigenvalues,

$$h_0^A\phi^0_{n_A}=\epsilon^0_{n_A}\phi^0_{n_A}, \tag{3.5a}$$

$$h_0^B\phi^0_{n_B}=\epsilon^0_{n_B}\phi^0_{n_B}. \tag{3.5b}$$

Channel wave numbers k_{n_A}, k_{n_B} are given by the relations

$$\hbar^2k^2_{n_A}/2\mu_A+\epsilon^0_{n_A}=E, \tag{3.6a}$$

$$\hbar^2k^2_{n_B}/2\mu_B+\epsilon^0_{n_B}=E. \tag{3.6b}$$

Let us further define explicit Cartesian and spherical components for each of the heavy particle coordinates:

$$\mathbf{R}_A\leftarrow(X_AY_AZ_A)\ \text{or}\ (R_A\Theta_A\Phi_A), \tag{3.7a}$$

$$\mathbf{R}_B\leftarrow(X_BY_BZ_B)\ \text{or}\ (R_B\Theta_B\Phi_B), \tag{3.7b}$$

$$\mathbf{R}\leftarrow(XYZ)\ \text{or}\ (R\Theta\Phi). \tag{3.7c}$$

We can now write down the boundary conditions for a scattering problem. For example, if A is the incident channel, then *at large* R_A, *finite* r_A,

$$\Psi\sim\phi^0_{m_A}(\mathbf{r}'_A)\exp(ik_{m_A}Z_A)+\sum_{n_A}\phi_{n_A}(\mathbf{r}'_A)f_{n_Am_A}(\Theta_A,\Phi_A)\exp(ik_{n_A}R_A)/R_A, \tag{3.8a}$$

while at large R_B, *finite* r_B,

$$\Psi\sim\sum_{n_B}\phi^0_{n_B}(\mathbf{r}'_B)f_{n_Bm_A}(\Theta_B,\Phi_B)\exp(ik_{n_B}R_B)/R_B. \tag{3.8b}$$

It should be noted that even when the heavy particles are electrically identical, i.e., the channel potentials V_0^A and V_0^B are identical functions of their respective arguments, the channel eigenstates and eigenvalues will still not be identical if $M_A\neq M_B$, because m_A and m_B will differ slightly (see Table III). It may also be noted that h_0^A differs from h_A^0 of Sec. II because of the difference between the rest mass of the electron and its atomic reduced mass. Likewise, the channel wave numbers will differ slightly, not only because $\epsilon^0_{n_A}\neq\epsilon^0_{n_B}$, but also because $\mu_A\neq\mu_B$. No approximations have been made here.

4. Definition and properties of Born-Oppenheimer states

Born-Oppenheimer eigenfunctions have been mentioned several times already, but it is now necessary to specify their properties more precisely. We define them to be eigenfunctions of the *electrostatic* part of the molecular electronic Hamiltonian. In the molecular frame, in which the nuclei lie on the z axis, these functions are denoted $\phi_n(\mathbf{r};R)$ and they satisfy the electronic Schrödinger equation

$$h_{\rm BO}(\mathbf{r};R)\phi_n(\mathbf{r};R)=\epsilon_n(R)\phi_n(\mathbf{r};R), \tag{3.9}$$

where

$$h_{\rm BO}(\mathbf{r};R)=-\frac{\hbar^2}{2m}\nabla^2_r+V. \tag{3.10}$$

These functions can be reexpressed in terms of space-fixed variables $(\mathbf{r}',\mathbf{R})$; the corresponding function of these new variables is designated $\phi_n(\mathbf{r}';\mathbf{R})$, and it represents the same molecular eigenstate tumbling in space with the moving nuclei.

For reasons that will be explained later, we deliberately omit spin-orbit coupling from the Born-Oppenheimer Hamiltonian, and we say that the full electronic Hamiltonian is the sum of the Born-Oppenheimer (electrostatic) part and the spin-orbit (magnetic) part,

$$h = h_{\mathrm{BO}} + h_{\mathrm{soc}}. \tag{3.11}$$

This is a convenient nomenclature, but it is not essential, and it is not universally followed in the literature.

The molecular Hamiltonian h differs from the atomic (channel) Hamiltonians h_A^0, h_B^0. (i) It contains the full potential $V(\mathbf{r};R)$, not just an asymptotic projection of it; (ii) the molecular electronic reduced mass m appears in the kinetic energy term. At large R, however, there is an approximate equality between the Born-Oppenheimer eigenstates and the atomic eigenstates.

We say a system is *symmetric* if the two atomic potentials V_0^A, V_0^B are identical functions of their respective arguments. In this case, the Born-Oppenheimer eigenfunctions are also parity eigenfunctions (g, u). If in addition $M_A = M_B$, we say the system is *homonuclear* (otherwise it is *heteronuclear*).

In the *asymmetric* case, each Born-Oppenheimer function is uniquely correlated to an atomic eigenfunction in one channel or the other (assuming no accidental asymptotic degeneracy); either

$$\phi_n(\mathbf{r};R) \xrightarrow[R\to\infty]{} \phi_{n_A}(\mathbf{r}_A) \simeq \phi_{n_A}^0(\mathbf{r}_A), \tag{3.12a}$$

with

$$\lim_{R\to\infty} \epsilon_n(R) \equiv \epsilon_{n_A} \simeq \epsilon_{n_A}^0, \tag{3.12b}$$

or else

$$\phi_n(\mathbf{r};R) \xrightarrow[R\to\infty]{} \phi_{n_B}(\mathbf{r}_B) \simeq \phi_{n_B}^0(\mathbf{r}_B), \tag{3.13a}$$

with

$$\lim_{R\to\infty} \epsilon_n(R) \equiv \epsilon_{n_B} \simeq \epsilon_{n_B}^0. \tag{3.13b}$$

The correspondences between ϕ_{n_A} and $\phi_{n_A}^0$ and between ϕ_{n_B} and $\phi_{n_B}^0$ are approximate rather than exact because the molecular electron mass m differs from the atomic ones m_A, m_B (cf. Table III).

For the symmetric case (whether or not it is homonuclear) the Born-Oppenheimer eigenfunctions correlate to g and u linear combinations of (approximate) atomic orbitals (LCAO):

$$\begin{aligned}\phi_n(\mathbf{r};R) &\xrightarrow[R\to\infty]{} 2^{-1/2}[\phi_{n_A}(\mathbf{r}_A) \pm \phi_{n_B}(\mathbf{r}_B)] \\ &\simeq 2^{-1/2}[\phi_{n_A}^0(\mathbf{r}_A) \pm \phi_{n_B}^0(\mathbf{r}_B)].\end{aligned} \tag{3.14a}$$

For both parities, n_A and n_B denote the same index, and

$$\lim_{R\to\infty} \epsilon_n(R) \equiv \epsilon_n(\infty) \simeq \epsilon_{n_A}^0 \simeq \epsilon_{n_B}^0. \tag{3.14b}$$

B. Perturbed-stationary-states theory and its problems

Because of the success of the Born-Oppenheimer approximation (Herzberg, 1950; Slater, 1963) for describing bound states of molecules, it is natural to expect that a simple generalization of this method will suffice for atomic collisions. In the original form of perturbed-stationary-states (PSS) theory (Mott and Massey, 1965, p. 429, Eq. 93) it was thought that the full wave function Ψ could simply be expanded in terms of Born-Oppenheimer states as

$$\Psi(\mathbf{R},\mathbf{r}') = \sum_n \chi_n(\mathbf{R})\phi_n(\mathbf{r}';\mathbf{R}). \tag{3.15}$$

More generally, the basis functions ϕ_n could be any linear combinations of Born-Oppenheimer states or other related functions; in what follows we shall only assume that they are orthonormal. Putting Eq. (3.15) into (3.1), using the form (3.2c), and taking scalar products with $\phi_m(\mathbf{r}';\mathbf{R})$, one obtains a system of coupled equations for $\chi_n(\mathbf{R})$, which we write in matrix notation,

$$\{(2\mu)^{-1}[(-i\hbar\nabla)^2 + 2\underline{\mathbf{P}}\cdot(-i\hbar\nabla) + \underline{B}^0] + \underline{\mathrm{h}} - E\}\underline{\chi}(\mathrm{R}) = 0, \tag{3.16}$$

where

$$\mathrm{P}_{jk} = \langle\phi_j| - i\hbar\nabla_R\phi_k\rangle, \tag{3.17}$$

$$B_{jk}^0 = \langle\phi_j| - \hbar^2\nabla_R^2\phi_k\rangle, \tag{3.18}$$

$$h_{jk} = \langle\phi_j|h|\phi_k\rangle. \tag{3.19}$$

It is understood that the operator ∇_R is a derivative with respect to the nuclear coordinate holding the electron coordinate fixed in the space-fixed frame, i.e., holding $\mathbf{r}'$ fixed. (Later we shall transform to the rotating molecular frame and write P in terms of spherical components. This will separate "radial" and "angular" couplings [cf. Eqs. (2.40), (2.45), and (2.66)], but for the moment all such couplings are left implicit in the vector $\underline{\mathbf{P}}$.)

Equations (3.16) can also be written in an alternative form. Using an identity which is valid for a complete set,

$$\underline{B}^0 = -i\hbar\nabla_R\cdot\underline{\mathbf{P}} + \underline{\mathbf{P}}\cdot\underline{\mathbf{P}}, \tag{3.20}$$

$\underline{B}^0$ can be eliminated in favor of $\underline{\mathbf{P}}$, and Eqs. (3.16) become

$$[(2\mu)^{-1}(-i\hbar\nabla + \underline{\mathbf{P}})^2 + \underline{h} - E]\underline{\chi}(\underline{\mathrm{R}}) = 0. \tag{3.21}$$

In a finite set of states, Eq. (3.20) is not exact, but it should be sufficiently accurate for most purposes.

Coupled equations of the form (3.16) or (3.21) are still used in many calculations of cross sections for slow atomic collisions. And, since the set of Born-Oppenheimer functions is formally complete, the expansion (3.15) would appear to be rigorous. But it is now known that truncation of this expansion, leading to a finite set of coupled equations, leads to errors that are comparable to the terms retained in these equations. In particular, we find in calculations that $\underline{\mathrm{P}}$-matrix elements typically have more or less sharp peaks superimposed on a smaller, smoothly varying background. The error in truncation of Eq. (3.15) is comparable to this smooth background; hence for any calculation involving that level of accuracy, a better approach is needed.

Among the problems implicit in Eqs. (3.16) are the following.

(a) Individual terms in the expansion (3.15) do not satisfy the scattering boundary conditions. As indicated by Eq. (3.8a) a possible form for the wave function in the A channel is $(\hbar = 1)$

$$\exp(i\mu_A vZ_A)\phi^0_{n_A}(\mathbf{r}'_A)=\exp(i\mu vZ)\exp[-im\tfrac{1}{2}(1-\lambda)vz']$$
$$\times\phi^0_{n_A}(\mathbf{r}'_A), \tag{3.22}$$

whereas the corresponding term of (3.15) would be

$$\exp(i\mu vZ)\phi_n(\mathbf{r}';\mathrm{R})\rightarrow\exp(i\mu vZ)\phi_{n_A}(\mathbf{r}'_A). \tag{3.23}$$

Even if there were no differences between $\phi_{n_A}(\mathbf{r}'_A)$ and $\phi^0_n(\mathbf{r}'_A)$, the second factor in Eq. (3.22) would still be missing from (3.23). That is the electron-translation factor (ETF). Since it depends on both the electron coordinate and the nuclear velocity, there is no trivial modification of Eq. (3.15) that can allow it to be incorporated.

Furthermore, as discussed earlier, the Born-Oppenheimer eigenfunctions do not exactly agree with the atomic states even in the channels because of the difference between the molecular reduced mass m and the atomic reduced masses m_A, m_B. However, this is a tiny discrepancy that is insignificant except at extremely low energies ($E \lesssim 0.1$ eV).

(b) As a consequence, the P *matrix contains couplings of infinite range.* Calculations of the radial component of this matrix

$$P^R_{mn}(R)=-i\hbar\left\langle\phi_m\left|\frac{\partial}{\partial R}\phi_n\right.\right\rangle \tag{3.24}$$

were first made for the $H_2{}^+$ system by Jepsen and Hirschfelder (1960), who computed the $\underline{P}^R$ matrix elements for several low-lying discrete states. They computed these by direct differentiation, using both exact and approximate $H_2{}^+$ wave functions.

For evaluation of such matrix elements, a form of the Hellman-Feynman theorem is simpler to use, and in *this* case gives more accurate results with approximate wave functions than direct differentation. By differentation of Eq. (3.9) with respect to R, and taking matrix elements, we obtain

$$P^R_{mn}(R)=-i\hbar\left\langle\phi_m\left|\frac{\partial h}{\partial R}\right|\phi_n\right\rangle\Big/[\epsilon_n(R)-\epsilon_m(R)]. \tag{3.25}$$

This form incidentally shows the characteristic conditions for violation of adiabatic behavior, namely that $P^R_{mn}(R)$ becomes large in a case of near-degeneracy, $\epsilon_n\sim\epsilon_m$. (Note, however, that P^R_{mn} does not become singular because eigenvalues of h can cross $[\epsilon_n(R_x)-\epsilon_m(R_x)=0]$ only if the matrix element of $\partial h/\partial R$ also vanishes at R_x).

Jepsen and Hirschfelder found that certain of the matrix elements $P^R_{mn}(R)$ do not tend to zero, but to constants, as $R\rightarrow\infty$. Using Eq. (3.25) this behavior becomes apparent: For $H_2{}^+$, one can show that

$$\frac{\partial h}{\partial R}=\frac{-e^2}{R^2}+e^2\left(\frac{z_B}{r_B^3}+\frac{z_A}{r_A^3}\right). \tag{3.26}$$

The infinite-range couplings arise because $\mathbf{r}$ is held fixed with respect to CMN rather than to either nucleus during differentiation. Evidently, as $R\rightarrow\infty$, where linear combinations of atomic orbitals represent the ϕ_n, atomic orbitals which are connected by the molecule axis (z) component of the dipole operator will also be connected by ($\partial h/\partial R$). This is what Jepsen and Hirschfelder found, e.g., the matrix element $\langle\sigma_g 1s|\partial/\partial R|\sigma_u 2p\rangle$ (separated-atom notation) tends to a constant as $R\rightarrow\infty$. Physically this just represents the displacement of the atomic orbitals relative to the CMN as R changes.

A scattering theory in which coupling matrix elements do not vanish asymptotically is obviously not well formulated, since no one could suggest that atoms somehow perturb each other at infinite range. These difficulties occur in the theory because the asymptotic wave function does not satisfy the asymptotic Schrödinger equation. [When the angular part of P is examined, it is found that there are couplings that fall off as R^{-1} (Bates and Sprevak, 1971); these also are fictitious, and are eliminated in a proper theory.]

(c) P contains some fictitious "origin-dependent" couplings. Consider symmetric heteronuclear systems such as HD^+. The Born-Oppenheimer eigenfunctions have (g,u) parity, and the electronic Hamiltonian does not couple g to u states. In any such systems, we expect to find tiny (g,u) couplings that are proportional to the difference between m_A and m_B. However, the P matrix also contains a much larger (g,u) coupling which arises because the center of mass of the nuclei is not at the geometric center of the molecule:

$$\begin{aligned}\mathbf{P}_{gu}&=\langle\phi_g|(-i\hbar\nabla_R)_{r'}|\phi_u\rangle\\&=\langle\phi_g|(-i\hbar\nabla_R)_{r'_g}-\tfrac{1}{2}\lambda(-i\hbar\nabla_{r'})_R|\phi_u\rangle\\&=-\tfrac{1}{2}\lambda\langle\phi_g|(-i\hbar\nabla_{r'})_R|\phi_u\rangle \qquad (3.27)\\&=(-\tfrac{1}{2}\lambda)(im/\hbar)(\epsilon_g-\epsilon_u)\langle\phi_g|\mathbf{r}'_g|\phi_u\rangle. \qquad (3.28)\end{aligned}$$

This matrix element vanishes within the manifold of a degenerate (g,u) pair as $R\rightarrow\infty$, but it has finite values at finite R; for HD^+ it is about $0.1\hbar/a_0$ as $R\rightarrow 0$. Note further that it does not depend on the atomic isotope splittings, which are proportional to (m_A-m_B); instead it is proportional directly to $\lambda=(M_A-M_B)/(M_A+M_B)$, which remains finite in the limit $M_A, M_B\rightarrow\infty$, m_0 fixed. This coupling is also an artifact of the inappropriate formulation of the theory.

A related problem is found in calculations of P-matrix elements for charge exchange at large internuclear distances. For example, Melius and Goddard (1972) calculated (among other things) the radial component of $\underline{\mathrm{P}}$ for the system

$$\mathrm{Li}^+ + \mathrm{Na} \rightleftharpoons \mathrm{Li} + \mathrm{Na}^+ .$$

They found that if they took ($\partial/\partial R$) holding $\mathbf{r}'_{\mathrm{Na}}$ fixed, the result was very different from that obtained by holding $\mathbf{r}'_{\mathrm{Li}}$ fixed. It might appear from the PSS theory that the derivative should be evaluated holding $\mathbf{r}'$ fixed (relative to CMN), but, as the HD^+ example shows, this is not necessarily best. To get a result that is invariant to the origin of coordinates, it is necessary to account for the displacement of the orbitals with the moving nuclei.

The word "fictitious" here has somewhat the same meaning that it has in classical mechanics when we speak of "fictitious forces in an accelerating frame": such forces are real enough in the accelerating frame, but there is a frame in which they do not appear. Likewise the "fictitious" infinite-range and origin-dependent couplings are a perfectly rigorous consequence of the PSS framework, and if the expansion (3.15) could include a complete set, the theory would give correct results. However, we shall show that there is another framework in which such couplings do not appear.

Implicit is the idea that the latter framework is better; it is more in accord with physical intuition, and truncation gives a smaller error.

(d) The matrix elements in this formulation do not contain momentum-transfer factors. We saw in Sec. II that the momentum-transfer factors $\exp(\pm imvz/\hbar)$ in the exchange matrix elements become very important when the nuclear velocity exceeds the electron velocity; these factors cause the sharp decrease in charge transfer cross sections at high velocities. At low velocities they are much less important, but they still lead to some observable effects. Consider for example the problem of calculating the angular and energy distribution of electrons autoionized from an atom, such as

$$\mathrm{He}^{**}(2p^2)\rightarrow \mathrm{He}(1s)+e^- . \tag{3.29}$$

If the atom is in motion, then the measured electron energy spectrum will show a Doppler shift associated with this motion. A similar Doppler shift has been observed in measurements of collisionally autoionized electrons in the system

$$\mathrm{He}^+ +\mathrm{Ca}\rightarrow (\mathrm{HeCa})^+ \rightarrow \mathrm{He}+\mathrm{Ca}^{++}+e^- \tag{3.30}$$

(Hultzsch *et al.*, 1979). In this case, the "source" of electrons is presumably the molecular ion (HeCa^+) that is formed momentarily in the collision. The Doppler shift is related to the motion of this source, and the theoretical description of the Doppler shift involves momentum-transfer factors.

In the PSS theory, these factors are completely absent from all the matrix elements, so such Doppler shifts cannot be described. In addition, without momentum-transfer factors, the coupled equations cannot go over to the correct classical limit, formulated in Sec. II. This is another manifestation of the fact that the theory is not well formulated.

(e) The couplings represented by the P matrix do not give a proper account of direct impact processes. Thorson and his collaborators (Thorson and Levy, 1969; Levy and Thorson, 1969; Lebeda, Thorson, and Levy, 1971; SethuRaman, Thorson, and Lebeda, 1973; Rankin and Thorson, 1979; Knudson, Kimura, and Thorson, 1979) have considered the impact ionization process

$$\mathrm{H}^+ +\mathrm{H}(1s)\rightarrow 2\mathrm{H}^+ +e^-$$

in the energy range 50–500 eV. Because the transition is not mediated by a degeneracy, the cross section in this energy range is very small. The P-matrix elements, however, are not only disturbingly large, but they are far too unselective: They are significant for as many as 40 to 50 partial waves of the electronic continuum, and they extend out to $R=30$ to 40 bohrs. When ETF's were included, Thorson *et al.* found that these unrealistic matrix elements were canceled to very high accuracy, leaving a much smaller residual coupling.

(f) Within the above framework, there is no acceptable formal definition of diabatic states. This will be discussed at length later.

All of the above problems have one common source. The $\underline{P}$ matrix represents the total change of the basis functions ϕ_n with changing R. This total change is made up of two kinds of change: (i) the rotation, distortion, polarization, and change of character of ϕ_n, and (ii) simple displacement of ϕ_n along with the atomic nuclei. Nonadiabatic transitions can occur as a result of the first kind of change of the basis functions, but as we saw in Sec. II, the part of $\underline{\mathrm{P}}$ that only represents displacement does not give real coupling between the states—this part must be canceled by the ETF's or their quantum analogs. In fact, one can show that *all of these defects would also arise in the classical trajectory formulation if ETF's were omitted from the theory.*

This makes the problem clear. We somehow have to incorporate the effects of ETF's into a fully quantum-mechanical formulation of atomic collision theory. But the ETF's given in Eqs. (2.17) or (2.52) contain the nuclear velocity, so they intrinsically involve a classical picture of the collision. Hence the ETF concept cannot be taken over directly, and the development of a better formulation involves careful reexamination of the fundamental ideas underlying the PSS framework.

In the following sections we shall develop a quantum-mechanical formulation which eliminates the defects discussed above. We shall show that the same corrections, which arise in the classical trajectory formulation as a consequence of ETF's, also arise in an improved quantum-mechanical formulation. In particular, the matrices $\underline{\mathrm{A}}$ and $\underline{\gamma}$ will again appear as corrections to $\underline{\mathrm{P}}$, and very similar modifications will be made to $\underline{B}^0$. (Recall that the matrix $\underline{A}$ cancels the displacement part of $\underline{\mathrm{P}}$, and $\underline{\gamma}$ comes from the low-velocity limit of momentum-transfer factors). In addition, a new matrix $\underline{I}$ arises, which contains electronic-reduced-mass corrections ("isotopic energy shifts"). This formulation resolves all of the above-mentioned defects of the unmodified PSS theory.

However, before launching our little boat into the waves of this new formulation, a parting remark about the PSS theory is appropriate. In presenting the long list of defects above, we might be giving the impression that the PSS theory [Eq. (3.15)] can only lead to disaster. This is not true. The above form of the theory would not have been used for so long if it did not successfully account for a great variety of slow collision processes.

One reason for its success has already been mentioned: The radial part of $\underline{\mathrm{P}}$ commonly has sharp peaks near degeneracies, representing sudden change of character of the basis functions; these peaks are relatively easy to describe by using simple models, and they usually dominate the behavior of the transition amplitude. It is the smaller, more slowly varying part of $\underline{\mathrm{P}}$ that causes problems, and calculations are now reaching the level of accuracy that these problems must be addressed. However, when this "background" in $\underline{\mathrm{P}}$ is negligible, or ineffective in causing transitions, then the theoretical modifications developed below will usually become computationally unimportant, and the system will be successfully described by the simpler unmodified PSS theory.

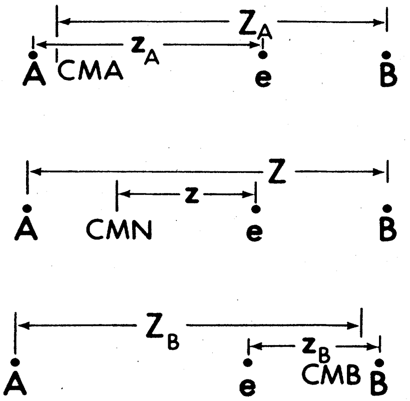

FIG. 11. Coordinates for collinear collision picture.

C. An improved formulation

The purpose of this section is to develop a more satisfactory quantum theory of slow atomic collisions. We shall show that the problems in the original formulation of PSS theory arise directly from the fact that the heavy-particle wave functions χ_n were taken to be functions of **R**. A better representation of Ψ is obtained if the heavy-particle coordinates are taken differently. We give a definition of appropriate coordinates, propose a new ansatz for Ψ, and then derive a set of coupled integro-differential equations, which provide a new foundation for the theory. Using approximations that are generally applicable for slow collisions, these integro-differential equations are reduced to differential equations, which replace Eqs. (3.16) as the basic equations of the theory of slow collisions.

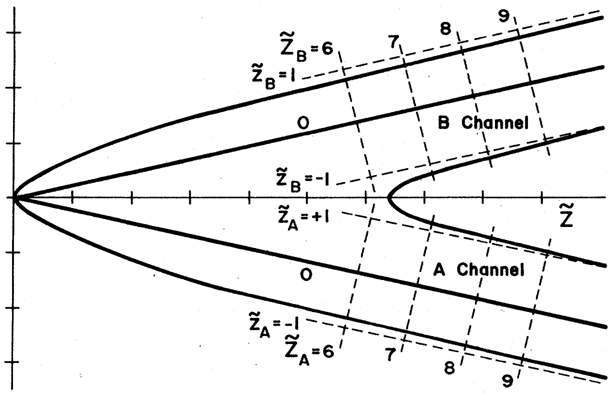

FIG. 12. Equipotential curves in mass-scaled coordinates. The axes are mass-scaled molecular coordinates, $\tilde{z}\tilde{Z}$. Dotted lines are lines of constant $\tilde{z}_A$, $\tilde{Z}_A$, $\tilde{z}_B$, or $\tilde{Z}_B$. Clearly, atomic mass-scaled coordinates provide two orthogonal grids related by rotations to molecular coordinates. Heavy lines are equipotentials, $V=-1,-\infty,-1$, marking centers and approximate width of the channels. Masses $M_A=M_B=$X, $m_0=1$ for this picture.

1. Mass-scaled-coordinate picture

Let us begin by presenting some pictures that show very clearly the essential defect in the original form of PSS theory. These pictures are based upon mass-scaled coordinates, which have been used for many years to study reactive scattering, especially collinear atom-diatom collisions (Glasstone, Laidler, and Eyring, 1941, p. 106; Pars, 1965, p. 537).

Mass-scaled coordinates are defined by

$$(\widetilde{\text{coordinate}})=(\text{associated mass})^{1/2}\times(\text{coordinate}), \tag{3.31}$$

where the associated masses were given in Table III; thus $\tilde{\mathbf{r}}_A=m_A^{1/2}\mathbf{r}_A$, $\tilde{\mathbf{R}}_A=\mu_A^{1/2}\mathbf{R}_A$, and so on. The conjugate momenta are transformed contragrediently, i.e., if $\mathbf{P}_A$ is conjugate to $\mathbf{R}_A$, then $\tilde{\mathbf{P}}_A=(\mu_A)^{-1/2}\mathbf{P}_A$, and so on; the transformation between scaled and unscaled coordinates is then canonical. From Eqs. (3.2), the transformed kinetic energy operators are given by

$$T=-\tfrac{1}{2}\hbar^2(\nabla^2_{\tilde{R}_A}+\nabla^2_{\tilde{r}_A'})=-\tfrac{1}{2}\hbar^2(\nabla^2_{\tilde{R}_B}+\nabla^2_{\tilde{r}_B'})=-\tfrac{1}{2}\hbar^2(\nabla^2_{\tilde{R}}+\nabla^2_{\tilde{r}'}) \tag{3.32}$$

so that we may now think of the collision as the motion of a single particle (of unit mass) on a six-dimensional potential surface.

We form an intuitive picture with a two-dimensional model. Consider the collinear cut of the potential surface, and think about the motion in the $(\tilde{z},\tilde{Z})$ plane (Fig. 11). We imagine that the electron may pass the nuclei, but the nuclei may not pass each other; hence $\tilde{Z}\geq 0$, but $\tilde{z}_A$, $\tilde{z}_B$, and $\tilde{z}$ may be positive or negative. In Fig. 12 are depicted the equipotential lines for this two-dimensional cut of the potential surface as a function of mass-scaled molecular coordinates, $(\tilde{Z},\tilde{z})$: each heavy line is a line of constant

$$V=-|z_A|^{-1}-|z_B|^{-1}+|Z|^{-1}.$$

The straight solid lines correspond to $z_A=0$ or $z_B=0$; these lines become the centers of the channels, which are the regions at large $|Z|$ bounded by $|z\mp\frac{1}{2}Z|\sim a$ few

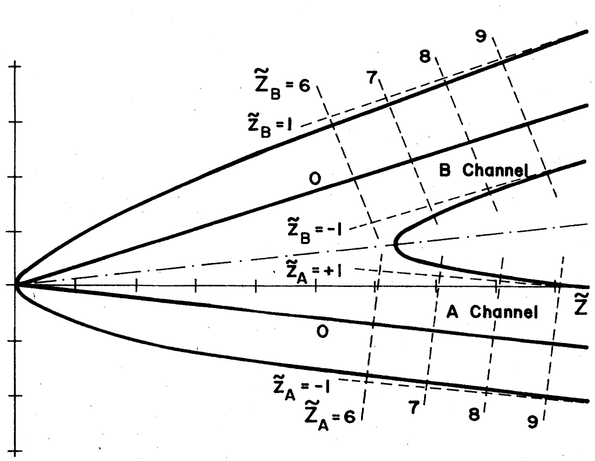

FIG. 13. Same as Fig. 12, but for $M_A=18$, $M_B=6$, $m=1$. The line bisecting the channels is the geometric center of the nuclei.

a_0. To draw this picture, we have taken $M_A = M_B = 9$, $m_0 = 1$; for a real molecule, with nuclear masses $\sim 2000 m_0$, the angle between the channels will be very tiny, of order $(m/\mu)^{1/2}$. Since the figure is drawn with $(\tilde{z}, \tilde{Z})$ orthogonal, one can show that $(\tilde{z}_A, \tilde{Z}_A)$ and $(\tilde{z}_B, \tilde{Z}_B)$ are also orthogonal, and these coordinates are represented by the dotted lines in the channels.

The situation for a symmetric but not homonuclear system is depicted in Fig. 13. The potentials are the same as those of the previous case, but the masses are now $M_A = 18$, $M_B = 6$, $m_0 = 1$. The picture is skewed off axis because z is measured not from the geometric center but from the center of mass of the nuclei (CMN). Again, however, atomic and molecular mass-scaled coordinates form orthogonal pairs which are related to each other by simple rotations.

Analogous pictures would be obtained from other cuts of the potential surface, and, though these figures are necessarily restricted to two dimensions, they provide insights applicable to the full six-dimensional problem. As mentioned earlier, the pictures are useful because they allow us to imagine the collision to be an elastic scattering process on a single potential surface. In classical mechanics we could imagine a particle oscillating back and forth in the A channel, between $\tilde{z}_A \simeq \pm 1$, and slowly approaching the molecular region. Here the other potential well becomes effective, and the particle's orbit is disturbed in some complicated way; eventually, however, it leaves the molecular region, oscillating out the B channel (charge exchange) or the A channel (no exchange). In quantum mechanics we may imagine a wave entering the A channel: on a line $\tilde{Z}_A = \text{constant}$ it looks like an exponential wave, mainly confined to the region between $\tilde{z}_A = \pm 1$, while on a line $\tilde{z}_A = \text{constant}$ it looks like a plane traveling wave approaching the molecular region. Upon reaching the molecular region the wave fronts are distorted in a complicated way, as the wave undergoes refraction, reflection, and diffraction in the double-well potential. Post-collision waves propagate back out both channels, representing the probability amplitudes for direct and exchange collisions.

Now let us examine the relationship between the basic ansatz of PSS theory, Eq. (3.15), and this picture. Consider a single term in that expansion, $\chi_0(\mathbf{R})\phi_0(\mathbf{r}'; \mathbf{R})$, and suppose ϕ_0 is the lowest molecular state of gerade symmetry. The function $\chi_0(\mathbf{R})$ must become some combination of plane waves $\exp(\pm i\mathbf{k}\cdot\mathbf{R})$ in the channels, and it must be more complicated in the molecular interaction region, but at the moment its precise form does not matter; all that matters is that it is a function only of $\mathbf{R}$. In the present two-dimensional picture, this term becomes $\chi_0(\tilde{Z})\phi_0(\tilde{z}; \tilde{Z})$. To be more specific, we might consider the function

$$\exp(i\tilde{k}\tilde{Z})[\exp(-|\tilde{z}_A|) + \exp(-|\tilde{z}_B|)] . \qquad (3.33)$$

The nodal lines of the real part of such a function are shown in Fig. 14(a), superimposed on a pair of equipotential curves from Fig. 12. Immediately we can see that there is something wrong about this picture. Schrödinger waves do not look like that. The nodal lines associated with a free traveling wave are supposed to be perpendicular to the direction of propagation of the wave. However, our ansatz requires that the nodal lines of each individual term, $\chi_n\phi_n$, be lines of constant Z, which are vertical, while the channels go off at an angle.[7]

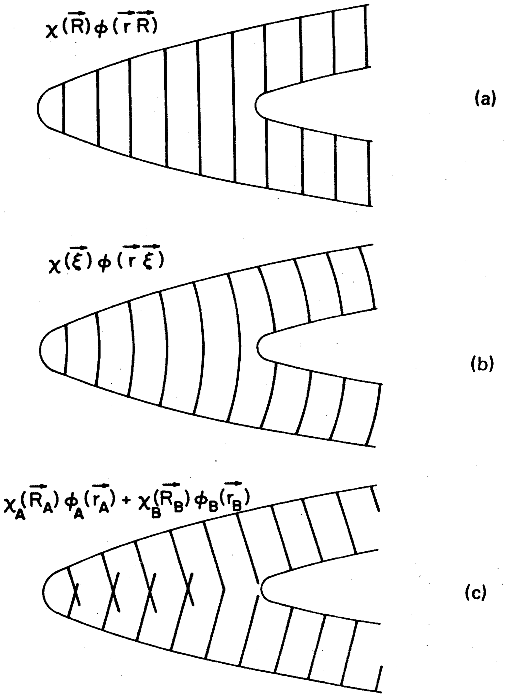

FIG. 14. (a): PSS ansatz. Nodal lines of a single term in a PSS-type ansatz are lines of constant R. In mass-scaled coordinates these are vertical lines. But Schrödinger waves don't look like this. The nodal lines are supposed to be perpendicular to the direction of propagation. (b): Curved-wave ansatz. If the nuclear wave function χ is taken to be a function of a curvilinear coordinate ξ, we get a picture like this. Now the nodal curves bend so that they can be properly aligned with the direction of propagation. (c): Intersecting-wave ansatz. A wave function of this form describes two intersecting wave trains. (Not shown): Intersecting-curved waves. The most general ansatz allows waves to be curved and to intersect.

We can now see ways of modifying the PSS ansatz to get a better description. One way is to use an expansion of the form

$$\Psi = \sum_{n_A} \chi_{n_A}(\mathbf{R}_A)\hat{\phi}_{n_A}(\mathbf{r}'_A) + \sum_{n_B} \chi_{n_B}(\mathbf{R}_B)\hat{\phi}_{n_B}(\mathbf{r}'_B) , \qquad (3.34\text{a})$$

where $\hat{\phi}_{n_A}$, $\hat{\phi}_{n_B}$ are states of atomic character centered on nucleus A or B. In the two-dimensional mass-scaled coordinate picture, such an ansatz might reduce to a function like

$$\exp(i\tilde{k}_A\tilde{Z}_A)\exp(-|\tilde{z}_A|) + \exp(i\tilde{k}_B\tilde{Z}_B)\exp(-|\tilde{z}_B|) . \qquad (3.34\text{b})$$

Such a function represents two intersecting wave trains [Fig. 14(c)]. Each wave train is oscillatory and propa-

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[7] In this figure, the relative nuclear momentum would be horizontal, and the electron momentum would be vertical. Therefore, the fact that the nodal lines are not properly oriented with the channels is directly related to the fact that individual terms in the PSS ansatz do not describe the momentum of the electron as it is carried along with a nucleus.

gating in a particular direction (toward increasing $\tilde{Z}_A$ or $\tilde{Z}_B$) but each is a localized exponential wave in the perpendicular direction ($\tilde{z}_A$ or $\tilde{z}_B$). Now the geometry of the nodal lines is compatible with the geometry of the channels.

A theory of slow collisions based upon an ansatz like Eq. (3.34a) was developed recently (Delos, 1981a). It has several obvious advantages over the earlier formulation. (i) The boundary conditions can be satisfied automatically by choosing some of the $\hat{\phi}_n$'s to correspond to the relevant asymptotic atomic states; hence the infinite-range couplings will not appear. This is intuitively clear in the mass-scaled picture because the coordinates are appropriately aligned with the channels. (ii) Molecular Born-Oppenheimer states often are known only in terms of states having atomic character (cf. the LCAO approximation); in this approach we circumvent the problems of PSS theory by refusing to make (or at least deferring) the transformation to molecular representation. (iii) Under appropriate restrictions on the atomic states, $\underline{P}$-matrix couplings can be canceled exactly or made negligibly small.

There is an important limitation to this approach, however. It requires that the elementary electronic basis states ϕ_{n_A}, ϕ_{n_B} have "single-center" character; each must be associated with, and propagating with, some specific center in the molecule: one or the other of the nuclei, the geometric center, the center of mass of the nuclei, etc. The theory also allows the basis states to be arbitrary linear combinations of single-center states, but in any case the decomposition of each basis function into single-center states must be available. Now, because of the near-adiabatic nature of slow atomic collisions, it is normally desirable to describe Ψ in terms of molecular electronic states (Born-Oppenheimer eigenfunctions, for example). Such states do not, in general, have single-center character, and the decomposition of such states into states of single-center character may be ambiguous, or it might simply not be available. In that case the ideas based on the intersecting wave-train picture cannot be used directly.

A different approach is more appropriate for this situation. Suppose we define a curvilinear heavy-particle coordinate $\tilde{\xi}(\tilde{\mathbf{R}}, \tilde{\mathbf{r}}')$ such that $\tilde{\xi} \to \tilde{\mathbf{R}}_A$ in channel A, and $\tilde{\xi} \to \tilde{\mathbf{R}}_B$ in channel B. Consider the ansatz

$$\Psi = \sum_n \chi_n(\xi)\hat{\phi}_n(\mathbf{r}'; \xi), \tag{3.35a}$$

where the functions $\hat{\phi}_n(\mathbf{r}'; \xi)$ represent some sort of molecular electronic basis states defined on surfaces of constant ξ. When expressed in mass-scaled coordinates, individual terms in Eq. (3.35a) would involve functions like

$$\exp\{(i\tilde{k}\,\tilde{\xi})[\exp(-|\tilde{z}_A|)+\exp(-|\tilde{z}_B|)]\}. \tag{3.35b}$$

The nodal lines of this function are lines of constant $\tilde{\xi}$; they curve in such a way that they give the right geometry in the channels [Fig. 14(b)]. We can see that these curved waves also provide a reasonable and intuitively pleasing picture.

Such a description of slow atomic collisions has also been fully developed (Thorson and Delos, 1978b), and it was found that it resolved most of the problems of PSS theory: scattering boundary conditions were satisfied, infinite-range couplings removed, and fictitious "origin-dependent" couplings eliminated. For most slow collision problems, therefore, this description was shown to be suitable.

Nevertheless, there was one significant restriction on the method as it was developed in that paper. Only one curvilinear coordinate was defined, and it was assumed that the same heavy-particle coordinate $\xi(\mathbf{R}, \mathbf{r}')$ was appropriate for every term in the expression (3.35a). As a consequence of this assumption, momentum-transfer factors did not appear in the matrix elements, variational techniques were somewhat restricted, and the formal definition of diabatic states was not fully encompassed by this approach.

There is an obvious generalization that combines the advantages of both of the above approaches. Let us consider the ansatz

$$\Psi = \sum_n \chi_n(\xi_n)\hat{\phi}_n(\mathbf{r}'; \xi_n). \tag{3.36}$$

Here the functions $\hat{\phi}_n(\mathbf{r}'; \xi_n)$ represent electronic basis states, each of which may have either atomic (one-center), or molecular (two-center) character. The set $\{\xi_n = \xi_n(\mathbf{R}, \mathbf{r}')\}$ is a set of heavy-particle coordinates. There is one for each basis state $|\hat{\phi}_n\rangle$. If $|\hat{\phi}_n\rangle$ is an A-atomic state, then ξ_n may be $\mathbf{R}_A$ or a constant times $\mathbf{R}_A$ (and likewise for B-atomic states); on the other hand, if $|\hat{\phi}_n\rangle$ is a two-center, molecular state, then ξ_n is a curvilinear coordinate. This generalization permits different heavy-particle coordinates for different electronic basis states, and it permits some or all of the coordinates to be curved. By suitable restrictions, it can be reduced to either the intersecting-wave or the curved-wave picture, so this generalization might be called the *intersecting-curved-wave* picture. This is the picture that will be developed into a theory in the following sections.

Equation (3.36) provides the basic ansatz for the calculation of Ψ, and there are three questions that have to be answered.

(1) How do we choose the set of basis functions $\{\phi_n\}$?

(2) How do we choose the corresponding set of heavy-particle coordinates $\{\xi_n\}$?

(3) What are the coupled equations for the functions $\chi_n(\xi_n)$?

It is the third question that we shall answer first. We shall show:

(a) that the functions $\chi_n(\xi_n)$ obey coupled integro-differential equations (3.42);

(b) that by very general approximations (suitable for slow collisions), these integro-differential equations can be reduced to coupled three-dimensional differential equations (3.61);

and finally

(c) that partial-wave expansion reduces these three-dimensional equations to radial equations (A10).

Mittleman was the first to recognize that an ansatz like (3.35a) could improve upon the PSS theory (Mittleman, 1969, 1974b; Mittleman and Tai, 1973). However, his definition of ξ was not quite adequate. It led to an implausible coupling between g and u states for isotopic systems (Mittleman, 1974a). Later, the introduction of mass-scaled-coordinate pictures (Thorson and Delos, 1978b) led to a better formulation. Related work has been done by Green (1981).

Mass-scaled coordinates were also used by Stechel, Schmalz, and Light (1979; see also Schmalz, Stechel, and Light, 1979). In their ansatz, they took atomic basis functions, as in (3.34a), but they took $\{\chi_n\}$ to be functions of R. Delos (1981a) criticized this last point, saying that each term in such an ansatz still has the behavior of the top diagram in Fig. 14.

Certain aspects of the theory of Chen and Watson (1968) are somewhat similar to the approach taken here. They also noted the incompatibility of PSS expansions with scattering boundary conditions, and their ansatz (which was never stated very clearly) involves molecular basis functions ϕ_n times functions $\chi_n(\mathbf{R}_j)$, $j=A, B$. Intrinsic to their formulation is an eikonal approximation to $\chi_n(\mathbf{R}_j)$, whereas no such approximation is made in the method developed here. See also Hatton *et al.* (1975).

Recently a curved-wave picture has also been used to describe proton exchange (Babamov and Marcus, 1981).

2. Coupled equations for heavy-particle motion

a. General properties of electronic basis states

We begin with a set of electronic basis states $|\phi_n\rangle$, which are assumed to have the same properties that were listed above Eq. (2.44): they are not necessarily eigenstates of any particular Hamiltonian, but they are assumed to be rotating, square-integrable states, of which a subset corresponds asymptotically to the important initial and final atomic states. As before, each state $|\phi_n\rangle$ is represented by either of two distinct functions, $\phi_n(\mathbf{r};R)$ or $\phi_n(\mathbf{r}';\mathbf{R})$, according to whether the electronic coordinates are referred to the internuclear axis or to the space-fixed frame.

b. Heavy-particle coordinates

For each basis state $|\phi_n\rangle$, we define a heavy-particle scattering coordinate $\xi_n = \xi_n(\mathbf{r}';\mathbf{R})$, in accordance with the discussion in Sec. III.C.1. Let us write

$$\xi_n(\mathbf{r}';\mathbf{R}) = \mathbf{R} + \frac{m}{\mu}\,\mathbf{s}_n(\mathbf{r}';\mathbf{R}) \tag{3.37}$$

and choose the function $\mathbf{s}_n(\mathbf{r}';\mathbf{R})$ such that ξ_n has the desired properties. The general principles concerning the choice of $\mathbf{s}_n(\mathbf{r}';\mathbf{R})$ are

(1) as stated earlier, if $|\phi_n\rangle$ is an A- or B-atomic state, then ξ_n should be proportional to $\mathbf{R}_A$ or $\mathbf{R}_B$, while if $|\phi_n\rangle$ has two-center character, ξ_n should be a curvilinear coordinate;

(2) the resulting coupled equations should be as simple as possible, and preserve as many of the molecular symmetries as possible;

(3) the coupled equations should go to the correct classical limit, i.e., they should correspond to one of the sets of coupled equations formulated in Sec. II.

One of the forms for $\mathbf{s}_n(\mathbf{r}';\mathbf{R})$ that is consistent with these principles is

$$\mathbf{s}_n(\mathbf{r}';\mathbf{R}) = \tfrac{1}{2}\,[f_n(\mathbf{r}';\mathbf{R})+\lambda]\mathbf{r}'_g - \tfrac{1}{8}\,(1-\lambda^2)\mathbf{R}\,, \tag{3.38}$$

where $f_n(\mathbf{r}';\mathbf{R})$ can be taken either to be ±1 (for states of atomic character) or to be a smooth switching function (for states of molecular character). With this definition of $\mathbf{s}_n$, the coordinate ξ_n goes approximately to $(\mu_J/\mu)^{1/2}\mathbf{R}_J$ $(J=A,B)$ in the channels.

There are many possible definitions of a corresponding scattering coordinate for the electron. The only requirement is that each (vector) value of the electron coordinate must specify a unique point on a surface of constant ξ in the configuration space. Otherwise, since in any case we will eventually integrate over electronic coordinates, the specific choice of these coordinates is not very important. It is easiest to continue to use $\mathbf{r}'$ (or $\mathbf{r}$) to describe the position of the electron. [In the mass-scaled-coordinate picture, the coordinates $(\tilde{\mathbf{r}}', \tilde{\xi}_n)$ are not orthogonal, but no great difficulty is caused thereby.]

The reader may have noticed that Eq. (3.38) is identical to (2.53). Obviously, this is not an accident. The same physical effects, which in the classical trajectory framework are described by electron-translation factors, are described in quantum mechanics by the intersecting–curved-waves pictures. Therefore we set up the equations such that the correspondence is as clear as possible.

c. Displacing the basis states onto surfaces of constant ξ

The electronic basis states $|\phi_n\rangle$ were represented by functions $\phi_n(\mathbf{r}';\mathbf{R})$, which are of course defined on surfaces of constant R. However, for each state $|\phi_n\rangle$, we have chosen a new scattering coordinate ξ_n, so we need to have basis functions which are defined on surfaces of constant ξ. Therefore let us pick up each of our original basis states $|\phi_n\rangle$ and move it from one surface to the other. In the mass-scaled-coordinate picture, we are starting with a function defined on a particular (vertical) surface of constant $\tilde{Z}$, and mapping it, (or displacing it) onto a surface of constant $\tilde{\xi}_n^z$. The displaced state is denoted $|\hat{\phi}_n\rangle$, and it is represented by a function $\hat{\phi}_n(\mathbf{r}';\xi_n)$. Algebraically, the mapping or displacement can be carried out simply by replacing R by ξ_n in the functional form. The new function $\hat{\phi}_n(\mathbf{r}';\xi_n)$ is not necessarily *equal to* the original function $\phi_n(\mathbf{r}';\mathbf{R})$ at any point in configuration space. However, *expressed in terms of the new variable ξ_n, it has the same functional form* as did the original, undisplaced function expressed in terms of the old variable R.

As an example, consider a system with the charge of nucleus B equal to unity. If we were to use a purely atomic-state expansion, as in Eq. (3.34), we would use the basis function

$$\phi^0_{1s_B}(\mathbf{r}_B;\mathbf{R}_B) = \exp(-m_B|\mathbf{r}_B|)\,.$$

This function happens to be independent of $\mathbf{R}_B$, but for the collision problem we would think of it as being defined on a set of surfaces of constant $\mathbf{R}_B$. For a molecular expansion, one of the basis functions that might be considered is

$$\phi_{1s_B}(\mathbf{r};\mathbf{R}) = \exp[-m\,|\mathbf{r}-\tfrac{1}{2}(1+\lambda)\mathbf{R}\,|]\,.$$

This differs from ϕ_{1s_B} in having a different electronic reduced mass, but more significant is the different way this function is used: We implicitly think of it as being defined on surfaces of constant R. For example, overlap integrals would be defined on surfaces of constant R (not of constant $\mathbf{R}_B$), and if we were to use a variable orbital exponent it would be regarded as a function of R (not $\mathbf{R}_B$). For the purposes of quantum chemistry, such things are done automatically, and it may be hard to imagine any other way of handling this function. However, we have seen that for collision problems, we must use basis functions defined on different surfaces.

In this case a possible choice is $\boldsymbol{\xi}=\mathbf{R}_B$. The mapping is done by *replacing* $\mathbf{R}$ by $\mathbf{R}_B$, so the displaced function is

$$\hat{\phi}_{1s_B}(\mathbf{r};\boldsymbol{\xi})=\exp[-m\,|\mathbf{r}-\tfrac{1}{2}(1+\lambda)\boldsymbol{\xi}\,|]$$
$$=\exp[-m\,|\mathbf{r}-\tfrac{1}{2}(1+\lambda)\mathbf{R}_B|\,].$$

Using Tables II and III this simplifies to

$$\hat{\phi}_{1s_B}(\mathbf{r}';\boldsymbol{\xi})=\exp(-m_B|\mathbf{r}_B|)=\phi^0_{1s_B}(\mathbf{r}_B;\mathbf{R}_B),$$

i.e., the displacement has converted it back to the original atomic state!

This example shows that if we were to use a basis of atomic states defined in atomic coordinates, the mapping step would be unnecessary (because it is already accomplished). However, since we usually have to use a molecular representation, in which states are defined on surfaces of constant R, some sort of displacement is necessary. Furthermore, if the basis function has a "two-center" character, then a curvilinear coordinate will be necessary, and the result of displacement will be less simple.

d. Expansion of Ψ

Now that each basis function $\phi_n(\mathbf{r}';\mathbf{R})$ is mapped onto its own set of surfaces of constant ξ_n, the full wave function is expanded as in Eq. (3.36),

$$\Psi\approx\sum_n \chi_n(\xi_n)\hat{\phi}_n(\mathbf{r}';\xi_n), \tag{3.39}$$

representing a superposition of wave trains, which may be intersecting and which may be curved. The Schrödinger equation is, of course,

$$0=(H-E)\Psi\approx\sum_n (H-E)\chi_n(\xi_n)\hat{\phi}_n(\mathbf{r}';\xi_n), \tag{3.40}$$

and there are two ways to develop it. Either we can reexpress each term as a function of $(\mathbf{r}',\mathbf{R})$ and act on it with H expressed in the same coordinates, or else we can transform H to the new coordinates $(\mathbf{r}',\xi_n)$ for action on each term. The latter course is more convenient for our purposes.

e. Coupled equations for $\{\chi_n(\xi_n)\}$

In principle the partial differential equation (3.40) specifies $\chi_n(\xi_n)$, but the electronic coordinates must first be eliminated. In the PSS theory this is done by taking scalar products with $\langle\phi_m|$, but now we have to pay attention to the fact that different states are expressed in different coordinates. *Hence for each m, we reexpress Eq. (3.40) in terms of $(\mathbf{r}',\xi_m)$, multiply by $\phi_m(\mathbf{r}',\xi_m)$, integrate over all $\mathbf{r}'$ holding ξ_m fixed, and set the result to zero.* That gives a set of coupled integro-differential equations that must be satisfied by the functions $\chi_n(\xi_n)$.

To translate these statements into equations, let us define $\mathcal{O}$ as

$$\mathcal{O}=\sum_n (H-E)\chi_n|\hat{\phi}_n\rangle\,. \tag{3.41a}$$

$\mathcal{O}$ is a sum of terms, $\mathcal{O}_n$, each of which is represented by a function of the configuration-space variables $(\mathbf{r}',\xi_n)$:

$$\mathcal{O}_n=\mathcal{O}_n(\mathbf{r}',\xi_n)=(H-E)\chi_n(\xi_n)\hat{\phi}_n(\mathbf{r}';\xi_n)\,. \tag{3.41b}$$

Moreover, each term, or the whole sum, can be expressed as a function of *any* pair of variables $(\mathbf{r}',\xi_m)$, so we write

$$\mathcal{O}=\mathcal{O}(\mathbf{r}',\xi_m)=\sum_n \mathcal{O}_n(\mathbf{r}',\xi_m)\,. \tag{3.41c}$$

The quantities $\mathcal{O}_n(\mathbf{r}',\xi_n)$ and $\mathcal{O}_n(\mathbf{r}',\xi_m)$ are different functions of different variables, but they represent the same physical quantity, namely the nth term in Eq. (3.41a), so the two functions are equal at corresponding points in configuration space. [Analogous notation was used in Eq. (2.44)].

If the ansatz (3.39) is a good one, then $\mathcal{O}$ should be small everywhere. Hence it is reasonable to impose the requirement that*

$$\int_{\text{fixed }\xi_m}\hat{\phi}^*_m(\mathbf{r}';\xi_m)\mathcal{O}(\mathbf{r}';\xi_m)d\mathbf{r}'=0\,. \tag{3.42}$$

This is the set of coupled integro-differential equations for $\{\chi_n(\xi_n)\}$.

To see this more explicitly, suppose we have

$$\hat{\phi}_m=\hat{\phi}_{1s_B}=\exp(-m_B|\mathbf{r}_B|),$$
$$\hat{\phi}_n=\hat{\phi}_{1s_A}=\exp(-m_A|\mathbf{r}_A|),$$
$$\xi_m=\mathbf{R}_B,\quad \xi_n=\mathbf{R}_A.$$

Then one of the terms in Eq. (3.42) is

$$-E\int\hat{\phi}_{1s_B}(\mathbf{r}_B)\chi_{1s_A}(\mathbf{R}_A)\hat{\phi}_{1s_A}(\mathbf{r}_A)d\mathbf{r}_B. \tag{3.43a}$$

Using Tables II and III, the integrand is reexpressed as a function of $\mathbf{r}_B$ and $\mathbf{R}_B$,

$$-E\int\exp(-m_B|\mathbf{r}_B|)\exp\left[-m_A\left|\left(1-\frac{m_0}{M_B+m_0}\right)\mathbf{r}_B+\mathbf{R}_B\right|\right]\chi_{1s_A}\left[\left(1-\frac{m_0}{M_A+m_0}\right)\mathbf{R}_B-\frac{m_0M_T}{(M_A+m_0)(M_B+m_0)}\mathbf{r}_B\right]d\mathbf{r}_B \tag{3.43b}$$

and the integral is to be evaluated at fixed $\mathbf{R}_B$. Equations of this type appear in Mott and Massey (1965, p. 424-8).

It is believed that these coupled integro-differential equations provide an adequate foundation for the quantum theory of discrete electronic transitions in atom-atom collisions.

f. Transformation of Hamiltonian

To evaluate each term $\mathcal{O}_n(\mathbf{r}',\xi_n)$ we need to express H in terms of these variables. Denoting components of any vector ρ by ρ^a ($a=x',y',z'$ or X,Y,Z), we have for any function $F(\mathbf{r}',\xi_n)$,

$$\begin{aligned}(\partial F/\partial R^a)_{\mathbf{r}'}&=(\partial\xi_n^b/\partial R^a)_{\mathbf{r}'}(\partial F/\partial\xi_n^b)_{\mathbf{r}'},\\(\partial F/\partial r'^a)_{\mathbf{R}}&=(\partial F/\partial r'^a)_{\xi_n}+(\partial\xi_n^b/\partial r'^a)_{\mathbf{R}'}(\partial F/\partial\xi_n^b)_{\mathbf{r}'}\end{aligned} \tag{3.44}$$

(summation over repeated indices implied). Taking the kinetic energy in the form (3.2c), applying (3.37) and using the notation

$$\Gamma_n^{ab}=\Gamma_n^{ab}(\mathbf{r}';\mathbf{R})=(\partial s_n^b/\partial R^a)_{\mathbf{r}'}\,, \tag{3.45a}$$

$$\gamma_n^{ab}=\gamma_n^{ab}(\mathbf{r}';\mathbf{R})=(\partial s_n^b/\partial r'^a)_{\mathbf{R}}\,, \tag{3.45b}$$

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*The Jacobian could be included in Eq. (3.42) but it is not really essential.

$$\begin{aligned} p^b &= -i\hbar(\partial/\partial r'^b)_{\xi_n}, \\ P^b &= -i\hbar(\partial/\partial \xi^b)_{\mathbf{r}'}, \end{aligned} \tag{3.45c}$$

then a straightforward but tedious derivation leads to

$$\begin{aligned} H(\mathbf{r}',\mathbf{R}) &= -\frac{\hbar^2}{2m}\nabla^2_{r'} - \frac{\hbar^2}{2\mu}\nabla^2_R + V = H(\mathbf{r}',\xi_n) \\ &= \frac{1}{2m}p^bp^b + V + \frac{1}{2\mu}\left[P^bP^b + 2\gamma_n^{ab}p^aP^b - i\hbar(\partial\gamma_n^{ab}/\partial r'^a)P^b + \frac{m}{\mu}[(\gamma_n^{ac}\gamma_n^{ab} + 2\Gamma_n^{cb})P^cP^b - i\hbar(\partial\Gamma_n^{ab}/\partial R^a)P^b] + \left(\frac{m}{\mu}\right)^2\Gamma_n^{ca}\Gamma_n^{cb}P^aP^b\right]. \end{aligned} \tag{3.46}$$

This expression is exact provided that the following interpretations are noted. V, Γ_n^{ab}, and γ_n^{ab} are originally given in terms of $(\mathbf{r}',\mathbf{R})$ and they have to be reexpressed as functions of ξ_n so that the whole operator is finally expressed in terms of $(\mathbf{r}',\xi_n)$. Likewise the drivative $(\partial\gamma_n^{ab}/\partial r'^a)$ is taken at fixed R and then is reexpressed in terms of $(\mathbf{r}',\xi_n)$.

3. Approximations suitable for slow atomic collisions

Except for the expansion of Ψ in a necessarily finite set of terms, no approximations have been made in the above development, so the coupled integro-differential equations (3.42) may be called "exact." Direct numerical solution of these equations would be quite difficult, however, so simplifying approximations should be sought. "First-order" and "semiclassical" approximations, which should be applicable to fast collisions, have been briefly examined by Mott and Massey (1965) and Delos (1981). Here we consider approximations that should be generally valid for slow atomic collisions.

As discussed earlier, a collision is slow if the heavy-particle speed is much less than the typical electron speed, and the ratio of these speeds may be taken to be the small parameter. If we regard the total electronic energy and the nuclear kinetic energy as being comparable in size, it follows that $(v_{nuc}/v_{el}) \sim (m/\mu)^{1/2}$.

Consider the action of $(1/2\mu)(P^aP^a)$ on the product $\chi_n\phi_n$. Three terms result: the one in which both P's act on χ is of order μv_{nuc}^2; the one in which one P acts on χ and one on ϕ is of order $mv_{nuc}v_{el}$; and the one in which both P's act on ϕ is of order $(m^2v_{el}^2/\mu)$. These terms may be considered to be of zeroth order, first order, and second order in v_{nuc}/v_{el}. In a similar way, every term in $H(\mathbf{r}';\xi_n)$ produces terms of various orders depending on whether P acts on ϕ or on χ.

The development below is based on the following approximations. All terms of zeroth order and first order in v_{nuc}/v_{el} are retained, and all terms of third order and higher are neglected. Most of the terms of second order in (v_{nuc}/v_{el}) are neglected, but we will retain a few of the more familiar of these terms. In particular, we will retain the second-order terms that appear in H unless they are also proportional to derivatives of, or differences between, functions f_n (Eq. 3.38). Second-order terms that are neglected include those which contain derivatives of switching functions or the related factor (f^2-1), and those (arising below) which are proportional to some power of $(\mathbf{s}_n-\mathbf{s}_m)$.

These approximations lead to immediate simplifications: the term $(2\mu)^{-1}(m/\mu)^2\Gamma_n^{ca}\Gamma_n^{cb}P^aP^b$ can be dropped, as well as

$$(2\mu)^{-1}(m/\mu)[(\gamma_n^{ac}\gamma_n^{ab} + 2\Gamma_n^{cb})P^cP^b - i\hbar(\partial\Gamma_n^{ab}/\partial R^a)P^b],$$

since we find from Eqs. (3.38) and (3.44) that these latter terms are at most of order $(v_{nuc}/v_{el})^2(f_n^2-1)$. The remaining terms in Eq. (3.46) are

$$H \simeq (2m)^{-1}p^ap^a + V + (2\mu)^{-1}[P^aP^a + 2\gamma_n^{ab}P^bp^a - i\hbar(\partial\gamma_n^{ab}/\partial r'^a)P^b], \tag{3.47}$$

and this can further be simplified by defining

$$D_n^a = P^a + \gamma_n^{ba}p^b. \tag{3.48}$$

Then to the same level of accuracy, we have

$$H = (2\mu)^{-1}[D_n^aD_n^a - i\hbar(\partial\gamma_n^{ba}/\partial r^{b\prime})D_n^a] + h_n', \tag{3.49a}$$

$$h_n' = (2m)^{-1}[p^ap^a - (m/\mu)\gamma_n^{ba}\gamma_n^{ca}p^bp^c] + V, \tag{3.49b}$$

and when this acts on $\chi_n|\hat{\phi}_n\rangle$, we obtain

$$\begin{aligned} \mathcal{O}_n = (2\mu)^{-1}\{&|\hat{\phi}_n\rangle D_n^aD_n^a\chi_n + 2[D_n^a|\hat{\phi}_n\rangle]D_n^a\chi_n \\ &+ [D_n^aD_n^a|\hat{\phi}_n\rangle]\chi_n - i\hbar(\partial\gamma_n^{ab}/\partial r'^a)|\hat{\phi}_n\rangle D_n^b\chi_n\} \\ &+ (h_n'-E)|\hat{\phi}_n\rangle\chi_n. \end{aligned} \tag{3.50}$$

Now, as stated earlier, this term is represented by a function of the variables $(\mathbf{r}',\xi_n)$, and it has to be reexpressed as a function of $(\mathbf{r}',\xi_m)$. For all of the functions that are given in advance, such as $\hat{\phi}_n$, $\mathbf{s}_n$, V, etc., this reexpression can in principle be done analytically, using the defined relationships between ξ_n and ξ_m. However, the reexpression cannot be done analytically for $\chi_n(\xi_n)$ or its derivatives, because these functions are not known until after the equations are solved. Hence, for $\chi_n(\xi_n)$, we use the approximation

$$\begin{aligned} \chi_n(\xi_n) &= \chi_n[\xi_m + (m/\mu)(\mathbf{s}_n-\mathbf{s}_m)] \\ &\simeq \chi_n(\xi_m) + (m/\mu)(\mathbf{s}_n-\mathbf{s}_m)\cdot\nabla_{\xi_m}\chi_n(\xi_m), \end{aligned} \tag{3.51a}$$

$$\nabla_{\xi_n}\chi_n(\xi_n) \simeq \nabla_{\xi_m}\chi_n(\xi_m) + (m/\mu)[(\mathbf{s}_n-\mathbf{s}_m)\cdot\nabla_{\xi_m}]\nabla_{\xi_m}\chi_n(\xi_m), \tag{3.51b}$$

and so on. When this approximation is used for χ_n, it is found that in every case the neglected terms are proportional at least to $(v_{nuc}/v_{el})^2$ and powers of $(\mathbf{s}_n-\mathbf{s}_m)$.

To see the effect of this approximation upon the form of the coupled equations, consider the last term in Eq. (3.50):

$$\begin{aligned} -E\hat{\phi}_n(\mathbf{r}';\xi_n)\chi_n(\xi_n) \simeq &-E\hat{\phi}_n(\mathbf{r}';\xi_m)\chi_n(\xi_m) \\ &+ (m/\mu)(\mathbf{s}_n-\mathbf{s}_m)\hat{\phi}_n(\mathbf{r}';\xi_m)\nabla_{\xi_m}\chi_n(\xi_m). \end{aligned} \tag{3.52a}$$

As in our earlier notation [cf. Eq. (3.41c)], $\hat{\phi}_n(\mathbf{r}';\xi_m)$ is a new function of new variables, obtained by reexpressing $\phi_n(\mathbf{r}';\xi_n)$ in terms of $(\mathbf{r}',\xi_m)$. In contrast, by virtue of the Taylor expansion (3.51), $\chi_n(\xi_m)$ is not a new function, but the old function $\chi_n(\xi_n)$ evaluated at a new point, ξ_m. We can now multiply (3.52a) by $\phi_m^*(\mathbf{r}';\xi_m)$, and integrate over $\mathbf{r}'$ (holding ξ_m fixed), to obtain

$$-E\int \hat{\phi}_m^*(\mathbf{r}';\xi_m)\hat{\phi}_n(\mathbf{r}';\xi_m)d\mathbf{r}'\chi_n(\xi_m)$$

$$-(m/\mu)E\int \hat{\phi}_m^*(\mathbf{r}';\xi_m)(\mathbf{s}_n-\mathbf{s}_m)\hat{\phi}_n(\mathbf{r}';\xi_m)d\mathbf{r}'\nabla_{\xi_m}\chi_n(\xi_m)\,. \tag{3.52b}$$

Continuing in this way for all terms in (3.50), discarding all new terms that are second order in (v_{nuc}/v_{el}), and noting that D_n^a acting on χ_n is just $-i\hbar\nabla\chi_n$, we find that the coupled integro-differential equations (3.42) are reduced to coupled differential equations, which we write in matrix form as

$$\begin{aligned}(2\mu)^{-1}\{[\underline{\hat{S}}&-(i\hbar/\mu)\underline{\hat{\sigma}}\cdot\nabla_{\xi_m}](-i\hbar\nabla_{\xi_m})^2\\ &+2\hat{\Pi}\cdot(-i\hbar\nabla_{\xi_m})+\underline{\hat{B}}\}\underline{\chi}(\xi_m)\\ +\{\underline{\hat{h}}'&-(i\hbar/\mu)\hat{\eta}\cdot\nabla_{\xi_m}\\ &-E[\underline{\hat{S}}-(i\hbar/\mu)\underline{\hat{\sigma}}\cdot\nabla_{\xi_m}]\}\underline{\chi}(\xi_m)=0\,,\end{aligned} \tag{3.53}$$

where

$$\begin{aligned}\hat{S}_{mn}&=\int \hat{\phi}_m^*\hat{\phi}_n d\mathbf{r}'\\ &=\int \hat{\phi}_m^*(\mathbf{r}';\xi_m)\hat{\phi}_n(\mathbf{r}';\xi_m)d\mathbf{r}'\,,\end{aligned} \tag{3.54a}$$

$$\hat{\sigma}_{mn}=(im/\hbar)\int \hat{\phi}_m^*(\mathbf{s}_n-\mathbf{s}_m)\hat{\phi}_n d\mathbf{r}'\,, \tag{3.54b}$$

$$\hat{\Pi}_{mn}=\int \hat{\phi}_m^*(D_n^a-\tfrac{1}{2}i\hbar\partial\gamma_n^{ba}/\partial r'^b)\hat{\phi}_n d\mathbf{r}'\,, \tag{3.54c}$$

$$\hat{B}_{mn}=\int \hat{\phi}_m^* D_n^a D_n^a\hat{\phi}_n d\mathbf{r}'\,, \tag{3.54d}$$

$$\hat{h}'_{mn}=\int \hat{\phi}_m^* h'_n\hat{\phi}_n d\mathbf{r}'\,, \tag{3.54e}$$

$$\hat{\eta}_{mn}=\int \hat{\phi}_m^*(\mathbf{s}_n-\mathbf{s}_m)h'_n\hat{\phi}_n d\mathbf{r}'\,. \tag{3.54f}$$

Each matrix element is evaluated according to the above discussion, and each is a function of ξ_m.

Because of the term $(2\mu)^{-1}(-i\hbar\hat{\sigma}\cdot\nabla)(-i\hbar\nabla)^2$, these equations are of third order. Nevertheless, they can be reduced to second order by an approximation that is consistent with neglect of new terms of order $(v_{nuc}/v_{el})^2$: We take

$$\underline{\hat{S}}(\underline{\hat{S}}-i\hbar/\mu\hat{\sigma}\cdot\nabla)^{-1}\simeq 1+(i\hbar/\mu)\underline{\hat{\sigma}}\cdot\nabla\underline{\hat{S}}^{-1}\,. \tag{3.55}$$

When Eq. (3.53) is multiplied on the left by (3.55), the factor $[\underline{\hat{S}}-(i\hbar/\mu)\underline{\hat{\sigma}}\cdot\nabla]$ is replaced by $\underline{\hat{S}}$, and only one significant new term is produced,

$$(i\hbar/\mu)\underline{\hat{\sigma}}\cdot\nabla\underline{\hat{S}}^{-1}\underline{\hat{h}}'\underline{\chi}\simeq(i\hbar/\mu)\underline{\hat{\sigma}}\underline{\hat{S}}^{-1}\underline{\hat{h}}\nabla\underline{\chi}\,.$$

Thus we obtain coupled second-order differential equations,

$$\begin{aligned}\{(2\mu)^{-1}[\underline{\hat{S}}(-i\hbar\nabla_{\xi_m})^2&+2(\underline{\hat{\Pi}}+\underline{\hat{\gamma}})\cdot(-i\hbar\nabla_{\xi_m})+\underline{\hat{B}}]+\underline{\hat{h}}'-\hat{S}E\}\\ &\times\underline{\chi}_n(\xi_n)=0\,,\end{aligned} \tag{3.56}$$

with

$$\underline{\hat{\gamma}}=\underline{\hat{\eta}}-\underline{\hat{\sigma}}\,\underline{\hat{S}}^{-1}\hat{h}'\,. \tag{3.57}$$

It is now convenient to define a "displaced" or "mapped" electronic Hamiltonian $\hat{h}_n$, which bears the same relationship to h that $\hat{\phi}_n(\mathbf{r}';\xi_n)$ bears to $\phi_n(\mathbf{r}';\mathbf{R})$. Expressed in terms of $(\mathbf{r}';\xi_n)$, $\hat{h}_n$ has the same functional form as does h expressed in terms of $(\mathbf{r}';\mathbf{R})$. Thus, for the $\mathrm{H}^+-\mathrm{H}$ system, for which spin-orbit coupling is negligible, and

$$\begin{aligned}h\rightarrow h_{\mathrm{BO}}&=-(\hbar^2/2m)(\nabla^2_{r'})_R+V\,,\\ V&=-e^2|\mathbf{r}-\mathbf{R}/2|^{-1}-e^2|\mathbf{r}+\mathbf{R}/2|^{-1}+e^2|\mathbf{R}|^{-1}\,,\end{aligned}$$

the "mapped" electronic Hamiltonian is

$$\begin{aligned}\hat{h}_n&=-(\hbar^2/2m)(\nabla^2_{r'})_{\xi_n}+\hat{V}_n\\ \hat{V}&=-e^2|\mathbf{r}-\xi_n/2|^{-1}-e^2|\mathbf{r}+\xi_n/2|^{-1}+e^2|\xi_n|^{-1}\,.\end{aligned} \tag{3.58}$$

We can also define

$$I_n=h'_n-\hat{h}_n \tag{3.59a}$$

$$=-(2\mu)^{-1}\gamma_n^{ba}\gamma_n^{ca}p^bp^c+V-\hat{V}_n \tag{3.59b}$$

$$\simeq-(m/\mu)\{(2m)^{-1}[\tfrac{1}{2}(f_n+\lambda)]^2p^ap^a+\mathbf{s}_n\cdot\nabla V\}\,. \tag{3.59c}$$

The latter two expressions are derived using Eqs. (3.49b), (3.45b), (3.45c), (3.37), and (3.38). Matrix elements of h'_n in the coupled equations are then replaced by those of $\hat{h}_n$ plus those of I_n.

Finally, let us look at the independent variables in Eqs. (3.56). These equations can be written more abstractly as

$$\sum_n M_{mn}(\xi_m)\chi_n(\xi_m)=0\,, \tag{3.60a}$$

where M_{mn} contains functions of ξ_m and derivatives with respect to ξ_m. In the development up to this point, the various heavy-particle coordinates are all distinct. However, for the purpose of integrating these equations they all play the same role: they are dummy integration variables, and to integrate the equations, we would set them *numerically* equal to each other. In other words, Eqs. (3.60a) are equivalent to

$$\sum_n M_{mn}(\bar{\mathbf{R}})\chi_n(\bar{\mathbf{R}})=0\,, \tag{3.60b}$$

where $\bar{\mathbf{R}}$ denotes the common numerical value of the coordinates ξ_m. [If more explanation of this step is needed, see Delos (1981) Appendix C.]

With these two modifications, we obtain the final form for the three-dimensional coupled equations for slow atomic collisions:

$$\begin{aligned}\{(2\mu)^{-1}[\underline{S}(-i\hbar\nabla_{\bar{R}})^2&+2(\underline{\Pi}+\underline{\gamma})\cdot(-i\hbar\nabla_{\bar{R}})+\underline{B}]+\underline{h}+\underline{I}-\underline{S}E\}\\ &\times\underline{\chi}(\bar{\mathrm{R}})=0\,,\end{aligned} \tag{3.61}$$

where each matrix is now a function of $\bar{\mathbf{R}}$. In this equation we have omitted the carets: For example, $\underline{h}$ should correctly be $\underline{\hat{h}}$. The reason for dropping these decorations will be clear in a moment.

4. Coupling matrices

Most of the matrices in the coupled equations (3.61) can be related to quantities that appeared in the classical trajectory formulation, and were discussed in Sec. II.C.3. Let us examine these matrices and their elements.

a. *Overlap matrix,* $\underline{S}$

Referring to Eq. (3.54a), the matrix element $\hat{S}_{mn}$ represents the overlap between two displaced electronic basis states. According to the discussion in Sec. III.C.2.c, the function $\hat{\phi}_n(\mathbf{r}';\xi_n)$ has the same functional form as does $\phi_n(\mathbf{r}';\mathbf{R})$. It follows that if ξ_m and ξ_n are identical (call them both ξ), then

$$\begin{aligned}\hat{S}_{mn} &= \int \hat{\phi}_m^*(\mathbf{r}';\xi)\hat{\phi}_n(\mathbf{r}';\xi)d\mathbf{r}'\\ &= \int \phi_m^*(\mathbf{r}';\mathbf{R})\phi_n(\mathbf{r}';\mathbf{R})d\mathbf{r}'\\ &= S_{mn}\,, \end{aligned} \tag{3.62}$$

i.e., the overlap between the states mapped onto a surface of constant ξ is the same as the overlap between the original, unmapped states. (In fact, we defined the mapping such that these overlaps would be invariant.)

If, on the other hand, ξ_m is not identical to ξ_n, then $\hat{S}_{mn}$ must be evaluated following the procedure given below Eq. (3.50): the function $\hat{\phi}_n(\mathbf{r}';\xi_n)$ has to be reexpressed in terms of the new variables $(\mathbf{r}';\xi_m)$ before integration is carried out. However, using a Taylor expression, we find that the correction resulting from this reexpression is proportional to

$$(m/\mu)(\mathbf{s}_n-\mathbf{s}_m)\cdot\nabla_{\xi_n}\hat{\phi}_n(\mathbf{r}';\xi_n)\,.$$

Hence this correction is of order $(v_{nuc}/v_{el})^2\times(\mathbf{s}_n-\mathbf{s}_m)$, i.e., it is as small as quantities that have already been neglected.

Within the accuracy of the present theory, therefore, the mapping of the basis states onto various surfaces of constant ξ_n does not affect these matrix elements, so they can be evaluated as if they were integrals involving ordinary electronic basis functions defined on surfaces of constant R. For this reason, we no longer have to distinguish between $\hat{\underline{S}}$ and $\underline{S}$.

b. *Electronic Hamiltonian matrix,* $\underline{h}$

By the same arguments, the matrix $\hat{\underline{h}}$ is the same as the matrix $\underline{h}$, which represents the original electronic Hamiltonian acting on the original basis functions. For example, from Eq. (3.58) we have

$$\begin{aligned}\hat{h}_{mn} &= \int \hat{\phi}_m^*(\mathbf{r}';\xi_m)\hat{h}_n\hat{\phi}_n(\mathbf{r}';\xi_n)d\mathbf{r}'\\ &= \int \hat{\phi}_m^*(\mathbf{r}';\xi_m)[(-\hbar^2/2m)(\nabla^2_{r'})_{\xi_n}+\hat{V}(\mathbf{r}';\xi_n)]\hat{\phi}_n(\mathbf{r}';\xi_n)d\mathbf{r}'\\ &= \int \phi_m^*(\mathbf{r}';\mathbf{R})[(-\hbar^2/2m)(\nabla^2_{r'})_{\mathbf{R}}+V(\mathbf{r}';\mathbf{R})]\phi_n(\mathbf{r}';\mathbf{R})d\mathbf{r}'\\ &\quad+O[(m/\mu)(\mathbf{s}_n-\mathbf{s}_m)]\\ &= h_{mn}+O[(m/\mu)(\mathbf{s}_n-\mathbf{s}_m)]\,, \end{aligned} \tag{3.63}$$

where again the corrections are proportional to $(v_{nuc}/v_{el})^2\times(\mathbf{s}_n-\mathbf{s}_m)$. The same argument applies to all of the other matrices, and it is implicit in the following evaluations.

c. *Corrected nonadiabatic coupling matrix,* $\underline{\Pi}$

From Eqs. (3.54) and (3.48), we have

$$\Pi^a_{mn}=\langle\hat{\phi}_m|P^a+\gamma_n^{ba}p^b-\tfrac{1}{2}i\hbar\partial\gamma_n^{ba}/\partial r'^a|\hat{\phi}_n\rangle\,. \tag{3.64a}$$

The first term is just the ath component of the $\underline{\mathbf{P}}$ matrix,

$$\mathbf{P}_{mn}=\langle\phi_m|-i\hbar\nabla_R\phi_n\rangle\,,$$

and the other two terms give the matrix called $\mathbf{A}$ [Eq. (2.61)], for

$$\gamma_n^{ba}p^b-\tfrac{1}{2}i\hbar\partial\gamma_n^{ba}/\partial r'^b=(im/\hbar)[h,s_n^a]\,, \tag{3.64b}$$

Hence,

$$\underline{\Pi}=\underline{\mathbf{P}}+\underline{\mathbf{A}}\,. \tag{3.65}$$

Recall that in the classical trajectory framework, we found that nonadiabatic couplings were represented by $\underline{\mathbf{P}}$ if electron-translation factors were neglected, but by $\underline{\mathbf{P}}+\mathbf{A}$ if these factors were included. To our delight, we now find that in quantum mechanics, this theory, based upon the intersecting-curved-waves picture, leads to exactly the same correction to $\underline{\mathbf{P}}$!

d. *Second-derivative matrix,* $\underline{B}$

In the PSS theory, there appeared a second-derivative matrix $B^0_{mn}=\langle\phi_m|-h^2\nabla^2_R\phi_n\rangle$. In the present approach we obtain a matrix $\underline{B}$ (capital Beta), which differs from $\underline{B}^0$ in almost the same way that $\underline{\Pi}$ differs from $\underline{\mathbf{P}}$. From Eqs. (3.54d) and (3.48),

$$\begin{aligned}B_{mn}&=\langle\phi_m|(P^a+\gamma_n^{ba}p^b)(P^a+\gamma_n^{ca}p^c)|\phi_n\rangle && (3.66\text{a})\\ &\simeq\langle\phi_m|[P^a+\tfrac{1}{2}(f_n+\lambda)p^a][P^a+\tfrac{1}{2}(f_n+\lambda)p^a]|\phi_n\rangle, && (3.66\text{b})\end{aligned}$$

neglecting derivatives of $f_n(\mathbf{r}';\mathbf{R})$. Like $\underline{\mathbf{P}}$, the matrix $\underline{B}^0$ involved the total change of the basis functions with internuclear distance. In $\underline{B}$, there appears the total change minus the part that only represents displacement of the basis functions with the moving nuclei.

e. *Momentum-transfer matrix,* $\underline{\gamma}$

Looking at Eq. (3.57), we see that the matrix $\underline{\gamma}$ appearing there is practically the same as the matrix $\underline{\gamma}$ appearing in Eq. (2.62), but the new $\underline{\gamma}$ involves h_n' instead of h. However, in our approximation scheme, the term $(2\mu)^{-1}\gamma\cdot(-i\hbar\nabla)\underline{\chi}$ is of order (v_{nuc}/v_{el}), and h_n' differs from h by terms that are of order (m/μ) $=(v_{nuc}/v_{el})^2$, so the modification is of order $(v_{nuc}/v_{el})^3$, and is smaller than terms already neglected. Thus we find again that this quantum framework gives results that are directly analogous to those obtained in Sec. II.C.

f. *Electron-reduced-mass matrix,* $\underline{I}$

The matrix $\underline{I}$ contains effects related to the reduced mass of the electron ("isotopic couplings"). As was noted earlier, the Born-Oppenheimer Hamiltonian contains the *molecular* electronic reduced mass, $m=m_0(M_A+M_B)/(m_0+M_A+M_B)$, while the channel Hamiltonians h_A^0, h_B^0 contain *atomic* reduced masses, $m_A=m_0M_A/(m_0+M_A)$. The matrix $\underline{I}$ is proportional to the difference between these reduced masses. Ac-

TABLE IV. Matrices appearing in the close-coupled equations. (i) Formulas here assume that basis states rotate with internuclear axis. (ii) Other forms for $\mathbf{s}_n$ are also possible. (iii) $\boldsymbol{\gamma}$ has no relationship to γ_n^{ab}.

$S_{kn}=\langle\phi_k\vert\phi_n\rangle=\int\phi_k^*(\mathbf{r};R)\phi_n(\mathbf{r};R)d^3r$	Overlap
$h_{kn}=\langle\phi_k\vert h\vert\phi_n\rangle$	Electronic Hamiltonian
$\mathbf{P}_{kn}=\langle\phi_k\vert -i\hbar\nabla_R\vert\phi_n\rangle$	Total change of ϕ_n
$P_{kn}^R=\langle\phi_k\vert -i\hbar\partial/\partial R\vert\phi_n\rangle$	
$P_{kn}^\Theta=-\langle\phi_k\vert L_y\vert\phi_n\rangle/R$	
$P_{kn}^\Phi=\langle\phi_k\vert L_x-\cot\Theta L_z\vert\phi_n\rangle/R$	
$\mathbf{A}_{kn}=(im/\hbar)\langle\phi_k\vert[h,\mathbf{s}_n]\vert\phi_n\rangle$	(Displacement part)
$A_{kn}^b=(im/\hbar)\langle\phi_k\vert\gamma_n^{ab}p^a-i\hbar\partial\gamma_n^{ab}/\partial r^a\vert\phi_n\rangle$	
$\gamma_n^{ab}=\partial s_n^b/\partial r^a$	
b component: $R\longleftrightarrow z,\ \Theta\longleftrightarrow x,\ \Phi\longleftrightarrow y$	
$\underline{\mathbf{\Pi}}=\underline{\mathbf{P}}+\underline{\mathbf{A}}$	Vector nonadiabatic coupling
$\underline{\Pi}^R=\underline{P}^R+\underline{A}^R$	"Radial" nonadiabatic coupling
$\underline{\boldsymbol{\gamma}}=\underline{\boldsymbol{\eta}}-\underline{\boldsymbol{\sigma}}\underline{S}^{-1}\underline{h}$	Momentum-transfer coupling
$\boldsymbol{\sigma}_{kn}=(im/\hbar)\langle\phi_k\vert(\mathbf{s}_n-\mathbf{s}_k)\vert\phi_n\rangle$	
$\boldsymbol{\eta}_{kn}=(im/\hbar)\langle\phi_k\vert(\mathbf{s}_n-\mathbf{s}_k)h\vert\phi_n\rangle$	
$B_{kn}^0=\langle\phi_k\vert -\hbar^2\nabla^2\vert\phi_n\rangle$	Second-derivative matrix
$B_{kn}=\langle\phi_k\vert(P^a+\gamma_n^{ba}p^b)(P^a+\gamma_n^{ca}p^c)\vert\phi_n\rangle$	Corrected second-derivative matrix
$\underline{I}$: Eq. (3.59)	Electron-reduced-mass correction matrix ("Isotopic coupling")
$\mathbf{s}_n=\frac{1}{2}(f_n+\lambda)\mathbf{r}_g-\frac{1}{8}(1-\lambda^2)\mathbf{R}$	

cordingly, it is very tiny, and can be ignored except at very low energies.

In the PSS theory, these reduced-mass effects are contained in the matrix $\underline{B}^0$, but it is difficult to distinguish them from fictitious infinite-range coupling. In the present theory, $\underline{B}$ goes to zero asymptotically, and reduced-mass effects are contained in $\underline{I}$.

These matrices, which represent the various mechanisms for coupling between electronic states in slow atomic collisions, are summarized in Table IV. Lest the reader should quail before the sight of this table, we must emphasize that in most problems it is not necessary to consider all of these matrices. $\underline{S}$, $\underline{h}$, and $\underline{\mathbf{P}}$ are generally the most important; $\underline{\mathbf{A}}$ is significant because it corrects the defects in $\underline{\mathbf{P}}$. $\underline{\gamma}$ and $\underline{I}$ are likely to be important only in special circumstances and in certain representations. Most of the rest of the matrices in the table are just convenient combinations of the basic ones. On the other hand, it must also be recognized that some of the terms that have been neglected can become significant at higher velocities. However, in that regime a full quantum treatment is not usually necessary (fortunately!).

5. Reduction to radial equations

Equations (3.61) are proposed as a theoretical starting point for quantum-mechanical calculations dealing with discrete electronic transitions in slow atomic collisions. For actual computations, however, these equations are difficult to use because the independent variable is a three-dimensional vector, $\bar{\mathbf{R}}$. The equations can, however, be reduced to a computationally tractable set of one-dimensional, radial equations by expansion in any convenient set of angular functions. There are at least half-a-dozen distinct ways to do this. In the appendix, we display the choices that are available, and we carry out the required manipulations for one possible choice.

The result is that if $\underline{\chi}(\bar{\mathbf{R}})$ is expanded in symmetric-top eigenfunctions, coupled radial equations have the form of Eq. (A10). Also, if in addition the initial state is spherically symmetric, then scattering amplitudes and cross sections are given by (A20) and (A21).

6. Generalization to multielectron systems

At the beginning of this chapter, the discussion was simplified by considering only one electron. However, all of the same considerations apply to multielectron systems. Although multielectron systems introduce well-known *computational* problems, there are no new *conceptual* problems.

The electronic coordinate $\mathbf{r}'$ (or $\mathbf{r}$) must be regarded as a collective coordinate representing the positions of all the electrons, $\phi_n(\mathbf{r};R)$ is a multielectron state, and $\Psi(\mathbf{r}';\mathbf{R})$ is the wave function for all electrons and nuclei. The mass-scaled-coordinate picture is generalized in a straightforward way. The coordinates for each electron can be chosen such that the kinetic energy has a separable form, and these coordinates can be scaled by the associated reduced masses to give a form like Eq. (3.32). For a collinear collision involving two electrons, Figs. 11 and 12 would be drawn in three dimensions, and there would be four channels. Curvilinear heavy-particle coordinates ξ_n would be defined as in Eq. (3.37), where $\mathbf{s}_n$ would be a function of the positions of all of the electrons.

Given appropriate $\mathbf{s}_n$, the rest of the formalism follows directly: h is a multielectron Hamiltonian, $\mathbf{L}$ is a total angular momentum operator for all electrons, and the final result is again Eqs. (3.42) or (3.61) or (A10), with the matrices given in Table IV. Thus, all the same formalism still holds. Of course, the problems of specifically defining and computing the basis functions and $\mathbf{s}_n$ become much more difficult as the number of active electrons increases, but we have deferred discussion of those problems to later sections.

7. Summary and closing

The mass-scaled-coordinate picture shows that the problems associated with the original form of PSS theory can be solved by modifying the coordinate used to describe the heavy-particle motion. For a completely satisfactory solution it is necessary to use different curvilinear coordinates for different states. Each electronic basis function $\phi_n(\mathbf{r}';\mathbf{R})$ is mapped onto a new surface of constant ξ_n, and the wave function is expanded as in Eq. (3.39). The one critical point is that the heavy-particle wave function χ_n is taken to be a function not of $\mathbf{R}$ but of ξ_n. For each term it is necessary to reexpress the Hamiltonian in the new coordinates $(\mathbf{r}';\xi_n)$. But then for each m, the whole sum is reexpressed in terms of $(\mathbf{r}';\xi_m)$, multiplied on the left by $\phi_m^*(\mathbf{r}';\xi_m)$, and integrated over all $\mathbf{r}'$ at fixed ξ_m. This gives a set of coupled integro-differential equations for the heavy-particle wave functions (3.42). Approximations suitable for slow collisions lead to the truncated three-dimensional close-coupled equations (3.61), which replace the PSS equations (3.16). Partial-wave analysis leads to one-dimensional close-coupled equations (Appendix).

In closing, let us review the relationship between the classical trajectory framework developed in Sec. II and the quantum-mechanical framework developed here. In the former, coupled equations for coefficients $b_n(t)$ were derived from the ansatz

$$\underline{\Upsilon} = \sum_n b_n(t)F_n(\mathbf{r}';\mathbf{R}(t))\phi_n(\mathbf{r}';\mathbf{R}(t)),$$

with the ETF F_n being given by

$$F_n = \exp(im\mathbf{v}\cdot\mathbf{s}_n/\hbar).$$

In the latter, coupled equations for heavy-particle wave functions χ_n were derived from the ansatz

$$\Psi = \sum_n \chi_n(\xi_n)\phi_n(\mathbf{r}';\xi_n),$$

with the coordinate ξ_n given by

$$\xi_n = \mathbf{R} + (m/\mu)\mathbf{s}_n.$$

The same basis functions and the same vector quantity $\mathbf{s}_n$ appear in both descriptions, so both sets of coupled equations contain the same matrices $\underline{S}, \underline{h}, \underline{P}, \underline{A}, \underline{\gamma}$.

We have therefore shown that *the very same corrections to* $\underline{P}$, *which arise in the classical trajectory framework as a consequence of* ETF's, *should also be incorporated into the quantum-mechanical framework.* In this framework, those corrections arise as a consequence of the intersecting-curved-waves ansatz. (This ansatz also provides related corrections to the second-derivative matrix, and it leads to a new matrix $\underline{I}$; neither of these matrices arise in the classical trajectory framework.)

The relationship between classical and quantum formulations might be more transparent if we note that the quantum-mechanical ansatz is approximately the same as

$$\Psi = \sum_n \hat{F}_n\chi_n(\mathbf{R})\phi_n(\mathbf{r}';\mathbf{R}),$$

with

$$\hat{F}_n = \exp[(i/\hbar)(m/\mu)(\mathbf{s}_n\cdot - i\hbar\nabla_R)].$$

Here we see that the displacement operator which (approximately) converts $\mathbf{R}$ to ξ_n has the same form as the ETF, but with the classical nuclear velocity $\mathbf{v}$ replaced by the corresponding quantum operator $(-i\hbar\nabla_R/\mu)$. This shows why $\mathbf{s}_n$ has to be the same quantity in both approaches.

IV. THE REPRESENTATION PROBLEM AND THE DESCRIPTION OF SPECIFIC SYSTEMS

In Secs. II and III of this article, formalisms were developed for the description of atomic collisions in classical trajectory or fully quantum-mechanical frameworks. The formalisms were very general: Only a few assumptions were made about the basis functions and about the quantity $\mathbf{s}_n$, which specifies the ETF or the heavy-particle scattering coordinate. Except for noting that an atomic representation is better for fast collisions, and a molecular representation is better for slow collisions, we carefully deferred all questions about how to choose basis functions and $\mathbf{s}_n$'s to describe specific collision systems.

In this section, we consider what basis functions $\{\phi_n\}$ might be chosen, what relationships exist among various representations, and how the quantities $\mathbf{s}_n$ might be specified. The questions to be answered include the following. (1) Besides atomic eigenstates and Born-Oppenheimer molecular eigenstates, what choices are available for the basis set $\{\phi_n\}$? (2) How should we select a specific set for describing a particular collision process? (3) In particular, should the basis functions be defined such that they rotate, following the internuclear axis, or should they be space-fixed? (4) Given a basis function ϕ_n, how should one chose the corresponding $\mathbf{s}_n$?

These questions are all inextricably linked with each other, and it is not possible to answer any one of them in isolation from the others. General principles governing the choice of representations are considered in Sec. IV.A, where we also discuss the calculation of switching functions and $\mathbf{s}_n$. Then the description of specific systems is taken up in Sec. IV.B. Through most of the text, we shall assume that the electronic basis functions rotate with the internuclear axis. The problem of rotating versus nonrotating electronic states, and other aspects that are too angular to fit with the rest of the text, are relegated to an appendix.

A. General principles

Obviously, the problems of choosing a representation would all be irrelevant if it were possible to make calculations using a complete set. Since this is not possible, it is necessary to seek a truncated set of functions and associated coordinates that will describe the collision in the most convenient and accurate way.

A calculation within a small manifold can be accurate only if couplings to states outside that manifold are negligible. This provides one criterion for optimizing the scattering coordinate: Given a basis set $\{\phi_n\}$ (usually adiabatic), the corresponding set $\{\mathbf{s}_n\}$ may be chosen such that nonspecific couplings (i.e., couplings to states outside a small manifold) are systematically minimized. This approach has been applied successfully to one-electron problems, but it is not easy to use. A second approach is much simpler. The purpose of $\underline{A}$ is to identify and cancel the displacement part of $\underline{\mathbf{P}}$; but what part of the change of a molecular state with $\mathbf{R}$ actually represents displacement? One way to answer this is to resolve the molecular state into atomic states, for which the displacement part is unambiguous. We shall show that for any molecular state that can be resolved into atomic states, there is a special definition of $\mathbf{s}_n$ that identifies the displacement part of $\underline{\mathbf{P}}$ through this resolution. Furthermore, since it has been found that a large part of the nonspecific couplings are "fictitious" effects of displacement, this method of identifying and eliminating displacement also reduces nonspecific couplings and increases the accuracy of truncation to a small manifold. A third approach to the calculation of $\mathbf{s}_n$ is presently under investigation. Given a reasonable guess about the form of $\mathbf{s}_n$, one can optimize parameters within that form by the use of a variational principle. To some extent, this method can also be used to optimize the form of $\mathbf{s}_n$. Results of these ways of calculating $\mathbf{s}_n$ will be reviewed in the first half of this section.

Once the set of ϕ_n's and $\mathbf{s}_n$'s has been chosen, and the basis truncated to the smallest set that will give accurate results, further changes of representation will not in general improve the accuracy of the calculation. In some cases, however, a change of representation within a small manifold can lead to further simplifying approximations or physical insight. For example, although for slow collisions truncation of the basis is usually most accurate if the states are adiabatic, many processes are much more easily described in some sort of "diabatic" representation.

The concept of adiabatic states is generally understood, but it is helpful to give a more precise definition, and we do so in Sec. IV.3.

The intuitive idea of a diabatic representation is a very old one, dating back at least to Zener's classic paper of 1932 on the curve crossing problem; in that paper he assumed that the basis functions being used were approximate eigenfunctions of the molecular electronic Hamiltonian, but that they did not have the sudden rapid "change of character" that is typical of exact molecular eigenstates near a crossing or avoided crossing. The word "diabatic" may have first appeared in a paper by Hellmann and Syrkin (1935), the word being chosen to suggest that the states do not adiabatically adjust to the instantaneous position of the nuclei. More recently Lichten (1963) and others have emphasized the importance of this concept for slow collision theory, and such states have been constructed and used to study a great variety of processes.

To understand the concept of diabatic states, we first have to consider the meaning of "nonadiabatic" transitions. Adiabatic electronic basis states adjust continuously to the changing molecular field; transitions between such states are produced, in a quantum description, by the nuclear kinetic energy operator (or, in a classical trajectory description, by the time-derivative operator $i\hbar\partial/\partial t = i\hbar\mathbf{v}\cdot\nabla_R$). Under appropriate conditions (Messiah, 1965, vol. II, p. 747) transition probabilities induced by the R dependence of adiabatic states must tend to zero at low velocities, and the system then actually follows the adiabatic behavior described by the adiabatic states. At higher velocities, however, the electrons do not have time to adjust to the changing molecular potential, and, in a sudden collision, the actual electronic wave function of the system may remain nearly fixed in character. Described in terms of changing adiabatic basis states, this "nonchange" of the system wave function appears as a transition.

A diabatic basis state is one that does not fully adjust to the changing molecular field. It may remain entirely fixed in character, or it may vary somewhat with R, but it is not permitted to have any sudden change of character. Such basis states are sought because they correspond more closely to the actual behavior of the system than do the fully adiabatic states. Typically such states are *not* eigenfunctions of the molecular electronic Hamiltonian, so the $\underline{h}$ matrix is not necessarily diagonal in a diabatic representation; however the nonadiabatic couplings Π^R (or more generally the "velocity-dependent" couplings $\Pi^R + \gamma^R$) in such a representation are assumed to be negligible. Atomic states have these properties, but they do not usually provide a satisfactory representation for a slow collision. Acceptable diabatic basis states must be slowly varying with R, such that they partially accommodate to the changing molecular environment, but such that "velocity-dependent" couplings can be neglected. There has never been any difficulty with this intuitive concept, and in any given situation it has always been possible to construct such states by physical reasoning.

On the other hand, a general formal definition of diabatic states has been more elusive. An attempt at such a definition was made earlier by Smith (1969): For radial coupling problems, he proposed that a diabatic basis is one in which $\underline{P}^R$ vanishes. This definition is almost correct, but it has a seemingly serious formal defect [Andreson and Nielson (1971); Gabriel and Taulbjerg (1974)]: If, for a given j, the scalar product of $d\phi_j(\mathbf{r};R)/dR$ with ϕ_i vanishes for all i in a complete set, then $(d\phi_j/dR)$ must itself be zero. If every matrix element $P_{ij}^R(R)$ vanishes for a complete set, then every state in that set must be completely independent of R. Not only do such basis states have none of the distortion, polarization, and change of character with changing R that is typical of molecular electronic states, but also they do not even translate along with the nuclei.

The formal theory presented earlier helps to point the way out of this difficulty. Since it is the change in character of adiabatic states with R which is responsible for the "transitions," then, if such change of character were represented by the d/dR operator, we could indeed construct suitable diabatic representations by making matrix elements of d/dR zero or negligibly small. In fact, however, $\underline{P}^R$ represents not only the effects of any change of character of basis functions, but also the effects of their simple translation with the moving nuclear centers. Since we want diabatic states to move along with the nuclei, we need a representation in which at most that portion of $\underline{P}$ representing polarization, distortion, and change of character of basis functions is made to vanish; but since A identifies and cancels the displacement of part of P, $(P+A)$ is that relevant part of P that really is responsible for nonadiabatic transitions. Therefore an appropriate formal definition of diabatic states can be given by a relation of the form

$$P+A=0\,. \tag{4.1}$$

In Sec. IV.3 below this definition is stated more precisely, its implications are considered, and various ways to construct a diabatic representation are discussed.

After a precise definition is given to diabatic and adiabatic representations, we take up the question of which type of representation is most convenient for a given collision problem. This requires a discussion of elementary degeneracy-mediated transitions, which we give in Sec. IV.A.4.

We conclude with a set of rules or guidelines for choosing a good representation, and then proceed to the discussion of specific systems.[8]

1. Changes of representation

Transformation theory (the theory of changes of representation) is a standard part of all quantum mechanics textbooks. However, certain minor modifications of the conventional treatment are made here. We want to separate the "static" parts of the calculation (the construction of molecular states using the machinery of quantum chemistry) from the "dynamic" parts (the definition of $\mathbf{s}_n$ and the calculation of its matrix elements). Hence we define transformations involving only the basis functions $\{\phi_n\}$ [Eq. (4.2), below]. This leads us to treat $\mathbf{s}_n$ as one of the operators. However, each $\mathbf{s}_n$ is originally defined in connection with a specific ϕ_n, from which it can never be fully separated. Hence we have operators which depend upon the functions on which they are acting. Furthermore, the operators necessarily refer back to an original representation in which they were defined.

A general change of representation may be defined in the following way. Suppose we have two sets of basis functions $\{\phi_n^1(\mathbf{r};R)\}$, $\{\phi_n^2(\mathbf{r};R)\}$ *defined on surfaces of constant* $\mathbf{R}$. Such states may be related to each other by a transformation matrix $\underline{U}$:

$$\phi_\mu^2(\mathbf{r};R)=\sum_n U_{n\mu}\phi_n^1(\mathbf{r};R)\,. \tag{4.2}$$

($\underline{U}$ is not necessarily unitary, but is certainly invertible, and may be a function of R.) Then it follows that matrices like $\underline{S}$, $\underline{h}$, $\underline{L}$, etc. which consist of matrix elements of operators that are defined *a priori*, independent of representation, transform as

$$\underline{M}^2=\underline{U}^\dagger\underline{M}^1\underline{U}\,, \tag{4.3}$$

except for $\underline{P}$, which obeys the rule

$$\underline{\mathbf{P}}^2=\underline{U}^\dagger\underline{\mathbf{P}}^1\underline{U}-i\hbar\underline{U}^\dagger\underline{S}^1\nabla_R\underline{U}\,. \tag{4.4}$$

Other matrices which appear in the theory (i.e., $\underline{\mathbf{A}},\underline{\eta},\underline{\sigma}$) are not composed of matrix elements of operators definable in a representation-independent way, since the scattering coordinates and $\mathbf{s}_n$'s are always defined in connection with some particular representation [in this case, the basis $\{\phi_n^1(\mathbf{r};R)\}$]. These matrices may nevertheless be transformed according to Eq. (4.3) as well. Finally, if we also define transformations of the functions χ_n according to

$$\underline{\chi}^2=\underline{U}^{-1}\underline{\chi}^1\,, \tag{4.5}$$

then under such invertible transformations *the form of the coupled equations* (2.59), (3.61), or (A10) *remains invariant.*

The fact that the form of the coupled equations is invariant under the above transformation does *not* imply that atomic and molecular representations of a collision process must be equivalent. The coupled equations have been formulated using atomic states ϕ_n and atomic $\mathbf{s}_n$'s and also using molecular states ϕ_μ and corresponding "molecular" $\mathbf{s}_\mu$'s. However, even if there is a relationship of the form (4.2) between atomic and molecular states, there is not *necessarily* any relationship between atomic $\mathbf{s}_n$'s and molecular $\mathbf{s}_\mu$'s. The $\mathbf{s}_\mu$'s in a molecular description may still be chosen quite arbitrarily.

2. Calculation of *s* and associated matrices

We now consider the problem of specifying the set of functions $\{\mathbf{s}_\mu\}$. Research on this problem is very active at present, and several calculations involving various schemes for defining $\mathbf{s}_\mu$ are in progress. Unfortunately, there are at the moment only a few published results available. One expects that much more will be known about this problem within a few years, but for the present, we can only summarize the ideas that have been proposed and the few calculations that have been made.

a. Method of Bates and McCarroll

The first method for defining $\mathbf{s}_\mu$ for a molecular state ϕ_μ was proposed by Bates and McCarroll (1958). Their proposal, reexpressed in the present notation, is to associate with each molecular state an "atomic" ETF, in which the r-dependent part of $\mathbf{s}_\mu$ is just

$$\mathbf{s}_\mu=\kappa_\mu\mathbf{r}'\,, \tag{4.6a}$$

where

$$\kappa_\mu=\tfrac{1}{2}(f_\mu+\lambda)\,,\quad f_\mu=\pm1\,. \tag{4.6b}$$

They take $f_\mu=-1$ if the molecular state correlates

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[8] The format of the present discussion follows that of Delos and Thorson (1979), who corrected and extended the ideas of Smith (1969). However, their developments were given only in the classical trajectory framework, whereas in the present article it is seen that the same discussion applies in either classical or quantum frameworks.

asymptotically to an A-atomic state, and $f_\mu = +1$ if it correlates asymptotically to a B-atomic state. (A related prescription is given for symmetric systems, for which molecular states correlate to linear combinations of atomic states.)

One criterion for choosing $\mathbf{s}_\mu$ is simplicity, and Eq. (4.6) is certainly the simplest possible $\mathbf{s}_\mu$ (except for $\mathbf{s}_\mu = 0$, which is the PSS theory).

Furthermore, (4.6) is a very good choice *if* the molecular state ϕ_μ retains single-center character at all internuclear distances. On the other hand, if ϕ_μ should change its character significantly as R changes (for example, if an electron is transferred from A to B, or shared approximately equally by the two nuclei), then (4.6) is not so reasonable. It describes an electron propagating always with velocity $\kappa_\mu v$, while the velocity of a shared or transferred electron may be quite different.[9]

b. Decomposition into atomic states

Another way of specifying $\mathbf{s}_\mu$'s is to decompose the molecular state into single-center states, and construct the molecular $\mathbf{s}_\mu$'s in terms of single-center $\mathbf{s}_n$'s.

Suppose we have an arbitrary set of class M electronic basis states $\{\phi_\mu^M\}$, and this is related to a set of class F basis states $\{\phi_n^F\}$ by an invertible transformation $\underline{U}$:

$$\phi_\mu^M = \sum_n U_{n\mu} \phi_n^F . \tag{4.7}$$

Now suppose further that we associate with the basis state ϕ_μ^M a "special" coordinate ξ_μ^M or ETF F_μ^M such that

$$\mathbf{s}_\mu^M \phi_\mu^M = \sum_n U_{n\mu} \mathbf{s}_n^F \phi_n^F . \tag{4.8}$$

Since $\mathbf{s}_n^F$ is unambiguously defined by Eq. (2.53) or (3.38) with $f_n = \pm 1$,

$$\mathbf{s}_n^F = \tfrac{1}{2}(\pm 1 + \lambda)\mathbf{r}_g' - \tfrac{1}{8}(1 - \lambda^2)\mathbf{R} , \tag{4.9}$$

it follows that $\mathbf{s}_\mu^M$ is also defined, given the matrix $\underline{U}$. In the classical trajectory framework, the full wave function was expanded as [Eq. (2.23)]

$$\Upsilon_F = \sum_n d_n^F F_n^F \phi_n^F \tag{4.10a}$$

or as

$$\Upsilon_M = \sum_\mu d_\mu^M F_\mu^M \phi_\mu^M . \tag{4.10b}$$

In the quantum-mechanical framework, the corresponding expansions are

$$\Psi_F = \sum_n \chi_n^F(\xi_n^F) \phi_n^F(\mathbf{r}'; \xi_n^F) , \tag{4.11a}$$

$$\Psi_M = \sum_\mu \chi_\mu^M(\xi_\mu^M) \phi_\mu^M(\mathbf{r}'; \xi_\mu^M) . \tag{4.11b}$$

If we choose $\mathbf{s}_\mu^M$ according to the special prescription (4.8) then it is easy to show, by expanding in powers of (m/μ) and neglecting terms of order $m/\mu\nabla f$ and smaller, that $\Upsilon_M = \Upsilon_F$ and that $\Psi_M = \Psi_F$, i.e., the wave function is invariant to the transformation (4.6) to the stated accuracy.

Since (4.6) implies the matrix transformation (4.3) it follows that

$$\underline{\sigma}_M = \underline{U}^\dagger \underline{\sigma}_F \underline{U} , \tag{4.12a}$$

where

$$(\sigma_M)_{\nu\mu} = (im/\hbar) \ \langle \phi_\nu^M | (\mathbf{s}_\mu^M - \mathbf{s}_\nu^M) | \phi_\mu^M \rangle , \tag{4.12b}$$

$$(\sigma_F)_{kn} = (im/\hbar) \langle \phi_k^F | (\mathbf{s}_n^F - \mathbf{s}_k^F) | \phi_n^F \rangle . \tag{4.12c}$$

The same result holds for $\underline{A} + \underline{\eta}$,

$$\underline{\mathbf{A}}_M + \underline{\eta}_M = \underline{U}^\dagger (\underline{\mathbf{A}}_F + \underline{\eta}_F) \underline{U} , \tag{4.13}$$

but not for $\underline{\mathbf{A}}$ *and* $\underline{\eta}$ *separately.* The mixing implied by (4.13) again emphasizes that we must distinguish between matrices $\mathbf{A}_M$ and matrices $\mathbf{A}_F$ and never assume that one goes into the other under any transformation.

A further result applies if the transformation $\underline{U}$ is such that the states ϕ_μ^M are eigenfunctions of h. In that case, we proved that

$$\underline{\gamma}_M = \underline{\eta}_M - \underline{\sigma}_M \underline{S}^{-1} \underline{h} = 0 ;$$

hence if we use the special switching functions (4.8) we obtain

$$\mathbf{A}_M = U^\dagger (\mathbf{A}_F + \gamma_F) U .$$

These "special" s_μ^M's defined by Eq. (4.8) provide a very specific identification of the "displacement part" of the R dependence of molecular states by resolving the molecular state into atomic states, for which the displacement part is unambiguous. Atomic and molecular descriptions are equivalent if and only if s_μ^M's are chosen in this way.

This method is not much more difficult to implement than the method of Bates and McCarroll, and it should give better results. One problem with this method is that decomposition into atomic states is not unique, and can be quite ambiguous at small R. On the other hand, molecular states are often known only in terms of some sort of LCAO expansion; in that case this approach might be as good as any. At the moment, no calculations using this method are available (though some are in progress).

c. Minimization of nonspecific couplings

This method evolved in connection with the study of a specific process, and it is the method for which the most detailed calculations are presently available. Some years ago Thorson recognized that unmodified PSS matrix elements $\underline{P}^R$ for impact ionization

$$\mathrm{H}^+ + \mathrm{H}(1s) \rightarrow 2\mathrm{H}^+ + e^-$$

were unrealistically large, and he recognized that these matrix elements were artifacts of the improper formulation—that they really represent displacement of the orbitals with the moving nuclei. He and his coworkers then began to develop a more satisfactory description (Thorson and Levy, 1969; Levy and Thorson, 1969a, 1969b; Lebeda, Thorson, and Levy, 1971; Sethu-Raman, Thorson, and Lebeda, 1973; Rankin and Thorson, 1979).

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[9] Crothers and Hughes (1978) have extended this approach by taking κ_μ to be a function of R. (Unfortunately, this paper contains a completely incorrect remark to the effect that the use of switching functions depending on $\mathbf{r}$ is a violation of the Heisenberg uncertainty principle. Reply to this was given by Ponce, 1979).

If the matrix elements in question really represent displacement, then certain patterns of behavior should follow. Since $\underline{A}^R$ is supposed to identify and cancel the effect of displacement in $\underline{P}^R$, we would then expect that for each bound molecular state there should exist a choice of $\mathbf{s}_\mu$ such that all "fictitious" couplings would simultaneously be reduced. They took

$$\mathbf{s}_\mu = \tfrac{1}{2}[f_\mu(\mathbf{r};R)+\lambda]\,\mathbf{r}'_g \tag{4.14}$$

and tried various forms for the switching function. (Of course, it was essential that the f's be restricted to *slowly varying*, *real* functions; otherwise they would not represent only the effects of electron translation.)

Consider the matrix element of $P^R + A^R$ between the ground Born-Oppenheimer state of $H_2{}^+$ and the continuum states of $2H^+ + e$. Since the electronic Schrödinger equation is separable in prolate spheroidal coordinates, the continuum states are labeled by three quantum numbers: $\lambda=\langle L_z\rangle/\hbar$, n_η, corresponding to the "angular" electronic coordinate $(r_A - r_B)/R$, and ϵ, the continuum state energy, which can be regarded as a quantum number for the "radial" electronic coordinate $(r_A + r_B)/R$. The matrix elements were written as, for example,

$$\langle \epsilon, n_\eta, \lambda=0, (g)|H'_R|1s\sigma(g)\rangle\,,$$

where H'_R is the operator whose matrix representation is $\underline{P}^R + \underline{A}^R$:

$$H'_R = -i\hbar[\partial/\partial R + \tfrac{1}{2}\nabla_r z f(\mathbf{r};R)\cdot\nabla_r + \tfrac{1}{4}\nabla_r^2 z f(\mathbf{r};R)]\,.$$

The switching function that led to the best results was

$$f(\mathbf{r};R) = \exp[-(r_A + r_B)/r_c]\tanh[\beta(R)(r_A - r_B)]\,,$$

where r_c and $\beta(R)$ are parameters to be determined by minimizing the problematic matrix elements. In the calculations, r_c was found to be unimportant, and the first factor was replaced by 1.

Figure 15 shows calculated matrix elements versus β at $R=12.4a_0$, $\epsilon=0.1$ hartree, with $n_\eta = 0, 2, 4, \ldots, 10$. It is seen that a value of β around 0.45 systematically reduces by orders of magnitude all except $n_\eta = 0$ and 2 matrix elements; the same value of β also reduces the matrix elements for $\epsilon = 1$ hartree. This shows that most of the large and long-range matrix elements were indeed "fictitious" effects of displacement, and only those for $n_\eta = 0, 2$ represented real nonadiabatic coupling.

Similar results were obtained for the HeH^{++} system [Rankin and Thorson (1979)]. For this case the switching function was taken to be

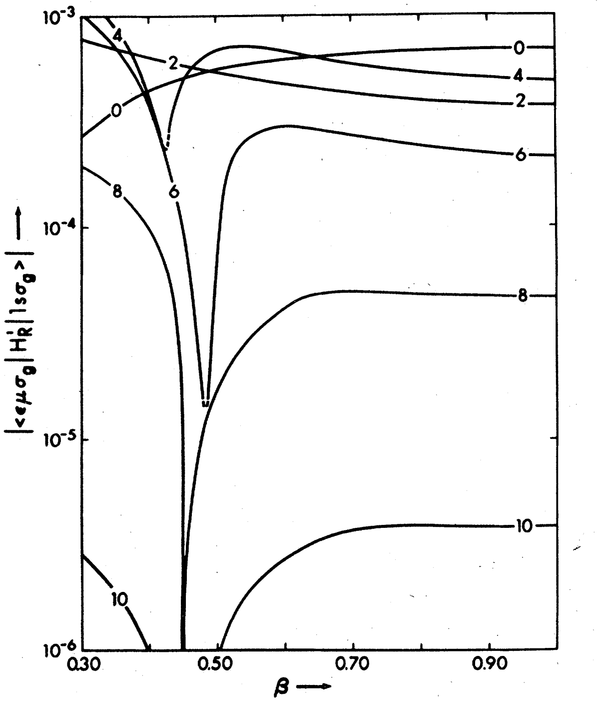

FIG. 15(a). For the H_2^+ system, logarithms of absolute values of matrix elements $\langle\epsilon n_\eta\sigma(g)|H'_R|1s\sigma(g)\rangle$ vs β for $R=12.4a_0$, $\epsilon=0.1$ hartrees, and $n_\eta=0, 2, 4, \ldots, 10$. One finds that there is a value of β that dramatically reduces most of these matrix elements. From Lebeda, Thorson, and Levy (1971).

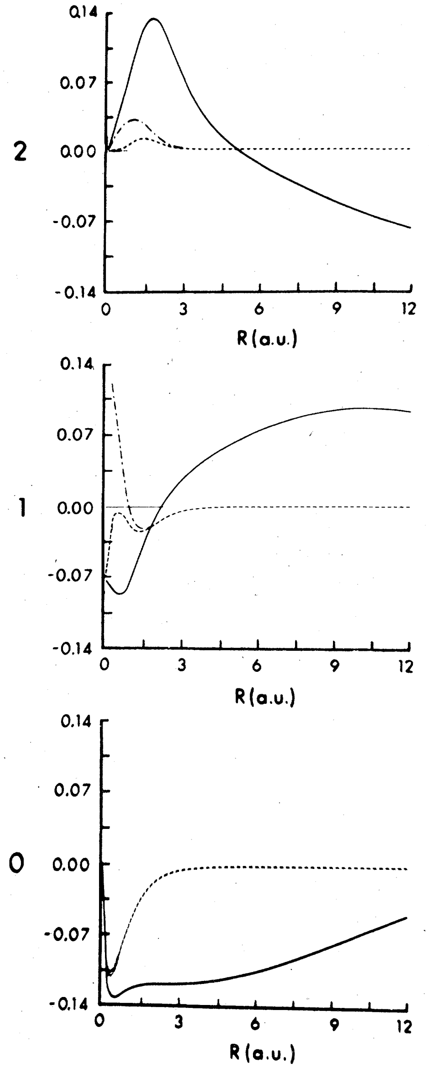

FIG. 15(b). Corresponding matrix elements between ground and continuum states for the HeH^{++} system for $\epsilon=0.5$, $n_\eta=0$, 1, 2. Solid line: P^R, which includes "fictitious" displacement coupling. Dot-dash line: $P^R + A^R$ with switching function equal to a constant, as in Bates-McCarroll method. Dash line: optimized $P^R + A^R$. From Rankin and Thorson (1979).

$$\tanh[\tfrac{1}{2}\beta(\hat{Z}_A+\hat{Z}_B)(r_A-r_B)+(\hat{Z}_A-\hat{Z}_B)R]+\alpha R\ln\hat{Z}_B/\hat{Z}_A\,,$$

where $\hat{Z}_A, \hat{Z}_B$ are the nuclear charges and α and β were varied. In Fig. 15(b) are shown uncorrected (P^R) and optimized corrected (P^R+A^R) matrix elements between the ground state and continuum states. Clearly the elimination of displacement gives a substantial and systematic reduction in these matrix elements.

In this case the ground-state wave function is essentially atomic in character and it is possible to account approximately for effects of displacement by taking f = constant, as in the Bates and McCarroll method. Results of such a calculation are shown as the dot-dash line in Fig. 15b; they are not far from the optimized results. However there are other bound states of HeH^{++} which have a two-center molecular character, and for which a constant-f approximation is quite unsatisfactory (Rankin and Thorson, 1979, Figs. 8,10,11).

Switching functions optimized in this way can be used for calculating all other matrix elements. This optimization procedure is difficult to apply in general, because continuum states used in the calculation are not readily available, and have only been obtained for these separable one-electron systems. However, the results of this method are the best ones available in the following sense: Insofar as this method minimizes nonspecific coupling matrix elements, it should also mimimize the error inherent in truncation of the coupled equations to a small set.

d. Euler-Lagrange variational principle

Riley and Green (1971) suggested that the Euler-Lagrange variational principle could be used to specify ETF's in the classical trajectory framework. The Lagrangian density for the one-electron Schrödinger equation is (Morse and Feshbach, 1953, p. 314)

$$\begin{aligned}\mathcal{L}=&(-\hbar^2/2m)(\nabla\psi)^*\cdot(\nabla\psi)\\&-(\hbar/2i)(\psi^*\dot{\psi}-\psi\dot{\psi}^*)-\psi^*V\psi\,,\end{aligned}\tag{4.15}$$

and this variational principle states that the exact solution to the Schrödinger equation is such that

$$I=\int_{t_1}^{t_2}dt\int d\mathbf{r}\,\mathcal{L}\tag{4.16}$$

is an extremum (t_1 and t_2 are arbitrary initial and final times). In using this principle, one considers only variations $\delta\psi$ that vanish at the boundaries ($t=t_1$ or t_2 and $|\mathbf{r}|\to\infty$). If we restrict ourselves to functions that are square integrable for all time and normalized to unity at $t=t_1$ and t_2, then I in Eq. (4.16) is equal to

$$I=-\int_{t_1}^{t_2}dt\int d\mathbf{r}\,\psi^*(h-i\hbar\partial/\partial t)\psi\,.\tag{4.17}$$

If one could find the extremum of I with respect to arbitrary variations $\delta\psi$, then one would have the exact solution to the Schrödinger equation. That is obviously not possible in general, and one can only consider restricted variations.

As an example, suppose we consider all possible functions of the form

$$\psi=\phi(\mathbf{r}',t)\exp[im\mathbf{v}\cdot\mathbf{s}(\mathbf{r};t)/\hbar]\,.\tag{4.18}$$

Here ϕ is some *given* real square-integrable electronic basis function, and the exponential factor is the ETF. We allow $\mathbf{s}$ to be any real function, and we ask: What condition must $\mathbf{s}$ satisfy in order that I be an extremum? Writing

$$g=m\mathbf{v}\cdot\mathbf{s}/\hbar\,,$$

one finds

$$\begin{aligned}\delta I=\int dt\int d\mathbf{r}\{&i[\delta g\;\phi e^{-ig}(h-i\hbar\partial/\partial t)\phi e^{ig}]\\&-i[\phi e^{-ig}(h-i\hbar\partial/\partial t)\phi e^{ig}\;\delta g]\}\,,\end{aligned}\tag{4.19a}$$

and integration by parts leads to

$$\delta I=\int dt\int d\mathbf{r}\,2i\,\delta g\,\mathrm{Im}[\phi e^{-ig}(h-i\hbar\partial/\partial t)\phi e^{ig}]\,.\tag{4.19b}$$

The extremum is obtained with respect to arbitrary (real) variation in g when

$$\mathrm{Im}[\phi e^{-ig}(h-i\hbar\partial/\partial t)\phi e^{ig}]=0$$

or

$$\hbar(2m)^{-1}(2\phi\nabla\phi\cdot\nabla g+\phi^2\nabla^2 g)+\phi\partial\phi/\partial t=0\,.\tag{4.20}$$

This is the equation that must be satisfied by g. If we write

$$\begin{aligned}&\mathbf{w}=\hbar\nabla g/m=\nabla(\mathbf{v}\cdot\mathbf{s})\,,\\&\rho=\phi^2\,,\end{aligned}\tag{4.21}$$

then Eq. (4.20) becomes

$$\nabla\cdot(\mathbf{w}\rho)+\partial\rho/\partial t=0\,.\tag{4.22}$$

This is just the continuity equation relating the electron density ρ and velocity field $\mathbf{w}$! Together with the equation $\mathrm{curl}\,\mathbf{w}=0$ (which follows from the fact that $\mathbf{w}$ is a gradient), and suitable boundary conditions, this equation determines $\mathbf{w}(\mathbf{r}',t)$ in terms of $\rho(\mathbf{r}',t)$ and its derivatives, all of which are known in principle since ϕ is given. [Riley and Green carried out a development similar to this one, but they obtained a different result because they did not restrict g to be real. Again, if the exponential factor in Eq. (4.18) is to represent an ETF, the restriction to real g is essential.]

The exact solution to Eq. (4.22) has not been constructed for any molecular function ϕ. However, suppose we use the approximation that the vector field $\mathbf{w}$ points only in the z direction, $\mathbf{w}=\hat{k}w_z$, and that for each internuclear distance, w_z is only a function of z, not of x or y. Then we can integrate Eq. (4.22) over x and y to obtain

$$\frac{d}{dz}\,w_z(z)\int\rho(x,y,z;R)dx\,dy+\frac{\partial}{\partial t}\int\rho(x,y,z;R)dx\,dy=0$$

or

$$w_z(z)=\frac{-dR/dt\int_0^z dz(\partial/\partial R)\int\rho(x,y,z;R)dx\,dy}{\int\rho(x,y,z;R)dx\,dy}\tag{4.23}$$

Ponce (1979) derived this equation (by a slightly different method), and he evaluated the resulting velocity field $w_z(z)$ for the three lowest states of the H_2^+ system. [Actually he obtained somewhat more: his full form for g is, in our notation, $g=g_1(z,t)+g_2(x,t)+w(t)xz$.] He then used the resulting ETF to compute transition probabilities for the processes

$$\mathrm{H}^+ + \mathrm{H}(1s) \rightarrow \mathrm{H}^+ + \mathrm{H}(2p)$$
$$\rightarrow \mathrm{H}(1s \text{ or } 2p) + \mathrm{H}^+ \tag{4.24}$$

at $E = 250$ eV and 1 keV. Good agreement was found with some experimental measurements.

Ponce did not compare his ETF with the one previously obtained by Thorson *et al*. The present author has made some comparison, and found the two ETF's to be somewhat different. However, it is known that for the processes studied, (4.24), calculated transition probabilities are not too sensitive to the form of the ETF. (As was mentioned earlier, for transitions mediated by a degeneracy at small R, even the unmodified PSS theory is often sufficiently accurate.)

Several interesting questions are rasied by these calculations. First, it is not known whether the form assumed by Ponce is an accurate solution to the continuity equation (4.22). Second, it is not yet known whether accurate solutions to (4.22) can be obtained for the problems of interest. Third, one can show that if the ETF were chosen to satisfy Eq. (4.22) exactly, then matrix elements of $P^R + A^R$ would vanish exactly. Couplings might then arise only from terms that were presumed to be negligible in the derivation of Eqs. (2.59) or (3.61). The full implications of this are not yet known. All of these questions need much more study.

To conclude this section we repeat that there is no final answer to the question of what is the best $\mathbf{s}_n$ for a molecular basis function. Of the available methods, one can say with reasonable confidence that the Bates and McCarroll form is an improvement on the unmodified PSS theory, that decomposition into atomic states should be even better, and that Thorson's method gives the best presently available results for the cases he studied. The Euler-Lagrange method looks promising, but has not yet led to definitive results.[10]

3. Definitions and constructions of adiabatic and diabatic representations

Equation (4.1) was suggested as a general definition of a diabatic representation, but its meaning was deliberately left ambiguous. First, we must distinguish between applications of (4.1) to the radial component $(\underline{P}^R + \underline{A}^R)$ only, and those which include all vector components. From this point on, we shall only apply this equation to the radial component. Second, we have shown that a distinction must be made between matrices of type $\underline{A}_V$ or $\underline{A}_F$ (based on single-center functions and coordinates) and those of type $\underline{A}_M$ (constructed explicitly using class M states and curvilinear coordinates); a corresponding distinction must be made between diabatic representations for which $(\underline{P}^R + \underline{A}_F^R) = 0$ (type F) and those for which $(\underline{P}^R + \underline{A}_M^R) = 0$ (type M). Third, Eq. (4.1) is also ambiguous in that it might hold only within a sharply truncated set of states, or only hold approximately.

Furthermore, though we have often referred to adiabatic basis states, we have avoided until now giving them a precise definition. This concept also requires some attention: In the past "adiabatic states" have usually been assumed to be the same as "Born-Oppenheimer states," but it is now convenient to draw a distinction between them.

For the purposes of this section, it is convenient to define a general coupling matrix $\underline{V}$ such that

$$\underline{V} = \text{electrostatic} + \text{magnetic} + \text{angular}$$
$$+ \text{electron-reduced-mass coupling matrices.} \tag{4.25a}$$

The specific form of this matrix depends on which set of coupled equations we are considering. For Eqs. (2.68),

$$\underline{V} = \underline{h} + v^\Theta(-\underline{L}_y/R + \underline{A}^\Theta + \underline{\gamma}^\Theta)\,. \tag{4.25b}$$

For Eqs. (A10),

$$\underline{V} = \underline{h} + \underline{I} + (2\mu R^2)^{-1}\{[K(K+1) - \underline{\Lambda}^2]\,\underline{S} + \underline{\hat{L}}_x^2 + \underline{\hat{L}}_y^2 - \underline{Q}\}\,. \tag{4.25c}$$

In general $\underline{V}$ includes all terms that can be collected into a (possibly velocity-dependent) "potential" coupling matrix, but it does not include $\underline{P}^R$, $\underline{A}^R$, $\underline{\gamma}^R$, or $\underline{B}^R$, which are related to $\partial/\partial R$ ("nonadiabatic") couplings.

a. Born-Oppenheimer representation

Recall that we defined the Born-Oppenheimer representation as the (orthogonal) set of eigenfunctions of the *electrostatic part* of the molecular electronic Hamiltonian,

$$h_{\mathrm{BO}}\phi_n(\mathbf{r};R) = \epsilon_n(R)\phi_n(\mathbf{r};R)\,. \tag{4.26}$$

We took h_{BO} to include only the electronic kinetic energy and electron-electron, electron-nuclear, and nuclear-nuclear Coulomb potential energy; we deliberately excluded spin-orbit couplings and other higher-order magnetic effects from h_{BO}. These states and their eigenvalues (and sometimes the important matrix elements of $\mathbf{P}$) are routinely calculated by quantum chemists. As suggested earlier, there are then two ways to obtain the $\mathbf{A}$ matrix and related terms ($\underline{I}, \gamma$, etc.): (i) Since the quantum-chemical calculation typically begins with a class V (or possibly a class F) basis, and the $\mathbf{s}_n$'s proper to such a basis are given in (4.9), the matrices $\underline{A}_V^R, \underline{\gamma}_V^R$ can be computed in the *original representation* of V or F states and then transformed into the Born-Oppenheimer representation according to Eqs. (4.12) and (4.13) by the same matrix $\underline{U}(R)$ which diagonalizes $\underline{h}_{\mathrm{BO}}$. (ii) Alternatively, once given the eigenstates of $\underline{h}_{\mathrm{BO}}$ and the matrix $\underline{P}^R$, switching functions may be chosen for each eigenstate and the matrix $\underline{A}_M^R$ is then computed directly using $\mathbf{s}$ as in Eq. (2.53).

We repeat that these two approaches are not necessarily identical within a finite basis, because no constraint has been placed on the choice of switching functions used to define $\underline{A}_M^R$. Only if the special switching functions of Eq. (4.8) are used is $\underline{A}_M^R$ equal to $\underline{A}_V^{R\prime} + \underline{\gamma}_V^{R\prime}$. Moreover, even in that case, $\underline{A}_V^{R\prime}$ is not to be identified with $\underline{A}_M^R$ because the invariance condition (4.13) only

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[10] Among significant computational studies that are ongoing at the present time, we mention the work of Thorson *et al*. (1981); Vaaben and Taulbjerg (1979); Macias, Riera, and Yáñez (1980); and Winter and Hatton (1980).

holds for $\underline{A}^R + \underline{\eta}^R$. We denote by $\underline{A}_M^R$ a matrix $\underline{A}^R$ computed originally in a molecular representation using switching functions, and any transform of such a matrix according to (4.3). $\underline{A}_F^R$ or $\underline{A}_V^R$ means any transform of an $\underline{A}$ matrix that was computed originally in class F or V basis with corresponding atomic coordinates.

b. Adiabatic representations

A representation is adiabatic with respect to a given type of interaction if the part of the $\underline{V}$ matrix representing that interaction is diagonal. This definition can be applied either to the complete set of states or to any subset.

For example, Born-Oppenheimer states as defined above are adiabatic with respect to electrostatic couplings, but they are *not* adiabatic with respect to spin-orbit couplings, angular couplings, or electronic-reduced-mass couplings (represented by the matrix $\underline{I}$); in fact we shall see that they are diabatic with respect to those couplings.

There is never any conceptual difficulty in constructing an adiabatic representation: It is done by diagonalizing the desired part of the V matrix. Thus, given a Born-Oppenheimer representation, one obtains the representation that is adiabatic with respect to both electrostatic interactions and spin-orbit couplings by calculating the matrix of the spin-orbit Hamiltonian $\underline{h}_{\mathrm{SO}}$, adding it to $\underline{h}_{\mathrm{BO}}$, and diagonalizing the result. Representations that are adiabatic with respect to other interactions or combinations of interactions are calculated similarly. Again this can be done for an entire matrix or any part of it.

c. Diabatic representations—definitions

We admit several different types of representations to the class of diabatic representations. We shall say that *a representation is diabatic if all, or a part, of the matrix* $(\underline{P}^R + \underline{A}^R)$ *either vanishes or is negligible*: The representation is *fully diabatic* if $\underline{P}^R + \underline{A}^R$ vanishes exactly in a complete set; it is *partially diabatic* if a selected subset $\{(m,n)\}$ of elements of $(\underline{P}^R + \underline{A}^R)$ vanishes; and it is *approximately diabatic* if the relevant portion of $(\underline{P}^R + \underline{A}^R)$ can be considered "negligibly small."[11] This terminology deliberately does *not* specify whether $\underline{A}^R$ is of type $\underline{A}_F^R$ or type $\underline{A}_M^R$.

(i) F-diabatic representations. An F-diabatic representation is defined by the condition $(\underline{P}^R + \underline{A}_F^R) = 0$. The properties of such representations follow from the simple and obvious *theorem*

$$[(\partial/\partial R)_{\mathbf{r}} + \kappa_n(\partial/\partial z)_R]\,\phi_n(\mathbf{r}; R) = 0 \tag{4.27a}$$

(with κ_n constant) if and only if

$$\phi_n(\mathbf{r}; R) = \phi_n(x, y, z - \kappa_n R)\,, \tag{4.27b}$$

i.e., if and only if ϕ_n is in class F. Since $\underline{P}^R$ is just the matrix of $-i\hbar\partial/\partial R$, and $\underline{A}_F^R$ is either the matrix of $(-i\hbar\kappa_n\partial/\partial z)$ or a transform of it, we have the following consequences.

(1) If every state in a representation is in class F, then $\underline{P}^R + \underline{A}_F^R \equiv 0$, i.e., a class F representation is fully F diabatic.

(2) If any particular state $\phi_k(\mathbf{r}; R)$ in a representation is in class F, then the kth column of $(\underline{P}^R + \underline{A}_F^R)$ vanishes.

(3) Any representation obtained by an R-*independent* invertible transformation from a representation based on class F states is also fully diabatic. (Hence, not every fully F-diabatic state is necessarily a class F state).

(4) Conversely to (1), if in some complete set we find that $\underline{P}^R + \underline{A}_F^R = 0$ *and* that $\underline{A}_F^R$ satisfies Eqs. (2.64a), i.e.,

$$(A_F^R)_{kn} = -i\hbar\langle\phi_k|\kappa_n\partial/\partial z|\phi_n\rangle \quad \text{all } k, n$$

then every state in that representation is in class F.

(5) Conversely to 2, if in some complete set we find that the entire kth column of $\underline{P}^R + \underline{A}_F^R$ vanishes *and* that

$$(A_F^R)_{kn} = \kappa_n(p_z)_{kn}\,,$$

where p_z is the z component of the electronic momentum, then $\phi_k(\mathbf{r}; R)$ is in class F.

Fully F-diabatic states meet one of the intuitive criteria that would be expected for diabatic states; these states move along with the nuclei to which they are attached, but do not change character in any way. But on the other hand these states have nonvanishing, velocity-dependent radial couplings $\underline{\gamma}^R$, and also they are not orthogonal.

A fundamental result follows as a trivial consequence of the above. If some molecular representation $\{\phi_\mu^M(\mathbf{r}; R)\}$ is constructed by matrix transformation of class F states as in Eq. (4.7), then

$$\begin{aligned}(\underline{P}^R + \underline{A}^R)^M &= \underline{U}^\dagger(\underline{P}^R + \underline{A}^R)^F\underline{U} - i\hbar\underline{U}^\dagger\,\underline{S}^F d\underline{U}/dR \\ &= -i\hbar\underline{U}^\dagger\,\underline{S}^F d\underline{U}/dR\end{aligned} \tag{4.28}$$

since $(\underline{P}^R + \underline{A}^R)^F$ vanishes in a class F representation. Thus the matrix representing the real nonadiabatic couplings in the molecular representation comes only from the R dependence of the coefficients of the transformation. This is equivalent to using the "special" s_μ^M's of Eq. (4.8), and it provides a way of identifying and eliminating the displacement part of P^R without the direct construction of an A^R matrix. An analogous result can be obtained if the original basis states are in class V; in this case nonadiabatic coupling comes from the R dependence of the coefficients and that of the parameters $\zeta_1 \cdots \zeta_J$.

(ii) M-diabatic representations. An M-diabatic representation is defined by the condition $(\underline{P}^R + \underline{A}_M^R) = 0$. Basis states for this type of representation have detailed properties that depend on the switching function used to calculate $\underline{A}_M^R$; they will *not* generally be the same as F-diabatic states.

As $R \to \infty$, $\frac{1}{2}[f_n(\mathbf{r}; R) + \lambda]$ assumes the proper value for κ_n near each center, and $\underline{\gamma}_F^R$ goes to zero. Therefore $\underline{A}_M^R$ and $\underline{U}^\dagger\underline{A}_F^R\underline{U}$ become identical, and the conditions $(\underline{P}^R + \underline{A}_F^R) = 0$ and $(\underline{P}^R + \underline{A}_M^R) = 0$ become equivalent. M-diabatic states must thus become either class F states or fixed linear combinations of such states, in the limit $R \to \infty$. (Of course, this result is rather trivial, since such an asymptotic correspondence to class F states holds for the basis states of any reasonable

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[11] In the quantum formulation, the intimate relationship between $\underline{P}^R + \underline{A}^R$ and $\underline{B}_R$ insures that if the former is negligible, so will be the latter.

representation.)

For symmetric systems, switching functions must have *ungerade* symmetry, and $(P+A)$ has no couplings between g and u states. For such systems, M-diabatic states retain the g or u symmetry and the two-center molecular character of the adiabatic states.

The really significant property of M-diabatic states is this: Provided that γ vanishes (or is negligible) in the original class M representation (Sec. II.C.3.e), then in the transformed equations *all velocity-dependent couplings are made to vanish* (or to be negligible). Hence the coupled equations in an M-diabatic representation have the form intuitively desired of a diabatic description. Although M-diabatic states are not class F, and must undergo some (presumably slow) change with R, and although their detailed nature depends upon the choice of switching functions used to define $\underline{A}_M^R$, this detailed behavior is of no concern to us if we are interested only in the actual solution of a collision problem; to solve the coupled equations one needs only to know the matrix elements of $\underline{h}$, $\underline{S}$, etc. in the diabatic representation.

$f_n(\mathbf{r};R)$ *independent of* n. One especially simple and convenient M-diabatic representation is obtained if the original class M states are orthogonal, and if we take the same switching function for all states, because then $\underline{A}_M^R$ is Hermitian. To find the diabatic representation we can require $\underline{U}(R)$ such that

$$\underline{U}^\dagger(\underline{P}^R+\underline{A}^R)\underline{U}-i\hbar\underline{U}^\dagger d\underline{U}/dR=0\ . \tag{4.29}$$

Since $(\underline{P}^R+\underline{A}_M^R)$ is Hermitian, it easily follows that $d/dR(\underline{U}^\dagger\underline{U})=0$, i.e., $\underline{U}^\dagger\underline{U}$ is a constant. But since we know that $(\underline{P}^R+\underline{A}_M^R)\to 0$ as $R\to\infty$, we can choose $\underline{U}(R\to\infty)=\underline{1}$ as our initial condition; then $\underline{U}^\dagger(R)\underline{U}(R)=\underline{1}$, $\underline{U}(R)$ is unitary, and the *diabatic basis states are orthogonal*.

d. Diabatic representations—construction

The definitions and properties given above suggest several methods for constructing diabatic representations; which method is appropriate depends upon the objectives of the problem, the required accuracy, and the amount of information available from earlier stages in the calculation.

(i). Partial or total decomposition of a known adiabatic construction. As noted earlier, a quantum chemist typically begins the construction of Born-Oppenheimer or adiabatic states with a set of basis functions based on atomic states or atomic orbitals; these may be class F or class V states. This basis is usually quite large compared to the number of adiabatic states calculated. Then the Born-Oppenheimer Hamiltonian is made diagonal by a transformation $\underline{U}(R)$ (or a series of transformations in stages, for the many-electron case), and a sharply truncated set of adiabatic states is obtained for use in a collision problem.

But since the original basis states are single-center states, there is no doubt about the correct forms for $\mathbf{s}_n^F$, and the resulting matrices $\underline{A}_F^R$ and $\underline{\gamma}_F^R$. If the matrix $\underline{U}(R)$ is available, we may then transform the matrices $\underline{P}^R$, $\underline{A}_F^R$, and $\underline{\gamma}_F^R$ according to Eqs. (4.3), and then truncate to the relevant square submatrices corresponding to the adiabatic states considered. Within this truncated subspace we may now identify in a piecewise manner each of the velocity-dependent couplings:

(1) $\underline{P}_F^{R'}=\underline{U}^\dagger\underline{P}_F^R\underline{U}$: that part of $\underline{P}^R$ which represents only displacement;

(2) $\underline{A}_F^{R'}=\underline{U}^\dagger\underline{A}_F^R\underline{U}$: this arises from ETF's or coordinate transformations in the original basis, and it exactly cancels $\underline{P}_F^{R'}$;

(3) $\underline{P}_\zeta^{R'}=\underline{U}^\dagger\underline{P}_\zeta^R\underline{U}$: that part of $\underline{P}^R$ which arises from the slow variations with R of the parameters in the class V functions;

(4) $\underline{P}_C^{R'}=-i\hbar\underline{U}^\dagger\underline{S}^{-1}(d\underline{U}/dR)$: the nonadiabatic couplings which arise from the (sometimes rapid) changes in the coefficients of transformation;

(5) $\underline{\gamma}_F^{R'}=\underline{U}^\dagger\underline{\gamma}_F^R\underline{U}$: the momentum-transfer couplings.

Obviously, only the last three pieces need actually be calculated. The advantage of this approach is that it allows us to identify the real couplings in the problem and to attribute each to a clearly distinguishable source. The transformation to a suitable truncated representation can then be carried out by a matrix $\underline{W}$ which can be defined in several ways; in any case it satisfies a differential equation of the form

$$i\hbar d\underline{W}/dR=\underline{D}\underline{W}\ . \tag{4.30}$$

We may take

(a) $\underline{D}=\underline{P}_C^{R'}$. In most cases this is the significant choice. It eliminates the rapid variations arising from changing coefficients, leaving only the smaller couplings due to slow variations in the parameters and to $\underline{\gamma}_F^{R'}$. If this were applied to the full (untruncated) space it would just take us back to the original class V basis. If the construction of the adiabatic representation is done in successive transformations (e.g., SCF-LCAO-MO calculation followed by configuration mixing), then $\underline{P}_C^{R'}$ will have separate pieces arising from each stage and the most significant of these may be retained while ignoring the rest.

(b) $\underline{D}=\underline{P}_C^{R'}+\underline{P}_\zeta^{R'}$. This also eliminates the couplings which arose from slow parameter variations. The resulting diabatic states will therefore be closer to class F than the original basis; in the limit of a complete set of states a fully F-diabatic representation will be obtained.

(c) $\underline{D}=\underline{P}_C^{R'}+\underline{P}_\xi^{R'}+\underline{\gamma}^{R'}$; this eliminates all velocity-dependent couplings from the new representation, which is therefore M diabatic. In general the new states are still molecular, but they should be slowly varying. Note, however, that in general $\underline{D}^\dagger\neq\underline{D}$ and the transformation is *not* unitary.

(ii). Direct synthesis of a practical A_M^R in adiabatic representation. It may happen that the information necessary to obtain the separate pieces of the nonadiabatic couplings as above is not readily available, or it may be that the labor required to do so is not justified by the approximations inherent in the collision problem considered. Then it is a reasonable procedure to introduce a suitable switching function directly into the adiabatic representation and calculate the matrix $\underline{A}_M^R$ and find the M-diabatic representation by solving Eq. (4.30) with $\underline{D}=\underline{P}^R+\underline{A}_M^R$. We have earlier discussed the particularly simple result that appears if a single switching function is used, i.e., the diabatic states are

orthonormal.

In many cases it may be possible to estimate $\underline{A}^R$ rather than compute it explicitly, and then just let $\underline{D}$ be the remaining "large" part of $\underline{P}^R$ which one wishes to eliminate. Also it is obvious that if $\underline{A}^R$ is negligible, then diabatic states within a small manifold can be constructed using Eq. (4.30) with $\underline{D}=\underline{P}^R$, as Smith originally proposed.

(iii). Partition of V matrix. Suppose that the V matrix can be partitioned in some way, $\underline{V}=\underline{V}_0+\underline{V}_1$, and we begin in a representation in which $\underline{V}_0$, a major part of $\underline{V}$, is diagonal, but $\underline{V}_1$ is not diagonal. For example, $\underline{V}_0$ might be $\underline{h}$, and $\underline{V}_1$ could be the angular coupling $\underline{Q}$ or the "isotopic" coupling $\underline{I}$; alternatively $\underline{V}_0$ might include only the electrostatic interactions h_{BO}, and $\underline{V}_1$ might be the spin-orbit terms. Frequently it will happen (usually because of symmetry) that the eigenstates of $\underline{V}_0$ have no (P^R+A^R) matrix elements connecting states that are coupled by V_1. It follows that the given representation is diabatic with respect to $\underline{V}_1$, though adiabatic with respect to $\underline{V}_0$. Let $U(R)$ be the matrix transforming to the fully adiabatic representation, in which $\underline{V}_0+\underline{V}_1$ is diagonal. The resulting velocity-dependent couplings are then

$$\underline{U}^\dagger(\underline{P}^R+\underline{A}^R+\underline{\gamma}^R)\underline{U}-i\hbar\underline{U}^\dagger\underline{S}d\underline{U}/dR\,.$$

Should we find that these couplings are out of hand, (i) we can be sure that the source of the trouble is the $d\underline{U}/dR$ term and (ii) the easy way to get to the diabatic representation required is *not* to integrate Eqs. (4.30) but to refrain from the damaging transformation $\underline{U}(R)$. Practically all useful diabatic representations have been constructed in this way.

4. Two model processes

The discussion in the preceding section gives precise definitions of adiabatic and diabatic representations, and it tells how such representations can be constructed from various starting points. However it does not answer one of the most important questions: Which type of representation is most convenient for a given collision process? A partial answer to this will be given in the following section; however, to understand this answer, some familiarity with elementary excitation mechanisms is needed, so we consider here two important models for degeneracy-mediated transitions.

a. Curve crossing

Consider a problem in which only two electronic states are important; suppose there exists an M-diabatic representation in which the states are orthogonal, all radial velocity-dependent couplings $\underline{P}^R+\underline{A}^R+\underline{\gamma}^R$ vanish or are negligible, and the diagonal matrix elements of $\underline{V}$ cross at some point R_X.

We can transform to the adiabatic representation using a 2×2 matrix $\underline{U}$ which diagonalizes $\underline{V}$. Then the diagonal elements will not cross, the basis vectors will depend significantly on R (and may change drastically and abruptly), and transitions between them are induced by this R dependence.

For any two-state problem, in an orthogonal diabatic representation, the coupled equations (2.68) or (A10) take the form

$$i\hbar\frac{d}{dt}\underline{d}^D=\underline{V}\,\underline{d}^D \tag{4.31a}$$

or

$$[(2\mu)^{-1}(-i\hbar d/dR)^2+\underline{V}]\underline{\chi}^D=E\underline{\chi}^D\,. \tag{4.31b}$$

Writing

$$\phi_k^A=\sum_j U_{jk}\phi_j^D\,, \tag{4.32}$$

with

$$\underline{U}^\dagger\underline{V}\,\underline{U}=\underline{\epsilon} \tag{4.33}$$

$\underline{U}$ is

$$\underline{U}=\begin{pmatrix}\cos\omega & \sin\omega\\ -\sin\omega & \cos\omega\end{pmatrix}, \tag{4.34}$$

where

$$\cot2\omega=(V_{22}-V_{11})/2V_{12}\equiv T(R) \tag{4.35}$$

and the eigenvalues $\epsilon_k(R)$ are

$$\epsilon_k=(V_{11}+V_{22})/2\mp\{[(V_{11}-V_{22})/2]^2+V_{12}^2\}^{1/2} \tag{4.36a}$$

$$=(V_{11}+V_{22})/2\mp V_{12}[1+T(R)^2]^{1/2}\,. \tag{4.36b}$$

Following the transformation rules Eq. (4.4), we have

$$[\underline{P}^R+\underline{A}^R+\underline{\gamma}^R]^A=\underline{U}^\dagger[\underline{P}^R+\underline{A}^R+\underline{\gamma}^R]^D\underline{U}-i\hbar\underline{U}^\dagger d\underline{U}/dR \tag{4.37a}$$

$$=-i\hbar\underline{U}^\dagger d\underline{U}/dR \tag{4.37b}$$

and evaluation of this expression gives

$$[\underline{P}^R+\underline{A}^R+\underline{\gamma}^R]_{12}^A=-i\hbar\,d\omega/dR\,. \tag{4.38}$$

The coupled equations in adiabatic representation are therefore

$$i\hbar\frac{d}{dt}\underline{d}^A=[\underline{\epsilon}+v^R(\underline{P}^R+\underline{A}^R+\underline{\gamma}^R)^A]\underline{d}^A \tag{4.39a}$$

or

$$\{(2\mu)^{-1}[-i\hbar d/dR+(\underline{P}^R+\underline{A}^R+\underline{\gamma}^R)^A]^2+\underline{\epsilon}\}\underline{\chi}^A=E\underline{\chi}^A\,. \tag{4.39b}$$

Before the role of ETF's or coordinate transformations was understood, the above analysis used to be applied in the PSS framework. It gave a way of finding the behavior of $\underline{P}^R$ matrix elements from assumptions about the adiabatic potential matrix $\underline{V}$. Now we see that the same models actually give information about $\underline{P}^R+\underline{A}^R+\underline{\gamma}^R$, which is the quantity of interest.

Equations (4.39) describe the same physics as do Eqs. (4.31), but in a different way. A crossing of V_{11} and V_{22} was indicated in Fig. 1(b). The corresponding ϵ_k's have an avoided crossing. When $T(R)\gg1$ $(R\to\infty)$ they approach V_{11} and V_{22}, and their separation at R_x is just $2V_{12}(R_c)$. Taking the conventions $V_{22}>V_{11}$ and $V_{12}>0$ at large R (the latter convention can be made to hold by suitable choice of the relative phases of ϕ_1^D and ϕ_2^D), Eq. (4.35) shows that ω passes from zero $[R\to\infty,\ T(R)\gg1]$ to $\pi/2$ $[T(R)\ll-1)]$ on going through the crossing, and the adiabatic states ϕ_k^A *change character*: e.g., for $T\to+\infty$, $\phi_1^A\to\phi_1^D$, while for $T\ll-1$, $\phi_1^A\to-\phi_2^D$. If V_{12}

is small, Eq. (4.35) shows that this change occurs over a short distance,

$$\Delta R \sim \left| \left(\frac{d\omega}{dR} \right)_{R_x} \right|^{-1} \approx \left| \frac{V_{12}}{(F_1 - F_2)} \right| , \tag{4.40}$$

where the force $F_k = -(dV_{kk}/dR)$. Thus if the coupling between the diabatic states V_{12} is smooth and weak, the coupling $d\omega/dR$ between adiabatic states will be abrupt and strong.

The above describes the behavior of the diabatic and adiabatic basis states. How does the actual wave function for the system behave? Various solvable models and approximation methods show that at low velocities the system wave function tends to follow the adiabatic states, while at higher velocities it tends to follow the diabatic states. This means that if such a higher-velocity collision is described in the diabatic representation, the probability of transition from one diabatic state to the other is small; however, if the *same* collision is described in the adiabatic representation, the probability of transition from one adiabatic state to the other is very large. This simply reflects the fact that in order to pass from the lower energy state to the higher energy state in Fig. 1(b), a transition is required in the adiabatic representation, but no transition in diabatic representation. Although any collision can be described in either representation, normally it is most convenient to use the representation in which couplings and transition probabilities are small.

One final point must also be noted. For a curve crossing there is a range of intermediate velocities in which the system is about equally likely to follow the diabatic or adiabatic states. This means that in either representation the transition probability is around $\frac{1}{2}$. Such situations intrinsically involve strong coupling, and there is no electronic basis set of the types normally considered in which the coupling is weak.

b. Asymptotic near degeneracy

When diabatic potential curves are strongly coupled but do not cross, there is a somewhat greater variety of possible behavior than appears in the crossing case. The case of asymptotic near degeneracy (also called "perturbed symmetric resonance") is the most complicated of the common situations, and it provides a basic model within which the simpler situations can also be understood. This case is frequently called the Demkov coupling mechanism (Demkov, 1964), and it is represented in Fig. 1(c).

Assume again that a system can be described by a pair of orthogonal M-diabatic states with negligible $\underline{P}^R + \underline{A}^R + \gamma^R$. Now suppose these states are nearly degenerate, with

$$V_{22} - V_{11} \equiv \Delta(R) \tag{4.41}$$

small and slowly varying, and assume they are coupled by $V_{12}(R)$ such that $2V_{12} \gg \Delta$ at small R but $V_{12} \to 0$ at large R. These two states form what we shall call the "external diabatic" representation.

Another diabatic representation can be formed by a fixed (R-independent) linear combination of these states. Using $\omega = \pi/4$ in Eq. (4.34), the resulting $\underline{V}$ matrix has the original $\Delta(R)$ off diagonal and the original $V_{12}(R)$ diagonal. Since the resulting basis states still have $\underline{P}^R + \underline{A}^R + \gamma^R = 0$, they constitute what we call the "internal diabatic" representation.

The adiabatic representation is as usual the one in which $\underline{V}$ is diagonal; it is related to the original external diabatic representation by a transformation matrix $\underline{U}$ in which ω goes from zero at large R to $\pi/4$ at small R; hence the adiabatic states vary continuously from external to internal diabatic states. Since ω will change most rapidly near R_c where $T(R_c) \simeq 1$, the adiabatic states are strongly coupled in this region.

In a very slow collision, the system wave function again tends to behave adiabatically, adjusting continuously to the changing Hamiltonian, as do the adiabatic basis states. In a fast collision, the system wave function tends to stay in the original precollision state. Therefore it is most convenient to use the adiabatic representation at low velocities and the external diabatic representation at high velocities.

There may be a range of intermediate velocities in which the system behaves adiabatically with respect to $V_{12}(R)$ in the internal region, and adiabatically with respect to $\Delta(R)$ in the external region; however it may pass *suddenly* from one region to the other. A "split diabatic" representation is suitable for describing this type of behavior: We may use the internal diabatic states at small R and the external diabatic states at large R, joining the two at some point near R_c. This split representation contains the physics of the sudden approximation, and is most convenient when the sudden approximation is appropriate. Like any other representation, it can also be used as the starting point of a close-coupling calculation even if the sudden approximation is not valid; solution of coupled equations is carried out on both sides of the boundary at R_c, and the solution joined there. Again, any representation can be used to solve any problem, but it is convenient to seek representations in which the coupling remains weak.[12]

5. Optimal representations

We now take up the question that underlies the whole discussion of changes of representation. *Of all the possible representations of a given collision system, can we pick the "optimal" one, in which coupling between the states is as weak as possible?* Although it is unlikely that a completely general answer to this question will ever be found, a cautiously affirmative answer can be given if the question is suitably restricted.

We consider only partially diabatic and partially adiabatic representations, in which the coupling between a pair of states (j,k) is represented *either* by V_{jk} or $P^R_{jk} + A^R_{jk} + \gamma^R_{jk}$. Even with this restriction, three more limitations are evident. First, the "optimal" repre-

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[12] It is worth remarking that asymptotic diabaticity, that is, the tendency for a colliding system to obey *sudden* rather than *adiabatic* connections between internal and external states in asymptotically near-degenerate manifolds, is a very common phenomenon. In Sec. IV.B, examples will be discussed in connection with isotope splittings, transitions among fine-structure levels, and near-resonant charge exchange.

sentation, if it exists at all, necessarily depends on the collision velocity. Second, for many collision processes, there is a range of intermediate velocities for which the system shows an intrinsic strong coupling, and for which there is no representation of the type considered here in which the coupling is weak. This point was emphasized for the curve crossing problem, but it also holds for other mechanisms.

A final limitation is also apparent. Since the "optimal" representation is the one that gives the best zero-order description of what actually happens in the collision, it is only possible to give general rules for the construction of optimal representations if there are general models that at least approximately describe the behavior of a wide variety of systems. For curve crossings, the Landau-Zener model has such broad applicability, and it has often been used to estimate the diabaticity or adiabaticity of a given collision. For states that are strongly coupled but do not cross, an appropriate model is one first suggested by Rosen and Zener. These models are based on a number of assumptions and approximations (two-state truncation, orthogonal M-diabatic representation, classical trajectory formulation, linear crossings, etc., etc.). Hence, they lead to formulas for the transition probability that may or may not be sufficiently accurate for the problem at hand. However, the accuracy of the formulas is not of concern to us here: Regardless of whether they are correct to within 1% or only to within a factor of two, they *can* provide the relatively gross distinction between essentially adiabatic and essentially diabatic behavior. We use the results of these models here only to help us choose a good representation, one in which an accurate solution may conveniently be obtained.

Within these limitations and restrictions, a simple prescription can be given for choosing a good representation. It must be recognized that we are asking quite a modest question: For each pair of states (j,k) in the system, is it better that the couplings between them be represented diabatically by V_{jk}, with $(\underline{P}^R+\underline{A}^R+\underline{\gamma}^R)_{jk}=0$, or adiabatically, by $(P^R+A^R+\gamma^R)_{jk}$, with $V_{jk}=0$? For a system with N states, we then have $\frac{1}{2}N(N-1)$ choices. *This set of choices can normally be made by a sequence of binary decisions, each decision involving only one pair of states.* Although one decision may influence another, a self-consistent set of choices can usually be reached by beginning with the most strongly coupled pairs.

The procedure for making the binary decisions can be condensed into a set of rules or guidelines. As stated here, the rules assume that the starting representation is diabatic between the given pair of states under consideration, so we are deciding whether to diagonalize V_{jk} or leave it off-diagonal. (For noncrossing problems, we assume that an external diabatic representation is the starting point.) The steps in the procedure are

1. Decide what collision velocity is of primary interest. The optimal representation necessarily depends on the collision velocity.

2. Examine the curves $V_{jj}(R)$ and $V_{kk}(R)$ for crossings. If they cross, apply rule 3; if not apply rule 4.

3. For crossing states, estimate the Landau-Zener parameter,

$$\zeta_{\rm LZ}=2\pi V_{jk}^2/\hbar v^R|F_j-F_k|, \tag{4.42}$$

where F_j is the force $-(dV_{jj}/dR)$ and v^R is the classical radial nuclear velocity at the crossing point. If $\zeta_{\rm LZ}\gg 0.69$, diagonalize V_{jk} to represent this coupling adiabatically; if $\zeta_{\rm LZ}\ll 0.69$, do not diagonalize V_{jk}.

4. For noncrossing states, estimate the two parameters

$$s_\infty=\int_{R_0}^{\infty}[V_{jk}(R)/\hbar v(R)]\,dR \tag{4.43a}$$

and

$$\zeta_{\rm RZD}=\bar{\Delta}d/\hbar v, \tag{4.43b}$$

where d is the distance over which $\Delta(R)=V_{jj}(R)-V_{kk}(R)$ is comparable to $V_{jk}(R)$, and $\bar{\Delta}$ is the average of $\Delta(R)$ over that region. Then

(a) If $s_\infty\ll 1$ and $\zeta_{\rm RZD}\ll 1$, do not diagonalize V_{jk}; use the external diabatic representation.

(b) If $s_\infty\gg 1$ and $\zeta_{\rm RZD}\gg 1$, diagonalize the $\underline{V}$ matrix to use the adiabatic representation.

(c) If $s_\infty\gg 1$ and $\zeta_{\rm RZD}\ll 1$, then the "split" representation may be used if convenient.

(d) If $s_\infty\ll 1$ and $\zeta_{\rm RZD}\gg 1$, weak coupling is obtained in both external diabatic and adiabatic representations.

5. In the intermediate cases (as for $\zeta_{\rm LZ}\simeq 1$ or $s_\infty\simeq 1$, $\zeta_{\rm RZD}\simeq 1$) the problem intrinsically involves strong coupling, and the choice of representation probably doesn't matter. Diagonalize $\underline{V}$ if you are a chemist; leave it off diagonal if you are a physicist.

Figure 16 summarizes the rules in a simple flow chart. Examples of their application will be given subsequently.

B. Representations and excitation mechanisms for specific systems

At last we consider the description of specific systems. The purpose of this part is to show how the general theory developed above is applied to real collision processes; in particular, the purpose is to display examples of the coupling matrices in Table IV, to show how diabatic and adiabatic representations have been constructed for specific systems, and to explain the various mechanisms leading to electronic excitations in slow collisions.[13]

It is useful to classify problems according to (1) the type of degeneracy, and (2) the specific physical interactions causing transitions. Table V shows the resulting catalog, with columns corresponding to degeneracy types and rows to the interactions. Some blocks contain two interactions because both may play a role in the process, or because they act in similar fashion. In some cases an example is given to illustrate the problem type.

A few general comments are appropriate here.

(a) "Radial coupling." Sometimes the expression "radial coupling" is used to denote the couplings which

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[13] On the other hand, we cannot give here any discussion of the methods for solving the coupled equations, or of the resulting features that appear in cross sections; those topics are outside the scope of the present article.

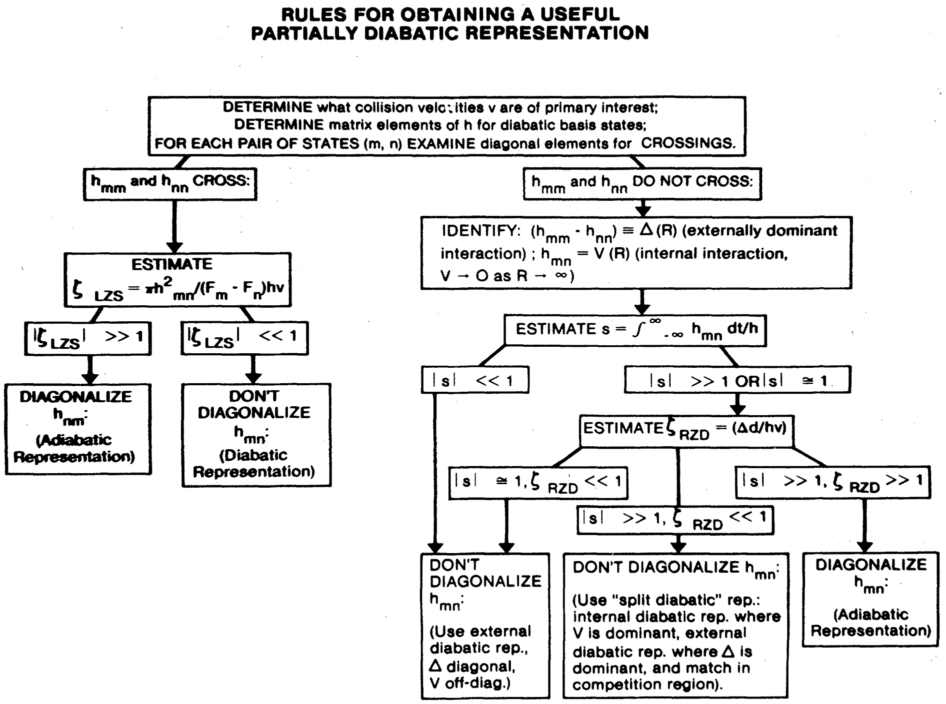

FIG. 16. Rules for obtaining a useful partially diabatic representation.

TABLE V. Degeneracies and interactions. The number in parentheses in each box indicates the subsection in which the corresponding problem is discussed.

Degeneracy type → Interaction ↓	$R=0$ (united atom)	$R=R_x$ (curve crossing)	$R\to\infty$ (asymptotic)	Continuum mediated
Isotopic splitting			$H^+ + D \to H + D^+$ (IV.B.5)	
Spin-orbit coupling		Triplet-singlet and other $\Delta S \neq 0$ transitions (IV.B.1)	Transitions among fine-structure multiplets and components (IV.B.7)	
Angular coupling	$H^+ + H(1s) \to H^+ + H(2p)$ (IV.B.2)	Rotational transitions ($\Delta\Lambda, \Delta\Omega \neq 0$)		
Electrostatic two-electron (CI)		Avoided crossings of valence-shell levels (CI of SCF configurations) (IV.B.3.a)	Resonant and near-resonant excitation and charge exchange (IV.B.4 and IV.B.6)	Electron detachment and collisional autoionization (IV.B.8)
Electrostatic one-electron (SCF effects)		Avoid crossing of inner-shell levels; covalent-ionic transitions (IV.B.3.b and IV.B.3.c)		

arise in an adiabatic representation due to the matrix $\Pi^R(R)$; in particular, this expression most often refers to the adiabatic representation of electrostatic couplings. "Radial coupling" is not, therefore, a separate physical interaction, but a way of describing any other type of interaction in an adiabatic representation.

In contrast, note that we have included the angular (Coriolis) coupling in the table. Like the radial coupling this is a dynamic interaction arising from the nuclear motion (in this case, the rotation of the molecular frame of reference). However, in a partial-wave expansion, angular coupling appears as a distinct "potential" matrix [see Eq. (4.25)], and it is easiest to think of it in this way.

(b) Russell-Saunders vs j-j coupling context. Here we normally assume the context of Russell-Saunders coupling; that is, we assume that the intrinsic strength of atomic spin-orbit interactions is substantially less than that of electrostatic interactions. While this situation is most common, there are of course problems where the opposite condition holds (j-j coupling scheme), and our discussion can be modified accordingly.

(c) Selection rules. There are two ways of using selection rules in atomic collision theory. One way is to examine the symmetries of the full quantum Hamiltonian H. One then finds the obvious conservation laws for total energy and total angular momentum. In addition, for identical nuclei, Ψ must be either symmetric or antisymmetric with respect to exchange, and this symmetry is, of course, conserved in any collision. Finally, also for identical nuclei, the parity of electronic states (symmetry on inversion of electrons through the center) is conserved. So we have the rigorous rules (see Herzberg, 1950, pp. 212–218 and 240–245)

$$\Delta E=0\,,$$

$$\Delta J=0\,,$$

$$\Delta M_J=0\,,$$

$$\left.\begin{array}{l}\text{sym} \not\to \text{anti}\\ \quad g \not\to u\end{array}\right\}\text{identical nuclei only.}$$

A second way of using selection rules involves examining a specific representation and asking which coupling matrices connect a given pair of basis states in that representation. The resulting selection rules then obviously depend upon the symmetries that are built into the chosen representation. Let us examine the selection rules associated with a Hund case a representation (appendix) in which the electronic states are denoted $|\epsilon\Lambda(\pi)\rangle|S\Sigma\rangle$. Besides the quantum numbers used to label the states, there are two other quantum numbers that can be considered: $\Omega=\Lambda+\Sigma$, and ($\pm$) symmetry of the electronic state on reflection through any plane containing the nuclei. This reflection operator does not commute with L_z, so in general a basis function cannot be characterized by *both* Λ and $\pm$ symmetry, but one can construct states having $\pm$ symmetry as combinations of pairs of states having $\langle L_z\rangle=\pm\Lambda\hbar$.

Table VI gives selection rules for each of the coupling matrices. Selection rules involving $\underline{\mathbf{A}}$, $\underline{\gamma}$, etc. were obtained on the assumption that $\mathbf{s}$ has the form (3.38) with f a cylindrically symmetric function. Parity (π) is a quantum number only for symmetric systems (equal nuclear charges). For systems with identical nuclei, none of the matrices connect states of opposite parity. For symmetric but heteronuclear (isotopic) systems $\mathbf{P}$ and $\mathbf{A}$ connect states of opposite parity, but $\mathbf{P}+\mathbf{A}$ does not (the two cancel). Parity-violating coupling for such systems is contained in the matrix $\underline{I}$.

Rules of this type are helpful in identifying the mechanism of a particular transition. For example, if one sees a transition for which $\Delta S=1$, one knows that it must arise from spin-orbit coupling, since no other matrix connects such states. Conversely, if one knows that spin-orbit coupling is negligible in a particular system, then one arrives at the additional selection rule $\Delta S=0$. One also notes that, for example, $\Delta\Lambda=\pm2$ does not appear anywhere in the table. This does *not* mean that such transitions are impossible; rather that they can only be described (in this representation) as occurring through a sequence of intermediate transitions having $\Delta\Lambda=\pm1$. Let us now examine specific cases.

1. Curve crossings coupled by spin-orbit interaction

Crossings between Born–Oppenheimer energy levels coupled by spin-orbit interactions are the paradigms for defining a diabatic representation by partitioning of the $\underline{V}$ matrix (Sec. IV.A.3.d.iii). Recall that we de-

TABLE VI. Selection rules for coupling matrices in case a representation. 0 means the quantity is conserved (e.g., $\underline{S}$ does not connect + to − states). See text regarding parity.

	Λ	π	$\pm$	S	Σ	Ω
$\underline{S},\underline{\boldsymbol{h}}_{\mathrm{BO}}$	0	0	0	0	0	0
$\underline{h}_{\mathrm{soc}}$	$\pm1,0$	0		$\pm1,0$	$\mp1,0$	0
$\underline{P}^R,\underline{A}^R,\underline{\Pi}^R,\underline{\gamma}^R,\underline{B}_R$	0	0	0	0	0	0
$\underline{P}^\Theta,\underline{A}^\Theta,\underline{\gamma}^\Theta$	$\pm1,0$	0	0	0	$\pm1,0$	±1
$\underline{P}^\Phi,\underline{A}^\Phi,\underline{\Pi}^\Phi,\underline{\gamma}^\Phi$	$\pm1,0$	0	$+,-\leftrightarrow+,-$	0	$\pm1,0$	$\pm1,0$
$\underline{I}$	0	$g,u\leftrightarrow g,u$	0	0	0	0
$\underline{Q}$	$\pm1,0$	0	$+\leftrightarrow+,-\leftrightarrow-$ $(+\leftrightarrow-,-\leftrightarrow+\text{ weak})$	0	$\pm1,0$	±1

fined the Born-Oppenheimer states as eigenfunctions of the electrostatic part of the electronic Hamiltonian, excluding spin-orbit coupling and other magnetic effects. These states (or more properly these molecular "terms") are then characterized by total spin S and by the molecular Z-axis component of electronic orbital angular momentum Λ.

Since the matrix elements of h_{BO} between states of different S or different Λ all vanish, it follows from the Hellmann-Feynman theorem that matrix elements of $\underline{P}^R$ between such states must also vanish, and it is easy to see that such elements of $\underline{A}^R$ also vanish.

When spin-orbit interactions are considered, they may have matrix elements linking such states. One form for the spin-orbit coupling operator is (Hirschfelder, Curtiss, and Bird, 1954, p. 1044)

$$h_{\mathrm{soc}} = (e^2\hbar/2m^2c^2)\sum_{i,\alpha}\frac{\hat{Z}_\alpha}{r_{\alpha i}^3}(\mathbf{r}_{i\alpha}\times\mathbf{p}_i)\cdot\mathbf{s}_i \tag{4.44}$$

where $\mathbf{p}_i$, and $\mathbf{s}_i$ are momentum and spin operators for each electron i, and $\mathbf{r}_{i\alpha}$ is the vector from nucleus α to electron i. Calculation of the corresponding matrix elements is not trivial, but often the desired ones can be estimated by referring to the separated atoms. In any case one can show from Eq. (4.44) that h_{SOC} connects states with $\Delta S=\pm 1,0$ and with $\Delta\Lambda=\pm 1,0$. Hence *Born-Oppenheimer states are adiabatic with respect to electrostatic couplings, but diabatic with respect to spin-orbit couplings.*

The adiabatic representation is formed in the obvious way by diagonalizing $\underline{h}_{\mathrm{BO}}+\underline{h}_{\mathrm{SOC}}$; coupling then results from the R dependence of the matrix $\underline{U}$ that accomplishes this transformation,

$$\underline{P}^R+\underline{A}^R=\underline{U}^\dagger(-i\hbar d/dR)\underline{U}\ .$$

As an example we may consider the process

$$\mathrm{O}^+(^4\mathrm{S})+\mathrm{He}\rightarrow\mathrm{O}^+(^2\mathrm{D})+\mathrm{He} \tag{4.45}$$

which was studied by Augustin, Miller, Pearson, and Shaeffer (1973). The atomic ground configuration of O^+, $1s^22s^22p^3$, yields Russell-Saunders terms ^4S, ^2D, ^2P, with further very small multiplet splitting by the atomic spin-orbit interaction. Process (4.45) is said to be "spin forbidden" ($\Delta S=1$); however, this does not mean that the process cannot occur, but only that it does not occur by electrostatic interactions. The molecular terms of $(\mathrm{OHe})^+$ are related to the atomic terms by the usual rules (Herzberg, 1950, p. 318),

$$^1S_g+{}^4S_u\rightarrow{}^4\Sigma^-$$

$$^1S_g+{}^2D_u\rightarrow{}^2\Sigma^-,{}^2\Pi,{}^2\Delta\ .$$

Calculations indicate that the $^4\Sigma^-$ and $^2\Pi$ terms cross each other at $R\simeq 2.2a_0$ (Fig. 17). The spin-orbit matrix element was estimated by approximately resolving the molecular wave function into atomic states and empirically estimating the corresponding atomic spin-orbit matrix elements; Augustin *et al.* obtained $\langle{}^2\Pi|h_{\mathrm{SO}}|{}^4\Sigma\rangle\simeq 106\ \mathrm{cm}^{-1}$. (Cross sections were calculated by a generalization of the Landau-Zener formula; the rather small coupling leads to a small total cross section, $\lesssim 10^{-2}$ Å^2.)

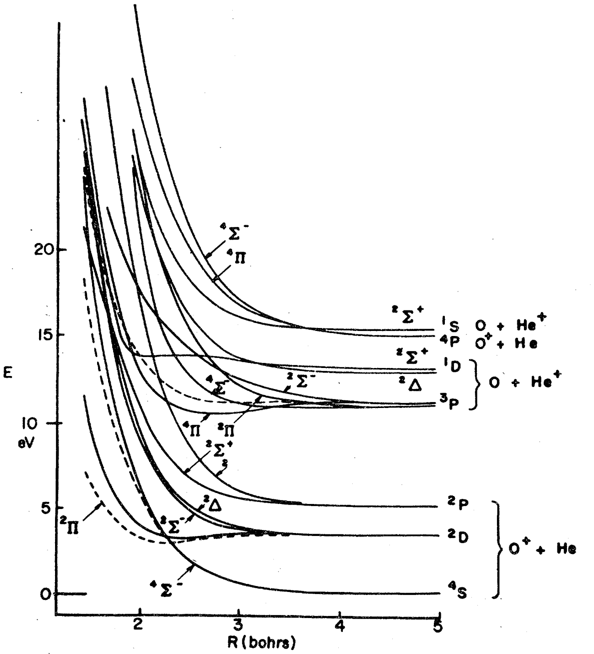

FIG. 17. Born-Oppenheimer energy curves for the lowest states of HeO$^+$. Transitions occur at the crossing between $^4\Sigma$ and $^2\Pi$ (from Augustin *et al.*, 1973).

As an illustration of the rules given in Sec. (IV.A.5), let us verify that the Born-Oppenheimer (diabatic) representation is the preferred one in this case. The collision energy range of interest is E (relative) = 1–10 eV, corresponding to $v\gtrsim .0035$ a.u. The calculations of Augustin *et al.* show that F_2-F_1 at the crossing is ~6–7 eV/a_0, giving $\zeta_{\mathrm{LZ}}\simeq 0.007$. Hence the

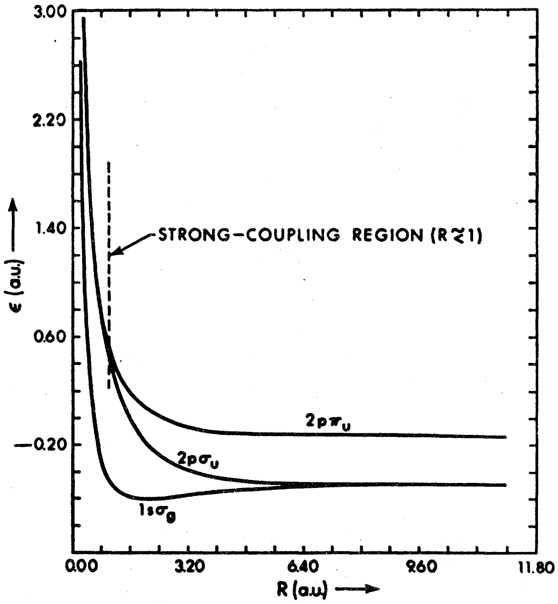

FIG. 18(a). Molecular energies of the three lowest states of H_2^+. Resonant charge exchange is reasonably described as coherent elastic scattering on the $1s\sigma_g$ and $2p\sigma_u$ curves. However, at small distances transitions from $2p\sigma_u$ to $2p\pi_u$ occur through rotation of the internuclear axis (from Knudson and Thorson, 1970).

Born-Oppenheimer states give a better zero-order description than do the adiabatic states.

2. Angular coupling in the united-atom limit

A very important class of transitions involves the angular or Coriolis coupling in the united-atom limit ($R \to 0$). Molecular levels which are orbitally degenerate (same n, l) as $R \to 0$ characteristically dissociate to very different energy levels of the separated products. Hence collisions which carry a system into the region of such orbital degeneracy can produce very efficient, strong-coupled excitation by angular coupling.

The prototype for such processes is the reaction

$$\mathrm{H}^+ + \mathrm{H}(1s) \to \mathrm{H}^+ + \mathrm{H}(2p)\,, \tag{4.46}$$

which was first treated by Bates and Williams (1964) using the straight-line-path impact parameter method; a more complete study was later done by Knudson and Thorson (1970) (see also Bates and Sprevak, 1970). The universality of this process as a mechanism for electronic excitation, and especially for inner-shell vacancy production, has been widely recognized, and numbers of calculations employing it have been done (Briggs and Macek, 1972; other references are in Sec. IV.B.3.b).

In the H_2^+ system the $2p\sigma_u$ level [which dissociates to $\mathrm{H}^+ + \mathrm{H}(1s)$] and the $2p\pi_u$ level [which dissociates to $\mathrm{H}^+ + \mathrm{H}(2p)$] are essentially degenerate for $R \lesssim 1.0$ a.u., as Fig. 18 shows. The two states are connected by angular coupling, $v(\underline{P}^{\ominus} + \underline{A}^{\ominus} + \underline{\gamma}^{\ominus})$ in the classical trajectory formalism (or $\underline{Q}$ in the quantum formalism). The momentum-transfer term $\gamma^{\ominus}$ vanishes because the basis states are eigenfunctions of h_{BO}. Coupling arises mainly from

$$v^{\ominus} P^{\ominus} = -(v^0 b/R^2)\langle 2p\pi_u | L_y | 2p\sigma_u\rangle\,, \tag{4.47}$$

v^0 being the asymptotic relative nuclear velocity and b the impact parameter corresponding to angular momentum $N\hbar$.

The $\underline{A}^{\ominus}$-matrix element can be neglected at small R, but at large R it cancels a long-range term in $\underline{P}^{\ominus}$ (as was shown in Sec. II.B.2.a and Sec. II.C.4). To see this, let us write the molecular states in LCAO approximation and consider the matrix element $\langle 2p_A | L_y | 1s_A\rangle$. Since the electron coordinates are defined relative to the center of mass of the nuclei, we may write

$$L_y = L_{y_A} + \tfrac{1}{2} i\hbar R\,\partial/\partial x_A\,,$$

where x_A, y_A are axes referred to atom A (cf. Fig. 5). The second term couples $1s_A$ and $2p_A$ states, and it increases linearly with R, giving $\underline{P}^{\ominus}$ a long-range R^{-1} behavior. This long-range coupling is physically meaningless, however, and it is canceled by the $A^{\ominus}$ matrix element, which therefore changes the molecular

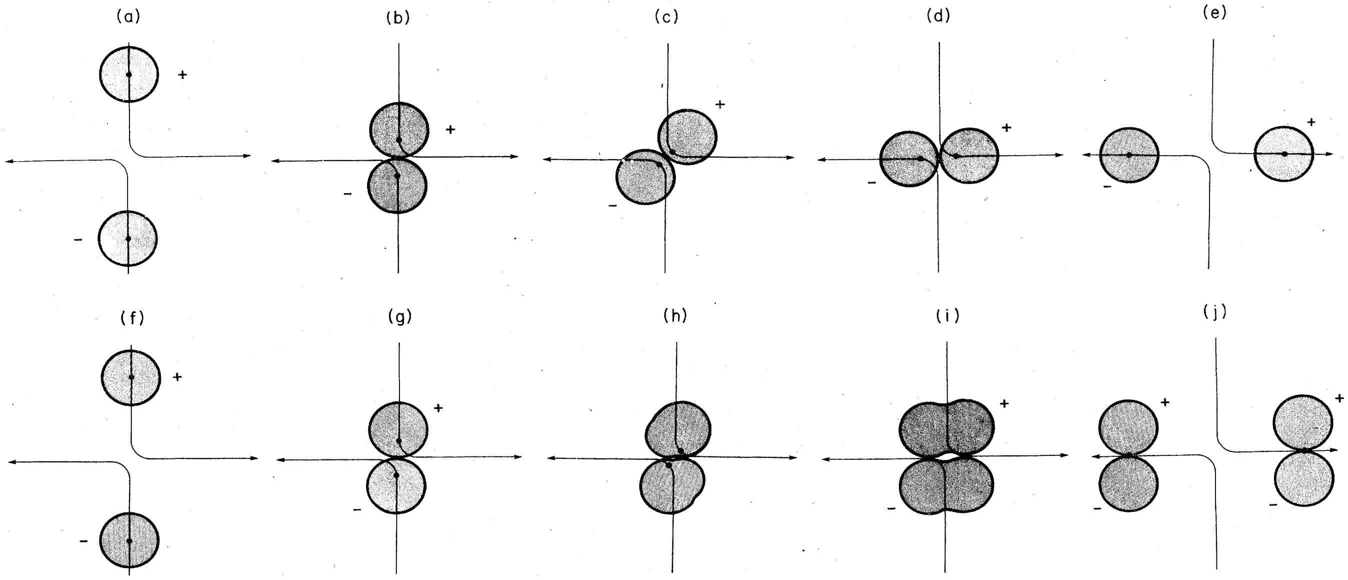

FIG. 18(b) Rotational coupling in the transition $\mathrm{H}^+ + \mathrm{H}(1s) \to \mathrm{H}^+ + \mathrm{H}(2p)$. Collisions in which the nuclei scatter to 90° are represented.

(a)–(e) illustrate a very slow collision.

(a) The electrons begin in the ungerade superposition of 1s atomic states.

(b) For small internuclear separations, this state becomes a $2p\sigma$ united-atom state.

(c), (d) If the internuclear axis rotates slowly, the electronic state follows.

(e) As the nuclei move apart, the electronic state again becomes the ungerade superposition of 1s states. No transition has occurred.

(f)–(j) Illustrate the consequences of more rapid motion on the same path.

(f), (g) Just as (a), (b).

(h) If the internuclear axis rotates too rapidly, the electronic state might not follow.

(i) As the axis rotates further, the electronic state becomes $2p\pi$.

(j) The $2p\pi$ molecular state dissociates into the ungerade superposition of separated-atom states. The transition occurred because the electrons could not follow the rapidly rotating internuclear axis.

L_y to the atomic L_{y_A} or L_{y_B}

Angular coupling arises as a dynamic effect from the rotation of the molecular frame of reference. However, for the purpose of defining diabatic and adiabatic representations, it is most convenient to treat it as "just another term" in $\underline{V}$, and to discuss it in exactly the same way that we discussed spin-orbit coupling. It connects Born-Oppenheimer states of different Λ ($\Delta\Lambda = \pm 1$) which are not connected by $\underline{h}_{\mathrm{BO}}$ or $\underline{P}^R$; hence Born-Oppenheimer states may be said to be "diabatic with respect to angular couplings." On the other hand, in a representation made up of nonrotating atomic or molecular states, angular coupling would not appear, and $\underline{h}$ would be nondiagonal; such a representation could be called "adiabatic with respect to angular couplings but diabatic with respect to electrostatic couplings." Such states are suitable for describing intermediate-to-high-velocity collisions, or other situations in which the coupling to the internuclear axis is weak (corresponding to Hund's cases d or e; see Appendix). Still another representation can be constructed which is adiabatic with respect to both electrostatic and angular couplings. It is obtained by diagonalizing $\underline{h}_{\mathrm{BO}} + v^{\Theta}(\underline{P}^{\Theta} + \underline{A}^{\Theta})$. Knudson and Thorson called this the X representation, and used it for some of their numerical calculations on the H_2^+ system. However, they found that it offers no particular advantages. By estimation of typical matrix elements and application of the rules of Sec. IV.A.5 one concludes that the "diabatic" Born-Oppenheimer representation is generally preferable to this fully adiabatic basis.[14]

3. Avoided crossings having electrostatic interactions

In the previous cases, diabatic and adiabatic states were constructed by partitioning the coupling matrix $\underline{V}$. Diabatic states were taken to be eigenstates of the electrostatic part of $\underline{V}$; the remaining part of $\underline{V}$ (spin-orbit or angular coupling) connected states of different symmetry, for which $\underline{P}^R + \underline{A}^R$ matrix elements vanish. In much of the literature it has been assumed that this partitioning technique constitutes the operational definition of diabatic states. Such partitioning runs into difficulty, however, when the transitions of interest are caused by electrostatic interactions, because the electrostatic part of the Hamiltonian does not separate itself neatly into large and small parts.

Certain partitionings have been found to give acceptable diabatic states in special cases. Writing

$$h_{\mathrm{BO}} = h_0 + h_1 ,$$

two possible partitionings are immediately apparent: (i) We might take h_0 = electron-nuclear and nuclear-nuclear interaction, h_1 = electron-electron interactions. Such an approach has been used for inner-shell transitions of heavy atoms, for which the interelectron repulsion is much smaller than the very strong attractive force of the nucleus. (ii) Alternatively we might take h_0 to be the Hamiltonian for Hartree-Fock self-consistent field (SCF) states; this includes an averaged part of the electron-electron interaction. h_1 would be the difference between the actual Hamiltonian and the SCF Hamiltonian. This method should work whenever the SCF method gives a sufficiently accurate description of the molecular states.

Unfortunately, these two partitionings frequently fail to give adequate diabatic states, and no other general partitionings of h_{BO} present themselves. The frustrations attendant on such calculations had led many workers to conclude that no satisfactory definition of diabatic states existed.

The approach taken here circumvents this difficulty in the following way. We say that partitioning does not provide the *definition* of diabatic states; instead it provides a *calculational technique* which may or may not be adequate for any given problem. The definition of diabatic states is given in Sec. IV.A by the requirement that selected parts of $\underline{P}^R + \underline{A}^R$ vanish. For those cases in which an acceptable partitioning cannot be found, diabatic states can be constructed by one of the other methods given therein. With this in mind, let us examine several specific cases.

a. Coupling of SCF configurations

The SCF method was used to define diabatic states for the $\mathrm{He}^+ - \mathrm{Ne}$ system. Theoretical analyses of experimental studies of the process

$$\mathrm{He}^+(1^2S) + \mathrm{Ne}(2\,^1S) \to \mathrm{He}^+(1\,^1S) + \mathrm{Ne}^*(3\,^{1,3}P) \qquad (4.48)$$

had already suggested that the transition was mediated by a crossing of $(\mathrm{HeNe})^+$ molecular terms (Smith, Marchi, Aberth, Lorents, and Heinz 1967; Coffey, Lorents, and Smith, 1969; Smith, Fleischmann, and Young, 1970; Olson and Smith, 1971; Baudon, Barat, and Abignoli, 1970; Bobbio, Doverspike, and Champion, 1973.) To calculate the relevant energy curves, Sidis and Lefebvre-Brion (1971) calculated SCF molecular orbitals by expansion in Slater-type orbitals with screening constants chosen to optimize the wave functions for the separated atoms. The resulting eigenvalues are shown in Fig. 19(a) and some of the significant configurations are identified in Table VII. Consider pairs of states such as (B, C) or (C, E) which differ by two or more orbitals. These are not coupled either by the SCF Hamiltonian or by $\underline{P}^R$, both of which are effectively one-electron operators. Normally the form of $\mathbf{s}_n(\mathbf{r}, \mathbf{R})$ will be chosen such that $\underline{A}^R$ is also the matrix of a one-electron operator, so it also will not connect such pairs. Since, however, these configurations are coupled by the two-electron part of the Hamiltonian, the SCF calculations are providing a partially diabatic representation of the system: The SCF representation is adiabatic with respect to the one-electron self-consistent field, but diabatic with respect to the remaining two-electron interactions in h_{BO}.

When the coupling matrix elements were examined, Sidis *et al.* found that those linking states C, E and $C'E'$ were quite large, 5 eV or more. Since the collision energies of interest were below 500 eV, rule 3 of Sec. IV.A.5 says that such pairs should be described

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[14] Angular couplings can also cause transitions at curve crossings involving states of different Λ with the selection rule $\Delta\Lambda = \pm 1$. Such situations are not unlike spin-orbit transitions, except that the coupling matrix element depends upon the collision velocity and the impact parameter [Eq. (4.47)]. Russek (1971) has examined this case.

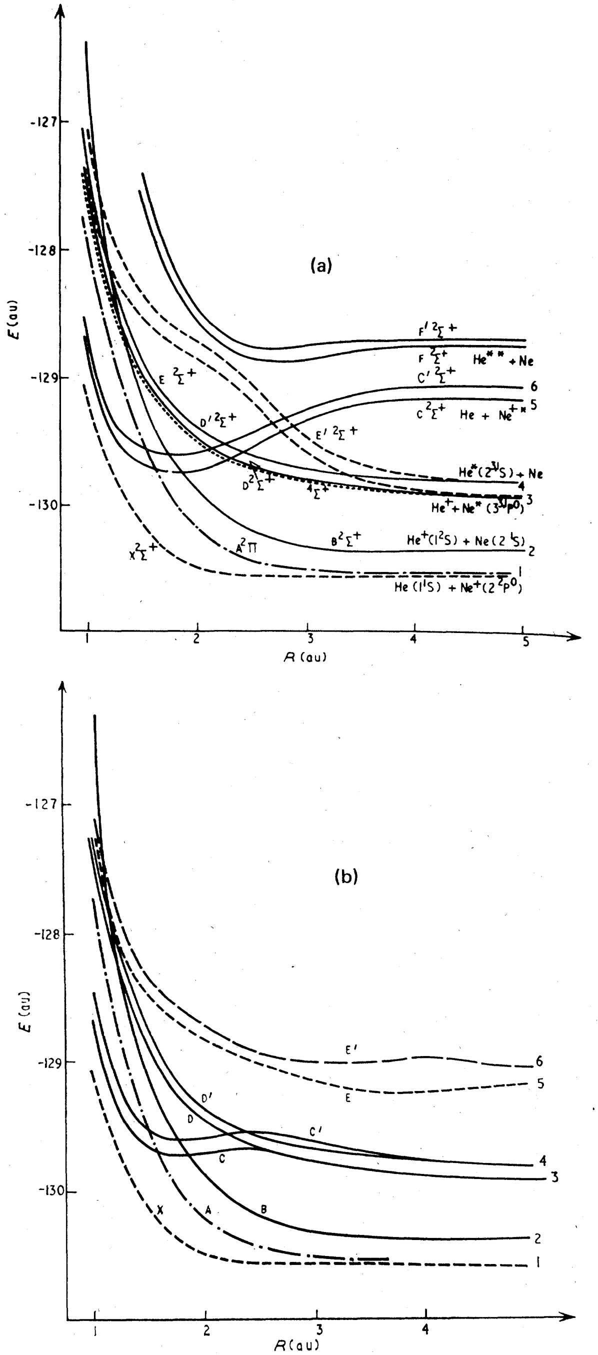

FIG. 19. (a) Potential energy curves for the (HeNe)$^+$ molecular ion computed in the single-configuration approximation. (b) Energy curves for the (HeNe)$^+$ system after diagonalization of the 4 × 4 $CC'EE'$ block of the Hamiltonian (from Sidis and Lefebre-Brion, 1971).

adiabatically, and this is exactly what Sidis and Lefebvre-Brion did. The resulting curves are shown in Fig. 19(b). There remains a crossing between B and new C, C' states for which the coupling is quite small (~0.25 eV). This could also be diagonalized if desired, but that would lead to a less convenient representation.

TABLE VII. Some $^2\Sigma^+$ configurations for the (He-Ne)$^+$ system.

X	$1\sigma^2$	$2\sigma^2$	$1\pi^4$	$3\sigma^2$	4σ	
C	$1\sigma^2$	$2\sigma^2$	$1\pi^4$	$3\sigma^2$	5σ	
C'	$1\sigma^2$	$2\sigma^2$	$1\pi^4$	$3\sigma^2$	6σ	
B	$1\sigma^2$	$2\sigma^2$	$1\pi^4$	3σ	$4\sigma^2$	
E	$1\sigma^2$	$2\sigma^2$	$1\pi^4$	3σ	4σ	5σ
E'	$1\sigma^2$	$2\sigma^2$	$1\pi^4$	3σ	4σ	6σ

b. Inner-shell excitations

Since inner-shell electrons are so much more tightly bound than those in valence shells, inner-shell collisional excitations occur only at energies much higher than those that are appropriate for slow-collision excitations of valence electrons. For collisions fast enough to disturb inner shells, effects on outer shells are violent and chaotic; not only can multiple ionizations and excitations by direct impact occur, but also a variety of complicated secondary electronic effects, and theoretical understanding of these is not yet very advanced (one approach has been developed by Garcia and Schmid, 1976, 1977).

However, if vacancies are created in inner shells, it is possible to identify these separately, from the high-energy electrons or photons subsequently emitted through autoionization, Auger effect, or x-ray emission, and such specific inner-shell processes have been the subject of much experimental study. Of course, if the collision energy is really high, inner as well as outer-shell excitations can be treated by Born-type approximations or classical models such as the binary encounter approximation. At lower energies, however, the observed selective nature of inner-shell excitations (especially the existence of rather sharp onset thresholds) soon led to the recognition that inner-shell molecular orbitals and their potential energy curves play a crucial role. Though "fast" for valence electrons, a collision may be "slow" for the much more tightly bound inner-shell electrons, and many concepts developed for valence shell processes can be applied to inner-shell problems too.

The special feature of inner shells of atoms is that the electron-nucleus attraction strongly dominates over the electron-electron repulsion. Because of this, the independent particle Hartree-Fock or molecular-orbital picture is more accurate for inner shells than for valence shells, and inner shell transitions can be described quite well by considering the behavior of one-electron orbitals and their energies.

Although (as usual) quantitative calculations would require knowledge of the orbital energies as functions of internuclear separation, a good deal of qualitative information can be obtained simply by examining the correlations between united-atom and separated-atom states.

Adiabatic correlation diagrams are obtained using rules given by Mulliken (1928) (see also Herzberg, 1950, p. 329). For equal nuclear charges the orbitals have conserved angular momentum about the internuclear axis (λ) and conserved parity (g, u); correlations are made by connecting united-atom and separated-atom states with no crossings between states of the same symmetry. Atomic orbital energies include effects of screening of the nuclear charge by the inner electrons, so, for example, the energy of the $2s$ orbital lies below that of the $2p$ orbital. The resulting correlation diagram is shown in Fig. 20(a).

Such a diagram can be used to suggest pathways for specific excitations by degeneracy-mediated transitions. For example, it shows that an electron could be excited from the $\sigma_u 1s = 2p\sigma_u$ orbital to the $2p\pi_u = \pi_u 2p$ orbital through the degeneracy in the united-atom limit, as discussed in Sec. IV.B.2. (Of course such a transition can take place only if the latter orbital is empty; hence workers in this area usually speak of the propagation of holes rather than of the excitation of electrons.) On the other hand the diagram also suggests that transitions involving the $2s\sigma_g = \sigma_g 2s$ orbital are very unlikely, because the energy of this state never closely approaches that of any other state of g symmetry.

As experiments in this area progressed, it was quickly recognized that this adiabatic correlation diagram was inadequate. Many specific and apparently degeneracy-mediated transitions occur that are not predicted by this diagram. This led Lichten to suggest that some sort of diabatic correlation diagram might be more appropriate (Lichten, 1963, 1967, 1980; Fano and Lichten, 1965; Barat and Lichten, 1972.)

Again because of the dominance of the electron-nucleus interaction in inner shells, one possible set of diabatic states is obtained by partitioning the electrostatic Hamiltonian into electron-nuclear and electron-electron parts. The Schrödinger equation for one electron in the field of two bare nuclei is separable in prolate spheroidal coordinates (Slater, 1963, p. 1), and each orbital is characterized by three quantum numbers, n_ξ, n_η, and $n_\phi \equiv \lambda$ [ξ and η are the spheroidal coordinates $(r_A + r_B)/R$ and $(r_A - r_B)/R$]. These quantum numbers correspond to conserved "symmetries" that provide a correlation between united-atom and separated-atom states.

To make this correlation for a symmetric molecule, let us first examine the orbitals close to the united-atom limit. Here the spheroidal coordinates (ξ, η, ϕ) go over to spherical coordinates (r, θ, ϕ), and the orbitals go continuously into hydrogenic united-atom states characterized by quantum numbers (n, l, m). Now n_ξ is the number of modes in the ξ-dependent factor in the wave function, and this must go to the number of radial modes in the hydrogenic state, $n_r = n - l - 1$. Likewise n_η is the number of modes in the η-dependent factor, and this must be equal to the number of θ modes, $n_\theta = l - m$.

The azimuthal quantum number λ for the molecule is the same as m for the atom. Hence we have the correspondence

$$\begin{array}{lcl} \text{united atom} & & \text{molecule} \\ n & = & n_\xi + n_\eta + \lambda + 1, \\ l & = & n_\eta + \lambda, \\ m & = & \lambda. \end{array} \qquad (4.49a)$$

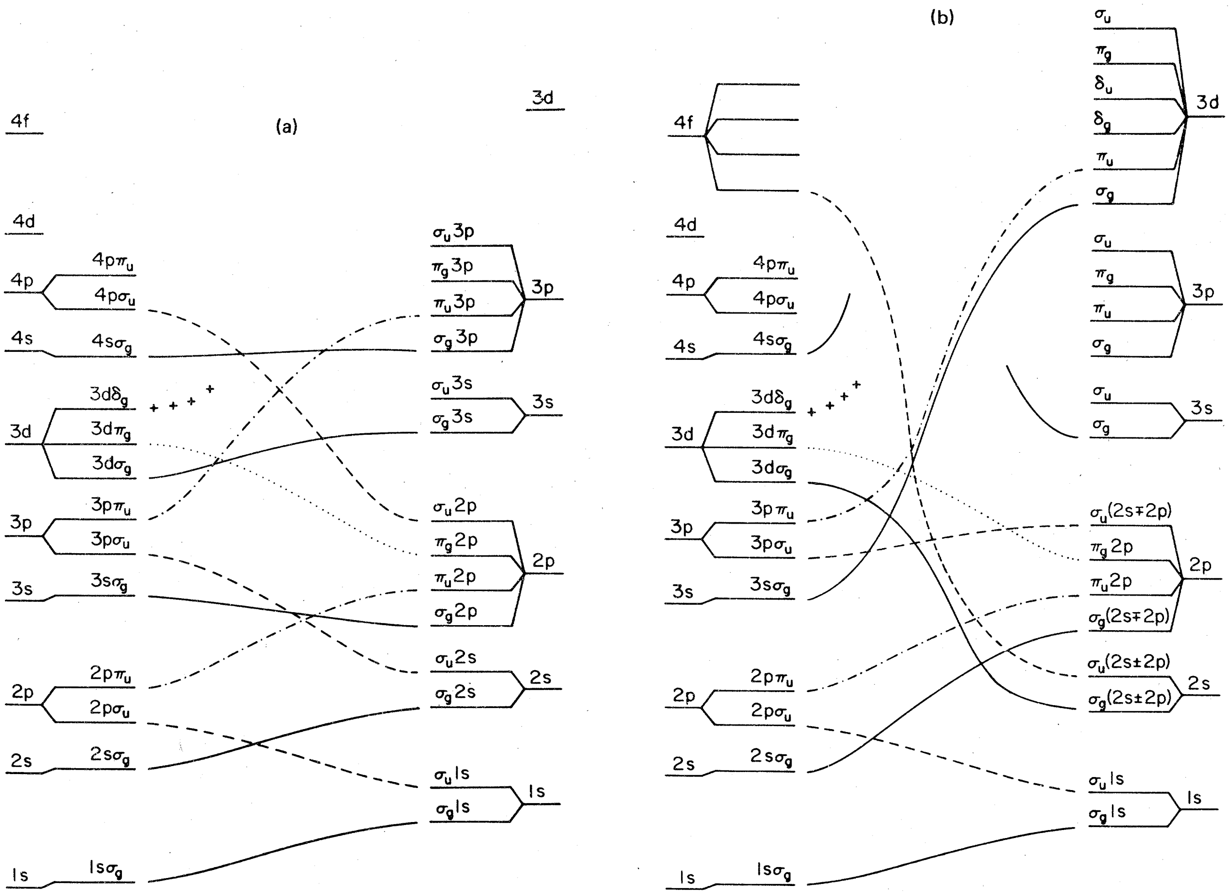

FIG. 20. (a) Adiabatic molecular orbital correlation diagram. (b) Diabatic molecular orbital correlation diagram.

The separated-atom limit is more complicated. The molecular orbitals do not correlate uniquely to atomic states of given (n,l,m): such states are mixed by the field of the other "distant" nucleus (Stark effect). For example, in the $n=2$ level, the appropriate separated atom eigenfunctions would be the linear combinations of degenerate states $2s+2p_z$, $2s-2p_z$, $2p_x$, $2p_y$. (The effects of screening of the nuclear field by inner electrons, which would split this degeneracy, are still being ignored.) Because of the Stark effect, the separated atoms should be described in parabolic coordinates, which are the limit of prolate spheroidal coordinates as $R\rightarrow\infty$ (see Condon and Shortley, 1959, p. 398; Bethe and Salpeter, 1957, p. 228).

The corresponding quantum numbers for the separated atoms are denoted n'_ξ, η'_η, $m'=\lambda$. These quantum numbers again count nodal surfaces of each type. Now, each ellipsoidal nodal surface of the molecule must go over to a parabolic nodal surface of the separated atoms, so we must have $n_\xi=n'_\xi$. The hyperbolic nodal surfaces of the molecule are divided between the two atoms: half go to A and half go to B, with possibly one left over. Thus we have the correlations,

$$\begin{array}{lcl} \text{molecule} & & \text{separated atoms} \\ \eta_\xi & = & n'_\xi, \\ n_\eta & = & 2n'_\eta \text{ or } 2n'_\eta+1, \\ \lambda & = & m'. \end{array} \tag{4.49b}$$

The resulting correlation diagram is shown in Fig. 21. It differs significantly from that in Fig. 20(a): the neglect of screening by inner electrons leaves more degeneracies in separated-atom and united-atom limits, but, more important, it allows a higher degree of "promotion" of orbitals and more crossings of states. Note, for example, the crossing of the $2s\sigma_g$ and $3d\sigma_g$ orbitals which might mediate a transition from the $2s\sigma_g$ level.

The effects of screening of the nuclear field by inner electrons are not easy to guess without a quantitative calculation. In the separated-atom limit and in the united-atom limit, this screening causes orbitals of higher l to have higher energy, and because of this, Barat and Lichten originally suggested another correlation diagram in which, for example, the crossing between $2s\sigma_g$ and $3d\sigma_g$ states does not appear. However, quantitative calculations made by Larkins (1972) and Eichler, Wille, Fastrup, and Taulbjerg (1976) showed that the Barat-Lichten correlations were incorrect in that one aspect. Correlations obtained by Eichler *et al.* are shown in Fig. 20(b).

Figure 22 shows their quantitative calculation of molecular orbital energies for the Ar-Ar system. Because screening was included, the crossings involving orbitals of the same symmetry are represented adiabatically as avoided crossings. Estimating the coupling strength and the forces in these regions, and using the Landau-Zener formula (rule 3 of Sec. IV.A.5), they showed that the system usually behaves diabatically at the collision velocities of interest, in accord with the correlation diagram [Fig. 20(b)].

At present there remains some uncertainty about the size of the h_{12} matrix element, and particularly about how its magnitude varies as different systems are considered. Obviously, whenever it is large, the system behaves adiabatically over a larger velocity range. The assumption of adiabatic behavior at the crossings in-

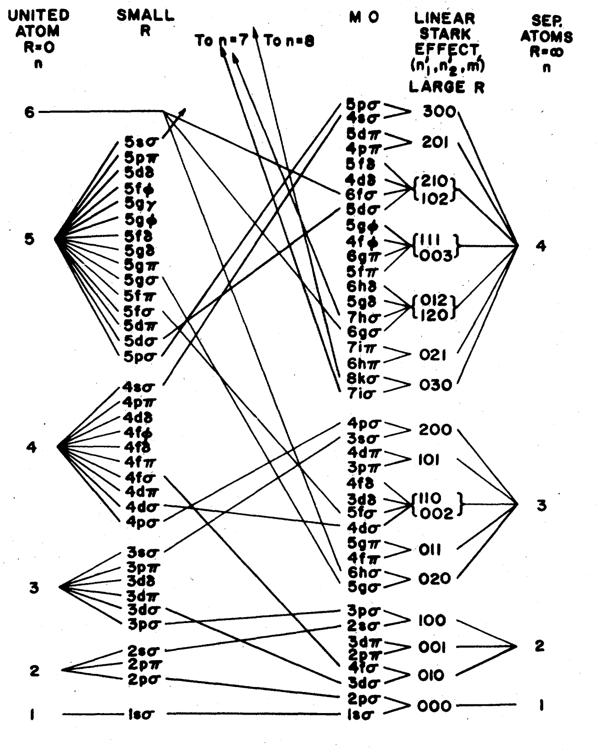

FIG. 21. Correlation diagram for σ states of a symmetric, one-electron system, as given by Barat and Lichten.

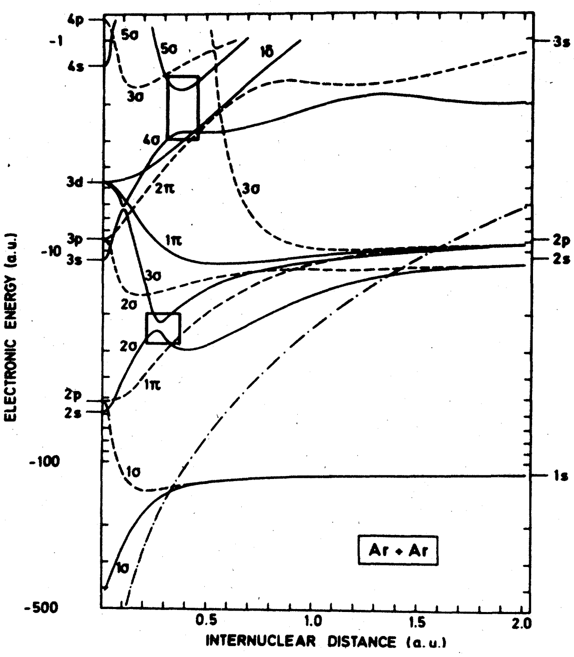

FIG. 22. Molecular orbital energies obtained by Eichler *et al.* (1976) for the Ar-Ar system. Energies of orbitals having the same symmetry avoid crossing, and the diabatic correlation diagram is obtained by drawing smooth crossing curves through these regions.

dicated by boxes in Fig. 22 leads to the Barat-Lichten correlation diagram. As of this writing, a definitive theoretical calculation of h_{ij} matrix elements is not available, but relevant experiments have been carried out by Meyerhof *et al.* (1979).[15]

c. Covalent-ionic transitions

Many systems of special interest in chemistry exhibit transitions from a covalent state, in which the active electron is shared by the two atoms, to an ionic state, in which the active electron is associated primarily with one atom. Transitions that occur by this mechanism include

$$\mathrm{Na} + \mathrm{Cl} \rightleftarrows \mathrm{Na}^+ + \mathrm{Cl}^-$$

and more generally

$$M + X \rightleftarrows M^+ + X^- \tag{4.50}$$

where M is an alkali atom and X is hydrogen or a halogen. Such systems have long been the subject of research (Polanyi, 1932; Magee, 1940, 1952; Bates and Boyd, 1956; Berry, 1957).

In the simplest model of such reactions, the energy of the covalent state is taken to be approximately independent of R at distances greater than about $5a_0$:

$$h_{11}(R) \sim \text{constant}, \quad \text{or perhaps} \sim -C_{\mathrm{cov}}/R^6 . \tag{4.51}$$

The ionic state has a higher energy as $R \to \infty$. The asymptotic energy gap Δ is equal to the difference between the ionization potential of M and the electron affinity of X. However, because of the long-range Coulomb attraction between the ions (and the smaller interaction between the charge and the induced dipole), the energy of the ionic state decreases substantially with decreasing R, so that at some (usually fairly large) distance it crosses the covalent curve. A good empirical representation of the ionic potential curve was proposed by Rittner (1951):

$$\begin{aligned} h_{22}(R) = {} & \Delta - 1/R - (\alpha_+ + \alpha_-)/2R^4 \\ & - 2\alpha_+\alpha_-/R^7 - C_{\mathrm{ion}}/R^6 + A\exp(-R/\rho) , \end{aligned} \tag{4.52}$$

where α_+ and α_- are the polarizabilities of the positive and negative ions, and the other constants are empirical or semitheoretical parameters. This intuitive picture immediately provides the crossing diabatic curves (Fig. 23), and much can be learned about the behavior of these systems by simply guessing a form for $h_{12}(R)$ and solving the resulting coupled equations (see, for example, the review by Baede, 1975, and work by Faist and Levine, 1976).

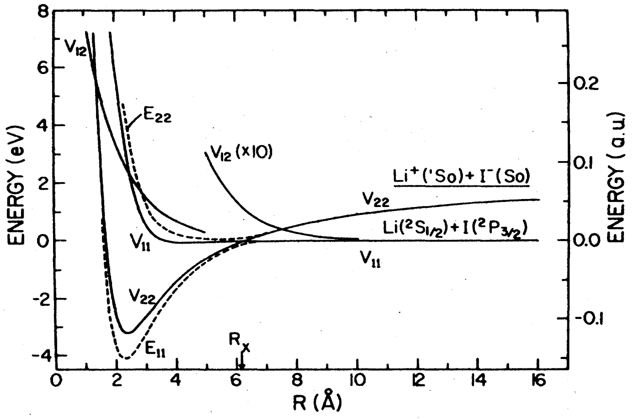

FIG. 23. Approximate diabatic and adiabatic potential energy curves for the Li-I system, showing the crossing between covalent and ionic states. E_{11} and E_{22} are the corresponding adiabatic levels, and the Li$^+$-I$^-$ asymptote is also shown (Faist and Levine, 1976).

A complete *ab initio* calculation would include evaluation of the coupling matrix element h_{12}, but obtaining a simple estimate of this quantity is not so easy. From a large amount of theoretical and experimental information on charge transfer processes, Olson, Smith, and Bauer (1971) obtained an empirical correlation between $h_{12}(R_x)$ and R_x. Their empirical correlation is given by the following formula: Define

$$H_{12}^* = h_{12}(R_x)/(I_1 I_2)^{1/2} ,$$

$$R_x^* = \tfrac{1}{2}[(2I_1)^{1/2} + (2I_2)^{1/2}]\, R_x ,$$

where I_1, I_2 are the ionization potential or electron affinity for the initial and final states of the exchanged electron; then

$$H_{12}^* = R_x^* \exp(-0.86R_x^*) . \tag{4.53}$$

Their graph of H_{12}^*/R_x^* vs R_x^* is shown in Fig. 24; the points represent values for various specific systems, and the solid line is the empirical correlation (4.53), which is a least-squares fit to the points. They find that 83% of the data fall within a factor of 3 of this line. This empirical correlation is helpful for first estimates, but it has limited usefulness for quantitative calculations because cross sections are often quite sensitive to the value of h_{12} (the Landau-Zener formula contains h_{12}^2 in an exponent), and a small error in h_{12} can become a large error in the calculated cross section.

For *ab initio* calculation of h_{12}, wave functions are needed for the covalent and ionic states. Alkali hydrides (e.g., LiH, NaH, etc.) can be treated in good approximation as "two-active-electron" systems, and the Heitler-London valence bond form gives a simple wave function for the covalent state:

$$[\phi_M(1)\phi_X(2) \pm \phi_X(1)\phi_M(2)][\alpha(1)\beta(2) \mp \beta(1)\alpha(2)] . \tag{4.54}$$

The ionic state is more difficult to describe accurately, but one possible wave function is

$$[\phi_X(1)\phi_X'(2) \pm \phi_X'(1)\phi_X(2)][\alpha(1)\beta(2) \mp \beta(1)\alpha(2)] \tag{4.55}$$

where ϕ_X' is usually taken to be a rather diffuse orbital centered on the X atom (Chandrasekhar, 1944; Shull and Lowdin, 1956; Goddard, 1968).

If ϕ_M, ϕ_X, and ϕ_X' are fixed so that they give the best possible description of the separated atoms, then these wave functions, [Eqs. (4.54) and (4.55)], form an F-diabatic basis. Using such a basis, Numrich and Truhlar

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[15] More detailed reviews of theory and experiments on inner-shell excitations have been written by Garcia, Fortner, and Kavanaugh (1973) and by Briggs (1976). Since then work in this area has remained very active; for an overview of recent work, the best source is the ICPEAC proceedings.

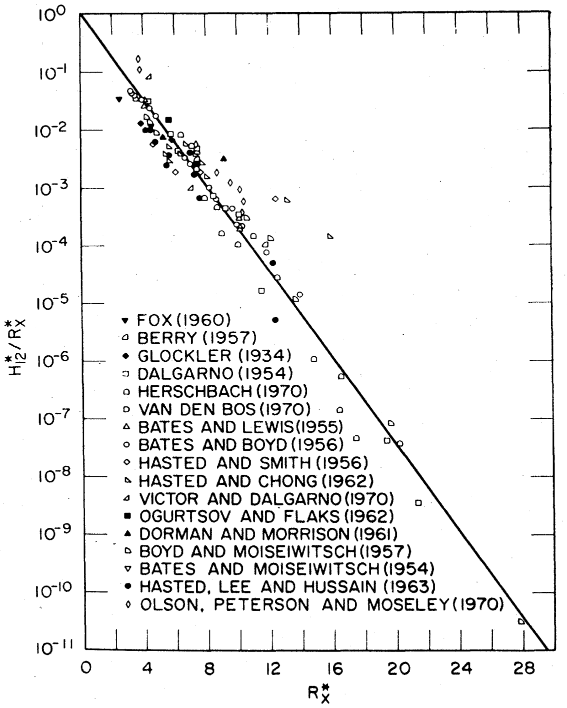

FIG. 24. Empirical correlation between H^*_{12} and R^*_x obtained by Olson, Smith, and Bauer (1971).

(1975) have carried out very detailed calculations of potential energy curves and coupling matrix elements for some alkali hydrides (NaH, KH, and MgH^+). Their calculations show quite clearly the problems associated with the use of limited F-diabatic basis sets. For example, since their basis was not large enough or flexible enough to account for polarization of the ions, they had to add an empirical polarization potential to the ionic curve. Also, since the wave functions $(\phi_u, \phi_x, \phi_x')$ did not represent exact atomic states, empirical adjustments to the energies were made at $R=\infty$. Even with such adjustments, it was found that the calculated energy curve for the ionic state of NaH was insufficiently attractive to cross the energy of the lowest covalent state. The existence of such a crossing is not disputed, however; more flexible wave functions should give lower energies, and perhaps show this crossing.

Calculations with larger or more flexible basis sets can be made; for example Brown and Shull (1968) obtained quite accurate energies for the LiH molecule using a many-term wave function containing explicit correlation. However, such calculations ultimately lead to the Born-Oppenheimer states, which provide the adiabatic, noncrossing representation. A partitioning of the electrostatic Hamiltonian that is suitable for accurate calculation of diabatic states for these systems has not been found.

However, this does not mean that diabatic states are not defined for such systems—it only means that they are not very accessible. They can still be defined by the requirement that selected parts of $\underline{P}^R+\underline{A}^R$ vanish. Probably the only way they can actually be constructed is by (i) obtaining adiabatic Born-Oppenheimer states and $\underline{P}^R$ matrix elements through a large variational calculation, (ii) identifying the displacement part of $\underline{P}^R$ either by inspection or by one of the methods for calculating $\underline{A}^R$, and (iii) calculating the transformation matrix $\underline{W}$ satisfying Eq. (4.30). The critical question in this approach is whether the results will be sensitive to $\underline{A}^R$, and if so, whether a suitable $\underline{A}^R$ can be specified. (Of course, once the adiabatic $\underline{P}^R+\underline{A}^R$ is available, it is not clear whether or not construction of diabatic states is worth the effort.[16])

4. Resonant charge exchange

Resonant charge exchange, as in

$$H^+ + H(1s) \rightarrow H(1s) + H^+ , \qquad (4.56)$$

has been well understood for many years (see, for example, Mott and Massey, 1965, pp. 430ff, and Mapleton, 1972, Chapters 1 and 2). As in Sec. II.B, an atomic state representation, which is diabatic with respect to the electrostatic interaction between the electron and the incident proton, is suitable at high collision velocities. Corresponding adiabatic states are just the Born-Oppenheimer electronic states for H_2^+, and their energies can be calculated exactly by separation of variables (Fig. 18). The lowest two states have, respectively, g and u symmetry, and they are therefore not coupled by electrostatic interactions or by $\underline{P}^R$.

As discussed in Sec. IV.A, the A matrix has been calculated for this system using several methods. Since the switching functions have ungerade symmetry, $\underline{A}$ does not couple g to u states, and it vanishes in the two-state $(1s\sigma_g, 2p\sigma_u)$ manifold. $\underline{\gamma}$ vanishes because the states are eigenfunctions of h, and for identical nuclei, none of the matrices in Table IV have couplings between g and u states. The $\underline{I}$ matrix has nonvanishing, but very small, diagonal matrix elements, which are usually neglected. Accordingly, resonant charge exchange is described as coherent elastic scattering on the two potential curves ϵ_g, ϵ_u (or $\epsilon_g + I_g, \epsilon_u + I_u$ if this level of accuracy is needed).

5. Charge exchange in isotopic systems

The process

$$H^+ + D(1s) \rightarrow H(1s) + D^+ \qquad (4.57)$$

is the paradigm for this type of collision, that involves symmetric but not homonuclear molecules. The reaction as written is endothermic by about 30 cm^{-1} $\simeq 0.0037$ eV, because the reduced masses for the electron are different on H and D. If this difference can be neglected, then it is intuitively obvious that this process must be identical to Eq. (4.56).

Such a result does not come directly out of the unmodified PSS theory, however. The Born-Oppenheimer wave functions and energy levels are essentially the same for H_2^+ as for HD^+, but the $\underline{P}$ matrix is quite different. Since ∇_R is to be evaluated holding $\mathbf{r}'$ fixed

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[16] Other calculations of h_{12} for covalent-ionic transitions have been made by Adelman and Herschbach (1977) and Janev and Radulović (1978). See also the review by Janev (1976).

relative to the center of mass of the molecule, a coupling between g and u states arises which does not go to zero as the nuclear masses go to infinity [Eq. (3.28)]. This fact was one of the reasons we developed the theory in Sec. III.C. It is now easy to show that the "fictitious" (g,u) coupling of Eq. (3.28) is exactly canceled by the $\underline{A}$-matrix element, so in this level of approximation the scattering in HD$^+$ is identical to that in H$_2{}^+$.

At very low energies (threshold to ~0.1 eV) the reduced-mass discrepancy becomes significant. Its effects are contained in the $\underline{I}$ matrix, which has both diagonal and off-diagonal (g,u) elements. In the limit as $R\to\infty$, one can show that the matrix elements of $\underline{I}$ between *degenerate* states are

$$I_{kn}(R\to\infty)=-\frac{\hbar^2}{2\mu}\langle\phi_k|\nabla_R^2|\phi_n\rangle \text{ for } \epsilon_k=\epsilon_n\,. \tag{4.58}$$

Consider the states ϕ_{n_A}, ϕ_{n_B} which were defined in Eq. (3.12); these are like atomic A and B states, but they are scaled by the molecular electronic reduced mass. As $R\to\infty$, the g and u Born-Oppenheimer states become linear combinations of these two states. It is easy to show from Eq. (4.58) that (at large R)

$$\begin{aligned}I_{AA}(R\to\infty)&=-\frac{\hbar^2}{2\mu}\langle\phi_{n_A}|\nabla_R^2|\phi_{n_A}\rangle\\&=-\tfrac{1}{2}\hbar^2(m_A^{-1}-m^{-1})\langle\phi_{n_A}|\nabla_{r_A}^2|\phi_{n_A}\rangle\,,\end{aligned} \tag{4.59}$$

$$\begin{aligned}I_{BB}(R\to\infty)&=-\frac{\hbar^2}{2\mu}\langle\phi_{n_B}|\nabla_R^2|\phi_{n_B}\rangle\\&=-\tfrac{1}{2}\hbar^2(m_B^{-1}-m^{-1})\langle\phi_{n_B}|\nabla_{r_B}^2\ \phi_{n_B}\rangle\,,\end{aligned} \tag{4.60}$$

$$I_{AB}(R\to\infty)=0\,.$$

and from this we obtain the matrix elements of $\underline{I}$ in the molecular representation

$$\begin{aligned}I_{gg}(R\to\infty)&=I_{uu}(R\to\infty)\\&=-\tfrac{1}{2}\hbar^2[\tfrac{1}{2}(m_B^{-1}+m_A^{-1})-m^{-1}]\langle\phi_{n_B}|\nabla_{r_B}^2|\phi_{n_B}\rangle\,,\end{aligned} \tag{4.61a}$$

$$\begin{aligned}I_{gu}(R\to\infty)&=I_{ug}(R\to\infty)\\&=-\tfrac{1}{2}\hbar^2\tfrac{1}{2}(m_B^{-1}-m_A^{-1})\langle\phi_{n_B}|\nabla_{r_B}^2|\phi_{n_B}\rangle\,.\end{aligned} \tag{4.61b}$$

Conversely, by starting from the Born-Oppenheimer states and diagonalizing $\underline{h}+\underline{I}$ as $R\to\infty$, essentially exact atomic state energies are recovered.

These collisions provide an example of asymptotic near-degeneracy. The Born-Oppenheimer states are adiabatic with respect to electrostatic interactions, which dominate at small R, but they are diabatic with respect to the electron-reduced mass ("isotopic") coupling $\underline{I}$, which dominates as $R\to\infty$. They therefore constitute the *internal* diabatic representation. There are several ways to choose an external diabatic representation. The atomic states ϕ_{n_A}, ϕ_{n_B} (or $\phi_{n_A}^0$, $\phi_{n_B}^0$) are F diabatic, but only suitable for fast collisions. An M-diabatic representation is obtained using linear combinations of exact Born-Oppenheimer states,

$$\begin{aligned}\tilde{\phi}_n^A&=(\phi_{n_g}-\phi_{n_u})/\sqrt{2}\,,\\\tilde{\phi}_n^B&=(\phi_{n_g}+\phi_{n_u})/\sqrt{2}\,.\end{aligned} \tag{4.62}$$

These two states go to ϕ_{n_A}, ϕ_{n_B} as $R\to\infty$, but they are orthogonal at all R. They are diabatic with respect to the electrostatic interaction within a given (g,u) pair, but they are adiabatic with respect to electrostatic couplings to other states, i.e.,

$$\langle\tilde{\phi}_k^A|h_{\mathrm{BO}}|\tilde{\phi}_n^B\rangle=0\,,\quad k\neq n$$

$$\langle\tilde{\phi}_k^A|h_{\mathrm{BO}}|\tilde{\phi}_k^B\rangle\neq 0\,.$$

For either definition of the external diabatic representation, $\underline{I}$ is diagonal at large R.

There is a representation which is adiabatic with respect to both electrostatic and isotopic coupling. It is obtained from the Born-Oppenheimer representation by a 2×2 matrix $\underline{U}$ which diagonalizes $\underline{h}+\underline{I}$. The states change their character continuously from atomic at large R to molecular at smaller R; the change is most rapid in the critical region in which h_{AB} is comparable to the isotopic energy gap, $I_{AA}-I_{BB}$. The eigenvalues W_k of $\underline{h}+\underline{I}$ are the energies of these states, and they also go continuously from atomic to molecular limits as indicated schematically in Fig. 25. Coupling between these adiabatic states is caused by the term $U^\dagger(-i\hbar\nabla_R\underline{U})$.

How does the system actually behave, and which representation is most convenient for describing that behavior? To illustrate the rules given in Sec. (IV.A.5), we carry them out in detail for this case. The energy range of interest is from 0 to 1 eV, corresponding to relative collision velocities <0.007 a.u. There are no crossings, so we go to rule 4. Starting naively with the F-diabatic $(1s_A, 1s_B)$ states, we find that electrostatic matrix elements h_{ij} to other atomic states $(2s_A\cdots)$ have magnitudes of several eV and ranges of a few a_0, so at the low velocities of interest, those couplings should be treated adiabatically (of course!).

Such a treatment brings us to the M-diabatic representation of Eq. (4.62). Now, examining

$$\hbar^{-1}\int\langle\tilde{\phi}_{1s_A}|h|\tilde{\phi}_{1s_B}\rangle dt\,,$$

we also find that this is large. To estimate η_{RZD}, Δ is

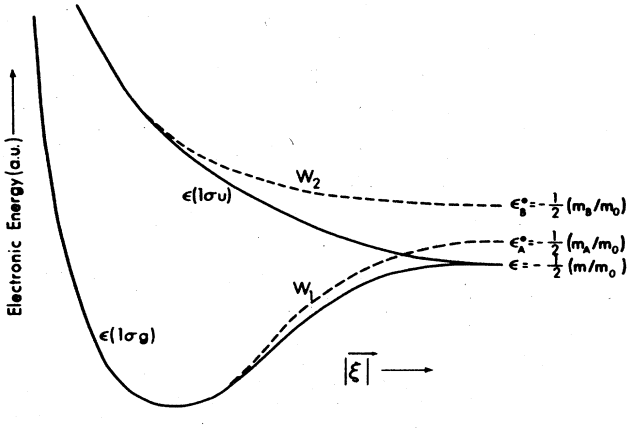

FIG. 25. Qualitative energy diagram for an electrically symmetric but heteronuclear ("isotopic") molecule. Solid lines are Born-Oppenheimer eigenvalues, $\epsilon(1\sigma g)$, $\epsilon(1\sigma u)$, vs R. Dotted lines are fully adiabatic eigenvalues, obtained by diagonalizing $\underline{h}+\underline{I}$. The isotopic splitting is exaggerated several thousandfold for clarity.

the isotope splitting (0.0037 eV), and d is the range parameter of $h_{1s_A 1s_B}$ (about $1a_0$). Hence for relative collision energies ~1 eV, we find $\delta_{\mathrm{RZD}} \sim 0.02$, and the system undergoes a sudden transition between atomic and molecular regimes. The "split" representation could be used for this problem, because it gives the best zero-order description. (In actual numerical calculations, usually the internal diabatic Born-Oppenheimer states have been used.[17])

6. Near-resonant charge exchange in unsymmetric systems

Charge exchange between unlike alkali ions and atoms,

$$M_1^{+} + M_2 \rightarrow M_1 + M_2^{+} \tag{4.63}$$

provides additional examples of transitions mediated by an asymptotic near-degeneracy. For example, for the reaction

$$\mathrm{Li}^{+} + \mathrm{Na} \rightleftarrows \mathrm{Li} + \mathrm{Na}^{+}, \tag{4.64}$$

the ionization potential of Li is 5.390 V and that of Na is 5.138 V, so the energy gap between initial and final states is only 0.25 eV. A very careful and complete study of process (4.64) was carried out by Melius and Goddard (1974b), and we shall follow their discussion.

Of the thirteen electrons in the (Li-Na)$^+$ molecule, twelve of them are in "core" orbitals that remain essentially unchanged over a large range of internuclear separations ($R \gtrsim 3.5a_0$); hence we can regard the molecule as a system having a single active electron moving in an effective potential field due to the nuclei and the core electrons. Melius and Goddard (1974a) constructed an effective potential based on a modified Hartree-Fock approximation, and obtained Born-Oppenheimer wave functions as eigenstates of a one-electron Hamiltonian containing this effective potential. Energies of these states are shown in Fig. 26.

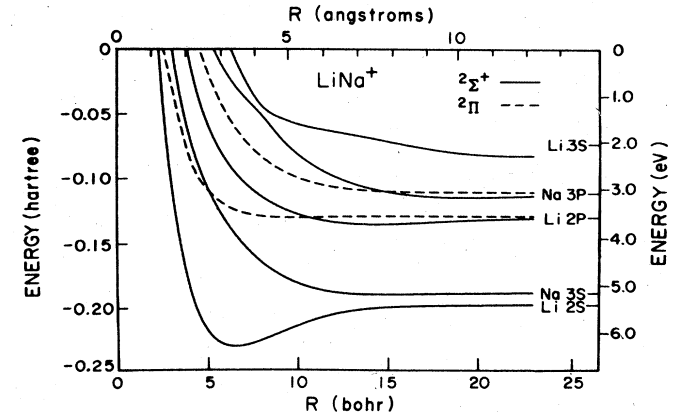

FIG. 26. Energy curves for the LiNa$^+$ system, as obtained by Melius and Goddard (1974b). Solid curves are $^2\Sigma$ and dashed curves are $^2\Pi$ states.

The two lowest Born-Oppenheimer wave functions, ϕ_1, ϕ_2, have atomic character at large R, since they correlate, respectively, to the Li($2s$) or Na($3s$) states, but they have molecular character at small R. Change of character occurs continuously over a fairly broad range of R, from about 10 to $16a_0$, and transitions between these states are most likely to occur in this "critical region" induced by the (1,2) matrix element of $\underline{P}^R + \underline{A}^R$.

As usual $\underline{P}^R$ represents the total change of the basis states with R, and $\underline{A}^R$ cancels the displacement part of $\underline{P}^R$. In this case $\underline{A}^R$ is substantial, so it must be calculated with a reasonable level of accuracy. Now, in view of the asymptotic correspondence to atomic states, we might estimate $\underline{A}^R$ by treating the states as if they were class F (or class V) states: $\mathbf{s}_n$ would then be given by Eq. (4.9), and $\mathbf{A}_{kn}$ by (2.64a), so

$$\begin{aligned}(P^R + A^R)_{12} &= -i\hbar\langle\phi_1|(\partial/\partial R + \kappa_2\partial/\partial z)|\phi_2\rangle\\ &= -i\hbar\langle\phi_1|(\partial/\partial R)_{r_{\mathrm{Na}}}|\phi_2\rangle \equiv -i\hbar M_{12}^{\mathrm{Na}},\end{aligned} \tag{4.65a}$$

$$\begin{aligned}(P^R + A^R)_{21} &= -i\hbar\langle\phi_2|(\partial/\partial R + \kappa_1\partial/\partial z)|\phi_1\rangle\\ &= -i\hbar\langle\phi_2|(\partial/\partial R)_{r_{\mathrm{Li}}}|\phi_1\rangle \equiv i\hbar M_{12}^{\mathrm{Li}}.\end{aligned} \tag{4.65b}$$

These quantities are displayed in Fig. 27. We see that the difference between M_{12}^{Na} and M_{12}^{Li} is very substantial; this difference is proportional to the non-Hermitian

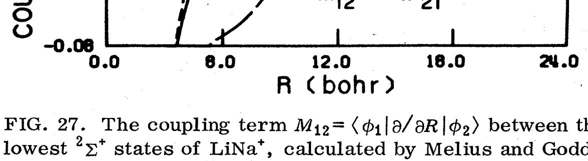

FIG. 27. The coupling term $M_{12} = \langle\phi_1|\partial/\partial R|\phi_2\rangle$ between the two lowest $^2\Sigma^+$ states of LiNa$^+$, calculated by Melius and Goddard (1974b). M_{12}^{Li} and M_{12}^{Na} refer to derivatives taken holding $\mathbf{r}_{\mathrm{Li}}$ or $\mathbf{r}_{\mathrm{Na}}$ fixed. M_{12}^{GTO} and M_{21}^{GTO} are nonadiabatic couplings calculated by what they called the generalized traveling orbital method, and what we call the "special-$\mathbf{s}_\mu$'s." M_{12} is the coupling matrix element they used in their calculations. (BM means Bates and McCarroll.)

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[17] Mott and Massey (1965, p. 433) did not recognize that the $\underline{P}$-matrix element was a "fictitious" coupling, so they gave a qualitative discussion of what effects it must have. We can now see that their comments are inappropriate.

Hunter and Kuriyan (1975, 1977b) made calculations on the HD$^+$ system at $E \lesssim 1$ eV using a modified form of PSS theory. They scaled the atomic wave functions to obtain exact asymptotic energies, but they did not eliminate the fictitious (g,u) coupling. It is believed that the error introduced thereby is negligible in this case at these very low energies; however, that error will increase at higher collision velocities. Another calculation was made by Davis and Thorson (1978) eliminating the fictitious coupling. Calculations on predissociation of some states of HD have been made by Thorson (1971) and Durup (1978), and predissociation in He^{3}He^4 has been examined by van Asselt, Maas, and Los (1976).

part of A_{12}^R, and it shows that A_{12}^R is not small.

The above method of calculation of A_{12}^R is unlikely to be accurate except at large R, because it is based on the assumption that the states have atomic character, whereas in fact their two-center molecular character increases with decreasing R. Therefore, Melius and Goddard also (indirectly) used what we call the "special" $\mathbf{s}_\mu$'s of Eq. (4.8) to calculate $P_{12}^R + A_{12}^R$, i.e., they expanded the Born-Oppenheimer states in terms of atomic states and attached an atomic $\mathbf{s}_n$ to each of the latter. (They called this the "generalized-traveling-orbital" or GTO method.) The resulting matrix elements of $P_{ij}^R + A_{ij}^R \equiv \pm i\hbar M_{ij}$ are also shown in Fig. 27. Since they differ significantly from the matrix elements in Eqs. (4.65) it is evident that this more difficult calculation is necessary. These GTO matrix elements should give a reasonable representation of the nonadiabatic couplings, and they could have been used in the calculation of cross sections.

The general theory discussed herein was not available when Melius and Goddard did their work, and they were not satisfied with the GTO matrix elements, partly because they were concerned about the uniqueness of the atomic orbital expansion, and perhaps partly because of the non-Hermitian character of the GTO coupling matrix (this last can now be recognized as a valid result). They therefore chose a different method, which can be described in the present framework in the following way. Suppose we take a switching function that depends on the nuclear coordinate R, but not on the electronic coordinate r: $f_n = f_n(R)$. Furthermore, let us use not only "different f's for different states" but also "different f's for different matrix elements." Thus we replace $f_n(R)$ by $f_{kn}(R)$, and Eq. (2.64a) becomes

$$\mathbf{A}_{kn} = \mathbf{p}_{kn} \kappa_{kn},$$

with

$$\kappa_{kn}(R) = \tfrac{1}{2}[f_{kn}(R) + \lambda].$$

Finally let us choose $\kappa_{kn}(R)$ such that

$$\kappa_{kn}(R) = \int |\phi_k \phi_n| z \, d^3r / R \int |\phi_k \phi_n| \, d^3r,$$

where, as usual, z is the electron coordinate parallel to the internuclear axis. This method is equivalent to using a certain weighted average of $\mathbf{r}_A$ and $\mathbf{r}_B$ as the electron coordinate which is to be held fixed in calculating $\partial/\partial R$. Since κ_{12} is the same as κ_{21}, the $\underline{A}^R$ matrix is Hermitian. The resulting $\underline{P}_{12}^R + A_{12}^R$ matrix element is also shown in Fig. 27 (denoted $M_{12}^{\bar{z}}$), and this is what Melius and Goddard used in their calculation.

Although the result is reasonable, this is probably not the best possible method of calculating nonadiabatic couplings. In using an f that is independent of r, this approach does not really account for the two-center, molecular character of the basis functions. Also, since it uses a matrix f_{kn} or κ_{kn}, displacement effects are not associated with each individual state; this is somewhat different from the intuitive picture we have been developing, in which $\partial\phi_n/\partial R$ can be separated into a displacement part and a coupling part.

Diabatic states for this system were also calculated by two methods. Again class F states were found to be an unacceptable representation for slow collisions, but an M-diabatic representation was obtained by integration of Eq. (4.30) using $D_{12} = -i\hbar M_{12}^{\bar{z}}$. [Actually Melius and Goddard effected the integration by fitting their $M_{12}^{\bar{z}}$ to an assumed analytic form of $\partial\omega/\partial R$, from which they were able to extract information about the diabatic Hamiltonian matrix. Later Dinterman and Delos (1977a) obtained substantially the same result by exact numerical integration of Eq. (4.30) using the same $M_{12}^{\bar{z}}$.] As in the paradigm of asymptotic near degeneracy considered in Sec. IV.A.4.b, it was found that the diabatic h_{11} and h_{22} are approximately parallel, and h_{12} has an exponential dependence on R.

7. Fine-structure transitions

One example of a collision leading to a fine-structure transition is

$$\mathrm{Na}(3p\,{}^2P_{3/2}) + G \rightarrow \mathrm{Na}(3p\,{}^2P_{1/2}) + G\,,$$

where G is a rare-gas atom or some other "inert" target. These transitions occur because of the competing effects of electrostatic, rotational, and spin-orbit coupling. Spin-orbit coupling is responsible for the energy gap between initial and final states, but as the internuclear separation decreases, the electrostatic interaction between the active electron and the target becomes much larger than the spin-orbit interaction. Also, in the rotating molecular frame, angular coupling increases as R decreases, so that it may also become stronger than the spin-orbit coupling. Thus the description of these collisions involves all of the machinery described in the appendix.

Let us examine the atomic states first. Neglecting spin-orbit coupling, the ${}^2P$ term would be characterized by (space-fixed) case d states $|\epsilon L M_L\rangle |S M_S\rangle$ (Table VIII). If these states were rotated to coincide with the molecular frame of reference, we would obtain a representation characterized by $|\epsilon L \Lambda\rangle |S \Sigma\rangle$. Such rotating atomic states are, of course, the asymptotic limit of the Born-Oppenheimer states [these are the states ϕ_{n_A} or $\phi_{n_A}^0$ of Eq. (3.12)].

Either of the above atomic basis sets can be combined into eigenstates of the total electronic (orbital + spin) angular momentum ($j^2, j_{z'}$, or j_z) by means of Clebsch-Gordan coefficients. Such combinations of space-fixed states give the case e representation $|\epsilon L S j m_j\rangle$, and the same combination of rotating states gives the $|\epsilon L S j \Omega\rangle$ representation, which is the asymptotic limit of a general case c representation. For the case of one electron outside a closed shell, if spin-orbit coupling is treated as a perturbation of the terms of the electrostatic Hamiltonian, and its matrix elements between different configurations are neglected, then these states are eigenfunctions of the atomic Hamiltonian including spin-orbit coupling (Condon and Shortley, 1959, p. 120).

For each of the above atomic representations there is a corresponding molecular representation. The electrostatic field from the target atom distorts the electronic orbitals, and eigenstates of the electrostatic part of the molecular electronic Hamiltonian (including the field from the target atom but excluding spin-orbit coupling) are the Born-Oppenheimer states, or the case b representation $|\epsilon\Lambda\rangle |S\Sigma\rangle$.

In the collision, transitions between Born-Oppenheimer states are produced by spin-orbit and angular couplings, and by the usual $P^R + A^R$ matrix elements. Frequently the interaction with the target atom is sufficiently weak that the Born-Oppenheimer states retain essentially atomic character; in that case, $\mathbf{A}$ can be calculated by Eq. (2.64a) and $(\mathbf{P} + \mathbf{A})$ becomes $-i\hbar\nabla_R$ with the electron coordinate held fixed relative to the alkali atom.

However, since collisions of this type are primarily of interest at thermal energies, it often is possible to truncate the Born-Oppenheimer representation to the manifold of states that correlate asymptotically to one atomic term. In the present cases such truncation would leave six coupled states, with $\Lambda = \pm 1, 0$ and $\Sigma = \pm \frac{1}{2}$. *Within such a manifold,* $P^R + A^R$ matrix elements all vanish because of symmetry, and the Born-Oppenheimer states satisfy the definition of an internal diabatic representation.

An external diabatic representation is obtained in the following way. The same Clebsch-Gordan coefficients that combine $|\epsilon LS\Lambda\Sigma\rangle$ states into $|\epsilon LSj\Omega\rangle$ states can be used to combine corresponding Born-Oppenheimer states into a new set that we shall call $|\epsilon S\Omega\rangle$ states. The electrostatic Hamiltonian is off-diagonal in this representation, but each of the states correlates uniquely as $R \to \infty$ to a molecule-fixed atomic eigenstate $|\epsilon LSj\Omega\rangle$. Since again $P^R + A^R$ matrix elements still vanish within the manifold considered, these states indeed provide an external diabatic representation.

We may also consider the states which are eigenfunctions of the full molecular electronic Hamiltonian, including both spin-orbit and electrostatic interactions; these provide the case *c* representation $|\epsilon, \Omega\rangle$, which is the adiabatic representation. At small R, where the electrostatic interaction dominates, these go to Born-Oppenheimer states, while at large R, where spin-orbit coupling dominates, they go to atomic $|\epsilon LSj\Omega\rangle$ states.

All of these representations have been used to solve the collision problem. Space-fixed states were used in the formulation given by Reid (1973), the adiabatic representation was chosen by Pascale (1978), and certain combinations of external diabatic states (times heavy-particle angular functions) were used by Mies (1973a, 1973b). (Born-Oppenheimer states are frequently considered in the formulation of the theory, but they have not been used in actual integration of the coupled equations because they are inappropriate at large R.)

In Fig. 28 adiabatic energy curves are shown for the Na($3p\,^2P$) + Ar system (Pascale and Olson, 1976). As mentioned above, they go to atomic energy levels at large R, but essentially to Born-Oppenheimer levels at smaller R. In this representation one can identify two main mechanisms that are responsible for transitions (Dashevskaya, Nikitin, and Reznikov, 1970). In a region around $R \simeq 12a_0$, the adiabatic states are changing their character from $|\epsilon S\Omega\rangle$ (approximately atomic) states to $|\epsilon\Lambda\rangle|S\Sigma\rangle$ (Born-Oppenheimer) states, and transitions are induced by $P^R + A^R$ matrix elements corresponding to this change of character. (This is called mechanism 1.) At smaller R, especially around the turning points for small b, angular couplings due to the rotation of the molecular frame induce transitions between the $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ states (mechanism 2). The relative importance of each of these mechanisms depends upon the particular system. For example, in collisions of Rb with rare gases, it has been found that mechanism 1 is dominant in Rb-He, but mechanism 2 dominates in Rb-Ne and Rb-Ar (Wilson and Shimoni, 1974).[18]

8. Collisional autoionization and electron detachment

The theory of electron detachment,

$$A^- + B \to A + B + e^-,$$

involves the electrostatic interaction of one or more discrete bound states with a continuum of free states. Usually it is assumed that there exists some representation in which the bound state crosses into the continuum. In the case of collisional autoionization,

$$A + B \to A^+ + B + e^-,$$

there is also an infinite series of high Rydberg states converging upon the continuum, and the initial bound state is assumed also to cross this series of levels.

For these processes, diabatic representations are almost always preferable to adiabatic ones. Application of the rules given in Sec. IV.A.5 leads directly to the conclusion that the effects of coupling are weaker in a diabatic representation. Consider for example the interaction between any given bound state ϕ_1 and a high Rydberg state ϕ_n. As the principal quantum number n increases, the Rydberg state becomes more and more diffuse, and any coupling matrix element V_{1n} must go to zero. Following rule 3, one concludes that the dia-

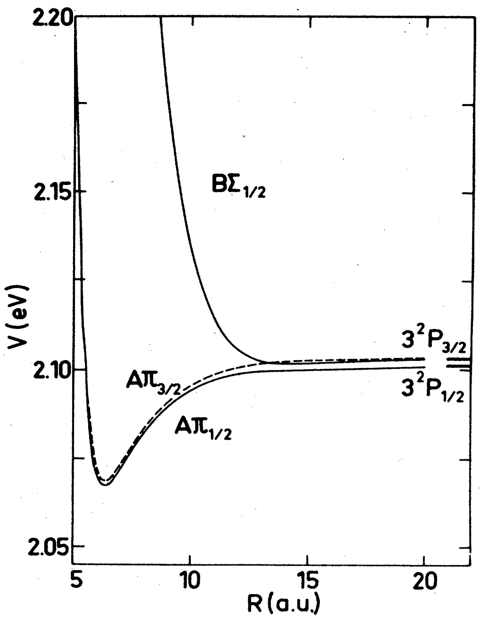

FIG. 28. Adiabatic energies for the Na($3\,^2P$) + Ar system (Pascale and Olson, 1976).

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[18] For further details on these processes, there is a very good review by Nikitin (1975), which contains references to earlier work. More recent papers include calculations by Pascale (1978), Pascale and Stone (1976), and a partly classical model developed by Miller and McCurdy (1978) and McCurdy, Meyer, and Miller (1979).

Another fine-structure transition, I($^2P_{3/2}$) + Br($^2P_{1/2}$) $\to$ I($^2P_{3/2}$) + Br($^2P_{3/2}$), occurs by a mechanism quite different from the two mentioned above; this one is mediated by a curve crossing (Faist and Bernstein, 1976).

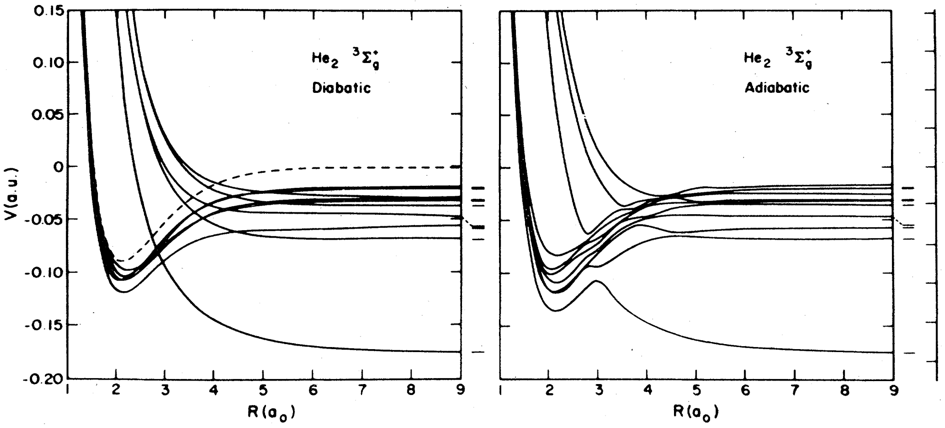

FIG. 29. Diabatic and adiabatic curves for the $^3\Sigma_g^+$ states of the He$_2$ system (Cohen, 1976a).

batic representation becomes more appropriate with increasing n; the same argument can be extended past the continuum boundary. Similarly, the matrix element of any *localized* interaction between two Rydberg states n and n' must also go to zero, so the representation should also be diabatic with respect to such interactions.

Moreover, even without the rules in Sec. IV.A.5 we would still wish to consider diabatic representations of these processes, and indeed diabatic representations were sought and constructed long before the rules were explicitly stated. In the Born-Oppenheimer representation (which in this case is adiabatic), the potential curves avoid crossing, and one must interpret ionization as a long series of transitions between strongly coupled Rydberg and continuum states. The diabatic picture is much simpler; ionization may occur by a single transition from the diabatic state to the continuum [compare Figs. 29(a) and 29(b)].

However, the construction of diabatic states for these systems is not a simple matter. The defining condition, in which appropriate matrix elements of $\underline{P}^R + \underline{A}^R$ are zero or negligible, provides the final test of whether a given representation is diabatic, but it does not tell us directly how to construct such a representation. Since many states are involved, it appears to be impossible (or at least impractical) to reconstruct a diabatic representation from an adiabatic representation by solving Eq. (4.30). We must instead consider the intuitive ideas underlying the formal definition, and use these ideas to guide the construction of a diabatic representation.

As discussed earlier, diabatic states are states that propagate with the nuclei, but otherwise have little or no variation with R. Class F states, which have no variation with R, are too stiff ("too diabatic"), so we must consider states which are carefully constructed to allow some partial (adiabatic) adjustment to the changing molecular field, but with their R variation somehow restricted.

A nice example of such a construction was provided by Cohen (1976a) for the excited triplet states of He$_2$. These excited states can be pictured as having a single electron in a diffuse Rydberg state around a He$_2^+$ core. The He$_2^+$ core has two states, one strongly binding [$^2\Sigma_u^+$; molecular orbital representation $(1s\sigma_g)^2(1s\sigma_u)$] and one strongly repulsive [$^2\Sigma_g^+$; molecular orbital representation $(1s\sigma_g)(1s\sigma_u)^2$]. These are, respectively, called the A core and the B core. The additional electron in a high Rydberg state feels the attractive Coulomb field of He$_2^+$, but otherwise interacts with the core only weakly. It follows that to each atomic Rydberg state there will correspond a pair of g and u molecular states for which the potential curves will be quite similar to those of He$_2^+$. Clearly the set of repulsive B-core curves will cross the set of attractive A-core curves, and the resulting series of crossings will mediate transitions between levels. The elementary transitions are two-electron processes, in which the core is deexcited ($B \rightarrow A$), giving its energy to the Rydberg electron, which then goes to a higher discrete state or to the continuum (autoionization).

In a typical collision between He* and He, the nuclear velocity is such that the He$_2^+$ core behaves essentially adiabatically; however the Rydberg electron behaves more diabatically, and the Rydberg core interaction is also best described diabatically. To describe the core, Cohen used a wave function of the form

$$|\phi_{AB}(\mathbf{r}_1)\phi_{AB}(\mathbf{r}_2)\phi'_{1s_B}(\mathbf{r}_3)| \pm |\phi_{BA}(\mathbf{r}_1)\phi_{BA}(\mathbf{r}_2)\phi'_{1s_A}(\mathbf{r}_3)|\ ,$$

where $\phi_{AB}(\mathbf{r}_1)$ is an elliptic orbital

$$\phi_{AB}(\mathbf{r}_1) = \exp\{-[(\delta+\gamma)r_{1A} + (\delta-\gamma)r_{1B}]/R\}\ .$$

The three orbital exponents, δ, γ, and the one implicit in $\phi'_{1s_{A,B}}$, were all optimized at each internuclear distance.

Rydberg orbitals for the molecular system were taken to be identical to separated-atom Rydberg orbitals, which, in turn, were taken to be hydrogenic (except for s states, which were obtained variationally as a linear combination of Slater-type orbitals). Then the diabatic electronic basis states for the full He*-H system were taken to be antisymmetrized valence-bond-type combinations of products like

$$\phi_{AB}(\mathbf{r}_1)\phi_{AB}(\mathbf{r}_2)\phi'_{1s_B}(\mathbf{r}_3)\phi^{\mathrm{Ryd}}_{nA}(\mathbf{r}_4)\ ,$$

where ϕ^{Ryd}_{nA} is an A-atomic Rydberg orbital. These basis states have exactly the desired properties: The He$_2^+$ core adjusts continuously to the changing position of the nuclei, the Rydberg states propagate with the nuclei, but otherwise are "frozen," and the core does not adjust to the presence of the Rydberg electron. Nonadiabatic couplings $(\underline{P}^R+\underline{A}^R)$ are associated only with the changing orbital exponents in the core, and they are believed to be negligible.

Some of the resulting diabatic energy curves are shown in Fig. 29. Crossings between discrete A-core and B-core curves are evident, as well as crossings between discrete B-core states and the A-core continuum $[\mathrm{He_2}^+ (A)+e^-]$.

Selected diabatic states for H_2, HeH^+, He_2^+, and He_2, had been calculated by O'Malley (1969) using similar ideas. Earlier, O'Malley (1967) had also shown that given one diabatic state, it is possible to calculate an associated "quasiadiabatic representation" by projecting that state out of the basis. Let $P=|\phi^D\rangle\langle\phi^D|$ be a projection operator for the given diabatic state, and let $Q=1-P$. Consider the basis made up from ϕ^D and the set of eigenfunctions $\{\phi^Q\}$ of QhQ (the latter set not including ϕ^D). The functions ϕ^Q may be considered to be adiabatic among themselves, since they are not connected by matrix elements of the electrostatic Hamiltonian. However transitions between ϕ^D and these states are represented diabatically. PhQ corresponds to the electrostatic matrix element coupling ϕ^D to $\{\phi^Q\}$, and the corresponding (P^R+A^R) matrix elements will be negligible if the variation of ϕ^D with R is sufficiently limited.

Actual construction of such an "O'Malley representation" has not been made, but it should not be difficult. However, it is important to note that in this representation all couplings except those involving ϕ^D (or some set of ϕ^D's) are represented adiabatically; as mentioned earlier, such a representation may not be advantageous for Rydberg states or for a continuum.

A definitive calculation of diabatic states has not been made for any negative-ion system, but Olson and Liu (1978) have obtained crossing ionic and neutral curves for HeH^-, ArH^-, and $ArCl^-$ systems using a Hartree-Fock approximation.

There is also another approach to the theory of collisional ionization and electron detachment. This other approach is based on the assumption that the state which crosses the continuum can be described as some sort of quasibound resonance (see, for example, the work of Bardsley, 1967, 1968; Herzenberg, 1967; Chapman and Herzenberg, 1972; Chen, 1967; Miller, 1970). Unfortunately, the relationship between a diabatic state and a quasibound resonance or a virtual state is not yet clear.

V. CONCLUSION

In this article, a part of the theory of electronic excitations in slow atomic collisions has been developed in a logically deductive way. Starting from the Schrödinger equation (in either classical trajectory or fully quantum-mechanical form), we first showed how to obtain a general set of close-coupled equations, then we discussed the general principles underlying the choice of representations, and finally we reviewed calculations on specific systems.

However (as one can see from the references cited in each section), the historical development of the topics considered here was quite different. In fact, calculations were made (successfully, in most cases) long before there was an acceptable underlying theory. The earlier quantum-mechanical calculations were based on unmodified PSS theory, **P** matrix elements were often estimated from models (see Sec. IV.A.4), or diabatic states were obtained by physical intuition. As calculations progressed, the difficulties inherent in this approach grew more and more clear.

What was missing was a proper quantum-mechanical form of close-coupling theory. In the classical trajectory framework, it has been known since the 1958 paper of Bates and McCarroll that electron-translation factors have to be incorporated in the expansion (Sec. II.C). However, an adequate quantum formulation was not developed until much later (the final version of this theory being given here, in Sec. III.C).

Now, starting from this approach, calculations can be set up logically and systematically. One of the pleasures of writing this article (especially Sec. IV.B) has been seeing how descriptions of so many different systems emerge as special cases of a general theory.

One must not conclude, however, that all of the problems in this area have been solved. There is still a great deal to be learned about the behavior of specific systems through computational investigations and comparison of theory with experiments.

Also, a problem still outstanding is that of finding simple but accurate forms for $\mathbf{s}_n$ for molecular states. Very little is known about what forms are "best" and what forms are "good enough" for a given system.

Furthermore, the whole close-coupling approach has obvious limitations. It is adequate if only a few coupled states are involved (and incorporation of good $\mathbf{s}_n$'s helps to reduce the number of states needed). Also, it can still be used for many-state systems if there is only weak coupling. But close-coupling methods are difficult to use to describe systems having strong coupling among many states. Systems in which the initial or final state is highly excited, systems showing ionization or electron detachment, and intermediate-velocity collisions typically involve a very large or an infinite set of coupled equations. In certain cases, techniques have been found for solving such equations; in other cases, the problem has been circumvented (and a new set of problems produced) by abandoning the close-coupling framework.

All of these problems are active subjects of current research.

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APPENDIX: ANGULAR ASPECTS OF THE REPRESENTATION PROBLEM

In most of the text, it is assumed that the electronic basis states can be represented by functions $\phi_n(\mathbf{r}; R)$ which depend only on the internuclear distance R and

TABLE VIII. Hund's coupling cases. (π) in $\lvert\epsilon\Lambda(\pi)\rangle$ means parity is possibly a quantum number for the electronic state. $\lvert JM_J(\Omega)\rangle\!\rangle$ is the abstract vector corresponding to $H^{(\Omega)}_{JM_J}(\Theta,\Phi)$. Ω is a parameter in this function.

Hund's case	Condition	Electronic state representation	Nuclear angular functions	Simple product and vector coupled representations
a	$\Delta\epsilon \gg \hbar\omega \gg \hbar\dot{\Theta}$	$\lvert\epsilon\Lambda(\pi)\rangle\!\rangle \lvert S\Sigma\rangle$	$\mathcal{H}^{(\Omega)}_{JM_J}(\Theta\Phi)$	$\lvert\epsilon\Lambda(\pi)\rangle\!\rangle \lvert S\Sigma\rangle \lvert JM_J(\Omega)\rangle\!\rangle$
b	$\Delta\epsilon \gg \hbar\dot{\Theta} \gg \hbar\omega$	$\lvert\epsilon\Lambda(\pi)\rangle\!\rangle \lvert SM_S\rangle$	$\mathcal{H}^{(\Lambda)}_{KM_K}(\Theta\Phi)$	$\lvert\epsilon\Lambda(\pi)\rangle\!\rangle \lvert SM_S\rangle \lvert KM_K(\Lambda)\rangle\!\rangle \xrightarrow[K+S=J]{} \lvert\epsilon\Lambda(\pi)\rangle\!\rangle \lvert KSJM_J(\Lambda)\rangle\!\rangle$
c	$\hbar\omega \gg \Delta\epsilon \gg \hbar\dot{\Theta}$	$\lvert\epsilon\Omega(\pi)\rangle\!\rangle$	$\mathcal{H}^{(\Omega)}_{JM_J}(\Theta\Phi)$	$\lvert\epsilon\Omega(\pi)\rangle\!\rangle \lvert JM_J(\Omega)\rangle\!\rangle$
		or $\lvert\epsilon j\Omega\rangle$		$\lvert\epsilon j\Omega\rangle \lvert JM_J(\Omega)\rangle\!\rangle$
		or $\lvert\epsilon LSj\Omega\rangle$		$\lvert\epsilon LSj\Omega\rangle \lvert JM_J(\Omega)\rangle\!\rangle$
d	$\hbar\dot{\Theta} \gg \Delta\epsilon \gg \hbar\omega$	$\lvert\epsilon LM_L\rangle \lvert SM_S\rangle$	$Y_{NM_N}(\Theta\Phi)$	$\lvert\epsilon LM_L\rangle \lvert SM_S\rangle \lvert NM_N\rangle \xrightarrow[L+N=K]{} \lvert\epsilon LNKM_K\rangle \lvert SM_S\rangle$
				$\xrightarrow[K+S=J]{} \lvert\epsilon LNKSJM_J\rangle$
e	$\hbar\omega \gg \hbar\dot{\Theta} \gg \Delta\epsilon$	$\lvert\epsilon LSjm_j\rangle$	$Y_{NM_N}(\Theta\Phi)$	$\lvert\epsilon LSjm_j\rangle \lvert NM_N\rangle \xrightarrow[j+N=J]{} \lvert\epsilon LSjNJM_J\rangle$
	or $\hbar\dot{\Theta} \gg \hbar\omega \gg \Delta\epsilon$	or $\lvert\epsilon jm_j\rangle$		$\lvert\epsilon jm_j\rangle \lvert NM_N\rangle \xrightarrow[j+N=J]{} \lvert\epsilon jNJM_J\rangle$

on the electronic coordinate **r** defined in Eq. (2.10) and Fig. 5. In other words, it is assumed that the basis functions rotate in space, maintaining a fixed orientation relative to the internuclear axis. Such a description is normally appropriate for slow atomic collisions. On the other hand, in Sec. II.B, we briefly considered the possibility of using space-fixed electronic basis states, and we mentioned that such states are generally more suitable than rotating states for the description of fast collisions. However, in neither case did we say anything about the spin part of the wave function; does it rotate or remain space fixed?

In the first part of this appendix, we consider these problems in more detail, and we ask under what conditions space-fixed or rotating spatial or spin states might be preferable. The discussion is simplest if we describe the collision in the classical trajectory formulation. Afterwards we shall consider the quantum-mechanical description of the nuclear motion, and present one form of partial-wave analysis.[19]

1. Electronic basis states—review of Hund's coupling cases

Coupled equations describing atomic collisions have been given in various forms. For the present purposes, we refer to Eqs. (2.68). Those equations contain the electronic Hamiltonian matrix $\underline{h}$, which can be divided into an electrostatic (Born-Oppenheimer) part and a magnetic (spin-orbit) part, and they contain the angular coupling matrix $(-\underline{L}_y/R+\underline{A}^{\theta})$, which arises because the basis states rotate with the molecular frame.

The relative strength of these three interaction matrices is of great importance in determining the outcome of the collision. For example, it is the electrostatic interaction between electrons and nuclei that makes the spatial part of the electronic wave function rotate with the molecular frame, so if this interaction is very weak, the wave function may remain more nearly space fixed.

Therefore we need a rough estimate of the strength of these interactions. Let us say $\Delta\epsilon$ represents the strength of that part of the electrostatic interaction which couples the electronic state to the internuclear axis; we can take $\Delta\epsilon$ to be the energy gap between any given state having $\langle L_z\rangle = \Lambda\hbar$ and the nearest state having $\langle L_z\rangle = (\Lambda\pm 1)\hbar$. Obviously this quantity depends on the internuclear distance, for it goes to zero both as $R\to\infty$ and as $R\to 0$, but it may have a magnitude of several eV for $R\sim$ a few Bohrs. Similarly, let $\hbar\dot{\Theta}$ represent the strength of the angular coupling, and $\hbar\omega$ represent the strength of the spin-orbit interaction; ω can be identified as the spin-orbit precession frequency, or $\hbar\omega$ as the spin-orbit energy splitting. Angular coupling vanishes as $R\to\infty$ (since $\dot{\Theta}\to 0$), but it may become very large at small R, while the spin-orbit interaction typically does not vary too much with R.

Now five cases arise, identified by Hund (1926) and Mulliken (1930); these are given in Table VIII, and pictorial representations of the corresponding electronic states are given in Fig. 30.

Consider first Hund's case a: Suppose the electrostatic interaction is much stronger than the spin-orbit interaction, and this, in turn, is much stronger than the angular coupling. Then the electrostatic interaction causes the spatial part of the electronic wave function $\underline{\Upsilon}$ to rotate, following the internuclear axis. In the rotating frame, angular couplings, being the quantum-mechanical representation of Coriolis and centrifugal forces, tend to "decouple" Υ from the internuclear axis; i.e., they would make it retain its space-fixed orientation. However, by hypothesis, these couplings

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[19] The problems discussed here are ancient, and their resolution, given by Hund, is familiar to molecular spectroscopists (Herzberg, 1950; Hougen, 1970; Mulliken, 1930, 1931). Recently these problems have again received attention because of their importance in atomic collisions. The presentation given here follows papers of Masnou-Seeuws and McCarroll (1974), Mies (1973), and Thorson (1961, 1965). We also note recent papers by Aquilanti and Grossi (1981), and Aquilanti, Casavecchia, Grossi, and Lagana (1981).

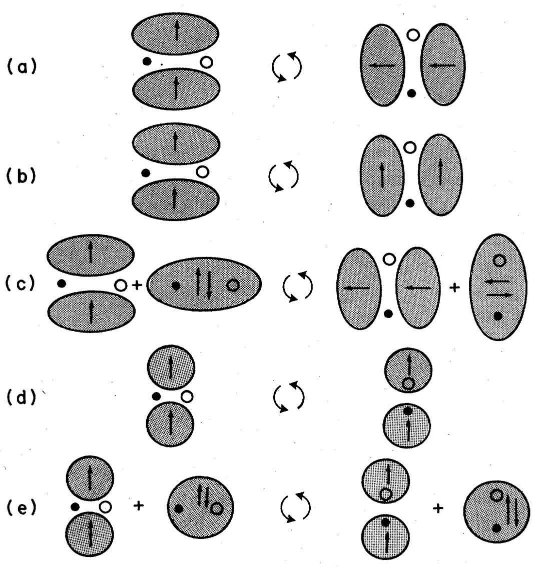

FIG. 30. Pictorial representation of electronic states in Hund's cases (a)–(e). On the left is the state with nuclei fixed on the horizontal axis. On the right is what happens to the electronic state when the nuclei are rotated $\pi/2$ counterclockwise.

(a) A $^3\Pi$ state (both spins up). Spatial and spin functions rotate with the nuclei.

(b) The spatial part rotates, but the spins stay space-fixed.

(c) For strong spin-orbit coupling this state is a superposition of $^3\Pi$ and $^1\Sigma$, and it rotates.

(d) Neither spatial nor spin parts rotate.

(e) Space-fixed state for strong spin-orbit coupling.

are weak. Therefore Υ, which itself follows the internuclear axis, is best described by an expansion in basis functions which also follow this axis. Such functions, which we have always written as $\phi_n(\mathbf{r};R)$, can be characterized by quantum numbers Λ (possibly parity, $\pi=g$ or u, for a symmetric system), and by their energy and any other quantum numbers, which we collectively denote ϵ. Thus these rotating basis functions are represented by kets $|\epsilon\Lambda(\pi)\rangle$.

Now, whenever the spatial part of the electronic wavefunction rotates with the internuclear axis, the spin-orbit interaction will tend to couple the spins to this same axis. In classical mechanics, spin-orbit coupling makes the electron-spin–angular-momentum vector **S** precess about the electron-orbital–angular-momentum vector **L**. However, in a molecule in which the spatial wave function rotates with the internuclear axis, only one orbital angular momentum component, $L_z \to \Lambda\hbar$ is quantized (conserved), so the spin must precess about the z (internuclear) axis. If this precession is rapid enough, compared to the rate of rotation of the molecule, then we can say that the electron spin follows the rotating molecular frame. Accordingly, the basis states should also have this property; we therefore use electron spin states $|S\Sigma\rangle$ oriented along (or "quantized on") the internuclear axis, with $\Sigma=\langle S_z\rangle/\hbar$.

In Hund's case b, the electrostatic interaction again dominates the other interactions, so the spatial part of Υ follows the internuclear axis. Now, however, the spin-orbit precession frequency is slower than the rate of rotation of the internuclear axis, so the spins cannot follow that axis, but tend to retain their original space-fixed orientation. Hence it is best to take the spin part of the basis states to be quantized on a space-fixed axis (z'), and we denote such spin states $|SM_s\rangle$, with $M_s=\langle S_{z'}\rangle/\hbar$.

Skipping case c for the moment, in cases d and e, angular coupling dominates coupling to the internuclear axis; this means simply that the electrostatic field is not strong enough to force Υ to rotate, so it tends to remain space fixed. Of course, the initial and final states of any collision are necessarily space fixed, but in addition there are several physical situations in which Υ might retain its original orientation throughout the entire collision. (i) In fast collisions, even if the electrostatic fields are strong, the electrons may not have enough time to adjust to them. (ii) In very distant collisions, the electrostatic fields may be too weak to cause rotation of the electronic state. (iii) Near the turning point of very close collisions, the field generated by the nuclei is nearly spherically symmetric, and the internuclear axis may rotate suddenly, so again the electrons might not go along. (iv) If an electron is in a high Rydberg state, such that its orbital radius is much larger than the internuclear separation, then again it "feels" mainly the spherically symmetric Coulomb attraction of the nuclei, and it need not follow the rotation of the internuclear axis.

In any of these situations, the spatial part of Υ tends to retain its original, space-fixed orientation. If, in addition, spin-orbit coupling is negligible (case d) then it is convenient to use basis states in which the spin part is separable from the spatial part (and is also space fixed, of course). Furthermore, in the above-mentioned situations, the major part (or the average of) the electrostatic field is spherically symmetric, so it is appropriate to describe Υ by an expansion in spherical harmonics (one-electron case) or eigenfunctions of L^2, L_z, (many-electron case). Thus a possible expansion basis is $|\epsilon LM_L\rangle|SM_s\rangle$.

If spin-orbit coupling is not negligible, but otherwise case d conditions are met, then we have case e. Within a given term (i.e., within the set of states having in common the quantum numbers ϵ, L, S), the matrix representing $h_{\rm soc}$ connects states of various M_L, M_s, and it is diagonalized by transformation to the $|\epsilon LSjm_j\rangle$ representation, using Clebsch-Gordan coefficients (Condon and Shortley, 1959; Edmonds, 1957). If the spin-orbit interaction is even larger than the energy gap between various terms (and if there is more than one electron outside a closed shell), then L and S cease to be "good quantum numbers," and the states can only be characterized by total electron angular momentum $|\epsilon jm_j\rangle$. (Of course, the use of j as a "good quantum number" involves the assumption that the interaction between the electrons and the pair of nuclei can be approximated in some way by a single, spherically symmetric field.)

Finally we turn to Hund's case c, with weak angular coupling and strong spin-orbit coupling. There are two quite different physical situations in which these conditions occur, and distinct representations should be used to describe them. If we have an atom in a given

$|\epsilon LSjm_j\rangle$ or $|\epsilon jm_j\rangle$ state, and it is only weakly perturbed by a distant, slowly moving atom or ion, then j (and possibly L and S) may remain a reasonably good quantum number, but the electronic state might slowly reorient itself, following the internuclear axis. Such a situation is best described by expansion in states $|\epsilon LSj\Omega\rangle$ or $|\epsilon j\Omega\rangle$, which are just case e states *rotated* so that they are quantized on the internuclear axis, with $\Omega=\langle j_z\rangle/\hbar$. Mulliken (1931, 1932, 1937) recognized the importance of such states in molecular spectroscopy, and they are also useful for describing fine-structure transitions (Sec. IV.B.7).

Case c can also arise at moderate internuclear distances, in situations for which j makes no sense as a quantum number. For example, suppose we have a system which we attempt to describe by case (a) basis states, $|\epsilon\Lambda(\pi)\rangle|S\Sigma\rangle$, but suppose we then find that matrix elements of the spin-orbit Hamiltonian (4.44)

$$\langle S'\Sigma|\langle\epsilon'\Lambda'(\pi)|h_{\text{soc}}|\epsilon\Lambda(\pi)\rangle|S\Sigma\rangle$$

between states with $S'=S\pm1$, $\Lambda'=\Lambda\pm1$ are at least as large as the (electrostatic) energy gap between these states. Then it may be preferable to transform to a representation in which the full electronic Hamiltonian matrix $\underline{h}=\underline{h}_{\text{BO}}+\underline{h}_{\text{soc}}$ is diagonal. Such states can no longer be characterized by definite values of Λ or Σ, but $\Omega=\Lambda+\Sigma$ is still a good quantum number, so these states are denoted $|\epsilon\Omega(\pi)\rangle$. These states constitute the adiabatic representation for the problems discussed in Sec. IV.B.1.

For bound molecules, since the internuclear distance is normally confined to a small range, it is usually found that *one* of Hund's cases applies, and often the electronic state is adequately described by a single ket from one of the above representations. In that situation, Hund's list of cases provides a scheme for classifying the actual physical states of various molecules.

For colliding atoms, on the other hand, since the relative strength of the interactions changes with R, and since the internuclear distance is not confined, the system passes from one case to another through an intermediate range where two interactions are comparable and no Hund case applies. For example, initial and final states must ultimately be referred to the space-fixed laboratory frame (case d or e), but at intermediate distances Born-Oppenheimer eigenfunctions often provide a good representation (case a or b).

The usual approach for collision problems, therefore, is to take any *one* representation and to solve the coupled equations in that representation.[20] Now Hund's scheme classifies the representations that can be used, and helps us to pick one that is appropriate to the problem at hand. The chosen representation may correspond to one of the Hund cases, or to an intermediate case, or it may change from one case to another either smoothly or suddenly with R. If the basis set is large enough, then any problem can be solved in any representation. Representations are chosen on the basis of convenience, and of accuracy of truncation to a small manifold. Some helpful rules for choosing a representation are given in Sec. IV.A.5.

2. Quantum-mechanical nuclear rotational functions

In the preceding section, the discussion of rotating and nonrotating electronic states was framed in the language of the classical trajectory formulation, but all of the same considerations still apply if a quantum-mechanical description of the nuclear motion is used. In addition, in the quantum description, we have to pick an appropriate set of eigenfunctions to describe the rotation of the nuclei or of the whole molecule.[21]

For cases (d) and (e), it is reasonable to use spherical harmonics $Y_{NM_N}(\Theta,\Phi)$, with N the quantum number corresponding to orbital angular momentum of the nuclei, and M_n the Z component. The assumption in these cases is that the coupling between nuclear and electronic angular momenta (N, and j or L) is weak. However, unless that coupling entirely vanishes, none of the quantum numbers j, m_j, NM_n (or LM_L) really represent conserved quantities. It may therefore be convenient to transform to a representation consisting of eigenfunctions of the *total* angular momentum J^2 and its Z component M_J, since these are rigorously conserved ($\mathbf{J}=\mathbf{N}+\mathbf{j}$ in the usual vector coupling sense).

In case (e), this transformation is accomplished by combining states of various m_j and M_N, using Clebsch-Gordan coefficients, into states characterized by $|\epsilon jNJM_J\rangle$ (or if L and S are good quantum numbers, states $|\epsilon LSjNJM_J\rangle$. In case d, since magnetic effects are by hypothesis negligible, one can leave the spin part separate, and combine states of various M_L and M_N into states $|\epsilon LNKM_K\rangle|SM_S\rangle$, where $\mathbf{K}=\mathbf{N}+\mathbf{L}=\mathbf{J}-\mathbf{S}$. (Subsequently, if desired, K and S can be vector-coupled into J.)

For cases (a) through (c), the electronic state follows the internuclear axis and may generate a nonzero angular momentum about that axis ($\Omega\hbar$ or $\Lambda\hbar$). Accordingly, the rotational wave functions should be symmetric-top eigenfunctions, $\mathcal{H}^{(\Lambda)}_{KM_K}(\Theta,\Phi)$ for case (b), or $\mathcal{H}^{(\Omega)}_{JM_J}(\Theta,\Phi)$ for cases (a) and (c). These functions satisfy the differential equations

$$-\left[(\sin\Theta)^{-1}\frac{\partial}{\partial\Theta}\sin\Theta\frac{\partial}{\partial\Theta}+(\sin^2\Theta)^{-1}\left(\frac{\partial}{\partial\Phi}-i\Omega\cos\Theta\right)^2-\Omega^2\right]\mathcal{H}^{(\Omega)}_{JM_J}=J(J+1)\mathcal{H}^{(\Omega)}_{JM_J}\,, \tag{A1a}$$

$$-i\frac{\partial}{\partial\Phi}\mathcal{H}^{(\Omega)}_{JM_J}=M_J\mathcal{H}^{(\Omega)}_{JM_J}\,. \tag{A1b}$$

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[20] If a representation is used in which the spin states rotate, following the internuclear axis (cases a and c), then the coupled equations (2.68) must be modified to incorporate the effects of the rotating frame on the electron spin. Essentially $\underline{L}_y$ must be replaced by $\underline{L}_y+\underline{S}_y$.

[21] For simplicity, in this section the radius and angles for the independent variable in the coupled equations are represented by the notation (R,Θ,Φ). In the corrected equations (3.61), the independent variable is $\bar{\mathbf{R}}$, and perhaps it would be better to write $(\bar{R},\bar{\Theta},\bar{\Phi})$, but we prefer to avoid excessively Baroque notation.

The operators on the left are differential representations of the square of the total angular momentum ($J^2/\hbar^2$), and its Z component ($J_z/\hbar$). The eigenvalues are $J(J+1)$ and M_J, while Ω plays the role of a *parameter* in these equations. (If we replace here $\Omega \to \Lambda, J \to K, M_J \to M_K$, then the operators represent K^2 and K_z.) For any given Ω, $\{\mathcal{H}^{(\Omega)}_{JM_J}(\Theta, \Phi)\}$ forms a complete and orthogonal set of angular functions.

The eigenfunctions $\mathcal{H}$ can be related to representations of finite rotations; using the conventions of Edmonds (1957),

$$\mathcal{H}^{(\Omega)}_{JM_J}(\Theta, \Phi) = ph_1\left(\frac{2J+1}{4\pi}\right)^{1/2} d^J_{M_J\Omega}(\Theta)\exp(iM_J\Phi). \quad \text{(A2)}$$

Two special cases are of interest: for integer J, M_J, Ω,

$$\mathcal{H}^{(\Omega)}_{J0}(\Theta, \Phi) = ph_2 Y_{J\Omega}(\Theta, \Phi = 0), \quad \text{(A3a)}$$

$$\mathcal{H}^{(0)}_{JM_J}(\Theta, \Phi) = ph_3 Y_{JM_J}(\Theta, \Phi). \quad \text{(A3b)}$$

These functions satisfy the differential recursion relation (Kronig, 1930),

$$\begin{aligned} Q_\pm \mathcal{H}^{(\Omega)}_{JM_J} &\equiv [\mp \partial/\partial\Theta + (i/\sin\Theta)(\partial/\partial\Phi - i\Omega\cos\Theta)]\mathcal{H}^{(\Omega)}_{JM_J} \\ &= ph_4[(J \pm \Omega + 1)(J \mp \Omega)]^{1/2}\mathcal{H}^{(\Omega\pm 1)}_{JM_J}. \end{aligned} \quad \text{(A3c)}$$

The quantities $ph_1 \cdots ph_4$ are phases, which can be selected arbitrarily but *not* independently. It is convenient to take $ph_4 = ph_3 = 1$; then ph_2 turns out to be $(-1)^\Omega$, and $ph_1 = (-1)^{M_J+\Omega}$ if $M_J \geq |\Omega|$ or if $M_J \leq -|\Omega|$ or if $M_J = 0$. The proof of this last statement is an exercise that is especially useful for building discipline and tolerance of pain.

These phases have caused some confusion in the past. The convention given by Kronig [1930, p. 62, Eq. (7)] is not consistent with $ph_4 = 1$, and a similar inconsistency appears in Thorson's 1961 and 1965 papers. The above form for ph_1 was given by Thorson and Delos (1978a), but it has not been proved that it is valid for $0 < |M_J| < |\Omega|$.

3. Partial-wave analysis

After suitable electronic basis functions and corresponding nuclear angular functions have been chosen, then the three-dimensional coupled equations (3.61) can be reduced to one-dimensional, radial equations. Truncation of this set of coupled equations to a small manifold finally yields a numerically tractable quantum-mechanical formulation. Examination of asymptotic behavior of the radial functions and comparison with scattering boundary conditions gives a formula for scattering amplitudes and cross sections in terms of the $\mathcal{S}$ matrix.

It should be obvious that the specific form of the coupled radial equations and the formulas for cross sections depend upon which set of nuclear angular functions is chosen. In the development below, we shall assume that the electronic basis functions belong within Hund's cases (*a*)–(*c*), so that the nuclear rotation is described by $\mathcal{H}$ functions, and we shall use notation of Hund's case (*b*), which seems to be most appropriate for typical slow collisions.

a. Further analysis of nonadiabatic coupling matrices $\underline{\mathbf{\Pi}}$ and $\underline{B}$

The first step is to put the nonadiabatic couplings into more explicit form. On the assumption that $\mathbf{s}_n(\mathbf{r}'; \mathbf{R})$ is given by Eq. (3.38), it is convenient to break the $\underline{\mathbf{A}}$ matrix into two parts. From Eq. (2.61), we have

$$\underline{\mathbf{A}} = \underline{\mathbf{A}}_0 + \underline{\mathbf{A}}_1, \quad \text{(A4a)}$$

$$(\mathbf{A}_0)_{mn} = \langle \phi_m | \tfrac{1}{2}(f_n + \lambda)\mathbf{p} | \phi_n \rangle, \quad \text{(A4b)}$$

$$(\mathbf{A}_1)_{mn} = (-i\hbar/2)\langle \phi_m | \nabla_r f_n + \tfrac{1}{2}\mathbf{r}_g(\nabla^2_r f_n) + \mathbf{r}_g[(\nabla_r f_n)\cdot\nabla_r] | \phi_n \rangle. \quad \text{(A4c)}$$

(The second term obviously vanishes if f_n is constant.) Define

$$\underline{\mathbf{\Pi}}_0 = \underline{\mathbf{P}} + \underline{\mathbf{A}}_0 \quad \text{(A5a)}$$

or, equivalently,

$$(\mathbf{\Pi}_0)_{mn} = \langle \phi_m | -i\hbar\nabla_R + \kappa_n \mathbf{p} | \phi_n \rangle, \quad \text{(A5b)}$$

with

$$\kappa_n = \tfrac{1}{2}(f_n + \lambda). \quad \text{(A5c)}$$

(κ_n may be a function of $\mathbf{r}'$ and $\mathbf{R}$). Now we can separate Π_0 into radial and angular components,

$$(\Pi^R_0)_{mn} \equiv (P^R + A^R_0)_{mn} = -i\hbar\left\langle \phi_m \middle| \frac{\partial}{\partial R} + \kappa_n\frac{\partial}{\partial r} \middle| \phi_n \right\rangle, \quad \text{(A6a)}$$

$$(\Pi^\Theta_0)_{mn} = (P^\Theta + A^\Theta_0)_{mn} = -R^{-1}\langle \phi_m | L^y_n | \phi_n \rangle, \quad \text{(A6b)}$$

$$(\Pi^\Phi_0)_{mn} = (P^\Phi + A^\Phi_0)_{mn} = R^{-1}(\langle \phi_m | L^x_n | \phi_n \rangle - \Lambda_n\hbar\cot\Theta\, S_{mn}), \quad \text{(A6c)}$$

where

$$L^x_n = -i\hbar\left(y\frac{\partial}{\partial z} - (z - \kappa_n R)\frac{\partial}{\partial y}\right) \quad \text{(A7a)}$$

$$L^y_n = -i\hbar\left((z - \kappa_n R)\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \quad \text{(A7b)}$$

are corrected electronic angular-momentum operators.

The second-derivative matrix $\underline{B}$ (Eq. 3.66b) contains the square of the operator $(-i\hbar\nabla_R + \kappa_n\mathbf{p})$, but when this is written in spherical components we have to distinguish between two interpretations of ∇_R: as a gradient and as a divergence. Writing

$$B_{mn} = \langle \phi_m | (-i\hbar\,\mathrm{div} + \kappa_n\mathbf{p})(-i\hbar\,\mathrm{grad} + \kappa_n\mathbf{p}) | \phi_n \rangle$$

and developing div and grad in spherical components, we obtain

$$\begin{aligned} B_{mn} = &-\hbar^2\left\langle \phi_m \middle| R^{-1}\left(\frac{\partial}{\partial R} + \kappa_n\frac{\partial}{\partial z}\right)^2 R \middle| \phi_n \right\rangle \\ &+ R^{-2}[\langle \phi_m | (L^x_n)^2 + (L^y_n)^2 | \phi_n \rangle \\ &\quad + \langle \phi_m | L^x_n | \phi_n \rangle(-2\Lambda_n\hbar\cot\Theta) \\ &\quad + \Lambda^2_n\hbar^2\cot^2\Theta\, S_{mn}]. \end{aligned} \quad \text{(A8)}$$

(To derive this equation, one must use the fact that components of $\mathbf{L}_n$ obey standard angular-momentum commutation relations, except for ignorable corrections related to derivatives of f_n.)

b. Coupled radial equations based on expansion in $\mathcal{H}$-functions

Partial-wave expansion in symmetric-top eigenfunctions takes the form:

$$\chi_n(\mathbf{R}) = R^{-1} \sum_{K=\Lambda_n}^{\infty} \sum_{M_K=-K}^{K} u_n^{KM_K}(R)\mathcal{H}_{KM_K}^{(\Lambda_n)}(\Theta, \Phi) . \tag{A9}$$

Here we are assuming that the electronic basis states are of Hund's case (*b*) type, and Λ_n is the eigenvalue of $L_z/\hbar$ for the *n*th basis function. To obtain radial equations one must insert this expansion (A9) into the three-dimensional equations (3.61), express $(-i\hbar\nabla)$ in spherical coordinates, use Eqs. (A4)–(A8), and write out the whole mess on a very large blackboard. Then the following things happen.

(1) The last term from (A8), the last term from (A4c) and the angular parts of ∇^2 combine via (A1a) into $[K(K+1) - \Lambda_n^2]/2\mu R^2$.

(2) The term from $\underline{B}$ in which $\partial/\partial R$ acts on R cancels a related term from $(\underline{\Pi} + \underline{\gamma}) \cdot (-i\hbar\nabla)\underline{\chi}$ (except for corrections related to γ/μ, which we have consistently neglected).

(3) Angular terms from $(\Pi + \gamma) \cdot (-i\hbar\nabla)$ together with the next-to-last term in (A8) combine into forms involving $Q_{\pm}$. Finally multiplying the *m*th differential equation by $\mathcal{H}_{K'M_{K'}}^{(\Lambda_m)}$ and integrating over angles, using orthogonality, selection rules on Λ, and the recursion relation (A3), we arrive at the coupled radial equations

$$\begin{aligned}\Big\{&(2\mu)^{-1}\Big[\underline{S}\Big(-i\hbar\frac{d}{dR}\Big)^2 + (\underline{\Pi}^R + \underline{\gamma}^R)\Big(-i\hbar\frac{d}{dR}\Big) + \underline{B}_R\Big] \\ &+ \underline{S}[K(K+1) - \underline{\Lambda}^2]/2\mu R^2 + (\hat{\underline{L}}_x^2 + \hat{\underline{L}}_y^2)/2\mu R^2 - \underline{Q}/2\mu R^2 + \underline{h} + \underline{I} - \underline{S}E\Big\}\underline{u}^{KM_K}(R) = 0 ,\end{aligned} \tag{A10}$$

where $\hat{\underline{L}}_x, \hat{\underline{L}}_y$ are the matrices of L_n^x, L_n^y defined in Eq. (A7), $\underline{\Lambda}$ is the diagonal matrix $\delta_{mn}\Lambda_n$, and

$$(B_R)_{mn} = -\hbar^2\Big\langle\phi_m\Big|\Big(\frac{\partial}{\partial R} + \kappa_n\frac{\partial}{\partial z}\Big)^2\Big|\phi_n\Big\rangle , \tag{A11}$$

$$\begin{aligned}Q_{mn} = {} & \delta_{\Lambda_m, \Lambda_n+1}[(K+\Lambda+1)(K-\Lambda)]^{1/2}\hbar\hat{\underline{L}}_+ \\ & + \delta_{\Lambda_m, \Lambda_n-1}[(K-\Lambda+1)(K+\Lambda)]^{1/2}\hbar\hat{\underline{L}}_- ,\end{aligned} \tag{A12a}$$

with

$$\begin{aligned}\hat{\underline{L}}_+ &= (\hat{\underline{L}}_x + i\hat{\underline{L}}_y) + R[(\underline{A}_1^{\Phi} + \underline{\gamma}^{\Phi}) - i(\underline{A}_1^{\Theta} + \underline{\gamma}^{\Theta})] , \\ \hat{\underline{L}}_- &= (\hat{\underline{L}}_x - i\hat{\underline{L}}_y) + R[(\underline{A}_1^{\Phi} + \underline{\gamma}^{\Phi}) + i(\underline{A}_1^{\Theta} + \underline{\gamma}^{\Theta})] .\end{aligned} \tag{A12b}$$

[This corrects a minor error in Eq. (3.23c), Thorson and Delos, 1978a.]

Equations (A10) can be solved numerically, or by any of a wide variety of approximation methods. Standard analysis of equations of this type (Child, 1974, Chap. 6; Mott and Massey, 1965, p. 369ff), shows that among the solutions there is a set of functions having the asymptotic form

$$\begin{aligned}u_n^{KM_K}(R) \sim (A_{KM_K}/k_n^{1/2})\{&\delta_{nn_0}\exp[-i(k_nR - K\pi/2)] \\ &- \mathcal{S}_{nn_0}^{K}\exp[+i(k_nR - K\pi/2)]\} .\end{aligned} \tag{A13}$$

The first term is the incoming wave in the initial (n_0) state; $\mathcal{S}_{nn_0}^{K}$ are the elements of the $\mathcal{S}$ matrix, to be determined by solving the coupled equations, and A_{KM_K} is a set of "normalization" coefficients, to be determined from the boundary conditions.

The exact $\mathcal{S}$ matrix is unitary and symmetric, and the $\mathcal{S}$ matrix calculated from the uncorrected PSS equations (3.16) will also have this property. However, the approximations used in have this property. However, the approximations used in deriving Eqs. (3.61) are such that symmetry and unitarity of the resulting approximate $\mathcal{S}$ matrix are not guaranteed. If errors of this type are found to be significant, it means that neglected higher-order terms in the Taylor expansion (3.51) have to be considered. With no further loss of accuracy, we shall later replace $(A_{KM_K}/k_n^{1/2})$ by $(A_{KM_K}/k_{n_J}^{1/2})$.

c. Scattering boundary conditions and cross-section formulas

The present form of partial-wave analysis is more complicated than the conventional ones for elastic or inelastic scattering (Mott and Massey, 1965; Child, 1974, Chaps. 3 and 6) because

(1) we are interested in transitions between electronic states;

(2) charge exchange constitutes a rearrangement such that different variables describe initial and final channels;

(3) in general the initial and final electronic states have a spatial orientation that must be considered.

None of these cause any more major conceptual difficulties, but they do make the formulas more complicated. We can simplify our considerations and still display the general principles by assuming that the initial atomic state is spherically symmetric ($L = 0$, or, if spin is important, $j = 0$). Generalization of the present formulas to other cases has been given by Thorson (1961, 1965).

Most of the formulas needed have been given already, but we collect them again here with some interpretation. The ansatz for the wave function (3.39) was

$$\Psi = \sum_n \chi_n(\xi_n)\hat{\phi}_n(\mathbf{r}'; \xi_n) .$$

We assumed that a subset of the electronic states $\hat{\phi}_n$ corresponds asymptotically to the important initial and final atomic states $\phi_{n_A}^0, \phi_{n_B}^0$, and we assumed that the coordinates go in the channels to constants times $\mathbf{R}_A$ and $\mathbf{R}_B$. Hence at large distances this expansion can be *reexpressed* in the form

$$\Psi = \sum_{n_A} \chi_{n_A}(\mathbf{R}_A)\phi_{n_A}^0(\mathbf{r}_A) + \sum_{n_B} \chi_{n_B}(\mathbf{R}_B)\phi_{n_B}^0(\mathbf{r}_B) . \tag{A14}$$

Since we are assuming that the basis functions $\phi_n(\mathbf{r}'; \xi_n)$ are oriented ("quantized") on the internuclear axis, this reexpression is simplest if we take the asymptotic atomic states $\phi_{n_A}^0(\mathbf{r}_A), \phi_{n_B}^0(\mathbf{r}_B)$ also to be quantized on the internuclear axis. Thus these are rotating atomic states, like the ones introduced in Sec. II.

Scattering boundary conditions (3.8) can be restated in terms of these rotating states: At large R,

$$\begin{aligned}\Psi \rightarrow\ & \phi^0_{m_A}(r_A)\exp(ik_{m_A}Z_A)\\ &+\sum_{n_A}\phi^0_{n_A}(\mathbf{r}_A)f_{n_Am_A}(\Theta_A)\exp(ik_{n_A}R_A)/R_A\\ &+\sum_{n_B}\phi^0_{n_B}(\mathbf{r}_B)f_{n_Bm_A}(\Theta_B)\exp(ik_{n_B}R_B)/R_B\,.\end{aligned} \tag{A15}$$

These f's are not identical to those in (3.8) because the latter refer to space-fixed states.

The scattering amplitudes do not depend on Φ_A or Φ_B because the initial state, $\phi^0_{m_A}\exp(ik_{m_A}Z_A)$, and all of the interactions, are cylindrically symmetric. Note that if the initial electronic state were not spherically symmetric, then reexpression of the first term of (A15) in terms of rotating states would be much more complicated, and scattering amplitudes would depend upon Φ_A and Φ_B.

Now we must note again the fact that the independent variable in the coupled equations is really $\overline{\mathrm{R}}$, that $\overline{\mathrm{R}}$ is the common numerical value of the coordinates ξ_n, and that these go to $(\mu_J/\mu)^{1/2}R_J$ $(J=A,B)$ in the channels. Also, noting that

$$\begin{aligned}k_{n_J}&=[2\mu_J(E-\epsilon^0_{n_J})]^{1/2}/\hbar\,,\\ \epsilon_{n_J}&=\lim_{\overline{R}\to\infty}[h_{nn}(\overline{R})+I_{nn}(\overline{R})]\,,\end{aligned} \tag{A16}$$

we see that k_n in Eq. (A13) differs from k_{n_J} by the factor $(\mu/\mu_J)^{1/2}$. Hence reexpression of (A13) in asymptotic coordinates gives

$$\begin{aligned}u^{KM_K}_{n_J}(R_J)\sim(A_{KM_K}/k^{1/2}_{n_J})\{&\delta_{n_Jm_A}\exp[-i(k_{n_J}R_J-K\pi/2)]\\ &-S^K_{n_Jm_A}\exp[+i(k_{n_J}R_J-K\pi/2)]\}\,.\end{aligned} \tag{A17}$$

Finally, we need the standard expansion of a plane wave in normalized spherical harmonics:

$$\exp(ik_{m_A}Z_A)\sim(2ik_{m_A}R_A)^{-1}\sum_n i^N[(4\pi)(2N+1)]^{1/2}Y_{N0}(\Theta_A,\Phi_A)\{-\exp[-i(k_{m_A}R_A-K\pi/2)]+\exp[+i(k_{m_A}R_A-K\pi/2)]\}\,. \tag{A18}$$

Then, combining (A3a), (A9), (A14), (A15), (A17), and (A18), we obtain

$$A_{KM_K}=\delta_{KN}\delta_{M_K0}(-1)i^N[(4\pi)(2N+1)]^{1/2}/2ik^{1/2}_{m_A}\,, \tag{A19}$$

and using (A3a), the scattering amplitude for excitation of the n_Jth state is

$$f_{n_J,m_A}(\Theta_J)=[2i(k_{m_A}k_{n_J})^{1/2}]^{-1}(-1)^{\Lambda_{n_J}}\sum_{K=\Lambda_{n_J}}[(4\pi)(2K+1)]^{1/2}Y_{K\Lambda_{n_J}}(\Theta_J,\Phi_J=0)(S^K_{n_Jm_A}-\delta_{n_Jm_A})\,. \tag{A20}$$

The differential cross sections are

$$\begin{aligned}\sigma_{n_A\leftarrow m_A}(\Theta_A)&=(k_{n_A}/k_{m_A})\,|f_{n_A,m_A}(\Theta_A)|^2\,,\\ \sigma_{n_B\leftarrow m_A}(\Theta_A)&=(k_{n_B}/k_{m_A})\,|f_{n_B,m_A}(\Theta_A)|^2\,,\end{aligned} \tag{A21}$$

If all electronic states have $\Lambda_n=0$, Eq. (A20) reduces to the standard form.

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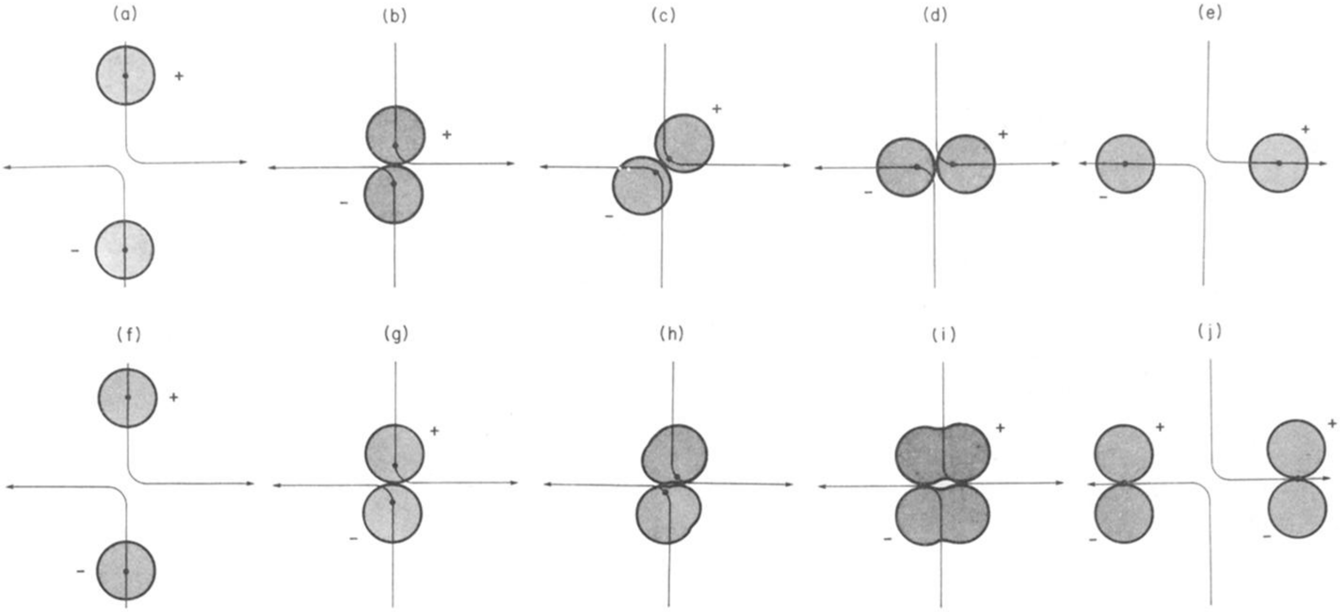

FIG. 18(b) Rotational coupling in the transition $H^+ + H(1s) \rightarrow H^+ + H(2p)$. Collisions in which the nuclei scatter to 90° are represented.

(a)–(e) illustrate a very slow collision.

(a) The electrons begin in the ungerade superposition of 1*s* atomic states.

(b) For small internuclear separations, this state becomes a $2p\sigma$ united-atom state.

(c), (d) If the internuclear axis rotates slowly, the electronic state follows.

(e) As the nuclei move apart, the electronic state again becomes the ungerade superposition of 1*s* states. No transition has occurred.

(f)–(j) Illustrate the consequences of more rapid motion on the same path.

(f), (g) Just as (a), (b).

(h) If the internuclear axis rotates too rapidly, the electronic state might not follow.

(i) As the axis rotates further, the electronic state becomes $2p\pi$.

(j) The $2p\pi$ molecular state dissociates into the ungerade superposition of separated-atom states. The transition occurred because the electrons could not follow the rapidly rotating internuclear axis.

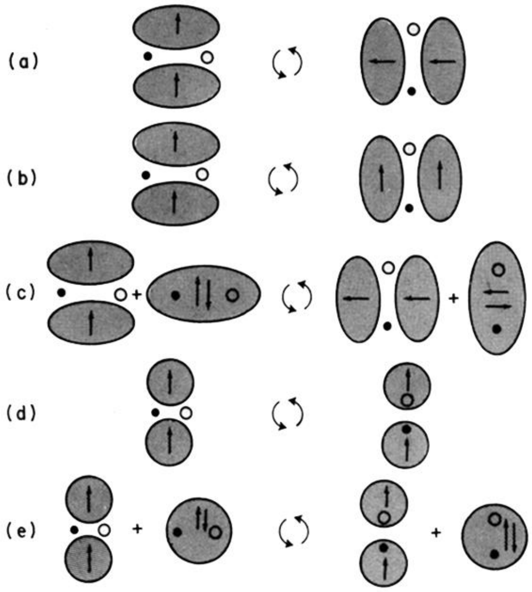

FIG. 30. Pictorial representation of electronic states in Hund's cases (a)–(e). On the left is the state with nuclei fixed on the horizontal axis. On the right is what happens to the electronic state when the nuclei are rotated $\pi/2$ counterclockwise.

(a) A $^3\Pi$ state (both spins up). Spatial and spin functions rotate with the nuclei.

(b) The spatial part rotates, but the spins stay space-fixed.

(c) For strong spin-orbit coupling this state is a superposition of $^3\Pi$ and $^1\Sigma$, and it rotates.

(d) Neither spatial nor spin parts rotate.

(e) Space-fixed state for strong spin-orbit coupling.

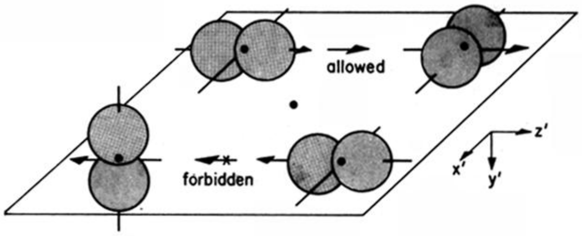

FIG. 6. Illustration of the ± symmetry selection rule. The motion of the two nuclei defines the collision plane, which is here taken to be the plane $y' = 0$. With respect to reflection through this plane, the $2p_{x'}$ and $2p_{z'}$ states have + symmetry, while the $2p_{y'}$ state has − symmetry. Hence $2p_{z'} \longleftrightarrow 2p_{x'}$, but $2p_{z'}$, $2p_{x'} \not\longleftrightarrow 2p_{y'}$.