MEMORANDUM

To: All Recipients of the DNA Reaction Rate Handbook (DNA 1948H)
From: The Editors
Subject: Revision Number 8

Enclosed herewith you will find a copy of Revision Number 8 to the Handbook. It comprises a completely revised and updated version of Chapter 8.

You should immediately discard the previous version of Chapter 8 and replace it with the enclosed. You should also enter on page iii in front of your Handbook the following information: Revision Number 8; Date of Issue - April 1979; Date of Receipt - whatever day you receive this; and sign your name in the last column.

Additional chapters in process of revision include numbers 2, 11, 13, and 20. These will be the subjects of future revisions.
# Reaction Rate Handbook

## Title
REACTION RATE HANDBOOK

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## Abstract
The chief theoretical methods involved in electronic structure calculations, radiative process calculations, dissociative recombination calculations, and atomic and molecular scattering calculations are reviewed in the light of their utilization in atmospheric and ionospheric modelling applications. This is a revision of a previous treatment of theory, within the context of the DNA Reaction Rate Handbook (1948H).
8. DATA-GATHERING METHODS BASED ON THEORETICAL ANALYSIS*

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8.1 INTRODUCTION

This chapter surveys theoretical methods for obtaining data needed to describe and understand either the natural or the perturbed atmosphere. The chapter is so organized as to reflect a natural division of the theoretical problems. Thus Section 8.2 is concerned with problems of molecular electronic structure, and Sections 8.3 and 8.4, respectively, deal with such processes as radiative transitions and dissociative recombinations which are immediately derivable from molecular wavefunctions. Section 8.5 is devoted primarily to collision processes, which require for the most part a different set of calculational techniques. In many cases solution of the collisional problem makes use of a great deal of information obtained from electronic structure considerations; in such instances the procedure usually falls into two distinct and separate components: one stage in which the fundamental information, e.g., wavefunctions, potential curves, matrix elements, is generated from molecular structure theory, and another stage in which these data are employed as input material for the specifically collisional aspects of the calculations.

There is a strong and persistent contrast in flavor between the two theoretical areas of electronic structure and collision processes. Electronic structure problems generally require heavily computerized calculations, drawing on a comparatively narrow and well-developed family of computing techniques; the family resemblances among these methods relate to the fact that the questions asked and the answers desired can usually be formulated in simple terms calling for energy levels,

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especially the lowest ones, and wavefunctions or their integrals, as functions of a few parameters, e.g., internuclear distances. Family resemblances are enhanced by the importance of the variational principle for the energy in stationary states.

Collision problems, by contrast, involve a wider spectrum of questions asked and energy ranges involved, with a broad spread of dynamical conditions including both heavy-particle and electron motion, and possibilities of three-body as well as two-body channels. Being non-stationary, the problems are not subject to the use of a simple and general variational principle. Instead, a much wider and more diverse set of methods must be used, depending on the conditions of the specific problem, the energy range involved, the accuracy desired, and many other factors. No exhaustive catalogue of such methods can be conveniently presented within the context of this chapter; besides, new techniques continue to evolve. In Section 8.5, therefore, some of the most important general methods of approach are outlined, and the reader is referred to a selection of texts and review articles in which more detailed and extensive information may be obtained.

The theoretical methods described in this chapter have been selected for their usefulness when applied to the understanding and prediction of the thermodynamic, radiative, and electromagnetic properties of the ionosphere in either its natural state or some perturbed condition. They will be particularly useful in evaluating the thermal, transport, and kinetic properties of heated air or of atmospheric mixtures under the influence of various types of electromagnetic and particulate radiation as well as hydrodynamic disturbances (Reference 8-1). Such properties are also of particular interest in plasma physics (Reference 8-2), gas laser systems, and basic studies of airglow and the aurora (Reference 8-3). This information also plays an important role in our understanding of re-entry physics, with applications in the areas of missile detection and discrimination. Calculations of electronic structure, radiative transitions, and collision processes are all important in these applications.

Present theoretical efforts, which are directed toward a more complex and realistic analysis of the transport and kinetic equations governing atmospheric relaxation and the propagation of artificial disturbances, require detailed information pertaining to thermal and non-thermal kinetics in regions of temperature and pressure where both atomic and molecular effects are important. Although various experimental techniques have been employed for both atomic and molecular systems, the older theoretical studies of radiative processes were largely confined to analyses of the properties of atomic systems (References 8-4, 8-5) owing in large part to the unavailability of reliable wavefunctions for diatomic molecular systems, particularly for excited states or states of open-shell structures. In later studies (References 8-6 through 8-8), reliable procedures have been prescribed for such systems, and these have resulted in the development of practical computational programs, including several of both an ab initio and semi-empirical nature which are outlined in Section 8.2. The utility of such procedures is discussed in Sections 8.3 and 8.4, in describing radiative processes and dissociative recombination, respectively, and related collisional processes are considered in Section 8.5.

8.2 ELECTRONIC STRUCTURE CALCULATIONS

The application of quantum-mechanical methods to the prediction of electronic structure has yielded a great deal of detailed information on atomic and molecular
properties (Reference 8-9). The availability of high-speed computers with large storage capacities has made it possible to examine both atomic and molecular systems using an ab initio approach, employing no empirical parameters (Reference 8-10). Variational calculations for molecules employ a Hamiltonian based on the nonrelativistic electrostatic interaction of the nuclei and electrons, and a wavefunction formed by antisymmetrizing a suitable many-electron function of spatial and spin coordinates. For most applications it is also necessary that the wavefunction represent a particular spin eigenstate and that it have appropriate geometrical symmetry.

In addition, it is assumed for most systems of interest here, that the electronic motion is fast relative to the kinetic motion of the nuclei and that the total wavefunctions can be separated into a product form, in which one term depends on the electronic motion and is parametric in the nuclear coordinates, and a second term describes the nuclear motion in terms of adiabatic potential hypersurfaces. This separation, based on the relative mass and velocity of an electron as compared with the mass and velocity of the nucleus, is known as the Born-Oppenheimer approximation.

The specific methods to be discussed below for electronic structure calculations may be broken down into three main classifications:

1) The variational methods, which in turn can be grouped into two categories:

   a) Self-consistent-field (SCF) procedures, which are based on wavefunctions consisting of a single term. SCF wavefunctions are characterized by the requirement that the spatial orbitals be chosen so as to optimize the energy, normally with certain occupancy and symmetry restrictions.

   b) Those methods based on configuration-interaction (CI) wavefunctions, i.e., on wavefunctions which are a linear combination of terms differing in either spatial or spin occupancy, each separate term being referred to as a configuration. Among the CI methods, a distinction may be drawn between those which are designed to optimize the description of a single electronic state and those which are applicable to the description of many states.

2) Methods based on many-body perturbation theory or on the use of Green's functions. These approaches have not yet been developed to a degree comparable with the SCF and CI methods, but they hold promise for the future and are worth serious consideration.

3) Methods derived as extensions of the original Hückel type of approach or from approximate solid-state models. Here certain difficult integrals are only approximately evaluated and/or a non-rigorous Hamiltonian is employed.

Regarding the accuracy of modern approaches, quantitative (~0.01 eV) studies have been carried out for atomic systems in the first or second row of the Periodic Table. For diatomic systems constructed from these atoms, an accuracy of 1-2 kcal in the potential curves is realizable. For polyatomic systems the situation is less clearcut owing to the great increase in computational difficulty. Probably a 5-10 kcal accuracy can be achieved for simple potential energy surfaces, although very few surfaces have been examined in detail.
8.2.1 Electronic States and Wavefunctions

Nearly all electronic structure calculations have been based on the use of one-electron orbitals and are of two types, viz., Hartree-Fock and configuration-interaction (Reference 8-11). Hartree-Fock calculations are based on a single assignment of electrons to spatial orbitals, following which the spatial orbitals are optimized, usually subject to certain restrictions. Most Hartree-Fock calculations have been based on the assumptions that the spatial orbitals are all doubly occupied, as nearly as possible, and that they are all of definite geometric symmetry. These restrictions define the conventional, or restricted, Hartree-Fock (RHF) method (References 8-12, 8-13). RHF calculations can be carried out with relatively large Slater-type orbital (STO) basis sets for diatomic molecules with first- or second-row atoms, and the results are convergent in the sense that they are insensitive to basis enlargement. Polyatomic systems have, for the most part, been examined using Gaussian-type orbitals. The RHF model is adequate to give a qualitatively correct description of the electron interaction in many systems, and in favorable cases can yield equilibrium interatomic separations and force constants. However, the double-occupancy restriction makes the RHF method inappropriate in a number of circumstances of practical interest. In particular, it cannot provide potential curves or surfaces for molecules dissociating into odd-electron atoms, e.g., NO at large internuclear separation, or into atoms having less electron pairing than the original molecule, e.g., \( \text{O}_2(\text{X}^{3}\Sigma_g^-) + \text{2 O}(3\text{P}) \). Moreover, it cannot handle excited states having unpaired electrons, e.g., the \( ^3\Sigma \) state of \( \text{O}_2 \) responsible for the Schumann-Runge bands. In general, it gives misleading results for molecules in which the extent of electron correlation changes with internuclear separation.

Configuration-interaction (CI) methods have the capability of avoiding the limitations of the RHF calculations. If configurations not restricted to doubly-occupied orbitals are included, a CI can, in principle, converge to an exact wavefunction for the customary Hamiltonian. However, many CI calculations have, in fact, been based on a restriction to doubly-occupied orbitals and therefore retain many of the disadvantages of the RHF method (Reference 8-11). The use of general CI formulations involves three considerations, all of which have been satisfactorily investigated. These are: the choice of basis orbitals, the choice of configurations (sets of orbital assignments), and the specific calculations needed to make wavefunctions describing pure spin states (Reference 8-7). The first and second of these considerations comprise the art associated with quantum-mechanical electronic structure calculations. Many methods, including iterative natural spin orbitals (I-NSO), perturbation selection, first-order CI, and others, have been advocated for the optimum choice of configurations. There are no firm rules, however, and the optimum choice is a strong function of the insight of the particular investigator. The third consideration enumerated above has proved difficult to implement, but computer programs in which it is included have been prepared, and the CI method has been found to be valuable in handling excited states and dissociation processes which cannot be treated with RHF techniques.

Either of the methods described above for \textit{ab initio} calculations reduces in practice to a series of steps, the most important of which are: the evaluation of molecular integrals, the construction of matrix elements of the Hamiltonian, and the optimization of molecular orbitals (RHF) or configuration coefficients (CI). For most molecules, these steps have comparable computing time requirements, so that no one bottleneck can be said to limit computation speed. In short: the integral evaluation involves the use of ellipsoidal or spherical coordinates and introduction

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of the Neumann or Laplace expansion for the interelectronic repulsion potential (Reference 8-14); the matrix element construction depends upon an analysis of the algebra of spin eigenfunctions (Reference 8-15); and the orbital or configuration optimization can be carried out by eigenvalue techniques (Reference 8-6). All these steps have become standard. All of them can be performed efficiently on a computer having approximately 65,000 words of core storage, a cycle time in the microsecond range, and several hundred thousand words of peripheral storage.

Both the RHF and CI methods yield electronic wavefunctions and energies as functions of the internuclear separation, the RHF method for one state, and the CI method for all states considered. The electronic energies can be regarded as potential curves, from which may be deduced equilibrium internuclear separations, dissociation energies, and constants describing vibrational and rotational motion, including anharmonic and rotation-vibration effects. It is also possible to solve the Schrödinger equation for the motion of the nuclei subject to the potential curves, in order to obtain vibrational wavefunctions for use in transition probability calculations. The electronic wavefunctions themselves can be used to estimate dipole moments of individual electronic states, transition moments between different electronic states, and other properties. While all of these calculations have been carried out on some systems, the unavailability of good electronic wavefunction and potential curves has limited actual studies of most of these properties to a small number of molecules.

8.2.2 Born-Oppenheimer Separation

For a system of \( n \) electrons and \( N \) nuclei, and considering only electrostatic interactions between the particles, the total Hamiltonian is:

\[
\mathcal{H} = \mathcal{H}^e + \mathcal{H}^n + \sum_{a=1}^{N} \frac{\hbar^2}{2m_\alpha} \nabla^2 + \sum_{i=1}^{n} \frac{\hbar^2}{2m_a} \left[ \sum_{j=1}^{N} \nabla_i \cdot \nabla_j \right],
\]

where:

\[
\mathcal{H}^e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla^2_i + \sqrt{\mathcal{E}^e} (\mathbf{r}_N, \mathbf{r}_N).
\]
where \( \psi_k(r_N, R_N) \) is an electronic wavefunction parametric in the nuclear coordinates as given in Equation (8-3), and \( X_k(R_N) \) are nuclear motion wavefunctions which satisfy (neglecting terms of the order of \( m_e/m_a \)):

\[
\left[ -\sum_{\alpha=1}^{N} \frac{\hbar^2}{2m_{\alpha}} \nabla_{\alpha}^2 + \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \nabla_{\alpha} \cdot \nabla_{\beta} + \sqrt{e^4}(r_{\alpha}, R_N) \right] X_k = \hbar \frac{\alpha_k}{t_k}. \tag{8-4}
\]

The cross term in \( \nabla_{\alpha} \cdot \nabla_{\beta} \) can be eliminated by a proper change of variables and Equation (8-4) then reduces to a (3N-3)-dimensional Schrödinger equation.

For most systems, where the velocity of motion of the nuclei is slow relative to the electron velocity, this decoupling of electronic and nuclear motion is valid and is referred to as the adiabatic approximation.

Equation (8-3) thus defines an electronic eigenstate \( \psi_k(r_N, R_N) \), parametric in the nuclear coordinates, and a corresponding eigenvalue \( E_k(r_N) \) which is taken to represent the potential energy curve or surface corresponding to state \( k \).

8.2.3 Variational Methods - ab initio

By an ab initio method is meant one which starts from a zero-order Hamiltonian which is exact except for relativistic and magnetic effects, and which involves the evaluation of electronic energies and other relevant quantities for wavefunctions which are properly antisymmetrized in the coordinates of all the electrons. For a system containing \( n \) electrons and \( M \) nuclei, the zero-order Hamiltonian depends parametrically on the nuclear positions and is of the form:

\[
\mathcal{H} = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \sum_{j=1}^{M} \frac{z_i z_j}{\left| \mathbf{r}_i - \mathbf{r}_j \right|} + \sum_{1 \leq i < j} \frac{z_i z_j}{\left| \mathbf{r}_i - \mathbf{r}_j \right|} + \sum_{1 \leq i < j} \frac{1}{\left| \mathbf{r}_i - \mathbf{r}_j \right|} \tag{8-5}
\]

where \( z_i \) and \( \mathbf{r}_i \) are the charge and position of nucleus \( i \), \( \mathbf{r}_j \) is the position of electron \( j \), and \( \nabla_i^2 \) is the Laplacian operator for electron \( i \). All quantities are in atomic units, i.e., lengths in bohrs, energies in hartrees (1 hartree = 2 rydbergs). The many-electron wavefunction consists of one term, or a linear combination of terms, of the form:

\[
\psi = \mathcal{A} \prod_{i=1}^{n} \phi_{i\mu}^* \theta_{\mu} \sigma_1 \ldots \sigma_n, \tag{8-6}
\]

where \( \phi_{i\mu}, \phi_{2\mu} \ldots \) are spatial orbitals occupied in \( \psi_{\mu} \), \( \theta_{\mu} \) \( \sigma_1 \ldots \sigma_n \) is an \( n \)-electron spin function, and \( \mathcal{A} \) is an antisymmetrizing projection operator. The spin function \( \theta_{\mu} \) may be required to be an eigenfunction of the spin operators \( S^2 \) and \( S_z \), and may therefore be characterized by quantum numbers \( S \) and \( M_S \), but these quantum numbers will not suffice completely to describe \( \theta_{\mu} \) except under certain conditions which cannot always be met. The spatial orbitals \( \phi_{i\mu} \) may be whatever basis orbitals have been introduced, arbitrary linear combinations thereof, or specific linear combinations.
determined pursuant to the particular calculational method in use.

The spatial orbitals $\phi_{i\mu}$, the spin functions $\theta_{i\mu}$, and the coefficients of different $\psi_{\mu}$ if a linear combination of $\psi_{\mu}$ is used, may be explicitly determined by invoking the variational principle:

$$\int \psi^* \frac{\partial \psi}{\partial t} \, dt = 0, \quad (8-7)$$

or they may be determined implicitly by the application of perturbation or other non-variational methods. Various specific methods for the determination of wavefunctions are described below. However, it should first be observed that the adequacy of an ab initio calculation, or for that matter any energy calculation, will depend crucially upon the extent to which the wavefunction can be qualitatively appropriate. Some of the considerations surrounding the choice of wavefunction are as follows:

(a) Necessity that the wavefunction possess sufficient flexibility to be able to describe dissociation to the correct atomic and molecular fragments as various internuclear separations are increased;

(b) Maintenance of equivalent quality of calculation for nuclear geometries differing in the nature or number of chemical bonds;

(c) Ability to describe degenerate or near-degenerate electronic states when they are pertinent;

(d) Ability to describe different electronic states to equivalent accuracy when their interrelation, e.g., crossing, is relevant, and in particular, ability to describe Rydberg–valence state mixing;

(e) Ability to represent changes in the coupling of electron spins as bonds are broken or re-formed.

The foregoing considerations indicate that it will often be necessary to consider wavefunctions with more than a minimum number of singly-occupied spatial orbitals, and that there will be many potential curves or surfaces for which a wavefunction consisting of a single $\psi_{\mu}$ cannot suffice. However, it will then be necessary to allow mixing of $\psi_{\mu}$ with different degrees of orbital single occupancy so as to obtain smooth transitions from the occupancies characteristic of separated atoms or molecules to those characteristic of a compound system or a different fragmentation. For example, a wavefunction for the system $O + N_2$ must be capable of describing the $^1P$ state of oxygen when it is far from the $N_2$ molecule, and this will require two singly-occupied spatial orbitals. But the compound system $N_2O$ may be well described in certain states using doubly-occupied orbitals only. Moreover, in regions where one nitrogen atom is separated from an NO molecule, as many as three singly-occupied spatial orbitals will be needed for the nitrogen atom, and there must be at least one singly-occupied orbital in any description of the NO molecule. Any calculational scheme which does not permit smooth transitions between
these various situations cannot be of comparable accuracy in all regions of space, and therefore may be misleading as to the shapes and sizes of features of the potential energy surfaces.

Another implication of the considerations surrounding the choice of wavefunction is related to the treatment of electron spin. Not only is it necessary to require that the wavefunction be an eigenfunction of $S^2$ and $S_z$, but it is also necessary to take account of the fact that under many conditions, there will be more than one spin eigenfunction of given $S$ and $M_S$. The different spin eigenfunctions correspond to different couplings among the individual spins. Since reactive processes involve the breaking and forming of electron-pair bonds, they must necessarily be accompanied by reorganizations of the spin coupling. A failure to take account of this will lead to qualitatively inappropriate wavefunctions.

8.2.3.1 SELF-CONSISTENT FIELD (SCF) METHODS

The simplest and most widely used SCF procedure is that known as Restricted Hartree-Fock (RHF). In the RHF procedure, the spatial orbitals are assumed insofar as possible to be doubly occupied, and if there is molecular symmetry, to be of a pure symmetry type. As a result of the occupancy assumption, the wavefunction usually takes the form of a single Slater determinant.

RHF calculations are most easily done after introducing an atomic orbital basis $\chi_1, ..., \chi_p$, in terms of which the orbitals take the form:

$$\phi_{ji} = \sum_{j=1}^{p} c_{ji} \chi_j.$$  \hspace{1cm} (8-8)

The variational condition determining the coefficients $c_{ji}$ is cubic in the unknowns, but iterative techniques permit these coefficients to be determined by repeated use of matrix diagonalization methods. Under most conditions it is possible to choose an iterative process facilitating convergence; there is much RHF experience and inordinate difficulties are not usually encountered. Because of the occupancy assumptions, it is possible without loss of generality to take the RHF spatial orbitals as orthogonal, and this is an important feature simplifying the calculations.

RHF wavefunctions are frequently unsatisfactory. For many systems they give poor descriptions of dissociation fragments; their use may preclude satisfactory description of intermediate situations in which one bond is partially formed while another is partially broken. In such cases, insistence upon an RHF formulation may force a discontinuous transition as the nuclear positions are changed, owing to changes in the energy ordering of the highest occupied RHF orbitals.

The great speed and other known properties of RHF calculations do not provide sufficient justification for a restriction to RHF methods when they are inherently inappropriate, as is the case for most potential energy surfaces which describe reactions, and many which describe dissociations. RHF methods are also of limited validity in many situations where two or more surfaces are at nearly the same energy.
Some of the disadvantages of the RHF method can be avoided by using a wavefunction consisting of an antisymmetrized spin-orbital product, thus not requiring orbitals of opposite spin to be pairwise spatially identical. This spin-polarized method has the disadvantage in turn of failing to yield spin eigenfunctions and is therefore a poor approach to the determination of relationships between states of definite spin multiplicities. The calculations are somewhat more cumbersome than RHF studies, and the advantages of the spin-polarized method are probably insufficient under most circumstances to favor its use. The disadvantage of not yielding a spin eigenfunction can be circumvented by spin projecting to an eigenstate after the spin-polarized orbitals have been determined, but the result obtained thereby is inferior to an energy optimization of the projected wavefunction.

An SCF procedure which avoids all the above conceptual difficulties involves the simultaneous optimization of the orbitals and the spin function. This yields satisfactory results only if the spatial orbitals are not required to be either identical or orthogonal, and the nonorthogonality greatly increases the computational complexity. Because of the free choice of spin eigenfunction, the spatial orbitals cannot be orthogonalized without serious loss of flexibility in the wavefunction. This simultaneous spin and spatial orbital optimization has been carried out for a few systems, and provides good results. However, computational complexities are prohibitive if there are many electrons, and under most circumstances it is more practical to achieve comparable or better results through a CI calculation with orthogonal orbitals.

8.2.3.2 CONFIGURATION-INTERACTION (CI) METHODS

The specific form for a CI wavefunction, \( \psi \), may be written as:

\[
\psi = \sum_{\mu} c_{\mu} \psi_{\mu},
\]

where each \( \psi_{\mu} \) is referred to as a configuration and has the general structure given in Equation (8-6). States of different symmetries are studied by restricting \( \psi \) to the appropriate form, and excited states of any symmetry can be handled by simultaneously determining \( \psi \) for the excited state of interest and for all lower-lying states of the same symmetry.

8.2.3.2.1 Single-state optimization methods

Variational optimization of Equation (8-9), where the principal concern is with only one projection of \( \psi \) corresponding to a particular electronic eigenstate, has been studied extensively. There exist at least two well-developed techniques for such situations, viz., the multiconfiguration SCF (MC-SCF) and iterative natural spin-orbital (I-NSO) approaches.

In the MC-SCF approach, the emphasis is on constructing the best possible spatial orbitals \( \phi_{\mu} \) within a CI framework which contains only those configurations necessary for proper wavefunction dissociation and those configurations necessary to handle, at least to first order, changes in pair correlation error as a function of internuclear separation. Typically only two or three configurations are required.
to account properly for correct atomic limit connections. A few tens of configurations which mainly include single orbital excitations are often added to the CI to handle the correlation problem. Various prescriptions have been proposed to handle the numerical aspects of obtaining optimum molecular orbitals within the chosen CI.

An analytic procedure has been suggested (Reference 8-11), similar to analytic Hartree-Fock methods whereby each molecular orbital is expanded as a linear combination of some simple basis functions over which all of the one- and two-electron integrals can be calculated efficiently. Thus:

\[
\hat{\phi}_{i\mu} = \sum_{ik} \hat{a}_{kj} u_{k} 
\]

where \( u_{k} \) is an elementary basis function such as a Slater-type orbital (STO) or a Gaussian-type orbital (GTO). The \( u_{k} \) are usually symmetry-restricted for a given \( \Phi_{i\mu} \) and the MO expansion coefficients \( \hat{a}_{kj} \) are found by non-linear matrix diagonalization techniques. An alternate and more direct procedure is to determine the \( \hat{a}_{kj} \) using Newton-Raphson techniques (Reference 8-17). In any event, the entire procedure involves a double iteration, first to estimate the MO coefficients \( \hat{a}_{kj} \), and then to solve the secular equation for the optimum CI coefficients.

The MC-SCF procedure has yielded excellent results in cases where there is a single dominant configuration in \( \Psi \), where there are no nearby degeneracies and where the principal interest has been the ground molecular state. The method fails, or is difficult to apply, when the total wavefunction \( \Psi \) may have two or more leading terms for proper chemical sense. Convergence difficulties have also been encountered in applying MC-SCF to excited electronic states of the same symmetry as the ground state. Nevertheless, MC-SCF is among the best available techniques for producing potential-energy surfaces accurate to within approximately one kcal.

The I-NSO approach is based upon the observation (Reference 8-18) of a unique orbital transformation which yields a CI having optimum convergence properties. The procedure for defining this orbital transformation requires, however, that a full CI be performed over an arbitrarily chosen basis set. The resulting CI coefficients can then be used to construct a unique one-particle density matrix (unique to the total Hilbert space represented by the basis functions) and this matrix can be diagonalized to yield the optimum orbital expansion coefficients for constructing the NSO's. This can never quite be accomplished in practice, owing to the rapid expansion of the size of a full CI with modest increases in the basis function size. Therefore, approximate iterative procedures have been suggested. One such (Reference 8-19) starts with a modest STO or GTO basis which is first converted into SCF form. All single, and possibly double, orbital excitations are then constructed from the SCF function using the unoccupied basis functions. The resulting CI is diagonalized and reduced to NSO form. These new orbitals now form a leading configuration and the basis set is augmented by the addition of new functions, possibly of higher orbital angular momentum, and the single, double, etc., excitations are constructed to form the CI. The procedure is cycled until some kind of internal consistency in the NSO's is achieved. Typically, several thousand configurations are handled in the CI as contrasted with the tens of configurations employed in MC-SCF.

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The two greatest deficiencies of I-NSO procedures are first, that the magnitude of effort involved is so large that only the biggest and most powerful computers prove to be useful in implementing this analysis, and second, that the method may converge to some non-physical state if the starting configuration is not a reasonable description of the total $\psi$. Care must be taken that the iterative procedure is producing a set of functions which are localized in the space of the eigenstate under study. The most accurate CI calculations available have been constructed using this procedure. The costs associated with the I-NSO method, as applied to potential-energy hypersurfaces, would appear to be prohibitive as developed thus far, except for a few isolated prototype calculations.

8.2.3.2.2 Multi-state analysis

For many applications, a single potential-energy surface will not suffice, and information may be required for a whole series of possibly intersecting hypersurfaces. In this case, ultimate wavefunction accuracy must be compromised for the sake of a consistent description of all the eigenstates of interest. The most successful approach has involved choosing a basis set optimum for all the ground and excited separated atomic and molecular dissociation products for a given system that are accessible within the energy range of interest. For example, the system MgO can be efficiently examined by first constructing optimum basis functions for Mg(3s, 3p, 3d) and O(2s, 2p). Such functions yield reasonable descriptions of the separate atomic states, and when mixed in a CI framework yield a set of potential-energy curves of consistent quality for all of the excited molecular states that can be constructed from this basis set. This is the main idea of the valence configuration-interaction (VCI) approach (Reference 8-7), where a complete or nearly complete CI is constructed from a few well-chosen atomic basis functions. The method applies without modification to studies of surfaces.

A key advantage of such an approach is that several eigenstates can be examined simultaneously with about the same overall accuracy. If the basis set is augmented by the addition of diffuse or Rydberg-type orbitals, Rydberg-valence state mixing can be studied. An important problem in this area is concerned with infrared radiation in the Rydberg bands of the NO molecule. Perturbations in the radiation characteristics of NO due to valence-state mixing have been examined quantitatively using a VCI approach. The principal drawback is the reliance on a full CI expansion of a limited basis set. Even modest extensions of the basis size make the method unwieldy owing to the large number of new configurations which result. Even with a minimum basis set, a typical triatomic system might have on the order of $10^4$-$10^5$ configurations in a full CI. It is therefore essential to identify and employ those configurations which describe the significant portion of the wavefunction. This objective may be accomplished in several ways, viz.: (a) by screening atomic orbital occupancies to eliminate those with excessive formal charge; (b) in a molecular-orbital framework, by eliminating those configurations having excessive numbers of antibonding orbitals; or (c) by carrying out an initial screening of configurations, using perturbation theory based on interaction matrix elements between some $\psi_0$ (possibly the Hartree-Fock function) and each constructed $\psi_\mu$, rejecting all $\psi_\mu$ which do not satisfy some energy criteria. This last procedure suffers from the fact that the total $\psi$ will be constructed from a different set of $\psi_\mu$ at different geometries of the nuclei.
8.2.4 Perturbation Methods

Non-variational methods have been of limited utility for electronic structure calculations, owing to a history of confusion of methods and a non-systematic approach to wavefunction expansion for higher order or more accurate analysis. Simple perturbation techniques based on a separable zero-order Hamiltonian and corresponding wavefunctions \( \psi_0 \) usually converge too slowly to be of use in describing molecular systems characterized by large changes in the charge distribution from the atomic states. Two systematic approaches which appear to have merit are described below:

8.2.4.1 MANY-BODY PERTURBATION THEORY (MBPT)

The non-variational method most often applied to atomic and molecular calculations is Many-Body Perturbation Theory (MBPT) (References 8-20, 8-21). The essence of the MBPT method is the identification of a soluble zero-order Hamiltonian wavefunction \( \mathcal{H}_0 \), and energy \( E_0 \), followed by the description of the actual wavefunction \( \psi \) and energy \( E \) as expansions in powers of matrix elements of \( \mathcal{H} = \mathcal{H}_0 - \mathcal{H} \), where \( \mathcal{H} \) is the actual Hamiltonian. If \( \mathcal{H}_0 \) is chosen to be a separable sum of one-electron operators, it is possible to cast the perturbation expansion in a diagrammatic form in which the energy is given as a sum of the contributions from connected diagrams. This result is known as the Linked Cluster Theorem.

The modern diagrammatic approach to MBPT has the great advantage that it helps organize the energy contributions in ways suggesting alternatives to the retention of all terms up to certain powers of matrix elements of \( \mathcal{H} \). In particular, it becomes clear how to sum certain classes of terms to infinite order in \( \mathcal{H} \), thereby reaching specific approximations not easily attained in other ways.

The suitability and rate of convergence of the MBPT expansion depends upon the choice of zero-order Hamiltonian \( \mathcal{H}_0 \). As has been shown in numerous studies (e.g., Reference 8-22) on atomic systems, satisfactory convergence can be obtained if \( \mathcal{H}_0 \) is so chosen as to be related to the Fock operator obtained by solving the SCF problem. Best results are achieved if the Fock operator is modified so that for unoccupied orbitals it describes interactions to one less than the total number of electrons, i.e., the so-called \( V_{n-1} \) potential. Otherwise the unoccupied orbitals are too diffuse to form a good basis for MBPT calculations. It has been shown (Reference 8-23) that highly satisfactory results are obtainable if numerical continuum orbitals (Reference 8-22) are avoided by the use of a discrete basis set.

Excellent results have been obtained for many properties of atoms and for a very small number of diatomic molecule problems (Reference 8-24). Relatively speaking, at such time as the effort invested in MBPT methods becomes equivalent to that expended in the SCF and CI approaches, the former will become highly competitive with the latter; this is not yet the case, however.

For potential-energy surface applications MBPT methods are subject to the limitation that they are readily applied to only one state at a time; moreover, the methods are most easily applied to non-degenerate ground states. However, there have been indications (Reference 8-25) as to how calculations can be extended to other situations, and studies have been reported (Reference 8-26) of some excited states of \( \text{H}_2 \).

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The greatest limitation to MBPT methods is their lack of a high degree of computational organization at this time. Programs for the systematic identification of diagrams are still in early stages of development, as are automated procedures for diagram evaluation. The scope of this limitation may perhaps be better appreciated by considering that no polyatomic system has as yet been studied by MBPT techniques.

8.2.4.2 GREEN'S FUNCTION APPROACH

A second group of relatively new non-variational methods includes those based on Green's functions (Reference 8-27). In a sense these methods correspond to closed forms of some of the MBPT equations. The underlying principle is that a complete knowledge of the two-particle Green's function will suffice to characterize all electronic states of a system, and that the one-particle Green's function suffices to determine all single-particle properties of all states. The difficulty is that the equations determining an n-particle Green's function are given in terms of the (n+1)-particle Green's function, so that its precise determination involves a complete solution for a many-electron wavefunction.

Green's function methods involve the introduction of approximations intended to break off the hierarchy of equations in a consistent manner. Different workers have introduced different decoupling schemes, and the results indicate that at least some of these can be highly accurate.

As indicated above, the principal importance of Green's function methods arises from their potential capability for handling many states at once. However, their practical limitation in this regard relates to the choice of the one-electron basis functions introduced when actual calculations are carried out. Additional limitations derive from inexperience and from a lack of the systematization from which other perturbation methods have usually benefited.

8.2.5 Semi-Empirical Methods

Since it is not always possible or practical to perform an ab initio or mathematically rigorous calculation of the electronic structure of a system containing a large number of electrons within a reasonable time, it may be both useful and desirable to resort to approximate methods, based on certain physical insights, for the sake of more rapid calculation. Three such groups of approximate methods have been studied extensively; following a brief overview of all three, two of them are discussed below in some depth. The third merely modifies the SCF methodology described above (subparagraph 8.2.3.1).

8.2.5.1 OVERVIEW OF SEMI-EMPIRICAL METHODS

One group of approaches is based upon the introduction of a local operator to circumvent the difficulties arising from the presence of the electronic energy. Because of the form of the local operators, these are referred to as $X_\alpha$ methods. The $X_\alpha$ approximation makes it unnecessary to keep track of individual electron wavefunctions in the energy expressions, and permits calculations to be reduced to sets of coupled one-electron equations. In practice, additional approximations are introduced to simplify the calculations further.
A second technique is to make the more drastic approximation that both direct and exchange contributions to the electron-electron interaction energy can be replaced by a simpler expression which depends only upon features of the charge distribution. For example, the extended Hückel procedures assume that electron-electron interactions can be characterized by net atomic charges, in place of a more detailed dependence on the charge density distribution.

These first two sets of methods, viz., Xα and Hückel, share whatever inadequacies come from approximating the detailed energy contributions, and in addition those which stem from reduction to non-specifically coupled one-electron formulations. This reduction washes out effects dependent upon spin or angular coupling of individual orbitals, and therefore makes it impossible to discuss the dependence of energy upon the spin multiplicity or angular symmetry state.

Moreover, these approaches normally share the defects of restriction to an orbital occupancy similar to that in \( \textbf{ab initio} \) RHF methods. However, if these deficiencies can be overcome, Xα or Hückel methods may facilitate the relatively rapid generation of qualitatively satisfactory potential surfaces in regions where high accuracy is not critical.

Finally, in the third set of methods calculations are carried out in an SCF formulation, but the computations are simplified with drastic integral approximations. Two levels of approximation have been identified: Either integrals are neglected altogether, as in Zero-Differential-Overlap (ZDO) methods, e.g., Complete Neglect of Differential Overlap (CNDO); or they are approximated as in the use of the Mulliken approximation. The ZDO route probably misrepresents the interatomic interactions too drastically to be a good starting point for approximate calculations, since it is the overlap which to a considerable extent is physically related to attractive or repulsive forces; neglect of this relationship cannot really be overcome by parametrization. Moreover, the situation here is far more stringent than in pi-electron systems, where internuclear separations are largely fixed by the sigma framework and where pi overlaps are relatively small anyway.

8.2.5.2 THE MULTIPLE-SCATTERING \((Xα)\) METHOD

In the Xα cluster method (Reference 8-28) as applied to molecules, the one-electron Schrödinger equation is set up within the so-called muffin-tin approximation to the true potential, spherically symmetric within spheres surrounding the several nuclei, constant in the region between adjacent spheres, and spherically symmetric outside an outer sphere which encloses the entire collection of nuclei. The resulting equations are solved by a multiple-scattering method, equivalent to the KKR method (Reference 8-29) often used for crystals. From the resulting charge densities, a total energy can be computed, using a statistical approximation for the exchange correlations. This approximation is defined apart from a multiplicative factor α, hence the designation "Xα method".

As a first step in calculating the total energy, occupation numbers \( n_i \) are required for the various spin orbitals. These numbers are not restricted to zero or unity but can take on fractional values for certain cases. A charge density for electron 1 can be written as:

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where each spin orbital is associated with a unique spin-up or spin-down function, \( \rho_+ (1) \) or \( \rho_- (1) \), respectively. The Hamiltonian is inexact, and is constructed from the following terms:

\[
\mathcal{H} = -\frac{1}{2} \sum_{i=1}^{n} v_{i}^2 - \sum_{i=1}^{n} \sum_{j=1}^{M} \frac{z_{j}}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} + \sum_{1 \leq i < j} \frac{z_{i} z_{j}}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} + \sum g_{ij},
\]

where \( g_{ij} \) is an approximate treatment of the two-electron operator. The total energy can be written in the form:

\[
E = \sum_{i} n_{i} \langle u_{i}^{+} | f_{i} | u_{i} \rangle + \frac{1}{2} \int \rho_+ (1) \left\{ \int \rho_+ (1) g_{12} \, d\tau_{2} + u_+ (1) \right\} \, d\tau_{1} \\
+ \frac{1}{2} \int \rho_- (1) \left\{ \int \rho_+ (1) g_{12} \, d\tau_{2} + u_- (1) \right\} \, d\tau_{1}.
\]

The first term is the expectation value of the one-electron operators in the Hamiltonian, namely the first three terms given in \( \mathcal{H} \) above. The second and third terms in \( E \) represent electron-electron interactions, first between electrons of the same spin and second between electrons of different spin. The first part of each integral is the Coulomb interaction \( \int \rho_+ (1) g_{12} \, d\tau_{2} \), which includes the self-interaction of an electron with itself; the second part of the integral represented by \( u_+ (1) \) removes this self-interaction term and accounts for all possible exchange terms. In the \( X_{\alpha} \) method the approximation is made that:

\[
u_{X_{\alpha}} (1) = -9a \left[ \frac{3}{4\pi} \rho_+ (1) \right]^{1/3} ;
\]

i.e., the self-interaction plus correlation energy is approximated by a term proportional to the one-third power of the density. The parameter \( \alpha \) can be shown to vary between the values of 2/3 and 1; the optimum value can be chosen such that \( E \) is made to agree with \( E_{HF} \) for the atomic case. This value is then carried over for each atom in the molecule. The one-electron energies are given by:

\[
\left[-\nu_{1}^2 + V_{c} (1) + u_{X_{\alpha}} (1) \right] u_{i}^{+} (1) = \varepsilon_{i}^{+} u_{i} (1),
\]

where \( V_{c} (1) \) represents the electrostatic energy and \( \varepsilon_{i} \) is the orbital energy.
corresponding to \( U_i \). The total energy, to first order, is then given by:

\[
E = \sum_i n_i \frac{\partial E}{\partial n_i} \sum_i n_i \epsilon_i x^\alpha_i.
\]  (8-16)

The \( X\alpha \) method has been very successful in predicting excitation energies in molecules and molecular ions but has met with only limited success in calculation of the total energy. The basic deficiency appears to lie in the muffin-tin approximation to the true potential rather than in the statistical treatment of the correlation energy. More rigorous extensions being examined include the use of simple polynomial forms for the potential between spheres. The method appears to have limited utility for constructing extensive regions of potential energy surfaces.

8.2.5.3 EXTENDED HÜCKEL METHOD

Modern extensions of the approximate calculational method originally introduced by Hückel for pi-electron systems are all based on the notion of an effective one-electron Hamiltonian which can be expressed in terms of atomic contributions. Single-center contributions on an atom are described by an alpha parameter, and two-center contributions by parameters either arbitrarily set, e.g., beta parameters, or calculated from alpha parameters and overlap integrals.

The alpha parameters are supposed to include all energetic effects, including those due to electron-electron interactions. For molecules with substantial charge inhomogeneities, best results are obtained if alpha is allowed to depend upon the net charge of the atom to which it applies. By iterative techniques, it is possible to solve the Hückel equations and adjust the alpha parameters so that the alpha values are consistent with the charge distribution.

Iterative Hückel calculations, in which overlap is included in evaluating two-center contributions, are capable of giving realistic gross distributions of net charge in many systems, and therefore give qualitatively satisfactory spectra, dipole moments, etc. Because of the arbitrariness of the energy representation, the method is somewhat unreliable in giving variations of energy with nuclear geometry. However, bond angles are frequently represented fairly well, and the method often gives good predictions of molecular shapes.

When applied to molecular collisions, the Hückel methods suffer from the limitations inherent in SCF-type wavefunctions. However, it is possible to use Hückel wavefunctions as a basis for crude approximations to CI studies, thereby using the Hückel method to obtain gross features of the charge distribution while leaving to further calculations the task of identifying effects dependent upon finer features of a good wavefunction.

8.2.6 Potential Energy Curves and Surfaces

Calculations of the dynamics of molecular collisions are ordinarily carried out with the aid of the Born-Oppenheimer separation of the electronic and nuclear

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motion. First, the electronic energy is calculated as a function of the positions of the nuclei, which are assumed to be stationary. This electronic energy, plus the electrostatic repulsion between the nuclei, defines a potential energy hypersurface which is useful for describing the kinetic motion of the nuclei. A potential energy hypersurface defined in this way is referred to as adiabatic, and is appropriate for describing the nuclear motion in the limit of low velocity. Many collisions exist for which an adiabatic potential-energy hypersurface provides an adequate description. However, most reactive collisions and many collisions which do not lead to reaction are inadequately described by an adiabatic potential energy hypersurface. These collisions are characterized by velocities of nuclear motion sufficient to affect the Born-Oppenheimer separation adversely, with the result that the overall wavefunction must be described as a superposition of terms involving different electronic energy states. Under these conditions, it will be useful to consider adiabatic potential energy hypersurfaces corresponding to all electronic states relevant to the overall wavefunction.

When the different potential energy hypersurfaces are well separated in energy, the nuclear motion can ordinarily be described in terms of motion on a single hypersurface. However, when two or more hypersurfaces are close in energy, they can be expected to mix appreciably in the overall wavefunction, and it will then be necessary not only to calculate the hypersurfaces but also to calculate the quantities needed to describe their mixing in the overall wavefunction.

The calculation of a point on a potential energy hypersurface is equivalent to calculating the energy of a diatomic or polyatomic system for a specified nuclear configuration, and therefore presents considerable practical computational difficulty. For certain problems or nuclear configurations, the maximum possible accuracy is needed and under these conditions relatively elaborate ab initio methods are indicated. Under other conditions, it may be possible to use less elaborate and more rapid computational methods, and semi-empirical or other approaches may then prove useful.

8.3 RADIATIVE PROCESSES

Given the electronic wavefunctions for a particular system, other static molecular properties can readily be calculated. These include dipole and higher multipole moments for any given electronic state, dipole and quadrupole transition probabilities between electronic states, atomic and/or molecular polarizabilities, spin densities at a nucleus, and many other observable properties of chemical interest. Atomic systems are adequately treated in standard reference works (Reference 8-30). The various molecular radiative processes which are amenable to theoretical analysis are described below, and estimates of their reliability are given.

8.3.1 Dipole-Allowed Diatomic Transition Probabilities

The electronic and vibrational-rotational wavefunctions of a pair of states can be used to calculate transition probabilities. If two molecular states are separated in energy by an amount $\Delta E = h c \nu$ (where $h = $ Planck's constant, $c = $ velocity of light, and $\nu = $ frequency in wave numbers), the semi-classical theory of radiation (References 8-31 through 8-33) yields for the probability of a spontaneous transition from an upper state $n$ to a lower state $m$:

$$A_{nm} = \frac{4 \Delta E^3_{nm}}{3 \pi^4 c^3 g_n} S_{nm}.$$  (8-17)

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Here $A_{nm}$ is the Einstein coefficient for spontaneous transition from level $n \rightarrow m$, $g_n$ is the total degeneracy factor for the upper state:

$$g_n = (2 - \delta_{0nA_n})(2S' + 1)(2J' + 1) \quad (8-18)$$

and $S_{nm}$ is the total strength of a component line in a specific state of polarization and propagated in a fixed direction. A related quantity is the mean radiative lifetime of state $n$, defined by:

$$\frac{1}{\tau_n} = \sum_{m<n} A_{nm}, \quad (8-19)$$

the summation being over all lower levels which offer allowed connections. The intensity of the emitted radiation is:

$$I_{nm} = \Delta E_{nm} N_n A_{nm} \quad (8-20)$$

where $N_n$ is the number density in the upper state $n$. This analysis assumes that all degenerate states at the same level $n$ are equally populated, which will be true for isotropic excitation. The total line strength $S_{nm}$ can be written as the square of the transition moment summed over all degenerate components of the molecular states $n$ and $m$:

$$S_{nm} = \sum_{i,j} |M_{ji}|^2, \quad (8-21)$$

where $j$ and $i$ refer to all quantum numbers associated collectively with upper and lower electronic states, respectively.

In the Born-Oppenheimer approximation, assuming the separability of electronic and nuclear motion, the wavefunction for a diatomic molecule can be written as:

$$\psi_{J\Lambda M} = \psi_e^i(R,R)\psi_v^j(R)\psi_{J\Lambda M}^i(\theta,\chi,\phi), \quad (8-22)$$

where $\psi_e^i(R,R)$ is an electronic wavefunction for state $i$ at fixed internuclear separation $R$, $\psi_v^j(R)$ is a vibrational wavefunction for level $v$ and $\psi_{J\Lambda M}^i(\theta,\chi,\phi)$ refers to the rotational state specified by electronic angular momentum $\Lambda$, total angular momentum $J$, and magnetic quantum number $M$. The representation is in a coordinate system related to a space-fixed system by the Eulerian angles $(\theta,\chi,\phi)$. The transition moment $M_{ji}$ can be written, using the wavefunction given by Equation (8-22), as:

$$M_{ji} = \int \psi_j^i \psi_v^j J' \Lambda' M' \left| \sum_{\Lambda'' M''} \psi_v^j J'' \Lambda'' M'' \right| \frac{d\tau}{d\tau} v \frac{d\tau}{d\tau} R. \quad (8-23)$$

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The subscripts e, v, and r refer to the electronic, vibrational, and rotational wavefunctions, and $\mathbf{M}^e$ and $\mathbf{M}^n$ are the electronic and nuclear electric dipole moments, respectively. Integration over the electronic wavefunction, in the Born-Oppenheimer approximation, causes the contribution of the nuclear moment $\mathbf{M}^n$ to vanish for $i \neq j$. The electronic dipole moment can be written (References 8-30, 8-32) in the form:

$$\mathbf{M}^e = - \sum_k e r'_{k} = - \left\{ \sum_k e r_{k} \right\} \Sigma(\theta, \chi, \phi),$$

(8-24)

where the primed coordinates refer to the space-fixed system, the coordinates $\Sigma_k$ refer to a molecule-fixed system, and $\Sigma(\theta, \chi, \phi)$ is a group rotation tensor whose elements are the direction cosines related to the Eulerian rotation angles $(\theta, \chi, \phi)$. Using bracket notation, Equations (8-23) and (8-24) can be combined to yield for the transition moment:

$$\mathbf{M}_{ji} = \mathbf{M}^e v' J'A'M',$$

$$= \left\langle jv' \right| - \sum_k e r_{k} \right| iv' \left. \right\rangle \cdot \left\langle J'A'M' \right| \Sigma(\theta, \chi, \phi) \left| J''A''M'' \right. \rangle. \quad (8-25)$$

An equivalent formulation, within the Born-Oppenheimer approximation, yields for the dipole velocity form of the transition moment:

$$\mathbf{m}_{ji} = \frac{1}{\Delta E_{nm}} \left\langle jv' \right| \left. \sum_k v_{k} \right| iv' \left. \right\rangle \cdot \left\langle J'A'm' \right| \Sigma(\theta, \chi, \phi) \left| J''A''m'' \right. \rangle. \quad (8-26)$$

The matrix elements $\langle J'A'm'|\Sigma(\theta, \chi, \phi)|J''A''m''\rangle$ determine the group selection rules for an allowed transition; these have been evaluated for many types of transitions (References 8-34 through 8-36). Summing Equation (8-24) over the degenerate magnetic quantum numbers $M'$ and $M''$ gives, from Equation (8-21):

$$S_{nm} = S_{mn}^{v' J'A'} = S_{mn}^{J'A'} P_{mv''},$$

(8-27)

where $S_{mn}^{J'A'}$ is the Hönöl-London factor (References 8-37, 8-38), and:

$$P_{mv''} = \sum_{i,j} \left\langle jv' \right| \left. \sum_k e r_{k} \right| iv'' \left. \right\rangle^2$$

(8-28)
is the band strength for the transition. Combining Equations (8-18), (8-20), and (8-27), the intensity of a single emitting line from upper level \( n \) is:

\[
I_{nm} = \frac{1}{3} \sum_{J''} \frac{4}{c^2} \frac{\Delta E_{nm}^J \rho_{nm}^J}{\hbar^3} \sum_{J'J''} S_{nm}^{J'J''} \left( \frac{4}{c^2} \right) \left( \frac{4}{c^2} \right) \left( \frac{4}{c^2} \right),
\]

(8-29)

where \( N_j \) is the number density in the upper rotational state \( J' \), and \( \omega_n = \left( \frac{2}{c^3} \right)^{-1} \) is the electronic degeneracy. Taking an average value of \( E_m^v J'' \), for the whole band, Equation (8-29) can be assumed to yield the total intensity in the \((v',v'')\) band:

\[
I_{mv}^{v'} = \sum_{J''} \frac{4}{3} N_{v'} \frac{4}{c^2} \frac{\Delta E_{mv}^v}{\hbar^3} \rho_{mv}^{v'},
\]

(8-30)

where \( \sum_{J''} S_{J''}^{J'J''} = (2J' + 1) \).

Comparing Equations (8-20) and (8-30) gives, for the Einstein spontaneous transition coefficient of the band \((v',v'')\):

\[
A_{mv}^{v'} = \frac{4}{3} \frac{\Delta E_{mv}^v}{\hbar c^3} \rho_{mv}^{v'},
\]

(8-32)

Similarly, the lifetime of an upper vibrational level \( v' \) of state \( n \) can be written:

\[
\frac{1}{\tau_n} = \sum_{m<n} \sum_{v''} A_{mv}^{v''},
\]

(8-33)

where the summation runs over all \( v'' \) for each lower state \( m \). Equation (8-32) can be cast in the computational form:

\[
A_{mv}^{v''}(\text{sec}^{-1}) = \left( \frac{21.41759 \times 10^9}{\omega_n} \right) \left[ \frac{\Delta E_{mv}^v (\text{a.u.})}{\rho_{mv}^{v''}(\text{a.u.})} \right]^3 \rho_{mv}^{v''}(\text{a.u.}),
\]

(8-34)
where $\Delta E_{m,v'}$, and $\rho_{m,v'}$, are in atomic units. It is also often convenient to relate the transition probability to the number of dispersion electrons needed to explain the emission strength classically. This number, the f-number or oscillator strength for emission is given by:

$$f_{nm,v',v''} = \frac{mc^2}{2e^2} \frac{A_{nv'}}{\Delta E_{mv''}}$$

(8-35)

The inverse process of absorption is related to the above development through the Einstein B coefficient. Thus for a single line in absorption, and corresponding to Equation (8-20):

$$I_{mn} = I_{mv''} = \int K(v)dv = \Delta E_{mn} N_m B_{mn}$$

(8-36)

where $K(v)$ is the absorption coefficient of a beam of photons of frequency $v$ and:

$$B_{mn} = B_{mv''} = \frac{2\pi}{3\hbar} \omega_m \omega_m (2J''+1)$$

(8-37)

is the Einstein absorption coefficient for a single line. Summing over all lines in the $(v'', v')$ band, and assuming an average band frequency, yields:

$$I_{mv''}^{nv'} = \sum_{J''} I_{mv''}^{J''v'} = \tilde{N}_{v''} \frac{2\pi}{3\hbar} \frac{2\tilde{\rho}_{mv''}^{nv'}}{\omega_m}$$

(8-38)

where $\tilde{N}_{v''} = \sum_{J''} N_{v''}$ is the total number density in the lower vibrational state $v''$. Corresponding to Equations (8-34) and (8-35), an f-number or oscillator strength for absorption can be defined as:

$$f_{mn,v'',v'} = \frac{2m}{3\hbar^2} \frac{\Delta E_{mv''}^{nv'}}{\rho_{mv''}^{nv'}}$$

(8-39)

In computational form, Equation (8-39) becomes:

$$f_{mn,v'',v'} = \frac{2}{3} \frac{\Delta E_{mv''}^{nv'}}{\omega_m} \tilde{\rho}_{mv''}^{nv'} (\text{a.u.})$$

(8-40)
where, as before, $\Delta E_{nm,v}$ and $\nu_{nm,v}$ are in atomic units. Combining Equations (8-32) and (8-35) and comparing with Equation (8-39), it may be seen that the absorption and emission f-numbers are related by:

$$f_{mn,v,v'} = \left( \frac{\nu_m}{\nu_n} \right) f_{nm,v,v'}.$$  \hspace{1cm} (8-41)

Some caution must be observed in the use of f-numbers as given by either Equation (8-35) or Equation (8-39), since both band f-numbers and system f-numbers have been defined in the literature. The confusion arises from the several possible band averaging schemes which can be identified.

An integrated and density-corrected absorption coefficient can be defined from Equation (8-38), as:

$$S_{v,v'} = \frac{1}{P_c} f_{nmv} = N_{v,v'} B_{v,v'} \left( 1 - \exp \left( -\frac{\hbar \nu_{v,v'}}{kT} \right) \right) \frac{\hbar \nu_{v,v'}}{p_c} ,$$  \hspace{1cm} (8-42)

where the exponential factor corrects for stimulated emission. Equation (8-42) can be written in terms of the absorption f-number as:

$$S_{v,v'} = \frac{\pi e^2}{m} \frac{N_{v'}}{p} \left( 1 - \exp \left( -\frac{\hbar \nu_{v,v'}}{kT} \right) \right) f_{mn,v,v'}.$$  \hspace{1cm} (8-43)

Using $\hbar c/k = 1.43880 \text{ cm}^{-1} \text{K}$, a computational formula is obtained for the integrated absorption coefficient, thus:

$$S_{v,v'} (\text{cm}^{-2} \text{ atm}^{-1}) =$$

$$\left( \frac{6.4974 \times 10^9}{T(K)} \right) \left( \frac{N_{v'}}{N_T} \right) \left( 1 - \exp \left( -1.43880 \nu_{v,v',(cm^{-1})} \right) \right) f_{mn,v,v'}.$$  \hspace{1cm} (8-44)

The total integrated absorption is found from:

$$S_{\text{TOTAL}} = \sum_{v''} \sum_{v'} S_{v'',v'},$$  \hspace{1cm} (8-45)

where only the first few fundamentals and overtones contribute to the summations, under normal conditions of temperature.

The developments presented above are rigorous for band systems where an average band frequency can be defined meaningfully. However, further approximations are
often made. For example, the electronic component of the dipole transition moment can be defined as:

\[ R_{ji}(R) = \langle j | \sum_k e c_k | 1 \rangle. \]  

(8-46)

This quantity is often a slowly varying function of \( R \) and an average value can sometimes be chosen. Equation (8-38) can then be written approximately in factored form as:

\[ \rho^{\nu \nu'}_{\mu \mu''} = q_{\nu' \nu''} | \sum_{i,j} | R_{ji}(R) |^2, \]  

(8-47)

where \( q_{\nu' \nu''} \), the square of the vibrational overlap integral, is called the Franck-Condon factor. \( R_{ji} \) is evaluated at some mean value of the internuclear separation \( R \). In addition, it is sometimes possible to account for a weak \( R \)-dependence in \( \rho^{\nu \nu'}_{\mu \mu''} \) by a Taylor-series expansion of this quantity about some reference value, \( R_{\alpha \beta} \), usually referred to the \((0,0)\) band. We have:

\[ R_{ji} = R_{ji}^{\alpha \beta} \left[ 1 + a (R - R_{\alpha \beta}) + b (R - R_{\alpha \beta})^2 + \ldots \right]. \]  

(8-48)

Substitution into Equation (8-38), followed by integration, yields:

\[ \rho^{\nu \nu'}_{\mu \mu''} = q_{\nu' \nu''} | \sum_{i,j} R_{ji}^{\alpha \beta} \left[ 1 + a (R_{\nu' \nu''} - R_{\alpha \beta}) + b (R_{\nu' \nu''} - R_{\alpha \beta})^2 + \ldots \right] |^2, \]  

(8-49)

where:

\[ (R_{\nu' \nu''} - R_{\alpha \beta}) = \frac{\langle \nu' \ R_{\nu' \nu''} - R_{\alpha \beta} \ R_{\nu''} \rangle \rangle}{\langle \nu' \ \nu'' \rangle} \]  

(8-50)

is the \( R \)-centroid for the transition and:

\[ (R_{\nu' \nu''} - R_{\alpha \beta})^2 = \frac{\langle \nu' \ (R_{\nu' \nu''} - R_{\alpha \beta})^2 \rangle \rangle}{\langle \nu' \ \nu'' \rangle} \]  

(8-51)
is the $R^2$-centroid. Note that the latter term differs, to the second order, from
the square of the $R$-centroid. An alternative procedure can be developed by eval-
uating Equation (8-46) at each $R$-centroid, $\bar{R}_{v',v''}$. Then:

$$\rho_{mv''}^{m'v'} = q_{v',v''} \sum_{i,j} | R_{ji}(\bar{R}_{v',v''}) |^2.$$  \hspace{1cm} (8-52)

Equation (8-52) assumes that the vibrational wavefunction product $\psi_{v'} \psi_{v''}$ behaves
like a delta function upon integration:

$$\psi_{v'} \psi_{v''} = \delta(R - \bar{R}_{v',v''}) \langle v' | v'' \rangle.$$  \hspace{1cm} (8-53)

The range of validity of Equation (8-52) is therefore questionable, particularly for
band systems with bad overlap conditions, such as the Schumann-Runge system of $O_2$.
The range of validity of the $R$-centroid approximation has been examined (Reference
8-39). For perturbed electronic systems, the transition dipole moment will show a
strong $R$-dependence, and $R$-centroid or other approximations will be invalid. A
direct evaluation of Equation (8-28) would therefore be required, using the fully
coupled system of electronic and vibrational wavefunctions to account properly for the
source of the band perturbations.

The final step in calculating transition probabilities is the determination of
$\rho_{ij}^i(R)$, the electronic dipole transition moment for the entire range of internuclear
separations $R$, reached in the vibrational levels to be considered. Expanding the
wavefunction in configuration interaction form:

$$\psi_{el}^i(R) = \sum_{\nu} c_{\nu}^i \psi_{\nu}(R),$$  \hspace{1cm} (8-54)

Equation (8-46) can be written as:

$$R_{ji}^i(R) = \sum_{\mu,\nu} c_{\mu}^j c_{\nu}^i \langle \psi_{\nu}^j(R) | M_{\nu}^\mu | \psi_{\nu}^i(R) \rangle.$$  \hspace{1cm} (8-55)

where $c_{\mu}^j$ and $c_{\nu}^i$ are expansion coefficients for $\psi_{\nu}^j$ and $\psi_{\nu}^i$, respectively. The matrix
elements appearing in Equation (8-55) can finally be reduced, by appropriate operator
algebra, to products of one-electron integrals over the spatial coordinates.

It is clear from Equation (8-47) that the Franck-Condon factor plays a dominant
role in the determination of intensities for a particular transition in a band system. The
experimental evidence (References 8-30, 8-33, 8-40 through 8-46) strongly suggests
that observed vibrational intensities can be correlated by a relative intensity scale
determined from the Franck-Condon factors, modified in some cases by a slowly varying
factor of the internuclear separation which is required to put the calculated
intensities on an absolute scale. This implies that an accurate solution to the
The vibrational-rotational wavefunctions \( \psi_{VJ}^i(R) \) satisfy:

\[
\frac{d^2 \psi_{VJ}^i(R)}{dR^2} + \frac{2\mu}{\hbar^2} \left( \epsilon_{VJ}^i - \left[ U^i(R) + \frac{J(J+1)B_e}{R^2} \right] \right) \psi_{VJ}^i(R) = 0 , \quad (8-56)
\]

where \( \mu \) is the reduced mass, \( U^i(R) \) is the total potential energy of interaction for the electronic state \( \psi^i \), and \( \epsilon_{VJ}^i \) are the vibrational energies belonging to this state. Studies of the sensitivity of the \( \epsilon_{VJ}^i \) to an assumed potential indicate that, with the possible exception of \( H_2 \) and \( HeH^+ \), theoretical estimates of \( U^i(R) \) which result from electronic structure calculations for a molecule are never as accurate as those obtained from spectroscopic data. The best procedure is to determine \( U^i(R) \) as a numerical function using the RKR technique (Reference 8-47) or modifications thereof (References 8-48 through 8-51).

The use of "experimental" RKR potential curves is especially critical where there is a bad Franck-Condon overlap, as in the Schumann-Runge system of \( O_2 \). Here a change in the potential of approximately one percent produces an order-of-magnitude change in predicted Franck-Condon factors. In addition, the use of potential functions derived from Hartree-Fock solutions to the electronic wavefunctions yields increasingly poor estimates of the Franck-Condon factors for higher vibrational levels, owing to the improper connections of Hartree-Fock wavefunctions in both the united and separated atom limits. The accurate numerical solution of Equation (8-56) using RKR potential functions is routine via a procedure (Reference 8-52) based on the Numerov method of integration. Convenient programs for accomplishing this type of calculation have been written (References 8-53, 8-54) for bound-bound transitions and (References 8-55, 8-56) for bound-free transitions. Using accurate RKR potentials based on spectroscopic data, Equation (8-56) can be solved routinely with errors no greater than \( \pm 1 \text{ cm}^{-1} \) in the derived spectroscopic levels.

The \textit{ab initio} calculation of electronic transition moments has not achieved accuracies of this high degree. Prior to 1968 only a few calculations of absolute oscillator strengths had been attempted. These included: The Lyman and Werner systems of \( H_2 \) by approximate LCAO wavefunctions (References 8-57, 8-58) and the Lyman system by improved CI wavefunctions (Reference 8-59); a very accurate analysis of the \( \Sigma - \Pi \) transitions in \( H_2 \) (Reference 8-60); the \( N_2^+ \) first negative system by LCAO wavefunctions (References 8-61 through 8-63); the Swan and D-standres-d'Azambuja systems of \( C_2 \) by LCAO wavefunctions within both dipole-length and dipole-velocity formulations (References 8-62, 8-63); the \( C_2 \) Swan bands using the dipole-length approximation within an SCF framework (Reference 8-64); the \( N_2 \) first and second positive systems (Reference 8-65); and the \( X^\Pi - A^2\Delta \) transition of \( CH \) using LCAO wavefunctions (References 8-66, 8-67).

Since 1968 the pace of work in this area has increased rapidly. Among the \textit{ab initio} calculations of transition moments which have been recorded during that period are studies involving: \( CH \) (Reference 8-68); \( BeH \) and \( MgH \) (References 8-69 through 8-71); a group of hydrides, e.g., \( BeH \), \( MgH \), \( OH \), \( SH \), \( SH^+ \), \( AlH^+ \), \( HPH^+ \), \( HCl^+ \) (Reference 8-72); the 13-electron system, e.g., \( N_2^+ \), \( C_2 \), \( CN \), \( CO^+ \), \( BO \), \( SF^+ \) (Reference 8-73);
and some very accurate theoretical results for band systems in H$_2$ (Reference 8-74) and NeH$^+$ (References 8-75, 8-76). Although definitive theoretical results are obtainable for two-to-four-electron molecules, calculations of electronic transition moments for heavier systems cannot be expected to have greater than order-of-magnitude accuracy. A major role of such calculations, however, lies in the possibility of their providing insight into the validity of R-centroid or other approximate analyses of band intensities.

8.3.2 Bound-Free and Free-Free Transitions

The general analysis for dipole-allowed diatomic transitions may be carried over to the case where one or both of the molecular states is either characterized by a repulsive potential curve or by the repulsive branch of a bound state where there exists a large difference in the equilibrium internuclear separations of the two states. In either case the bound state wavefunction is replaced by a continuum wavefunction $\psi^R (r, R, \epsilon_R)$ with positive energy $\epsilon_R$. The radiation intensity is now a continuous function of $\epsilon_R$ for bound-free transitions or a continuous function of $\epsilon_R - \epsilon_S$ for a system where both molecular states have a positive energy relative to their separated atomic limits.

A well known example of a bound-free transition is the Schumann-Runge continuum in O$_2$. Free-free transitions are known in N$_2$ but are difficult to analyze theoretically owing to conditionally convergent integrals which arise in evaluating the band strengths. In general, free-free transitions are relatively weak in molecular systems.

8.3.3 Forbidden Transitions

The theory of forbidden transitions in atomic and molecular has been described elsewhere (Reference 8-77). In atomic spectra, all transitions which violate the strict selection rules for electric dipole radiation are classified as forbidden transitions. These include magnetic-dipole, electric-quadrupole and two-photon transitions.

The coupling operator for magnetic dipole radiation is given by:

$$ m = -\frac{e}{2mc} (L + 2S), \quad (8-57) $$

where $L$ and $\mathbf{S}$ are the total angular momentum and spin operators, respectively. Selection rules can be derived for the various electron coupling schemes in an atomic system. The quadrupole coupling operator is a tensor of rank two, and can be written as:

$$ Q = -e \sum_{i=1}^{n} 3r'_{ij} r''_{ij} - r''_{1} (ij + jj + kk). \quad (8-58) $$

The general formulae for the transition probabilities are difficult to formulate for quadrupole radiation for an arbitrary atomic configuration. In general, the intensity of optical transitions arising from these operators is weak. Detailed calculations for a number of atoms have been reported (Reference 8-78).
For diatomic molecular systems, additional selection rules governing angular momentum changes must be considered, and other symmetry constraints may be imposed by the particular molecular configuration. Interestingly, the well-known Lyman-Birge-Hopfield bands of $N_2$ are a dipole-forbidden transition, and coupling must occur through the magnetic dipole operator. This band system is fairly strong with a lifetime of the order of $10^{-4}$ seconds. Other magnetic dipole molecular transitions are known, particularly in $O_2$, where inter-system transitions ($\Delta S \neq 0$) have been observed. Electric quadrupole transitions are rare in molecular spectra.

The general theory has been worked out (Reference 8-79) for vibronic and electronic transitions in polyatomic systems. In general, fewer symmetry constraints are found, and most transitions are allowed. Certain organic molecules exhibit forbidden transitions between states coupled by either vibronic motion or spin-orbit interaction. Observed lifetimes vary from 0.1 msec to 100 seconds.

8.3.4 Photoionization and Photodetachment

If an atomic or molecular neutral or ionic system absorbs a photon and is raised in energy to the continuum state of the electron, this process is called photoionization, or in the case of negative ions, photodetachment. The reaction can be written as:

$$A, AB + h\nu \rightarrow A^+, AB^+ + e.$$  \hspace{1cm} (8-59)

There are available in the literature, to a degree exceeding both the scope of coverage and the space limitations of this chapter, discussions outlining the basic theory of photoionization (Reference 8-80) and reviewing photoionization cross-section calculations (References 8-81, 8-82). The reader is referred to these and to an in-depth treatment of photoionization (Reference 8-83) and a review of both theoretical and experimental aspects of photodetachment (Reference 8-84) for greater detail than can be presented here. For purposes of this chapter, however, the general theoretical model of photoionization or photodetachment may be written as:

$$\sigma_{AB}(\nu) = \frac{8}{3} \frac{\pi^3 \nu^3}{C W_A} \left| \sum \psi_A \cdot \sum \psi_B \right|^2,$$  \hspace{1cm} (8-60)

where $\psi_A$ and $\psi_B$ represent the initially bound atomic or molecular state and final continuum state of the system, respectively, and where the coupling is by the dipole-moment operator. Direct evaluation of Equation (8-60) involves integration over continuum functions, and several techniques, e.g., Hartree-Fock, close-coupling, and the method of polarized orbitals, have been applied for its solution. The energy dependence of the cross-section has been formulated (Reference 8-85) for the case of photodetachment at threshold.

The photoionization cross-sections for atomic oxygen (Reference 8-86) and nitrogen (Reference 8-87) are of fundamental importance in the quantitative understanding of the ionosphere. Photoionization of ions of oxygen and nitrogen have also been examined (References 8-88, 8-89). The very few molecular systems which have been examined include the photoionization of $N_2$ (References 8-90, 8-91) and the photodetachment of $O_2^-$ and $N_2O^-$ (References 8-92, 8-93).
8.4 DISSOCIATIVE RECOMBINATION

Two-body electron-ion recombination coefficients several orders of magnitude larger than those associated with the recombination of electrons and atomic ions have been observed in recombining plasmas, both in the laboratory and in the upper atmosphere. These relatively large recombination coefficients have been explained in terms of the dissociative recombination of electrons and molecular ions (Reference 8-94), i.e.:

\[ \text{AB}^+ + \text{e} \rightarrow (\text{AB})^* \rightarrow \text{A} + \text{B}. \]  

(8-61)

Dissociative recombination appears to be the dominant recombination mechanism in neon and argon plasmas (References 8-95, 8-96). By preparing an ionized gas containing only Ar\(_2^+\) ions, for example, it was shown that the recombination rate for the atomic ions is less than 10\(^{-3}\) times the rate measured for gases containing Ar\(_2^+\) molecular ions (Reference 8-95). Additional aspects of dissociative recombination have been confirmed in studies of the emission spectra of recombining plasmas, including observations of excited rare gas atoms formed in the process. Thus when Doppler broadening of the spectral lines was examined in neon, the kinetic energy of the radiating atoms was deduced and found to be much greater than the expected thermal energy, suggesting the eventual deactivation of the excited atoms (References 8-97, 8-98). Convincing experimental evidence indicates that the recombination rates of more than 10\(^{-7}\) cm\(^3\)sec\(^{-1}\) observed in many plasmas are attributable to dissociative recombination (References 8-99, 8-100). This evidence is sufficiently strong to warrant the devotion of a great deal of attention to determination of the temperature dependence of the dissociative recombination coefficient (References 8-101 through 8-111). However, comparatively little effort has been devoted to analyses of the temperature-dependent product ratios of such reactions, especially in atmospheric gases where several dissociative channels are available, e.g., O\(_2^+\), N\(_2^+\), and N\(_3^+\).

8.4.1 Temperature Dependence of Rate Coefficients

Dissociative recombination proceeds by radiationless transitions through the initial formation of a temporary molecular complex (AB)* (Equation (8-61)), which is subsequently stabilized by dissociation. The process is most efficient if the bound-free Franck-Condon overlap of the molecular ion and the dissociating neutral molecular state is favorable. The recombination rate can be shown to vary with electron temperature as \(T_e^{-\frac{5}{2}}\) for low-energy attachment. At high electron temperatures the rate drops off as \(T_e^{-\frac{7}{2}}\), which can be shown to be a theoretical limit for simple attachment.

The theory of capture of an electron by a positive molecular ion has been developed for both direct attachment processes (References 8-94, 8-99, 8-112 through 8-114) and for several possible indirect processes, some of which involve the formation of an intermediate excited Rydberg state belonging to the molecular-ion core configuration (References 8-115, 8-116). Let \(\Psi_f(\tau, R, \xi)\) represent the continuum wavefunction describing the free electron with energy \(\xi\) plus the (n-l)-electron bound system of the molecular ion. Let \(\Psi_d(\tau, R)\) represent the wavefunction for an eigenstate of the neutral molecule which can be written, in the Born-Oppenheimer approximation,
as the product of an electronic and a nuclear wavefunction in the form:

\[ \psi_d(r, R) = \psi^e_d(r, R) \xi_d(R). \]  (8-62)

The cross-section for electron capture in dissociative recombination is determined by the asymptotic form of the nuclear wavefunction \( \xi_d(R) \). Let the incident flux of electrons per unit area be:

\[ \omega_e = \frac{k^2}{2\pi \hbar} \delta \epsilon, \]  (8-63)

where \( \delta \epsilon \) is a measure of the energy spread of the incoming beam and \( k \) is the wave number associated with the incoming electron. The outgoing flux of atoms is given by:

\[ \xi_a = \frac{\hbar k \delta \epsilon}{\mu} \left| \xi_d(R) \right|^2, \]  (8-64)

where \( \hbar k / \mu \) is the relative velocity of the separating neutral atoms. Equations (8-63) and (8-64) yield for the cross-section:

\[ \sigma(\epsilon, \Gamma) = \lim_{R \to \infty} \frac{2\pi \hbar^2 k}{\mu k^2} \left| \xi_d(R) \right|^2. \]  (8-65)

Equation (8-65) in turn must be averaged over all rotational orientations as:

\[ \sigma(\epsilon) = \frac{1}{4\pi} \int \sigma(\epsilon, \Gamma) d\Gamma. \]  (8-66)

Assuming that the total cross-section can be written as the product of a resonant capture cross-section and a survival factor, in the form:

\[ \sigma(\epsilon) = \sigma_{cap}(\epsilon) S(\epsilon), \]  (8-67)

then:

\[ \sigma_{cap}(\epsilon) = \frac{\pi \hbar^2}{2\epsilon \omega_{AB}} \left| \frac{\omega_{AB}}{\omega_{AB}^+} \right| \gamma_d(r, \epsilon) \left| V(R, \epsilon) \right| \psi^e_d(r, R) \right|^2, \]  (8-68)

where the factor \( \omega_{AB}/\omega_{AB}^+ \) is the ratio of the electronic degeneracies of the neutral and ionic states, respectively. The capture width \( \Gamma_c(R, \epsilon) \) is determined by integrating over the coordinates of the electronic wavefunctions.
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\[ \Gamma_c(R, \varepsilon) = 2\pi \left( \frac{\omega_{AB}^+}{\omega_{AB}^+} \right) \frac{1}{2\pi} \left( \frac{\omega_{AB}^+}{\omega_{AB}^+} \right) \frac{\partial}{\partial R} \left( \begin{array}{c} \xi_{AB}^+ (R) \varepsilon_{AB}^+ (R) f(\varepsilon, R) \cr V(R, \varepsilon) \psi_d(R) \xi_{AB}^+ (R) \end{array} \right) \frac{1}{2\pi \hbar} \frac{\partial}{\partial R} \left( \begin{array}{c} \xi_{AB}^+ (R) \varepsilon_{AB}^+ (R) f(\varepsilon, R) \cr V(R, \varepsilon) \psi_d(R) \xi_{AB}^+ (R) \end{array} \right) \right) \]  

Thus the capture cross-section can be written as:

\[ \sigma_{\text{cap}}(\varepsilon) = \frac{2}{\pi} \frac{\hbar^2}{2mc} \left( \frac{\omega_{AB}^+}{\omega_{AB}^+} \right) \frac{1}{2\pi} \left( \frac{\omega_{AB}^+}{\omega_{AB}^+} \right) \frac{\partial}{\partial R} \left( \begin{array}{c} \xi_{AB}^+ (R) \varepsilon_{AB}^+ (R) f(\varepsilon, R) \cr V(R, \varepsilon) \psi_d(R) \xi_{AB}^+ (R) \end{array} \right) \frac{1}{2\pi \hbar} \frac{\partial}{\partial R} \left( \begin{array}{c} \xi_{AB}^+ (R) \varepsilon_{AB}^+ (R) f(\varepsilon, R) \cr V(R, \varepsilon) \psi_d(R) \xi_{AB}^+ (R) \end{array} \right) \right) \]  

or in the equivalent:

\[ \sigma(\varepsilon) = \frac{2}{\pi} \frac{\hbar^2}{2mc} \left( \frac{\omega_{AB}^+}{\omega_{AB}^+} \right) \frac{1}{2\pi} \left( \frac{\omega_{AB}^+}{\omega_{AB}^+} \right) \frac{\partial}{\partial R} \left( \begin{array}{c} \xi_{AB}^+ (R) \varepsilon_{AB}^+ (R) f(\varepsilon, R) \cr V(R, \varepsilon) \psi_d(R) \xi_{AB}^+ (R) \end{array} \right) \frac{1}{2\pi \hbar} \frac{\partial}{\partial R} \left( \begin{array}{c} \xi_{AB}^+ (R) \varepsilon_{AB}^+ (R) f(\varepsilon, R) \cr V(R, \varepsilon) \psi_d(R) \xi_{AB}^+ (R) \end{array} \right) \right) \]  

The nuclear wavefunction \( \xi_{AB} \) is energy-normalized such that asymptotically:

\[ \xi_{AB} \sim \frac{\sqrt{2\pi}}{\hbar} \frac{1}{R} \frac{1}{\pi k} \sin(kR+\eta). \]  

Equation (8-71) can be cast into the computational form:

\[ \sigma(\varepsilon, V) \text{cm}^2/\text{sec} = \frac{1.38188 \times 10^{-6}}{\varepsilon \text{(a.u.)}} \frac{\omega_{AB}^+}{\omega_{AB}^+} \frac{1}{2\pi} \left( \frac{\omega_{AB}^+}{\omega_{AB}^+} \right) \frac{1}{2\pi \hbar} \frac{\partial}{\partial R} \left( \begin{array}{c} \xi_{AB}^+ (R) \varepsilon_{AB}^+ (R) f(\varepsilon, R) \cr V(R, \varepsilon) \psi_d(R) \xi_{AB}^+ (R) \end{array} \right) \frac{1}{2\pi \hbar} \frac{\partial}{\partial R} \left( \begin{array}{c} \xi_{AB}^+ (R) \varepsilon_{AB}^+ (R) f(\varepsilon, R) \cr V(R, \varepsilon) \psi_d(R) \xi_{AB}^+ (R) \end{array} \right) \right) \]  

where the electron energy \( \varepsilon \) and the capture width \( \Gamma_c \) are in atomic units.

Assuming a Maxwellian temperature distribution for the electrons, the rate coefficient can be written as:

\[ a_v(T_e) = \frac{2}{\sqrt{\pi}} \frac{1}{(kT_e)^{3/2}} \int_0^\infty \sigma(\varepsilon, V) x e e^{-c/kT_e} \varepsilon d\varepsilon, \]  

or in the equivalent:

\[ a_v(T_e) = \frac{2 \sqrt{2}}{\sqrt{\pi} m(kT_e)^{3/2}} \int_0^\infty \sigma(\varepsilon, V) \varepsilon e^{-c/kT_e} \varepsilon d\varepsilon. \]  

The capture width \( \Gamma_c \) can be calculated by examining the high members of the Rydberg series of neutral states which have the structure of a ground-state molecular ion coupled to an electron in a diffuse hydrogenic orbital of large effective principal quantum number. A direct calculation of the capture width requires a knowledge of the continuum wavefunction for the electron as a function of the interparticle coordinates. This approach is computationally very difficult and may be expected to lead to errors of at least the same magnitude as an extrapolation procedure of the corresponding neutral Rydberg states.

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Chapter 16 of this Handbook presents a great deal of information on experimental studies of dissociative recombination. Further experimental studies (i.e., reported since the most recent revision of Chapter 16) indicate an E^{-1} energy dependence in the recombination cross-section for all gases, at sufficiently low (\leq 60.1 \text{eV}) collisional energies (References 8-117 through 8-121). These results differ quantitatively from those reported earlier (e.g., in the most recent revision of Chapter 16) with respect to predicted recombination rates, especially for the atmospheric ions. There is also work in progress (References 8-122 through 8-124) on the recombination of clustered ions, e.g., NH₃(NH₃), which show essentially no temperature dependence of the recombination rate. The field continues to be active.

8.5 ATOMIC AND MOLECULAR SCATTERING CALCULATIONS

Atomic and molecular collision processes which may occur in the upper atmosphere include: rotational, vibrational, and electronic excitation; translational energy and momentum transfer; dissociation and recombination associated with radiative or electron emission and absorption; excitation- and charge-transfer; ionization and neutralization; and a wide variety of other physical and chemical reactions. These interactions must be studied on a microscopic level in order to calculate the macroscopic behavior of the atmosphere reliably, but in principle, they may all be understood within a single, unified quantum theory. Such a general formulation is of limited practical value, however, because the total computation required for the exact solution of any realistic problem would be overwhelming. As in some of the processes considered in preceding sections, approximations are usually necessary to obtain numerical answers to any specific problem, and again, the reliability of these answers is determined by the extent to which such approximations are justified.

Accordingly, this section presents a broad survey of commonly used approximations and a discussion of the particular types of problems to which each is applicable. Three broad classes of collision phenomena are considered in this manner. These are: (1) heavy-particle, i.e., proton or heavier, collisions which can be treated using Born-Oppenheimer potential curves; (2) electron-impact phenomena; and (3) collisions involving transitions between bound states and a continuum, e.g., Penning ionization, electron detachment, or dissociative recombination. Generally speaking, the computational techniques involved in treating each of these classes are different, and are therefore discussed separately.

8.5.1 Heavy-Particle Collisions

The importance and utility of the Born-Oppenheimer, or adiabatic, approximation was described in subsection 8.2.2, for the case of electronic structure calculations. Its significance is no less in calculating heavy-particle collisional scattering. For most thermal-energy collision phenomena, the assumption that the nuclear motion is much slower than the electronic motion is justified. Hence it is accurate to assume that the nuclear motion is governed by a potential surface (or surfaces, if different electronic states are involved) obtained by solving the electronic-structure problem for several different values of the nuclear coordinates. For heavy-particle collisions, this potential surface is generally assumed to be an exact starting point for the calculation. Where electronic excitation or electron transfer occurs, two or more potential curves or surfaces are necessarily involved, and the most important case of this type is that of a curve-crossing between at least two of the electronic curves (or surfaces). The collisional processes discussed below fall into two classes, depending on whether a single potential surface suffices to describe the situation, or whether a curve-crossing is involved.
8.5.1.1 COLLISIONS INVOLVING A SINGLE POTENTIAL SURFACE

Collisions in which electronic excitation and electron transfer are unimportant, and a single Born-Oppenheimer potential surface can be assumed to govern the heavy-particle motion, include such relatively simple cases as elastic collisions, and rotational and vibrational excitation of molecules by a projectile. More difficult, in general, are the chemically reactive collisions, the prototype of which is:

\[ A + BC \rightarrow AB + C. \]  

(8-76)

8.5.1.1.1 The Coupled Channel Expansion

Beginning with the appropriate potential surface, the equations governing nuclear motion may be rigorously formulated using the close-coupling, or coupled channel method (Reference 8-125). This method is not restricted to collisions involving only one potential surface, notwithstanding the limitation of the present discussion to such processes. An important problem of this class for which satisfactory numerical solutions exist is the rotational-vibrational excitation or deexcitation of a target by a structureless projectile. In this case, it is desired to solve the Schrödinger equation in the form:

\[ (\mathcal{H} - E) \psi (\vec{R}, \vec{r}) = 0, \]  

(8-77)

in which the Hamiltonian \( \mathcal{H} \) is given by:

\[ \mathcal{H} = \frac{\hbar^2}{2M} \nabla_{\vec{R}}^2 + \mathcal{H}_{\text{target}} (\vec{r}) + V(\vec{R}, \vec{r}), \]  

(8-78)

where the kinetic energy operator for the incident projectile is equal to \( -\frac{\hbar^2}{2M} \nabla_{\vec{R}}^2 \) and \( \mathcal{H}_{\text{target}} \) is the internal Hamiltonian for the target, the eigenfunctions and eigenvalues of which are assumed to be known:

\[ \mathcal{H}_{\text{target}} (\vec{r}) \psi_n (\vec{r}) = E_n \psi_n (\vec{r}); \]  

(8-79)

\[ \langle \psi_n | \psi_m \rangle = \delta_{nm}. \]  

(8-80)

The interaction potential coupling the projectile with the internal motion of the target is \( V(\vec{R}, \vec{r}) \). The solution to Equation (8-77) is obtained by assuming:

\[ \psi (\vec{R}, \vec{r}) = \sum_{n=1}^{\infty} F_n (\vec{R}) \psi_n (\vec{r}), \]  

(8-81)

and substituting this into Equation (8-77) to obtain an infinite set of coupled differential equations for the functions \( F_n (\vec{R}) \). Expansion (8-81) is rigorous; an approximate solution is obtained by truncating this series and solving the resulting...
finite set of coupled equations. If enough target states are included in the calculation, a convergent solution is obtained, which is generally considered to be exact.

The theoretical treatment of scattering thus outlined depends on obtaining the solution of the time-independent Schrödinger equation at a particular collision energy. Since a collision is clearly a time-dependent process, one may question whether the necessary information is contained in a purely spatial wavefunction. The answer is that the scattering information lies in the asymptotic form of the wavefunction, which is required to satisfy certain boundary conditions.

The coupled channel expansion is most practical at low energies, where the projectile may excite only a few low-lying excited states. The number of such open (i.e., energetically accessible) channels increases very rapidly with energy. When vibrational excitation is not possible, many calculations assume the target to be a rigid rotor (Reference 8-126). Even in such a case, e.g., He–H₂ at a collision energy of 1.2 eV, there are 49 open channels corresponding to the H₂ rotational levels \( j = 0, 2, \ldots, 12 \). If vibrational excitation is also considered, the rotational levels corresponding to each vibrational state must be included. Consequently, the computation involved at higher energies may not be feasible. However, some calculations have included as many as about 100 channels (Reference 8-127), but the time required to accomplish this was virtually prohibitive.

It should be emphasized that a rigorous quantum-mechanical scattering calculation yields detailed state-to-state transition amplitudes at a particular energy. Since this calculation must generally be repeated at each energy, substantial averaging may then be required in order to obtain the desired end results. Thus rate constants are obtainable as functions of temperature by averaging over the energy distribution appropriate to each temperature. Similarly, cross-sections for particular vibrational transitions must be obtained by summing over the corresponding vibrational-rotational transitions. The calculation of such averages is a relatively minor part of the total computational effort, so further approximations are generally oriented toward obtaining state-to-state transition amplitudes by simpler procedures.

8.5.1.1.2 Simplification of the Coupled Equations

The most effective way to reduce the number of coupled equations is to neglect the coupling terms and then solve for each \( F_n \) separately. This comprises the distorted wave approach (Reference 8-125), which may be justified when the coupling between the various channels is weak. Transition amplitudes are obtained by taking matrix elements of the coupling terms between \( F_{n+1} \) and \( F_n \).

Another method, which has been applied to the problem of the excitation of a rigid rotor, is the infinite-order sudden (IOS) approximation (References 8-128, 8-129). "Sudden" approximations generally involve an assumption that the collision time is short compared to the time in which the internal coordinates of the target can change significantly (Reference 8-130). Thus an important parameter is the ratio of a collision time (estimated from the speed of the projectile and the range of the potential) to a rotational or vibrational period of the target. Concerning the nomenclature of approximations in general, and of the sudden approximation in particular, it should be noted that there are often many variants of a technique, which share a family resemblance, but which may differ markedly in details. The assumptions employed by a given author must therefore always be scrutinized carefully. In the case of IOS approximations, two basic assumptions are made. One is
that the energy separations between states among which transitions are likely to occur are small compared to the collision energy. This is related to the "sudden" limit of very fast collisions. The other assumption is that the anisotropic part of the potential $V(R, r)$ is dominated by a single term.

For a rigid rotor, the latter potential depends only on the target-projectile distance $R$ and the relative orientation $\theta$. It is generally expressible as a sum:

$$V(R, r) = v_0(R) + \sum_{n=1}^{\infty} v_n(R) P_n(\cos \theta), \quad (8-82)$$

and in fact many realistic systems exist for which one $P_n$ term is dominant.

Given these assumptions, it has been shown (References 8-128, 8-129) that the coupled differential equations may be transformed into $N$ uncoupled equations, which are solved sequentially. The method is quite accurate even when the $N$ states are strongly coupled, so long as the "sudden" condition is fulfilled.

A third approach often used to reduce the number of coupled equations is the $j_z$-conserving approximation (References 8-131 through 8-133). In describing the IOS approximation, the coupled equations were expressed in terms of a "space-fixed" center-of-mass coordinate system, where the origin moves with the center of mass but the direction of the axes is fixed. Alternatively, the quantum dynamics may be formulated in a "body-fixed" coordinate system, where the origin remains at the center of mass, but the axes rotate with the rotating target. If the Coriolis terms arising from the rotating coordinate system are neglected, the equations partially decouple, and a great simplification is achieved. This approximation may be used for vibrational as well as rotational excitation; it has proved to be accurate to within 30% of the close-coupling results for many systems (References 8-134 through 8-139).

8.5.1.1.3 Perturbation Techniques

Systems in which the interaction potential is regarded as a small perturbation may be treated by several methods, including the distorted-wave approximation described above. Additional techniques are best presented in terms of the integral formulation of quantum dynamics, where the Schrödinger differential-form equation is replaced by an integral equation (References 8-125, 8-140).

Let $H_0$ represent the "unperturbed" Hamiltonian for which the solution is known, and let $V$ be a perturbation. Then:

$$(H_0 + V - E) \psi = 0, \quad (8-83)$$

may be rewritten as:

$$(E - H_0) \psi = V \psi. \quad (8-84)$$

Using the Green's function $G_0$ for the inverse operator $(E - H_0)^{-1}$, the formal solution to this equation may be written as:

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\[ \psi = \psi_0 + (E - \mathcal{H}_0)^{-1} \psi, \quad (8-85) \]

or as:
\[ \psi = \psi_0 + \int G_0 \psi \, d\tau, \quad (8-86) \]

where \( \psi_0 \) is a known solution to the homogeneous equation:
\[ (E - \mathcal{H}_0) \psi_0 = 0. \quad (8-87) \]

Equation (8-86) is the starting point for a number of related approximations by which \( T \) may be obtained. The simplest such approximation is the Born approximation (Reference 8-125), in which \( \psi \) is replaced under the integral by \( \psi_0 \):
\[ \psi \approx \psi_0 + \int G_0 \psi_0 \, d\tau. \quad (8-88) \]

Higher-order terms in this approximation are obtained by substituting this improved expression for \( \psi \) into Equation (8-86), and then iterating. A formal series is thus obtained:
\[ \psi = \psi_0 + \int G_0 \psi_0 \, d\tau + \int \int G_0 \psi_0 \psi_0 \, d\tau + \ldots. \quad (8-89) \]

In most applications only the expression (8-88) is used. For the scattering of a particle of momentum \( k \) from a potential \( V(R) \), it is easily shown that the Born amplitude for a transition to a state of momentum \( k' \) is:
\[ f(k, k') = \frac{2M}{4\pi \hbar^2} \int \exp(-i\mathbf{R} \cdot \mathbf{R}') V(R) \exp(i\mathbf{k} \cdot \mathbf{R}) \, d^3R. \quad (8-90) \]

For a radial potential \( V(R) \), \( k \) and \( k' \) have the same magnitude and differ in direction by an angle \( \theta \). Then \( f(k, k') \) gives the amplitude for elastic scattering at an angle \( \theta \). For more complicated types of interaction, Equation (8-90) must be generalized.

The value of the Born approximation is that for many potentials the scattering amplitude can be evaluated analytically. The technique works best for high-energy scattering at small angles.

A related but more sophisticated technique is the Eikonal approximation (Reference 8-141), in which a more complex expression than \( \psi_0 \) is substituted for \( \psi \) under the integral sign in Equation (8-86):
\[ \psi(R) \approx C \exp \left( \frac{iS_0(R)}{\hbar} \right). \quad (8-91) \]

An approximate solution is used for \( S_0(R) \):
\[ S_0(R) = \frac{\hbar k}{2} - \frac{1}{V} \int_{-\infty}^{\infty} V(x, y, z') \, dz'. \quad (8-92) \]
where \( v \) is the velocity at the particle, and \( R \) is considered in terms of its components \( x, y, \) and \( z \), only the last of which is varied as shown. The Eikonal approximation is equally as good as the Born in the high-energy limit, but its range of validity extends to lower energies, and it is therefore more broadly applicable. Physically, a straight-line path through the potential is assumed, but effects arising from the changing phase and velocity of the particle are included. Another, very similar approximation (Reference 8-142) produces the same result for potential scattering but differs somewhat for inelastic transitions.

8.5.1.1.4 Classical Mechanics as an Approximation to Quantum Mechanics

In many important cases none of the methods discussed above are feasible. Fortunately, in the extreme where the number of quantum states involved is hopelessly large, classical mechanics often provides a reasonable approximation (Reference 8-143). The range of application of classical mechanics may be illustrated by emphasizing those cases in which it is not applicable. But first, two important contrasts between classical and quantum scattering theory should be pointed out:

First, as was previously mentioned, quantum scattering theory may be formulated in a time-independent fashion. By contrast, a classical trajectory is explicitly time-dependent (Reference 8-144). That is, suitable initial conditions are chosen and then the classical equations of motion are integrated with time as a parameter to trace the evolution of the system. Quantum transitions are usually identified by assuming the quantum numbers to be continuous parameters and then using some sort of histogram scheme (References 8-145 through 8-147).

The second contrast is related to the information obtainable from a single computational step. On the one hand, the calculation of a given wavefunction provides detailed state-to-state transition amplitudes at a particular energy. Then a suitable average is taken over energies and the initial and final states. In the classical case on the other hand, each trajectory can be calculated very rapidly, but it contains much less information than the full wavefunction does. This typically necessitates the adoption of a Monte Carlo approach. Initial conditions are generated randomly according to a desired distribution of initial states, and the distribution of final states is statistically analyzed for a large number of trajectories. In general, the less the detailed information that is required, the fewer the trajectories that must be computed to obtain statistical reliability. A classical trajectory study thus corresponds very closely to the physical scattering system, in that the measured or calculated results are averaged over a large number of individual events. The difference lies in the use of classical dynamics. Certain situations exist, in which resort to the latter approach may overlook important quantum effects. Three of the most common examples of such a result may be cited, as follows:

(a) Quantum mechanics calculations frequently yield interference patterns of an oscillating nature (Reference 8-141); classical mechanics tends to smooth these oscillations, producing an average over the oscillating structure. Such quantal oscillations are actually observable in properly designed experiments, as in the interactions between particles in sharply defined beams (Reference 8-148), and are thus capable of providing excellent comparisons of theory and experiment. On the other hand, when a bulk experiment is performed such as to measure some gross quantity, the smoothed or averaged output of a classical calculation will tend to compare more favorably to the test results than would a quantized output.

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(b) The quantum phenomenon of leakage through a potential barrier (Reference 8-141), with a characteristic declining exponential behavior as a function of the barrier parameters, is a well-known situation where pure classical mechanics would indicate that the transition is totally forbidden. A purely classical treatment is unsatisfactory in such a case, unless the transition probability is in any event so small that it can safely be neglected within the accuracy desired.

(c) In the transition region at the edge where classical motion stops and quantal tunneling would begin, a purely classical solution very frequently shows a sharp cusp, where some property such as a transition probability may even appear to become infinite. Such classical cusps are always integrable, with only a finite area beneath them, and smoothed to a finite height by fluctuations. The corresponding quantum solution generally shows an intensity maximum near the location of the classical cusp and a smooth turnover going ultimately to the exponential decline in the classically forbidden region, as described above, while the part of the curve in the classically allowed region leads smoothly into the oscillations of any interference structure that may be present. Again, if the structure is observed in the presence of much averaging through the use of coarse methods of observation, the smoothed-over classical cusp may adequately represent the true quantum solution within the accuracy desired. Although these types of phenomena cannot be included in a "pure" classical description, they can often be correctly represented using a combination of classical and quantum treatments.

8.5.1.1.5 Semiclassical methods

Semiclassical mechanics occupies the middle ground between purely classical and purely quantum mechanics. An important contribution in this area has been made by showing how the oscillatory behavior of elastic scattering cross-sections could be understood in terms of the interference between different classical trajectories corresponding to the same scattering angle (Reference 8-149). Similar results have been obtained by considering quantum mechanics in the limit \( \hbar \to 0 \) (References 8-150 through 8-152). In general, semiclassical methods are those which combine interference effects with an otherwise predominantly classical description. However, the term is often used in a much looser sense to denote any mixture of quantum and classical methodologies.

It is characteristic of Miller's theoretical treatment (References 8-150, 8-151) that particular initial and final states may be connected by more than one classical trajectory. These states are labelled by so-called "quantum numbers" which are really continuous variables. The intent is to identify those trajectories which correspond to initial and final integer values of the quantum numbers. If more than one such trajectory is possible, the relative phase of each is determined by the classical action integral for that trajectory. In this way, the transition amplitude for a given process is expressed as a sum of probability factors, each multiplied by an appropriate phase factor. This technique is of great conceptual value, but for systems with many degrees of freedom the search for the desired trajectories has proven to be quite difficult.

8.5.1.2 CURVE CROSSINGS

In certain circumstances the interaction of electronic states can produce striking effects, even in elastic scattering. For example, interference patterns and rainbows may appear, or especially long-lived collision complexes may be produced.

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More often, the transfer of electronic energy may give rise to interesting problems involving electronic excitation, vibrational excitation, or dissociation. Such problems can usually be treated through the use of two or more Born-Oppenheimer surfaces. When this is the case, the regions of close approach or intersection of these surfaces (crossings and pseudo-crossings) are particularly important for electronic transitions. Electron transfer from one species to another also necessarily involves more than one electronic state.

With specific reference to curve crossings, it sometimes happens that two or more potential surfaces corresponding to a particular system in different electronic states are nearly degenerate for certain values of the nuclear coordinates (Reference 8-125). These "avoided crossings" (or perhaps actual crossings) of potential surfaces occur for an important class of phenomena, e.g., charge exchange, for which application of the Born-Oppenheimer approximation requires some modification. From the standpoint of quantum mechanics, such modification is achievable through the explicit inclusion as correction terms of certain of the non-adiabatic coupling terms neglected in the standard Born-Oppenheimer approximation procedure. A simpler method is based on the recognition that the system behaves as if there were a certain probability for "jumping" from one surface to the other at the point of closest approach. This probability $P$ is approximated by the well-known classical Landau-Zener relationship (References 8-125, 8-153, 8-154):

$$ P = e^{-2\gamma}, \quad (8-93) $$

where:

$$ \gamma = \left[ \frac{2\pi V_{12}^2}{d(R)(V_{11} - V_{22})} \right]^{1/2} \quad (8-94) $$

and it is assumed that the electronic wavefunctions $\phi_1(R;r_i)$ and $\phi_2(R;r_i)$ correspond to the same or nearly the same electronic energy at $R_0$ (R denotes nuclear coordinates; $r_i$ denotes all the electronic coordinates). Then $V_{11}$, $V_{12}$, and $V_{22}$ are defined as matrix elements of the Hamiltonian $\mathcal{H}$ as:

$$ V_{ij}(R) = \langle \phi_j | \mathcal{H} | \phi_i \rangle, \quad (8-95) $$

where $V_{11}$ and $V_{22}$ are the conventional Born-Oppenheimer potential surfaces corresponding to the adiabatic electronic states $\phi_1$ and $\phi_2$. $V_{12}$ is the coupling between these states and arises from terms normally neglected but which may be large when $V_{11} = V_{22}$, $R_0$ is the point of crossing, and $v$ is the velocity at the crossing point.

If the colliding species begin asymptotically on an initial surface, the crossing point will be encountered, in the classical view, twice during the collision, and two sequences of events may thus lead to a condition in which the post-collision species are on the final surface. Either the crossing may occur with a probability $P$ on the inbound part of the trajectory, and with no crossing on the outbound part, i.e., probability equal to $(1-P)$, or the crossing may be delayed until the outbound...
swing, with probability designations suitably reversed, viz., \((1-P)\) inbound and \(P\) outbound. Hence the final total probability for a change of electronic state due to the curve crossing is equal to \(2P(1-P)\).

While the Landau-Zener formulation is the most generally useful simple tool for dealing with interactions between two electronic states, sometimes more accurate methods are needed. One of the more useful of these involves the application to the Landau-Zener equation of corrections (Reference 8-155) expressed in terms of the curve-crossing parameters. The transition probability can also be presented in analytical form (Reference 8-156), but care must be taken to apply the correct formulation, of several available, in treating a given set of curve-crossing parameters. It is ordinarily very difficult to estimate the magnitude of \(V_{12}\) in the Landau-Zener equation, without resorting to a complicated \textit{ab initio} potential energy calculation. Only for the case of charge transfer have parametric forms for \(V_{12}\) been given (References 8-157, 8-158).

When two electronic states do not cross, but nevertheless interact through an off-diagonal term \(V_{12}(R)\), other useful approximations (References 8-159 through 8-161) may apply when \([V_{11}(R) - V_{22}(R)]\) is roughly constant and \(V_{12}(R)\) falls off, either inversely (to some integral power), or exponentially, in \(R\), i.e., as \(A/R^n\) or \(A \exp (-bR)\), respectively.

Velocity-dependent coupling terms may also come into play, as when angular momentum coupling at a curve crossing causes transitions between states of different angular momentum symmetry. Thus, cross-sections in one such case have been expressed successfully in terms of the crossing parameters (Reference 8-162). For endoergic reactions and threshold collision velocities, the standard Landau-Zener approach has also been found to be exceedingly effective (Reference 8-163), since the large-impact-parameter collisions are classically forbidden from the product channel.

8.5.2 Electron-Impact Phenomena

Electron-impact phenomena are distinguishable from the types of collision treated above in at least two important respects: First, potential curves are not as easily defined for the former, because the Born-Oppenheimer separation of nuclear and electronic motion is not appropriate. One must find the total electronic wavefunction for the target plus the additional electron. Second, since the incident electron is identical to the bound electrons in the target species, the possibility of exchange must be included in the wavefunction. Nevertheless, as in the systems discussed above, the general problem of electron scattering may be formulated as a coupled-channel expansion.

Beginning with a relatively simple treatment and adding refinements, the first approach to consider is that for which elastic scattering is assumed in the static-field approximation (Reference 8-125). Here, the possibility of exchange is ignored, and the incident electron is assumed to be affected by, but not to affect in turn, a potential field associated with an average charge distribution determined for the unperturbed target. This leads to a rather poor approximation at low energies, owing primarily to the lack of exchange terms in the wavefunction. In the next higher order is the static-exchange approximation (Reference 8-125), where the same static potential is used, but the required exchange terms are included in the wavefunction. Somewhat improved results are achieved thereby, but important resonance effects may still be missed.
The difficult problem of including distortion or polarization effects in the wavefunction can often be surmounted by using an extra polarization potential, determined, for example, from the polarizability of the target (Reference 8-164). Alternatively, resort may be had to R-matrix theory (References 8-165 through 8-168), where the electronic wavefunction near the target is expanded in a basis set of arbitrary anti-symmetrized \((n+1)\) electron functions. The asymptotic behavior of this expansion is examined in the limit of any electron coordinate \((r_1 \rightarrow \infty)\) and carefully matched to analytic forms from which the required scattering information is extracted.

In many important systems, rotational excitation by electron impact can be calculated from the Coulomb potential alone. For example, in a moderate energy \((\gtrsim 1 \text{ eV})\) collision between an electron and a molecule with a permanent dipole moment, the target can be treated as a rigid rotor and the dipole potential without exchange can be used. Such cases have been treated by close-coupling.

Yet another technique (Reference 8-169) is based on an application of semi-classical theory (cf. subparagraph 8.5.1.1.5). Here the dynamics is treated classically using perturbation theory, and then the S-matrix is constructed according to the procedure of References 8-150, 8-151. The advantage is that all results are obtainable analytically, enabling the effect of changing various parameters of the collision to be easily evaluated. The method yields quite good agreement with close-coupling calculations for total elastic and rotational excitation cross-sections.

### 8.5.3 Bound State \(\rightarrow\) Continuum Transitions

Many important processes may be understood in terms of a quasi-bound state weakly coupled to a background continuum of states. Such a system begins in the quasi-bound state but in the course of time decays into the continuum, usually by electron emission. For example, given an impact by metastable helium upon a target \(A\), Penning or associative ionization of \(A\) is possible whenever the electronic excitation energy of the helium \((\sim 20 \text{ eV})\) exceeds the ionization potential of the target:

\[
\text{He}^+ + A \rightarrow \text{He} + A^+ + e \quad (8-96)
\]
\[
\rightarrow \text{HeA}^+ + e. \quad (8-97)
\]

Electron ejection in this case is a purely electronic transition which can occur even in the limit of zero collision energy. This type of reaction may be treated within the general framework of the Born-Oppenheimer approximation, but certain modifications are necessary. A formal theory exists (References 8-170, 8-171) such that the quasi-bound, i.e., for finite internuclear separation, state \(\text{He}^+ A\) may be approximately decoupled from the continuum of states \(\text{HeA}^+ + e\). An effective potential curve \(V^*(R)\) is thereby defined for the interaction of \(\text{He}^+ A\). Then the transition rate \(\Gamma(R)/\hbar\) may be calculated from the coupling term, and its reciprocal \(\hbar/\Gamma(R)\) is the lifetime for molecular autoionization of \(\text{He}^+ A\) if the nuclei are imagined "frozen" at separation \(R\).

Several methods are available for the calculation of \(V^*(R)\) and \(\Gamma(R)\). The stabilization method (References 8-172 through 8-176), for example, has proven quite useful in calculating \(V^*\) for a variety of systems, but it necessitates a further, often troublesome, calculation (References 8-177, 8-178) for the determination of \(\Gamma\).
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Another approach, in the style of References 8-170, 8-171, is capable of yielding both $V^*$ and $\Gamma$ with very little additional effort (Reference 8-179). This method has been applied successfully to the system He(1s2s$^3$S)H$_2$. An empirical approach to obtaining $\Gamma$ is also available (Reference 8-180).

Given known values for $V^*$ and $\Gamma$, the system may then be treated in several ways. Conceptually, the simplest of these involves a classical trajectory approach. Here the collision of He* with the target $\text{A}$ proceeds along the potential curve $V^*$ according to classical mechanics. Physically, however, there is a probability during each time step that the system will ionize. Should this occur, it must be imagined that the remainder of the trajectory is determined by the potential surface $V^*$ for HeA*, which can be calculated by standard methods described earlier in this chapter. The important assumptions then are that the positions and momenta of the nuclei do not change during the ionization, and that the electron leaves very rapidly and has no further influence on the system. A reasonably realistic model has been developed on this basis (Reference 8-181), in which a number of classical trajectories are computed, for each of which a random number scheme is used to determine whether or not ionization occurs at any time step.

The quantum-mechanical formulation of the problem entails the use of a complex potential $(V^* - \frac{i}{2} \Gamma)$ to compute elastic and ionization cross-sections. The imaginary part of this potential causes a loss of flux corresponding to particles which disappear as a result of ionization. Following formal development of this approach (References 8-182 through 8-186), calculations have been carried out for the systems He(1s2s$^3$S)Ar (Reference 8-187) and He(1s2s$^3$S)H$_2$ (References 8-179, 8-188). While a comparison of the results of classical and quantum calculations demonstrates the general reliability of the classical approach, the role of quantum effects in this type of process is still incompletely understood. Thus no definitive conclusion may yet be stated as to a preferred line of attack.

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