

# The Physics of Low-energy Electron–Molecule Collisions: A Guide for the Perplexed and the Uninitiated

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## Abstract

The essential physical features of low-energy electron–molecule scattering are described in a qualitative fashion. The context for this discussion is provided by the frame-transformation picture, which entails a 'partitioning' of the quantum scattering problem according to the relative importance of various physical interactions. This picture is then used as the basis for a qualitative overview of several contemporary theoretical techniques for solving the quantum scattering problem that are based on eigenfunction expansions of the system wavefunction and for representing the electron–molecule interaction potential. Finally, progress in three specific problem areas of recent interest is surveyed. The emphasis throughout is on non-resonant elastic scattering and ro–vibrational excitation.

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### Part I. General Introduction

An enormous amount of research has been carried out in the field of low-energy electron-molecule scattering theory since the pioneering work of Fisk, Massey, and others in the 1930s. Since the mid-1960s, the pace of research in this branch of collision physics has increased dramatically. Indicative of this level of activity is the large number of recent workshops, symposia and satellite meetings that have been devoted to low-energy electron-molecule collisions\* and the many reviews that have recently appeared or are forthcoming. Indeed, electron-molecule scattering theory has come of age!

Table 1. Selected theoretical approaches to low-energy electron-molecule scattering

Theoretical approach	Selected reference
<i>L<sup>2</sup> variational methods</i>	
<i>R</i> matrix	Schneider (1975)
<i>T</i> matrix	Rescigno <i>et al.</i> (1974)
Schwinger variational	Watson <i>et al.</i> (1980)
<i>Eigenfunction-expansion methods</i>	
Frame transformation	Chang and Fano (1972)
Coupled channel	Morrison <i>et al.</i> (1977)
Adiabatic nuclei	Shugard and Hazi (1975)
Hybrid theory	Chandra and Temkin (1976)
Lab-frame close-coupling	Henry and Lane (1969)
Weak coupling:	
Born approximation	Breig and Lin (1965)
Distorted wave	Ardill and Davison (1968)
<i>Other</i>	
Continuum multiple scattering	Dehmer <i>et al.</i> (1978)
Glauber approximation	Narasimham <i>et al.</i> (1982)
Semiclassical perturbation scattering	Smith <i>et al.</i> (1975)

A vast number of collision processes can take place when an electron collides with a molecule, including non-rearrangement processes (for example, elastic scattering and excitation of electronic and/or nuclear states of the molecule) and rearrangement processes (for example, dissociative attachment, ionization and dielectronic recombination). But at 'low' scattering energies (less than about 10 eV), the theorist can focus mainly on the first class of processes, the rearrangement channels usually being closed. Scattering in this energy regime is fully quantal. Hence the theoretical problems one encounters in this field are of interest from the fundamental perspective of quantum mechanics.

The theoretical treatment of electron-molecule systems is complicated by certain special features of these systems. (Many of these features are discussed in Part II.)

\* For example, a Symposium on Electron-Molecule Collisions was held at the University of Tokyo on 6-7 September 1979 in association with the XIth International Conference on the Physics of Electron and Atomic Collisions. A Workshop on Electron-Molecule and Photon-Molecule Collisions was held in August of 1978 at Asilomar, California. [The proceedings have been published; see Rescigno *et al.* (1979).] The present paper is an expansion of a talk presented at a Symposium on the Current State of Electron-Molecule Scattering as part of the Eleventh Annual Meeting of the Division of Electron and Atomic Physics of the American Physical Society, held in Houston, Texas in December 1979.

One consequence of this fact is the need for large and powerful computers in the calculation of cross sections for many collision processes. Until rather recently, such facilities were not available. This is one reason why this field is not as advanced as, say, the theory of low-energy electron-atom scattering (cf. the review by Nesbet 1975). Nevertheless, considerable advances have been made in our qualitative and quantitative understanding of low-energy electron-molecule collision phenomena.

Upon digging into the literature of this field, one is immediately struck by its size and by the diversity of theoretical approaches that have been brought to bear on the problem. Some of the latter are shown (with a representative reference) in Table 1. Fortunately for the newcomer, who may be understandably appalled at this abundance of riches, there is available a number of reviews that cover various aspects of the theory and its applications (see the Appendix).

Rather than a review, the present paper is an attempt to provide three things: (1) a qualitative introduction to the principal physical features of electron-molecule collisions and the special difficulties attendant upon their theoretical analysis (Part II); (2) a description of the essential ideas behind several approaches to this problem that are currently under investigation (Part II, Section 3); and (3) comments on a few outstanding problems that seem to be particularly important and on work in the field since 1980 (Part III).

Thus, following this introduction, Part II contains an introductory overview of current concerns in electron-molecule scattering theory and how they are dealt with in continuing research in the field. This discussion was written expressly for the experimentalist, general reader and inquisitive graduate student with a minimal background in scattering theory. Therefore it contains (virtually) no mathematics or theoretical formulae.

Section 1 sets the stage by reviewing the quantum scattering problem and begins the discussion of the difficulties we face in trying to solve it. This theme (that 'electron-molecule scattering is non-trivial') continues throughout Part II. After a description of the idea behind eigenfunction-expansion theories, we embark on a description of the basic physics of electron-molecule scattering. This discussion, which occupies Section 2, is limited to concerns that are related to the solution of the Schrödinger equation for the collision. Following the description in Section 3 of several current theoretical methods that derive from these concerns, we take up the 'other half' of the theoretical problem—the electron-molecule interaction potential—in Section 4. This section is an attempt to provide readers, who have never encountered electron-molecule collision theory, with a sufficient background so that they can understand the aims and ideas behind much of the current theoretical research in this field.

Part III speaks for itself; it should be approached keeping in mind the caveat that the particular selection of problems and results discussed therein is rather subjective and most emphatically does *not* reflect on work not mentioned.

In keeping with its purpose, the present paper makes no claim to comprehensiveness and gives scant attention to many valuable theoretical studies.\* The emphasis herein is on a widely used class of theoretical methods based on eigenfunction expansions of the electron-molecule wavefunction. Hence the reader will find very little information concerning ' $L^2$  variational methods', which represent an important alternative approach to the electron-molecule problem. In addition, the focus of

\* The recent review by Lane (1980) contains a thorough critical discussion of applications of the theory up to early 1980.

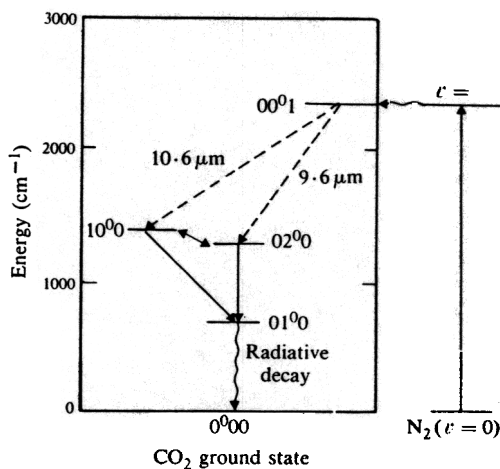
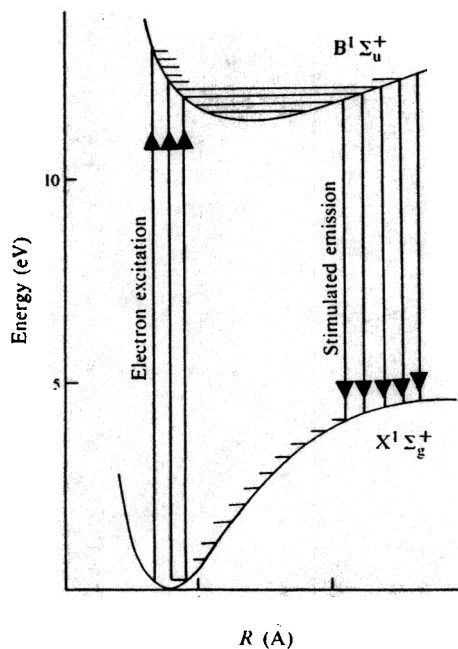


Fig. 1. Vibrational energy levels of  $\text{N}_2$  and  $\text{CO}_2$  that participate in the operation of the  $\text{CO}_2/\text{N}_2/\text{He}$  laser. Collisional energy transfer from  $\text{N}_2(v=1)$  to  $\text{CO}_2(00^01)$  and cascade from higher levels (not shown) lead to a population inversion. For further details see Patel (1968).

Fig. 2. Electron-induced electronic excitation in  $\text{H}_2$  followed by stimulated emission to the ground electronic state. This process is important in laser isotope separation processes (cf. Phelps 1980).



the present work is almost exclusively on non-resonant elastic scattering and ro-vibrational excitation.

Before concluding this introduction, it seems appropriate to mention the surprisingly diverse range of scientific and technological problems for which an understanding of electron-molecule collision processes is required.\* Among these are astrophysics (the study of the solar corona), the physics of planetary atmospheres (modelling of, say, the Martian and Venusian atmospheres), materials damage in fusion-powered reactors, and pollution control (the study of impurities in the air).

\* The recent article by Phelps (1980) contains a detailed discussion of various applications and related needs.

Data regarding electron-molecule collisions are also of importance in energy-related technology. For example, CO<sub>2</sub> lasers are widely employed in energy technology; they are highly efficient and capable of emitting a great deal of power. The CO<sub>2</sub>/N<sub>2</sub>/He laser operates, as indicated in Fig. 1, via radiative decay from a particular low-lying vibrational energy level of CO<sub>2</sub>. This level is populated by energy transfer from a (near-resonant) vibrationally excited state of N<sub>2</sub> and by cascade from higher lying vibrational levels of CO<sub>2</sub>. Therefore, to understand the basic physical processes that are operative in this laser, one requires cross sections for all electron-induced low-lying vibrational excitations of CO<sub>2</sub> and N<sub>2</sub>, as these processes can excite the particular molecular states that participate in the energy transfer.

An additional example of the usefulness of electron-molecule scattering data to energy technology is provided by laser isotope separation. Processes for isotope separation exist that use electron-beam-initiated high-power gas lasers that operate in the visible or ultraviolet region. The kinds of electron-molecule excitations that are involved in these processes are illustrated by the H<sub>2</sub> system. As shown in Fig. 2, a population inversion in molecular hydrogen can be achieved by excitation of the B<sup>1</sup>Σ<sub>u</sub><sup>+</sup> electronic state followed by stimulated emission to excited vibrational levels of the ground state.

These important applications notwithstanding, it is fair to say that much of the appeal of electron-molecule collision *theory* derives from its interest as fundamental physics. The quantum-mechanical problem of solving the Schrödinger equation for the scattering states of a particle in a non-central non-local potential presents an intriguing challenge, as do the intricacies of molecular structure, which are also part of the problem. In addition, low-energy electron-molecule collision processes provide a context for the study of some important fundamental physical interactions (for example, exchange and polarization) and some quite interesting phenomena (for example, resonances and threshold effects). In Part II, we shall take a qualitative look at the field from a fundamental point of view.

## Part II. A Bird's-eye View of Electron-Molecule Scattering Theory

### 1. *The problem—and an approach to its solution*

To begin this overview of electron-molecule collision theory we briefly review the quantum scattering problem to be solved, giving due attention to physical features peculiar to electron-molecule systems and the difficulties these features cause. This review will provide a context for the subsequent survey of recent attempts at solving the problem.

#### (a) *Schrödinger Equation*

The *system* that confronts us, which consists of an electron and a target molecule, is sketched in Fig. 3 in a coordinate system fixed in space. Quantum mechanically, this system is described by a (nonrelativistic) Hamiltonian\*

$$\mathcal{H} = \hat{T} + \hat{V}, \quad (1)$$

where  $\hat{T}$  and  $\hat{V}$  are operators for the kinetic and potential energies of all particles of the system (nuclei, bound electrons and scattering electron).

\* All magnetic interactions, such as spin-orbit coupling, are neglected throughout this discussion, as they are in nearly all current studies in this field. The justification for this assumption is simply that these interactions are weaker than the Coulomb terms in the Hamiltonian (1).

This Hamiltonian can conveniently be written as the sum of the Hamiltonian of the isolated molecule  $\hat{\mathcal{H}}_m$ , the kinetic-energy operator for the scattering electron  $\hat{T}_e$ , and the electron-molecule interaction potential energy  $\hat{V}_{\text{int}}$ , namely

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_m + \hat{T}_e + \hat{V}_{\text{int}}. \quad (2)$$

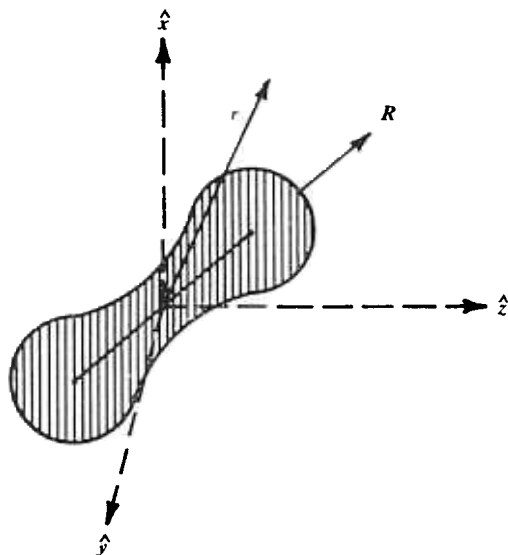


Fig. 3. Schematic representation of an electron (with coordinate  $r$ ) and a molecule (with internuclear axis  $R$ ) in a space-fixed ('lab') reference frame  $\hat{x}\hat{y}\hat{z}$ . This coordinate system is used in lab-frame close-coupling theories.

The molecular Hamiltonian  $\hat{\mathcal{H}}_m$  includes kinetic-energy operators for the nuclei and molecular electrons as well as Coulomb potential-energy terms for all pairs of these particles. The last term in (2) arises from the electrostatic (Coulomb) forces between the scattering electron and the constituent nuclei and electrons of the target, i.e.

$$\hat{V}_{\text{int}} = \hat{V}_{\text{elec-nucl}} + \hat{V}_{\text{elec-mol.elec}}. \quad (3)$$

The Coulomb potential provides a mechanism by which the quantum-mechanical 'motion' of the scattering electron influences and is influenced by that of the molecular constituents. This inherently dynamical effect, which will be discussed in Section 1b, gives rise to serious complications in performing scattering calculations.

With the system Hamiltonian (2) in hand, we can (in principle!) obtain the stationary state wavefunctions for total system energy  $E$  by solving the time-independent Schrödinger equation

$$\hat{\mathcal{H}}\Psi_E = E\Psi_E. \quad (4)$$

The energy  $E$  is just the sum of the (asymptotic) kinetic energy of the scattering electron and the energy of the target molecule. Equation (4) confronts us with a many-body problem and, since the aforementioned dynamical interaction of electron and target 'motion' prohibits an exact separation of variables in the Schrödinger equation, we must turn to approximate strategies. Pre-eminent among these are the *truncated eigenfunction-expansion methods* to be described in Section 3 and the  *$L^2$  variational methods* noted in Table 1.

However we choose to go about it, our objective is to solve equation (4) subject to the usual scattering boundary conditions: as the scattering electron moves into the

asymptotic region (where the detector and the experimentalist are located), the system wavefunction must reduce to the sum of an undistorted incident wave and a scattered wave. The latter term, which is 'altered' by the effect of the interaction potential, contains the scattering information. Letting  $r$  denote the coordinate of the scattered electron and  $\tau_m$  collectively represent all the coordinates\* (*nuclear and electronic*) of the target molecule, we write this boundary condition as

$$\Psi_E(r, \tau_m) \xrightarrow{r \rightarrow \infty} \underbrace{\exp(i k_i \cdot r) \Phi_i(\tau_m)}_{\text{Initial state}} + \sum_f \underbrace{\frac{\exp(i k_f \cdot r)}{r} \Phi_f(\tau_m) f_{i \rightarrow f}(\hat{r})}_{\text{Altered states}} \quad (5)$$

The incident wave term in (5) is the product of a plane wave  $\exp(i k_i \cdot r)$ , representing the scattering electron with initial wave vector  $k_i$ , and the initial-state molecular wavefunction  $\Phi_i(\tau_m)$ . This wavefunction is an eigenfunction of  $\mathcal{H}_m$ .

The scattered wave terms in (5) are more interesting. There is one such term for each *energetically accessible* final state of the molecule  $\Phi_f(\tau_m)$ . Each term is a product of a final-state molecular wavefunction, an outgoing spherical wave  $\exp(i k_f \cdot r)/r$  with wave number  $k_f$  corresponding to that of the electron after the collision, and the scattering amplitude for the transition  $f_{i \rightarrow f}(\hat{r})$ . This amplitude is the fundamental quantity of the theory; given it, we can compute any desired cross section.

#### (b) Special Difficulties

Thus far, the problem we have described may look like a rather standard, if potentially messy, application of quantum scattering theory. However, there are features of *electron-molecule* systems that pose special difficulties.

Some of these difficulties arise because the scattering particle is an *electron*. First, the scattering electron is *indistinguishable* from the molecular electrons. Hence the system wavefunction must obey the Pauli Principle (for fermions), i.e.  $\Psi_E$  must be *antisymmetric* under interchange of any two electrons. This requirement gives rise to EXCHANGE EFFECTS, which are demonstrably important in the calculation of cross sections for low-energy collisions. Second, because the scattering electron is a charged particle, it will distort the target charge cloud. This distortion gives rise, in turn, to POLARIZATION EFFECTS, which are also important in low-energy scattering. The problems attendant upon proper inclusion of exchange and polarization effects are considerable; we shall return to them in Section 4.

Other difficulties are involved because the target is a *molecule*. The fact that, in general, the target has several nuclei gives rise to a fundamental question: *In what coordinate system do we formulate the collision theory?* This question does not arise in the theory of electron-atom scattering, where the single nucleus of the target *atom* provides an obvious origin for a spherical coordinate system. This choice places the potentially troublesome (Coulomb) singularity due to the electron-nucleus interaction at the origin, where it can do minimal damage.

\* In this article we shall not explicitly consider spin functions or coordinates, but restrict our attention to electronically elastic scattering from a closed-shell molecule in a  $^1\Sigma$  ground electronic state. The theory for the more complicated general case has been reviewed by Lane (1980).

If the target is a *diatomic* molecule, as in Fig. 3, we could use prolate-spheroidal coordinates, with the foci of the elliptical and hyperbolic coordinates located at the nuclear centres. The numerical solution of the scattering problem as formulated in these coordinates is decidedly non-trivial, but prolate-spheroidal coordinates have been used in both eigenfunction-expansion and  $L^2$  variational methods (cf. Crees and Moores 1977 and Schneider 1975 respectively).

However, in the general problem of electron scattering from *polyatomic* molecules, one is forced to contend with one or more Coulomb singularities in the interaction potential that are located away from the coordinate origin(s). The complications caused by this seemingly obvious feature of the electron-molecule collision problem permeate most theoretical approaches for solving the Schrödinger equation (4). They are especially worrisome in eigenfunction-expansion methods that entail partial-wave expansions, such as CLOSE COUPLING (Section 3b), forcing the practitioner to include a large number of partial waves, most of which do not actually contribute to the (asymptotic) cross section.

A second troublesome consequence of the molecular nature of the target derives from the aforementioned interaction of the motion of the scattering electron and that of the nuclei, due to the term  $\hat{V}_{\text{elec-nucl}}$  in equation (3). This dynamical interaction is responsible for the non-separability of the Schrödinger equation which, as we shall see, makes its solution extremely difficult numerically. A similar problem enters molecular structure calculations, in which we seek to solve the time-independent Schrödinger equation for the *molecule* (with the Hamiltonian  $\mathcal{H}_m$ ) for *bound* stationary-state wavefunctions  $\Phi(\tau_m)$  and energies. In this case, the interaction of the motion of the nuclei and molecular electrons is usually dealt with by invoking the Born-Oppenheimer approximation, which is an *approximate* separation of the two types of motion (cf. Ch. 12 of Morrison *et al.* 1976).

A Born-Oppenheimer separation can be applied to the electron-molecule Schrödinger equation *under certain* (rather imprecisely defined) *circumstances*. The resulting ADIABATIC-NUCLEI methods will be described in Section 3a. Alternatively, we can let the scattering electron and the nuclei interact dynamically; this strategy leads to CLOSE-COUPLING methods (Section 3b). However, the latter choice forces us to incorporate into the theory a huge number of rotational and vibrational nuclear quantum states. These greatly complicate the implementation of close-coupling methods even on large computers.

### (c) Eigenfunction Expansions

The Schrödinger equation (4) for the electron-molecule system is a second-order partial differential equation in several variables, and direct solution of it is impossible. Eigenfunction-expansion methods are a convenient way to reduce this equation to a more tractable *set* of equations that depend only on the *radial* coordinate of the scattering electron.

Typically, such methods proceed in two steps. First, the system wavefunction is expanded in a complete set of target states (eigenfunctions of  $\mathcal{H}_m$  in the electron-molecule case), namely

$$\psi_E = \hat{\mathcal{A}} \sum_{\text{target states}} \left( \begin{array}{c} \text{one-particle} \\ \text{scattering function} \end{array} \right) \left( \begin{array}{c} \text{target} \\ \text{eigenfunctions} \end{array} \right) \quad (6)$$



The 'expansion coefficients' in this eigenfunction expansion contain the dependence of  $\Psi_E$  on the coordinate  $r$  of the scattering electron; they are therefore *one-particle scattering functions*. The operator  $\mathcal{A}$  in equation (6) is an antisymmetrizer; it merely ensures that the Pauli Principle is satisfied by  $\Psi_E$ . In principle, the target state expansion of (6) must include eigenfunctions for all bound *and continuum* states of the target. The set consisting of these functions is complete in the molecular coordinates  $\tau_m$ .

A set of equations for the one-particle scattering functions is obtained by substituting (6) into the Schrödinger equation (4) and performing some relatively painless algebra.

The resulting one-particle scattering equations are still hard to solve, since they contain radial and angular coordinates of the electron. To eliminate the latter from the problem, we can take the second step of introducing a further complete-set expansion of the one-particle scattering functions in *angular functions*, i.e. eigenfunctions of suitably chosen angular momentum operators,

$$\left( \begin{array}{c} \text{one-particle} \\ \text{scattering function} \end{array} \right) = \sum_{\text{partial states}} \left( \begin{array}{c} \text{radial} \\ \text{scattering function} \end{array} \right) \left( \begin{array}{c} \text{angular} \\ \text{functions} \end{array} \right). \quad (7)$$

The angular functions contain the full dependence of the scattering functions on the angular variables. Thus the 'expansion coefficients' here are *radial scattering functions*. Equation (7) is often called a 'partial-wave expansion' (cf. Ch. 11 of Taylor 1972). This expansion leads—by substitution into the equations for the one-particle scattering functions followed by suitable algebraic contortions—to a set of equations for the *radial scattering functions*.

The equations in this set are *not* independent of one another. Terms in the molecular Hamiltonian and the *non-spherical* electron-molecule interaction potential lead to 'coupling' between the equations for the various radial scattering functions. Consequently, the entire set of equations must be solved simultaneously in order to obtain any individual scattering function. [Symmetry properties of the electron-molecule system can lead to considerable simplification of this chore, in that they cause the huge set of equations that one obtains by implementing the expansions (6) and (7) to separate into a number of *independent* smaller sets of coupled equations.]

To solve this set of coupled equations, which is (in principle) infinite, we *truncate* it, obtaining a *finite* set of equations that, ideally, is small enough to be solvable on a computer and that leads to highly accurate approximations to the desired cross sections. This is the idea behind CLOSE-COUPLED THEORIES.\*

An additional operational difficulty arises from the sad fact that the coupled equations for the radial scattering functions are *integrodifferential* equations. The integral terms in these equations, which are particularly odious, are characterized

\* This name has its origin in the fact that the target states in the expansion (6) that are most important to the determination of a cross section for a given transition and, hence, which must be retained in the truncation are 'close' (in energy) to the initial and final states. In applications of this theory, one neglects the continuum and most of the discrete (bound-state) target eigenfunctions. The energetically inaccessible states thereby left out *are* germane to the scattering; they represent second-order distortion effects ('polarization'). This severe truncation necessitates the inclusion of polarization effects by other means (see Section 4b). For details concerning truncation and convergence of the scattering equations, the courageous reader is referred to the technical article by Morrison (1979).

by the presence of the (unknown) radial scattering function in an integrand. These integral terms arise from the action of the antisymmetrizer  $\mathcal{A}$  in equation (6) and are often referred to in the literature as *exchange terms*. [We shall discuss exchange further in Section 4a. Here we shall note only that these exchange terms can formally be incorporated into the equations for the one-particle functions of equations (6) or (7) by introducing a *non-local*\* 'exchange potential'  $\hat{V}_{ex}$  into the single-particle Hamiltonian for the collision, cf. equation (1).]

The necessity of taking account of the effects of exchange markedly complicates the calculation of cross sections for electron scattering from atoms or from molecules. The resulting computational difficulties are exacerbated in the electron–molecule case by the partial-wave coupling due to the non-spherical character of the interaction potential  $\hat{V}_{int}$ .

## 2. Body and laboratory frames: The physics of electron–molecule collisions

Keeping in mind the background laid in Section 1, let us turn now to one of the fundamental conundrums of electron–molecule theory: How should we take into account the effects of the *nuclear motion*? In particular, does the physics of the collision permit us to treat the motion of the scattering electron separately from that of the nuclei? That is, can we justifiably assume that the scattering electron responds *adiabatically* to changes in the positions of the nuclei as they go about their rotational and vibrational motions? This assumption amounts to invoking the Born–Oppenheimer approximation *for the electron–molecule system* (Shugard and Hazi 1975); it leads to the ADIABATIC-NUCLEI THEORY to be discussed in Section 3a. If, on the other hand, we do *not* invoke this adiabatic separation, then we must explicitly retain the interaction of the motion of the scattering electron and that of the nuclei. In theories that adopt this viewpoint, the electron is allowed to respond dynamically to the nuclear motion. For example, including the non-adiabatic coupling of the *orbital* motion of the scattering electron to the *rotational* motion of the nuclei leads to the ROTATIONAL CLOSE-COUPLED METHOD described in Section 3b.

As pointed out in Section 1c, it is certainly desirable to implement an adiabatic separation if it is valid, since doing so eliminates the need to cope with extensive coupling of nuclear states. This observation leads us to the central question of this section: *Under what circumstances is the Born–Oppenheimer approximation justified for the electron–molecule system?*

To address this question, we adopt the viewpoint of the *frame-transformation* theory of Chang and Fano (1972). This theory will provide a 'framework' for our discussion, in Section 3, of various strategies currently being used to calculate electron–molecule cross sections. Moreover, the frame-transformation idea focuses our attention on the essence of the physics of the collision.

The central point of this idea, as elucidated by Fano (1970) and most recently reviewed by Lane (1980), is that *neither* of the above approaches to the problem of nuclear motion is really appropriate to the electron–molecule collision. The reason is that, as the electron approaches, interacts with and then leaves the molecule, it finds itself in fundamentally different physical environments.

\* A local potential  $V(r)$  is simply a function of the position coordinate  $r$ . In contrast, a *non-local* potential cannot be specified in this way, since its value at any single point  $r$  depends on its value throughout space.

To a great extent, this fact is a consequence of the nature of the system Hamiltonian (2). For purposes of the present discussion, it is desirable to write the *molecular* Hamiltonian  $\mathcal{H}_m$  as the sum of an electronic Hamiltonian for the molecule  $\mathcal{H}_m^{(e)}$  and a nuclear Hamiltonian  $\mathcal{H}_m^{(n)}$  (cf. Ch. 11 of Morrison *et al.* 1976). Then the *system* Hamiltonian takes on the form

$$\mathcal{H} = \mathcal{H}_m^{(e)} + \mathcal{H}_m^{(n)} + \hat{T}_e + \hat{V}_{\text{int}} \quad (8)$$

The electronic Hamiltonian in this expression contains the kinetic-energy operators for the molecular electrons, the attractive electron-nucleus and repulsive electron-electron Coulomb potential energies for these electrons, and (by convention) the repulsive nucleus-nucleus potential energy. The nuclear Hamiltonian is just the nuclear kinetic-energy operator, which can be separated into the sum of terms that describe the rotational and vibrational motion.

Now, the behaviour of the scattering electron at any position  $r$  is, in large part, determined by the relative importance of the various terms in (8). In a particular region of space, for example near the target, the dominant term in this Hamiltonian determines which physical observables are (approximately) conserved in the collision. As we shall see, knowledge of these *approximate constants of the motion* is a useful guide in formulating a physically appropriate collision theory. The salient point is that the relative importance of the  $\mathcal{H}_m^{(n)}$  and  $\hat{V}_{\text{int}}$  terms depends on the proximity of the scattering electron to the target.

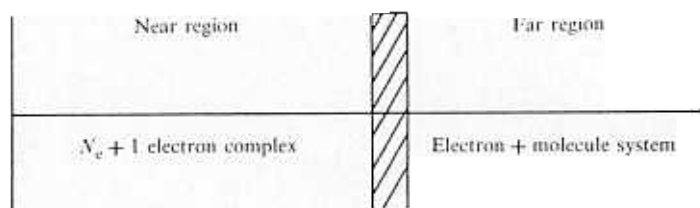


Fig. 4. Partitioning of space according to the proximity of the scattering electron at distance  $r$  from the target molecule. The (fuzzy) boundary at  $r_1$  subdivides space according to the physical picture appropriate to the collision near and far from the target.

To elucidate the above remarks, let us imagine a boundary dividing space into two regions, one 'near' the target and the other 'far' from it, as shown in Fig. 4. This boundary is not necessarily sharply defined. Moreover, its location need not be specified precisely. Crudely speaking, one can envisage the boundary as a *surface* immediately outside the molecular charge cloud, at the approximate radius  $r_1$ . We shall now consider in turn the physical environment of the electron in each region.

#### (a) Inner (Near-target) Region

In the 'inner' region, the scattering electron finds itself in the same physical environment as the  $N_e$  molecular electrons; indeed, as pointed out above, all electrons in the system must be treated quantum mechanically as 'indistinguishable' from one another. One is therefore tempted to treat the system theoretically as an  $N_e + 1$

electron complex, as indicated in Fig. 5. This idea is the basis (*sic*) of the aforementioned  $L^2$  variational methods\* (cf. the references in Table 1).

In terms of the Hamiltonian (8), the inner region is distinguished by the dominance of the electron–molecule interaction potential  $\hat{V}_{\text{int}}$ , which is strongly attractive near the nuclei. In the determination of the behaviour of the scattering electron in this region, this term dominates the nuclear Hamiltonian. This fact diminishes the relative importance of the troublesome coupling of different nuclear target states, which is due to the nuclear Hamiltonian. Because of the dominance of this strongly attractive, axially symmetric potential energy, the projection of the orbital angular momentum of the electron along the internuclear axis is quantized (to a very good approximation), and the angular dependence of the one-electron scattering function (cf. equation 7) is most appropriately described by angular functions *referred to this axis of quantization* (for example, spherical harmonics).

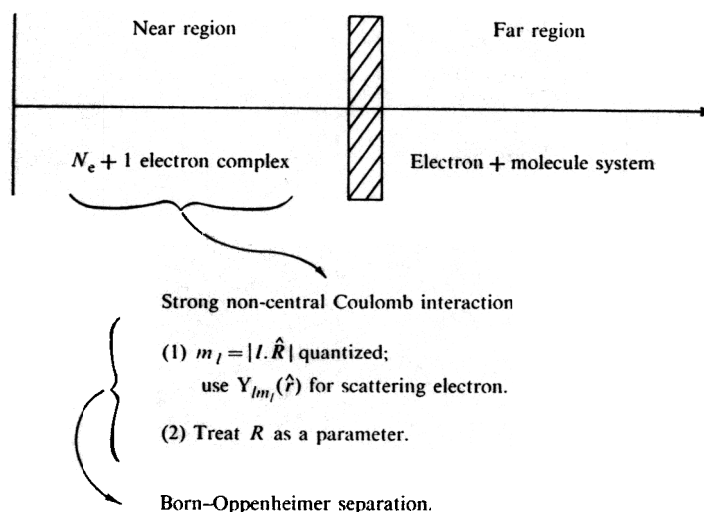


Fig. 5. Summary of the physics of the 'inner region'

For this reason, the theory in the near-target region is optimally formulated in the 'body-fixed' coordinate system shown in Fig. 6. Unlike the 'space-fixed' (or 'lab') system of Fig. 3, the body-fixed system rotates with the molecule. In such a formulation, the internuclear axis always lies along the polar  $z$ -axis. This choice of coordinate system facilitates *neglect of the rotational Hamiltonian in the inner region*, an approximation which is justified by the dominance of the interaction potential in this inner region.

What about the other contribution to the nuclear Hamiltonian in (8), the vibrational term? If we think about the behaviour of the electron in the inner region in semi-classical language for a moment, we can imagine it 'speeding up' as it nears the nuclei and is exposed to increasingly strong attractive Coulomb forces. The speed

\* For example, in the *R-matrix method* one solves the molecular structure problem for this complex in the inner region using the variational principle. The resulting 'inner solutions' are matched at the boundary to 'outer solutions' that obey appropriate scattering boundary conditions. The *R matrix* is just a mathematical device for effectuating this matching procedure.

of the electron in the inner region will be much greater than that of the motion of the nuclei. This picture suggests that the electron is moving so rapidly that, in effect, it 'sees' a fixed nuclear geometry; in particular, it will (to a good approximation) adjust instantaneously to changes in the internuclear separation  $R$ . Consequently, in the near-target region it makes sense to treat  $R$  as a parameter in determining the wavefunction of the scattering electron.

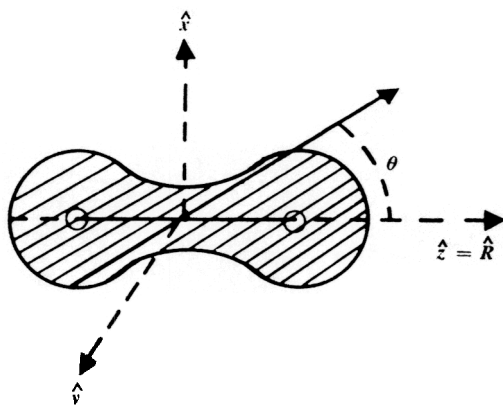


Fig. 6. Schematic of the electron-molecule system in the body-fixed coordinate system, which is defined so that  $\hat{z} = \hat{R}$ . This coordinate system is used in fixed- and adiabatic-nuclei formulations.

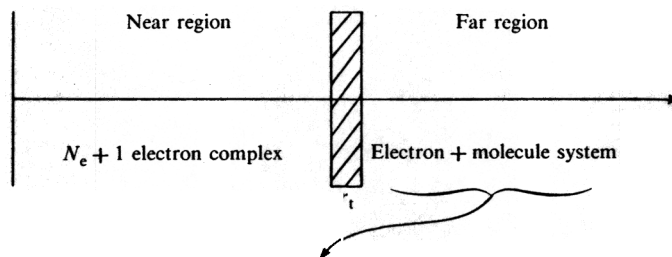
Our ruminations have partly answered, at least for the 'near' region, the question posed in the introduction to this section: Under what circumstances is the Born-Oppenheimer approximation justified for the electron-molecule system? The physical picture that emerges as appropriate to this region of space is a simple one: Invoking the Born-Oppenheimer approximation in a body-fixed reference frame, we 'freeze' the spatial locations of the nuclei for the duration of the collision and determine the scattering function for the electron in this 'fixed-nuclei approximation'. Computational schemes based on this theoretical picture have several highly desirable features, not the least of which are the ensuing simplifications of the set of coupled equations for the radial scattering functions of equation (7). For example, the equation that describes *electronically elastic* collisions for a diatomic target can be treated by the partial-wave method, the 'coupled channels' being labelled\* by  $l$  and  $m_l$ , the quantum numbers corresponding to the orbital angular momentum of the scattering electron and its projection along the internuclear axis respectively. In the approximation that the orientation of the internuclear axis is fixed, channels with different values of  $m_l$  are not coupled. This fact is a consequence of the absence of the  $z$  projection  $\hat{L}_z$  of the orbital angular momentum operator in the Hamiltonian in this approximation; it leads to a reduction in the number of simultaneous equations one must solve in this formulation. Further simplifications in these equations ensue if we can fix the internuclear axis, since the vibrational degree(s) of freedom of the nuclei do not explicitly appear.†

\* Channels are conventionally labelled by the quantum numbers appropriate to the asymptotic states of the system, in the present case being the spherical harmonics  $Y_{lm_l}(\hat{r})$ . [See Ch. 16 of Taylor (1972) for an excellent discussion of channels in collision theory.]

† The usual parlance in electron-molecule theory is to use the 'fixed-nuclei approximation' to describe the formulation in which the internuclear orientation *and* separation are frozen throughout the collision. The phrase 'fixed-nuclear-orientation approximation' is sometimes used to describe a formulation in which only *rotational* degrees of freedom are frozen.

(b) *Outer (Far) Region*

The electron–molecule interaction potential, which is dominant in the near-target region, diminishes in strength with increasing distance from the origin. Consequently, the assumption that we can neglect the nuclear Hamiltonian in determining the wavefunction of the scattering electron becomes increasingly questionable in the region of space outside the molecular charge cloud.



Interactions other than Coulomb are important.

- (1) Angular momentum coupling  $\hat{j} + \hat{l} = \hat{J}$
- (2)  $m_l = |l \cdot \hat{R}|$  is not a good quantum number.
- (3)  $\hat{H}_{\text{rot}}$  and  $\hat{H}_{\text{vib}}$  are important.

Include dynamical interaction of electron and nuclei.

Fig. 7. Summary of the physics of the 'far region'

Strictly speaking, this outer region includes values of the electron radial coordinate  $r$  that are so large that  $\hat{V}_{\text{int}}$  is negligible. This is the *asymptotic region*, where we extract the scattering amplitude from the scattering function. However, in the present instance we are interested in *non-asymptotic* values of  $r$  beyond our imaginary boundary, where  $\hat{V}_{\text{int}}$  is still important but not dominant. This is the 'far' region shown schematically in Fig. 7.

Because of the diminished strength of  $\hat{V}_{\text{int}}$  in this region, the projection of the orbital angular momentum of the electron along the nuclear axis is no longer quantized, i.e.  $m_l$  is not even approximately a good quantum number. In this region, competing terms in the Hamiltonian significantly influence the quantum behaviour of the electron. For example, we must acknowledge the coupling of the rotational angular momentum of the nuclei and the orbital angular momentum of the scattering electron; in our semiclassical conceptualization of the collision this coupling can be thought of as arising from the mutual interaction of the corresponding torques. This *angular momentum coupling* can be conveniently taken into account by formulating the collision theory in the 'space-fixed' (lab) coordinate system of Fig. 3.

In the far region, the scattering electron is slow moving, and the conceptual picture of it being scattered by the field of *fixed nuclei*, on which we based the approximate Born–Oppenheimer separation of Section 2a, breaks down. Instead, we should take full account of the rotational and vibrational Hamiltonians accepting, with some reluctance, the concomitant increase in complexity of the close-coupling equations owing to the explicit appearance of the nuclear wavefunctions.

This unfortunate feature of the theory in the far region is mitigated somewhat by the fact that in this region the coupling between different nuclear states and

that between different partial waves is comparatively weak.\* The rotational and orbital angular momenta are only weakly coupled, and the corresponding quantum numbers for the magnitudes of these observables are the most appropriate channel labels for an eigenfunction expansion of the system wavefunction.

Thus in the region outside the molecular charge cloud, the most suitable way to formulate the collision theory is in a 'space-fixed' reference frame, taking explicit account of the effects of the nuclear motion on the wavefunction of the scattering electron. It is advantageous to explicitly couple the rotational and orbital angular momenta in such a formulation, since the resultant *total* angular momentum and its projection along the lab polar axis are constants of the motion (cf. Section 16.6 of Merzbacher 1970). Finally, we should note that a lab reference frame is also convenient because (obviously) measurements are made in such a reference frame. If one likes, one can view the *body frame* of Section 2a as a theoretical artifice introduced because it leads to a formulation of the problem that is more suitable to the physics of the collision near the target.

### (c) Frame Transformation

In seeking a theoretical formulation of the quantum mechanics of electron-molecule scattering that most accurately reflects the essential physics of the collision, we have been led, in the preceding subsections, to a 'dual description' of the system. The division of space into two regions was motivated by the relative importance of various terms in the Hamiltonian near and far from the target. The dominant terms are different in the two regions, a fact which evokes distinct physical pictures in these regions and leads to correspondingly different approximations (for example, different physical observables are approximate constants of the motion in the two regions). In addition to the insight this scheme provides, it is beneficial in practical ways; for example, in reducing the fraction of one's computer budget that must be consumed in solving coupled equations!

We have not yet addressed the question of how to relate the scattering function in the inner region to its counterpart in the outer region. This step is essential, since we must eventually determine the wavefunction in the *asymptotic* region ( $r \rightarrow \infty$ ) in order to obtain the desired scattering information.

A mechanism for 'connecting' the scattering functions in the two regions is the *frame-transformation* procedure of Chang and Fano (1972). The rather evocative name of this procedure derives from its operational details. At the boundary radius ( $r_1$  in Fig. 4), one uses a (unitary) transformation to *transform* the *body-frame/fixed-nuclei* scattering function *into* the lab reference frame. Letting  $\hat{U}$  symbolically denote the transformation, we can write the frame transformation schematically as†

$$\begin{pmatrix} \text{lab-frame} \\ \text{scattering function} \end{pmatrix} = \hat{U}^\dagger \begin{pmatrix} \text{body-frame} \\ \text{scattering function} \end{pmatrix} \hat{U}. \quad (9)$$

\* The possible exception to this statement is that of a system in which the target is a strongly polar molecule. In this case, the strong long-range  $r^{-2}$  dipole interaction induces significant coupling of partial waves with  $\Delta l = 1$  (see Section 3d or, for more detail, the review by Norcross and Collins 1982).

† The transformation (9) actually accomplishes *two* things: (1) it rotates the body-fixed coordinate system (Fig. 6) into the space-fixed (lab) system (Fig. 3); (2) it 'removes' the fixed-nuclei approximation.

The function on the right-hand side of (9) embodies the effects of the inner region on the scattering electron. Once this function has been appropriately transformed into the lab frame, its behaviour in the outer region—and, most importantly, at large values of  $r$ —can be investigated. The definition of the function on the left-hand side of (9) incorporates the fact that  $j$  and  $l$  are approximately good quantum numbers in the outer region and explicitly couples these angular momenta to introduce the total angular momentum  $J = j + l$ , which is conserved in the collision (recall Fig. 7). Thus, the frame transformation  $\hat{U}$  relates two equivalent forms of the scattering function at  $r_t$ , one form appropriate to the physics of the inner region, the other appropriate to that of the outer region.

Operationally, one can envisage a computational procedure based on this dual description of the collision. Starting at the origin, we could propagate the body-frame/fixed-nuclei scattering function (of Fig. 6) through increasing values of  $r$  (by solving the appropriate Schrödinger equation numerically) until we reach  $r = r_t$ . At this point, the frame transformation (9) is invoked, putting us in the lab-frame formulation. We then continue propagating the scattering function out from  $r_t$  to some value of  $r$  large enough so that we can extract scattering information from it.\*

It is worth noting that the frame-transformation procedure involves no approximations other than the fixed-nuclei approximation in the near-target region. Indeed, in their original discussion, Chang and Fano (1972) distinguished the frame transformation as such from the additional assumptions of the fixed-nuclei theory, which lead to the adiabatic-nuclei and related methods (see Section 3a).

In spite of the power and physical appeal of frame-transformation theory, few applications of it have been reported. The most complete study to date is that of Chandra (1977) for e-CO scattering. This theory has been discussed by Le Dourneuf *et al.* (1979), who have introduced some interesting modifications to the original formulation of Chang and Fano.

### 3. Various strategies—and a few applications

In this section, we shall use the frame-transformation idea as a springboard for the discussion of several theoretical schemes for calculating cross sections for low-energy electron-molecule scattering.

Two widely used procedures, the adiabatic-nuclei theory and the close-coupling method, will be obtained in Sections 3a and 3b by the simple expedient of moving the (imaginary) boundary between the inner and outer regions to infinity or to the origin. Variants and combinations of these methods will be examined in the third subsection, and an alternative type of frame transformation that is especially useful in the study of electron polar molecule scattering will be described in Section 3d.

#### (a) Adiabatic-nuclei Method

In Section 2, we saw that the most appropriate description of the essential physics of an electron-molecule collision in the region of space near the target is different

\* Chandra and Gianturco (1974) have proposed frame transforming the  $R$  matrix rather than the radial wavefunctions. This idea has been implemented by Chandra (1977) in a study of e-CO collisions. Strictly speaking, the method described in this section should be called a 'radial' frame-transformation theory to distinguish it from 'angular' frame-transformation theories (Section 3d). Clark (1979) has contributed a variant on the method of Chang and Fano (1972) that is especially designed to treat systems in which the target is a polar molecule and the electron-dipole interaction is dominant at intermediate and large values of  $r$ .



from that appropriate to the far region. In the former region, a Born-Oppenheimer separation of nuclear and electronic motion is justified for the electron-molecule system because of the dominance of the attractive Coulomb potential. In the far region, on the other hand, the dynamic interaction of the quantum motions of the scattering electron and molecular nuclei must be taken into account. The two regions thus defined are separated by a boundary, as shown in Fig. 4.

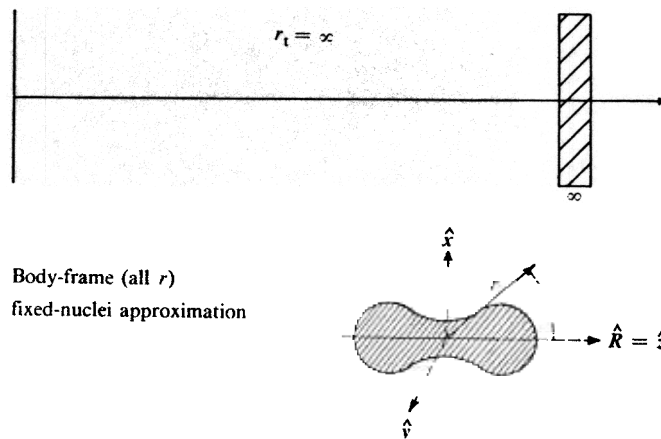


Fig. 8. Adiabatic-nuclei theory regained from the 'dual region' picture of Fig. 4. This theory is usually (but not necessarily) formulated in the body-fixed coordinate system with use made of the fixed-nuclei approximation.

Suppose we place this boundary in the asymptotic region, i.e. 'at infinity', as shown in Fig. 8. In the resulting picture, the collision takes place entirely in the body-fixed reference frame, and the *fixed-nuclei approximation* is made throughout all of space.\* This approximation, which, because of the increasing importance of the nuclear Hamiltonian, is more severe far from the target than in the inner region, is the essential assumption of the *adiabatic-nuclei* method.

To understand this widely used method, it is important to keep in mind the physical assumptions that underly it. Essentially, these assumptions amount to an extension of the picture of Section 2a to all of space. We are invoking an adiabatic separation of electronic and nuclear motion throughout space; for this separation to be valid, the effects of the interaction potential must dominate those of the nuclear Hamiltonian so that the latter can be neglected in the determination of the scattering wavefunction.

The adiabatic-nuclei theory can be implemented in either the body frame or the lab frame (see Shugard and Hazi 1975) although, of the resulting computational schemes, the body-frame formulation is more convenient and hence is always used in practical applications. It is important to note that adiabatic-nuclei theory as such is based on the picture of the electron scattering from a 'frozen' nuclear geometry rather than on a particular choice of coordinate axes.

\* Choi and Poe (1977a, 1977b) have proposed a 'moving body-frame' formulation of electron-molecule scattering that does not require making the fixed-nuclei approximation. However, to date no application of this method has been published.

The simplest incarnation of adiabatic-nuclei theory is based on the assumption that no *electronic* excitation of the molecule takes place; the resulting formulation does allow for nuclear excitations (rotations and vibrations). Assuming that the molecule remains in the ground electronic state and making the fixed-nuclei approximation reduces the target-state expansion of equation (6) to a single term (in the body frame). Coupled equations for the radial scattering functions are then simply obtained via the partial-wave expansion (7).

Once the coupled equations, or their lab-frame counterparts, have been solved and a fixed-nuclei scattering amplitude obtained, the differential cross section can be calculated by averaging the squared magnitude of this amplitude over all nuclear orientations. Subsequent integrations of this cross section over *lab-frame* scattering angles lead to integrated and momentum-transfer cross sections. We should emphasize that none of these 'fixed-nuclei cross sections' correspond to *elastic* scattering. A detailed perusal of the theory reveals that each of these is a 'total' cross section, i.e. the sum of the cross sections for elastic scattering and for all rotational excitations.\*

From our description of the physical picture on which the adiabatic-nuclei theory is based, the reader might reasonably conclude that the assumptions of the theory prohibit the determination of cross sections for rotational and/or vibrational excitation. Not so! In point of fact, the essential result of the adiabatic-nuclei theory is that one *can* obtain approximate inelastic cross sections from the *fixed-nuclei* scattering amplitude. Let us denote this latter quantity by  $f^{\text{FN}}(\theta, \phi; \mathbf{R})$ , where  $\theta$  and  $\phi$  are the scattering angles in the lab reference frame (of Fig. 3) and where  $\mathbf{R}$  denotes the *parametric* dependence of this quantity on the internuclear separation and orientation.†

Once we have obtained the lab-frame fixed-nuclei scattering amplitude, it is an easy matter to calculate the amplitude for any desired ro-vibrational excitation. Suppose we are interested in the cross section for excitation from an initial state  $i$  to a final state  $f$ . For example, we might want to determine the cross section for ro-vibrational excitation of a diatomic molecule from an initial state  $i$ , denoted by vibrational and rotational quantum numbers  $v_0$  and  $j_0$  respectively, to a final state  $f$ , denoted by  $v$  and  $j$ . In the adiabatic-nuclei theory, the scattering amplitude for this excitation is computed from the nuclear wavefunctions  $\chi_i(\mathbf{R})$  and  $\chi_f(\mathbf{R})$  according to the simple formula

$$f_{i \rightarrow f}(\theta, \phi) = \int \chi_f^*(\mathbf{R}) f^{\text{FN}}(\theta, \phi; \mathbf{R}) \chi_i(\mathbf{R}) d\mathbf{R} \quad (10)$$

\* In the adiabatic-nuclei theory, the quantity formed by adding all rotational-excitation cross sections from an initial state  $j_0$  to all (energetically accessible) final states  $j$  turns out to be independent of the *initial-state* quantum number  $j_0$ . Hence, it is meaningful to talk about a 'total cross section' without specifying a particular initial rotational state. This lack of dependence on initial-state quantum numbers is uniquely a feature of the adiabatic-nuclei theory *for rotation* and does not hold in the corresponding theory for vibration.

† If the usual radial scattering equations are solved in the *body-frame/fixed-nuclei* formulation, an intermediate step must be inserted into this analysis: In this step we obtain the 'lab' scattering amplitude  $f^{\text{FN}}(\theta, \phi; \mathbf{R})$  from 'body-frame' scattering quantities that we extract from the radial scattering function in the asymptotic region. This step entails a standard rotation of coordinates (cf. Rose 1957) and introduces *no* new approximations.

From this scattering amplitude we can calculate differential, integral or momentum-transfer cross sections using standard equations (cf. Lane 1980). Equation (10) is *the* central result of adiabatic-nuclei theory.

To fully explain why this simple integration produces an approximate scattering amplitude for inelastic scattering would entail a more mathematical exposition of the collision theory than befits the present overview. However, the structure of equation (10) provides a clue to what is happening. In determining the fixed-nuclei scattering amplitude  $f^{\text{FN}}(\theta, \phi; \mathbf{R})$  we completely neglect the effects of the nuclear Hamiltonian  $\mathcal{H}_m^{(n)}$  on the wavefunction of the scattering electron. In the adiabatic-nuclei theory these effects are introduced approximately ('after the fact') by 'averaging' the fixed-nuclei amplitude over the nuclear coordinates  $\mathbf{R}$ , the 'weighting factor' in this averaging being the product of the initial and final target states,  $\chi_i^*(\mathbf{R})\chi_f(\mathbf{R})$ .

In a number of adiabatic-nuclei calculations, the internuclear *separation* is held fixed throughout, allowing one to calculate only rotational excitation cross sections via equation (10). In these 'adiabatic nuclear rotation' studies, vibrational motion of the nuclei is *completely ignored*. In considering the results of calculations that use the adiabatic nuclear rotation theory, it is important to keep in mind that the internuclear separation is fixed at its equilibrium value. Thus, such calculations ignore the zero-point motion of the nuclei as well as the effects of open and closed vibrational states. Phenomena such as vibrational broadening of resonance peaks and structure in the cross sections due to vibrational motion will not be seen in the results of such studies. The consequences of this freezing of the internuclear separation have been discussed by Klonover and Kaldor (1979).

The adiabatic-nuclei theory has been widely used in the last several years. The essential ideas elucidated above can be implemented in the context of eigenfunction-expansion,  $L^2$  variational, or other formulations. An extensive discussion of these applications and illustrative results for a variety of systems can be found in the review by Lane (1980).

Thus far in this section, we have treated all of the nuclear motion, i.e. rotation and vibration, adiabatically. One need not do this; variations on this theme have been used in which one or the other motion is treated non-adiabatically. We return to these 'hybrid theories' in Section 3c.

### (b) Close-coupling Methods

The adiabatic-nuclei method of Section 3a was obtained from the frame-transformation picture by placing the boundary between the inner and outer regions at infinity. Suppose, instead, that we consider the other extreme and put the boundary at the coordinate origin ( $r_i = 0$ ), as shown in Fig. 9. This stratagem leads to *lab-frame close-coupling theories*.

These theories are usually formulated by implementing eigenfunction expansions\* in the space-fixed (lab) reference frame shown in Fig. 3. The expansions that one introduces to simplify the many-particle electron-molecule Schrödinger equation are just those of Section 1c: for electronically elastic collisions, the electron-molecule system wavefunction is expanded (as in equation 6) in target eigenfunctions, each of which is a product of the (same) ground-electronic-state molecular wavefunction  $\Phi_g(\tau_m)$  and a nuclear wavefunction  $\chi_\alpha(\mathbf{R})$ . The summation in this target-state expansion runs over  $\alpha$ , which collectively denotes the set of rotational and vibrational quantum numbers. A further partial-wave expansion (7) leads (via some algebra)

to a set of coupled equations for the radial scattering functions. [In most applications of lab-frame close-coupling theory, one takes advantage of the fact that the total angular momentum *of the system* and its projection on the (space-fixed)  $z$ -axis are constants of the motion by coupling the orbital angular momentum of the scattering electron to the rotational angular momentum of the molecule (Arthurs and Dalgarno 1960). This angular momentum coupling does not affect the treatment of the vibrational states in the expansion (6).]

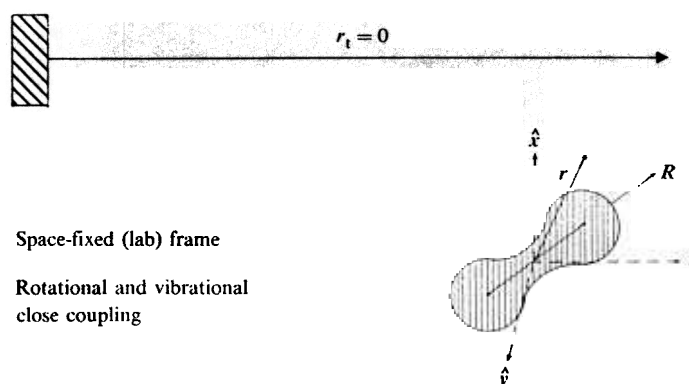


Fig. 9. Lab-frame close-coupling theory regained from the 'dual region' picture of Fig. 4. Close-coupling theories can also be formulated in the body-fixed reference frame (cf. Choi and Poe 1977a).

The essential feature of the physical picture that distinguishes close-coupling methods is the way in which they incorporate the effects of the nuclear motion on the scattering electron. The electron is allowed to respond dynamically, rather than adiabatically, to the motion of the nuclei. (This interaction appears in the radial scattering equations as the coupling of different nuclear states by the interaction potential energy.) This approach is more accurate than the adiabatic-nuclei method, since it does not assume the Born-Oppenheimer separation that characterizes the latter theory. (It is in this sense that close-coupling theories can meaningfully be described as 'non-adiabatic'.)

In addition to being more accurate than the theory of Section 3a, the present formalism is somewhat easier to understand. Here we need not introduce the rather artificial body-fixed reference frame, with the attendant rotation of coordinates back to the space-fixed frame. Moreover, we do not average over nuclear coordinates in calculating cross sections. Indeed, in lab-frame close-coupling methods the lab-frame scattering amplitude  $f_{i \rightarrow f}(\theta, \phi)$  is computed directly from the radial scattering functions in the asymptotic region, and cross sections can be obtained immediately.

Thus the lab-frame close-coupling theory is easier to comprehend and more accurate than the adiabatic-nuclei theory of Section 3a. Nonetheless, it has been

\* The close-coupling idea need not be restricted to eigenfunction-expansion theories. Kaldor (1979) has shown formally how to allow for coupling of nuclear states in the context of an  $L^2$  variational method, although no applications of this theory have been published to date. Moreover, Choi and Poe (1977a) have formulated full ro-vibrational close-coupling theory in a body-fixed reference frame.

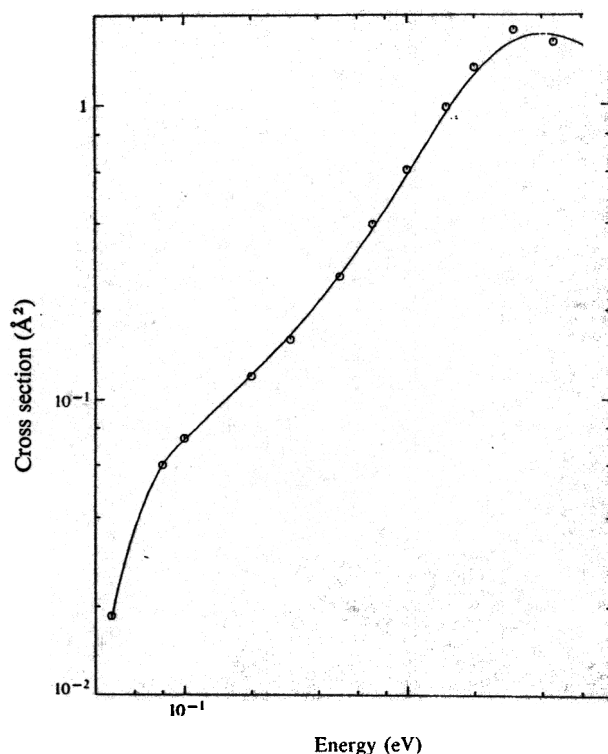
used only sparingly in the study of electron-molecule scattering (see Lane 1980). The reason for this seeming contradiction is the plethora of coupled equations that one must solve in this case. Because of the small energy spacing between rotational and vibrational states (typically, tenths of a meV for rotational states and tenths of an eV for vibrational states), a huge number of nuclear target states will be energetically accessible even at very low scattering energies. Many (or all) of these must be included in the target-state expansion (6) to obtain accurate cross sections. Moreover, it may be necessary to include some or all of the infinity of target states that are energetically inaccessible. (These states correspond to distortion, or 'polarization', of the target by the scattering electron; see Section 4*b*.) Each nuclear target state gives rise, through the partial-wave expansion (7), to a host of coupled equations.

By contrast, a comparatively small number of coupled radial scattering equations is obtained in the adiabatic-nuclei theory. This happy fact is a consequence of ignoring the nuclear motion in solving the 'electronic' (fixed-nuclei) scattering problem. To some extent, this pragmatic computational consideration—*how many coupled equations must we solve simultaneously?*—is responsible for the widespread use of methods based in whole or part on the Born-Oppenheimer theory of Section 3*a*, rather than the admittedly more accurate theory of the present subsection. Nevertheless, the lab-frame close-coupling formalism is useful in understanding the physics of electron-molecule scattering, is an essential part of the frame-transformation theory, and *may* be (computationally) feasible in circumstances where the adiabatic-nuclei method is not applicable owing to a breakdown of the Born-Oppenheimer approximation.

Full lab-frame ro-vibrational close-coupling theory using a reasonably realistic representation of the electron-molecule interaction potential has been applied only to low-energy e-H<sub>2</sub> scattering (Henry 1970). However, a number of studies have been reported using *rotational close coupling*, in which the vibrational states are not included in the target-state expansion (6). The most convenient way to implement this approximation is to simply 'freeze' the internuclear separation at its equilibrium value. This is the *rigid-rotator* model of the molecule. Like the *adiabatic nuclear rotation* method discussed at the end of Section 3*a*, rotational close-coupling studies *completely* neglect the vibrational motion, including the zero-point motion of the molecule. It is advisable to keep this fact in mind when trying to interpret and use the results of rotational close-coupling calculations.

A few applications of the rotational close-coupling method to intermediate-energy electron-molecule collisions have been reported by Truhlar and collaborators; notable among these are recent studies by Onda and Truhlar (1980) of e-CO scattering at 10 eV, and by Thirumalai *et al.* (1981) of e-C<sub>2</sub>H<sub>2</sub> collisions. Other applications are discussed in the reviews by Lane (1980) and by Takayanagi and Itikawa (1970).

From the standpoint of agreement between theoretically calculated and experimentally measured cross sections, the calculations of Henry and Lane (1969), Hara (1969) and Feldt *et al.* (1983) on rotational excitation of H<sub>2</sub> are particularly noteworthy. In Fig. 10 theoretical results from the last study, which entailed a full ro-vibrational close-coupling calculation for the excitation  $j_0 = 0 \rightarrow j = 2$  within the ground vibrational state, are compared with the highly accurate cross sections of Crompton *et al.* (1969), which were determined indirectly from data taken in swarm experiments (cf. the review by Crompton 1969).



**Fig. 10.** Cross section for the rotational excitation  $j_0 = 0 \rightarrow j = 2$  of  $H_2$  by electron impact as calculated by Feldt *et al.* (1983) using ro-vibrational close-coupling theory. The open circles are the experimental values of Crompton *et al.* (1969).

### (c) Hybrid Theories

The adiabatic-nuclei and lab-frame close-coupling methods adopt fundamentally different approaches to the problem posed by the nuclear motion. Both procedures suffer from disadvantages: On the one hand, the approximations underlying the adiabatic-nuclei method are invalid in several situations: for example, scattering near threshold for an inelastic transition, scattering near a shape resonance, excitations involving high-lying nuclear states, and collisions with strongly polar targets. On the other hand, the (more accurate) close-coupling procedures are usually inapplicable in practice because of the huge number of coupled equations that must be solved.

Regardless of which of the approaches described in Sections 3a and 3b is adopted, the theorist will run into special difficulties in the study of electron scattering from polar molecules. [This subject has been recently reviewed by Itikawa (1978) and by Norcross and Collins (1982).] The long-range electron-dipole interaction potential characteristic of such systems exacerbates the partial-wave coupling and the attendant numerical worries. Worse yet, the total integrated cross section as calculated in the adiabatic-nuclei theory for electron polar molecule scattering is infinite, owing to an artificial divergence of the total differential cross section in the forward direction. (This problem does not plague the momentum-transfer cross section, which can be calculated with this method.)

In the light of these difficulties, some attention has been given recently to the development of 'hybrid methods' that combine elements of the two strategies discussed in Sections 3a and 3b. The spirit of these methods is similar to that of the radial

frame-transformation theory discussed in Section 2c: one treats various parts of the collision problem with simplifying approximations based on appropriate physical pictures. To implement such a philosophy, it is necessary to 'partition' the problem in some way. In the radial frame-transformation theory of Section 2c, this partitioning is easily visualized (*à la* Fig. 4), since it corresponds to an imaginary separation of space into inner and outer regions. In each region, the dominant terms in the Hamiltonian dictate suitable approximations and a formulation of the Schrödinger theory. The hybrid methods to be discussed in this and the following section are a bit more subtle in their approach. Hence, a qualitative exploration of these methods can lead us to further insight into the physics of electron-molecule scattering.

The first of these hybrid methods we shall discuss was introduced by Chandra and Temkin (1976) in an attempt to extend the adiabatic-nuclei theory to the study of shape resonances such as the 2.3 eV resonance in e-N<sub>2</sub> scattering. The lifetime of these resonances is about 10<sup>-14</sup> s. In time-dependent collision theory, this is a rough measure of the time the scattering electron spends near the molecule. But this time is roughly comparable with the vibrational period of the nuclear motion. Hence it is unreasonable to assume, as we did in the adiabatic-nuclei theory, that the electron is unaffected by the vibrational motion. This argument suggests that the dynamic interplay of the motion of the electron and the nuclear vibrational motion may be quite important for scattering at energies near a resonance.

The characteristic period for rotation (typically about 10<sup>-12</sup> s) is longer than that for vibration. Hence, even for scattering near a resonance of lifetime ~10<sup>-14</sup> s, the response of the scattering electron to the *rotational* motion may be adiabatic. To take advantage of this possibility, we could fix the *orientation* of the nuclei for the duration of the collision. To obtain excitation cross sections, we could use a variant of equation (10) in which we let  $\chi_i$  and  $\chi_f$  denote initial and final *rotational* target functions, and integrate over the angular coordinate  $\hat{R}$  only.

This was precisely the strategy adopted by Chandra and Temkin (1976): working in a body-fixed reference frame, they used vibrational close coupling to treat resonance scattering, and adiabatic-nuclei theory for everything else. However, knowing in advance the computational difficulties attendant on full close-coupling calculations, Chandra and Temkin used this theory only where absolutely necessary. To do so, they took advantage of the fact that in the fixed-nuclei/body-frame theory (see Section 2a), the set of coupled equations that must be solved actually consists of several smaller independent sets of coupled equations. Although equations within each set are coupled to one another, there is no coupling between equations in different sets. Consequently each set can be solved separately. Once this has been done, the desired scattering cross section, for example, can be determined by summing the 'partial cross sections' that were obtained from each set of equations.

These independent sets of coupled equations are labelled according to the symmetry properties of the electron-molecule system. Typically, one speaks of  $\Sigma_g, \Sigma_u, \Pi_g, \Pi_u$  etc. symmetries, where the capital Greek letter refers to the projection of the total electronic angular momentum *of the electron-molecule system* along the internuclear axis (the  $\hat{z}$ -axis in the body-frame fixed-nuclei theory of Fig. 6). In particular, we use  $\Sigma, \Pi, \Delta, \dots$  for values of this projection equal to 0,  $\hbar, 2\hbar, 3\hbar, \dots$ . The subscripts g and u indicate the parity of the electronic wavefunction *of the electron-molecule system* under simultaneous inversion of all electron coordinates through the

origin: g for even parity and u for odd parity.\* (This label is inapplicable for heteronuclear targets.) The partial cross section obtained by solving, say, the coupled equations for the  $\Sigma_g$  symmetry is referred to as the ' $\Sigma_g$  cross section'.

It is important to keep in mind that this nomenclature is a theoretical artifact. Strictly speaking, there is no such thing as a ' $\Sigma_g$  cross section'. Cross sections for comparison with experimental data or for applied needs must be 'assembled' by the theorist, including contributions from all important symmetries. This theoretical separation of the scattering problem into various symmetry contributions is analogous to the partial-wave separation one employs in potential or electron-atom scattering theory (cf. Ch. 11 of Taylor 1972). For example, in potential scattering, one speaks of 's-wave scattering' and 'd-wave cross sections', knowing full well that the *measurable* cross sections are comprised of contributions from all (non-negligible) partial cross sections.

One of these partial cross sections may be so large that it completely dominates all the other contributions to the summed cross section. For example, the scattering cross section at energies near the peak of a shape resonance is often accurately approximated by the partial cross section in a single symmetry. An illustration of this phenomenon is found in  $e\text{-N}_2$  cross sections, where a large peak, rich with structure (for example, oscillations), occurs in the vicinity of 2.3 eV (cf. Golden 1966). Near this energy, the cross section is due almost entirely to the  $\Pi_g$  contribution. Therefore, we speak of this peak as a ' $\Pi_g$  shape resonance'.

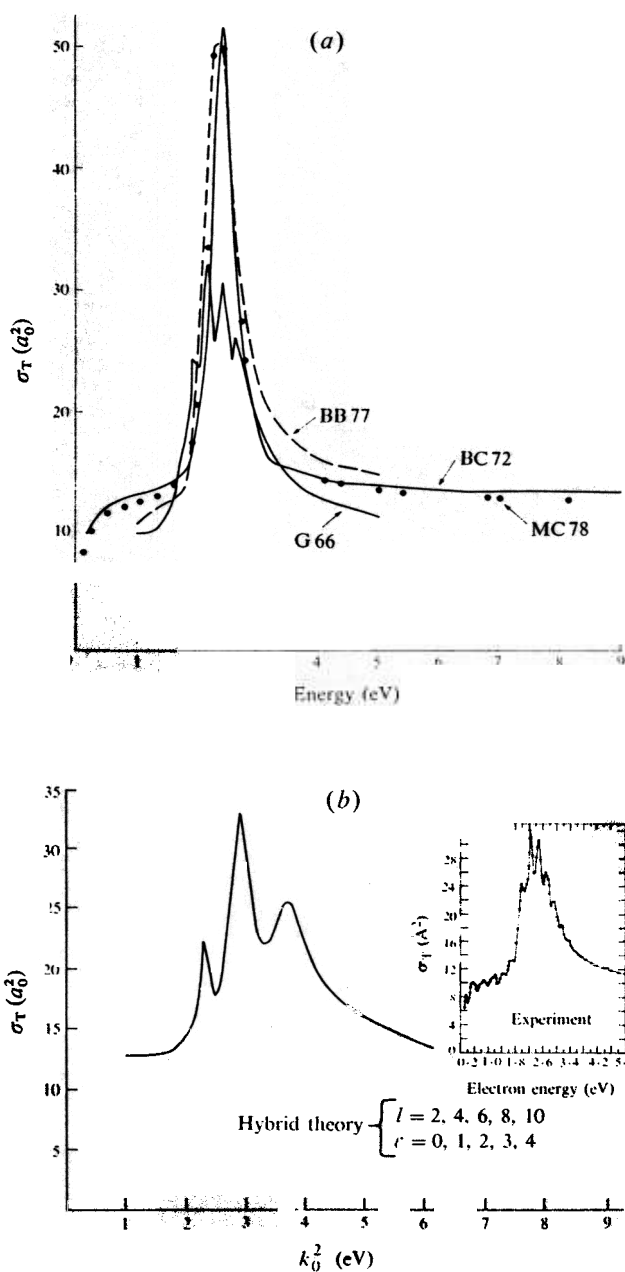
Returning now to the hybrid theory of Chandra and Temkin (1976), we can understand how they were able to *treat only the resonance scattering with vibrational close-coupling theory*. Thus the contribution to the cross section in the (resonant)  $\Pi_g$  symmetry was calculated by solving the body-frame coupled equations that are obtained when the *orientation* of the internuclear axis is fixed but the nuclei are allowed to vibrate during the collision. The contributions in other symmetries were calculated using standard adiabatic-nuclei vibration theory (cf. Section 3a).

In spite of this minimal use of close-coupling theory, extensive partial-wave coupling in the  $\Pi_g$  symmetry led to computational difficulties in the calculations of Chandra and Temkin. At the time of the present writing these authors have not reported fully converged vibrational-excitation cross sections. However, their work clearly demonstrates the importance of properly accounting for the dynamical interaction of the nuclear and electronic motion in certain electron-molecule scattering events. For example, in a full adiabatic-nuclei calculation of the total cross section for  $e\text{-N}_2$  scattering near 2 eV, one sees the experimentally measured peak, as illustrated in Fig. 11a, but none of the oscillatory structure that is known to be present in these cross sections (cf. the experimental results of Golden 1966). When the dynamical interaction is included via the hybrid theory of Chandra and Temkin, the experimentally observed oscillations do appear; recent results of hybrid theory calculations by these authors are illustrated in Fig. 11b. The hybrid theory also produces oscillatory structure in the vibrational-excitation cross sections; such structure is observed in cross sections near the resonance (cf. Srivastava *et al.* 1976).†

\* These designations label the irreducible representations of the point group of the electron-molecule system (cf. Ch. 7 of Tinkham 1964).

† In a very recent piece of work (A. Temkin 1983, personal communication), Onda and Temkin repeated the  $e\text{-N}_2$  calculations using the hybrid theory and an *ab initio* polarization potential determined via the method of polarized orbitals. Their new results are in much better agreement with experimental cross sections; the qualitative conclusion presented here remains unchanged.





**Fig. 11.** (a) Total integrated cross sections for  $e\text{-N}_2$  collisions from several theoretical calculations based on a fixed-nuclei body-frame formulation and from the experiment of Golden (1966). Theoretical results are from Morrison and Collins (1978), Buckley and Burke (1977) and Burke and Chandra (1972).

(b) Total integrated cross sections for  $e\text{-N}_2$  scattering in the vicinity of the 2.3 eV shape resonance as calculated using the hybrid theory of Chandra and Temkin (1976). The inset shows the experimental results of Golden (1966). [From Temkin (1979).]

The 2.3 eV e-N<sub>2</sub> resonance has been the subject of considerable study, but this is not the place to review this subject (see Schulz 1973; Moiseiwitsch 1977; Lane 1980). However, we should note that one does not *have* to use vibrational close-coupling theory to take account of the important electron nuclear motion effects in resonance scattering. Indeed, it is possible to apply the Born-Oppenheimer approximation to this case. However, because of the long lifetime of the resonance, one must do so in a way that takes account of the effect of the scattering electron on the target. This entails (Schneider 1976) separating the electronic and nuclear motions of the temporary negative N<sub>2</sub><sup>-</sup> ion with full allowance for distortion of the N<sub>2</sub> molecular orbitals and resulting changes in the nuclear motion. This point was recently illustrated by Schneider *et al.* (1979), who used the *R*-matrix method in a fully *ab initio* determination of resonant e-N<sub>2</sub> vibrational-excitation cross sections which are in excellent agreement with experimental results.

The emerging physical picture of resonances such as those that occur in low-energy e-N<sub>2</sub> and e-CO<sub>2</sub> scattering is one in which the resonant excitation of vibrational levels of the temporary negative ion is responsible for the oscillations in the cross sections. Competition between nuclear vibrations in the temporary negative ion and autoionization of the electron causes these oscillations to be located at different relative energies for different excitations. This complicated collision process has been successfully modelled by the 'boomerang' model of Birtwistle and Herzenberg (1971), which has been recently studied by Hazi *et al.* (1981).

#### (d) Angular Frame-transformation Theories

The *radial* frame-transformation theory of Section 2c is predicated on the fact that in the region of space near the molecule, the Coulomb interaction is the dominant term in the electron-molecule Hamiltonian, while far from the target the nuclear Hamiltonian terms must be taken into account. Recently, alternatives to this theory have been proposed. In the present article, these methods will be referred to as *angular frame-transformation theories*. Like the radial frame-transformation theory, these methods entail a 'partitioning' of the collision problem. However, rather than base this partitioning on the radial distance of the electron from the origin, they focus on its orbital angular momentum quantum number *l*, and on the effects of the associated centrifugal potential energy on the radial scattering functions.

This potential energy appears in the coupled equations for the radial scattering function when a partial-wave expansion is introduced (cf. equation 7). Specifically, a term of the form  $l(l+1)/r^2$  appears in the operator that acts on the scattering function. Since  $l > 0$ , this is a repulsive potential. Conceptually, we can think of this term as introducing a 'centrifugal barrier'. The net effect of this barrier is to dramatically reduce the magnitude of the scattering function at small values of *r*. This reduction becomes more pronounced with increasing *l*, as the 'barrier' becomes more repulsive.

Centrifugal-potential effects are important in a wide range of familiar problems, from the determination of stationary states of the one-electron atom to simple potential scattering theory. However, care must be exercised in using arguments based on centrifugal effects in discussing electron-molecule collisions, because *the radial scattering functions for these systems are coupled in l and thus cannot be rigorously identified with a single partial wave*. With this caveat in mind, the notion that high-*l*

partial waves are relatively impervious to the interaction potential in the region of space near the target, because they are 'kept out' of this region by centrifugal barriers, is quite valuable. [A useful discussion of the effects of the centrifugal potential in electron-molecule collisions can be found in the article by Fano (1970).]

This idea is the basis of angular frame-transformation theories. The development of these new methods was stimulated by the inordinate difficulty theorists encountered in calculating cross sections for electron polar molecule scattering, and all applications to date have been to such systems. (There is no inherent reason, however, why these techniques could not be used for systems in which the target is non-polar.) In angular frame-transformation methods, different formulations of the Schrödinger theory are used depending on the magnitude of  $l$ , which is often referred to as the *partial-wave order*. Typically, three ranges of  $l$  values are identified: small  $l$ , intermediate  $l$ , and large  $l$ . No precise rule can be given for how to determine the particular partial-wave order at which one should leave one range and enter another. These 'boundaries' must be determined by trial and error for each system studied (and, in some cases, for each energy region of interest). Fortunately, the physical premise of the theory provides some qualitative guidance in choosing these boundaries.

The centrifugal barrier associated with *small- $l$*  partial waves will be quite weak (and zero for  $l = 0$ ). Therefore, to a good approximation, one can argue that the radial scattering functions with small values of  $l$  are not excluded from the region of space near the molecule, where the electron-molecule interaction potential is strong and the collision physics is best described by the body-frame picture of Section 2*a*. To determine these small- $l$  functions, one can invoke the Born-Oppenheimer approximation, working in the body-frame fixed-nuclei formulation. As we have noted before, the coupled scattering equations of this formulation are more easily solved than those of the full lab-frame close-coupling theory.

As the value of  $l$  increases, the physical picture on which the body-frame fixed-nuclei formulation is predicated becomes less appropriate. Once the centrifugal barrier term becomes large, terms in the Hamiltonian that prevail in the 'outer region' (see Fig. 4) become important in the determination of the distortion of the radial functions. That is, the effects on the intermediate- and large- $l$  partial waves due to the rotational Hamiltonian cannot properly be neglected, as they are in a fixed-nuclei treatment. *Ergo*, one must resort to procedures that incorporate these effects, such as the lab-frame close-coupling theory of Section 3*b*.

Electron polar molecule collisions are especially awkward computationally because these systems are characterized by a *very* long-range strong  $r^{-2}$  interaction potential that arises from the permanent dipole moment of the target. This electron-dipole interaction necessitates the inclusion of huge numbers of partial waves (for example, hundreds) in a scattering calculation, with concomitant appalling increases in the computer time required. In the angular frame-transformation theories, this invidious feature of electron polar molecule systems is turned into an advantage by noting that the centrifugal barriers for very large values of  $l$  are so strong that the corresponding radial functions are distorted *only* by the long-range electron-dipole interaction. This interaction is rather weak; its great importance derives from its long-range nature and from the coupling mechanism it provides. Hence, one is justified in using 'weak

potential theories' like the (first) Born approximation\* (for a point dipole) to solve the scattering equations for these 'large- $l$ ' partial waves. Weak potential methods require only very simple computations, news which should come as a relief after the difficulties presented by the rest of the problem!

To summarize: In angular frame-transformation theories, one uses centrifugal barrier arguments to determine strategies for solving the collision problem, which is partitioned according to the angular momentum quantum number  $l$  of the scattering electron. In their implementation of this strategy, Collins and Norcross (1978) carried out very accurate calculations of cross sections for electron scattering from *strongly* polar molecules. Their procedure entails the following blend of theoretical procedures:

- small  $l$ :            body-frame fixed-nuclei theory, approximation to the electron-molecule interaction potential;
- intermediate  $l$ :    lab-frame rotational close coupling;
- large  $l$ :            first Born approximation.

The research of Collins and Norcross is of further significance in that it demonstrated conclusively the importance of using an accurate representation of the electron-molecule interaction *throughout* space in calculations of electron polar molecule cross sections. (Most earlier calculations had used extremely crude models of this interaction that all but neglected the 'short-range' or 'inner' region, where electrostatic and exchange effects predominate.)

A variant on this angular frame-transformation theory for electron polar molecule collisions is the 'hybrid  $S$ -matrix theory'† of Siegel *et al.* (1980, 1981). Like the computational method of Collins and Norcross (1978), this theory also entails a partitioning of the scattering problem according to partial-wave order. Hybrid  $S$ -matrix theory differs from the procedure described above in only two respects:

First, the electron-molecule interaction potential  $\hat{V}_{int}$  in the coupled equations for small values of  $l$  which are solved using body-frame fixed-nuclei theory is modelled by the *continuum multiple-scattering method* (cf. the review by Dehmer and Dill 1979). This approximation leads to an electron-molecule potential energy less accurate than the one used by Collins and Norcross; it will be discussed briefly in Section 6.

The second new feature of hybrid  $S$ -matrix theory is a very efficient method for calculating the contributions to the cross sections of the 'intermediate- $l$ ' partial waves. Collins and Norcross used the lab-frame close-coupling method to solve the radial scattering equations for these partial waves. Subsequently, Clark and Siegel (1980) found that in the region of space where significant distortion of the scattering functions for these partial waves occurs, the projection of the electron orbital angular momentum along the internuclear axis is approximately conserved. This feature arises from the strong electron-dipole interaction. One can exploit it by using

\* The Born approximation to the  $S$  matrix is the first term in a perturbation expansion of this quantity. Physically, this approximation amounts to neglecting the distortion of the scattering function to first order. The  $S$  matrix in the Born approximation is given by an integral over undistorted plane waves and the interaction potential. (For more details see Ch. 9 of Taylor 1972.)

† This name is derived from the way in which this particular angular frame-transformation theory is implemented. The scattering matrix  $S_{ll'}^{(m)}$  is literally 'built up', elements of the matrix (corresponding to different partial waves) being selected from various calculations according to the values of the partial-wave order that label these elements.

body-frame fixed-nuclei theory for the 'intermediate- $l$ ' partial waves. In the coupled equations of this theory, one can represent the interaction potential by an electron point dipole term. The resulting equations are *very* easy to solve; the  $S$ -matrix elements one needs to determine cross sections have simple analytic forms and are independent of the scattering energy.

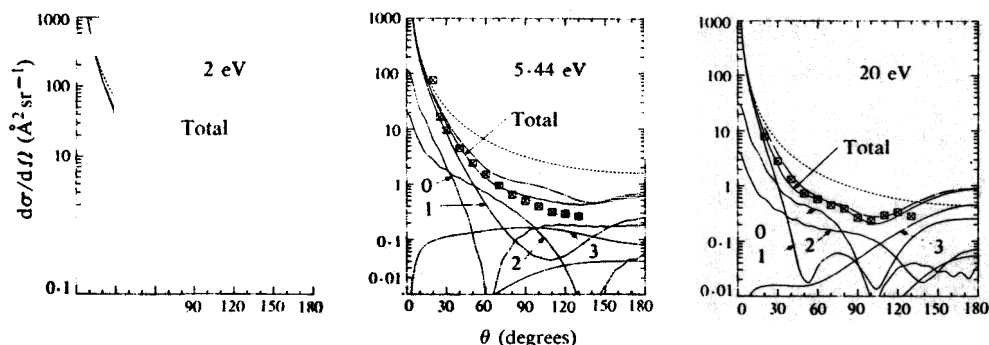


Fig. 12. Differential cross sections for e-LiF scattering at the three energies shown: solid curve, the hybrid  $S$ -matrix calculations of Siegel *et al.* (1980); dashed curve, the first Born approximation; dot-dash curve, the calculation of Collins and Norcross (1978). The squares are the experimental results of Vušković *et al.* (1978). [From Siegel *et al.* (1980).]

Both of the features introduced in hybrid  $S$ -matrix theory result in substantial savings of computer time over that required to perform lab-frame close-coupling calculations. Siegel *et al.* (1980, 1981) have recently applied hybrid  $S$ -matrix theory to e-LiF scattering; their differential cross sections are compared with those of Collins and Norcross and with experimental results in Fig. 12.

To conclude this section on hybrid methods, we should note the appeal of their underlying philosophy: namely, to partition the collision problem into essentially separate parts, acknowledging the complex and often subtle nature of the physics of the electron-molecule interaction and using our knowledge of this physics to arrive at appropriate (i.e. efficient and accurate) computational methods for solving each part of the problem.

This philosophy extends beyond the theoretical issues discussed in this subsection of the present article. For example, Norcross and Padial (1982) have adopted it in a recent study of the applicability of adiabatic-nuclei theory to the scattering of electrons from polar molecules. They have proposed a multipole-extracted adiabatic-nuclei (MEAN) theory in which a factorization of the differential cross section for ro-vibrational excitation is introduced. Specifically, this cross section is written as the sum of two terms. The first term describes long-range scattering of the huge number of large-order partial waves that are required in any electron strong-dipole calculations. The MEAN method exploits the weak nature of the long-range interaction, which is primarily just the aforementioned electron-dipole potential, by calculating this first term using a simple approximate theory like the first Born approximation. To take account of the nuclear Hamiltonian, these calculations are carried out in lab-frame coordinates and the nuclear geometry is *not* fixed. The second term in the MEAN approximation to the differential cross section corrects

the first term by, in effect, replacing the low-order partial-wave contributions in the first Born approximation with more accurate contributions calculated using adiabatic-nuclei theory. These terms in the cross section should be valid for small values of  $l$  since, as discussed above, the body-frame fixed-nuclei approximation is quite good for low-order partial waves.

It is likely that future theoretical assaults on electron-molecule scattering problems, especially those involving polar targets, will require combined procedures like the hybrid and frame-transformation methods we have been discussing. The exploration of such theories may open the doors to the accurate calculation of cross sections for a much wider range of systems than are currently tractable. Moreover, they provide further insight into the endlessly rich physics of electron-molecule scattering.

#### 4. Electron-molecule interaction potential

One can view the situation confronting the theorist undertaking the study of a particular collision in terms of two classes of questions. *First*, how does one formulate the scattering theory? For example, does one base the theory on the time-dependent or time-independent Schrödinger equation? In what reference frame and coordinate system does one work? And, most importantly, what physical approximations are to be invoked in order to turn the problem into one that can reasonably be tackled, both computationally and conceptually? *Second*, how does one treat the various aspects of the interaction between the electron and the molecule that influence low-energy scattering? Thus far, we have discussed questions that fall into the first category; we now turn to the representation of the interaction potential.

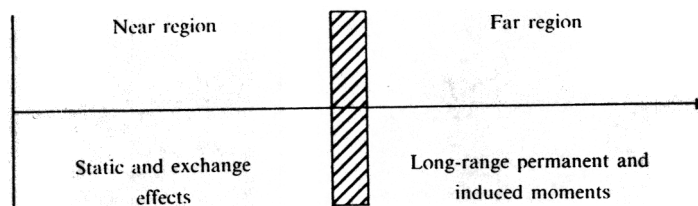


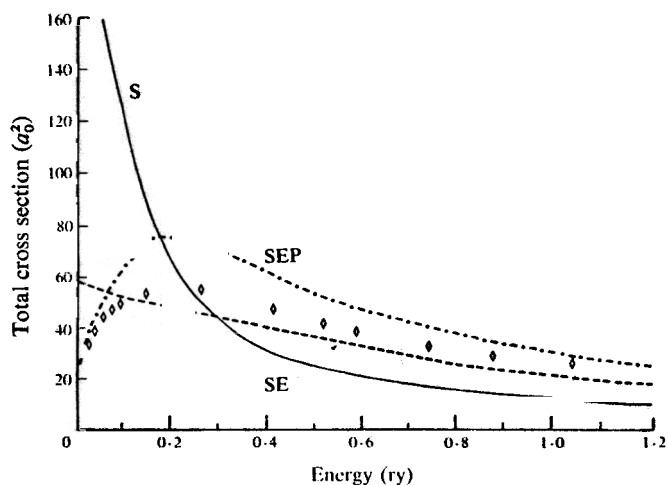
Fig. 13. Summary of the components of the electron-molecule interaction potential.

We can identify three physically distinct effects that influence the scattering of low-energy electrons. These can conveniently (if crudely) be characterized in terms of the region of space in which they predominate. Thus, as illustrated in Fig. 13, near the target the 'short-range' *static* and *exchange* effects are dominant in distorting the scattering function. Far from the target, the most important terms in the potential are the 'long-range' interactions between the electron and the permanent and induced moments of the molecule. Let us look briefly at each of these interactions.

We have already described the *static* potential energy in Section 1a; it is represented by the term  $\hat{V}_{\text{int}}$  in the electron-molecule Hamiltonian (2). Arising from the Coulomb forces between the scattering electron and the constituents of the target (cf. equation 3), the static potential energy has a strong, attractive, non-spherical short-range component and a weaker long-range component that consists of a sum of terms, each of which is proportional to one of the permanent moments of the molecule (for example, dipole or quadrupole).

The short-range static component is the most important interaction in the inner region; it is responsible for the fact that the  $\hat{z}$  projection of the orbital angular momentum of the scattering electron is approximately conserved in this region. This fact is the cornerstone of the body-frame theory (Section 2a). At very low scattering energies, say less than about 1.0 eV, the *long-range* interactions play a significant role in determining cross sections. For example, these interactions are of great importance for scattering near the threshold for a ro-vibrational excitation.

The state of the art is now such that the determination of an accurate static potential for electron scattering from diatomic molecules poses no significant problems. Packages of very efficient computer programs for this purpose are readily available (Morrison 1980; Collins *et al.* 1980b). These codes produce the static potential, in a form suitable for use in scattering calculations, from accurate *ab initio* (near Hartree-Fock) wavefunctions for the target which are easily accessible in the literature for a vast array of molecules.\*



**Fig. 14.** Total cross sections for e-H<sub>2</sub> collisions calculated using the fixed-nuclei approximation employing three model interaction potentials: S, static only; SE, static and exchange; SEP, static, exchange and polarization. The diamonds are the experimental data of Golden *et al.* (1966). (The theoretical results shown here were calculated using rather crude model potentials. They are designed to show *qualitative* behaviour only. (Note: 1 ry = 27.212 eV.)

The static interaction alone is not sufficient to accurately describe low-energy electron collisions. To emphasize this point, we compare in Fig. 14 the measured total integrated cross section for e-H<sub>2</sub> scattering and the results of three theoretical studies. The latter differ only in their representation of the interaction potential: one includes only the static (S) potential, one the static and exchange (SE) effects,

\* If a less accurate representation of the static potential is acceptable, one can use approximate theories like the INDO or related methods. The calculation of these model static potentials is extremely fast on present-day computers. For a review of these approximations see Truhlar (1981).

and the third static, exchange and polarization (SEP) effects. The point is that the first two studies yield *qualitatively incorrect* cross sections.\*

(a) *Exchange Effects*

In the panoply of physical interactions, exchange holds a special place because it is purely quantum mechanical; it has no classical analogue. Thus, the challenge of understanding the physics of exchange is especially provocative (and non-trivial).

Exchange effects pose practical difficulties as well. As mentioned briefly in Section 2b, in solving the time-independent Schrödinger equation for the electron-molecule system, care must be taken to ensure that the system wavefunction  $\Psi_E$  is *antisymmetric* under pairwise interchange of electrons. This requirement is a consequence of the fact that electrons (which are spin- $\frac{1}{2}$  fermions) are *identical particles* and, hence, are physically indistinguishable. This important facet of quantum theory is codified in the Pauli Principle. In eigenfunction-expansion methods, this requirement is formally satisfied by introducing an 'antisymmetrizer' (the operator  $\mathcal{A}$  in equation 6).

Operationally, however, the presence of this operator gives rise to *integral* terms in the coupled scattering equations we must solve. These terms have the disconcerting property that the unknown radial scattering functions appear in their integrands. Hence one must know the values of the unknown functions throughout space (i.e. from  $r = 0$  to  $\infty$ , the limits of these integrals) in order to evaluate terms in the very equations that one wants to solve for the scattering function. As one might expect, the task of solving large sets of coupled integrodifferential equations is quite formidable—even on a CRAY-1 computer! Numerical procedures for coping with this predicament exist (see Collins *et al.* 1980c, and references therein), but their implementation is arduous and limited to a few systems. Nevertheless, as illustrated by the results shown in Fig. 14, the effects of exchange on low-energy cross sections cannot be neglected.

The integral exchange terms are sometimes represented symbolically by an operator, for example  $\hat{V}_{ex}$ , that operates on the scattering functions. As discussed above, one effect of  $\hat{V}_{ex}$  is to push the function on which it operates under an integral. Such an operator is said to be 'non-local' (because it requires knowledge of the integrand throughout space, rather than only at a single point). The exchange operator formally appears in the Schrödinger equation along with the other terms in the Hamiltonian, namely

$$(\mathcal{H}_m + \hat{T}_e + \hat{V}_{int} + \hat{V}_{ex})\Psi_E = E\Psi_E. \quad (11)$$

In the literature,  $\hat{V}_{ex}$  is often referred to as the *exchange potential*. It is a non-local potential that is not spherically symmetric and that depends on the scattering energy. (Note carefully that  $\hat{V}_{ex}$  is *not* a 'potential energy' in the classically meaningful sense of the term; in contrast, the static potential  $\hat{V}_{int}$  does have a conventional classical counterpart.)

\* Having gazed at Fig. 14, the reader may wonder about the vast amount of research in the literature in which exchange and/or polarization are neglected. The purpose of such studies is to investigate particular component(s) of the full SEP interaction, rather than to produce cross sections for comparison with experiment. For example, in studies of exchange (Section 4a), one usually works in the 'static-exchange approximation', neglecting polarization effects which might obscure the effects of exchange.



In response to the interpretive puzzles and computational conundrums posed by exchange, a two-pronged attack on the problem has been mounted over the past several years. On the one hand, a number of computational procedures have been devised which include exchange effects 'exactly', i.e. in which the aforementioned coupled integrodifferential equations are solved numerically. On the other hand, a number of theorists have sought to develop approximate treatments of exchange, that is, models of the exchange potential that are physically comprehensible and computationally tractable.

Studies of exact and approximate treatments of the exchange potential are almost always carried out in the static-exchange approximation; this approximation is defined by the neglect of polarization of the target molecule. (Polarization effects will be discussed in Section 4b.)

Exact static-exchange calculations have been carried out by a variety of researchers (see the review by Lane 1980). These theorists have used a variety of strategies to solve the Schrödinger equation (11), including  $L^2$  variational and eigenfunction-expansion formulations of the scattering theory. Pioneering work on this problem using the latter formulations was performed by Tully and Berry (1969) on  $e\text{-H}_2$  collisions and by Burke and Sin Fai Lam (1970) on  $e\text{-N}_2$  scattering. More recently, further work on the latter system using the numerical methods of Burke and Sin Fai Lam was reported by Buckley and Burke (1977). Very recently, a rash of new procedures for solving the integrodifferential static-exchange equations has greatly widened the range of systems for which exact static-exchange results are available. These new methods include the *iterative static-exchange method* of Collins *et al.* (1980c), which has been applied to electron scattering from  $\text{H}_2$ ,  $\text{N}_2$ , LiH, CO, LiF and a number of molecular ions, the *linear-algebraic method* of Schneider and Collins (1981), and a *multi-channel Kohn variational method* of Collins and Robb (1980).

The details of these various computational strategies are less important for the purposes of this article than the fact that these studies have made available very valuable 'benchmark' results for electron scattering from small molecules. The calculations this work entails are arduous, to say the least, and require computer facilities that are unavailable to most theoreticians. Even with state-of-the-art computers, it is unlikely that exact static-exchange calculations of cross sections for a large number of collision processes and/or for scattering from large many-electron polyatomic targets will be feasible in the foreseeable future.

Acknowledging this situation, some theorists have recently pursued an alternative tactic for taking account of exchange effects: the use of *approximate treatments*, which are loosely called 'model exchange potentials'. The goal of this research is to devise a local potential energy that mocks, in some average sense, the effects on the scattering functions of the complex non-local exchange potential discussed above. An additional benefit accrues from the study of model exchange potentials, in that they provide insight into the physics of this acutely nonclassical effect.

In reports of studies of exchange in electron-molecule scattering, one very frequently finds tables and graphs of 'eigenphase sums' rather than the more familiar cross sections. The extensive use of eigenphase sums is motivated partly by their convenience and partly by their sensitivity to the interaction potential. (Furthermore if, as is often the case in these studies, polarization effects are neglected, the resulting cross sections are of less immediate physical significance. Indeed, unless these cross sections are interpreted with great care, they can lead to serious misconceptions

regarding the physics of the collision.) Because of their wide use, we need to digress briefly to contemplate these quantities.

Eigenphase shifts play a role in electron–molecule scattering theory analogous to that of phase shifts in the theory of scattering from a spherically symmetric potential (cf. Ch. 6 of Taylor 1972). In the latter problem, there is no partial-wave coupling, and the radial scattering equations that result from implementing a partial-wave expansion are completely independent of one another. In this happy situation, a phase shift can be defined *for each partial wave* (for example,  $l = 0$ , s-wave phase shift;  $l = 1$ , p-wave phase shift) and determined from the corresponding radial scattering function in the asymptotic region.

As we have seen, the interaction potential for an electron–molecule system is not spherically symmetric, and no such separation of the problem into independent partial waves occurs. However, as discussed in Section 3c, the coupled equations one obtains in the body-frame fixed-nuclei theory *do* separate according to the electron–molecule symmetry ( $\Sigma_g, \Sigma_u, \Pi_g$  etc. for homonuclear diatomic targets). Within each symmetry, we can examine the asymptotic values of all of the radial scattering functions and, by suitable mathematical machinations (cf. Morrison 1979), determine a set of ‘eigenphase shifts’. The *sum* of these numbers is, sensibly, called the eigenphase sum. Thus, at a given scattering energy  $E$ , we have a  $\Sigma_g$  eigenphase sum, a  $\Sigma_u$  eigenphase sum etc. The significance of the eigenphase sum is illustrated by its behaviour at energies near a shape resonance (Hazi 1979). As the scattering energy varies through the resonance energy, the eigenphase sum in the resonant symmetry increases by (roughly)  $\pi$  radians (see Fig. 15b). In this and other ways, the physics of an electron–molecule scattering event can be studied by drawing on the analogy between the eigenphase sum and the partial-wave phase shifts of potential scattering theory. With this digression out of the way, let us return to the subject at hand, model exchange potentials in electron–molecule scattering.

Recent investigations in this area have focused on three approximate treatments of exchange. The first of these uses a class of models called free-electron-gas exchange potentials. Two approximations provide the theoretical foundation for these potentials. First, the electron charge cloud of the molecule is modelled by a free-electron (Fermi) gas, i.e. a collection of *non-interacting* fermions with a density equal (at each point in space) to the quantum-mechanical charge density of the molecule. Second, the scattering electron is approximated by a plane wave, i.e. distortions of the electron wavefunction from a plane wave are neglected (to zeroth order). It is important to note that these two (rather drastic) assumptions are applied *only* in the integral exchange terms in the scattering equations. Implementing these two assumptions reduces the exchange operator in equation (11) to a *local* model exchange potential. Like the exact exchange potential, the free-electron-gas exchange potential is non-spherical and energy dependent; however, its local character greatly facilitates the determination of the radial scattering functions, which can now be obtained by solving sets of coupled *differential* equations.

Free-electron-gas exchange potentials have been used in recent years to study electron scattering from a variety of molecules (cf. Morrison and Collins 1981). The availability of benchmark results from *exact* static-exchange calculations has made possible careful evaluation of the accuracy of these models.

To illustrate the use of free-electron-gas exchange potentials in electron–molecule scattering, we show two applications in Fig. 15. In Fig. 15a, eigenphase sums for

$e$ - $N_2$  scattering calculated using free-electron-gas potentials are compared with results of an exact static-exchange calculation for the (non-resonant)  $\Sigma_g$  symmetry. A similar comparison for the (resonant)  $\Pi_u$  symmetry of the  $e$ - $CO_2$  system is shown in Fig. 15b.\*

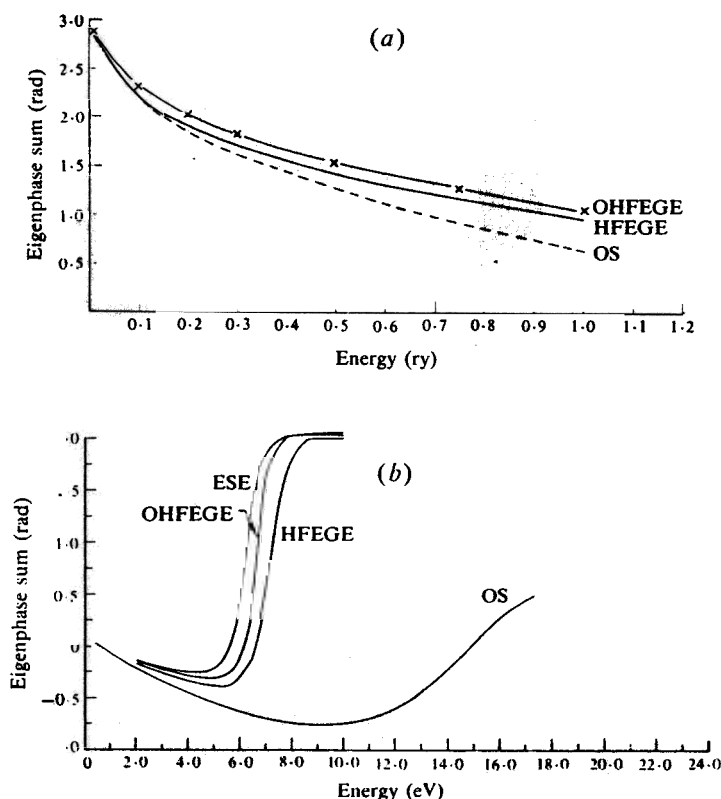


Fig. 15. Static-exchange eigenphase sums calculated using exact and approximate treatments of exchange for (a)  $e$ - $N_2$  scattering in the  $\Sigma_g$  symmetry [from Morrison and Collins (1981)] and (b)  $e$ - $CO_2$  scattering in the  $\Pi_u$  symmetry [from Collins and Morrison (1982)]. Results are shown for the orthogonalized-static (OS) method, the Hara free-electron-gas exchange (HFEGE) potential, and the HFEGE potential with orthogonalization (OHFEGE). Exact static-exchange (ESE) results are represented by crosses in (a) and by a curve in (b).

A second class of model exchange potentials was introduced by Riley and Truhlar (1975), based on the research of Furness and McCarthy (1973) on electron-atom collisions. These models are called semiclassical exchange potentials because they derive from a semiclassical (short-wavelength) approximation for the radial scattering function. This approximation is implemented in the integral exchange terms to

\* Cross sections and eigenphase sums for scattering at energies near a shape resonance are especially sensitive to exchange effects and, consequently, provide very stringent tests of approximate exchange potentials. This enhanced sensitivity near resonance is due to the fact that the scattering function at a near-resonant energy is predominantly localized very near the target, where the (short-range) effects of exchange are very important (see Fig. 14).

extricate the scattering function from under the integral, resulting in an approximate local potential energy. The validity of this semiclassical assumption is questionable at *low* scattering energies (less than say 10.0 eV), where the de Broglie wavelength of the electron is quite long, and most applications of semiclassical exchange potentials have been in the intermediate-energy range from about 10 eV to about 100 eV (cf. Rumble and Truhlar 1980; Onda and Truhlar 1980). However, theoretical arguments based on the idea of a 'local' ( $r$  dependent) wavelength for the scattering electron suggested the possible utility of this model at low scattering energies. Gibson and Morrison (1981) have explored this suggestion for e-H<sub>2</sub> scattering (with and without polarization effects).

A totally different approach to the problems posed by exchange is adopted in the 'orthogonalized-static' method, which was originally proposed by Burke and Chandra (1972). This method is based on the fact that in the *exact* static-exchange theory of electron scattering from a *closed-shell* molecule, the radial scattering functions are necessarily orthogonal to the bound orbitals of the target molecule (see Morrison and Collins 1981 for details). In a sense, we can think of this condition as imposing constraints on the scattering functions; for example, the (nonzero) values of  $r$  at which each radial scattering function is zero—the 'nodes' of this function—must conform to these orthogonality conditions. These constraints are *not* the only effect of the exact non-local exchange terms on the scattering functions, but Burke and Chandra argued that they may be the most important ones. One can derive the scattering equations of their procedure by starting in the *static* approximation, in which exchange is completely neglected, and then *imposing* suitable orthogonality constraints on the solutions of these equations. The resulting orthogonalized-static approximation has been widely applied; recent studies include electron scattering from H<sub>2</sub>, CO, HCl, HF, CH<sub>4</sub>, H<sub>2</sub>O and H<sub>2</sub>S (see Morrison and Collins 1981 for references).

Because model exchange potentials greatly simplify the computational chore of solving the scattering equations, they may facilitate the study of systems for which exact static-exchange calculations are not feasible. However, the treatments discussed above are all *ad hoc* to some extent; that is, they cannot be *rigorously* derived from quantum theory. (They are, after all, *models*.) To evaluate such models, it is necessary to try them out on a diverse range of electron-molecule systems, comparing exact and approximate results wherever possible.

Several such comparative studies have quite recently been reported: by Morrison and Collins (1981) for electron collisions with H<sub>2</sub>, CO, N<sub>2</sub> and LiH; by the same authors (Collins and Morrison 1982) for e-CO<sub>2</sub> scattering; by Collins and Norcross (1978) for e-LiF collisions; and by Collins *et al.* (1980a) for e-HCl scattering. This collection of studies encompasses a wide variety of *types* of targets: non-polar diatomics, a triatomic, and polar diatomics with a wide range of values of dipole moment. They therefore provide a foundation for extrapolation of the model potentials to the many systems for which exact results are not (nor likely to become) available.

The detailed conclusions of this research need not concern us here. Suffice it to say that, taken together, these studies indicate that model exchange potentials can provide reliable and, in some cases, surprisingly accurate approximations to the non-local exchange operator. For collisions at low scattering energies, models based on the free-electron-gas theory have proven to be particularly successful. In many

cases, the results of these calculations can be improved by combining orthogonality constraints with model exchange potentials. However, in nearly all cases studied, the orthogonalized-static procedure *alone* was an inadequate representation of exchange. It is likely that more research along these lines, perhaps involving polyatomic targets and new approximate treatments of exchange, will be forthcoming in the near future.

(b) *Induced Polarization Effects*

Electrostatic and exchange effects dominate the near-target region. Further from the molecule, a new interaction that becomes important is the induced polarization interaction. The importance of taking account of polarization of the molecule by the scattering electron in electron-molecule collision theory is evident from the cross sections of Fig. 14. Polarization is an *induced* effect that can, perhaps, best be understood in terms of a *time-dependent* semiclassical picture.

Let us imagine the encounter of the scattering electron with the target. As it approaches, interacts with the molecule, and departs, the electron, being a charged particle, establishes a *time-varying* electric field throughout space. This field will, of course, distort the charge cloud of the target, inducing a dipole moment. This 'polarized' charge cloud exerts forces on the electron; these forces, which are different from those exerted by a neutral charge cloud, distort the scattering function. This induced distortion is the 'polarization effect' that so dramatically changes the cross sections in Fig. 14. Because of the polarization of the molecule, the total energy of the electron-molecule system is *lowered* from its value for the neutral case. The energy *shift* due to these induced polarization effects is called the *polarization potential* and, for a given electron position  $r$ , is denoted by  $V_{\text{pol}}(r)$ .

The origin of polarization effects in the quantum-mechanical *time-independent* collision theory of Section 1c is buried in the target-state expansion of equation (6). To see this, let us suppose that, as befits a 'low-energy collision', the electron has insufficient kinetic energy to induce a transition from the ground electronic state to any of the excited electronic states of the target. Since equation (6) is an expansion in a complete set of functions, we formally must include the infinity of excited target states, even though all of them are inaccessible energetically. A rather complicated analysis of the Schrödinger equation reveals (Castillejo *et al.* 1960) that these states give rise to terms in the scattering equation that represent the induced polarization effects. (Because they correspond to nonphysical transitions, these terms are sometimes said to represent 'virtual excitations'.)

Now, we have seen that the numerical solution of the scattering equations of electron-molecule collision theory can be very difficult even if only one target electronic state, the ground state, is retained in the eigenfunction expansion (6). It should therefore come as no surprise to learn that the solution of the equations that result from the exact quantal treatment of polarization described above is even more complicated. Indeed, even in electron-atom scattering, exact solution of these equations is impossible. This predicament is exacerbated in the present case by the nuclear degrees of freedom and by partial-wave coupling. So, once again, we must turn to approximate treatments and models.

The most widely used procedure for incorporating induced-polarization effects in studies of electron-molecule collisions derives from the fact that at low energies the 'polarization terms' in the scattering equations take on a simple form in the

asymptotic region. The idea is this: If the electron is moving very slowly, we can treat its motion *adiabatically*, i.e. we can assume that the distortion of the molecular charge cloud in response to the electric field of the scattering electron occurs very rapidly compared with changes in the position of the electron. In effect, this approximation amounts to assuming that the distortion ‘follows’ the electron as it moves through space. Making this approximation, one finds (cf. Castillejo *et al.* 1960) that at very large values of  $r$  (far from the target) the polarization terms in the quantum-mechanical scattering equations give rise to an ‘asymptotic polarization potential’ of the following form:

$$V_{\text{pol}}(\mathbf{r}) \xrightarrow{r \rightarrow \infty} -\alpha(\hat{\mathbf{r}})/2r^4. \quad (12)$$

In this equation,  $\alpha(\hat{\mathbf{r}})$  is the *polarizability* of the molecule. This quantity is an intrinsic property of the molecule, being a quantitative measure of its capability to distort in response to an electric field directed along  $\hat{\mathbf{r}}$ . The asymptotic polarization potential is not spherically symmetric; it provides a mechanism for coupling partial waves in the large- $r$  region of space.

Equation (12) describes only the *asymptotic form* of the polarization potential. To solve the scattering equations, we require values of  $V_{\text{pol}}$  for all  $r$ . The adiabatic picture described above is predicated on the electron moving slowly. At large (but not *asymptotic*) values of  $r$ , this picture may still be viable even though the simple form (12) may be inapplicable due to the breakdown of other approximations that go into its derivation. However, as the electron nears the target (in our time-dependent semiclassical conceptualization) it speeds up, primarily due to the short-range attractive Coulomb forces. Therefore, near the target, our adiabatic approximation is invalid since the distortion of the charge cloud will ‘lag behind’ the position of the electron. Under these circumstances, the polarization potential depends on the position *and velocity* of the scattering electron. The resulting potential is much more complex than its adiabatic counterpart; it is, sensibly, referred to as a ‘non-adiabatic polarization potential’. Theoretical studies of non-adiabatic corrections for simple electron-atom systems (for example, e-He) have revealed that these corrections *weaken* the polarization potential at small values of  $r$ , so that it is less strongly attractive than its adiabatic counterpart.

To properly take account of non-adiabatic effects and deviations from the simple asymptotic form (12), a full quantum-mechanical treatment of polarization would be required. As this is not feasible, a crude model potential has been introduced that seeks to describe these deviations in a highly approximate fashion. The form of this model polarization potential is

$$V_{\text{pol}}(\mathbf{r}) = C(r)\{-\alpha(\hat{\mathbf{r}})/2r^4\}, \quad (13)$$

where  $C(r)$  is a spherically symmetric ‘cutoff function’. This function bears full responsibility for taking account of a breakdown in the adiabatic approximation and of deviations of  $V_{\text{pol}}(\mathbf{r})$  from its asymptotic dependence on  $r$ . It usually takes the form  $1 - \exp\{- (r/r_c)^6\}$ , where  $r_c$  is an adjustable parameter.\* Regardless of the explicit

\* In a system with well-established physical features, such as a shape resonance at an accurately known energy, the cutoff parameter is usually chosen so that the calculated cross sections reproduce this feature. In other situations, one must guess a reasonable value of  $r_c$ . In interpreting the results of studies which use a parametrized polarization potential, one should be cognizant of the influence of ‘tuning’ of the cross sections via adjustment of the cutoff radius (or other parameters).

mathematical form of  $C(r)$ , its purpose is to ensure that at values of  $r$  near the target,  $V_{\text{pol}}(r)$  of equation (13) is weaker (less attractive) than its asymptotic form  $-\alpha(\hat{r})/2r^4$ . Surprisingly, this simple model potential works rather well (cf. Lane 1980 and references therein).

In spite of its success, this model polarization is unsatisfactory in many respects, not the least of which is the presence of the adjustable parameter  $r_c$  in the cutoff function. Unfortunately, more accurate treatments of polarization effects entail considerable computational effort. However, quite recently 'pseudostate' (Schneider 1977) and 'optical potential' (cf. Klonover and Kaldor 1978; Schneider and Collins 1982) methods have been successfully applied to e-H<sub>2</sub> scattering. These more accurate and sophisticated theories provide *parameter-free* approximations to the polarization potential. However, their complexity and difficulty of implementation makes widespread use of them unlikely in the foreseeable future.

The study of the validity of the assumptions inherent in the crude form (13) for  $V_{\text{pol}}(r)$  and the search for more accurate approximate polarization potentials continues. For example, Morrison and Hay (1979) investigated deviations of the *adiabatic* polarization potential from the asymptotic  $-\alpha(\hat{r})/2r^4$  form for the e-N<sub>2</sub> and e-CO<sub>2</sub> systems. Truhlar and collaborators reported adiabatic polarization potentials for a number of systems. Onda and Truhlar (1980) have proposed new treatments of polarization effects for intermediate-energy electron-molecule collisions. Also, Gibson and Morrison (1981) have generated an *ab initio* (parameter-free) non-adiabatic polarization potential for the e-H<sub>2</sub> system.

The topics of exchange and polarization have been discussed here at some length because they are essential to an understanding of the physics of electron-molecule scattering and because they are likely to be the subjects of continuing research in the next several years. Be that as it may, these are theoretical concerns and may seem rather remote from the immediate needs of experimentalists, i.e. theoretical cross sections for various excitations and physical insight into collision phenomena. In the next part of this article, we shall consider some specific *types* of collisions that pose particular challenges to electron-molecule theory.

### Part III. Problems—and Progress in Their Solution

Next we shall look briefly at several specific problems in the theory of low-energy electron-molecule collisions that seem to be of immediate interest. In the course of this discussion, we shall note recent progress on these problems, although these comments will, of necessity, be brief.

#### 5. *Threshold structures in vibrational-excitation cross sections*

One of the most intriguing discoveries in recent years in the field of electron-molecule scattering is that of sharp threshold 'spikes' in cross sections for vibrational excitation of a variety of molecules. (For a review of experimental results see Rohr 1979.) These peculiar structures were first observed by Rohr and Linder (1975) in their measured cross sections for vibrational excitation of the hydrogen halides HF, HCl and HBr. In Fig. 16, threshold peaks can be seen in the differential cross sections for excitation from the ground ( $v_0 = 0$ ) to the first excited ( $v = 1$ ) vibrational

states of these molecules.\* Characteristically, these spikes are quite narrow (i.e. widths of the order of 0.1 eV), their peaks occurring very near threshold (i.e. roughly 0.1 eV above the threshold energy). In the energy range of the peaks, the differential cross sections for vibrational excitation are observed to be isotropic.

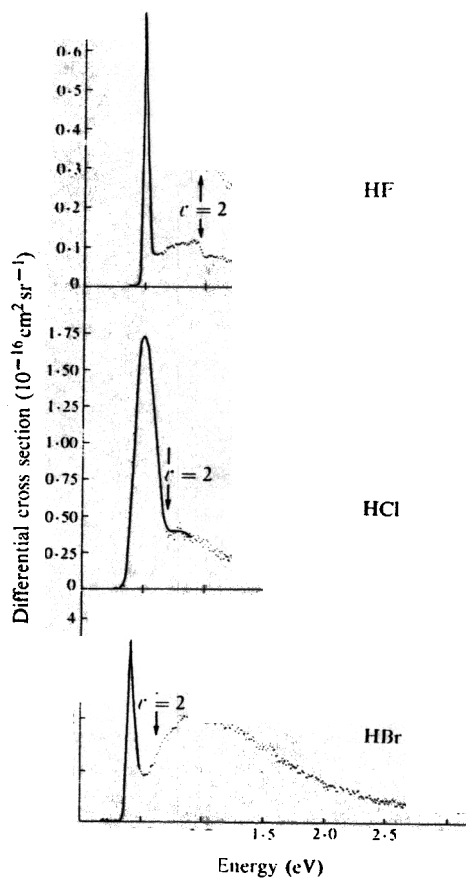


Fig. 16. Experimentally determined differential excitation functions for the  $v_0 = 0 \rightarrow v = 1$  vibrational excitation of HF, HCl and HBr at a scattering angle of  $120^\circ$ . [From Rohr (1979).]

Threshold peaks occur in vibrational-excitation cross sections for molecules other than the hydrogen halides. Indeed, these structures have been observed in cross sections for electron scattering from strongly polar diatomic (HF, HCl, HBr) and polyatomic ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ) molecules, weakly polar ( $\text{CFCl}_3$ ) and non-polar ( $\text{CH}_4$ ,  $\text{SF}_6$ ) polyatomics, and in the excitation cross section for the non-polar (symmetric stretch) mode of  $\text{CO}_2$  (S. Wong 1980, personal communication). Threshold peaks have *not*

\* Similar peaks are seen in excitations from the ground state ( $v_0 = 0$ ) to other final vibrational states ( $v > 1$ ) in, for example, e-HBr and e-HCl collisions. In certain cases, one must use caution in interpreting these experimental results. As Azria *et al.* (1980) have noted, 'when the vibrational levels of a molecule are in the energy range of negative ions formed by dissociative attachment with no kinetic energy, their corresponding excitation functions will exhibit peaks due to these negative ions.' For example, the peaks in the excitation of HBr from  $v_0 = 0$  to  $v = 3, 4$  and  $5$  are due to  $\text{Br}^-$  ions, not electrons.



been observed in electron collisions with non-polar or weakly polar diatomic molecules.

As might be expected, the discovery of these unusual structures brought an immediate response from the theoretical community, and in the years since 1975 several attempts have been made to understand the physical mechanism responsible for threshold peaks. In this quest, particular attention has been given to e-HCl collisions. Among the mechanisms that have been explored for this system are resonant states of  $\text{HCl}^-$  that dissociate to  $\text{H}^- + \text{Cl}$  and  $\text{Cl}^- + \text{H}$  (Taylor *et al.* 1977); a virtual state (Dubé and Herzberg 1977; Nesbet 1977); a final-state interaction (Gianturco and Rahman 1977); and most recently a non-adiabatic phenomenon related to the 3 eV shape resonance in e-HCl scattering (Domcke and Cederbaum 1980). This 'catalogue of theories' is presented to suggest the extent of the research that has been carried out on this particularly provocative problem. A discussion of much of this work can be found in a recent review by Herzberg (1979). Suffice it to say here that at the present writing the question of *why* threshold peaks occur in vibrational excitation cross sections for many molecules has not been fully answered; this mystery will probably continue to attract attention until it is.

In addition to the aforementioned studies of very low-energy e-HCl collisions, some recent theoretical attention has been given to threshold structures in the vibrational excitation of  $\text{CO}_2$ . This case is of some interest because the target is non-polar in the initial and final vibrational target states and because a likely mechanism for producing the threshold peak has been verified computationally. Morrison and Lane (1979) predicted a sharp threshold peak in the cross section for excitation by electron impact of the first symmetric-stretch vibrational level of  $\text{CO}_2$  from the ground vibrational state. This structure was also exhibited in simultaneous experimental measurements by S. Wong (1980, personal communication). The theoretical study of Morrison and Lane was based on the adiabatic-nuclei theory (see Section 3a) for vibration, which must be treated with caution near threshold. Subsequently, Morrison (1982) presented evidence that a virtual state is present in the e- $\text{CO}_2$  interaction potential used to calculate the theoretical vibrational-excitation cross sections. A virtual state mechanism explains the threshold structure in this cross section (Nesbet 1977) and is consistent with observed total and momentum transfer cross sections for e- $\text{CO}_2$  collisions.

Before leaving the topic of near-threshold electron-molecule scattering, we should note two related areas that are currently receiving considerable theoretical attention. The first topic pertains to the formulation of the scattering theory. As noted in Section 3a, the adiabatic-nuclei theory is expected to break down near threshold for a ro-vibrational excitation. This fact leaves one without a theory for calculation of cross sections in this energy range (except for extremely simple systems), full close-coupling theories being impossible to implement. A number of formulations that go beyond the adiabatic-nuclei picture are currently being studied (Nesbet 1979; Domcke *et al.* 1979; Norcross and Padial 1982; Feldt and Morrison 1982). The second topic encompasses the vast array of phenomena that occur when electrons scatter from strongly polar molecules (cf. Collins *et al.* 1980a, and the review by Norcross and Collins 1982). The recent interest in this area of research is due to the importance of such collisions to applied areas such as energy technology and partly because (for some systems) classical and semiclassical scattering techniques can be interwoven into the quantum theory (Allan and Dickinson 1981).

### 6. Electron collisions with polyatomic molecules

Even a cursory perusal of the literature on electron–molecule collision theory will reveal that the overwhelming majority of studies that have been carried out to date have dealt with systems with simple targets such as  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{CO}$ —rather small diatomic molecules with comparatively few electrons. This emphasis is understandable in a ‘new’ field in which researchers are trying to cope with problems of the magnitude of those discussed in Part II. Indeed, we have seen that extensive use of approximations and models is necessary to cope even with these ‘small systems’.

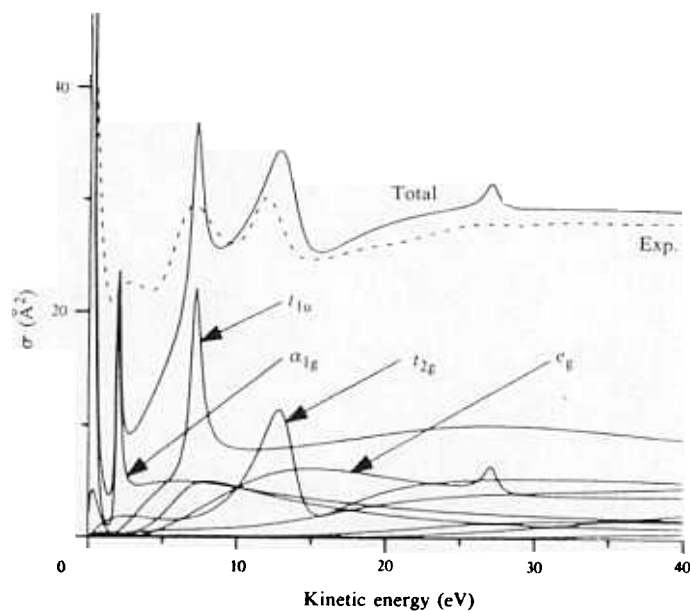


Fig. 17. Total elastic cross section for  $e\text{-SF}_6$  scattering as calculated using the continuum multiple scattering method (solid curve) of Dehmer *et al.* (1978). Experimental data give the absolute cross section (dashed curve) of Kennerly *et al.* (1979). Also shown are partial cross sections for the resonant electron–molecule symmetries. [From Dehmer and Dill (1979).]

Nevertheless, most molecules are not small in this sense. Polyatomic molecules typically have a rich and complex nuclear and electronic structure. Hence, cross sections for electron collisions with polyatomic targets display a rich diversity of phenomena not seen in their counterparts for diatomic systems. Thus, an important part of the electron–molecule collision theory is the question of how to treat scattering from complicated polyatomic targets with *many* electrons, for example  $\text{SF}_6$  (70 electrons) or  $\text{CFCl}_3$  (66 electrons). Much of the study of model interaction potentials and approximate collision theories (cf. Part II) that has been carried out for electron *diatomic* molecule collisions will provide an essential foundation for future research on polyatomic systems. But very extensive modelling may be required to treat these systems, and the task of reducing the scattering problem to tractable size without approximating away all the important physics in the process poses a substantial theoretical challenge.

One promising new strategy for tackling electron collisions with polyatomic molecules is the *continuum multiple scattering method* (see the review by Dehmer and Dill 1979). Briefly, this method is based on a model of the entire electron-molecule interaction potential. This potential is replaced by a form that is similar to the 'muffin tin' potentials of solid-state physics. Essentially, this model potential consists of a collection of finite-range spherically symmetric potentials centred on the nuclei. Exchange and long-range polarization effects are approximately taken into account, the former by a free-electron-gas potential (cf. Section 4a). Dehmer and collaborators have carried out a huge number of applications of this method; their total cross section for e-SF<sub>6</sub> scattering is compared with the absolute experimental results of Kennerly *et al.* (1979) in Fig. 17.

Recently, Rumble and Truhlar (1980) reported a careful quantitative investigation of the validity of several key approximations inherent in the continuum multiple scattering method. These authors showed that for e-N<sub>2</sub> scattering in the energy range from 5 to 30 eV, this method leads to errors of about 30% in the total integrated cross section. However, the study of Rumble and Truhlar confirmed the usefulness of multiple scattering theory for the generation of realistic *semi-quantitative* results for e-N<sub>2</sub> scattering.

To obtain more accurate cross sections for electron polyatomic molecule collisions, one might try to apply one of the theories of Section 3 to the problem. Doing so requires great care and (often) patience. Nevertheless, a few such calculations have been reported, and more are likely to be undertaken in the future. For example, adiabatic-nuclei theory with a free-electron-gas exchange potential was used by Morrison *et al.* (1977) to study e-CO<sub>2</sub> collisions, the lab-frame rotational close-coupling method was used by Thirumalai *et al.* (1981) to calculate elastic scattering and rotational excitation cross sections for e-C<sub>2</sub>H<sub>2</sub> scattering, and the orthogonalized-static procedure (Section 4a) was employed by Gianturco and Thompson (1980) to investigate electron collisions with CH<sub>4</sub>, H<sub>2</sub>O and H<sub>2</sub>S.

### 7. *Electronic excitation*

Although it is a bit outside the stated confines of this paper, the topic of electronic excitation of molecules by electron impact must be mentioned, for it is an important and very difficult problem in this field. In confronting electronic excitation, one must deal with all the difficulties described in Part II, i.e. partial-wave coupling due to the non-spherical Coulomb interaction, the nuclear degrees of freedom and their interaction with electronic motion, exchange effects, and so forth, *plus* the redistribution of the molecular charge cloud in the final state of the system.

Early progress on electronic excitation was made by applying 'weak coupling' theories like the Born approximation. These highly approximate theories are not uniformly successful [cf. the discussion in the papers by Cartwright *et al.* (1977a, 1977b) and by Chutjian *et al.* (1977)]. More recently the ideas of  $L^2$  variational theory have been combined with the distorted-wave method by Rescigno, McKoy, and collaborators to study electronic excitation of H<sub>2</sub>, N<sub>2</sub> and F<sub>2</sub> (cf. Fliflet *et al.* 1980). This work represents a significant advance in sophistication of the theory, as do the two-state close-coupling calculations of Chung and Lin (1978) of cross sections for several electronic transitions in H<sub>2</sub> and the research of Holley *et al.* (1981) on e-N<sub>2</sub> scattering.

Comparison of the close-coupling results of Chung and Lin (1978) with those obtained in weak coupling calculations reveals that the two theoretical formulations produce striking differences in the predicted cross sections. Further research will be essential to understanding and resolving these substantial differences; the extensive use of weak coupling theories in calculations of electronic excitation makes such research all the more imperative.

Most recent studies have treated *spin-forbidden* transitions (for example, singlet-triplet excitations), which are dominated by exchange effects. In an important complementary theory, Hazi (1981) has proposed a semiclassical impact parameter method for *optically allowed* excitations of linear molecules. This theory, which is formulated within the Born-Oppenheimer approximation (Section 2a), uses *classical* straight-line trajectories to describe the motion of the scattering electron. The rest of the formulation is quantum mechanical. In addition, two approximations are made in the interaction potential: exchange effects are ignored (hence the method is applicable *only* to spin-allowed transitions) and only the large- $r$  (asymptotic) electron-molecule interaction is retained (hence the method is applicable at intermediate and high energies where large-order partial waves are important). Hazi has applied this semiclassical impact parameter method of optically allowed transitions in  $H_2$ ,  $N_2$  and  $F_2$  and obtained very accurate integrated cross sections.

In spite of these substantial advances, much more research needs to be done on electronic excitation in electron-molecule scattering before we can have confidence in the explanatory and predictive capabilities of the theory. There is a great need for further close-coupling calculations on systems such as  $e-N_2$  and  $e-H_2$ . Some way must be found to take account of coupling to all the relevant electronic states, i.e. to converge the cross sections. Comparison of the results of these calculations with those obtained from studies based on  $L^2$  variational and/or weak coupling theories will be useful in resolving the substantial discrepancies that can be found in the current literature. Finally, the complexity of calculations for electronic excitation necessitates further research on approximations, both to the interaction potential and to the collision theory.

#### Part IV. Concluding Remarks

Progress in electron-molecule scattering theory is being made at a rapid pace, and there is no indication of a slackening of interest in this field. Theorists have advanced our understanding of the physics of the collision process as well as developed tools for the qualitative and quantitative study of low-energy collisions with 'small' targets. Work is currently underway on the difficult problems of near-threshold scattering, electronic excitations, rearrangement collisions (for example, dissociative attachment), and scattering from polyatomic molecules.

This article has surveyed the principal physical features of low-energy electron-molecule theory, emphasizing non-resonant electronically elastic scattering as treated using eigenfunction expansions. We have seen how an understanding of these qualitative ideas has led to theoretical approaches that circumvent some of the serious difficulties that arise from the nature of these systems. Finally, we have examined a few areas of current (and future) research interest in this endlessly fascinating area of collision physics.

Clearly, there is much work yet to be done in understanding the fundamental interactions that govern the collision, in improving the accuracy with which we can calculate cross sections, and in extending the range of energies and systems that theoreticians can confidently tackle. In these endeavours, communication and collaboration between theorists of various persuasions and among theorists and experimentalists will continue to be of paramount importance.

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## Appendix. Selected Recent Reviews of Electron-Molecule Scattering Theory

### Long Reviews and Monographs

- Takayanagi, K. (1967). *Prog. Theor. Phys. Jpn Suppl.* **40**, 216: Emphasizes non-resonant processes.
- Chandra, N., and Joshi, S. K. (1970). *Adv. Astron. Astrophys.* **2**, 7: Detailed explication of theory for ro-vibrational excitation, with emphasis on eigenfunction-expansion methods.
- Takayanagi, K., and Itikawa, Y. (1970). *Adv. At. Mol. Phys.* **6**, 105: Treats rotational excitation only, including a rather detailed discussion of the Born approximation.
- Schulz, G. J. (1973). *Rev. Mod. Phys.* **45**, 423: Resonances in electron-molecule scattering.
- Rescigno, T. N., McKoy, V., and Schneider, B. I. (1979). 'Electron-Molecule and Photon-Molecule Collisions' (Plenum: New York): Contains several useful reviews of various theoretical gambits, emphasizing computational and practical details.
- Itikawa, Y. (1978). *Phys. Rep.* **46**, 117: Survey of electron polar molecule studies.
- Brown, S. C. (Ed.) (1979). 'Electron-Molecule Scattering' (Wiley: New York): Contains a survey of vibrational excitation, articles on applications of electron-molecule data, and a short review of the state of the theory.

- Burke, P. G. (1979). *Adv. At. Mol. Phys.* **15**, 471: Survey of theoretical techniques for electronically elastic collisions, including illustrative results and recent calculations.
- Lane, N. F. (1980). *Rev. Mod. Phys.* **52**, 29: Contains a thorough explication of the main theoretical approaches and a critical discussion of applications up to 1980.
- Norcross, D. W., and Collins, L. A. (1982). *Adv. At. Mol. Phys.* **18**, 341: Emphasizes electron scattering from highly polar molecules.
- Golden, D. E., Lane, N. F., Temkin, A., and Gerjuoy, E. (1971). *Rev. Mod. Phys.* **43**, 642: Discusses experimental techniques and theoretical procedures; close-coupling and adiabatic-nuclei methods only.

#### Short Reviews and Comments

- Phelps, A. V. (1968). *Rev. Mod. Phys.* **40**, 399: Discusses experimental determination of cross sections for ro-vibrational excitation.
- Takayanagi, K. (1972). *Comments At. Mol. Phys.* **2**, 95.
- Temkin, A. (1976). *Comments At. Mol. Phys.* **6**, 27; **5**, 129.
- Herzenberg, A. (1978). In 'Electron and Atomic Collisions' (Ed. G. Watel), p. 1 (North-Holland: Amsterdam): Discussion of treatments of vibrational excitation.
- Truhlar, D. G. (1981). In 'Chemical Applications of Atomic and Molecular Electrostatic Potentials' (Eds P. Politzer and D. G. Truhlar), p. 123 (Plenum: New York).

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