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CORRECTIONS TO THE BORN-OPPENHEIMER APPROXIMATION

by

Russell T Pack

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CORRECTIONS TO THE BORN-OPPENHEIMER APPROXIMATION*

by

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ABSTRACT

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Although the Born-Oppenheimer separation is usually an excellent approximation, it need not be for either very large or very small nuclear separations. And even near the equilibrium separation, highly accurate calculations such as those of Kolos and Wolniewicz make the evaluation of corrections essential. In addition, due to rotational degeneracies, the usual single product of an electronic and a nuclear wavefunction is not always a proper zeroth-order solution of the Schrödinger equation.

In this study the center of mass and rotational motions of an arbitrary diatomic system are exactly separated off. The removal is simplified by the use of the rotation operator itself rather than the representations of the rotation group. The Breit-Pauli Hamiltonian (which allows magnetic and relativistic corrections to be included) is carried through the transformations.

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Coupled equations for internal motion are obtained which form a basic starting point for any exact treatment of diatomic molecules. Use of angular momentum raising and lowering operators allows the coupled equations to be expressed in a simpler form than they have been previously.

The equations are treated here by perturbation methods which start from the adiabatic and Born-Oppenheimer approximations. Selection rules and formulas for the corrections to long range interatomic potentials are given, and significant corrections to the centrifugal potential are found. Finally, the interaction of two hydrogen atoms is treated as an example.

Author

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I. INTRODUCTION

A. The Problem

Although the Born-Oppenheimer (BO) separation[1,2] is usually an excellent approximation, recent accurate calculations make it necessary to evaluate corrections to it. These corrections have two basic effects: they shift the intermolecular potential curve and the associated vibrational and rotational energies, and they induce transition probabilities between different electronic states and their associated potential curves.

A formalism is presented in this paper which is valid for any state of an arbitrary diatomic system and which allows corrections to the BO approximation to be treated to any desired accuracy. The results are applied to the calculation of corrections to long range interatomic potentials.

In this section we sketch the BO approximation, discuss the effects of the corrections, and outline our treatment of the problem.

B. The Born-Oppenheimer Approximation

In this paper we use the term "Born-Oppenheimer" (BO) approximation[1,2] to refer only to the simplest and most common type of separation of electronic and nuclear motion. This separation is fundamental to most molecular quantum mechanics. In the usual[3] "derivations" one first neglects the kinetic energy of the nuclei, T_R, in the total Hamiltonian, $H = T_R + H_e$, and solves the remaining

electronic equation

$$\mathcal{H}_e \Psi_i(r;R) = \mathcal{E}_i(R)\Psi_i(r,R). \tag{1-1}$$

Here r represents the electronic variables, and R represents a parametric dependence of the electronic wave functions and energy on the nuclear variables. This electronic energy, $\mathcal{E}_i(R)$, is then used as the potential energy governing the nuclear motion,

$$[T_R + \mathcal{E}_i(R)]\chi_{i\nu}^{BO}(R) = E_{i\nu}^{BO}\chi_{i\nu}^{BO}(R). \tag{1-2}$$

This form of the BO approximation usually works remarkably well and is commonly used for all molecular quantum mechanics, both bound and unbound states, for all ranges of the internuclear distances. But such uses are often not really justified. The original derivation of Born and Oppenheimer[1,2] is a rigorous perturbation treatment (in which the common BO approximation given above is only the zeroth-order approximation), but the treatment is only valid for bound state molecules in non-degenerate electronic states with the nuclei executing small oscillations about their equilibrium positions. For other states one needs to know the errors introduced by the approximation.

Corrections to the BO approximation are of two types; 1) <u>adiabatic</u> corrections arising from the action of T_R on Ψ_i, and 2) <u>nonadiabatic</u> corrections involving electronic states other

than ψ_i . They arise from the inability of one electronic function to adequately describe the system. We now discuss these two types of corrections and their effects.

C. The Adiabatic Approximation

The common BO approximation given above assumes that the solution of the complete Schrödinger equation,

$$\mathcal{H}\,\Psi_{i\nu} = E_{i\nu}\,\Psi_{i\nu}, \tag{1-3}$$

is adequately given by the product $\chi_{i\nu}\psi_i$. However, if this product is substituted into (1-3), multiplied by ψ_i^* and integrated over electronic coordinates, there are some correction terms $\mathcal{E}_{i\mu}(R)$, arising from the action of T_R on ψ_i , which add to $\mathcal{E}_i(R)$. If they are retained, the equation for nuclear motion is altered slightly,

$$\left[T_R + \mathcal{E}_i(R) + \mathcal{E}_{i\mu}(R) - E_{i\nu}^{ad}\right]\chi_{i\nu}^{ad}(R) = 0. \tag{1-4}$$

This approximation is called by Born[2] the <u>adiabatic</u> approximation, so that the $\mathcal{E}_{i\mu}(R)$ are thus the adiabatic corrections to the intermolecular potential.

The sign of $\mathcal{E}_{i\mu}(R)$ deserves mention. Epstein[4] has shown that the BO approximation, if solved accurately enough, gives a

lower bound to the total energy. But in the adiabatic approximation, $\chi_{i\nu}^{ad}\psi_i$ is treated simply as an approximate solution and must provide an upper bound to the total energy by the variation principle. Hence, retention of $\mathcal{E}_{i\mu}(R)$ raises the total energy calculated. However, rather than calculating the total energy in (1-4) one usually solves it with the zero point of energy chosen so that the effective potential $\mathcal{E}_i(R) + \mathcal{E}_{i\mu}(R) \longrightarrow 0$ as $R \rightarrow \infty$. With the corrections to the separated atoms thus subtracted off, $\mathcal{E}_{i\mu}(R)$ may either raise or lower the BO potential, depending on the value of R and the system being considered.

The $\mathcal{E}_{i\mu}(R)$ must be retained in order to obtain accurate values of molecular rotational energies[1,2], isotope shifts and observed constants in molecular spectra[5,6] and effective intermolecular potentials. Considerable work on these corrections has been done recently in attempts to produce perfect agreement between calculated and spectroscopic potential energy curves, mostly on the hydrogen molecule-ion[7-10], the hydrogen molecule[10-15] and their mesonic and isotopic analogs. Most of the work done has been on bound state molecules in low vibrational states. The corrections found have been very small, as expected, since this is precisely the case in which Born and Oppenheimer[1,2] proved their approximation is most accurate. Consider, for example, the extremely accurate calculations of Kolos and Wolniewicz[11] on the ground state of H_2. The adiabatic corrections to the total electronic energy are 114.6 cm^{-1} at the equilibrium

internuclear distance, but the corrections to the dissociation energy are much smaller, due to the fact that the corrections for the separated atoms are subtracted off. Kolos and Wolniewicz's most recent values and the experimental values are as follows[11]:

	D_o (cm^{-1})	$D_e - D_o$ (cm^{-1})
Experimental	36113.6 ± 0.3	2179.2 ± 0.2
Born-Oppenheimer	36112.2	2180.5
Adiabatic	36118.0	2179.6

Here D_o is the dissociation energy, D_e the binding energy, and $D_e - D_o$ the zero point energy. The agreement here is excellent, but the fact that the adiabatic dissociation energy is <u>larger</u> than the experimental value is producing considerable discussion[6,11,15]. Kolos and Wolniewicz[16] have also made a completely nonadiabatic calculation on H_2 which is discussed later. Their result[11] was $D_o = 36114.7\ cm^{-1}$, but the calculation was not carried to the same accuracy as the adiabatic calculations. More accurate nonadiabatic calculations are expected to give a D_o within $1\ cm^{-1}$ of but <u>larger</u> than the <u>adiabatic</u> result[11,14].

One expects the corrections to be more important in either the long or short range parts of the potential. Adiabatic corrections extending into the short range (repulsive) part of the potential have been calculated for a few states of the hydrogen molecule-ion[8-10],

the hydrogen molecule[10,11,14] and their analogs. For the potentials treated which have an attractive well, the short range corrections are repulsive but appear to grow less important as the internuclear distance decreases. The short range corrections to purely repulsive potentials grow large as does the potential, but whether or not they become relatively more important as R decreases is not clear from the work that has been done. Calculation of accurate short range potentials is difficult and present calculated potentials still lie above the experimentally inferred potential. From the work that has been done, it appears that calculation of the adiabatic corrections would probably usually raise the short range potential and result in poorer agreement with experiment. However, Thorson[17,18] has calculated nonadiabatic corrections to H^+ - H and He - He short range potentials and shown that they lower the short range potential considerably. It is clear that more work needs to be done on short range potentials, but in this study they not treated explicitly. However, our methods can certainly be used and in Appendices A and B, we present the Hamiltonian for internal motion in coordinates convenient for short range work.

Adiabatic corrections to the long-range (van der Waals) intermolecular potentials have been calculated by Wu and Bhatia[19] and by Dalgarno and McCarroll[10]. Wu and Bhatia's results are in error, and neither treatment is easily generalized either to higher accuracy or to other systems besides H_2^+ and H_2 to which they were applied. As a result, these calculations do not show clearly what

the size, nature, and importance of the corrections to long range BO potentials are. Therefore, in this work we consider in detail the corrections to the long range potentials between arbitrary pairs of atoms. We treat a few systems explicitly and give selection rules and formulas which allow the corrections for an arbitrary diatomic system to be readily evaluated.

Another development which adds impetus to the calculation of corrections to the long range potential is the recent calculation of the relativistic and magnetic corrections to the long range potential[20,21]. As a result of these calculations, some interesting new terms in the potential have been discovered. These relativistic terms are of $\mathcal{O}(\alpha^2) \approx \mathcal{O}(5 \times 10^{-5})$, where $\alpha = 1/137$ is the fine structure constant. As we show in this work, the adiabatic corrections due to nuclear motion are of $\mathcal{O}(\mu^{-1})$, where for a diatomic system, μ is the reduced mass of the nuclei in atomic units. For possible diatomic systems, $(10^{-5} \leq \mu^{-1} \leq 10^{-3})$; hence, the relativistic and adiabatic corrections are of very much the same order of magnitude, and it hardly seems consistent to calculate the one without accounting for the other. Thus, one of our reasons for calculating corrections to the long range potential is to see what relationship they have to the relativistic corrections already calculated.

D. Nonadiabatic Corrections

To go beyond the adiabatic approximation, one must allow for the effects of other electronic states. One way to do so has been suggested by Born[22,23]. He expands the exact solution in the complete set of electronic wave functions,

$$\Psi_j = \sum_i \chi_{ji}(R)\psi_i(r,R). \tag{1-5}$$

The nuclear wave functions, χ_{ji}, are in principle determined by solving the infinite set of coupled equations that results when Eq. (1-5) is substituted into the Schrödinger equation and the electronic coordinates integrated over. Matrix elements coupling different electronic states produce radiationless transitions between different adiabatic potential curves. These transitions are responsible for or important in such observable effects as rotational distortion of spin multiplets and Λ-type doubling[24], the Jahn-Teller and Renner effects[25], molecular autoionization[26], inelastic collisions[27], certain types of predissociation[28], certain perturbations in molecular spectra[28], and natural line widths[28] of potential energy curves. The transition probability, which is highest near the pseudo-crossing points of the adiabatic potentials, has been studied by a number of authors[29-31].

E. The Concept of a Potential

When one attempts to treat nonadiabatic corrections to the BO approximation, problems with the concept of an intermolecular potential energy curve arise. In the BO and adiabatic approximations the nuclei move in a single, well-defined potential. And as long as the coupling between different electronic states is small enough to be treated by perturbation theory, the single potential is still retained. The effects of the transitions are contained in the second order energy, and their influence on the potential can be estimated[6,14,17]. We discuss this in detail in Section IV. However, when the total energy lies in a region where two or more potential energy curves whose states are connected by T_R are close together, one has a problem in degenerate perturbation theory. The transition probabilities and second order energy become large, so that the line width of the potentials becomes large and the potentials fuzzy. The solution must be taken as a linear combination of the states involved, and the concept of a potential in which the nuclei move loses its meaning. However, it may still be a useful mathematical artifact to think of the set of coupled equations as a set of equations involving a family of potentials[32].

Another problem which arises is that the electronic equation (1-1) is always solved in coordinates fixed on the nuclei, while the nuclear coordinates are relative to space-fixed axes. In the BO approximation the effect is neglected, but in higher approximations one must rotate axes and transform properly, as

Kronig did[33,34] or one is led to wrong results. The other alternative would be to solve the electronic equation in space-fixed coordinates. However, this is so difficult as to be utterly impractical, except for high energy scattering in which the Born approximation is applicable[17], and if solved accurately would lead to a very complicated angle-dependent potential.

The rotation of the system produces yet another problem. The component, Ω , of angular momentum along the molecular axis of a diatomic system is only a good quantum number in lower approximations. Higher approximations couple states of different Ω . One example of this is the Λ -type doubling[24] of molecular spectra. In it the states of $+\Omega$ and $-\Omega$ (which in lower orders are degenerate) are coupled to form states $|\Omega|^{\pm}$ which are symmetric or antisymmetric to reflection through a plane containing the nuclei and which differ slightly in energy. The effect is basically similar to the Jahn-Teller and Renner effects[25] which occur in polyatomic spectra but is much smaller. Coupling between the Ω and $\Omega \pm 1$ states also occurs, and we discuss it in detail in Section III. Bates[35] has emphasized repeatedly that in scattering problems this $\Omega \pm 1$ coupling is important and cannot be neglected. Curtiss and co-workers[32,36] have considered this coupling, and Bates and Williams[37] have carried out some detailed calculations on H^+ - H collisions which show strong coupling. The $\Omega \pm 1$ coupling in collisions arises physically from the fact that the directions of the body-fixed axes change (often rapidly) during the course of a collision, as pointed

out by Hornig and Hirschfelder[38]. The change in the proper axes of quantization during the course of a collision has also been discussed in detail by Thorson[17]. These difficulties with the body-fixed axes and the resulting Ω coupling lead us to the conclusion that the proper zeroth order solutions (which transform as the irreducible representations of the group of the complete Hamiltonian) cannot be written in general as the product of a single nuclear and a single electronic wave function. Rather, as is well-known in degenerate perturbation theory, they must be linear combinations of the states involved. We handle this problem by exactly removing rotational motion in Section II.

F. Outline of this Study

Throughout this study we use the Breit-Pauli Hamiltonian[20] for an arbitrary diatomic system. This Hamiltonian gives the relativistic and magnetic corrections to the Schrödinger equation accurate through $\mathcal{O}(\alpha^2) \approx \mathcal{O}(5 \times 10^{-5})$. However, it omits higher order terms in the fine structure constant α such as the Lamb shift[39] of $\mathcal{O}(\alpha^3 \ln \alpha) \approx \mathcal{O}(2 \times 10^{-6})$. One is thus only justified in calculating corrections to $\mathcal{O}(\alpha^2)$, and this is done by first order perturbation theory. Hence, we consistently omit terms of higher order, as for example, the terms explicitly containing nuclear spin, which are of $\mathcal{O}(\alpha^2/\mu) \lesssim \mathcal{O}(5 \times 10^{-8})$ where μ is the reduced mass of the nuclei. We show how to calculate some terms of $\mathcal{O}(\mu^{-2}) \lesssim \mathcal{O}(10^{-6})$, but one is not in

general justified in including them due to the accuracy of the Hamiltonian.

In addition, when the Breit-Pauli Hamiltonian is used to calculate long-range interatomic potentials, it can only be used for internuclear separations $R < \lambda\!\!\!^{-}$, where $\lambda\!\!\!^{-}$ is the reduced wavelength characteristic of allowed transitions in one of the atoms. For a typical case (H atoms) $\lambda\!\!\!^{-} \sim 350$ a.u. For $R \geq \lambda\!\!\!^{-}$, there are strong retardation effects, and quantum electrodynamics must be used to calculate the interaction[21].

In Section II the center of mass motion is first separated off and the Breit-Pauli Hamiltonian is cast into relative coordinates convenient for calculations at large internuclear distances. The importance of removing the center of mass motion and of the choice of relative coordinates has been discussed by Jepsen and Hirschfelder[34,40] and by Fröman[13]. We next remove (exactly) two coordinates[41] describing the overall rotation of the system. The method used is based on a series of papers[42-46] which we call the HWC series, begun by Hirschfelder and Wigner and continued by Curtiss and co-workers, in which the rotation is removed using group theoretical methods. Group theory has also been used by a number of other authors[47-48] to remove rotational coordinates. The methods used by most are particularly suited to the treatment of polyatomic systems, and owing to the difficulty of choosing relative coordinates of any general usefulness in polyatomic systems, this study is kept limited to diatomics. While our method is based on the HWC series[42-46], we

are able, using the operators themselves, to derive the equations for internal motion much more simply.

After removing rotation, one is left with a set of $2J + 1$ coupled equations involving the different components Ω, of the total angular momentum J, along the molecular axis. The equations are expressed in a particularly simple way and the coupling arises from physically meaningful operators. These equations are exact, are written entirely in body-fixed coordinates and form a good starting point for almost any calculation on a diatomic system. Symmetry conditions on the solutions are derived and are easily satisfied.

The Ω coupling is discussed. It is found that energy restrictions usually limit the number of equations for which the coupling is not negligible to just a few, regardless of the value of J. And in the case $J = 0$ there is, of course, only one equation. The $J = 0$ internal equation of motion has been solved by direct variational methods, without any separation of nuclear and electronic motion, for H_2^+, H_2 and their analogs[16,49]. The results have been excellent, and the method looks very promising, but it is presently limited to very small systems. While these previous nonadiabatic treatments of diatomic molecules only include detailed work for the $J = 0$ case, some include coupled equations for $J \neq 0$ equivalent to those obtained herein. However, the coupled equations are expressed in a much more complicated form than those here.

After discussing the coupling, we then treat the internal equations of motion by perturbation theory. The adiabatic approximation gives a proper zeroth-order solution to these internal equations unless the total energy lies in the neighborhood of a psuedo-crossing point of the adiabatic potentials. In this work a particularly natural adiabatic approximation is used which gives the energy fully accurate through $\mathcal{O}(\mu^{-1})$. In addition a method, which was developed by Herman and Asgharian[6] for Σ state diatomics, is extended to other diatomic states, enabling one to calculate approximate nonadiabatic corrections to the potential itself.

The formalism developed is then applied to the calculation of long range interatomic potentials. The electronic equation is solved for large R by an R^{-1} perturbation series expansion and selection rules on the corrections are obtained for an arbitrary pair of atoms. The R^{-1} dependence of the effective potential is shown clearly. The meaning of this long range effective potential is discussed, and particular emphasis is put on the fact that the corrections all arise from the radial and centrifugal motion of the nuclei and must not be interpreted as part of the static interatomic potential[10]. Most of the adiabatic corrections obtained are small. Special systems in which they could be important are suggested. The most important corrections are those to the centrifugal potential, some of which were found by Dalgarno and McCarroll[10]. Finally, to illustrate the method and the results, the corrections to the long range potentials of two 1s-hydrogen atoms are presented and discussed.

II. TRANSFORMATION OF THE BREIT-PAULI HAMILTONIAN

In this section the center of mass and rotational motion is removed and the internal equations of motion relative to body-fixed axes are derived.

A. Removal of Center of Mass Motion. Relative Coordinates.

Let us consider a system consisting of N electrons and two nuclei (a and b) in the absence of any external field. Then the center of mass motion is separable. In this subsection we present the Hamiltonian for relative motion of the particles. The particular system of relative coordinates chosen is the "separated atom" system in which N_a electrons are arbitrarily centered on nucleus a and $N-N_a$ on nucleus b. This system is chosen because it is convenient for our treatment of long range potentials later in this paper. It has the disadvantage that it contains awkward nuclear-electronic cross derivatives. For this reason the relative Hamiltonian is presented in Appendix A in two other coordinate systems which avoid the cross-derivatives[40]. One of those two systems is suited to short range potentials; the other may be physically significant at long range.

The "separated atom" system of center of mass and relative coordinates[50] is defined by (see Figure 1):

$$\underset{\sim}{C} = \frac{1}{M}\left(m_a \underset{\sim}{r}_a + m_b \underset{\sim}{r}_b + \sum_{i=1}^{N} \underset{\sim}{r}_i\right),$$

$$\underset{\sim}{R} = \underset{\sim}{r}_b - \underset{\sim}{r}_a, \tag{2-1}$$

$$\underset{\sim}{r}_{ia} = \underset{\sim}{r}_i - \underset{\sim}{r}_a, \quad 1 \leq i \leq N_a, \quad \text{and}$$

$$\underset{\sim}{r}_{jb} = \underset{\sim}{r}_j - \underset{\sim}{r}_b, \quad N_a + 1 \leq j \leq N.$$

Here the $\underset{\sim}{r}_q$, where q = a,b,1...N, are the laboratory-fixed coordinate vectors of the particles. Throughout this work we use Hartree atomic units (mass in units of the electron mass, charge in units of the proton charge, e, length in Bohr radii, a_o, energy in units of e^2/a_o, and $\hbar = 1$). Then, the total mass of the system is

$$M = m_a + m_b + N. \tag{2-2}$$

Thus, $\underset{\sim}{C}$ is the center of mass of the system and $\underset{\sim}{R}$ is the internuclear vector. The set (2-1) is independent and spans the configuration space of the system.

The transformation of the Breit-Pauli Hamiltonian into these coordinates and the separation of the center of mass motion is carried out in Appendix A. The resulting relative Hamiltonian[51] is:

$$\mathcal{H} = \frac{1}{2\mu}\underset{\sim}{p}_R^2 + \frac{1}{\mu}\underset{\sim}{P}\cdot\underset{\sim}{p}_R + \mathcal{H}_e, \tag{2-3}$$

where $\mu = m_a m_b/(m_a + m_b)$ is the reduced mass of the nuclei; $\mathcal{P}_q = \frac{1}{i}\nabla_q$, where q is any member of the set (2-1); and

$$\underset{\sim}{P} = \frac{\mu}{m_a}\underset{\sim}{P}_a - \frac{\mu}{m_b}\underset{\sim}{P}_b . \tag{2-4}$$

Here

$$\underset{\sim}{P}_a = \sum_{i=1}^{N_a} \mathcal{P}_{ia} , \quad \text{and}$$
$$\underset{\sim}{P}_b = \sum_{j=N_a+1}^{N} \mathcal{P}_{jb} . \tag{2-5}$$

The electronic Hamiltonian, H_e, contains all terms not explicitly depending on the motion of the nuclei. It is

$$\mathcal{H}_e = T_e + V + \frac{1}{2m_a}\underset{\sim}{P}_a^2 + \frac{1}{2m_b}\underset{\sim}{P}_b^2 + \alpha^2 \mathcal{H}_\alpha \tag{2-6}$$

Here T_e is the electronic kinetic energy,

$$T_e = \frac{1}{2}\sum_{i=1}^{N_a} \mathcal{P}_{ia}^2 + \frac{1}{2}\sum_{j=N_a+1}^{N} \mathcal{P}_{jb}^2 \tag{2-7}$$

V is just the total Coulombic potential energy, naturally expressed in the relative coordinates. α is the fine structure constant ($\alpha = e^2/\hbar c = 1/137$), and H_α contains the relativistic and magnetic corrections. The transformation of H_α to these coordinates is discussed in Appendix A. Since we do not use H_α

explicitly in this work, we do not write it out but carry it along for generality. The properties which we use in our transformation can easily be checked by the interested reader by simply referring to the explicit forms given by Meath and Hirschfelder[20], for example. H_α is grouped with H_e at this point simply for convenience.

The $\underset{\sim}{P}_a^2$ and $\underset{\sim}{P}_b^2$ terms are the mass polarization[52] operators of the separated atoms. Including them in the electronic Hamiltonian insures dissociation to the right limit as pointed out by Fröman[13].

B. Symmetry. Removal of Rotation

In this subsection a simple plausibility argument is used to separate off the rotational motion of the system, and the Schrödinger equation and constants of the motion are expressed in separated atom coordinates relative to body-fixed axes. In Appendix B the transformation is carried out in more detail using the representations of the rotation group and the methods of the HWC series[42-46]. The results using the simpler center of mass of the nuclei coordinates are also presented in Appendix B.

1. Notation

Before making the transformation we discuss the notation used. The space-fixed axes and coordinates are denoted by primes in this section, and the body-fixed quantities are left plain. When operators are written in terms that apply only to the space-fixed coordinates, they will also be denoted by primes . Thus, we let

$$\mathbf{x}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \tag{2-8}$$

symbolize any or all of the separated atom electronic coordinates relative to the space-fixed (primed) axes and let $\mathbf{X}'$ similarly symbolize the coordinates of $\underset{\sim}{R}$. We then write the wave function in the space-fixed system as

$$\Psi = \Psi(\mathbf{x}', \mathbf{X}')$$

suppressing the spin variables and quantum numbers unless they are explicitly needed. The action of the operators on $\mathbf{x}'$ and $\mathbf{X}'$ will be considered explicitly. From that action, their effects on the components of the linear momenta;

$$\mathbf{p} = \frac{1}{i} \underset{\sim}{\nabla}, \tag{2-9}$$

and angular momenta,

$$\underset{\sim}{l} = \underset{\sim}{r} \times \mathbf{p}, \tag{2-10}$$

are easily obtained. Spin angular momenta must also transform as Eq. (2-10).

The rotation operator is denoted by $\mathcal{R}$, and $\mathbb{R}$, with elements $\mathbb{R}_{ij}$, is the matrix of Euler angles which represents the action of $\mathcal{R}$ on the coordinates. (But $\underset{\sim}{R}$ is the internuclear

vector and $R = |\underset{\sim}{R}|$ its magnitude.)

The Breit-Pauli Hamiltonian, H, does not contain the nuclear spins; hence, the total angular momentum of the system, $\underset{\sim}{J}$, is

$$\underset{\sim}{J} = \underset{\sim}{L} + \underset{\sim}{j} . \tag{2-11}$$

Here $\underset{\sim}{L}$ is the orbital angular momentum of the nuclei, $\underset{\sim}{L} = \underset{\sim}{R} \times \underset{\sim}{p}_R$ and $\underset{\sim}{j}$ is the total electronic angular momentum. $\underset{\sim}{j}$ is given by

$$\underset{\sim}{j} = \underset{\sim}{\mathcal{L}} + \underset{\sim}{S} , \tag{2-12}$$

where $\underset{\sim}{\mathcal{L}}$ and $\underset{\sim}{S}$ are the electronic orbital and spin angular momenta, respectively. The total orbital angular momentum is denoted by $\underset{\sim}{K}$ and is

$$\underset{\sim}{K} = \underset{\sim}{L} + \underset{\sim}{\mathcal{L}} . \tag{2-13}$$

2. <u>Constants of the Motion</u>

In the absence of external fields the Hamiltonian is invariant under all rotations, and the system possesses the following set of commuting observables (constants of the motion)[53],

$\mathcal{H}$ -- the Hamiltonian,

$\underset{\sim}{J}^2$ -- the square of the total angular momentum,

$J_{z'}$ -- the z' component of angular momentum,

$\mathcal{I}$ -- inversion of the coordinate axes, (2-14)

$\mathcal{P}_{ij}$ -- exchange of any electrons i and j , and

$\bar{\mathcal{P}}_{ab}$ -- exchange of the nuclei a and b .

The bar ($\bar{\ }$) above $\mathcal{P}_{ab}$ implies that it is only included in the set if the nuclei are identical, $m_a = m_b$ and $Z_a = Z_b$.

Each of the operators in (2-14) is quantized. Their eigenvalue equations are

$$\mathcal{H}\Psi = E_i \Psi, \tag{2-15}$$

$$\underset{\sim}{J}^2 \Psi = J(J+1)\Psi, \tag{2-16}$$

$$J_{z'} \Psi(x', \chi') = M \Psi(x', \chi'), \tag{2-17}$$

$$\mathcal{I}\Psi = (-1)^{P}\Psi, \tag{2-18}$$

$$\mathcal{P}_{ij}\Psi = -\Psi, \text{ and} \tag{2-19}$$

$$\bar{\mathcal{P}}_{ab}\Psi = (-1)^{P_{ab}}\Psi. \tag{2-20}$$

Eq. (2-19) just expresses the Pauli principle, but the parity under exchange of identical nuclei, $\mathcal{P}_{ab}$, may be even or odd depending on the nuclear spin functions used[54] and the number of nucleons per nucleus. These equations make it clear that the quantum numbers on which Ψ depends are

$$\Psi = \Psi(J, M, \mathcal{P}, i, \bar{\mathcal{P}}_{ab}). \tag{2-21}$$

The bar again implies that $\mathcal{P}_{ab}$ appears only if the nuclei are identical.

Two other operators that are of interest, besides the set (2-14), are the other components $J_{x'}$ and $J_{y'}$ of $\underset{\sim}{J}$. They do not commute with $J_{z'}$ and, as a result, are not quantized. However, space is isotropic, and they commute with all the other operators of (2-14). Hence, the raising and lowering operators

$$J_{\pm'} = J_{x'} \pm i J_{y'} , \tag{2-22}$$

have their familiar property[55],

$$J_{\pm'} \Psi(J, M, \mathcal{P}, i, \bar{\mathcal{P}}_{ab}) = \lambda_{\pm}(J, M)\, \Psi(J, M \pm 1, \mathcal{P}, i, \bar{\mathcal{P}}_{ab}), \tag{2-23}$$

where the constants $\lambda_{\pm}$ are given by

$$\lambda_{\pm}(J, M) = [J(J+1) - M(M \pm 1)]^{1/2} = [(J \pm M + 1)(J \mp M)]^{1/2}. \tag{2-24}$$

The transformation to body-fixed axes must begin from the coordinate representations of the operators in the space-fixed system. Let us now state the actions of each of the operators on the space-fixed coordinates. Only the action on the configuration space is given explicitly, but $\mathcal{H}$ depends on electron spin through $\mathcal{H}_\alpha$, and unless $\mathcal{H}_\alpha$ is negligible, the operators in (2-14) will only be constants of the motion if they act on the spin space as well as the configuration space and treat spins as angular momenta.

The representation of $\mathcal{H}$ relative to space-fixed axes is given by Eq. (2-3). Coordinate representations of $\underset{\sim}{J}^2$ and $J_{z'}$ are easily obtained from Appendix A. However, all the information needed about $\underset{\sim}{J}^2$ and $J_{z'}$ is contained in Eq. (2-16, 17 and 23), and it is convenient to regard the components of the total angular momentum solely as formal operators. The actions of the other three constants of the motion on the space-fixed separated atom coordinates are derived in Appendix A and are

$$\mathcal{I}'\Psi(\mathbf{x}',\mathbf{X}') = \Psi(-\mathbf{x}',-\mathbf{X}'), \tag{2-25}$$

$$\mathcal{P}'_{ij}\Psi(\mathbf{x}'_{ic},\mathbf{x}'_{jd},\mathbf{X}') = \Psi(\mathbf{x}'_{jc},\mathbf{x}'_{id},\mathbf{X}'), \tag{2-26}$$

where $i \neq j,\ 1 \leq i,j \leq N,$ and $a \leq c, d \leq b.$

$$\bar{\mathcal{P}}'_{ab}\,\Psi(\mathbf{x}'_{ia},\mathbf{x}'_{jb},\mathbf{X}') = \Psi(\mathbf{x}'_{ib},\mathbf{x}'_{ja},-\mathbf{X}'), \tag{2-27}$$

where $1 \leq i \leq N_a$ and $N_a+1 \leq j \leq N$. However, instead of using $\bar{\mathcal{P}}_{ab}$ as a member of the set of observables, it is convenient to use the operator $\bar{\mathcal{J}}_e \equiv \mathcal{I}\bar{\mathcal{P}}_{ab}$, which does not affect $\mathcal{X}'$. One sees that

$$\bar{\mathcal{J}}_e \Psi = (-1)^{p_e} \Psi, \tag{2-28}$$

and

$$\bar{\mathcal{J}}_e' \Psi(\mathcal{X}_{ia}', \mathcal{X}_{jb}', \mathcal{X}') = \Psi(-\mathcal{X}_{ib}', -\mathcal{X}_{ja}', \mathcal{X}'), \tag{2-29}$$

where $p_e = p + p_{ab}$. $\bar{\mathcal{J}}_e$ clearly only applies if the nuclei are identical, and it commutes with all the members of set (2-14). Since $\bar{\mathcal{P}}_{ab} = \mathcal{I}\bar{\mathcal{J}}_e$, the nuclear parity remains well defined. We choose $\bar{\mathcal{J}}_e$ to be a member of the set (2-14) in place of $\bar{\mathcal{P}}_{ab}$. It inverts the electronic coordinates through the geometrical center of the nuclei and gives rise to the familiar gerade (g) and ungerade (u) states of homonuclear diatomic molecules.

3. <u>Rotations</u>. <u>The Body-fixed Axes</u>.

The transformation to body-fixed coordinates is made by applying a rotation to Eq. (2-15 to 20) and Eq. (2-25 to 29). In the conventions used here the rotation operator $\mathcal{R}$ of an arbitrary rotation can be written in the form[56]

$$\mathcal{R} = e^{i\gamma J_{z'}} e^{i\beta J_{y'}} e^{i\alpha J_{z'}} , \tag{2-30}$$

where α , β , and γ are the Euler angles of the rotation, and all rotations are performed about space-fixed axes. $\mathcal{R}$ clearly commutes with all the operators of set (2-14) except $J_{z'}$.

The particular $\mathcal{R}$ desired here is the one which rotates the space-fixed axes into the body-fixed axes. It is defined to bring the new z axis to lie along $\underset{\sim}{R}$, the internuclear vector, but leave the new y axis in the old xy plane. Then, the new (body-fixed) axes, $\hat{e}_i$, are just the unit vectors of $\underset{\sim}{R}$ in spherical polar coordinates,

$$\hat{e}_x = \hat{e}_\theta , \quad \hat{e}_y = \hat{e}_\varphi , \quad \hat{e}_z = \hat{e}_R . \tag{2-31}$$

Here R, θ, and φ are the spherical polar coordinates of $\underset{\sim}{R}$ relative to the space-fixed axes. This particular choice of body-fixed axes makes the Euler angles α , β , and γ of the rotation become φ , θ and 0 , respectively. And the particular rotation wanted is just

$$\mathcal{R} = e^{i\theta J_{y'}} e^{i\varphi J_{z'}} . \tag{2-32}$$

The matrix representation, $\mathbb{R}$, of this particular rotation[57] is given explicitly in Appendix B. It was used by Kolos and Wolniewicz[16]

and by Thorson[17]. The body-fixed coordinates are

$$\mathbf{x} = \mathbb{R}\mathbf{x}'$$

and

$$\mathbf{X} = \mathbb{R}\mathbf{X}' = \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix}. \tag{2-33}$$

4. Rotation of the Wavefunction

In applying the rotation operator to Eq. (2-15 to 20) we adopt the functional convention (see Appendix B) whenever a rotation is applied to Ψ . That is,

$$\mathcal{R}^{-1}\Psi(\mathbf{x}',\mathbf{X}') = \Psi(\mathbb{R}\mathbf{x}', \mathbb{R}\mathbf{X}') = \Psi(\mathbf{x},\mathbf{X}). \tag{2-34}$$

Using Eq. (2-33), this will be written as

$$\Psi(\mathbf{x},\mathbf{X}) = \Psi(\mathbf{x},R), \tag{2-35}$$

to emphasize the fact that the rotated wavefunction does not depend on θ and φ : it is a function of two less coordinates than $\Psi(\mathbf{x}',\mathbf{X}')$.

The effect of a rotation on Ψ can also be expressed in terms of the representations, $D^{J}_{\Omega M}$, of the rotation group as follows.

$$\mathcal{R}\,\Psi(x',X';J,M) = \sum_{\Omega=-J}^{J} D^{J}_{\Omega M}(\mathcal{R})\,\Psi(x',X';J,\Omega). \tag{2-36}$$

Combining Eq. (2-34 and 36), one obtains

$$\Psi(x',X',J,M) = \mathcal{R}\,\mathcal{R}^{-1}\,\Psi(x',X';J,M)$$

$$= \sum_{\Omega} D^{J}_{\Omega M}(\mathcal{R})\,\Psi(x,R,J,\Omega). \tag{2-37}$$

In Appendix B the operators are transformed by applying them directly on this equation, but here the transformations are made using $\mathcal{R}$ itself.

5. <u>Rotation of Constants of the Motion other than H</u>.

If A' is the representation in space-fixed coordinates of any of the set (2-14), and if a is its eigenvalue, then application of $\mathcal{R}^{-1}$ to its eigenvalue equation makes it clear that

$$A = \mathcal{R}^{-1} A' \mathcal{R} \tag{2-38}$$

represents A' in the body-fixed coordinates and has the eigenvalue a. In addition, the fact that the members of (2-14) commute is an operator relationship and must hold in any coordinate system. We now proceed to transform the operators of (2-14) and obtain representations in the body-fixed axes by applying $\mathcal{R}^{-1}$ to the

equations which they satisfy.

The angular momentum operators are treated as formal operators[58]. From Eq. (2-16, 17, 23 and 38) it is clear that the result is simply

$$\underset{\sim}{J}^2 \Psi(\mathbf{x}, R; J, \Omega) = J(J+1)\, \Psi(\mathbf{x}, R; J, \Omega), \tag{2-39}$$

$$J_z \Psi(\mathbf{x}, R; J, \Omega) = \Omega\, \Psi(\mathbf{x}, R; J, \Omega), \tag{2-40}$$

and

$$J_\pm \Psi(\mathbf{x}, R; J, \Omega) = (J_x \pm i J_y) \Psi(\mathbf{x}, R; J, \Omega) = \lambda_\pm(J, \Omega)\, \Psi(\mathbf{x}, R; J, \Omega \pm 1), \tag{2-41}$$

where everything is relative to body-fixed axes, and the index Ω is (rather than M) used for the component of J along the internuclear axis, in accord with standard notation.

From the form (2-32) of the rotation operator, it is clear that the representation of an operator in body-fixed coordinates will differ from its representation in space-fixed coordinates only if the operator affects θ and φ (or χ'). The operators $\mathcal{J}_e$ and $\mathcal{P}_{ij}$ do not affect θ and φ . Hence, they act on the body-fixed coordinates in the same way they acted on the space-fixed coordinates, and their representations are obtained by just dropping the primes in Eq. (2-26 and 29).

To transform Eq. (2-25), one could just let $\mathcal{J} = \mathcal{R}^{-1} \mathcal{J}' \mathcal{R}$ and obtain

$$\mathcal{I}\,\Psi(\mathbf{x},\mathbf{X}) = \Psi(-\mathbf{x},-\mathbf{X}). \tag{2-42}$$

But from Eq. (2-33) this is

$$\mathcal{I}\,\Psi(\mathbf{x},R) = \Psi(-\mathbf{x},-R), \tag{2-43}$$

and $R = |\underset{\sim}{R}|$ should be positive. In addition, Eq. (2-43) leaves the body-fixed z axis (which points in the $\underset{\sim}{R}$ direction) ill-defined. To avoid these difficulties one must find another way to represent the conditions on $\Psi(\mathbf{x},R)$ which are sufficient to give $\Psi(\mathbf{x}',\mathbf{X}')$ definite parity under $\mathcal{I}'$. To do so, we apply $\mathcal{I}'$ directly on Eq. (2-37) and use the properties of the $\mathbb{D}^{J}(\mathcal{R})$. The details are given in Appendix B, where it is shown that if

$$\sigma_{yz}\,\Psi(\mathbf{x},R;J,\Omega) = (-1)^{p-J}\Psi(\mathbf{x},R;J,-\Omega) = \Psi\left[\begin{pmatrix}-x\\ y\\ z\end{pmatrix},R;J,\Omega\right], \tag{2-44}$$

then $\Psi(\mathbf{x}',\mathbf{X}')$ has parity p under $\mathcal{I}'$. Here σ_{yz} is reflection in the body-fixed yz plane. For $\Omega = 0$, it gives rise to the familiar + and - states of diatomic molecules. We use σ_{yz} in place of $\mathcal{I}$.

6. The Rotation of H.

Having obtained representations of the other constants of motion in the body-fixed coordinates, we now transform $\mathcal{H}$. From Eq. (2-3), $\mathcal{H}$ is

$$\mathcal{H} = \frac{1}{2\mu} \mathcal{P}_R^2 + \frac{1}{\mu} \underset{\sim}{P} \cdot \mathcal{P}_R + \mathcal{H}_e , \tag{2-45}$$

with the momenta in space-fixed coordinates given by the usual gradient formulas. $\mathcal{H}$ is invariant to rotations. Since $\mathcal{H}_e$ does not affect θ and φ , its coordinate representation in body-fixed coordinates is simply given by Eq. (2-6) using the usual formulas. However, the components of $\mathcal{P}_R$ do affect θ and φ , and we now seek a representation of the first two terms of (2-45) in the body-fixed coordinates. The scalar products are invariant to rotation,

$$\mathcal{P}_g \cdot \mathcal{P}_\ell = \sum_{k'=1}^{3} (\mathcal{P}_g)_{k'} (\mathcal{P}_\ell)_{k'} = \sum_{k=1}^{3} (\mathcal{P}_g)_k (\mathcal{P}_\ell)_k , \tag{2-46}$$

for any g and ℓ .

To find the components of $\mathcal{P}_R$ in the body-fixed coordinates, let us look at the nuclear orbital angular momentum, $\underset{\sim}{L}$. Since $\underset{\sim}{R}$ lies along the z axis,

$$\underset{\sim}{L} = \underset{\sim}{R} \times \mathcal{P}_R = R \hat{e}_z \times \mathcal{P}_R , \tag{2-47}$$

and one readily finds that

$$(p_R)_x = L_y/R \ , \ (p_R)_y = -L_x/R \ , \quad \text{but} \quad L_z = 0 , \tag{2-48}$$

in these coordinates. The L_i are explicitly represented below. Since the body-fixed axes are the spherical polar axes of $\underset{\sim}{R}$, the z component of p_R , $(p_R)_z$ is just the familiar radial momentum[59], p_R ,

$$(p_R)_z \equiv p_R = \frac{1}{i}\frac{1}{R}\frac{\partial}{\partial R}R . \tag{2-49}$$

Use of these results in Eq. (2-45) gives

$$\mathcal{H} = \frac{1}{2\mu}p_R^2 + \frac{L^2}{2\mu R^2} + \frac{1}{\mu}\left[\frac{1}{R}(P_x L_y - P_y L_x) + P_z p_R\right] + \mathcal{H}_e . \tag{2-50}$$

The electronic momenta P_i do not affect θ and φ , so that they again have the usual gradient representation.

Eq. (2-50) gives $\mathcal{H}$ in terms of operators in the body-fixed system. And coordinate representations of all of them are known except the components of $\underset{\sim}{L}$. Since $\Psi(x,R)$ does not depend on θ and φ , the components of $\underset{\sim}{L}$ cannot be expressed in terms of the usual derivatives with respect to θ and φ . Instead, one must evaluate the action of the components of $\underset{\sim}{L}$ on $\Psi(x,R)$ as follows. Eq. (2-11) is

$$\underset{\sim}{L} = \underset{\sim}{J} - \underset{\sim}{j} . \tag{2-51}$$

The components of the electronic angular momentum $\underset{\sim}{j}$ are representable in these coordinates in the usual way, and the components of $\underset{\sim}{J}$ are taken to be formal operators[58] and evaluated using Eq. (2-39 to 41). Thus Eq. (2-51) provides a suitable representation of $\underset{\sim}{L}$ in the body-fixed coordinates.

To write Eq. (2-50) out in terms of $\underset{\sim}{J}$ and $\underset{\sim}{j}$, one notes from Eq. (2-48) that the only angular momentum along the internuclear axis is electronic angular momentum,

$$J_z = j_z . \tag{2-52}$$

Using this and the commutation relations of the angular momenta, one obtains $\underset{\sim}{L}^2$ in the form

$$\underset{\sim}{L}^2 = \underset{\sim}{J}^2 - 2J_z^2 + \underset{\sim}{j}^2 - j_- J_+ - j_+ J_- . \tag{2-53}$$

Here $j_\pm = j_x \pm i j_y$ are the electronic raising and lowering operators. In addition, if the components of $\underset{\sim}{P}$ are written in terms of irreducible spherical tensors (see Appendix D), then

$$P_x L_y - P_y L_x = \frac{1}{\sqrt{2}\, i} \left[P_1^{-1} L_+ + P_1^{1} L_- \right] , \tag{2-54}$$

$$= \frac{1}{\sqrt{2}\, i} \left[P_1^{-1} (J_+ - j_+) + P_1^{1} (J_- - j_-) \right] . \tag{2-55}$$

The Hamiltonian (2-50) is thus expressible entirely in terms of operators whose action on the wave function in body-fixed coordinates is known. It is

$$\mathcal{H} = \frac{-1}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left(\mathcal{J}^2 - 2\mathcal{J}_z^2 + \mathcal{J}^2 - \mathcal{J}_-\mathcal{J}_+ - \mathcal{J}_+\mathcal{J}_-\right) +$$

$$\frac{1}{\mu i}\left\{\frac{1}{\sqrt{2}\,R}\left[P_i^{-1}(\mathcal{J}_+ - \mathcal{J}_+) + P_i^{1}(\mathcal{J}_- - \mathcal{J}_-)\right] + \frac{P_z}{R}\frac{\partial}{\partial R}R\right\}, \qquad (2\text{-}56)$$

completing the exact removal of the rotational coordinates θ and φ from the wave function and the equations for all the constants of the motion. The problem now is to solve for $\Psi(\mathbf{x}, R; \mathcal{J}, \Omega, p, i, \bar{p}_e)$ using

$$\mathcal{H},\ \mathcal{J}^2,\ \mathcal{J}_z,\ \mathcal{P}_{ij},\ \bar{\sigma}_{yz},\ \text{and}\ \bar{\mathcal{I}}_e\,. \qquad (2\text{-}57)$$

$\bar{\mathcal{I}}_e$ is a constant of the motion only for identical nuclei, and $\bar{\sigma}_{yz}$ is a constant of the motion only if $\Omega = 0$. However, Eq. (2-44) must hold for all Ω. Once $\Psi(\mathbf{x}, R)$ has been determined for $\Omega = -\mathcal{J}, -\mathcal{J}+1, \cdots, \mathcal{J}$, for the given energy E_i, the space-fixed solution $\Psi(\mathbf{x}', \mathbf{X}')$ is given by Eq. (2-37).

7. Hund's Cases.[60]

The set (2-14) of constants of the motion contains only the exact constants of motion of the Breit-Pauli Hamiltonian. However, in some systems, there are other quantities which, to a very good approximation, are constants of the motion and are conveniently included in the set. The coupling of the various angular momenta determines the approximate constants of the motion and can be discussed in terms of Hund's cases[60] for diatomic molecules. The general case worked out above corresponds to Hund's case c) in which the coupling between $\underset{\sim}{\mathcal{L}}$ and $\underset{\sim}{S}$ and between $\underset{\sim}{\mathcal{L}} + \underset{\sim}{S} = \underset{\sim}{j}$ and $\underset{\sim}{L}$ is quite strong. However, in most bound-state diatomic molecules, the coupling between $\underset{\sim}{\mathcal{L}}$ and $\underset{\sim}{S}$ is small enough that $\mathcal{L}_z$ and S_z can simultaneously be considered quantized,

$$\begin{aligned} \mathcal{L}_z \, \Psi(x,R) &= \Lambda \, \Psi(x,R) , \\ S_z \, \Psi(x,R) &= \Sigma \, \Psi(x,R) , \end{aligned} \tag{2-58}$$

and since $J_z = j_z = \mathcal{L}_z + S_z$, $\Omega = \Lambda + \Sigma$. Then, the set (2-57) becomes

$$\mathcal{H}, \; \underset{\sim}{J}^2, \; J_z , \; \mathcal{L}_z , \; S_z , \; \mathcal{P}_{ij}, \; \bar{\sigma}_{4z} , \text{ and } \bar{\mathcal{J}}_e . \tag{2-59}$$

This corresponds to Hund's case (a). In addition, there is Hund's case b), which usually applies to the Σ states of light molecules.

In such a case, $\Lambda = 0$ and $\underset{\sim}{S}$ is not coupled with $\underset{\sim}{L}$. (This is also equivalent to having $\mathcal{H}_\alpha$ in $\mathcal{H}$ be very small.) Then, the total orbital angular momentum can be taken to be quantized

$$\underset{\sim}{K}^2 \Psi = K(K+1)\Psi . \tag{2-60}$$

In addition, in Hund's case b) the spins are usually left relative to space-fixed axes. Then, J_z is not defined, $\underset{\sim}{J}^2$ is not of interest, and the set of constants of the motion is

$$\mathcal{H}, \underset{\sim}{K}^2, K_z, \underset{\sim}{S}^2, S_{z'}, \mathcal{P}_{ij}, \bar{\sigma}_{yz}, \text{and } \bar{\mathcal{J}}_e . \tag{2-61}$$

Here σ_{yz} and $\mathcal{J}_e$ are now assumed to affect only the configuration space. In Hund's case b) $\underset{\sim}{K}$ plays the role that $\underset{\sim}{J}$ did in the general case worked out above, and it becomes the formal operator. $K_z = \mathcal{L}_z$ plays the role of J_z . The only significant change made in any of the equations of this section is that Eq. (2-13),

$$\underset{\sim}{L} = \underset{\sim}{K} - \underset{\sim}{\mathcal{L}} , \tag{2-62}$$

is used instead of Eq. (2-51) in Eq. (2-50).

III. THE COUPLED EQUATIONS

In the previous section the center of mass and rotational motions were removed, and the Schrödinger equation for internal motion in the body-fixed coordinates was obtained. Examination shows readily, however, that what was obtained is really a set of coupled equations. In this section we discuss the coupling. Some special cases of small coupling are pointed out, and possible methods of treating the equations are discussed.

A. The Ω Coupling

1. The Nature of the Coupling

That the exact removal of rotation leads to $2J + 1$ equations coupled in the different Ω components is well known[42-48]. But the coupled equations obtained have usually been written in a very complicated fashion. That the coupling is done simply by the components of $\underline{L}$ and that the coupled equations could be written as simply as Eq. (2-50) or (2-56) does not seem to have been realized. Eq. (2-50) also makes it clear that the coupling arises from and simply expresses the fact that the nuclear angular momentum $\underline{L}$ is not a constant of the motion. (In relative coordinate systems which do not have the nuclear-electronic cross derivatives, the equations are even simpler. See Appendix B, Eq. (B-72).)

The body-fixed Schrödinger equations should form a basic starting point for almost any high accuracy treatment of diatomic

systems. We now write out the coupling explicitly and discuss these equations. Applying the formal operators in (2-56) to the wave function and leaving only operators expressible in the internal coordinates, one obtains

$$E_i \, \Psi(x,R;J,\Omega) = \mathcal{H} \, \Psi(x,R;J,\Omega)$$

$$= \mathcal{H}_{\Omega,\Omega-1} \Psi(J,\Omega-1) + \mathcal{H}_0 \Psi(J,\Omega) + \mathcal{H}_{\Omega,\Omega+1} \Psi(J,\Omega+1) \tag{3-1}$$

Here

$$\mathcal{H}_0 = \frac{1}{2\mu} P_R^2 + \frac{1}{2\mu R^2}\left[J(J+1) - \Omega^2 + j_x^2 + j_y^2\right] + \mathcal{H}_e +$$

$$\frac{1}{\mu i}\left[\frac{-1}{\sqrt{2}\,R}\left(P_1^{-1} j_+ + P_1^{1} j_-\right) + \frac{P_z}{R}\frac{\partial}{\partial R} R\right], \tag{3-2}$$

and

$$\mathcal{H}_{\Omega,\Omega\pm1} = \frac{\lambda_\pm(J,\Omega)}{\mu R}\left(\frac{-1}{2R} j_\mp + \frac{1}{\sqrt{2}\,i} P_1^{\mp 1}\right). \tag{3-3}$$

The constants $\lambda_\pm(J,\Omega)$ are defined by Eq. (2-24). Thus, we have an equation (3-1) for each of the $2J+1$ allowed values, and each of the equations is coupled to the equations for $\Omega + 1$ and $\Omega - 1$.

2. The Ω Coupling in Collisions

The importance of this Ω coupling is not known yet and the question needs further study. However, some things can be said about it. For example, it appears that the coupling may be of considerable importance in collisions[35]. The reason may be seen from a semiclassical discussion of a collision. Before the collision (at time $t = -\infty$) the system consists of two atoms with magnetic quantum numbers relative to space-fixed axes. If we choose the space-fixed axes and body-fixed axes to coincide at $t = -\infty$, then Eq. (2-37) becomes

$$\Psi(x', X', J, M, t = -\infty) = \Psi(x, X, J, M, t = -\infty) . \qquad (3\text{-}4)$$

That is, at $t = -\infty$, there is only one Ω component, namely M, and $\Psi(x, X, J, M \pm 1, t = -\infty) = 0$ in Eq. (3-1). The solution (3-4) is known and is just the product of two atomic wavefunctions and a plane wave nuclear wavefunction. We now let the system evolve through the collision subject to the time dependent analog of Eq. (3-1). The body-fixed axes change direction during the collision and no longer coincide with the space-fixed axes; hence, the importance of the various Ω components must change during the collision. If the Ω coupling in (3-1) is neglected the system appears locked in one Ω state. At the end of the collision, the system must again consist of two atoms with space-fixed magnetic quantum numbers. Furthermore, the total space-fixed M value must be conserved.

That is, at the end,

$$\Psi(\mathbf{x}', \mathbf{X}', J, M, t=\infty) = \sum_{\Omega} D^{J}_{\Omega M}(\mathcal{R}_{\infty})\, \Psi(\mathbf{x}, \mathbf{X}, J, \Omega, t=\infty), \qquad (3\text{-}5)$$

and the various Ω components must have just the weights to make this true. If the Ω coupling in (3-1) is neglected it will not be true, and the space-fixed M will not appear to be conserved. Furthermore, the adiabatic interaction potentials and associated nuclear equations of motion differ considerably for different Ω values, so that other calculated quantities may also be considerably affected by omission of the Ω coupling. Thorson[17] and Bates[35] have discussed this problem in detail, and their calculations[37,18] on $He-He$ and $H^{+}-H$ collisions show the importance of the coupling in some collision processes.

3. <u>The Ω Coupling in Diatomic Molecules</u>

The Ω coupling gives rise to the Λ-doubling in molecular spectra discussed in Section I. The fact that this effect is small and also the success of the BO approximation, in which the coupling is neglected, indicate that the <u>coupling</u> is very small and usually unimportant in bound state diatomic molecules, and we now consider such cases.

In discussing the Ω coupling, it is important to clearly identify the states involved. From Eq. (2-23) and (2-41) one sees that

$$J_{\pm}\,\Psi(\mathbf{x}, R; J, \Omega, p, i, \bar{p}_e) = \lambda_{\pm}(J,\Omega)\,\Psi(\mathbf{x}, R, J, \Omega\pm 1, p, i, \bar{p}_e).$$

That is, the wavefunctions involved have the same energy, total angular momentum, and parity. They differ only in the component of angular momentum along the internuclear axis. And Eq. (2-37) appears to be a linear combination of degenerate states. However, Ω is not exactly a good quantum number, and from Eq. (2-37),

$$\Psi(\mathbf{x}', \mathbf{X}', J, M) = \sum_{\Omega} D^{J}_{\Omega M}(\mathbf{R})\,\Psi(\mathbf{x}, \mathbf{X}, J, \Omega),$$

one sees that there is really only <u>one</u> state, and the functions for different Ω values are <u>components</u> of that state.

However, it is known experimentally that to an excellent approximation, Ω <u>is</u> a good quantum number. To connect that fact with the exact result, let us write the set of equations (3-1) in matrix form,

$$(\mathbb{H} - E_i \mathbb{I})\,\Psi = 0. \tag{3-6}$$

$\mathbb{I}$ is the unit matrix, and the elements of $\mathbb{H}$ are labeled by $\mathcal{H}_{\Omega,\Omega'}$, where from (3-2) and (3-3),

$$\mathcal{H}_{\Omega,\Omega} = \mathcal{H}_0(\Omega), \tag{3-7}$$

the $\mathcal{H}_{\Omega,\Omega\pm1}$ are given by Eq. (3-3), and all other $\mathcal{H}_{\Omega,\Omega'}$ are zero. The indices Ω run in order over the values

$$\Omega = -J, -J+1, \cdots, J. \tag{3-8}$$

Eq. (3-6) is essentially a secular equation. If one solves it exactly, he obtains a set of energy eigenvalues, E_i, and with each eigenvalue a column vector $\Psi(i)$ with components $\Psi(J,\Omega,i)$. It is these different components of a given state that are coupled in Eq. (3-1).

As the coupling between equations grows smaller, for a given E_i a particular Ω component, say $\Psi(J,\Omega',i)$, will dominate in size and importance, and in the limit of zero coupling will be the only component of $\Psi(i)$. In this limit, one can label E_i by Ω as well as i, and this designation will be that of the spectroscopic Ω state. It is usually a convenient and adequate designation. Let us call the solution neglecting Ω coupling $\tilde{\Psi}(J,\Omega)$. The spectroscopic states $\tilde{\Psi}(J,\Omega)$ and $\tilde{\Psi}(J,\Omega\pm1)$ will differ in energies in general, and the larger the difference in these energies, the smaller one expects the coupling to be in the exact equations.

In connection with the generally strong dependence of the energy on Ω and the resulting small coupling in bound states, we mention the following. In this body-fixed coordinate system, $J_z = j_z$. Hence, since

$$\mathcal{J}_z^2 \leq \mathcal{J}_x^2 + \mathcal{J}_y^2 + \mathcal{J}_z^2 = \mathcal{J}^2,$$

one has the restriction

$$-\langle \mathcal{J}^2 \rangle^{1/2} \leq \Omega \leq \langle \mathcal{J}^2 \rangle^{1/2}, \tag{3-9}$$

in addition to the restriction (3-8). This latter restriction keeps Ω small for most states of interest even though J may be large. We discuss examples of Ω coupling in Section VII and show how the smallness of the coupling reduces the number of equations that must be considered in practice.

When the relativistic corrections $\mathcal{H}_\alpha$ are small enough that the total orbital angular momentum K can be taken as quantized, then K and Λ play the roles of J and Ω in the cases discussed above. But there are also some additional simplifications. Whereas the $\Omega \pm 1$ coupling will couple the different components of a spin multiplet and split them apart, the $\Lambda \pm 1$ coupling leaves them uncoupled. For example, the three states of a $^3\Sigma$ have $\Omega = -1, 0$ and 1 and are coupled if J and Ω are used. But if K and Λ can be taken quantized, they all have $\Lambda = 0$ and are unaffected by the $\Lambda \pm 1$ coupling.

In addition to these cases of small and negligible coupling just discussed, it will be shown in Section IV that in the adiabatic approximation, the number of coupled equations can always be exactly reduced to $J + \frac{1}{2}$ or $J + 1$ equations (whichever is an integer)

instead of the $2J + 1$ equations considered here.

4. The $J = 0$ Case

When $J = 0$, from Eq. (3-8), there is only one allowed value of Ω, and it is well known that Eq. (3-1) becomes just

$$\mathcal{H}_0 \Psi(\mathbf{x}, R; 0,0) = E_i \Psi(\mathbf{x}, R; 0,0). \tag{3-10}$$

Equations equivalent to Eq. (3-10) have been used in the previous nonadiabatic treatments[49,16] of diatomic molecules. In those cases, Eq. (3-10) was treated by direct variational techniques with excellent results. In the adiabatic approximation of the next section, the state $J = 0$ will also play an important role, it leading to the fundamental interatomic potential and the higher states to a family of effective potentials.

B. The Nonadiabatic Coupling

In addition to the Ω coupling discussed above, there is another obstacle to high accuracy solution of Eq. (3-1). In this formalism it is distinct from but similar to the Ω coupling. We call it the "nonadiabatic" coupling. It is due to the fact that the dependence of $\Psi(\mathbf{x},R)$ on $\mathbf{x}$ and R is not separable. And except for very small systems in which $\Psi(\mathbf{x},R)$ can be obtained by direct variational methods[16,49], it is necessary at present to achieve some separation of electronic and nuclear motion. The exact

solution $\Psi(x,R)$ could be expanded in the complete set[22] of electronic wave functions, $\psi(x;R)$,

$$\Psi(x,R,J,\Omega,p,i,\bar{p}_e) = \sum_{j=1}^{\infty} \chi(R;i,j,J,\Omega,p)\,\psi(x;R,j,\Omega,\bar{p},\bar{p}_e), \tag{3-11}$$

where the j index the electronic energy. However, any serious application of Eq. (3-11) is impossible because it leads to an infinite set of coupled equations which have to be solved to obtain the χ_{ij} .

Fortunately, in actual practice one need never take more than two or three terms in the sum to obtain excellent accuracy. The reason for this is as follows. All the constants of the motion except $\mathcal{H}$ are independent of R . Thus, the symmetry properties of Ψ are given by the $\psi(j)$ in the sum, and all of them in the sum must have exactly the same symmetries. Hence, the $\psi(j)$ are just those states for which the non-crossing rule[62] holds. And on the basis of the Franck-Condon principle[63] we expect the coupling between them to be small unless the total energy is near a pseudocrossing of two or more electronic energy curves. Most of these electronic energy curves are separated by large differences in energy, and situations in which more than two of these curves have pseudocrossings in the same energy region are very rare. Hence, one only need include electronic states in (3-11) having pseudocrossings in the

energy range of interest. The rest of the electronic states can be treated by perturbation theory.

C. Methods of Solution. Special Cases

We now discuss possible methods of solution of Eq. (3-1). For this purpose it is convenient to distinguish four special cases: In case 1) both the Ω and nonadiabatic couplings are important; in 2) the nonadiabatic coupling is important and the Ω coupling is unimportant; in 3) the nonadiabatic coupling can be moderately important, but the Ω coupling is unimportant; and in 4) the nonadiabatic coupling is unimportant, but the Ω coupling is important. We discuss these cases in order. In all cases it is assumed that the electronic wavefunctions and energies are known.

1. Both Ω and Nonadiabatic Coupling Important

One expects that both Ω and nonadiabatic couplings will be important simultaneously only very rarely, because the Franck-Condon[63] principle is expected to be valid for both kinds of coupling, and the potentials rarely lie close together. And when such cases occur, they can best be treated individually. If the atoms involved are very small, it seems likely that for small J, direct variational techniques similar to those of Kolos and Wolniewicz[16] could be extended to obtain the simultaneous solution of Eq. (3-1). At present such an approach is clearly limited to small systems and very few equations, but as the size and speed of computers grows,

this approach should become more and more attractive. For larger systems one could use a two or three term sum of the form of (3-11) and treat both the Ω coupling and psuedocrossing coupling simultaneously by standard numerical techniques to obtain the nuclear wave functions[61]. This is essentially an extension of the "perturbed stationary states" method[27] of scattering theory. Examples have been treated by Bates and Williams[37] and Kouri[32]. We do not consider this case any further in this work.

2. Nonadiabatic Coupling Important, Ω Coupling Unimportant

In this case the Ω coupling can be neglected in first approximation and treated afterward by iteration methods. Thus, the major problem here is the solution of

$$\mathcal{H}_0 \Psi(\mathcal{J},\Omega) = E_i \Psi(\mathcal{J},\Omega) \tag{3-12}$$

when E_i lies near the pseudocrossing of two or more adiabatic potential curves. This problem can be treated by degenerate perturbation theory, time-dependent perturbation theory[30], or by simultaneous numerical solution of the coupled equations. It has been treated extensively by several authors[29-31]. It is discussed as one limit of Case 3) below but not treated in this work.

3. Nonadiabatic Coupling not Too Important, Ω Coupling Unimportant

In this case the Ω coupling can again be treated last by iteration methods. For collision problems the proper treatment of the nonadiabatic coupling ranges here from simple first order evaluation of the transition matrix elements with adiabatic or Born-Oppenheimer functions to any of the treatments of case 2 above, depending on the importance of the nonadiabatic coupling. However, for bound or metastable states the coupling can be treated by perturbation theory starting from the adiabatic approximation, and the nonadiabatic effects on the total energy and also on the potential itself can be estimated. This latter case is treated in detail in Section IV.

4. Nonadiabatic Coupling Unimportant, but Ω Coupling Important

In this case the adiabatic approximation can be used for $\Psi(x,R)$ and the electronic variables integrated out. Then one just has coupled equations depending on one variable, R , to solve for the nuclear wavefunctions, χ . Each $\chi(\Omega)$ is coupled only to its nearest neighbors $\chi(\Omega+1)$ and $\chi(\Omega-1)$, so that the set of equations form a Jacobian Normal Form matrix. Numerical methods for handling such equations are well developed[61], so that once the adiabatic potentials have been obtained, the χ should be obtainable for J not too large. This case is discussed in more detail in the next section, and it is shown that the parity restriction on the wavefunctions reduces the number of these equations from $2J + 1$ to $J + \frac{1}{2}$ or $J + 1$, the nearest integer larger than J .

IV. ADIABATIC APPROXIMATIONS

In this section the internal equations of motion, Eq. (3-1), are treated by perturbation theory for the cases 3) and 4) just discussed. Adiabatic wavefunctions are used as the zeroth order approximation. The two cases are treated in order. In case 3) the adiabatic approximation is extended to allow an approximate estimation of nonadiabatic corrections to the potential. In case 4) the Ω coupling is discussed in the adiabatic approximation.

A. The Extended Adiabatic Approximation

It is assumed that case 3) of the previous section holds, and the Ω coupling is ignored at present. The equation to be solved is the diagonal part of Eq. (3-1),

$$\mathcal{H}_0 \Psi(J,\Omega) = E_i \Psi(J,\Omega), \tag{4-1}$$

where

$$\begin{aligned} \mathcal{H}_0 = {} & \frac{1}{2\mu} p_R^2 + \frac{1}{2\mu R^2}\left[J(J+1) - \Omega^2 + j_x^2 + j_y^2 \right] + \\ & \frac{1}{\mu}\left[\frac{i}{\sqrt{2}R}\left(P_1^{-1} j_+ + P_1^{1} j_- \right) + P_z p_R \right] + \mathcal{H}_e . \end{aligned} \tag{4-2}$$

We now treat Eq. (4-1) by perturbation methods. The higher order corrections obtained are quite restricted in applicability, but the discussion of the restrictions is postponed until the end of this subsection. We assume that

$$\Psi = \sum_n \beta^n \Psi^{(n)}, \tag{4-3}$$

where $\beta = 1$ is a perturbation ordering parameter. The zeroth order wavefunction chosen is an adiabatic approximation,

$$\Psi^{(0)}(x, R; J, \Omega, p, i, \bar{p}_e) = \chi(R; J, \Omega, p, j, \nu)\, \psi(x; R; \Omega, \bar{p}, j, \bar{p}_e). \tag{4-4}$$

The ψ here are electronic wave functions and the χ are nuclear wavefunctions. The equations they satisfy will be derived below. It is seen that the energy index $i \to j, \nu$ where j specifies the electronic energy and ν specifies the nuclear state which goes with J to give $E_i^{(0)}$ as the total energy,

$$E_i^{(0)} = E_{j\nu}^{(0)}. \tag{4-5}$$

In what follows everything is diagonal in the good quantum numbers J, Ω, p, $\bar{p}_e$, and they are usually not written explicitly.

The electronic wavefunctions $\psi(x; R)$ are allowed to depend only parametrically on R and are assumed orthonormal for all R,

$$\langle \psi(') | \psi( ) \rangle_x = \delta_{jj'} \, \delta_{\ell\ell'} \, \bar{\delta}_{pp'} \, \bar{\delta}_{p_e p_e'} \, . \tag{4-6}$$

The symbol $\langle | \rangle_x$ implies integration over the electronic space, and the bars on p and p_e were explained at Eq. (2-57).

The exact choice of the equations satisfied by χ and ψ is somewhat arbitrary. However, a convenient choice has been made by Herman and Asgharian[6], and we use it here. Let $\Psi^{(0)}$ be substituted into Eq. (4-1). The result is

$$\mathcal{H}_0 \Psi^{(0)} = \frac{\psi}{2\mu} p_R^2 \chi + \chi \mathcal{H}_0 \psi - \frac{1}{\mu} \frac{\partial \psi}{\partial R} \frac{\partial \chi}{\partial R} + \frac{1}{\mu i} P_z \psi \frac{\partial \chi}{\partial R} , \tag{4-7}$$

where H_0 is given by (4-2). The electronic wavefunction is now chosen to satisfy the effective electronic equation,

$$\mathcal{H}_0 \psi = \mathcal{E}_j(R; \mathrm{eff}) \psi . \tag{4-8}$$

The restriction (4-6) on ψ makes it clear that the terms in (4-8) which contain derivatives of ψ with respect to R are to be treated by perturbation theory only. $\mathcal{E}_j(R; \mathrm{eff})$ is the <u>effective interatomic potential</u>. Eq. (4-8) is treated in more detail in Section V. In this section it is assumed that its solutions are known to some consistent order in μ^{-1}. (2nd order in this case). Then, the nuclear wavefunctions are chosen to satisfy the following equation,

$$\left[\frac{1}{2\mu} p_R^2 + \mathcal{E}_j(R;\mathrm{eff}) + \beta^2 U_j^{nad}(R)\right] \chi(j\nu) = E_{j\nu}^{(0)} \chi(j\nu) . \tag{4-9}$$

$U_j^{nad}(R)$ will be chosen to make the second order corrections to $E_{j\nu}^{(0)}$ vanish and thus give approximately the nonadiabatic corrections to the effective potential. This method is equivalent to the method used by Van Vleck[5], Fisk and Kirtman[14], and Herman and Asgharian[6] to obtain nonadiabatic corrections to the potential itself rather than just to the total energy.

Use of Eq. (4-8 and 9) in Eq. (4-7) allows it to be written in the form,

$$\mathcal{H}_0 \Psi^{(0)}(j\nu) = E_{j\nu}^{(0)} \Psi^{(0)}(j\nu) + \beta \mathcal{H}_0^{(1)} \Psi^{(0)}(j,\nu) + \beta^2 \mathcal{H}_0^{(2)} \Psi^{(0)}(j\nu), \tag{4-10}$$

where

$$\mathcal{H}_0^{(1)} \Psi^{(0)}(j\nu) = \frac{1}{\mu}\left[\left(P_z + \frac{1}{i}\frac{\partial}{\partial R}\right)\psi(j)\right] \frac{1}{i}\frac{\partial \chi(j\nu)}{\partial R}, \tag{4-11}$$

and

$$\mathcal{H}_0^{(2)} \Psi^{(0)}(j\nu) = -\psi(j)\, U_j^{nad}(R)\, \chi(j\nu). \tag{4-12}$$

Eq. (4-11) just consists of the leftover terms. They are considered to be of order β . One sees that the perturbations $\mathcal{H}_0^{(1)}$ and $\mathcal{H}_0^{(2)}$ are operators and are only well defined when acting on the

zeroth order wavefunction. However, it is proved in Appendix C that a perturbation solution for Ψ is still possible if $E_{j\nu}^{(0)}$ is non-degenerate, and if $\Psi^{(n)}$ is always expanded in the zeroth order solutions,

$$\Psi^{(n)}(j\nu) = \sum_{j',\nu'} c^{(n)}(j'\nu', j\nu)\, \Psi^{(0)}(j'\nu'). \tag{4-13}$$

If these conditions can be satisfied, then from Appendix C,

$$E_{j\nu}^{(1)} = \langle \Psi^{(0)}(j\nu) \,|\, \mathcal{H}_0^{(1)} \Psi^{(0)}(j\nu) \rangle , \tag{4-14}$$

and

$$E_{j\nu}^{(2)} = \langle \Psi^{(0)}(j\nu) \,|\, \mathcal{H}_0^{(2)} \Psi^{(0)}(j\nu) \rangle - \sum_{j'\nu' \neq j\nu} \frac{\langle \mathcal{H}_0^{(1)} \Psi^{(0)}(j\nu) | \Psi^{(0)}(j'\nu') \rangle \langle \Psi^{(0)}(j'\nu') | \mathcal{H}_0^{(1)} \Psi^{(0)}(j\nu) \rangle}{E_{j'\nu'}^{(0)} - E_{j\nu}^{(0)}} . \tag{4-15}$$

From Eq. (4-11) the first order energy is given by

$$E_{j\nu}^{(1)} = \frac{1}{\mu i} \langle \chi(j\nu) \langle \psi(j) | P_z + \frac{1}{i}\frac{\partial}{\partial R} | \psi(j) \rangle_R \frac{\partial \chi(j\nu)}{\partial R} \rangle_R . \tag{4-16}$$

In Appendix D the integral over electronic coordinates is shown to vanish identically. Therefore,

$$E_{j\nu}^{(1)} \equiv 0 . \tag{4-17}$$

Eq. (4-12) and Unsöld's approximation can be used to simplify the second order energy. The Unsöld approximation consists of replacing the energy differences $E^{(0)}_{j'\nu'} - E^{(0)}_{j\nu}$ by a mean value $\Delta_{j\nu}$ and using the closure relations to perform the sum. The result is

$$E^{(2)}_{j\nu} = -\langle \chi(j\nu) | U^{nad}_j(R) | \chi(j\nu) \rangle_R - \frac{1}{\Delta_{j\nu}} \langle \mathcal{H}^{(1)}_0 \Psi^{(0)}(j\nu) | \mathcal{H}^{(1)}_0 \Psi^{(0)}(j\nu) \rangle . \quad (4\text{-}18)$$

The problems involved in the Unsöld approximation will be discussed later. From Eq. (4-11) let

$$F_j(R) \equiv \langle (P_z + \tfrac{1}{i}\tfrac{\partial}{\partial R}) \psi(j) | (P_z + \tfrac{1}{i}\tfrac{\partial}{\partial R}) \psi(j) \rangle_x . \quad (4\text{-}19)$$

And from Eq. (2-49) or Appendix B , Eq. (B-51), one sees that

$$\langle \mathcal{H}^{(1)}_0 \Psi^{(0)}(j\nu) | \mathcal{H}^{(1)}_0 \Psi^{(0)}(j\nu) \rangle = \frac{1}{\mu^2} \langle \chi(j\nu) | \left(\frac{1}{i}\frac{\partial}{\partial R} + \frac{2}{iR} \right) \frac{F_j(R)}{i} \frac{\partial \chi}{\partial R} \rangle_R , \quad (4\text{-}20)$$

$$= \frac{1}{\mu^2} \langle \chi(j\nu) | -\frac{\partial F_j(R)}{\partial R} \frac{\partial}{\partial R} + F_j(R) p_R^2 | \chi(j\nu) \rangle_R , \quad (4\text{-}21)$$

where p_R is given by Eq. (2-49). Let $U^{nad}_j(R)$ now be chosen to be

$$U^{nad}_j(R) = \frac{1}{\mu^2 \Delta_{j\nu}} \left[\frac{\partial F_j(R)}{\partial R} \frac{\partial}{\partial R} - F_j(R) p_R^2 \right] . \quad (4\text{-}22)$$

Then, the second order corrections vanish,

$$E_{j\nu}^{(2)} = 0 . \tag{4-23}$$

This $U_j^{nad}(R)$ is a velocity dependent potential. It represents contributions of states other than the single adiabatic state $\Psi^{(0)}$ to the effective potential. It is hence a nonadiabatic correction due to the pseudocrossing type of coupling. Setting $\beta = 1$ in Eq. (4-9) and using these results, one finds the nuclear equation of motion,

$$\left[\left(\frac{1}{2\mu} - \frac{F_j(R)}{\mu^2 \Delta_{j\nu}}\right) p_R^2 + \frac{1}{\mu^2 \Delta_{j\nu}} \frac{\partial F_j(R)}{\partial R} \frac{\partial}{\partial R} + \mathcal{E}_j(R;\mathrm{eff}) - E_{j\nu}^{(0)} \right] \chi(j\nu) = 0 . \tag{4-24}$$

Solution of Eq. (4-24) provides nuclear wave functions and total energies.

Let us now discuss some of the difficulties and restrictions connected with Eq. (4-24). Most of them involve the sum in Eq. (4-15),

$$\langle \chi | U_j^{nad}(R) | \chi \rangle_R = - \sum_{j'\nu' \neq j\nu} \frac{|\langle \Psi^{(0)}(j'\nu') | \mathcal{H}_0^{(1)} \Psi^{(0)}(j\nu) \rangle|^2}{E_{j'\nu'}^{(0)} - E_{j\nu}^{(0)}} . \tag{4-25}$$

Firstly, it should be clear that the R dependence of $U_j^{nad}(R)$ should not be taken too seriously[64]. Eq. (4-23) and (4-25) are the only necessary and significant restrictions on U_j^{nad}. Secondly, if U_j^{nad} is really of $O(\mu^{-2})$ as Eq. (4-22) appears to be, then it is

negligible, as pointed out in the introduction. However, $\mathcal{U}_1^{nad}$ can be considerably larger than $\mathcal{O}(\mu^{-2})$ depending on the size of $\Delta_{j\nu}$. To discuss its size, let us write Eq. (4-25) in more detail,

$$\langle \chi | \mathcal{U}^{nad} | \chi \rangle_R = -\sum_{j'\nu' \neq j\nu} \frac{\left| \langle \chi(j'\nu') \langle \psi(j') | (P_z + \frac{1}{i}\frac{\partial}{\partial R}) \psi(j) \rangle_x \frac{1}{i} \frac{\partial \chi(j\nu)}{\partial R} \rangle_R \right|^2}{E^{(0)}_{j'\nu'} - E^{(0)}_{j\nu}} .$$

From equation (4-17) the matrix elements vanish if $j' = j$. Also, all the states in the sum have the same symmetry. One thus sees that if there can exist an electronic state j' of the same symmetry as j with nuclear energy ν' such that $E^{(0)}_{j'\nu'} = E^{(0)}_{j\nu}$, then the term in Eq. (4-26) can blow up, and Eq. (4-24) becomes nonsense. In such a case the adiabatic approximation (4-4) is not justified and the whole procedure here for calculating these higher order corrections is invalid[65]. One must then either limit the calculation to lower accuracy or treat it as case 2) of the preceding section.

For most bound states of diatomic molecules and some metastable and very low energy collision states[66] no degeneracy is possible and Eq. (4-24) is valid. However, in higher energy collisions, due to the fact that the relative translational energy (indexed by ν) is continuous, Eq. (4-24) is not usually applicable.

For the ground state and the lowest state of each symmetry, $\Delta_{j\nu}$ can be estimated in a straightforward way using the Hylleraas variation principle[67,68]. The procedure for the particular kind of perturbation encountered here is given in detail in Appendix C.

The result is

$$\tilde{\Delta}_{j\nu} = \frac{\langle \mathcal{H}_0^{(1)} \Psi^{(0)}_{(j\nu)} | \mathcal{H} - E_c^{(0)} | \mathcal{H}_0^{(1)} \Psi^{(0)}_{(j\nu)} \rangle}{\langle \mathcal{H}_0^{(1)} \Psi^{(0)}_{(j\nu)} | \mathcal{H}_0^{(1)} \Psi^{(0)}_{(j\nu)} \rangle} . \tag{4-26}$$

The value, $\tilde{\Delta}_{j\nu}$, is a upper bound to $\Delta_{j\nu}$, so that the estimated value of the sum is an upper bound to its true value. Since $\Delta_{j\nu}$ must be known before χ and $\Psi^{(0)}$ can be determined, Eq. (4-26) must be evaluated using some approximation such as BO wavefunctions for $\Psi^{(0)}$, which makes the approximate nature of Eq. (4-24) all the more apparent. We consider U_j^{nad}(R) in more detail for a special case in Section VII.

B. The Adiabatic Approximation

Case 4) of Section III is now assumed to hold. The Ω coupling is important, but the pseudocrossing coupling is negligible. In the treatment that follows there is a hidden approximation; namely, the $\mathcal{H}_{\Omega,\Omega\pm1}$ of Eq. (3-3) are not allowed to influence the choice of electronic wavefunctions. Even so, it should be an excellent approximation for many systems.

Let us assume that $\Psi(J,\Omega)$ is adequately described by a function of the form of Eq. (4-4),

$$\Psi^{ad} = \chi^{ad} \Psi. \tag{4-27}$$

The electronic wavefunction, Ψ, is again assumed to satisfy Eq. (4-8) to a consistent order in μ^{-1}. That is first order in

this case, and this procedure will give all corrections through $\mathcal{O}(\mu^{-1})$. To determine the equations satisfied by χ^{ad}, we substitute Ψ^{ad} into Eq. (3-1), multiply by $\psi^*(\Omega)$ and integrate over electronic space. Eq. (4-16 and 17) still hold because of ψ, and the result is

$$E^{ad}_{j\nu}\chi^{ad}(\Omega) = h^{(R)}_{\Omega,\Omega-1}\chi^{ad}(\Omega-1) + \left[\frac{1}{2\mu}p_R^2 + \mathcal{E}_j(R;\mathrm{eff})\right]\chi^{ad}(\Omega) + h^{(R)}_{\Omega,\Omega+1}\chi^{ad}(\Omega+1). \tag{4-28}$$

Here the functions $h^{(R)}_{\Omega,\Omega\pm1}$ are the matrix elements

$$h^{(R)}_{\Omega,\Omega\pm1} = \langle\psi(\Omega)|\mathcal{H}_{\Omega,\Omega\pm1}|\psi(\Omega\pm1)\rangle_*, \tag{4-29}$$

with $\mathcal{H}_{\Omega,\Omega\pm1}$ given by Eq. (3-3). The quantum numbers not written are implied to be the particular values listed in Eq. (4-4). If Eq. (4-28) is satisfied, then

$$E^{ad} \equiv \langle\Psi^{ad}(\Omega)|\mathcal{H}|\Psi^{ad}(\Omega)\rangle, \tag{4-30}$$

so that this approximation includes all first order corrections.

The set (4-28) of $2J + 1$ coupled equations now involves only one variable, R. Since $\mathcal{E}(R;\mathrm{eff}) = \mathcal{E}(R;\Omega;\mathrm{eff})$, this is a set of nuclear equations involving a family of effective potentials. The concept of the single potential to be used in a radial Schrödinger equation is thus modified.

The coupling in (4-28) is subject to Eq. (3-8) and (3-9) and

has the same cases of vanishing or reduced coupling discussed in Section III. The adiabatic approximation also produces additional simplifications. The wavefunction, Ψ^{ad} , used here must satisfy Eq. (2-44),

$$\sigma_{yz}\, \Psi^{ad}(x,R\,;J,\Omega) = (-1)^{p-J}\, \Psi^{ad}(x,R\,;J,-\Omega). \tag{4-31}$$

But from Eq. (4-27) this is

$$\sigma_{yz}\, \Psi^{ad} = \chi(R\,;\Omega)\, \sigma_{yz}\, \psi(x;R;\Omega)\,, \tag{4-32}$$

since σ_{yz} does not affect R . For a ψ built of the usual kinds of functions, it is shown in Appendix B, Eq. (B-69 and 70), that for $\Omega \neq 0$, the electronic functions can always be taken to satisfy

$$\sigma_{yz}\, \psi(x;R;\Omega) = \psi(x\,;R\,;-\Omega). \tag{4-33}$$

But if $\Omega = 0$, the electronic functions can either be odd (-) or even (+) under reflection[69],

$$\sigma_{yz}\, \psi(x;R,0) = (-1)^{\sigma}\, \psi(x;R,0). \tag{4-34}$$

Substituting Eq. (4-33 and 34) into the left side of Eq. (4-31) one sees that the proper behavior under σ_{yz} is given by choosing

$$(-1)^{\sigma} = (-1)^{p-J}, \quad \text{for} \quad \Omega = 0, \tag{4-35}$$

and

$$\chi(R;-\Omega) = (-1)^{p+J}\chi(R;\Omega), \quad \text{for } \Omega \neq 0. \tag{4-36}$$

The only difference between $\chi(R;-\Omega)$ and $\chi(R;\Omega)$ is their relative phase. This means that some of the 2J + 1 equations are redundant. The redundant ones can be removed from the set as follows. We write the set (4-28) in matrix form,

$$(\mathbb{h} - E^{ad}_{j\nu}\mathbb{I})\mathbb{X} = 0, \tag{4-37}$$

where the rows and columns start from $\Omega = -J$ and run to $\Omega = J$. $\mathbb{I}$ is the unit matrix. The elements $h_{\Omega\Omega'}$ of $\mathbb{h}$ are zero except for $h_{\Omega,\Omega\pm1}$ given by Eq. (4-29) and

$$h_{\Omega\Omega} = \frac{1}{2\mu}p_R^2 + \mathcal{E}_j\,(R;\Omega^2;\text{eff}). \tag{4-38}$$

That $\mathcal{E}_j(\text{eff})$ depends only on Ω^2, rather than on Ω, is well known and can be seen from Eq. (4-2).

Let us consider in order the cases in which J (and hence Ω) is an integer or a half integer. If J is an integer, then the $\Omega = 0$ equation appears in the set. It reads

$$h_{0,-1}\chi(-1) + (h_{00} - E)\chi(0) + h_{0,1}\chi(1) = 0. \tag{4-39}$$

From Eq. (4-36) $\chi(-1) = (-1)^{\rho+J}\chi(1)$, and in Appendix D it is shown that

$$h_{0,-1} = (-1)^{\rho-J} h_{0,1} . \tag{4-40}$$

Thus, Eq. (4-39) becomes

$$(h_{00} - E)\chi(0) + 2h_{01}\chi(1) = 0. \tag{4-41}$$

This completely uncouples the equations for 0 or positive Ω from those for negative Ω . Then Eq. (4-37) can be taken to include only the values $\Omega = 0$, ... J . The set of 2J + 1 equations thus reduces to a maximum of J + 1 equations, in which all the elements are the same as before except for the $2h_{01}$ in Eq. (4-41).

If J is a half integer, then $\Omega = 0$ cannot occur. The two closest values are $\Omega = -\frac{1}{2}$ and $\frac{1}{2}$. The equation for $\Omega = \frac{1}{2}$ is

$$h_{\frac{1}{2},-\frac{1}{2}}\chi(-\tfrac{1}{2}) + (h_{\frac{1}{2},\frac{1}{2}} - E)\chi(\tfrac{1}{2}) + h_{\frac{1}{2},\frac{3}{2}}\chi(\tfrac{3}{2}) = 0. \tag{4-42}$$

From Eq. (B-66), we drop the J in Eq. (4-36) for this half integral case. Then $\chi(-\frac{1}{2}) = (-1)^{\rho}\chi(\frac{1}{2})$, and Eq. (4-42) becomes

$$\left[h_{\frac{1}{2},\frac{1}{2}} + (-1)^{p} h_{\frac{1}{2},-\frac{1}{2}} - E \right] \chi(\tfrac{1}{2}) + h_{\frac{1}{2},\frac{3}{2}} \chi(\tfrac{3}{2}) = 0. \qquad (4\text{-}43)$$

This completely uncouples the equations for negative Ω from the rest of the set. The matrix is split in half and we are left with $J + \frac{1}{2}$ equations for the values $\Omega = \frac{1}{2}, \frac{3}{2}, \ldots, J$. All the equations except the $\Omega = \frac{1}{2}$ equation remain unchanged.

At this point the origin of the Λ - and ρ -type splittings in molecular spectra is clear. The parity appears explicitly in Eq. (4-43) and the two choices of p make $h_{\frac{1}{2},-\frac{1}{2}}$ come into the equation with a positive or a negative sign and shift the energy up or down. In Eq. (4-41) the electronic wave function $\psi(0)$ which appears in h_{01} may be either even or odd under reflection, and its choice affects the value of h_{01}, producing slightly different energy eigenvalues. In bound state molecules the coupling and splittings are small effects, and to obtain the spectroscopic states and energies, one usually need consider no more than three equations. If one is interested in the state Ω, he can consider the equations for Ω, $\Omega + 1$, and $\Omega - 1$, but neglect the coupling to the $\Omega \pm 2$ equations. An example is discussed in Section VII.

C. The Born-Oppenheimer Approximation

For the sake of clarity, let us show the connection between these adiabatic approximations and the Born-Oppenheimer approximation. In the BO approximation one takes

$$\Psi^{BO} = \chi_s \psi_s , \qquad (4\text{-}44)$$

But in treating the equivalent of Eq. (4-8) for Ψ_s, many of the terms in Eq. (3-2) are neglected, and Ψ_s just satisfies the static or fixed-nucleus electronic equation,

$$\left[\mathcal{H}_s + \frac{J(J+1)}{2\mu R^2}\right] \Psi_s(j) = \mathcal{E}_{js}(R;\mathrm{eff})\, \Psi_s(j) \tag{4-45}$$

$\mathcal{H}_s$ is the static electronic Hamiltonian obtained by neglecting the mass polarization terms (and usually also H_α) in Eq. (2-6). The effects of both Ω and nonadiabatic coupling are neglected, and the nuclear wavefunctions just satisfy

$$\left[\frac{1}{2\mu} p_R^2 + \mathcal{E}_{js}(R;\mathrm{eff})\right] \chi_s(j\nu) = E_{j\nu}^{BO}\, \chi_s(j\nu). \tag{4-46}$$

The effective potential is now

$$\mathcal{E}_{js}(R;\mathrm{eff}) = \frac{J(J+1)}{2\mu R^2} + \mathcal{E}_{js}(R), \tag{4-47}$$

where $\mathcal{E}_{js}(R)$ is the usual electronic energy. It should be noted that in this approximation only one term in Eq. (2-37) need be taken, and the $D^J_{\Omega M}(\mathcal{R})$ reduce[70] to the spherical harmonics $Y^{\Omega}_{\tilde{}}(\theta,\varphi)$. Thus both of the adiabatic approximations used in this section reduce to the Born-Oppenheimer approximation if one simply neglects the correction terms. This close connection allows one to start from the BO approximation and treat the various corrections by perturbation methods.

V. THE ELECTRONIC EQUATION

In the previous section it was assumed that the solutions of the effective electronic equation, Eq. (4-8), were known. In this section that equation is treated by perturbation methods. A detailed treatment is presented for the special case of neutral atoms interacting at large separations. All matrix elements $\langle | \rangle$ in this section and the next only involve integration over the electronic space, and for simplicity the subscript $\mathbb{X}$ will be omitted.

A. The Effective Electronic Equation

In Section IV the electronic wave functions $\psi(\mathbb{X}; R; \Omega, \bar{p}, j, \bar{p}_e)$ were introduced. They depend only parametrically on R and are solutions of the effective electronic equation,

$$\mathcal{H}_0 \psi = \mathcal{E}_j(R; \mathrm{eff}) \psi. \tag{5-1}$$

From Eq. (4-2) and (2-6) $\mathcal{H}_0$ can be written as

$$\mathcal{H}_0 = \mathcal{H}_s + \mu^{-1} \mathcal{H}_\mu + \alpha^2 \mathcal{H}_\alpha + \mu^{-1} \mathcal{H}_c, \tag{5-2}$$

where H_s is the static or BO electronic Hamiltonian,

$$\mathcal{H}_s = T_e + V, \tag{5-3}$$

and the $\mathcal{H}_\mu$ are the adiabatic corrections,

$$\mathcal{H}_\mu = \frac{1}{2}p_R^2 + \frac{1}{2R^2}(j_x^2 + j_y^2) + \frac{i}{\sqrt{2}R}\left(P_1^{-1} j_+ + P_1^{1} j_-\right) + P_z p_R + \frac{\mu}{2m_a} P_a^2 + \frac{\mu}{2m_b} P_b^2 . \tag{5-4}$$

The relativistic and magnetic corrections, $\mathcal{H}_\alpha$, are given in these body-fixed coordinates by Meath and Hirschfelder[20]. The last term,

$$\mathcal{H}_c = \mathcal{E}_c(R) = \frac{1}{2R^2}\left[J(J+1) - \Omega^2\right], \tag{5-5}$$

is the centrifugal potential[71]. It is just an additive constant in the electronic equation. It should be noted that it is the rotational energy of a symmetric top rather than that of a BO rigid rotator. This choice of the centrifugal potential is common in spectroscopy[24,33].

The effective electronic equation is most conveniently treated by perturbation theory. Both α^2 and μ^{-1} are small parameters, and the associated terms usually make only small contributions to $\mathcal{E}_j(R;\mathrm{eff})$. In fact, $\mathcal{H}_\alpha$ must be treated only to first order in α^2 because of the limitations of the Hamiltonian. And the derivatives with respect to R in p_R must be treated as perturbations to maintain only a parametric dependence of Ψ on R . If such a

perturbation expansion is made, the effective potential can be written as

$$\mathcal{E}_j(R;eff) = \mathcal{E}_{js}(R) + \alpha^2\mathcal{E}_{j\alpha}(R) + \mu^{-1}\mathcal{E}_{j\mu}(R) + \mu^{-2}\mathcal{E}_{j\mu\mu}(R) + \mu^{-1}\mathcal{E}_c(R). \tag{5-6}$$

All higher order terms are negligible in the Breit-Pauli approximation. The $\mathcal{E}_{js}(R)$ is the BO electronic energy obtained from the familiar electronic equation,

$$\mathcal{H}_s \psi_{js} = \mathcal{E}_{js}(R)\psi_{js} \tag{5-7}$$

where j labels the state and s stands for "static". The relativistic and magnetic contribution, $\mathcal{E}_{j\alpha}$, is

$$\mathcal{E}_{j\alpha}(R) = \langle \psi_{js} | \mathcal{H}_\alpha | \psi_{js} \rangle. \tag{5-8}$$

The first order adiabatic correction, $\mathcal{E}_{j\mu}$, is

$$\mathcal{E}_{j\mu}(R) = \langle \psi_{js} | \mathcal{H}_\mu | \psi_{js} \rangle, \tag{5-9}$$

and except at crossing points where $\mathcal{E}_{j6}(R)$ is degenerate, the second order adiabatic correction, $\mathcal{E}_{j\mu\mu}(R)$ is

$$\mathcal{E}_{j\mu\mu}(R) = -\sum_{i}{}' \frac{\langle \psi_{js} | \mathcal{H}_\mu | \psi_{is} \rangle \langle \psi_{is} | \mathcal{H}_\mu | \psi_{js} \rangle}{\mathcal{E}_{is}(R) - \mathcal{E}_{js}(R)} . \qquad (5\text{-}10)$$

The prime on the sum implies that the term i = j is omitted.

The sum in (5-10) involves only the electronic energy index i because $\mathcal{H}_e$ is diagonal in the good quantum numbers Ω , p , and $\mathcal{P}_e$. Hence, all the ψ_{is} involved have the same symmetries as ψ_{js} . For most systems and most values of R , the denominator in Eq. (5-9) is very large and $\mathcal{E}_{j\mu\mu}(R)$ negligible. However, when two BO potential energy curves $\mathcal{E}_{ks}(R)$ and $\mathcal{E}_{js}(R)$ involved in the sum come close together or cross, $\mathcal{E}_{j\mu\mu}(R)$ becomes very large, and the effective potential of Eq. (5-6) becomes undefined. In such a region one must treat the problem by degenerate perturbation theory[65,68]. Linear combinations ψ_{ks}' and ψ_{js}' of the degenerate wave functions ψ_{js} and ψ_{ks} are chosen which diagonalize $\mathcal{H}_\mu$. This procedure splits apart the degenerate energies and gives rise to the non-crossing rule[62]. Eq. (5-9) can be shown to still be the appropriate second order energy except that now ψ_{js}' appears in place of ψ_{js} and $l = k$ is also omitted from the sum. The problems associated with these almost crossings have been investigated in detail[29-31] and are not treated in this work.

Because $\mathcal{E}_{j\mu\mu}(R)$ is small except near crossing points of potentials, it will generally be neglected throughout the rest of this paper. However, two points about it should be noted. Firstly, it is of about the same order of magnitude as the nonadiabatic

corrections, $U_j^{nad}(R)$, of Eq. (4-22 and 25), and one should not calculate $U_j^{nad}(R)$ without at least estimating $\mathcal{E}_{j\mu\mu}(R)$. This has not always been done[6]. Secondly, $\mathcal{E}_{j\mu\mu}(R)$ is an adiabatic correction since Eq. (5-1) involves only one adiabatic electronic function, but it could also be considered a nonadiabatic correction in the sense that it involves many BO wavefunctions.

When $\mathcal{E}_{j\mu\mu}(R)$ is neglected, all that is needed to obtain the first order corrections is the BO electronic wavefunction.

B. Perturbation Treatment for Large R .

Once the BO electronic wavefunctions and energies are obtained by any of the methods of molecular quantum mechanics, the evaluation of the above corrections is straightforward. To continue this discussion with some degree of generality, let us restrict the discussion to large R ; that is, let R be sufficiently large that the charge distributions of the two atoms do not overlap[72], but not large enough to involve the retardation[21] effects mentioned in Section I. A typical allowed range of R values would be

$$10a_0 \leq R \leq 350a_0 \quad .$$

For this range of R , the exchange of electrons[72] between the atoms can be neglected, and, in addition, the BO electronic Hamiltonian can be expanded in a power series in R^{-1} ,

$$\mathcal{H}_s = \sum_{n=0}^{\infty} R^{-n} \mathcal{H}_s^{(n)} , \tag{5-11}$$

where the zeroth order Hamiltonian, $\mathcal{H}_s^{(0)}$, is

$$\mathcal{H}_s^{(0)} = \mathcal{H}_s^{(0)}(a) + \mathcal{H}_s^{(0)}(b). \tag{5-12}$$

Here $\mathcal{H}_s^{(0)}(a)$ and $\mathcal{H}_s^{(0)}(b)$ are the nonrelativistic fixed-nucleus Hamiltonians of the isolated atoms. The higher terms in (5-11) are obtained from the two-center multipole expansion[73-75] of the electrostatic potential, V , of Eq. (A-3) and can be written as

$$\mathcal{H}_s^{(n)} = \sum_{\ell=0}^{n-1} \sum_{m=-\ell_<}^{\ell_<} G(n,\ell,m)\, \mathcal{M}_\ell^m(a)\, \mathcal{M}_{n-1-\ell}^{-m}(b) . \tag{5-13}$$

where $\ell_<$ is the lesser of ℓ and $n-1-\ell$, and

$$G(n,\ell,m) = 4\pi(-1)^{n-1-\ell}(n-1)!\left[(2\ell+1)(2n-2\ell-1)(\ell-m)!(\ell+m)!(n-1-\ell-m)!(n-1-\ell+m)!\right]^{-1/2}$$

The tensors $\mathcal{M}_\ell^m$ are the 2^ℓ -pole moments of the atoms

$$\mathcal{M}_\ell^m(a) = \sum_{i=0}^{N_a} Z_i\, r_{ia}^\ell\, Y_\ell^m(\theta_{ia},\varphi_{ia}), \quad \text{and} \tag{5-15}$$

$$\mathcal{M}_{n-1-\ell}^{-m}(b) = \sum_{j=N_a+1}^{N+1} Z_j\, r_{jb}^{n-1-\ell}\, Y_{n-1-\ell}^{-m}(\theta_{jb},\varphi_{jb}). \tag{5-16}$$

The Z_i are the charges of the particles. The particles 0 and N+1 in the sums are the nuclei a and b, respectively. These 0 and

N+1 terms in the sums only contribute to the monopoles of the atoms. This is because in the body-fixed separated atom coordinates (see Figure 2), the nuclei are at the centers of the atomic coordinate systems:

$$(r_{0a}, \theta_{0a}, \varphi_{0a}) = (r_{N+1,b}, \theta_{N+1,b}, \varphi_{N+1,b}) = (0,0,0).$$

There are problems associated with the convergence[76] and analyticity[77] of the expansion Eq. (5-11), but it is convenient and meaningful in the use made of it here.

We now treat Eq. (5-7) by perturbation theory, using R^{-1} as a natural perturbation parameter. Let us assume that

$$\psi_{js} = \sum_{n=0}^{\infty} R^{-n} \psi_{js}^{(n)}, \tag{5-17}$$

and that

$$\mathcal{E}_{js}(R) = \sum_{n=0}^{\infty} R^{-n} \mathcal{E}_{js}^{(n)}, \tag{5-18}$$

where the coefficients in these series are independent of R. Then, the relativistic and adiabatic corrections to the potential also take the form

$$\mathcal{E}_{j\mu}(R) = \sum_{n=0}^{\infty} R^{-n} \mathcal{E}_{j\mu}^{(n)}, \quad \text{and} \tag{5-19}$$

$$\mathcal{E}_{j\alpha}(R) = \sum_{n=0}^{\infty} R^{-n} \mathcal{E}_{j\alpha}^{(n)} . \tag{5-20}$$

We thus have an ordinary perturbation theory problem. The detailed formulas are derived in Appendix C for the Hamiltonian in the form (5-11). The general results and the problems with degeneracy are discussed in the following subsections.

C. The General Form of the Long Range Potentials for Neutral Atoms

1. Neutral Atoms

The discussion is now restricted to include only the interaction of two neutral atoms. The application to ion-ion and ion-atom interactions is straightforward and is omitted largely for lack of space. The static interactions of neutral atoms are smaller than those of ions, and the small corrections are expected to be relatively more important.

The charge or monopole, $\mathcal{M}_0^0$, of a neutral atom is zero. Thus, in Eq. (5-13) one has

$$\mathcal{H}_s^{(1)} = \mathcal{H}_s^{(2)} = 0 , \tag{5-21}$$

and its sum over ℓ only need run from $\ell = 1$ to $\ell = n-2$. From Eq. (5-21) it can be shown (see Appendix C) that

$$\psi_{js}^{(1)} = \psi_{js}^{(2)} = 0 . \tag{5-22}$$

Using this, we now give the general forms of the potential and corrections. Many of the terms listed will be shown to vanish in Section VI.

2. The Static Potential

The static or BO long-range potential is represented by Eq. (5-18), and the n=0 term is

$$\mathcal{E}_{js}^{(0)} = \mathcal{E}_{js}^{(0)}(a) + \mathcal{E}_{js}^{(0)}(b), \tag{5-23}$$

where $\mathcal{E}_{js}^{(0)}(a)$ is the energy of the separated atom a . The higher terms are given by Eq. (C-49),

$$\mathcal{E}_{js}^{(1)} = \mathcal{E}_{js}^{(2)} = 0, \tag{5-24}$$

$$\mathcal{E}_{js}^{(k)} = \langle \psi_{js}^{(0)} | \mathcal{H}_s^{(k)} | \psi_{js}^{(0)} \rangle, \quad k = 3, 4, \text{ or } 5, \tag{5-25}$$

$$\mathcal{E}_{js}^{(6)} = \langle \psi_{js}^{(0)} | \mathcal{H}_s^{(6)} | \psi_{js}^{(0)} \rangle + \langle \psi_{js}^{(0)} | \mathcal{H}_s^{(3)} | \psi_{js}^{(3)} \rangle. \tag{5-26}$$

Here $\mathcal{E}_{js}^{(6)}$ is the van der Waals energy. It is known to be non-zero and quite large. In the allowed range of R , it will dominate the following terms. Hence, we do not carry the expansion of $\mathcal{E}_{js}$ past $\mathcal{O}(R^{-6})$, and in particular, we do not keep any of the small correction terms past this order.

3. Relativistic Corrections to the Potential

The terms, $\mathcal{E}_{j\alpha}^{(n)}$, in the expansion (5-20) have been worked out in detail, together with their selection rules, by Meath and Hirschfelder[20]. Some of their results are used for a specific example in Section VII, but no details are presented here, and the relativistic corrections are entirely omitted from the discussion of Section VI.

4. Adiabatic Corrections to the Potential

Let us now consider the coefficients in Eq. (5-19). They give the first order adiabatic corrections to the Born-Oppenheimer potential. To discuss them it is convenient to split $\mathcal{H}_\mu$ in Eq. (5-4) into four parts according to the nature of the terms. Let

$$\mathcal{H}_\mu = \mathcal{H}_\mu(r) + \mathcal{H}_\mu(c) + \mathcal{H}_\mu(x) + \mathcal{H}_\mu(m), \tag{5-27}$$

where $\mathcal{H}_\mu(r)$ arises from the radial motion of the nuclei,

$$\mathcal{H}_\mu(r) = \frac{1}{2} p_R^2, \tag{5-28}$$

$\mathcal{H}_\mu(c)$ are corrections due to the centrifugal motion of the nuclei,

$$\mathcal{H}_\mu(c) = \frac{1}{2R^2}\left(\mathcal{J}_x^2 + \mathcal{J}_y^2\right) = \frac{1}{2R^2}\left(\mathcal{J}^2 - \Omega^2\right), \tag{5-29}$$

$\mathcal{H}_\mu(m)$ contains the atomic mass polarization corrections,

$$\mathcal{H}_\mu(m) = \frac{\mu}{2m_a} P_a^2 + \frac{\mu}{2m_b} P_b^2 , \tag{5-30}$$

and $\mathcal{H}_\mu(x)$ arises from the nuclear-electronic cross derivatives,

$$\mathcal{H}_\mu(x) = \frac{i}{\sqrt{2}R}\left(P_1^{-1} j_+ + P_1^{1} j_-\right) + P_z p_R . \tag{5-31}$$

$\mathcal{H}_\mu(x)$ seems to be largely an artifact of the coordinate system and has rather limited physical significance. (See Appendix A, Eq. (A-48)). Use of Eq. (5-27) also splits up the adiabatic corrections to the potential in a similar fashion,

$$\mathcal{E}_{j\mu}(R) = \mathcal{E}_{j\mu}(R;r) + \mathcal{E}_{j\mu}(R;c) + \mathcal{E}_{j\mu}(R;x) + \mathcal{E}_{j\mu}(R;m), \tag{5-32}$$

and

$$\mathcal{E}_{j\mu}^{(n)} = \mathcal{E}_{j\mu}^{(n)}(r) + \mathcal{E}_{j\mu}^{(n)}(c) + \mathcal{E}_{j\mu}^{(n)}(x) + \mathcal{E}_{j\mu}^{(n)}(m). \tag{5-33}$$

This division makes it convenient to treat the corrections, and it also emphasizes the fact that they arise from the motion of the nuclei. They are corrections to the <u>effective</u> potential, not corrections to the usual static interatomic potential. Let us now consider the general R^{-1} dependence of each of the terms.

a. The mass polarization corrections.

The mass polarization correction, $\mathcal{H}_\mu(m)$ is independent of

R . Its R^{-1} expansion is just

$$\mathcal{H}_\mu(m) = \mathcal{H}_\mu^{(0)}(m). \tag{5-34}$$

From Eq. (C-50) the terms in Eq. (5-19) for $\mathcal{E}_{j\mu}(R', m)$ are

$$\mathcal{E}_{j\mu}^{(0)}(m) = \langle \Psi_{js}^{(0)} | \mathcal{H}_\mu^{(0)}(m) | \Psi_{js}^{(0)} \rangle, \tag{5-35}$$

$$\mathcal{E}_{j\mu}^{(1)}(m) = \mathcal{E}_{j\mu}^{(2)}(m) = 0, \tag{5-36}$$

$$\mathcal{E}_{j\mu}^{(k)}(m) = 2\mathrm{Re} \langle \Psi_{js}^{(k)} | \mathcal{H}_\mu^{(0)}(m) | \Psi_{js}^{(0)} \rangle, \quad k = 3, 4, 5, \tag{5-37}$$

$$\mathcal{E}_{j\mu}^{(6)}(m) = 2\mathrm{Re} \langle \Psi_{js}^{(6)} | \mathcal{H}_\mu^{(0)}(m) | \Psi_{js}^{(0)} \rangle + \langle \Psi_{js}^{(3)} | \mathcal{H}_\mu^{(0)}(m) | \Psi_{js}^{(3)} \rangle. \tag{5-38}$$

b. The corrections to the centrifugal potential.

The expansion in R^{-1} for $\mathcal{H}_\mu(c)$ also contains only one term,

$$\mathcal{H}_\mu^{(2)}(c) = \frac{1}{2}(\mathcal{J}^2 - \Omega^2). \tag{5-39}$$

And from Eq. (C-50) we obtain

$$\mathcal{E}_{j\mu}^{(k)}(c) = 0, \quad k = 0, 1, \tag{5-40}$$

$$\mathcal{E}^{(2)}_{j\mu}(c) = \langle \Psi^{(0)}_{js} | \mathcal{H}^{(2)}_{\mu}(c) | \Psi^{(0)}_{js} \rangle , \tag{5-41}$$

$$\mathcal{E}^{(k)}_{j\mu}(c) = 0, \quad k = 3, 4, \tag{5-42}$$

$$\mathcal{E}^{(n)}_{j\mu}(c) = 2\,\mathrm{Re}\, \langle \Psi^{(n-2)}_{js} | \mathcal{H}^{(2)}_{\mu}(c) | \Psi^{(0)}_{js} \rangle , \; n = 5, 6. \tag{5-43}$$

c. The radial motion potential.

The corrections due to the radial motion of the nuclei are

$$\mathcal{E}_{j\mu}(R;r) = \langle \Psi_{js} | -\frac{1}{2}\frac{\partial^2}{\partial R^2} - \frac{1}{R}\frac{\partial}{\partial R} | \Psi_{js} \rangle . \tag{5-44}$$

However, it is shown in Appendix D that the second integral vanishes for all R , and the first integral can be put into the simpler form,

$$\mathcal{E}_{j\mu}(R;r) = \frac{1}{2} \left\langle \frac{\partial \Psi_{js}}{\partial R} \middle| \frac{\partial \Psi_{js}}{\partial R} \right\rangle . \tag{5-45}$$

But with Eq. (5-22), this becomes

$$\mathcal{E}_{j\mu}(R;r) = \frac{9}{2} R^{-8} \langle \Psi^{(3)}_{js} | \Psi^{(3)}_{js} \rangle + \mathcal{O}(R^{-9}), \tag{5-46}$$

so that the lead term here will be of $\mathcal{O}(1/\mu R^8)$, in the effective potential. For all allowed large R values, this is negligible

compared to the $\mathcal{O}(R^{-6})$ term contributed by Eq. (5-26), notwithstanding Wu and Bhatia's[19] claims to the contrary.

d. The cross derivative corrections.

The correction due to the nuclear-electronic cross derivatives, $\mathcal{H}_\mu(X)$, can be written as

$$\mathcal{H}_\mu(X) = R^{-1}\mathcal{H}_\mu^{(1)}(X) + P_z p_R , \tag{5-47}$$

where

$$\mathcal{H}_\mu^{(1)}(X) = \frac{i}{\sqrt{2}}\left(P_1^{-1} j_+ + P_1^{1} j_-\right). \tag{5-48}$$

The terms in the expansion of $\mathcal{E}_{j\mu}(R;X)$ due to $\mathcal{H}_\mu^{(1)}(X)$ are obtained directly from (C-50). The second term here is

$$\langle \psi_{js} | P_z p_R | \psi_{js} \rangle = \frac{1}{i}\langle \psi_{js} | P_z \frac{\partial \psi_{js}}{\partial R} \rangle + \frac{1}{iR}\langle \psi_{js} | P_z | \psi_{js} \rangle . \tag{5-49}$$

The second integral vanishes for all R as shown in Appendix D. The expansion of the first integral is obtained by direct substitution of Eq. (5-17) and (5-22). Combining the result with the expansion obtained from Eq. (5-48), we obtain

$$\mathcal{E}^{(0)}_{j\mu}(x) = 0 , \tag{5-50}$$

$$\mathcal{E}^{(1)}_{j\mu}(x) = \langle \psi^{(0)}_{js} | \mathcal{H}^{(1)}_{\mu}(x) | \psi^{(0)}_{js} \rangle , \tag{5-51}$$

$$\mathcal{E}^{(2)}_{j\mu}(x) = \mathcal{E}^{(3)}_{j\mu}(x) = 0 , \tag{5-52}$$

$$\mathcal{E}^{(k)}_{j\mu}(x) = 2\mathrm{Re} \langle \psi^{(k-1)}_{js} | \mathcal{H}^{(1)}_{\mu}(x) | \psi^{(0)}_{js} \rangle + i(k-1) \langle \psi^{(0)}_{js} | P_z | \psi^{(k-1)}_{js} \rangle , \tag{5-53}$$

where k = 4, 5, and 6.

To obtain details and selection rules on all the above matrix elements one needs information about the wavefunctions. This problem is discussed next.

D. Degeneracy. Correct Zeroth-order Wavefunctions

1. Degeneracy

The degeneracies which occur in the electronic energy are not actually handled as simply as was indicated in connection with Eq. (5-10). The effective electronic equation (5-2) is a double perturbation problem, and when restricted to large R, it becomes a triple perturbation problem. Its zeroth order solutions are products of atomic wavefunctions and often highly degenerate. This

degeneracy can sharply limit the validity of the assumption of this section that the wavefunctions and energies could all be expanded in a triple series of the form,

$$\psi_j = \sum_{n,\ell,m=0}^{\infty} R^{-n} \mu^{-\ell} \alpha^{2m} \psi_j^{(n,\ell,m)} . \tag{5-54}$$

The perturbation theory of the behavior of a <u>singly</u> perturbed degenerate level is complicated but well developed[65,78,79]. But the treatment of <u>more than one</u> perturbation of a degenerate level is much more difficult. The major problem is that an expansion of the form (5-54) is not possible unless there exists a set of degenerate zeroth-order wavefunctions which simultaneously diagonalizes all the perturbations. That is, one must have $\psi_{is}^{(0)}$ such that

$$\langle \psi_{is}^{(0)} | H_q^{(k)} | \psi_{js}^{(0)} \rangle = \text{Const.}\ \delta_{ij} , \tag{5-55}$$

where i and j belong to the degenerate set. This must hold for the low orders of k and for q=s, μ or α . As Hirschfelder, Byers Brown, and Epstein[73] pointed out, this is usually not possible. If it is not possible, then one cannot make the simultaneous expansion (5-54) but must group the perturbations together and treat their sum as a single perturbation.

The perturbations involved in this treatment of the effective electronic equation are not in general simultaneously diagonalizable. In particular, the spin-orbit coupling terms of the separated atoms

in $\mathcal{H}_\alpha^{(0)}$, the corrections to the centrifugal potential, $\mathcal{H}_\mu^{(2)}(c)$ and some of the multipole moments $\mathcal{H}_s^{(n)}$, are not always simultaneously diagonalizable. However, for any given value of R , the perturbations usually differ widely in magnitude. If so, the problem can be treated by diagonalizing the perturbations in the order of their size, each perturbation being diagonalized only on the subsets left degenerate by the larger perturbations. If such a procedure is followed, the largest perturbation can be treated in higher order, but any perturbation which is not diagonal on the whole degenerate set cannot be treated in higher than first order. We assume that such a procedure is adequate and has been carried out on the systems treated here. Chang[80] has made a calculation of a long range potential at values of R for which the perturbations are the same size and cannot be treated separately.

Regardless of the way in which the perturbations must be treated, the correct zeroth order wavefunctions are always some linear combination of the original degenerate wavefunctions. We next write the zeroth order wavefunctions in the general form of a linear combination and show in Section VI that this is all that is needed to obtain the selection rules on the long range effective potential.

2. <u>The Zeroth-order Wavefunctions</u>

From Eq. (5-12) the zeroth-order equation is

$$\left(\mathcal{H}_s^{(0)} - \mathcal{E}_{js}^{(0)}\right)\psi_{js}^{(0)} = 0 , \tag{5-56}$$

where $\mathcal{H}_s^{(0)}$ consists of the nonrelativistic, fixed-nucleus Hamiltonians of the separated atoms,

$$\mathcal{H}_s^{(0)} = \mathcal{H}_s^{(0)}(a) + \mathcal{H}_s^{(0)}(b). \tag{5-57}$$

Eq. (5-56) is separable. For the values of R considered, electron exchange is negligible, and the equation has as solutions the products Φ of atomic eigenfunctions,

$$\Phi = \Upsilon(a)\,\Upsilon(b). \tag{5-58}$$

A complete set of the atomic wavefunctions, $\Upsilon(c)$, where c = a or b , is assumed known. The atomic wavefunctions are characterized by a set of quantum numbers,

$$\Upsilon(c) = \Upsilon(\mathbf{x}_{ic}, k_c, M_{L_c}, M_{S_c}), \tag{5-59}$$

where M_{L_c} and M_{S_c} are the (body-fixed) z components of the orbital and spin angular momenta, respectively, of atom c = a or b . The symbol k_c represents the set of quantum numbers,

$$k_c \equiv (n_c, p_c, L_c, S_c), \tag{5-60}$$

where L_c and S_c are the orbital and spin angular momenta, p_c is the parity of the atomic state, and n_c specifies the energy of the atom. The energy is assumed to be non-degenerate in k_c, and L_c and S_c are assumed to be good quantum numbers. This

restriction allows the treatment of almost any pair of atoms in any state. However, it excludes the very heavy atoms which must be treated by j-j coupling. But for such heavy atoms the Breit-Pauli Hamiltonian is not adequate, anyway. It also excludes the excited states of the hydrogen atom since they are degenerate in p_c and L_c. The procedure below could be extended to include excited hydrogen atoms by summing over L_c, and this problem has been treated by Dahler and Hirschfelder[72], but it is not convenient to include it here, and k_c is considered fixed.

The energies of these nonrelativistic atoms are degenerate in M_{L_c} and M_{S_c}. Hence, the product functions $\Phi = \gamma(a)\gamma(b)$ are g-fold degenerate, where

$$g = (2L_a+1)(2S_a+1)(2L_b+1)(2S_b+1), \tag{5-60}$$

and if the atoms are alike the total degeneracy may be 2 g.

The choice of quantum numbers in (5-59) corresponds to LS coupling in the atoms. Since the relativistic corrections, $\mathcal{H}_\alpha$, are included in the Hamiltonian, it is convenient to work with eigenfunctions $\phi(k_c, J_c, M_c)$ of the total atomic angular momentum, $\mathbf{J}_c = \mathbf{L}_c + \mathbf{S}_c$, with

$$\begin{aligned} \mathbf{J}_c^2\, \phi(c) &= J_c(J_c+1)\,\phi(c), \qquad \text{and} \\ (\mathbf{J}_c)_z\, \phi(c) &= M_c\, \phi(c). \end{aligned} \tag{5-61}$$

The functions $\phi(c)$ are easily constructed using projection operators[82], $\mathcal{O}_{J_c, M_c}$. It is convenient here to represent $\phi(c)$ by the sum,

$$\phi(x_{ic}, k_c, J_c, M_c) = \mathcal{O}_{J_c, M_c} \gamma(x_{ic}, k_c, M_{L_c}, M_{S_c})$$
$$= \sum_{M_{L_c} M_{S_c}} \langle \gamma(c) | \phi(c) \rangle \gamma(x_{ic}, k_c, M_{L_c}, M_{S_c}) . \tag{5-62}$$

From the initial set of $\gamma(c)$, this produces $\phi(c)$ having the J_c values,

$$J_c = |L_c - S_c|, \; |L_c - S_c| + 1, \; \cdots, \; L_c + S_c . \tag{5-63}$$

The products Φ^J of these functions ϕ ,

$$\Phi^J = \phi(x_{ia}, k_a, J_a, M_a) \, \phi(x_{ib}, k_b, J_b, M_b) , \tag{5-64}$$

are all still degenerate in the nonrelativistic equation (5-56) and can be used as the basic degenerate set.

The construction of the proper zeroth-order solutions is greatly simplified by projecting functions out of the Φ^J which are eigenfunctions of the exact constants of motion of the total effective electronic Hamiltonian, $\mathcal{H}_0$, of Eq. (5-2); namely, of J_z , $\bar{\sigma}_{yz}$, and $\bar{\mathcal{J}}_c$. However, at large R , $\mathcal{J}_c$ itself is not convenient to use, because as defined at Eq. (2-29) it has the effect of interchanging electrons between the two atoms,

$$\mathcal{I}_e \psi_j(\mathbf{x}_{1a}, \cdots \mathbf{x}_{N_a,a}, \mathbf{x}_{N_a+1,a}, \cdots \mathbf{x}_{N,b}) = \psi_j(-\mathbf{x}_{1b}, \cdots -\mathbf{x}_{N_a,b}, -\mathbf{x}_{N_a+1,a}, \cdots -\mathbf{x}_{N,a}). \tag{5-65}$$

But when $\mathcal{I}_e$ is applicable for a system of two neutral atoms, the atoms have equal numbers of electrons as well as identical nuclei. Instead of using $\mathcal{I}_e$ itself, we use a simpler operator; namely,

$$\bar{\mathcal{I}}_e = \mathcal{P}_{1,N_a+1} \times \mathcal{P}_{2,N_a+2} \cdots \times \mathcal{P}_{N_a,N} \, \mathcal{I}_e, \tag{5-66}$$

where the $\mathcal{P}_{ij}$ are electron exchange operators defined at Eq. (2-26). The product of the $\mathcal{P}_{ij}$ exchanges each electron in a with one in b. If ψ_j is the exact solution, it is clear that

$$\bar{\mathcal{I}}_e \psi_j = (-1)^{N_a+p_e} \psi_j. \tag{5-67}$$

The action of $\bar{\mathcal{I}}_e$ on the product Φ^J is

$$\bar{\mathcal{I}}_e \phi(\mathbf{x}_{ia}, k_a, J_a, M_a)\, \phi(\mathbf{x}_{jb}, k_b, J_b, M_b) = \phi(-\mathbf{x}_{jb}, k_a, J_a, M_a)\, \phi(-\mathbf{x}_{ia}, k_b, J_b, M_b),$$

$$= (-1)^{p_a+p_b} \phi(\mathbf{x}_{ia}, k_b, J_b, M_b)\, \phi(\mathbf{x}_{jb}, k_a, J_a, M_a). \tag{5-68}$$

Here p_a and p_b are the parities of the two atomic functions under atomic inversion. Thus, $\bar{I}_e$ essentially exchanges the <u>functions</u> or quantum numbers of the two atoms without exchanging the electrons. We will choose our correct zeroth order functions to satisfy Eq. (5-67) just as the exact solution does. The wavefunctions in (5-68) will usually be abbreviated and written in the form $\phi(c;d)$ where the first letter, c , represents the set of electronic coordinates centered on atom c and the second letter , d , represents the set of quantum numbers k_d , J_d amd M_d . Then, Eq. (5-68) becomes

$$\bar{I}_e\, \phi(a;a)\, \phi(b;b) = (-1)^{p_a+p_b}\, \phi(a;b)\, \phi(b;a) \tag{5-69}$$

The correct zeroth-order functions can now be constructed[82]. One starts with $\bar{\Phi}^J$ and applies successively the projection operators O_{J_z} , $\bar{O}_{\sigma_{4z}}$, and $\bar{O}_I$ to produce eigenfunctions of the good quantum numbers. On the subsets that still remain degenerate and incompletely specified one diagonalizes the perturbations in the order of their size until each wavefunction is uniquely specified. The resulting correct zeroth order wavefunctions can always be written in the form,

$$\Psi^{(0)}_{js}(\Omega,\bar{p},\bar{p}_e) = \sum_{J_a,J_b}\sum_{M_a,M_b} \langle \bar{O}_I\, \phi(a;a)\phi(b;b) | \Psi^{(0)}_{js} \rangle\, \bar{O}_I\, \phi(a;a)\, \phi(b;b)\,. \tag{5-70}$$

Here M_b is restricted to the values $M_b = \Omega - M_a$. The behavior under σ_{1z} restricts the values of the coefficients $\langle 1 \rangle$ in the sum. The sum over the J_a, J_b can take the values of Eq. (5-63) in general, but in many problems, it collapses to just one or two terms. One obtains a solution of this form for each value over the interval,

$$-(L_a + S_a + L_b + S_b) \leq \Omega \leq (L_a + S_a + L_b + S_b), \tag{5-71}$$

and for each Ω value, j runs over the interval $1 \leq j \leq g_\Omega \leq g$, where g_Ω is the degeneracy of the Ω subset.

This general form (5-70) for the wavefunction also allows the inclusion of the LS coupling method. Substitution of Eq. (5-62) into (5-70) still leaves a sum of basically the same form as (5-70) over the LS products Φ .

It is convenient now to distinguish two cases. They will be discussed in Section VI.

<u>The "Resonant" Case</u>. This occurs for <u>like</u> atoms in states of <u>different</u> energies $(k_a \neq k_b)$. Then $\bar{O}_I$ is applied in (5-70), and after normalization the result can be written in the form

$$\psi^{(0)}_{js}(\Omega, \bar{p}, p_e) = \sum_{J_a, J_b} \sum_{M_a, M_b} \langle \sqrt{2}\, O_I\, \phi(a;a)\, \phi(b;b) \,|\, \psi^{(0)}_{js} \rangle \times$$

$$\frac{1}{\sqrt{2}} \left[\phi(a;a)\, \phi(b;b) + (-1)^{\delta}\, \phi(a;b)\, \phi(b;a) \right], \tag{5-72}$$

where $q = p_a + p_b + N_a + p_e$, and the state is labeled g or u as p_e is even or odd. The true case of resonant interatomic forces is a subcase of this.

The "Non-resonant" Case. This occurs for unlike atoms in any states, or like atoms in states of the same energy ($k_a = k_b$) . In this case the $\bar{O}_I$ is omitted from Eq. (5-70) because even if the atoms are alike, $\bar{O}_I$ is redundant; the sum already contains the terms $\bar{O}_I$ produces.

Finally, from the orthonormality of the atomic eigenfunctions and of the correct zeroth-order functions, it is clear that the coefficients in Eq. (5-70) and (5-72) form a unitary matrix,

$$\delta_{ij}\,\delta_{\Omega\Omega'}\,\delta_{\bar{p}\bar{p}'}\,\delta_{\bar{p}_e\bar{p}_e'} = \sum_{J_a,J_b}\sum_{M_a,M_b} \langle \sqrt{2}\,O_I\,\phi(a;a)\phi(b;b)\,|\,\psi_{js}(\Omega',\bar{p}',\bar{p}_e')\rangle^* \times$$

$$\langle \sqrt{2}\,O_I\,\phi(a;a)\,\phi(b;b)\,|\,\psi_{is}(\Omega,\bar{p},\bar{p}_e)\rangle . \tag{5-73}$$

3. Higher Order Wavefunctions

The wavefunctions $\psi_{js}^{(n)}$ for n = 3, 4, and 5 are solutions of "first-order" type equations from (C-47). They can be expressed in spectral expansions[65,68] over the complete set of atomic wavefunctions, $\{\psi_{js}^{(0)}(\Omega),\ \Phi_{\ell>q}^{J}\}$. The $\Phi_{\ell>q}^{J}$ are products in the form of (5-64), and $\ell>q$ implies that the set includes all such products not belonging to the degenerate set. The expansion of the "first order"

solutions can then be written in the form,

$$\Psi_{js}^{(n)}(\Omega,\bar{p},\bar{p}_e) = \sum_{k}^{g\Omega}{}' \left\langle \Psi_{ks}^{(0)}(\Omega,\bar{p},\bar{p}_e) \middle| \Psi_{js}^{(n)}(\Omega,\bar{p},\bar{p}_e) \right\rangle \Psi_{ks}^{(0)} -$$

$$\sum_{\ell>g} \frac{\left\langle \Phi_\ell^J \middle| \mathcal{H}_s^{(n)} \middle| \Psi_{js}^{(0)}(\Omega,\bar{p},\bar{p}_e) \right\rangle \Phi_\ell^J}{\mathcal{E}_{\ell s}^{(0)} - \mathcal{E}_{js}^{(0)}} \, . \qquad (5\text{-}74)$$

The prime on the first sum implies omission of the $k = i$ term. The explicit forms of the coefficients $\left\langle \Psi_{ks}^{(0)} \middle| \Psi_{js}^{(n)} \right\rangle$ depend on the particular problem and are not needed to determine the selection rules in the next section.

The sixth-order wavefunction, $\Psi_{is}^{(6)}$, is only needed for one integral. It appears in Eq. (5-38), and its selection rules will be obtained without writing $\Psi_{is}^{(6)}$ out in any detail.