AN INTRODUCTION TO THE ELECTRONIC STRUCTURE OF MOLECULES

By

EVANGELOS THEODORE SKOUMBOURDIS

Bachelor of Science
Tennessee Technological University
Cookeville, Tennessee
1970

Bachelor of Science
Tennessee Technological University
Cookeville, Tennessee
1972

Master of Science
Tennessee Technological University
Cookeville, Tennessee
1974

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1982

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Thesis Approved:

Paul W. Westhaus
Thesis Adviser

Robert B. Kamm

Geoff M

John J. Hardin

Norman N. Durham
Dean of the Graduate College

PREFACE

This work is an exposition of the electronic structure of molecules. The ethane molecule is used throughout the thesis as an illustrative example to the theory. It is hoped that this work will be of use to biochemists at the beginning graduate level as well as for physics majors at the senior and graduate level.

I would like to express my deepest gratitude to my adviser, Dr. Paul Westhaus, for the many hours which he spent with me in writing out the details of this work.

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CHAPTER I

INTRODUCTION AND BACKGROUND

In this thesis we attempt to introduce the student to a number of concepts dealing with the structure of molecules. The audience is envisioned as advanced undergraduate students of physics and chemistry, as well as beginning graduate students in these fields. However, we hope our attempts at explaining the material might also be useful to students in related fields such as biochemistry. To this end we shall try to avoid the pitfalls of mathematical rigor and concentrate rather on the physical ideas that are necessary to interpret what, in a word, may be called molecular structure. In no way, however, is this a comprehensive treatment of such a broad and diversified subject. On the contrary, as a pedagogical device, we have decided to concentrate on a single molecule, ethane, explaining in some detail those concepts used in carrying out molecular structure calculations in the framework of modern quantum chemistry.

Below we shall summarize the topics to be covered in the chapters of this thesis. In writing them we had in mind the possibility that each might stand by itself even as it was part of the more unified picture of the entire work. Thus the student may want to concentrate his readings on a particular chapter, though we hope eventually he may find it rewarding to read the entire thesis. We shall assume that our reader is acquainted with the basic elements of quantum mechanics, having perhaps encountered them at the level of an undergraduate "modern physics" course. At the end of each chapter we shall provide a small bibliography for the student to "brush up" on some more elementary concepts which we shall necessarily have to presume and to "follow up" in greater detail some of the treatments which unfortunately we leave incomplete.

After summarizing the remaining chapters here, we shall make some remarks on the interpretations and mathematical framework of quantum theory. We must hasten to add that this will be our only attempt at presenting the interpretation scheme; for the most part our efforts are directed toward the calculational aspects of the problem. In this spirit the thesis is much more like a grammar textbook than a literary work.

To illustrate the concepts, we return again and again to a specific molecule, ethane, the chemical formula for which C_2H_6 indicates there are N=18 electrons about A=8 nuclear centers. Figure 1.1 presents a picture of ethane with the atomic nuclei labeled in accordance with the scheme we shall adopt throughout the thesis. Most generally, however, our derivations treat a collection of N electrons and A nuclei with charges -e and Z_a e, a=1,2,...,A respectively.

Chapter II formulates the problem of finding the stationary states of ethane in the so-called Born-Oppenheimer approximation. Here, we discuss the "separation" of the electronic and nuclear "motions" according to the traditional arguments of quantum chemistry. Emphasis shifts to focus upon the states of the nuclear motion as determined by the various "electronic potential energy" surfaces for ethane. Indeed, the concept of potential energy surface is important not only in chemical physics' contexts but also in biochemical problems of molecular conformations. Consequently, we devote some effort to introducing terminology generally

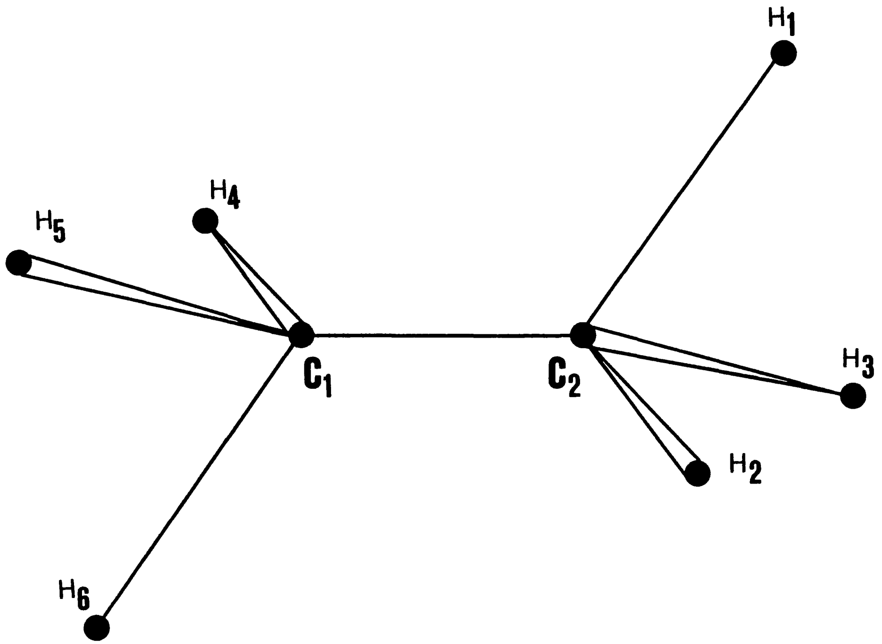

Figure 1.1. The Ethane Molecule

encountered in research papers on this subject. The numerical data used in the illustrations are, of course, specific to the well-studied ethane molecule. Among the topics discussed in Chapter II are configuration space, normal coordinates, and barriers of rotation. Both the classical picture of atomic nuclei rolling around on electronic potential energy surfaces subject to Newton's laws and the stationary state concept resulting from quantizing these nuclear motion degrees of freedom are presented. Then we turn to the problem of finding the electronic stationary states in Chapters III and V. Here, our cue is taken from the Rayleigh-Ritz variational principle which leads us eventually to detail discussions of self-consistent-field theory and configuration interaction. As preliminary groundwork, however, we discuss in Chapter III the notions of electronic orbitals and the exclusion principle in the context of an independent particle model of atoms. Some details pertaining to atomic and molecular orbitals are reserved for Appendix A. In Chapter IV we derive the closed shell Hartree-Fock equations for molecules. We indicate how they may be approximated in a finite dimensional space and formulated in terms of a matrix diagonalization problem. Finally, Chapter V applies the results to ethane, and in so doing introduces some of the common concepts and approximations used in quantum chemical calculations. In particular, the notions of group theory developed more fully in Appendices B and C are used to classify the orbitals and facilitate the matrix diagonalization.

Now clearly any one of the above chapters could become a thesis and indeed has so become many times over. Thus, it is without shame that we now inform our reader that our emphasis among these topics is not balanced. We have devoted our primary efforts to the electronic structure calculations presented in Chapters III through V. Hopefully, the reader will be able to overcome our bias by freely using the suggested bibliography which was compiled with our intended audience in mind. In all that follows, mathematical rigor is intentionally sacrificed for clarity and physical insight. However, our ultimate aim has been to reveal the practicality of quantum theory as a calculational tool, an aim which clearly must use mathematics. It might be useful to the reader to know that the inspiration for this thesis arose out of seeing the great diversity of applications of quantum physics in such complicated fields as biology and biochemistry. While we in no way begin to touch on such problems in this thesis, we hope it may be the introduction for some into this fascinating area of twenty-first century science.

As mentioned above, we propose to spend a little time now discussing the formal concepts (interpretations and mathematical framework) of quantum theory. In this spirit, it might be useful to back up just a bit and recall the classical ideas developed for describing the motion of particles. Allowing each particle to move in three dimensions, a collection of N particles has 3N degrees of freedom. At a given instant the dynamical state of any particle is completely specified by its position $\vec{r}$ and momentum $\vec{p}$. Thus, with the particle label $\alpha=1,2,\ldots,N$, the dynamical state of the N particle system is, at each instant, specified by a point $\{\vec{p}_1,\vec{r}_1,\ldots,\vec{p}_\alpha,\vec{r}_\alpha,\ldots,\vec{p}_N,\vec{r}_N\}$ in a 6N dimensional "phase space". As time goes on, the "system point" evolves along a trajectory in this phase space, with each such point along the trajectory yielding the exact instantaneous position and the momentum of each and every one of the N particles. The motion of the "system point" through phase space is governed by a formidable looking set of 6N coupled first order differential equations, Hamilton's equations. According to classical mechanics, one obtains the equations of motion (Goldstein, 1980, pp. 339-342)

$$\dot{p}_\lambda = - \frac{\partial H}{\partial q_\lambda} (p_1,p_2,\ldots,p_{3N},q_1,q_2,\ldots,q_{3N}), \tag{1.1}$$

$$\dot{q}_\lambda = \frac{\partial H}{\partial p_\lambda} (p_1,p_2,\ldots,p_{3N},q_1,q_2,\ldots,q_{3N}), \quad \lambda=1,2,\ldots,3N.$$

As usual, the dot indicates the time derivative. Here, the index λ runs over the 3N degrees of freedom, with each λ including the notions of both particle label $\alpha=1,2,\ldots,N$ and the Cartesian component x,y, or z.

It should be noted for instance, that the symbol p_λ plays a dual role; not only does it denote the time dependent function $p_\lambda(t)$ for the momentum of the λth degree of freedom, but it also labels the corresponding p axis in the 6N dimensional phase space. In fact, the Hamiltonian function appearing in (1.1)

$$H = \sum_{\alpha=1}^{N} \frac{p_{x_\alpha}^2 + p_{y_\alpha}^2 + p_{z_\alpha}^2}{2m_\alpha} + \sum_{1\leq\alpha<\beta\leq N} U(\vec{r}_\alpha,\vec{r}_\beta) \tag{1.2}$$

$$= \sum_{\lambda=1}^{3N} \frac{p_\lambda^2}{2m_\lambda} + U(q_1,q_2,\ldots,q_{3N})$$

is defined for all points in phase space, not simply along a trajectory of the system. In this expression for H (which, incidentally, is not its most general form), the first term is the sum of the kinetic energies of all N particles, while the second term is their mutual potential energy of interaction. For a collection of charged particles their interactions are dominated by the electrostatic Coulomb potential energy, and thus we write for the molecular Hamiltonian function

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m_e} + \sum_{a=1}^{A} \frac{\vec{p}_a^{\,2}}{2m_a} + \sum_{i=1}^{N} \sum_{a=1}^{A} \frac{-Z_a e^2}{|\vec{r}_i - \vec{r}_a|} \tag{1.3}$$

$$+ \sum_{1 \le i < j \le N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{1 \le a < b \le A} \frac{Z_a Z_b e^2}{|\vec{r}_a - \vec{r}_b|} .$$

The Latin letters i,j,k,... indicate electrons, while Latin letters a,b, c,... denote nuclei. Z_a is the atomic number of nucleus a while e is the electronic charge. We will use this notation throughout this thesis, and we reiterate that for our molecule of interest, ethane (C_2H_6), N=18, the number of electrons, and A=8, the number of nuclear centers. Gaussian units are used here. Solving Equation (1.1) as a set of 6N first order coupled differential equations includes 6N constants of integration which, in turn, may be specified in terms of the initial coordinates and momenta of the system point in phase space. Needless to say, the subsequent position in phase space of the system point depends not only on being able to solve the classical equations of motion (which presumably can be done, since this is "just" a mathematics problem), but also upon imposing the initial conditions (which implies measuring some initial values for all the p_λ's and q_λ's).

The parenthetical statements above are more significant than they may first appear, for it is in fact the physical impossibility of carrying out the measurement of the exact initial position in phase space which ultimately necessitates abandoning this classical description. It is indeed a real physical limitation imposed by nature itself--rather than, say, a technical infeasibility--which no longer allows the same completeness in our description of the dynamical state of the system as was envisioned in classical physics. We shall discuss this limitation more fully below. It is interesting to recall that it was another limitation on the measurement of the exact initial state of the system which led to the development of statistical mechanics, augmenting the developments of classical mechanics. In that case, the limitations arose (at least in classical physics) from the sheer size of the system, as N the number of particles became very large. Thus, as a practical matter it was simply infeasible to determine the precise initial state (a definite point in phase space) and this led Gibbs, among others, to see the necessity of averaging over all possible initial states consistent with our admittedly incomplete knowledge of the dynamical state of the classical system. In fact, classical statistical mechanics itself possesses some almost quasi-quantum mechanical insights: recall, for instance, the fact that with N identical particles, those N! different phase space points corresponding to simply relabeling the particles somehow ought not to be counted as different possible dynamical states. Thus, in a very real sense even identical classical particles possess some remnant of the ascribed quantum mechanical trait of indistinguishability. The point of this digression into what is admittedly not the scope of our undertaking, statistical mechanics, is to emphasize the importance of measurement as the basis of physical theory. Of course, it is not only in "preparing" the initial dynamical state of the system but also in subsequently "testing" it in order to verify the predictions of the formalism that measurement enters as the keystone of science. At the heart, then, of the classical dilemma is the real impossibility of verifying its predictions. The Heisenberg Uncertainty Principle states essentially that the "simultaneous" measurements of p_λ and q_λ--conjugate variables--is impossible. The better defined is the momentum p_λ the worse defined is the position q_λ.

Having made the point about measurements, we now regrettably inform the reader that we will not delve into the subject (which surely is at the very heart of appreciating quantum theory) but rather turn immediately to state more or less matter of factly the mathematical description and physical consequences of the impossibility of realizing the measurements envisioned by classical physics. First and foremost is the fact that phase space is no longer the proper medium for describing the quantized system. Indeed, the impossibility of assigning values to variables like q_λ and p_λ necessitates the introduction of mathematical entities called linear operators whose operands are functions--the so-called wavefunctions--in a multidimensional vector space. The operators do not commute in general with one another--the order in which two operate upon the wave functions is generally not interchangable. This non-commutativity of the operators is the mathematical framework leading to the impossibility of assigning definite values to all the variables at will. The interpretation given to some operators, called observables, and to the information they may abstract from the wave functions summarizes our understanding of the modern quantum theory of matter. The measurements and their possible outcomes will be depicted by the observables and their eigenvalues, while information about the state of the system, including predictions of the relative probability of various possible outcomes occuring, is contained in the wave functions. Our bibliography contains some of the more important works which pursue the formal consequences in terms of measurement theory.

Thus, formally in the quantum description of matter we speak of the variables q and p of classical phase space being replaced by operators which operate upon vectors in an infinite dimensional vector space. To be sure, we let

$$\begin{aligned} p_\lambda &\longrightarrow \hat{p}_\lambda, \quad q_\lambda \longrightarrow \hat{q}_\lambda; \\ \vec{p}_\alpha &\longrightarrow \hat{\vec{p}}_\alpha, \quad \vec{r}_\alpha \longrightarrow \hat{\vec{r}}_\alpha. \end{aligned} \tag{1.4}$$

Although the vectors $|\Psi\rangle$ (Dirac, 1978, pp. 14-22) may be defined abstractly in terms of their axiomatic properties, for our purposes we represent each vector by the traditional "wave function" $\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)$ of wave mechanics, a complex function defined over the 3N dimensional configuration space of the system (Merzbacher, 1976, pp. 294-307). The wavefunctions have the properties of "vectors" in a linear vector space $\mathcal{S}$. That is, if the complex functions Φ and χ are both elements in $\mathcal{S}$, then with α and β any two complex numbers the linear superposition

$$\Psi = \alpha\Phi + \beta\chi \tag{1.5}$$

is also an element of $\mathcal{S}$.

Moreover, we shall define an inner product on $\mathcal{S}$ as we associate with each ordered pair of complex functions, a complex number defined by the 3N-dimensional configuration space integral

$$(\Phi,\chi) = \int d\vec{r}_1 \int d\vec{r}_2 \ldots \int d\vec{r}_N \; \Phi^*(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)\,\chi\,(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t). \qquad (1.6)$$

This is simply a generalization of the scalar product encountered in introductory quantum mechanics. We recall some of the basic terminology found there. The "norm" of the wave function $\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)$ is the square root of the inner product of Ψ with itself:

$$||\Psi||^2 = (\Psi,\Psi) = \int d\vec{r}_1 \int d\vec{r}_2 \ldots \int d\vec{r}_N \; \Psi^*(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)\,\Psi\,(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t). \qquad (1.7)$$

The quantity $||\Psi||^2$ is clearly never negative and in fact vanishes only if $\Psi \equiv 0$. We are interested in vector spaces where $||\Psi||$ is finite, a so-called Hilbert space. Also from the scalar product definition we note that

$$([\alpha_1\Phi_1 + \alpha_2\Phi_2],[\beta_1\chi_1 + \beta_2\chi_2]) = \alpha_1^*\beta_1(\Phi_1,\chi_1) + \alpha_2^*\beta_1(\Phi_2,\chi_1) + \alpha_1^*\beta_2(\Phi_1,\chi_2) + \alpha_2^*\beta_2(\Phi_2,\chi_2). \qquad (1.8)$$

All these properties will be necessary in the standard interpretation of quantum mechanics.

Although the momentum and position operators can be defined abstractly by the commutation relationships

$$[\hat{q}_\lambda,\hat{p}_{\lambda'}] = i\hbar\,\delta_{\lambda\lambda'} \;, \qquad (1.9)$$

where "the commutator"

$$[\hat{A},\hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}, \tag{1.10}$$

in wave mechanics these operators may be represented by

$$\vec{p}_\alpha \longrightarrow \hat{\vec{p}}_\alpha = \frac{\hbar}{i}\vec{\nabla}_\alpha = \frac{\hbar}{i}[\hat{e}_x \frac{\partial}{\partial x_\alpha} + \hat{e}_y \frac{\partial}{\partial y_\alpha} + \hat{e}_z \frac{\partial}{\partial z_\alpha}] \tag{1.11}$$

and

$$\vec{r}_\alpha \longrightarrow \hat{\vec{r}}_\alpha = \vec{r}_\alpha = x_\alpha \hat{e}_x + y_\alpha \hat{e}_y + z_\alpha \hat{e}_z . \tag{1.12}$$

Clearly this representation of the momentum and position operators does satisfy the commutation relations in the spirit that for any wave function Ψ

$$[q_\lambda \frac{\hbar}{i} \frac{\partial}{\partial q_{\lambda'}} - \frac{\hbar}{i} \frac{\partial}{\partial q_{\lambda'}} q_\lambda]\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t) = i\hbar\, \delta_{\lambda\lambda'}\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t) . \tag{1.13}$$

The q_λ's and $\frac{\hbar}{i}\frac{\partial}{\partial q_\lambda}$'s are examples of linear operators. In general $\hat{A}$ is a linear operator if for all wavefunctions Φ and χ and complex numbers α and β

$$\hat{A}(\alpha\Phi + \beta\chi) = \alpha\hat{A}\Phi + \beta\hat{A}\chi . \tag{1.14}$$

Thus, the mathematics of quantum theory may be described as concerned with linear operators on a linear vector (function) space with a well-defined scalar product (Heisemberg, 1930, pp. 105-138).

Here, as in all non-relativistic physics, time plays the role of a parameter. It should be noted that the operators introduced here $\hat{q}_\lambda$ and $\hat{p}_\lambda$ are themselves time independent with all the time dependence carried by the wavefunction. This defines what is called the "Schrödinger Picture" of quantum mechanics. There are in fact other--indeed infinitely many other--ways of incorporating the time dependence into quantum theory, with the result that operators (and in general both operators and wave functions) may carry the time dependence of the system.

An observable is any operator which represents a property of the system which can be measured. According to the interpretation of quantum theory only the so-called "characteristic values" (proper values, or eigenvalues) of an observable may result from a measurement on the physical system. Mathematically, the characteristic values, or eigenvalues, are those numbers a_n for which there exist a corresponding function Ψ_n such that

$$\hat{A}\Psi_n = a_n\Psi_n . \tag{1.15}$$

Generally, there are many solutions (in fact infinitely many) to this eigenvalue problem. Here n indexes the linearly independent solutions (we have assumed they are denumerable) with the set of eigenvalues $\{a_n\}$ constituting the spectrum of $\hat{A}$. In general, a_n and $a_{n'}$ $(n \neq n')$ differ, but two or more a's may be equal whence we speak of their corresponding eigenfunctions as degenerate. Indeed, the set of eigensolutions $\{\Psi_n, a_n\}$ is, from the formal mathematical point of view, a complete characterization of the operator $\hat{A}$ itself. Now clearly, only real numbers result from measuring real properties of the system. Consequently, we require that the eigenvalues a_n of the observable $\hat{A}$ must be real. This in turn implies $\hat{A}$ is a Hermitian (self-adjoint) operator. Quite generally, the adjoint $\hat{B}^\dagger$ of the operator $\hat{B}$ is defined so that for all Φ and χ,

$$(\Phi,\hat{B}\chi) = (\hat{B}^\dagger\Phi,\chi). \tag{1.16}$$

Our conclusion that $\hat{A}$ an observable be Hermitian is then stated

$$\hat{A} = \hat{A}^\dagger. \tag{1.17}$$

It may easily be verified that the q_λ's and $\frac{\hbar}{i}\frac{\partial}{\partial q_\lambda}$'s are indeed Hermitian operators.

As in classical physics where other dynamical variables of the system could be constructed as functions of the phase space variables, so too here the observables of the quantum mechanical system are envisioned to be constructed as functions of the noncommuting operators $\hat{q}_\lambda$ and $\hat{p}_\lambda$. This noncommutativity, however, coupled with our subsequent interpretation requires that in constructing "analogous" functions for the classical dynamical variables, we take "symmetrized" combinations of the q and p . Thus, for instance, in order to insure a Hermitian operator we must replace

$$\vec{p}\cdot\vec{r} \longrightarrow \frac{1}{2}(\hat{\vec{p}}\cdot\hat{\vec{r}} + \hat{\vec{r}}\cdot\hat{\vec{p}}). \tag{1.18}$$

It is shown in quantum mechanics texts (Messiah, 1966, p. 199-202) that if two observables $\hat{A}$ and $\hat{B}$ commute (i.e., if their commutator is the null operator)

$$[\hat{A},\hat{B}] = \hat{0} \tag{1.19}$$

they have a common set of eigenfunctions. That is, there exists a set of eigenfunctions $\{\Psi_n\}$ satisfying

$$\hat{A}\Psi_n = a_n\Psi_n \tag{1.20}$$

and

$$\hat{B}\Psi_n = b_n\Psi_n . \tag{1.21}$$

Here, $\{a_n\}$ and $\{b_n\}$ constitute the spectrum of $\hat{A}$ and $\hat{B}$ respectively, with n enumerating all the linearly independent solutions Ψ_n. Indeed, this theorem can be extended to sets of three or more pairwise commuting operators, so that with

$$[\hat{A},\hat{B}]=\hat{0},[\hat{A},\hat{C}]=\hat{0},[\hat{B},\hat{C}]=\hat{0},\ldots,[\hat{A},\hat{G}]=\hat{0},\ldots,[\hat{F},\hat{G}]=\hat{0} \tag{1.22}$$

a set of simultaneous eigenfunctions may be found satisfying

$$\begin{aligned} \hat{A}\Psi_n &= a_n\Psi_n \\ \hat{B}\Psi_n &= b_n\Psi_n \\ &\vdots \\ \hat{G}\Psi_n &= g_n\Psi_n . \end{aligned} \tag{1.23}$$

If in fact there is no other observable which commutes with $\hat{A},\hat{B},\hat{C},\ldots,\hat{G}$, then they are said to form a complete set of observables. In turn this means that each eigenfunction Ψ_n corresponds to a unique set of eigenvalues. That is, the particular set of eigenvalues $a_n, b_n, c_n, \ldots, g_n$ does not occur with any other eigenfunction, say $\Psi_{n'}$ $(n \neq n')$; for if such were the case one could in fact find an additional operator to be included with $\hat{A}, \hat{B}, \hat{C}, \ldots, \hat{G}$. But the uniqueness of a set of eigenvalues of a complete set of commuting observables suggests that the eigenfunctions themselves be enumerated by these eigenvalues. Thus, we write

$$
\begin{aligned}
\hat{A}\, \Psi_{abc\ldots g}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) &= a\, \Psi_{abc\ldots g}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \\
\hat{B}\, \Psi_{abc\ldots g}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) &= b\, \Psi_{abc\ldots g}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \qquad (1.24) \\
&\vdots \\
\hat{G}\, \Psi_{abc\ldots g}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) &= g\, \Psi_{abc\ldots g}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N).
\end{aligned}
$$

The set of eigenfunctions $\{\Psi_{abc\ldots g}\}$ may be chosen orthonormal in that the inner product

$$
\begin{aligned}
(\Psi_{a'b'c'\ldots g'}, \Psi_{a''b''c''\ldots g''}) &= \int d\vec{r}_1 \int d\vec{r}_2 \ldots \int d\vec{r}_N \Psi^*_{a'b'\ldots g'}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \\
&\quad \Psi_{a''b''\ldots g''}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \delta_{a'a''}\, \delta_{b'b''}\, \delta_{c'c''} \ldots \delta_{g'g''}. \qquad (1.25)
\end{aligned}
$$

Here, the primes and double primes distinguish sets of eigenvalues and the Kronecker delta satisfies

$$
\delta_{k'k''} = \begin{cases} 0, & k' \neq k'' \\ 1, & k' = k'' \end{cases} . \qquad (1.26)
$$

The above prescription for constructing the time independent observables of the Schrödinger picture necessarily leads to time independent eigenfunctions.

A word about the spectra of the commuting observables is in order here. We have assumed that the spectrum of each observable is discrete--that is, the different eigenvalues of $\hat{A}$, for instance, form a countable set, $a', a'', a''', \ldots$. Thus each set of eigenvalues, $a', b', c', \ldots, g'$ can be indexed by a single integer. Indeed this notation is implied by our original enumeration of the eignefunctions with the index n, i.e., Ψ_n. In fact, the spectrum of an operator may include a continuous and so uncountable distribution of eigenvalues. Still the eigenfunctions, though they do not form a countable set, may be labeled with the eigenvalues. Some technical problems arise--the normalization must include the notion of Dirac delta functions as well as Kronecker deltas--but they may be handled with proper care (Messiah, 1966, pp. 178-184). The "sums" over the eigenvalue spectra must be replaced by integrals. Both in notation and spirit we will simply bypass these modifications.

The wave function $\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{t})$ evolves in time according to the Schrödinger equation of motion

$$\hat{H}\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) \tag{1.27}$$

where $\hat{H}$ is the Hamiltonian operator for the system. The fundamental problem of microscopic quantum mechanics is, given the initial (t=0) wave function $\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, 0)$, to integrate the quantum mechanical equation of motion (that is the Schrödinger equation) in order to find $\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t)$. All the information about the state of the system at time t is contained in the wave function $\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)$. Now we consider how this information is to be extracted from Ψ in order to predict the results of measurement.

A fundamental ansatz of quantum mechanics is that any normalizable wavefunction $\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)$ may be expanded in terms of the set of orthonormal eigenfunctions $\{\Psi_{abc\ldots g}\}$

$$\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t) = \sum_a \sum_b \cdots \sum_g C_{abc\ldots g}(t)\; \Psi_{abc\ldots g}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N). \quad (1.28)$$

Here, we have expanded the time dependent wavefunction for the system $\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)$ in terms of the set of time-independent eigenfunctions $\{\Psi_{abc\ldots g}\}$ of a complete set of commuting observables. The "expansion coefficients" $C_{abc\ldots g}(t)$ occurring in (1.28) are given by

$$C_{abc\ldots g}(t) = \int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_N\; \Psi^*_{abc\ldots g}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$
$$\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t). \quad (1.29)$$

This follows from the orthogonality of the complete set of eigenfunctions. In the terminology of vector spaces the eigenfunctions are "basis vectors" and the expansion coefficients "components". Thus at a given instant t we have resolved a vector (the wavefunction $\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)$) into a set of components (the $C_{abc\ldots g}(t)$'s, expansion coefficients) by choosing a specific basis $\{\Psi_{abc\ldots g}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)\}$. A different choice of a complete set of commuting observables--say $\{\hat{U},\hat{V},\hat{W},\ldots,\hat{Z}\}$--leads to a different orthonormal basis $\{\Psi_{uvw\ldots z}(\vec{r}_1,\vec{r}_2,\vec{r}_N)\}$ and thus a different resolution of a given wavefunction

$$\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t) = \sum_u \sum_v \sum_w \cdots \sum_z C_{uvw\ldots z}(t)\ \Psi_{uvw\ldots z}(\vec{r}_1,\ldots,\vec{r}_N). \qquad (1.28')$$

These mathematical properties of linear vector spaces lead to an interesting physical interpretation of the wave function in terms of measurements. For indeed we postulate that it is only the eigenvalues of operators which occur as the result of measurement and only commuting observables which can be measured simultaneously. Further the probability that the simultaneous measurements of $\hat{A},\hat{B},\hat{C},\ldots,\hat{G}$ will give the particular set of eigenvalues a,b,c,...g is

$$P_{abc\ldots g}(t) = |C_{abc\ldots g}(t)|^2. \qquad (1.30)$$

To illustrate the point about complete sets we consider a particle in an isotropic harmonic oscilator potential energy

$$V(\hat{x},\hat{y},\hat{z}) = \tfrac{1}{2}\, k\ (x^2 + y^2 + z^2). \qquad (1.31)$$

The Hamiltonian (which we call $\hat{H}_o$) is then

$$\hat{H}_o = -\frac{\hbar^2}{2m}\ \nabla^2 + V(\hat{x},\hat{y},\hat{z}). \qquad (1.32)$$

There is also a vector angular momentum operator which according to the above operator constructing prescription is

$$\hat{\vec{\ell}} = \hat{\vec{r}}\times\hat{\vec{p}} = \left\{\hat{e}_x\left(y\,\frac{\hbar}{i}\,\frac{\partial}{\partial z} - z\frac{\hbar}{i}\,\frac{\partial}{\partial y}\right) + \hat{e}_y\left(z\,\frac{\hbar}{i}\,\frac{\partial}{\partial x} - x\,\frac{\hbar}{i}\,\frac{\partial}{\partial z}\right) + \hat{e}_z\left(x\,\frac{\hbar}{i}\,\frac{\partial}{\partial y} - y\,\frac{\hbar}{i}\,\frac{\partial}{\partial z}\right)\right\}. \qquad (1.33)$$

We find that the components of $\hat{\vec{\ell}}$ do not commute; rather we obtain

$$[\hat{\ell}_x,\hat{\ell}_y] = i\hbar\hat{\ell}_z, \; [\hat{\ell}_y,\hat{\ell}_z] = i\hbar\hat{\ell}_x, \quad \text{and} \quad [\hat{\ell}_z,\hat{\ell}_x] = i\hbar\hat{\ell}_y. \tag{1.34}$$

On the other hand, each component $\hat{\ell}_x$, $\hat{\ell}_y$, $\hat{\ell}_z$ commutes with $\hat{H}_o$ and with

$$\hat{\ell}^2 = \hat{\ell}_x^2 + \hat{\ell}_y^2 + \hat{\ell}_z^2 \tag{1.35}$$

which itself commutes with $\hat{H}_o$. Thus $\hat{H}_o$, $\hat{\ell}^2$ and any one of the components of $\hat{\vec{\ell}}$ form a set of commuting observables. For instance $\{\hat{H}_o,\hat{\ell}^2,\hat{\ell}_z\}$ is a set of pairwise commuting observables as are $\{\hat{H}_o,\hat{\ell}^2,\hat{\ell}_x\}$ and $\{\hat{H}_o,\hat{\ell}^2,\hat{\ell}_y\}$. Using any of these three sets one shows (Messiah, 1966, pp. 451-454) that the three eigenvalue equations are satisfied by

$$\begin{aligned} \hat{H}_o\,\Psi_{n\ell m} &= (n + \tfrac{3}{2})\hbar\sqrt{k/m}\;\Psi_{n\ell m} \\ \hat{\ell}^2\,\Psi_{n\ell m} &= \ell(\ell + 1)\hbar^2\,\Psi_{n\ell m} \\ \hat{\ell}_i\,\Psi_{n\ell m} &= m\hbar\,\Psi_{n\ell m}, \quad (i = x, y, \text{or } z). \end{aligned} \tag{1.36}$$

The precise functional dependence of $\Psi_{n\ell m}$ on x,y,z depends on which of the three sets of commuting observables is used. Another notational development often used is shown here. Rather than the cumbersome eigenvalues, a set of numbers (the "quantum numbers") is used to index the eigenfunctions. The values of these quantum numbers found in this isotropic harmonic oscillator problem are restricted by a heirarchy of conditions; namely that while n may take on any integral value (n=0,1, 2...), ℓ must satisfy (ℓ=n,n-2,...,$\{^0_1\}$) for a given n $\{^{\text{even}}_{\text{odd}}\}$ and m, for a given n and ℓ may take on values ($m=-\ell,-\ell+1,\ldots,\ell-1,\ell$). A given triplet of quantum numbers $n\ell m$ thus labels each eigenstate.

Often, in order to simplify the notation, each set of eigenvalues abc...g is enumerated by the single index. Thus, reverting to the earlier scheme instead of (1.28) we write

$$\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)=\sum_n C_n(t)\ \Psi_n(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N). \tag{1.37}$$

However, the reader should keep in mind that the implied summation is over the spectra of sets of commuting observables as stated most explicitly in (1.28). In this notation, then, (1.29) becomes

$$C_n(t) = \int d\vec{r}_1 \int d\vec{r}_2 \ldots \int d\vec{r}_N\ \Psi_n^*(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)\ \Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t). \tag{1.38}$$

In carrying out the "fundamental problem" of evolving the wave function in time it often happens that the full Hamiltonian governing the evolution of the system can be expressed as the sum

$$\hat{H} = \hat{H}_o + \hat{V}(t). \tag{1.39}$$

Contrary to our above presumption we now allow $\hat{V}$ to be time-dependent. In fact, this time dependence arises from "degrees of freedom" of the entire system which are not quantized. Thus, while $\hat{H}_o$ and $\hat{V}$ do depend upon the $\hat{q}$'s and $\hat{p}$'s of the particles, there may be in addition other aspects of the problem which are still described classically. Perhaps the prototype of this situation is that of an electron in a harmonic oscillator well described quantum mechanically, interacting with a classically described electromagnetic field. With $\hat{H}_o$ given by (1.32), one finds that to a certain approximation

$$\hat{V}(t) = \frac{1}{2}(\hat{\vec{p}}\cdot\vec{A}(\hat{\vec{r}},t) + \vec{A}(\hat{\vec{r}},t)\cdot\hat{\vec{p}}). \tag{1.40}$$

Here $\hat{A}$ is the classical vector potential in which $\vec{r}$ is replaced by $\hat{\vec{r}}$. Nevertheless the field itself is described by the time-dependent amplitudes. In passing we remark that (1.40) is a good illustration of the symmetrization rule discussed above for constructing Schrödinger operators, albeit in this instance with the classical electromagnetic field, a time-dependent Schrödinger operator.

In carrying out the expansion (1.37) it is both mathematically convenient and formally significant to choose a set of commuting observables which include $\hat{H}_o$, the Hamiltonian of the isolated matter system. The formal significance arises from the fact that measurements (either directly or indirectly) focus upon the initial and final energy of the isolated system. Thus, in effect we prepare the system in an eigenstate of $\hat{H}_o$ (implying only one or, at worst, a very selective subset of the $C_n(0)$'s are non-zero) and measure the final state energy of the isolated atom and thereby collapsing the state function to a particular energy degenerate subspace. It is, of course,the intention of the theoretician to predict the relative probabilities that one state as opposed to another will be found by the final measurement. In the meantime it is the perturbation of the external electromagnetic field (as depicted by $\hat{V}(t)$) which is responsible (in the causal evolutionary sense) for the transition from the initially prepared state to the final state. To see the mathematical connotations we employ (1.39) in the Schrödinger equation (1.27) finding upon inserting the expansion (1.37)

$$\sum_n \{E_n C_n(t)\ \Psi_n + \hat{V}(t) C_n\ \Psi_n\} = \sum_n i\hbar \dot{C}_n(t)\ \Psi_n; \tag{1.41}$$

then after taking the inner product of both sides with $\Psi_{n'}$, we obtain

$$E_{n'} C_{n'} + \sum_n V_{n'n}(t) C_n(t) = i\hbar \dot{C}_{n'} \tag{1.42}$$

(for any and all states n'). Here we used our stipulation that $\hat{H}_o$ was one of the observables included in the complete set of commuting observables defining the orthonormal basis $\{\Psi_n\}$:

$$\hat{H}_o\ \Psi_n(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = E_n\ \Psi_n(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N). \tag{1.43}$$

The time-dependent matrix element is

$$V_{n'n}(t) = \int d\vec{r}_1 \int d\vec{r}_2 \ldots \int d\vec{r}_N\ \Psi^*_{n'}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)\hat{V}(t)\ \Psi_n\ (\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N). \tag{1.44}$$

This set of coupled first order differential equations (1.42) in time is in all respects equivalent to the original Schrödinger equation (1.27). Moreover, they may be cast into a most revealing form by letting

$$C_n(t) = \exp(-iE_n \frac{t}{\hbar}) a_n(t) \tag{1.45}$$

and noting that the $a_n(t)$'s satisfy a somewhat simpler appearing set of coupled equations:

$$\dot{a}_{n'}(t) = \sum_{n} V_{n'n}(t) \exp(i\omega_{n'n} t)\, a_n(t) \tag{1.46}$$

(for any and all n'). Here, we have defined the "transition frequency"

$$\omega_{n'n} = (E_{n'} - E_n)/\hbar \tag{1.47}$$

and point out that the initial conditions become

$$a_{n'}(0) = C_{n'}(0). \tag{1.48}$$

In fact if there were no external field, $\hat{V}(t) = \hat{0}$, then all the matrix elements $V_{n'n}(t)$ vanish, all $\dot{a}_n(t) = 0$, and so for all time t

$$a_n(t) = a_n(0) = C_n(0). \tag{1.49}$$

Then clearly the exact solution is

$$C_n(t) = \exp(-i\, E_n \frac{t}{\hbar})\, C_n(0). \tag{1.50}$$

Each coefficient simply oscillates sinusoidally in time with an amplitude proportional to its initial value. More to the point, we have

$$|C_n(t)|^2 = |C_n(0)|^2 \tag{1.51}$$

implying, not surprisingly, that no transitions occur. The eigenstates $\Psi_n(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ (where the complete set of observables includes $\hat{H}_o$) are called "stationary states".

A complete exposition of spectroscopy would surely include a detailed analysis of the time-dependent perturbation $\hat{V}(t)$ as well as a survey of the techniques for approximately solving the coupled set of equations (1.46). As we have indicated, however, the stationary states (the eigenstates of $\hat{H}_o$ as well as those additional pairwise commuting operators which also commute with $\hat{H}_o$) play a central role in this analysis. In this thesis our efforts are limited to obtaining, at least approximately, these stationary states for molecules. The bibliography does include some of the better explanations of the other topics.

Among the observables of importance in our discussion of molecules is the Hamiltonian operator obtained from that classical form found in (1.3) according to the above prescription:

$$\hat{H} = \sum_{i=1}^{N} \frac{-\hbar^2}{2m_e} \nabla_i^2 + \sum_{a=1}^{A} \frac{-\hbar^2}{2m_a} \nabla_a^2 + \sum_{i=1}^{N} \sum_{a=1}^{A} \frac{-Z_a e^2}{|\vec{r}_i - \vec{r}_a|} + \sum_{1\leq i<j\leq N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{1\leq a<b\leq A} \frac{Z_a Z_b e^2}{|\vec{r}_a - \vec{r}_b|} . \qquad (1.52)$$

In addition, the vector operator for the total orbital angular momentum of the system of N electrons and A nuclei

$$\hat{\vec{L}} = \sum_{i=1}^{N} \hat{\vec{\ell}}_i + \sum_{a=1}^{A} \hat{\vec{\ell}}_a = \sum_{i=1}^{N} \vec{r}_i \times \left(\frac{\hbar}{i} \vec{\nabla}_i\right) + \sum_{a=1}^{A} \vec{r}_a \times \left(\frac{\hbar}{i} \vec{\nabla}_a\right) \qquad (1.53)$$

also plays a central role. It follows from the commutation relations (1.34) that for the αth particle

$$[\hat{\ell}_{\alpha x}, \hat{\ell}_{\alpha y}] = i\hbar\hat{\ell}_{\alpha z},$$

$$[\hat{\ell}_{\alpha y},\hat{\ell}_{\alpha z}] = i\hbar\hat{\ell}_{\alpha x}, \text{ and} \tag{1.54}$$

$$[\hat{\ell}_{\alpha z},\hat{\ell}_{\alpha x}] = i\hbar\hat{\ell}_{\alpha y}.$$

Consequently with the stipulation that all operators belonging to degrees of freedom associated with different particles commute, it follows that

$$[\hat{L}_x,\hat{L}_y] = i\hbar\,\hat{L}_z$$

$$[\hat{L}_y,\hat{L}_z] = i\hbar\,\hat{L}_x, \text{ and} \tag{1.55}$$

$$[\hat{L}_z,\hat{L}_x] = i\hbar\,\hat{L}_y$$

In fact, relations (1.55) will serve as the definition of angular momentum operators. While the components of angular momentum do not commute among themselves, it is easily shown (again by using the commutation relations themselves) that all of the components commute with the operator for the square of the total orbital angular momentum

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 . \tag{1.56}$$

That is to say,

$$[\hat{L}^2,\hat{L}_x] = 0,\ [\hat{L}^2,\hat{L}_y] = 0, \text{ and } [\hat{L}^2,\hat{L}_z] = 0. \tag{1.57}$$

Now it may be shown that each component of the total orbital angular momentum operator of the system of electrons plus nuclei as well as $\hat{L}^2$ commutes with the Hamiltonian (1.52). Thus, we may, for example, include in a complete set of observables $\hat{L}^2$, $\hat{L}_z$ and $\hat{H}$.

Often models of atoms (A=1) treat only the electrons, fixing the nucleus at the origin to provide an "external" Coulomb field in which the electrons, also interacting with themselves via the Coulomb interaction, move. In such a model each component of the total orbital angular momentum for the N electrons themselves--i.e., considering only the first sum in Equation (1.53)--commutes with $\hat{L}^2$ for the electronic system and with the so-called electronic Hamiltonian,

$$\hat{H}_o = \sum_{i=1}^{N} \frac{-\hbar^2}{2m_e} \nabla_i^2 + \sum_{i=1}^{N} \frac{-Ze^2}{r_i} + \sum_{1\leq i<j\leq N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} . \tag{1.58}$$

We may simply envision in (1.52) the mass of the atomic nucleus to become infinite.

There are other "degrees of freedom" observed in quantum systems which have no classical analogue. The prototype of these degrees of freedom is the intrinsic spin (Tipler, 1968, pp. 301-305) of a particle. Thus, one is faced with the task of introducing Hermitian operators (observables) to describe these degrees of freedom in the quantum mechanical sense of predicting outcomes of measurements made with these observables. In fact, the intrinsic spin of an electron is described by a generalized angular momentum (vector) operator; that is, a set of three operators $\hat{s}_x$, $\hat{s}_y$, and $\hat{s}_z$ obeying the angular momentum commutation rules,

$$\begin{aligned} [\hat{s}_x,\hat{s}_y] &= i\hbar\ \hat{s}_z \\ [\hat{s}_y,\hat{s}_z] &= i\hbar\ \hat{s}_x \\ [\hat{s}_z,\hat{s}_x] &= i\hbar\ \hat{s}_y . \end{aligned} \tag{1.59}$$

Once again for an N-electron system we take the total electronic spin operators to be

$$\hat{S}_x = \sum_{i=1}^{N} \hat{s}_{ix}, \quad \hat{S}_y = \sum_{i=1}^{N} \hat{s}_{iy}, \quad \hat{S}_z = \sum_{i=1}^{N} \hat{s}_{iz}. \tag{1.60}$$

The nuclei also have an intrinsic spin. The spin of nucleus a is depicted by $\hat{\vec{s}}_a$, with

$$\begin{aligned} [\hat{s}_{ax}, \hat{s}_{ay}] &= i\hbar\, \hat{s}_{az} \\ [\hat{s}_{ay}, \hat{s}_{az}] &= i\hbar\, \hat{s}_{ax} \\ [\hat{s}_{az}, \hat{s}_{ax}] &= i\hbar\, \hat{s}_{ay}. \end{aligned} \tag{1.61}$$

One can define a spin operator for the total (N+A) particle system by

$$\hat{\vec{S}} = \sum_{i=1}^{N} \hat{\vec{s}}_i + \sum_{a=1}^{A} \hat{\vec{s}}_a \tag{1.62}$$

with all the generalized angular momentum relations holding for $\hat{\vec{S}}$.

The eigenvalue problem for spin operators (ignoring for the moment other degrees of freedom) is quite analogous to that for orbital angular momentum. The fact that any of the components commutes with the squared operator

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \tag{1.63}$$

implies that $\hat{S}^2$ and any one component have a common set of eigenvectors. Typically, we choose $\hat{S}^2$ and $\hat{S}_z$. It is found that

$$\hat{S}^2|S\ M_S\rangle = S(S+1)\hbar^2|S\ M_S\rangle \tag{1.64}$$

$$\hat{S}_z\ |S\ M_S\rangle = M_S\ \hbar|S\ M_S\rangle \tag{1.65}$$

where the possible values for the quantum number S are 0, 1/2, 3/2, 2,... and for a given S, M_S ranges from -S to +S in steps of unity:

$$-S \leq M_S \leq S. \tag{1.66}$$

It should be remarked that the eigenvalues of the orbital angular momentum operators may be found in a similar fashion, but additional restrictions on the wave function limit the corresponding values of L to integers (Winter, 1979, pp. 209-223).

For the moment we focus upon a single particle. The eigenstates of the single particle spin operator are limited to a particular choice of the quantum number s. For half-integral values of s, the particle is a fermion, while for integral values s the particle is termed a boson. The electron, for example, has an intrinsic spin of 1/2 (s=1/2) and is thus a fermion. Nuclei, on the other hand are composites of protons and neutrons (each of which has s=1/2), but from the point of view of atomic and molecular physics (that is our point of view) the "spin" of the nucleus will be the overall s value of the composite proton-neutron system. Typically, even number of protons and neutrons have a total spin of s=0, and an odd number of one type and an even number of the other type nucleon will give rise to an s=1/2 spin state. Thus, for example, the carbon 12 isotope has an intrinsic spin of s=0 while carbon 13 has s=1/2.

Aside from the dynamical interactions associated with spin, as is evidenced when placing charged particles in a magnetic field, there are what are termed statistical correlations (constraints) placed upon the wave functions for systems of identical particles. To be specific we might consider only the N-electron system itself. We may, for instance, imagine again the nucleus as simply a fixed force center providing an external Coulomb field in which the electrons move. More generally, any set of N particles all of which have the same intrinsic quantum properties like mass, charge, spin, constitutes a system of N identical particles. To investigate the "statistical correlations" of such a system, we first note that the configuration space of each particle must be extended from three to four-dimensions to include this intrinsic degree of freedom, spin. This discrete spin index takes on a finite set of values. For an electron, somewhat picturesquely, we might refer to this discrete configuration space label as spin "up" or spin "down". In any event, the configuration space variable for particle i is now to be understood as

$$x_i \longrightarrow \vec{r}_i \, \xi_i, \tag{1.67}$$

while the inner product now involves the sum over the values of the discrete spin index ξ as well as integration over the continuum of spatial variables

$$\int dx \longrightarrow \sum_{\xi} \int d\vec{r}. \tag{1.68}$$

In this spirit, the wave function is defined over the 4N-dimensional configuration space of an N-particle system.

Now, for N identical particles, the wave function

$$\Psi(x_1,x_2,\ldots,x_N;t) = \Psi(\vec{r}_1\xi_1,\vec{r}_2\xi_2,\ldots,\vec{r}_N\xi_N;t) \tag{1.69}$$

must be either totally symmetric or antisymmetric under the interchange of any pair of particles labels. Moreover, if the intrinsic spin of the individual particle is half-integral then the wave function must be antisymmetric under the interchange of any pair of particle labels; but if the intrinsic spin of the particles is integral, the wave function must be symmetric under the interchange of any pair of particle labels. Thus there is a connection between the intrinsic spin of an individual particle and the statistical correlation properties of the wavefunctions describing a collection of these identical particles. Once again the source of this restriction is our interpretation of quantum mechanics as the predictor of the outcome measurements on the system of particles. As such the wave function must include all our knowledge of the system, but must also reflect the limitations of that knowledge. In this instance, that limitation is the belief that identical particles are in fact indistinguishable in the sense of not allowing themselves to be subjected to any measurement which might be able to follow in time a specific one of the identical particles.

In our discussion of the electronic structure of molecules the facts introduced above are most important. Specifically, the requirement that the wavefunction describing a system of N electrons must be antisymmetric (Schiff, 1968, p. 364) under the interchange of particle labels severely restricts the allowed states of that system. Specifically, in Chapters III through V we will be seeking the so-called electronic eigenstates of a many-body Hamiltonian, making certain approximations along the way to compute at least approximately these states. However, at each level of approximation the antisymmetry requirement will be invoked, constraining us to approximations which reflect--at least to this extent--the nature of a system of N identical electrons. Perhaps, the reader is familiar already with the orbital Auf-Bau model in which a many electron system is "built up" by adding electrons, the state of each being described by its own individual wavefunction (orbital), but insuring that no two electrons "occupy" (i.e. their states are not described by) the same orbital. Thus, one says, in conformity with the so-called Pauli Exclusion Principle, that no more than one electron may "occupy" each orbital (Kramers, 1937, pp. 308-314). This is the way of incorporating the antisymmetry requirement into an orbital model of an atom.

We end this brief introduction into the principles of quantum mechanics and turn to the more specific problem of molecular structure. We list in our bibliography what we have found to be useful references in outlining these general principles. We assure the conscientious reader that many of these points require a lifetime of thought to be fully appreciated. Thus, if he now feels a little uneasy, we can only suggest that with the following chapters more concerned with specific techniques rather than abstract principles and interpretations, the usefulness of quantum mechanics may become more apparent.

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CHAPTER II

THE BORN-OPPENHEIMER APPROXIMATION AND MOLECULAR VIBRATIONS

Consider a molecule consisting of N electrons and A nuclei in relative motion to one another. We speak of the "degrees of freedom" of the system, recognizing that each particle can move in three dimensions as in classical physics. Generally, as mentioned in Chapter I, quantum particles have another, intrinsic degree of freedom called spin. Thus the configuration space of each particle is extended to four dimensions with the fourth coordinate denoted ξ. The coordinate ξ is discrete, taking on two possible values "spin up" or "spin down" for an electron. A point in the configuration space of each electron is specified by the values assigned three continuous $\vec{r} = (x,y,z)$ space and one discrete spin coordinate ξ. Thus a point in the configuration space of N electrons can be denoted by the set of 4N space and spin coordinates. We shall use the capital letter X_i to indicate collectively the space and spin coordinates of the ith electron: $X_i = x_i,y_i,z_i,\xi_i$. Similarly, for the A nuclei, we label the space and spin coordinates by $X_a = x_a,y_a,z_a$ and ξ_a, where a=1,2,...,A. The inner products which we encounter now imply a sum over the discrete spin coordinates and as well as an integration over all spatial coordinates $\vec{r}_i$ and $\vec{r}_a$.

Let $\hat{T}_e$ and $\hat{T}_n$ denote the kinetic energy operators of the electrons and nuclei, and $\hat{V}_{ee}$, $\hat{V}_{nn}$, $\hat{V}_{ne}$ denote the Coulomb potential energy operators for the electron-electron, nucleus-nucleus, and the nucleus-electron interactions respectively. Thus the Hamiltonian operator of the system is the sum of the five terms

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{ne}. \tag{2.1}$$

The mass of the ath nucleus will be denoted by M_a and the mass of each electron by m. In the wave mechanics formulation we write the kinetic energy operator of the electrons

$$\hat{T}_e = \sum_{i=1}^{N} \frac{-h^2}{2m} \nabla_i^2 = \sum_{i=1}^{N} \frac{-\hbar^2}{2m} [\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}]. \tag{2.2}$$

Similarly, the kinetic energy of the nuclei is

$$\hat{T}_n = \sum_{a=1}^{A} \frac{-h^2}{2M_a} \nabla_a^2 = \sum_{a=1}^{A} \frac{-\hbar^2}{2M_a} [\frac{\partial^2}{\partial x_a^2} + \frac{\partial^2}{\partial y_a^2} + \frac{\partial^2}{\partial z_a^2}] \tag{2.3}$$

The potential energy operators are

$$\hat{V}_{ee} = \sum_{1 \leq i < j \leq N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \tag{2.4}$$

where $\vec{r}_i$, $\vec{r}_j$ are the position vectors of the ith and jth electrons, $-e$ is the electron charge, and the sum $(i<j)$ is over all pairs of electrons;

$$\hat{V}_{nn} = \sum_{1 \leq a < b \leq A} \frac{Z_a Z_b e^2}{|\vec{r}_a - \vec{r}_b|}, \tag{2.5}$$

where Z_a, Z_b are the atomic numbers, and $\vec{r}_a$, $\vec{r}_b$ are the position vectors of the ath and the bth nucleus; and finally

$$\hat{V}_{ne} = \sum_{i=1}^{N} \sum_{a=1}^{A} \frac{-Z_a e^2}{|\vec{r}_i - \vec{r}_a|} . \tag{2.6}$$

We now come to the central problem of this thesis: we seek the stationary states, that is, all solutions to the eigenvalue problem

$$\hat{H} \Psi_\mu (\{X_i\},\{X_a\}) = E_\mu \Psi_\mu (\{X_i\},\{X_a\}). \tag{2.7}$$

Here, $\{X_i\}$ and $\{X_a\}$ denote collectively the electronic $X_1,X_2,\ldots,X_N$ and nuclear $X_1,X_2,\ldots,X_A$ space-spin coordinates respectively. $\Psi_\mu(\{X_i\},\{X_a\})$ is the many-body eigenstate labeled by μ, a collection of eigenvalues (or perhaps more simply quantum numbers) specifying the stationary state. E_μ is the energy found when the system is in the state $\Psi_\mu(\{X_i\},\{X_a\})$. As outlined in Chapter I, these stationary states are important in expanding the wave function of the molecule as it evolves, say, under the influence of an external electromagnetic field. In their own right these stationary states depict the static properties of various states of the isolated molecule. Finally, we must mention that the stationary state index μ contains, along with the eigenvalue E_μ, eigenvalues of other operators which commute with $\hat{H}$. By and large we shall not be concerned with these other operators at this point, but simply mention that they arise--at least in some approximate fashion--as we pursue the eigenvalue problem (2.7).

Ideally, we want the exact solutions to the eigenvalue problem; this requires solving a multidimensional partial differential equation which, because of the interactions between pairs of particles, is not separable. To make progress in obtaining at least approximations to these stationary states, we must turn from (2.8) as a strictly mathematical problem and incorporate physical ideas into a more tractable reformulation of the problem. In this instance, the simplifying feature for this system is the disparity in the masses of the electrons and nuclei, the ratio M/m ranging from about 2×10^3 to 5×10^5. At the same time, the Coulomb forces experienced by the electrons and nuclei are, by Newton's third law, comparable in magnitude. Consequently, from a classical viewpoint the motion of the nuclei should be much slower than the motion of the electrons. Thus to a good approximation we can treat the motions of the nuclei and the electrons separately: as the nuclei move slowly, the electrons, due to their mutual repulsions and the attractions of the nuclei, redistribute themselves fast enough so that, to a first approximation, they experience the nuclei as fixed force centers. In turn, the nuclei subsequently move subject to the electrical forces provided by their mutual repulsion and the new electronic charge distributions. Hopefully the eigenvalue problem (2.7) can be reformulated (approximately) to reflect these intuitive notions. Such a reformulation of the problem must provide a prescription for determining the wave functions depicting these electronic and nuclear "motions".

We will proceed with such a reformulation by substituting the Born-Oppenheimer ansatz (Gasiorowicz, 1974, pp. 313-326).

$$\Psi_\mu(\{X_i\},\{X_a\}) \cong \chi_{\ell;\Lambda}(\{X_a\})\ \Psi_\ell(\{\vec{r}_a\};\{X_i\}) \qquad (2.8)$$

into equation (2.7) realizing the "approximately equal sign $\cong$" is a hoped for result to be obtained with optimum choices for each factor. Here, our notion anticipates that the electronic factor $\Psi_\ell(\{\vec{r}_a\};\{X_i\})$ is parametrized by the nuclear positions $\vec{r}_a$, while the nuclear factor $\chi_{\ell;\Lambda}(\{X_a\})$ will depend on the "electronic state" ℓ. Each of the indices ℓ and Λ will represent a collection of quantum numbers specifying the "states" of the electrons and nuclei in the presence of the other. Shortly, we shall see how the parametrization of $\Psi_\ell(\{\vec{r}_a\};\{X_i\})$ arises and the significance of the new quantum numbers.

We consider applying the total molecular Hamiltonian to this form (2.8) for the "approximate eigenfunction". Although the Laplacian operator ∇_i^2 for the ith electron operates only upon the electronic factor $\Psi_\ell(\{\vec{r}_a\},\{X_i\})$, the Laplacian ∇_b^2 for the bth nucleus operates upon both the "nuclear" factor $\chi_{\ell;\Lambda}(\{X_a\})$ and, because of its parametric dependence on the $\vec{r}_a$'s, the "electronic" factor. Explicitly there are three terms

$$\nabla_b^2\left(\chi_{\ell;\Lambda}(\{X_a\})\Psi_\ell(\{\vec{r}_a\};\{X_i\})\right) = \nabla_b^2\left(\chi_{\ell;\Lambda}(\{X_a\})\right)\Psi_\ell(\{\vec{r}_a\};\{X_i\})$$

$$+ 2\vec{\nabla}_b\chi_{\ell;\Lambda}(\{X_a\})\cdot\vec{\nabla}_b\Psi_\ell(\{\vec{r}_a\};\{X_i\}) + \nabla_b^2\left(\Psi_\ell(\{\vec{r}_a\});\{X_i\})\right)\chi_{\ell;\Lambda}(\{X_a\}). \tag{2.9}$$

Neglecting the second and third terms and setting the resulting approximate expression for $\hat{H}\chi_{\ell;\Lambda}(\{X_a\})\Psi_\ell(\{\vec{r}_a\};\{X_i\})$ equal to $E_\mu\chi_{\ell;\Lambda}(\{X_a\})$ $\Psi_\ell(\{\vec{r}_a\};\{X_i\})$ so as to "enforce" the eigenvalue equation, we obtain

$$\Psi_\ell(\{\vec{r}_a\};\{X_i\})[\sum_{a=1}^{A}\frac{-\hbar^2}{2M_a}\nabla_a^2\chi_{\ell;\Lambda}(\{X_a\})] + [\{\sum_{i=1}^{N}\frac{-\hbar^2}{2m}\nabla_i^2 + \sum_{i=1}^{N}\sum_{a=1}^{A}\frac{-Z_a e^2}{|\vec{r}_i - \vec{r}_a|}$$

$$+ \sum_{1\le i<j\le N}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}\}\Psi_\ell(\{\vec{r}_a\};\{X_i\}) + \Psi_\ell(\{\vec{r}_a\};\{X_i\})\sum_{1\le a<b\le A}\frac{Z_a Z_b e^2}{|\vec{r}_a - \vec{r}_b|}]\chi_{\ell;\Lambda}(\{X_a\})$$

$$= E_\mu\Psi_\ell(\{\vec{r}_a\};\{X_i\})\chi_{\ell;\Lambda}(\{X_a\}). \tag{2.10}$$

We now notice that if the positions of the nuclei $\vec{r}_a$ were fixed in place and $\Psi_\ell(\vec{R}_a;X_i)$ were an eigenfunction of the electronic Hamiltonian operator, that is to say, if

$$\left[\sum_{i=1}^{N} \frac{-\hbar^2}{2m}\nabla_i^2 + \sum_{i=1}^{N}\sum_{a=1}^{A} \frac{-Z_a e^2}{|\vec{r}_i - \vec{R}_a|} + \sum_{1\leq i<j\leq N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}\right]\Psi_\ell(\{\vec{R}_a\};\{X_i\})$$

$$= E_\ell(\{\vec{R}_a\})\Psi_\ell(\{\vec{R}_a\};\{X_i\}), \tag{2.11}$$

where the fixed positions of the nuclei $\vec{R}_a \equiv \vec{r}_a$ are now treated as parameters, then the electronic wave function $\Psi_\ell(\{\vec{r}_a\};\{X_i\})$ would occur as a factor in equation (2.10) leaving us simply with

$$\Psi_\ell(\{\vec{r}_a\};\{X_i\})\Big[\sum_{a=1}^{A} \frac{-\hbar^2}{2M_a}\nabla_a^2\chi_{\ell;\Lambda}(\{X_a\}) + \Big\{E_\ell(\{\vec{r}_a\})$$

$$+ \sum_{1\leq a<b\leq A} \frac{Z_a Z_b e^2}{|\vec{r}_a - \vec{r}_b|}\Big\} - \mathcal{E}_\mu\Big]\,\chi_{\ell;\Lambda}(\{X_a\}) = 0. \tag{2.12}$$

This, in turn, implies that since $\Psi_\ell(\{\vec{r}_a\};\{X_i\})$ is not zero, $\chi_{\ell;\Lambda}(\{X_a\})$ is to be found as the solution to the nuclear motion eigenvalue problem

$$\left[\sum_{a=1}^{A} \frac{-\hbar^2}{2M_a}\nabla_a^2 + \Big\{E_\ell(\{\vec{r}_a\}) + \hat{V}_{nn}(\{\vec{r}_a\})\Big\} - \mathcal{E}_\mu\right]\chi_{\ell;\Lambda}(\{X_a\}) = 0. \tag{2.13}$$

To emphasize the fact that the nuclei have been "frozen" in place as we consider the electronic eigenvalue problem (2.11) we use capital letters $\vec{R}_a$ for the fixed nuclear positions.

Equation (2.13) may be written more concisely

$$[\sum_{a=1}^{A} \frac{-\hbar^2}{2M_a} \nabla_a^2 + U_\ell(\{\vec{r}_a\}) - E_\mu]\chi_{\ell;\Lambda}(\{X_a\}) = 0, \qquad (2.14)$$

where

$$U_\ell(\{\vec{r}_a\}) = E_\ell(\{\vec{r}_a\}) + \hat{V}_{nn}(\{\vec{r}_a\}). \qquad (2.15)$$

Here we see that $U_\ell(\{\vec{r}_a\})$ containing $E_\ell(\{\vec{r}_a\})$, an eigenvalue obtained in solving the electronic eigenvalue equation (2.11), plays the role of a potential energy operator for the subsequent motion of the nuclei. Thus, we see the significance of the indices ℓ and Λ: the index ℓ labels the electronic eigenstates obtained as solutions of equation (2.11) while for each ℓ, the index Λ distinguishes among the different nuclear motion eigenstates of equation (2.14). Each $U_\ell(\{\vec{r}_a\})$ provides an electronic "potential energy surface" in the configuration space of the nuclei. The $\chi_{\ell;\Lambda}(\{X_a\})$ are the nuclear eigenstates delineated by Λ on the ℓth surface.

The subsequent motion of the nuclei is then obtained for the stationary state by solving the nuclear eigenvalue problem (2.14). In fact, the nuclear motion problem is often treated classically with $U_\ell(\{\vec{r}_a\})$ considered the potential energy function used in Hamilton's equations (1.1). From this point of view the "massive" nuclei are classical particles following Hamiltonian trajectories in phase space. This approach has proven very fruitful in constructing what might be called a "semiclassical picture" of chemical reactions. Needless to say, these classical theories approximate quantum mechanics in the spirit of the correspondence principle. Our perspective, however, focuses exclusively on the quantum mechanical problem defined in terms of seeking the eigenstates of

(2.14).

We could consider the nuclear eigenvalue problem on any and all of these potential energy surfaces and so envision a set of approximate stationary states specified by the electronic quantum numbers (those which indexed the solutions of (2.11)) and nuclear quantum numbers (those associated with the solutions of (2.14) on the appropriate electronic potential energy surface). The set $\{\Psi_\ell(\{\vec{r}_a\};\{X_i\})\chi_{\ell;\Lambda}(\{\vec{r}_a\})\}$ is assumed complete in the sense that the most general molecular wave function may be expanded in terms of these functions. These so-called adiabatic states are not the exact eigenfunctions of $\hat{H}$. Shortly we shall see just what these nuclear quantum numbers may be, while the electronic problem is considered in detail in Chapters III-V. For now, let us simply make the point that with the entire procedure of separating the electronic and nuclear motions being approximate, one may obtain better approximations for the exact stationary states by treating the herethereto neglected coupling terms in equation (2.9) as a perturbation and proceding in the usual perturbation theory expansions based upon the adiabatic states obtained here as the so-called "unperturbed states". Such considerations are beyond the scope of our present discussion but are of real importance in looking at the details of molecular spectroscopy.

A few remarks about the potential energy surfaces of ethane are now in order. Recall that the configuration space of the nuclei (ignoring spin) is twenty-four dimensional; that is, each point is located by specifying the coordinates--three Cartesian coordinates, for example--of each of the eight atomic nuclei. We envision solving the electronic Schrödinger equation (2.11) for each such configuration and thereby obtaining a set of energy eigenvalues at each point in configuration space.

Moving from one configuration space point to another we generate a set of electronic energy surfaces. To be sure, there are only eighteen "internal" nuclear coordinates upon which the electronic potential energy could depend. For surely any rigid translation of the nuclei in space (in any of three independent directions) or any reorientation of the carbon-carbon bond in space (requiring two angles) or any rotation of the molecule about the carbon-carbon axis (through any arbitrary angle) must not affect the electronic energy of the system. Thus, we must anticipate that there are six directions in the twenty-four dimensional configuration space along which the electronic potential energy surface is "flat". In general there are, for a molecule with A nuclei, 3A-6 internal coordinates upon which the electronic energy depends and 6 ignorable coordinates.

It would be virtually impossible to convey all the information about all these electronic potential energy surfaces. Indeed, there are "infinitely many". Even just a few (say the ground state and the low-lying electronic exited states) of these multidimensional surfaces cannot be effectively plotted. Often a schematic presentation as in Figure 2.1 is sufficient to convey general information (such as symmetry and minimum energy) about the surfaces. In Figure 2.1 the darker curves $\ell=1$, $\ell=2$ indicate two electronic potential energy surfaces, while the lighter horizontal lines indicate the total energy of the quantum state labeled $\mu = \ell\Lambda$. But one should realize that the "configuration" coordinate R in this figure may stand for a whole collection of atomic coordinates. This point may be aptly illustrated by Figure 2.2a where the electronic ground state barrier of rotation curve is sketched. Ostensibly we envision one "umbrella" of hydrogen atoms (say H_1,H_2,H_3) rotated as in Figure 2.3 with respect to the other umbrella (say H_4,H_5,H_6). As indicated in Figure

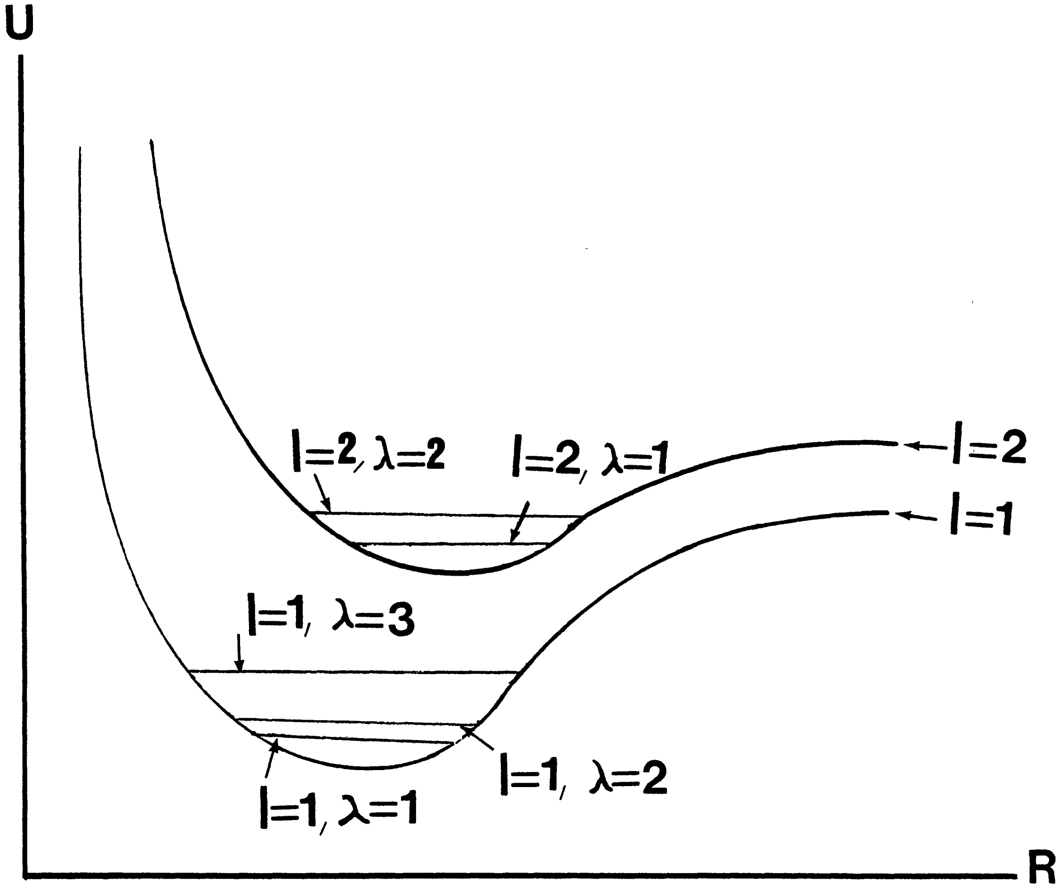

Figure 2.1. Schematic Presentation of Two Electronic Potential Energy Surfaces with Molecular States Indicated by Horizontal Lines as a Function of the "Configuration Coordinate" R

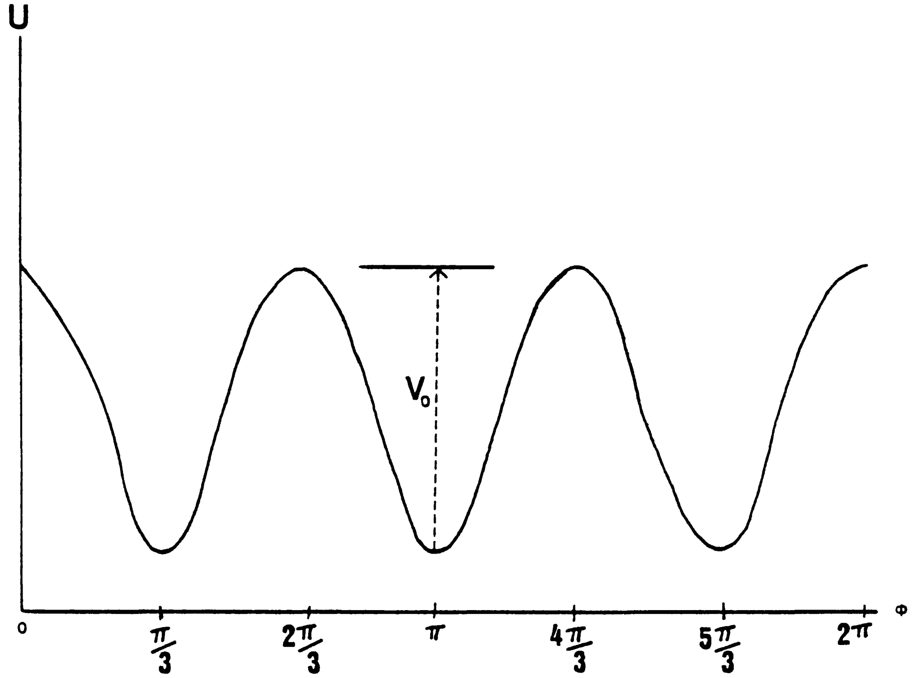

Figure 2.2a. Rotational Barrier in Ethane as a Function of the Dihedral Angle $\phi = H_1C_1C_2$, $H_5C_1C_2$

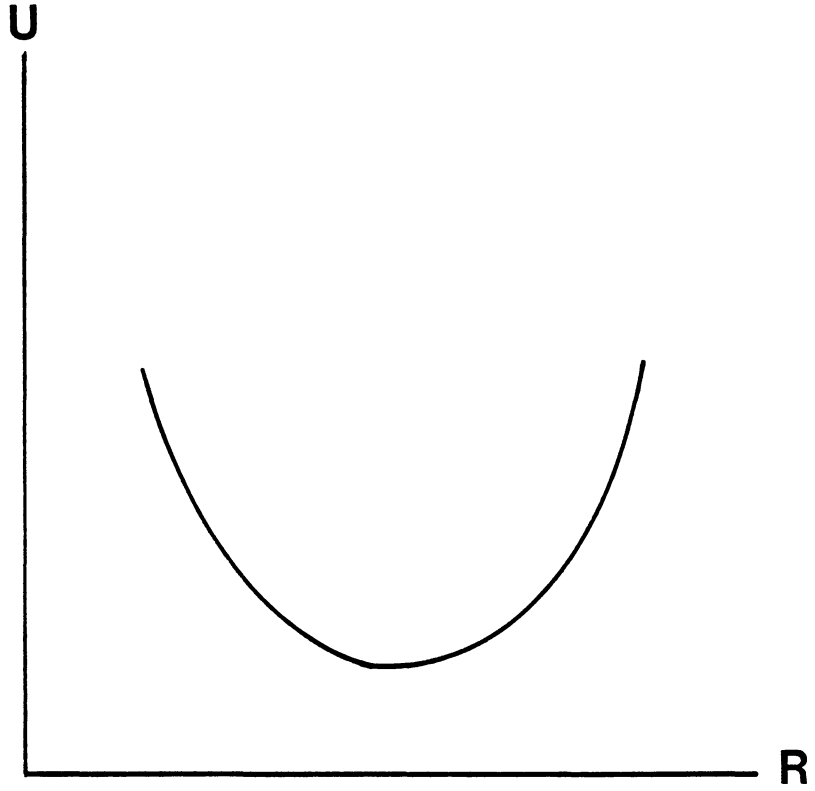

Figure 2.2b. Bond Energy as a Function of C-C Bond Length

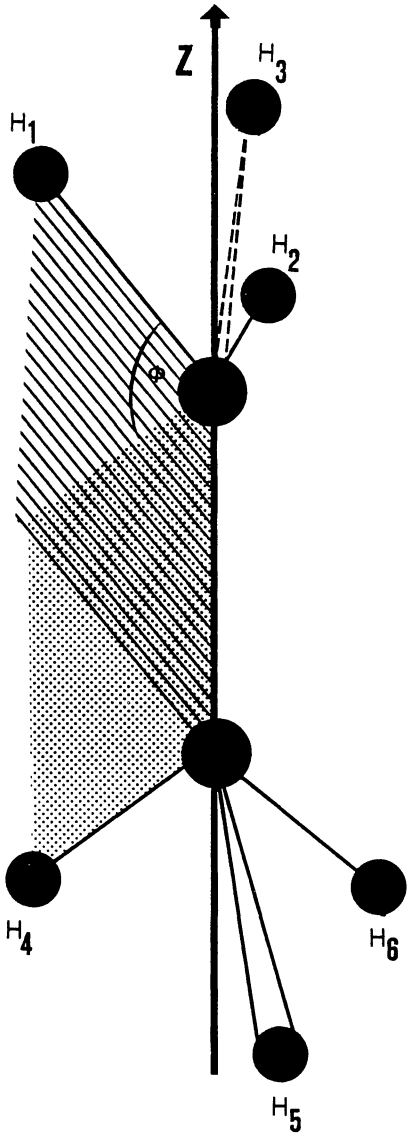

Figure 2.3. Dihedral Angle φ

2.2a, the energy increases as the umbrellas advance from the "staggered" to the "eclipsed" position. The curve could represent a cut of the ground state potential energy surface in which all the other geometrical parameters of ethane are fixed while only the dihedral angle between the two umbrellas is changed. On the other hand a similar curve (but not the identical curve by any means) can schematically represent the situation in which, as the dihedral angle ϕ is varied, the other geometrical parameters are allowed "to relax". For example the H-C-H angles and the C-C bond length may be reoptimized for each choice of ϕ so that the minimum electronic energy (for a given ϕ) is achieved. One might call the first curve in which the "configuration coordinate" is rigorously ϕ the "rigid geometry" case, while the second curve in which the "configuration coordinate" includes the notion of not only changing the dihedral angle but also relaxing the bond lengths the "optimized geometry" case.

In their electronic structure calculations, Clementi and Popkie (1972), obtain the results for the "barrier height" V_o listed in Table I for the "rigid" and "optimized" geometry cases. V_o is the energy differ-

TABLE I

BARRIERS OF ROTATION IN ETHANE

Geometry	R(C-C) (Å)	V_o(ev)
Rigid	1.2011	0.0206
Rigid	1.3450	0.0117
Rigid	1.5513	0.0054
Optimized	1.5511 (ϕ=60°) 1.5693 (ϕ=0°)	0.0052

ence, U(eclipsed) - U(staggered). Here the "rigid" C-H bond lengths and the fixed H-C-H face angles are those of the absolute minimum electronic energy (vide infra) obtained in D_{3d} symmetry. The "rigid geometry" calculations imply that only ϕ is changed in computing the barrier height. Three such calculations are presented in Table I for three choices of R_{CC}. The fourth entry in this table allows R_{CC} (as well as $\measuredangle$ H-C-H (not given)) to change as the umbrellas are rotated. The changes of these quantities upon optimizing are small. The salient point to be made here is that, in general, such changes must be understood in plotting schematically potential energy surfaces vs. the "configuration coordinate".

In the same vein we have also plotted in Figure 2.2b the ground state electronic potential energy as a function of the C-C bond length with ϕ=60°. Again this may be an actual cut on the potential energy surface if all the other geometrical parameters are fixed, or more generally it schematically gives the energy as some of the remaining parameters are optimized as R_{CC} is varied. Perhaps in this latter instance we should envision these schematic plots as "projections" (rather than cuts) of a path on the potential energy surface into the corresponding U-R_{CC} plane.

In fact, we will eventually illustrate our concepts using the ground electronic potential energy surface of ethane. Much of what follows is based upon intuition, but the reader may be assured of its ultimate correctness and rigor as evidenced by many years of successful application to this well-advanced field of spectroscopy. As we move from point to point in this twenty-four dimensional configuration space there is found a configuration of the atomic nuclei where the total electronic energy (including the nuclear repulsion terms) attains its lowest value. In fact, according to very sophisticated electronic structure calculations, this minimum electronic energy is obtained for the so-called "staggered" configuration of ethane (D_{3d} symmetry; $\phi=60°$ in Figure 2.3) with the geometry parameters (e.g., bond lengths and angles) given in Table II. It should be emphasized, of course, that these are indeed theoretical--i.e., calculated--values, since in reality there is no such entity as an electronic system with fixed nuclear coordinates. In fact, even at the classical level of picturing this molecule, we envision the nuclei as making small amplitude vibrations about this minimum energy position. We will find that, as in all such quantum phenomena, there is indeed a zero point motion which belies our thinking of the nuclei as fixed. At the same time, however, it is the existence of the calculated minimum of the electronic energy in the nuclear configuration space that points the way to a general analysis of the nuclear eigenvalue problem. In fact the nuclear motion eigenvalue problem is usually subject to further approximations resulting in the internal motion of the nuclei able to be described simply in terms of independent harmonic oscillators. Before presenting our ethane illustration we shall take up this approximation of treating the nuclear motion eigenvalue problem. The procedure commences by expanding the electronic potential energy as a function of the nuclear coordinates about the minimum point in configuration space.

Returning now to our general notation for a molecule with A nuclei we expand the electronic potential energy function $U_\ell(\{\vec{R}_a\})$ in a Taylor series about the minimum energy point $\{\vec{R}^\circ_a\}$ in configuration space. Although this procedure may be done for any electronic potential energy surface, we envision our attention focused on the ground state ($\ell=0$). Moreover to keep the notation simple, we omit the electronic state label

ℓ. Keeping only the quadratic terms and recalling the first derivative terms vanish, we need to evaluate the mixed second partial derivatives at the minimum energy point $\{\vec{R}^{o}_{a}\}$. Thus, we write

$$U(\ldots,x_{ai},\ldots) = U(x^{o}_{11},\ldots,x^{o}_{ai},\ldots)$$

$$+\frac{1}{2}\sum_{i=1}^{3}\sum_{a=1}^{A}\sum_{j=1}^{3}\sum_{b=1}^{A}\xi_{ai}\left[\frac{\partial^{2}U}{\partial x_{ai}\,\partial x_{bj}}\right]_{\{\vec{R}^{o}_{a}\}}\xi_{bj} \tag{2.16}$$

where the Cartesian displacement (from equilibrium) coordinates are

$$\xi_{ai} = x_{ai} - x^{o}_{ai}, \quad i=1,2,3;\ a=(1,2,\ldots,A). \tag{2.17}$$

TABLE II

BOND LENGTHS AND ANGLES FOR THE "STAGGERED" ETHANE MOLECULE

C-H (Å)	C-C (Å)	∢ H-C-H
1.093	1.534	109° 45'

The approximation (2.16) includes what will be termed "harmonic" forces for reasons which will be clear shortly. The neglected "anharmonic" terms, however, play a crucial role in such phenomena as energy migration. These are beyond the scope of this thesis. Our preceeding remarks, of course, suggest that the above expansion may be re-expressed in terms of just 3A-6 internal coordinates, rather than the 3A displacement coordinates introduced here. To see this, we now proceed by a rather standard, "brute force" method anticipating a more elegant approach to follow. We note that the potential energy and also the kinetic energy operators may be expressed as a bilinear form in the displacement coordinates and the partial derivatives with respect to the displacement coordinates respectively. Thus, it is that we have in matrix terms

$$U = U_o + \frac{1}{2} \underset{\sim}{\xi}^T \underset{\sim}{K} \underset{\sim}{\xi} \tag{2.18}$$

and

$$T = - \frac{\hbar^2}{2} \underset{\sim}{\nabla}_\xi^T \underset{\sim}{M}^{-1} \underset{\sim}{\nabla}_\xi . \tag{2.19}$$

The two column matrices are

$$\underset{\sim}{\xi} = \begin{bmatrix} \vdots \\ \xi_{ai} \\ \vdots \end{bmatrix} \quad \text{and} \quad \underset{\sim}{\nabla}_\xi = \begin{bmatrix} \vdots \\ \dfrac{\partial}{\partial \xi_{ai}} \\ \vdots \end{bmatrix} \tag{2.20}$$

while the symmetric "force constant" matrix is

$$\underset{\sim}{K} = \left[K_{ai\,bj} = \left(\frac{\partial^2 U}{\partial x_{ai} \partial x_{bj}}\right)\Bigg|_{\{\vec{R}^o_a\}} \right] \tag{2.21}$$

and the diagonal mass matrix is

$$\underset{\sim}{M} = [M_{ai\,bj} = M_a \delta_{ab} \delta_{ij}] . \tag{2.22}$$

Note that the row and column indices of these column (3A×1) or square (3A×3A) matrices contain both a nucleus a (a=1,2,...,A) and a Cartesian coordinate i (i=x,y,z). We envision the arrangement ai to follow dictionary order. $\underset{\sim}{M}^{-1}$ is the matrix with the reciprocals of the masses placed along the diagonal and likewise the real diagonal matrices $\underset{\sim}{M}^{\frac{1}{2}}$ and $\underset{\sim}{M}^{-\frac{1}{2}}$ have the corresponding mass factors in the appropriate places along the diagonal. With this in mind, we define the so-called mass weighted displacement coordinates

$$\underset{\sim}{\tau} = \underset{\sim}{M}^{\frac{1}{2}}\underset{\sim}{\xi} = \begin{bmatrix} \vdots \\ \sqrt{M_a}\ \xi_{ai} \\ \vdots \end{bmatrix} \tag{2.23}$$

and correspondingly

$$\underset{\sim}{\nabla}_{\tau} = \underset{\sim}{M}^{-\frac{1}{2}}\underset{\sim}{\nabla}_{\xi} = \begin{bmatrix} \vdots \\ \dfrac{1}{\sqrt{M_a}}\dfrac{\partial}{\partial \xi_{ai}} \\ \vdots \end{bmatrix} \tag{2.24}$$

so that now

$$U = U_o + \frac{1}{2}\underset{\sim}{\tau}^T \underset{\sim}{M}^{-\frac{1}{2}} \underset{\sim}{K} \underset{\sim}{M}^{-\frac{1}{2}} \underset{\sim}{\tau} \tag{2.25}$$

and

$$T = -\frac{\hbar^2}{2} \underset{\sim}{\nabla}_{\tau}^T \underset{\sim}{\nabla}_{\tau}. \tag{2.26}$$

Our purpose is now made clear upon recognizing that the real symmetric matrix $\underset{\sim}{M}^{-\frac{1}{2}}\ \underset{\sim}{K}\ \underset{\sim}{M}^{-\frac{1}{2}}$ may now be brought to diagonal form by an orthogonal transformation $\underset{\sim}{S}$ among the $\underset{\sim}{\tau}$ coordinates. Indeed, anticipating the choice of $\underset{\sim}{S}$ so that $\underset{\sim}{S}^{-1} = \underset{\sim}{S}^{T}$, we define the so-called normal coordinates

$$\underset{\sim}{\eta} = \underset{\sim}{S}^{-1}\ \underset{\sim}{\tau} \qquad (2.27)$$

and correspondingly the gradient matrix

$$\underset{\sim}{\nabla}_{\eta} = \underset{\sim}{S}\ \underset{\sim}{\nabla}_{\tau}. \qquad (2.28)$$

Then choosing the orthogonal transformation matrix $\underset{\sim}{S}$ to diagonalize $\underset{\sim}{M}^{-\frac{1}{2}}\ \underset{\sim}{K}\ \underset{\sim}{M}^{-\frac{1}{2}}$,

$$\underset{\sim}{S}^{T}\{\underset{\sim}{M}^{-\frac{1}{2}}\ \underset{\sim}{K}\ \underset{\sim}{M}^{-\frac{1}{2}}\}\underset{\sim}{S} = \underset{\sim}{\Omega}^{2}, \qquad (2.29)$$

we find that both the potential energy and the kinetic energy operators are diagonal quadratic forms in the normal coordinates. More to the point the Hamiltonian operator is "separable" in this normal mode representation. With λ indexing the normal modes we write

$$\mathcal{H} = \sum_{\lambda=1}^{3A} \left[\frac{1}{2}\left(\frac{\hbar}{i}\frac{\partial}{\partial\eta_{\lambda}}\right)^{2} + \frac{1}{2}\,\Omega_{\lambda}^{2}\,\eta_{\lambda}^{2}\right] + U_{o}. \qquad (2.30)$$

The normal mode index λ reflects the fact that any given normal mode involves the displacement of many (in general all) of the atoms and is not just a single nuclear displacement. On the other hand, the matrix $\underset{\sim}{S}$ clearly does not depend upon the coordinates themselves (since neither $\underset{\sim}{K}$

nor $\underset{\sim}{M}^{-\frac{1}{2}}$ does) and so each normal coordinate η_λ is simply linearly dependent upon the mass weighted Cartesian displacement coordinates τ_{ai}. Finally, as suggested by our discussion of the internal coordinates we must anticipate that six of the eigenvalues Ω_λ^2 vanish corresponding to the six ignorable rigid translations and rotations of the molecule which leave the 3A-6 internal coordinates unchanged. The normal coordinates corresponding to the non-zero frequencies may be expressed in terms of the 3A-6 internal coordinates. Often, we refer to 3A-6 "genuine" and 6 "non-genuine" normal modes. One may now proceed with the solution of (2.14) with the nuclear Hamiltonian approximated by (2.30): clearly the latter is the sum of Hamiltonians for simple (uncoupled) harmonic oscillators, whence the term "harmonic" approximation.

Before discussing the eigenstates of (2.30) let us mention the "elegant" formulation for classifying the normal modes alluded to previously in our discussion. This a priori classification of the normal modes is based upon the fact that there is a symmetry to the nuclear framework of the molecule in ordinary space. Such symmetry is most appropriately discussed in terms of group theory. Indeed, we will also find group theoretical arguments a most powerful tool in discussing electronic structure. Thus, we give a sketchy outline of its essential content in Appendices B and C. Here, we want in a more or less intuitive way to mention how the so-called irreducible representation of the symmetry group may be used to classify the normal modes. It is only the classification by symmetry that is obtained here; the details of the normal modes--e.g., the frequencies Ω_λ--are found only by considering the dynamics incorporated by the masses and force constants.

We return to the specific example of ethane. In its equilibrium (minimum energy) configuration the symmetry group of the ethane molecule is D_{3d}. A small but otherwise arbitrary displacement of the molecule in the twenty-four dimensional configuration space corresponds to such a displacement of each of the eight atoms in real space. Each such real-space displacement of the atoms might, for example, be represented by a set of eight vectors in three dimensional space indicating the relative magnitude and the direction of the displacement of each atom. In turn the displacement is able to be written for each of the eight atoms as the sum of three basis vectors with the appropriate amplitude coefficients. That is to say, we write an arbitrary displacement of the ethane molecule

$$\delta\vec{R} = \sum_{a=1}^{8} \sum_{i=1}^{3} \delta\xi_{ai}\, \hat{e}_{ai} \tag{2.31}$$

where the symbol "δ" is used to connote small amplitudes. The potential energy U, a function of the configuration space displacement $\delta\vec{R}$, depends not only on $\delta\xi_{ai}^2$ but crossterms like $\delta\xi_{ai} \cdot \delta\xi_{bj}$. Keeping this in mind, recall also that under certain operations in three dimensional space--the operations of the D_{3d} symmetry group--the molecule is brought into coincidence with itself. Consequently, the potential energy function must be invariant under these symmetry operations. However, the 24 atomic basis vectors $\{\hat{e}_{ai},\ a=1,2,\ldots,8;\ i=1,2,3\}$ transform among themselves under these symmetry operations according to reducible representations. The normal modes may be classified in terms of those linear combinations of atomic basis vectors which transform as irreducible representations of the symmetry group of the molecule. Indeed, with $\{\hat{e}_\lambda,\ \lambda=1,2,\ldots,24\}$ such a set of vectors, we may write

$$\delta\vec{R} = \sum_{\lambda} \delta\eta_{\lambda}\, \hat{e}_{\lambda} \tag{2.32}$$

where this time U depends only on the $\delta\eta_{\lambda}^{2}$.

Thus, beginning with a set of atomic displacements, we consider those combinations which transform as basis vectors for the irreducible representations of the symmetry group D_{3d}. Such a displacement of atoms in real physical space then corresponds to the displacement of the molecule along a single normal coordinate in configuration space. We need not limit ourselves to Cartesian displacements but, guided by our intuition, may begin with a set of unit displacement vectors which already contain some of the symmetry of the molecule. To that end, we consider the displacement vectors of the nuclei indicated in Figure 2.4. The displacement vectors of the two carbons are simply the Cartesian vectors defined by the coordinate axes at the center of the C-C bond. The displacement vectors of any of the six hydrogen atoms are those spherical polar vectors defined (as shown in the figure) with respect to the nearer carbon atom (in its equilibrium position) as origin, the C-C axis as the polar axis, and the C-H vector as the radius vector. The twenty-four vectors shown fall into five different sets, each of which is said to span a reducible representation:

$[\hat{e}_{C_{1z}}, \hat{e}_{C_{2z}}]$

$[\hat{e}_{C_{1x}}, \hat{e}_{C_{1y}}, \hat{e}_{C_{2x}}, \hat{e}_{C_{2y}}]$

$[\hat{e}_{H_{i\phi}}, i=1,2,\ldots,6]$

$[\hat{e}_{H_{i\theta}}, i=1,2,\ldots,6]$

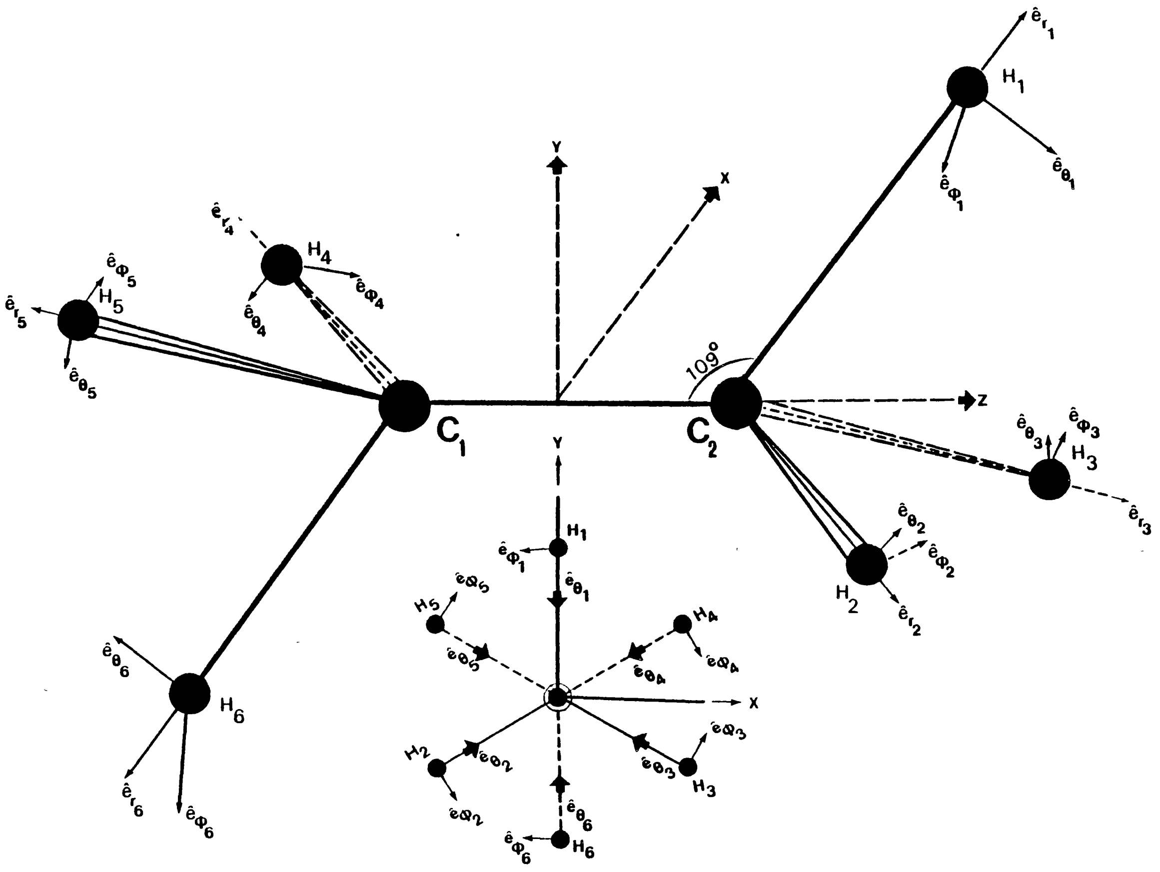

Figure 2.4. Displacement Vectors of the Nuclei in Ethane

$[\hat{e}_{H_{ir}}, i=1,2,\ldots,6]$.

Taking the results outlined in the appendix, the transformation properties of each of these sets of vectors may be fully delineated by a group of twelve matrices, each matrix depicting how the vectors in any one set transform among themselves under one of the twelve symmetry operations of the group D_{3d}. We have listed in Table III each of these sets of matrices; however, both $\{\hat{e}_{H_{ir}}\}$ and the $\{\hat{e}_{H_{i\theta}}\}$ vectors (i=1,2,..., 6) transform in exactly the same way, and thus the same set of twelve matrices describes the transformations ($\underset{\sim}{D}^{(\hat{\theta})}(R) = \underset{\sim}{D}^{(\hat{r})}(R)$) of each set of vectors. The problem of classifying the normal modes thus hinges upon being able to find the occurences of the irreducible representations contained in the reduction of these five reducible representations. We obtain by the scheme outlined in the Appendix B the number of occurences of each of the six irreducible representations in our five reducible representations. To this end we present Table IV listing according to classes the characters in the various irreducible representations, together with the characters of the five reducible representations. Carrying out the algebra given in equation (C.1) leads to the results presented in Table V, listing the sought-for occurrences. Clearly, the number of occurrences times the dimensionality of the irreducible representations must add up to twenty-four, the number of basis vectors in configuration space. In the language of group theory the 24 dimensional representation is reducible to the direct sum of the six irreducible representations with these occurrences. We write

$$\Gamma = 3A_{1g} \oplus 1A_{1u} \oplus 3A_{2u} \oplus 1A_{2g} \oplus 4E_g \oplus 4E_u . \qquad (2.33)$$

TABLE III

THE REDUCIBLE REPRESENTATIONS $\{\underset{\sim}{D}^{(\hat{z})}(R)\}$, $\{\underset{\sim}{D}^{(\hat{xy})}(R)\}$, $\{\underset{\sim}{D}^{(\hat{\phi})}(R)\}$, $\{\underset{\sim}{D}^{(\hat{\theta})}(R)\}$, $\{\underset{\sim}{D}^{(\hat{r})}(R)\}$

$\underset{\sim}{D}^{(\hat{z})}(R)$:

$$I: \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad C_3: \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad C_3^2: \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad C_2': \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

$$C_2'': \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \qquad C_2''' \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \qquad i: \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \qquad \sigma_d': \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\sigma_d'': \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \sigma_d''': \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad S_6: \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \qquad S_6': \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

$\underset{\sim}{D}^{(\hat{xy})}(R)$:

$$I: \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad C_3: \begin{pmatrix} -\frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{-\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \qquad C_3^2: \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{-\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{-\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

TABLE III (Continued)

$$C_2': \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \qquad C_2'': \begin{pmatrix} 0 & 0 & -\frac{1}{2} & \frac{-\sqrt{3}}{2} \\ 0 & 0 & \frac{-\sqrt{3}}{2} & \frac{1}{2} \\ -\frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 & 0 \\ \frac{-\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \end{pmatrix} \qquad C_2''': \begin{pmatrix} 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \end{pmatrix}$$

$$i: \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \qquad S_6: \begin{pmatrix} 0 & 0 & \frac{1}{2} & \frac{-\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \end{pmatrix} \qquad S_6': \begin{pmatrix} 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{-\sqrt{3}}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{-\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \end{pmatrix}$$

$$\sigma_d': \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \qquad \sigma_d'': \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \sigma_d''': \begin{pmatrix} \frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 & 0 \\ \frac{-\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & \frac{-\sqrt{3}}{2} \\ 0 & 0 & \frac{-\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

TABLE III (Continued)

$\underline{\underset{\sim}{D}^{(\hat{\phi})}(R)}$:

$$I: \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad C_3: \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \quad C_3^2: \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

$$C_2': \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad C_2'' \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \quad C_2''': \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$i: \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \sigma_d': \begin{pmatrix} 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & -1 & 0 \end{pmatrix} \quad \sigma_d'': \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}$$

TABLE III (Continued)

$$\sigma_d''': \begin{pmatrix} 0 & -1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \end{pmatrix} \quad S_6: \begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \end{pmatrix} \quad S_6': \begin{pmatrix} 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \end{pmatrix}$$

$\underset{\sim}{D}^{(\hat{r})}(R) = \underset{\sim}{D}^{(\hat{\theta})}(R)$:

$$I: \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad C_3: \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \quad C_3^2: \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

$$C_2': \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad C_2'': \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \quad C_2''': \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}$$

TABLE III (Continued)

$$i: \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \sigma'_d: \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \quad \sigma''_d: \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\sigma'''_d: \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix} \quad S_6: \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix} \quad S'_6: \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

TABLE IV

CHARACTER TABLE FOR IRREDUCIBLE AND REDUCIBLE REPRESENTATIONS

	I	$2S_6$	$2C_3$	i	$3C_2$	$3\sigma_d$
Class:						
	1	2	3	4	5	6
Number of Operations:						
	1	2	2	1	3	3
Irreducible Representations:						
A_{1g}:	1	1	1	1	1	1
A_{1u}:	1	-1	1	-1	1	-1
A_{2g}:	1	1	1	1	-1	-1
A_{2u}:	1	-1	1	-1	-1	1
E_g:	2	-1	-1	2	0	0
E_u:	2	1	-1	-2	0	0
Reducible Representations:						
z:	2	0	2	0	0	2
xy:	4	0	-2	0	0	0
ϕ:	6	0	0	0	0	-2
r ; θ	6	0	0	0	0	2

TABLE V

OCCURRENCES OF IRREDUCIBLE REPRESENTATIONS

	z	xy	ϕ	r	θ
A_{1g}	1	0	0	1	1
A_{1u}	0	0	1	0	0
A_{2g}	0	0	1	0	0
A_{2u}	1	0	0	1	1
E_g	0	1	1	1	1
E_u	0	1	1	1	1

The number of occurrences of irreducible representation μ in a given reducible representation is

$$N_\mu = \frac{1}{12} \sum_{i=1}^{6} n_i \chi_i^{(\mu)} \chi_i^{*}.$$

Here i runs over the six classes; n_i, $\chi_i^{(\mu)}$, χ_i are respectively the number of elements and the characters of the irreducible and reducible representations of class i.

Six of the basis vectors span irreducible representations corresponding to rigid translations and rotations of the molecule. These correspond to the zero frequency modes arising in the diagonalization (2.29). Indeed, the non-genuine modes may be immediately subtracted leaving only the genuine modes expressed in terms of basis vectors displaying the motion of the internal coordinates. According to standard group theory tables the six rigid translation/rotation basis vectors span

$$\{A_{2u} \oplus E_u\} \oplus \{A_{2g} \oplus E_g\}$$

leaving the internal modes

$$3A_{1g} \oplus 1A_{1u} \oplus 2A_{2u} \oplus 3E_g \oplus 3E_u.$$

We can also find a set of basis vectors transforming according to the irreducible representations by applying the projection operator techniques developed in Appendix B. In the case of more than a single occurence of a given irreducible representation--or indeed an irreducible representation of dimensionality greater than one--there is no way of finding the precise normal coordinates by symmetry considerations alone. Rather, one must diagonalize the matrix according to (2.29). Indeed one must always do this to find the normal mode frequencies. Nevertheless group theory remains a valuable tool in the classification scheme.

To illustrate the concept of potential energy surfaces we focus upon a two-dimensional subspace in configuration space corresponding to two specific normal modes of the ethane molecule. The first normal mode is the symmetric stretch of the C-C bond, with the in and out motion of each umbrella keeping the C-H bonds and angles fixed within each umbrella. This symmetric stretch is an A_{1g} mode. The stretching motion maintains the total momentum of the molecule (which, of course, is zero in the center of momentum frame). The second normal mode is the torsional motion of the two sets of the umbrella hydrogens about the C-C bond, the two sets simultaneously twisting in opposite directions (e.g., clockwise vs. counterclockwise as viewed along the C-C bond) so as to preserve the total angular momentum of the molecule. This twisting motion is an A_{1u} mode. As our intuition suggests--and indeed as our earlier analysis demonstrated--both these normal modes are simple harmonic oscillations about the equilibrium C-C bond length and the equilibrium dihedral angle.

According to the vibrational analysis of Duncan et al. (1983) the quadratic approximation to the electronic potential energy surface--at least within the two-dimensional subspace depicted by the stretching and twisting modes--can simply be written in terms of the internal coordinates $\delta R = \left(R - R_e\right)$ and $\delta\phi = \left(\phi - \phi_e\right)$ as

$$U = \frac{1}{2}[K_{A_{1g}} (\delta R)^2] + \frac{1}{2}[K_{A_{1u}} (\delta\phi)^2]. \tag{2.34}$$

The stretching and twisting force constants are $K_{A_{1g}} = 4.25 \times 10^{-3}$ dyne/Å and $K_{A_{1u}} = .081 \times 10^{-3}$ dyne × Å respectively. R_e and ϕ_e are the minimum energy values for the C-C bond length and dihedral angle. Thus, in this harmonic approximation within a particular two-dimensional subspace (where each direction corresponds to a specific collective motion of the atoms) we can envision the potential energy surface as a paraboloid. In Figure 2.5 we sketch such a surface, noting that $\delta(R)$ and $\delta(\phi)$ are re-

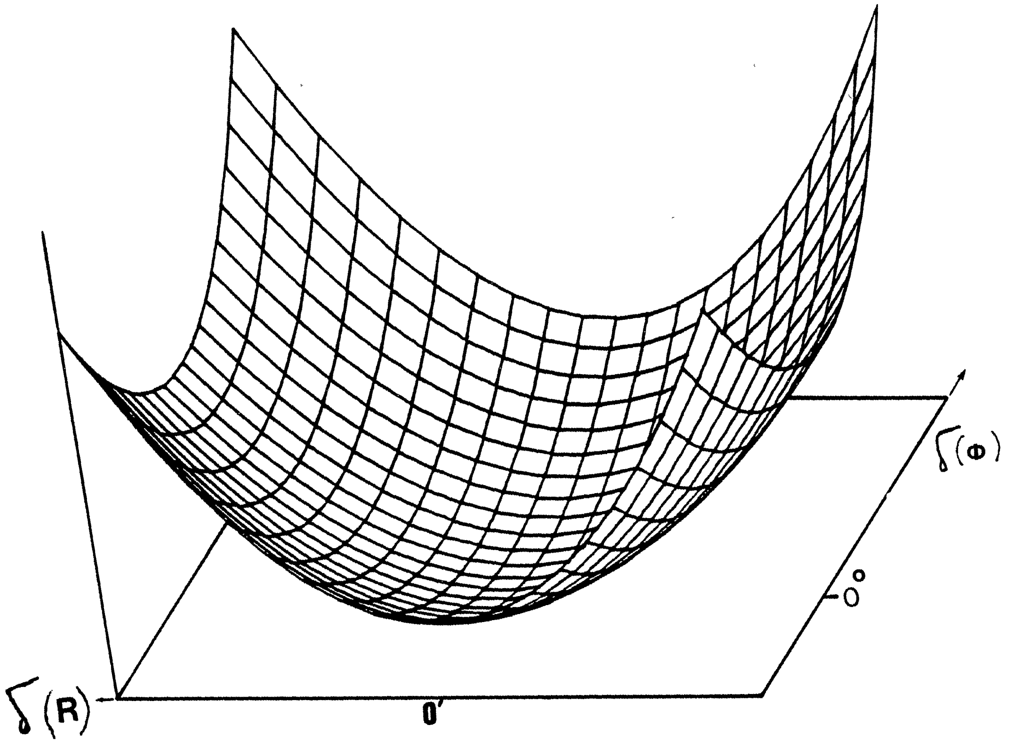

Figure 2.5. Paraboloid

lated to the normal coordinates for the two modes under consideration. The frequency of the stretching (A_{1g}) mode is, according to Duncan et al. (1983), $\bar{\nu} = 994\ \mathrm{cm}^{-1}$. The "wave number" designation $\bar{\nu}$ for "frequency" ν or the angular frequency Ω arises from the relationship, familiar in optics, $\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{\Omega}{2\pi c}$. In optics, of course, these quantities refer to the transition energy. Here, on the contrary they are used to express stationary state eigenvalues. Similarly, the torsional (A_{1u}) mode frequency is $\bar{\nu} = 291\ \mathrm{cm}^{-1}$. Both frequencies may be found to within 2% by a simple "back of the envelope" calculation taking the mass of each umbrella to be 2.50×10^{-23} gm and a moment of inertia about the C-C bond to be 5.23×10^{-24} gm $\mathring{A}^2$. These values for the CH_3 moiety are easily found in terms of the atomic masses and equilibrium geometry. In more traditional language we find the stretching normal mode frequency

$$\begin{aligned} \Omega_{A_{1g}} &= \{4.25 \times 10^{-3}\ \mathrm{dyne}/\mathring{A}\}/\{0.5 \times 2.50 \times 10^{-23}\ \mathrm{gm}\}^{\frac{1}{2}} \\ &= 1.84 \times 10^{14}\ \mathrm{Hz} \end{aligned} \tag{2.35}$$

and the twisting mode frequency

$$\begin{aligned} \Omega_{A_{1u}} &= \{0.081 \times 10^{-3}\ \mathrm{dyne}\ \mathring{A}\}/\{0.5 \times 5.23 \times 10^{-24}\ \mathrm{gm}\ \mathring{A}^2\}^{\frac{1}{2}} \\ &= 5.56 \times 10^{13}\ \mathrm{Hz}. \end{aligned} \tag{2.36}$$

Of course, it is precisely by working "backwards" from the measured frequencies that the force constants are obtained by Duncan et al.

In better approximations, one envisions the points on the potential energy surface as generated, configuration by configuration, by detailed solutions to the electronic eigenvalue problem (2.11). We sketch in Figure 2.6 an artist's concept of the potential energy surface in which only R and ϕ are allowed to change. The paraboloid Figure 2.5 is then simply an approximation to the region about the minimum (R=1.534 Å, ϕ = 60°) in Figure 2.6. The surface is no longer simply expressed as in equation (2.34) but surely contains "coupling" terms in the ϕ and R coordinates. Returning now to our earlier considerations we see that the curves in Figure 2.2a and 2.2b may be "cuts" of the surface 2.6 at constant R and constant ϕ respectively. Or in the spirit of these earlier remarks the curves of Figures 2.2a for instance may schematically represent a more general path along the surface in Figure 2.6 where, as ϕ is varied, R also is allowed to relax. In fact, the other sixteen internal displacement coordinates ought to be allowed to relax to generate the surface in Figure 2.6 which itself is then seen as some optimum "path" in a higher dimensional space.

In the harmonic approximation the problem of finding the internal states of the nuclear motion (on a given potential energy surface) is now reduced to the familiar harmonic oscillator problem for each of the non-trivial internal normal modes. The form of the Hamiltonian (2.30) is just the sum of one dimensional harmonic oscillators, one for each of the 3A normal modes. (Of course, 6 of the frequencies Ω_λ are zero, so that in fact six of the terms are simply free-particle kinetic energy operators corresponding to rigid translational and rotational states of the whole molecule.) As detailed in the next chapter an eigenfunction is just the product of eigenfunctions for each term in $\mathcal{H}$ while the eigenvalues are simply the sum of the individual eigen-

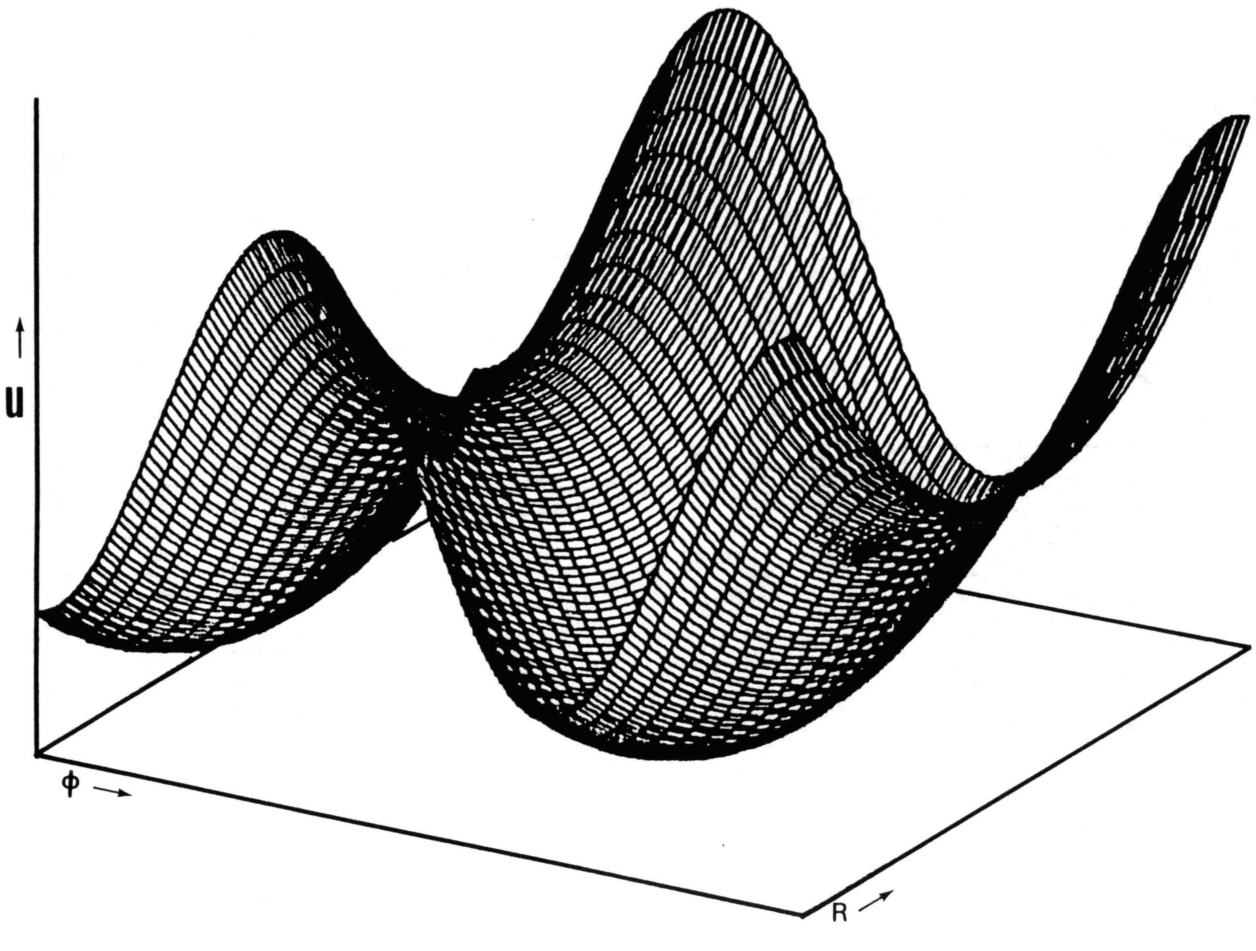

Figure 2.6. Potential Energy Surface as a Function of R and ϕ

values. We refer the reader to any standard quantum mechanics text such as Schiff (1968). The eigenfunction for the internal vibrational motion is $\prod_{\lambda=1}^{3A-6} \psi_{\nu_\lambda}(\sqrt{\alpha}\,\eta_\lambda)$, the product of one dimensional harmonic oscillator eigenfunctions, and the eigenvalue (including the constant U_0) is

$$E_{\nu_1\nu_2\cdots\nu_{3A-6}} = \sum_{\lambda=1}^{3A-6} (\nu_\lambda + \tfrac{1}{2})\hbar\,\Omega_\lambda + U_0. \tag{2.37}$$

Here, the ν's are integral quantum numbers ν_λ (= 0,1,2,...) and now the normal mode index λ runs over all non-zero frequency modes.

We conclude this chapter by bringing together the ideas introduced here, namely the Born-Oppenheimer approximation and the harmonic approximation for the nuclear motion. We have found that, in these approximations, the internal eigenstate of the molecule is specified by the electronic index ℓ (in reality a collection of quantum numbers arising in solving the electronic problem) and the vibrational quantum numbers $\nu_1, \nu_2, \nu_3, \ldots, \nu_{3A-6}$ for the (3A-6) genuine normal modes. The internal energy of a molecule in an eigenstate specified by these quantum numbers is

$$E = U_{o\ell}(R_{o\ell}) + \sum_{\lambda=1}^{3A-6} [(\nu_\lambda + \tfrac{1}{2})\hbar\,\Omega_{\lambda\ell}]. \tag{2.36}$$

Here, $R_{o\ell}$ stands for the nuclear configuration coordinates of the minimum energy point on the potential energy surface for electronic state ℓ, and $U_{o\ell}$ is the electronic energy (as given by Equation (2.15) at this configuration. The $\Omega_{\lambda\ell}$, $\lambda=1,2,\ldots,3A-6$, are the (angular) frequencies of the genuine normal modes obtained on this ℓth electronic potential energy surface. (Recall that the electronic label ℓ had been suppressed just prior to Equation (2.16).) The vibrational quantum number ν_λ (= 0,1,2,

...) depicts the level of excitation of the λth ($\lambda=1,2,3,\ldots,(3A-6)$) normal mode. Clearly, arriving at these values requires sufficiently detailed electronic structure calculations to obtain accurately not only the minimum electronic energy $U_{o\ell}$ but also the second partial derivatives of the potential energy $\frac{\partial^2 U_\ell}{\partial X_{a_i} \partial X_{b_j}}$ evaluated at $\{\vec{R}_{o\ell}\}$. These latter quantities, of course, enter the calculation of the normal mode frequencies via the prescriptions discussed above.

In addition to the internal energy given by (2.36) we must include for the total energy eigenvalue the translational and rotational energies of the molecule. Indeed, there are six additional quantum numbers to express these degrees of freedom of the molecule. One must specify these quantum numbers as well as the internal quantum numbers to delineate the eigenstate of the molecule. They may, for example, be the three components of the center of mass momentum $\vec{p}$ and the three quantum numbers for a rigid top. (See Chapter XIII, Landau and Lifshitz, Quantum Mechanics.)

Similarly, the internal energy of a second molecular eigenstate with electronic index ℓ' and vibrational quantum numbers $\nu_1', \nu_2', \ldots, \nu_{3A-6}'$ may be expressed as

$$E' = U_{o\ell'}(R_{o\ell'}) + \sum_{\lambda=1}^{3A-6} [(\nu_\lambda' + \tfrac{1}{2})\hbar\, \Omega_{\lambda\ell'}] \tag{2.37}$$

Here we must note that the minimum energy $U_{o\ell'}$--and indeed the configuration space coordinates themselves--depend on the electronic index ℓ'. Also, the normal mode frequencies $\Omega_{\lambda\ell'}$ depend on the electronic state ℓ', since clearly we must anticipate the "shapes" of various electronic potential energy surfaces are reflected in different curvatures. In fact, the precise nature of the normal mode could change from one potential energy surface to another, say as a molecule undergoes a conformational change. The point to be emphasized here is simply that once again detailed electronic structure calculations must be performed to obtain these various parameters even within the framework of the harmonic approximation.

Finally, ignoring the translational and rotational energy changes, as a molecule undergoes a transition from one internal state (with quantum indices $\ell, \nu_1, \nu_2, \ldots, \nu_{3A-6}$) to another (with quantum indices $\ell', \nu_1', \nu_2', \ldots, \nu_{3A-6}'$) we obtain for the transition energy

$$\Delta E = E' - E = U_{o\ell'}(R_{o\ell'}) - U_{o\ell}(R_{o\ell}) + \sum_{\lambda=1}^{3A-6} \{\frac{1}{2}\hbar\,(\Omega_{\lambda\ell'} - \Omega_{\lambda\ell}) \\ \hbar(\nu_\lambda'\,\Omega_{\lambda\ell'} - \nu_\lambda\,\Omega_{\lambda\ell})\}. \tag{2.38}$$

On the same electronic potential energy surface--that is, with $\ell = \ell'$ so that $\Omega_{\lambda\ell} = \Omega_{\lambda\ell'}$ for all $\lambda = 1, 2, \ldots, (3A-6)$--only vibrational excitation of the molecule takes place, with the result that

$$\Delta E = \sum_{\lambda=1}^{3A-6} \{\hbar(\nu_\lambda' - \nu_\lambda)\Omega_{\lambda\ell}\}. \tag{2.39}$$

Most often only one of the vibrational quantum is changed and that only in unit steps. If, for a given normal mode σ, $\nu_\sigma' = \nu_\sigma \pm 1$ while $\nu_\lambda' = \nu_\lambda$ $\lambda \neq \sigma$, then the excitation energy becomes simply

$$\Delta E = \pm\hbar\,\Omega_{\sigma,\ell}. \tag{2.40}$$

The transition energy in this case depends on one normal mode frequency--

the σth--on a particular electronic potential energy surface--the ℓth. Again we note that although the electronic energy is no longer required, the second partial derivatives at the equilibrium configuration of the molecule for this particular electronic state are necessary to evaluate accurately the vibrational excitation energy. In the past twenty years with the coming of age of computers much progress has been made in computing these electronic state parameters for various molecules. We shall spend the next three chapters discussing some of the essential ideas which underlie these electronic structure calculations.

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CHAPTER III

ELECTRONIC STRUCTURE

Consider a system of N electrons interacting with A fixed nuclei and pairwise with each other via coulomb potentials. The electronic Hamiltonian $\hat{H}_o$ is

$$\hat{H}_o = \sum_{i=1}^{N} \left(\frac{-\hbar^2}{2m} \nabla_i^2 + \sum_{\alpha=1}^{A} \frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|}\right) + \sum_{1 \leq i < j \leq N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \tag{3.1}$$

There are other interactions among the particles (e.g., magnetic effects) which we shall neglect. To get started we consider a system consisting of one nucleus--an atom: then with A=1 and $\vec{R}_1$ located at the origin of the coordinate system, the Hamiltonian becomes

$$\begin{aligned} \hat{H}_o &= \sum_{i=1}^{N} \left(\frac{-\hbar^2}{2m} \nabla_i^2 + \frac{-Ze^2}{|\vec{r}_i|}\right) + \sum_{1 \leq i < j \leq N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \\ &= \sum_{i=1}^{N} (\hat{h}_i) + \sum_{1 \leq i < j \leq N} \hat{v}(i,j). \end{aligned} \tag{3.2}$$

We seek the eigenstates of $\hat{H}_o$:

$$\hat{H}_o \Psi_\mu = E_\mu \Psi_\mu .$$

The eigenstate index μ--which will be explained more fully below--distinguishes the linearly independent solutions. The partial differential equation (3.3) cannot be solved exactly because the electron pairwise interaction is included in the Hamiltonian $\hat{H}_o$. Thus as a first attempt at atomic structure calculations we might replace the Coulomb Hamiltonian with a "model Hamiltonian" which, while having the basic physics, may have tractable solutions. In fact, in general terms this is what theoretical physics is all about. We thus replace the Hamiltonian $\hat{H}_o$ with another Hamiltonian $\hat{\mathcal{H}}_o$, the sum of N one-body operators

$$\hat{\mathcal{H}}_o = \hat{h}_o(1) + \hat{h}_o(2) + \dots + \hat{h}_o(N) = \sum_{i=1}^{N} [\hat{h}(i) + \hat{U}(r_i)]. \tag{3.4}$$

We shall call this model based on the sum of one-body Hamiltonians an "independent particle model". The details of the one-body Hamiltonian--the same form for each of the N-identical electrons--remain to be specified, but we shall assume it will have the general structure

$$\hat{h}_o(i) = \frac{-\hbar^2}{2m} \nabla_i^2 + \frac{-Ze^2}{r_i} + \hat{U}(r_i). \tag{3.5}$$

$\hat{U}(r_i)$ accounts for the effects upon electron i of the presence of the other N-1 electrons in some average fashsion. For instance, as $|\vec{r}_i|$ approaches zero, electron i is close to the nucleus and we expect $\hat{U}(r_i)$ to approach a constant value indicative of the region inside a spherical charge distribution. On the other hand as $|\vec{r}_i|$ approaches infinity we anticipate $\hat{U}(r_i)$ behaves like $(N-1)e^2/r_i$, the Coulomb potential energy of electron i outside the charge distribution of the remaining electrons. In fact, we assumed here that $\hat{U}(r_i)$ is "local"--the effects incorporated into $\hat{U}$ depend only upon the position $\vec{r}_i$ of electron i. More generally, we shall later develop the approach of choosing the "best" $\hat{U}(r_i)$ according to the Hartree-Fock variational procedure. There it happens that $\hat{U}$ will be a non-local operator. Since the electrons are identical particles, the eigenvalue problem

$$\hat{h}_o(i)\ \varphi_\lambda(i) = \varepsilon_\lambda\ \varphi_\lambda(i), \tag{3.6}$$

has the same spectrum for any particle label $i=1,2,...,N$. The single particle eigenfunctions φ_λ will be called orbitals. The orbital index λ distinguishes the linearly independent solutions, and consists of a set of eigenvalues of operators, including $\hat{h}_o$ itself, which commute pairwise among themselves. Often λ, in addition to the orbital eigenvalue ε, will include "quantum numbers" directly related to the symmetry of the problem. A general discussion of orbitals is given in Appendix A, while symmetry properties of finite point groups are reserved to Appendix C.

With the inclusion of a spherically symmetric effective potential energy $\hat{U}(r)$ in the effective Hamiltonian for the atomic problem, we seek spatial eigenfunctions of the form

$$\varphi_\lambda = R_{\varepsilon\ell}(r)\ Y_\ell^m(\theta,\phi). \tag{3.7}$$

This follows, as detailed in many textbooks (Messiah, 1966, Vol. I, pp. 343-368), because the partial differential equation in spherical polar coordinates

$$\left[\frac{-\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\ \frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\ \frac{\partial^2}{\partial\phi^2}\right\} + \frac{-Ze^2}{r}\right.$$

$$\left. + \hat{U}(r)\right]\ \varphi_\lambda = \varepsilon_\lambda\,\varphi_\lambda \tag{3.8}$$

is separable. Here the $Y_\ell^{m_\ell}(\theta,\phi)$ are the usual spherical harmonics, where because of the single-valuedness and boundedness required of the orbitals, ℓ is restricted to nonnegative integers ($\ell=0,1,2,\ldots$) and for a given ℓ, m may take integral values between $-\ell$ and $+\ell$ ($-\ell\leq m_\ell<+\ell$). These orbitals are simultaneously eigenfunctions of the square of orbital angular momentum

$$\hat{\ell}^2 = -\hbar^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}] \tag{3.9}$$

as well as the z-component

$$\hat{\ell}_z = -i\hbar\frac{\partial}{\partial\phi} \tag{3.10}$$

of orbital angular momentum, the eigenvalues of which are respectively $\ell(\ell+1)\hbar^2$ and $m_\ell\hbar$. We refer to $\ell=0,1,2,\ldots$ as s,p,d,... orbitals in accord with early spectroscopic notation. The so-called radial factor must then satisfy

$$[\frac{-\hbar^2}{2m}\{\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) - \frac{\ell(\ell+1)}{r^2}\} + \frac{-Ze^2}{r} + U(r)]R_{\varepsilon\ell}(r) = \varepsilon R_{\varepsilon\ell}(r). \tag{3.11}$$

For a given ℓ, we anticipate a number of solutions $\{R_{\varepsilon\ell},\varepsilon\}$ of this ordinary differential equation. The boundary conditions on R lead to acceptable solutions for only certain choices of ε. This set of allowed ε's—the so-called spectrum of $\hat{h}_o$—depends upon the details of the effective potential U(r). In (3.11) we have used the energy eigenvalue itself to enumerate the acceptable solutions of the radial equation. Thus, for each ℓ we may have finite or an infinite number of solutions, and in the latter case the spectrum may also include a continuum of allowed energy eigenstates. In this case, however, the radial functions $R_{\varepsilon\ell}(r)$ though bounded and single-valued are not square-integrable--that is, $\int_0^\infty r^2\,dr\,|R_{\varepsilon\ell}(r)|^2$ does not exist. Nevertheless, they must be included in forming a "complete set" of one-particle functions.

Notwithstanding these rather general remarks it is good to consider the "pure Coulomb" case where the effective potential

$$\hat{U}(r) = -(Z - z)\frac{e^2}{r} \tag{3.12}$$

simply replaces the actual nuclear charge Ze with an effective charge ze. In this case the solutions are the well-known "hydrogen-like" functions. For each ℓ there are indeed an infinite number of square integrable functions labeled $R_{N\ell}(r)$ and corresponding (negative) eigenvalues

$$\varepsilon_{N\ell} = \frac{-me^4z^2}{2\hbar^2(N+\ell)^2}. \tag{3.13}$$

N, which we refer to as the "ordinal" quantum number, assumes (for each ℓ) all positive integral values, N=1,2,3,.... The more traditional labeling scheme (which arises naturally in solving the radial equation for the bound states), however, introduces the "principal" quantum number

$$n = N + \ell. \tag{3.14}$$

Clearly the radial functions may be relabeled $R_{n\ell}$ and the energy eigenvalues reexpressed in terms of n alone. Besides this countable set of bound state solutions for each ℓ, there is an uncountable set of nonsquare-integrable functions for the continuum of positive energy values $\varepsilon > 0$.

Returning to the more general form of U(r) we see that the "ordinal" indexing scheme (N=1,2,3,...) remains valid for the bound states. Indeed, N simply "orders" the solutions of the radial equation according to energy, for instance, by making

$$\varepsilon_{N\ell} \leq \varepsilon_{N+1,\ell}. \tag{3.15}$$

On the other hand, the principal quantum number labeling scheme for the atomic orbitals can also be adopted for the general effective potential simply by defining n as in (3.14). This time there may be no "intrinsic" reason (such as solving the differential equation) leading to the notion of principal quantum number and $\varepsilon_{n\ell}$ may be expected to depend both on n and ℓ. Nevertheless, adopting this principle quantum number scheme to label the atomic orbitals will prove worthwhile. For the case of atoms considered here, λ will, in addition to n (or ε), include the square of the orbital angular momentum and z-component of angular momentum quantum numbers ℓ and m_ℓ. Moreover, as discussed in the first chapter, electrons possess an intrinsic degree of freedom, spin, depicted by an intrinsic angular momentum operator. The square of the spin angular momentum and its z-component quantum numbers, s and m_s, are also included in λ. Thus, with $\hat{h}_o$, $\hat{\ell}^2$, $\hat{\ell}_z$, $\hat{s}^2$, $\hat{s}_z$, forming a set of five commuting operators λ consists of a set of five quantum numbers: $\{\varepsilon, \ell, m_\ell, s, m_s\} \equiv \lambda$. That is, we may write for a given orbital

$$\begin{aligned}
\hat{h}_o(i)\ \phi_\lambda(i) &= \varepsilon\ \phi_\lambda(i) \\
\hat{\ell}^2(i)\ \phi_\lambda(i) &= \ell(\ell+1)\hbar^2\phi_\lambda(i) \\
\hat{\ell}_z(i)\ \phi_\lambda(i) &= m_\ell\hbar\ \phi_\lambda(i) \\
\hat{s}^2(i)\ \phi_\lambda(i) &= s(s+1)\hbar\ \phi_\lambda(i) \\
\hat{s}(i)\ \phi_\lambda(i) &= m_s\hbar\ \phi_\lambda(i).
\end{aligned} \tag{3.16}$$

In fact, the quantum number s is always 1/2 for electrons. Understanding this fixed value for s, we may omit it from explicit enumeration of the set λ, and write more simply $\lambda = \{\varepsilon, \ell, m_\ell, m_s\}$, where the possibilities are restricted to $m_s = \pm\frac{1}{2}$, $-\ell \leq m_\ell \leq \ell$, $\ell=0,1,2,\ldots$, and ε found in solving (3.11).

In passing, we remark that the "atomic orbital" $\phi_{\varepsilon\ell m_\ell m_s}$ is a basis function for the m_ℓth row of the ℓth irreducible representation of the atomic symmetry group. In the molecular case, there will arise analogously a set of "molecular orbitals" labeled $\phi_{\varepsilon\mu i m_s}$, each of which, it shall turn out, is a basis function spanning the ith row of the μth irreducible representation of the finite point symmetry group of the molecule.

Having discussed the single particle eigenfunctions of $\hat{h}_o(i)$--the orbitals--we now turn to the construction of eigenfunctions of the independent particle model Hamiltonian $\hat{H}_o$. We find that with $\hat{H}_o$ being the sum of single particle operators, each simple product of orbitals is one of its eigenfunctions. For example, if we have a three electron system with the independent particle Hamiltonian

$$\hat{H}_o = \hat{h}_o(1) + \hat{h}_o(2) + \hat{h}_o(3), \tag{3.17}$$

then the direct product of any three orbitals

$$\phi_\Lambda = \varphi_{\lambda_1}(X_1)\, \varphi_{\lambda_2}(X_2)\, \varphi_{\lambda_3}(X_3), \tag{3.18}$$

is an eigenfunction of $\hat{H}_o$. To see this we apply $\hat{H}_o$ to ϕ_Λ with the understanding that in operating on ϕ_Λ, $\hat{h}_o(1)$ operates on $\varphi_{\lambda_1}(X_1)$:

$$\begin{aligned}\hat{h}_o(1)[\,\varphi_{\lambda_1}(X)\, \varphi_{\lambda_2}(X)\, \varphi_{\lambda_3}(X)] &= \varphi_{\lambda_2}(X_2)\, \varphi_{\lambda_3}(X_3)[\hat{h}_o(1)\, \varphi_{\lambda_1}(X_1)] \\ &= \varphi_{\lambda_2}(X_2)\, \varphi_{\lambda_3}(X_3)[\varepsilon_{\lambda_1}\, \varphi_{\lambda_1}(X_1)],\end{aligned} \tag{3.19}$$

and similarly for $\hat{h}_o(2)$ and $\hat{h}_o(3)$. If we focus on a specific set of three orbitals a,b,c, and choose $\lambda_1 = a$, $\lambda_2 = b$, $\lambda_3 = c$, then we find

$$\begin{aligned}\hat{H}_o\phi_\Lambda &= \{(\hat{h}_o(1) + \hat{h}_o(2) + \hat{h}_o(3)\}\phi_\Lambda \\ &= \varphi_b(X_2)\, \varphi_c(X_3)[\hat{h}_o(1)\, \varphi_a(X_1)] + \varphi_a(X_1)\, \varphi_c(X_3)[\hat{h}_o(2)\, \varphi_b(X_2)] \\ &\quad + \varphi_a(X_1)\, \varphi_b(X_2)[\hat{h}_o(3)\, \varphi_c(X_3)] \\ &= (\varepsilon_a + \varepsilon_b + \varepsilon_c)\phi_\Lambda.\end{aligned} \tag{3.20}$$

The point to be made is that we could have chosen $\lambda_1 = c$, $\lambda_2 = a$, $\lambda_3 = b$, or any other permutation of this set, thereby generating different (linearly independent) eigenfunctions, but each having the same energy eigenvalue, $\varepsilon_a + \varepsilon_b + \varepsilon_c$.

For general N the eigenfunctions of $\hat{H}_o$ are of the form

$$\phi_\Lambda = \prod_{i=1}^{N} \varphi_{\lambda_i}(X_i), \tag{3.21}$$

that is,

$$\hat{H}_o \phi_\Lambda = [\hat{h}_o(1) + \ldots + \hat{h}_o(N)] \prod_{i=1}^{N} \varphi_{\lambda_i}(X_i) = (\varepsilon_{\lambda_1} + \ldots + \varepsilon_{\lambda_N}) \prod_{i=1}^{N} \varphi_{\lambda_i}(X_i)$$

$$= E_\Lambda \phi_\Lambda. \tag{3.22}$$

Various choices of the orbitals $\lambda_1, \lambda_2, \ldots, \lambda_N$ lead to various eigenstates. Note the correspondence between particle label and orbital label at this point. Thus, a permutation of the orbital label leads in general to a different (linearly independent) eigenfunction, but one having the same eigenvalue, namely $\varepsilon_{\lambda_1} + \varepsilon_{\lambda_2} + \ldots + \varepsilon_{\lambda_N}$. We speak of "permutational degeneracy" of the eigenstates. In that special case in which $\lambda_i = \lambda_j$ the transposition does not produce a linearly independent eigenfunction. Of course, any linear combination of these product eigenfunctions for a given set of labels $\lambda_1, \lambda_2, \ldots, \lambda_N$ is once again an eigenfunction of the model Hamiltonian.

In quantum mechanics we cannot distinguish the motions of each of the N identical electrons. Since electrons are identical particles--each has the same mass, charge, and spin--, the interchange of any pair will leave the system physically unchanged. That is to say, there is no way physically to detect such an interchange by direct measurement. Thus we can never determine which of the electrons we have found at a certain point because the electrons are physically indistinguishable particles. This fact must be incorporated into a "correct" description of the wavefunction.

It may be shown (Messiah, 1966, Vol. II, p. 582) that as a consequence of this indistinguishability of the identical particles the wavefunction $\Psi(X_1,X_2,\ldots,X_N)$ depicting the system of particles must be even or odd under the interchange of any pair of particle labels:

$$\Psi(X_1,X_2,\ldots,X_N) = \pm\Psi(X_1,X_2,\ldots,X_N). \tag{3.23}$$

In turn this implies that the Hamiltonian eigenfunctions themselves have this "particle permutation symmetry". We can then use the permutational degeneracy of the product eigenfunctions

$$\phi_\Lambda = \prod_{i=1}^{N} \mathfrak{P}_{\lambda_i}(X_i) \tag{3.24}$$

to insure that the eigenfunctions of the model Hamiltonian do indeed have this symmetry. In particular, if the intrinsic spin quantum number s is half-intergral, as indeed it is for electrons, the system's wave function must be antisymmetric under the exchange of any pair of particle labels. We may use the degeneracy of the simple product functions $\prod_{i=1}^{N} \mathfrak{P}_{\lambda_i}(X_i)$ to form antisymmetrized products which are also eigenfunctions of the model Hamiltonian.

Before writing the general prescription for these antisymmetrized model eigenfunctions, we first continue with our three particle example. There are in fact 6 = 3! permutations of the particle labels 1,2,3 among themselves. We define, for instance, the permutation operator $\hat{P}_{\substack{123\\321}}$ by

$$F(X_3,X_2,X_1) = \hat{P}_{\substack{123\\321}} F(X_1,X_2,X_3), \tag{3.25}$$

and introduce the antisymmetrizer

$$\hat{a}(3) = \frac{1}{\sqrt{3!}} \sum_P (-1)^{\sigma_P} \hat{P} \tag{3.26}$$

which incorporates the sum over all 3! permutations of the particle labels, with the factor $(-1)^{\sigma_P}$ being +1 or -1 depending upon whether the number of transpositions composing $\hat{P}$ is even or odd. A transposition is the interchange of two labels, one with the other, and the most general permutation may be envisioned simply as a succession of transpositions.

To illustrate, we apply $\hat{a}(3)$ to the simple direct product ϕ_Λ to obtain the antisymmetrized product Φ_Λ:

$$\Phi_{\lambda_1\lambda_2\lambda_3}(X_1,X_2,X_3) = \hat{a}(3) \prod_{i=1}^{3} \phi_{\lambda_i}(X_i)$$

$$= \frac{1}{\sqrt{3!}} \sum_P (-1)^{\sigma_P} \hat{P}_{\substack{1\,2\,3\\i_1 i_2 i_3}} [\phi_{\lambda_1}(X_1)\, \phi_{\lambda_2}(X_2)\, \phi_{\lambda_3}(X_3)]$$

$$= \frac{1}{\sqrt{3!}}[\phi_{\lambda_1}(X_1)\phi_{\lambda_2}(X_2)\phi_{\lambda_3}(X_3) - \phi_{\lambda_1}(X_2)\phi_{\lambda_2}(X_1)\phi_{\lambda_3}(X_3) - \phi_{\lambda_1}(X_3)\phi_{\lambda_2}(X_2)\phi_{\lambda_3}(X_1)$$

$$- \phi_{\lambda_1}(X_1)\phi_{\lambda_2}(X_3)\phi_{\lambda_3}(X_2) + \phi_{\lambda_1}(X_3)\phi_{\lambda_2}(X_1)\phi_{\lambda_3}(X_2) + \phi_{\lambda_1}(X_2)\phi_{\lambda_2}(X_3)\phi_{\lambda_3}(X_1)]. \tag{3.27}$$

We see that the result of applying $\hat{a}(3)$ is a linear combination of 6 (=3!) simple product eigenfunctions, all corresponding to the one eigenvalue $(\varepsilon_{\lambda_1} + \varepsilon_{\lambda_2} + \varepsilon_{\lambda_3})$. Thus, as indicated above, the antisymmetrized product itself is an eigenfunction of the model Hamiltonian corresponding to this eigenvalue. If the orbitals were rearranged in the simple product function, that is, if

$$\phi_{\Lambda'} = \varphi_{\lambda_1}(X_3)\,\varphi_{\lambda_2}(X_2)\,\varphi_{\lambda_3}(X_1) \tag{3.28}$$

then, it is easily shown that the resulting antisymmetrized product

$$\Phi_{\Lambda'} = \hat{a}(3)\phi_{\Lambda'} \tag{3.29}$$

is not linearly independent of Φ_Λ, but rather

$$\Phi_{\Lambda'} = (\pm 1)\Phi_\Lambda. \tag{3.30}$$

This follows from the fact that the set of permutation operations form a group, so that multiplication of $\hat{a}(3)$ by any group element $\hat{P}$ gives

$$\hat{a}(3)\hat{P} = \hat{P}\hat{a}(3) = (-1)^{\sigma_P}\,\hat{a}(3). \tag{3.31}$$

In the example given here

$$\phi_{\Lambda'} = \hat{P}_{\substack{123\\321}}\,\phi_\Lambda \tag{3.32}$$

and so

$$\Phi_{\Lambda'} = \hat{a}(3)\phi_{\Lambda'} = \hat{a}(3)\hat{P}_{\substack{123\\321}}\,\phi_\Lambda = (-1)^{\sigma_{\substack{123\\321}}}\,\hat{a}(3)\phi_\Lambda = -\Phi_\Lambda. \tag{3.33}$$

From these considerations, we conclude that only distinct combinations of three orbitals give rise to linearly independent, antisymmetrized eigenfunctions. Thus, for a given set of orbitals λ_1, λ_2, λ_3 rather than having six electronic eigenfunctions we have at most one. Indeed, unless all three orbitals λ_1, λ_2, λ_3 are different the antisymmetrized product vanishes. Of course, such a function may not be included in our list of independent eigenfunctions of $\hat{H}_o$.

Having six linearly independent simple products originally, ($\lambda_1 \neq \lambda_2 \neq \lambda_3$) we must have five additional independent functions besides the one antisymmetrized acceptable electronic eigenfunction. To be sure these additional functions have particle permutation symmetries other than being odd (i.e., changing sign) under the interchange of any pair of particle labels. One such function is even under the interchange of any pair of particle labels. The four remaining functions have more complicated transformation properties under particle interchanges. All these functions may be classified according to their belonging to irreducible representations of the symmetric group S_3. Be that as it may, the point to be made here is that the antisymmetric requirement on electronic wave functions restricts the number of acceptable eigenfunctions of the model Hamiltonian.

A careful examination of Equation (3.27) shows that the result of applying $\hat{a}(3)$ on the product of three orbitals $\phi_{\lambda_1}(X_1)\phi_{\lambda_2}(X_2)\phi_{\lambda_3}(X_3)$ may be written as a 3×3 determinant

$$\hat{a}(3)\phi_\Lambda(X_1,X_2,X_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \varphi_{\lambda_1}(X_1) & \varphi_{\lambda_2}(X_1) & \varphi_{\lambda_3}(X_1) \\ \varphi_{\lambda_1}(X_2) & \varphi_{\lambda_2}(X_2) & \varphi_{\lambda_3}(X_2) \\ \varphi_{\lambda_1}(X_3) & \varphi_{\lambda_2}(X_3) & \varphi_{\lambda_3}(X_3) \end{vmatrix} . \qquad (3.34)$$

The Pauli exclusion principle for the independent particle model may now be stated: No acceptable electronic eigenstate exists in which more than one orbital has the same set of quantum numbers $\lambda \equiv (\varepsilon,\ell,m_\ell,m_s)$. For instance, if we let $\lambda_1 = \lambda_3$, the first and the third column of (3.34) will be identical, resulting in a vanishing determinant.

Now let us generalize these considerations for an N electron system. We construct an antisymmetric wave function by applying the N particle antisymmetrizer $\hat{a}(N)$ to the product $\prod_{i=1}^{N} \varphi_{\lambda_i}(X_i)$. The antisymmetrizer $\hat{a}(N)$ is the sum of N! permutations $\hat{P}_{\substack{1\ 2\ 3\ \dots N \\ i_1 i_2 i_3 \dots i_N}}$ interchanging the particle labels among themselves. These permutation operations form the symmetric group of order N!. Thus, with

$$\hat{a}(N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^{\sigma_P} \hat{P}_{\substack{1\ 2\ \dots N \\ i_1 i_2 \dots i_N}} \qquad (3.35)$$

applied to the simple product $\prod_{i=1}^{N} \varphi_{\lambda_i}(X_i)$ we get

$$\Phi_\Lambda(X_1 \dots X_N) = \Phi_{\lambda_1 \dots \lambda_N}(X_1 \dots X_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\lambda_1}(X_1) & \varphi_{\lambda_2}(X_1) & \cdots & \varphi_{\lambda_N}(X_1) \\ \varphi_{\lambda_1}(X_2) & \varphi_{\lambda_2}(X_2) & \cdots & \varphi_{\lambda_N}(X_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\lambda_1}(X_N) & \varphi_{\lambda_2}(X_N) & \cdots & \varphi_{\lambda_N}(X_N) \end{vmatrix} . \quad (3.36)$$

Provided all the λ_i's are different Φ_Λ is antisymmetric under the interchange of particle labels; here $\Lambda = \{\lambda_1, \lambda_2, \ldots, \lambda_N\}$ is a collection of N sets of orbital quantum numbers $(\varepsilon, \ell, m_\ell, m_s)$, one for each λ_i. All the analogous statements made above for $N = 3$ hold in general here. In particular, all N λ_i's must be different in each determinant and distinct combinations of the $\{\lambda_1 \ldots \lambda_N\}$ (not simply permutations) give rise to linearly independent electronic eigenfunctions. Therefore we see that the antisymmetric function $\Phi_\Lambda(X_1, X_2, \ldots, X_N)$ is an eigenfunction of $\hat{H}_o$ with eigenvalue $(\varepsilon_{\lambda_1} + \varepsilon_{\lambda_2} + \ldots + \varepsilon_{\lambda_N})$. Indeed, by noting that the commutator $[\hat{H}_o, \hat{a}(N)]$ vanishes, that is $\hat{H}_o$ and $\hat{a}(N)$ commute, we obtain

$$\begin{aligned} \hat{H}_o\Phi = \hat{H}_o[\hat{a}(N)\phi_\Lambda] = \hat{a}(N)[\hat{H}_o\phi_\Lambda] &= \hat{a}(N)[\varepsilon_{\lambda_1} + \ldots + \varepsilon_{\lambda_N}]\phi_\Lambda \,. \\ &= [\varepsilon_{\lambda_1} + \ldots \varepsilon_{\lambda_N}]\hat{a}(N)\phi_\Lambda \\ &= [\varepsilon_{\lambda_1} + \ldots \varepsilon_{\lambda_N}]\Phi_\Lambda . \end{aligned} \tag{3.37}$$

We form the complete set of so-called "Slater determinants" $\{\Phi_\Lambda\}$--that is, the "Slater" basis which spans the N-particle Hilbert space such that any antisymmetric function Ψ can be written as a linear combination of the said basis--by considering all possible combinations of sets of N-orbitals $\Lambda = \{\lambda_1, \lambda_2, \ldots, \lambda_N\}$. Here we are presuming that $\{\varphi_\lambda\}$ is a complete set of single particle functions. We envision the orbitals $\{\varphi_\lambda\}$ to be ordered in some fashion--say by a dictionary prescription for arranging the quantum numbers $\varepsilon, \ell, m_\ell, m_s$. Then we may use this ordering to arrange $\lambda_1 < \lambda_2 < \ldots < \lambda_N$ in defining Λ, recalling that no permutations of a given Λ be considered in enumerating the complete set $\{\Phi_\Lambda\}$. If the orbitals themselves form an orthonormal set $\{\varphi_\lambda\}$ in the sense that

$$\int {}^{*}_{\lambda}(X)\ {}_{\lambda'}(X)\ dX = \delta_{\lambda\lambda'}, \tag{3.38}$$

then the set of Slater determinants $\{\Phi_\Lambda\}$ is also an orthonormal set in the sense that

$$\int dX_1 \ldots \int dX_N\ \Phi^*_\Lambda(X_1 \ldots X_N)\ \Phi_{\Lambda'}(X_1 \ldots X_N) = \delta_{\Lambda\Lambda'}. \tag{3.39}$$

Here the Kroneker delta $\delta_{\Lambda\Lambda'}$ is zero if the two ordered N-tuples

$$\Lambda = \{\lambda_1 < \lambda_2 < \ldots < \lambda_N\} \tag{3.40}$$

and

$$\Lambda' = \{\lambda'_1 < \lambda'_2 < \ldots < \lambda'_N\} \tag{3.41}$$

are different. This orthonormality of the Slater determinants may be seen by expanding the left and right Slater determinants into N! terms. Then of the $(N!)^2$ products in the integrand of (3.39) only those with the same orbitals occurring from the left as from the right for all N particle labels $X_1, X_2, \ldots, X_N$ integrate to unity, the other terms vanish. Clearly, if $\Lambda \neq \Lambda'$ no such coincidence occurs since the two sets have at least one mismatch. Thus, the orthogonality of the Slater determinant follows. If $\Lambda = \Lambda'$ then, of the $(N!)^2$ terms only those N! terms corresponding to the same permutation on the left as on the right yield one upon integrating. This observation, coupled with the fact that the product of phase factors is always +1 and the occurrence of 1/N! from the two antisymmetrizers, indicates that the Slater determinants are normalized to unity. Thus, the Slater determinants $\{\Phi_\Lambda\}$ form a complete orthonormal basis for expanding N electron wave functions.

At this point we step back to survey the problem which is to be studied in detail. The outline closely follows what we have done so far for atoms. We seek to find the solutions to the exact molecular electronic eigenvalue problem

$$\hat{H}_o \Psi_\mu = E_\mu \Psi_\mu . \tag{3.42}$$

With $\hat{H}_o$ given by Equation (3.1), we cannot solve Equation (3.42) exactly. Our first step is to obtain a model Hamiltonian which has solutions that are in some as yet vague sense a good approximation to those of $\hat{H}_o$. Specifically, we investigate the independent particle model, a sum of one body operators. We assume a complete set of one-particle eigenstates

$$\hat{h}_o \phi_\lambda(X) = \varepsilon_\lambda \phi_\lambda(X) \tag{3.43}$$

where $\phi_\lambda(X)$ are the eigenfunctions and ε_λ are the eigenvalues. Again, we envision

$$\hat{h}_o(i) = \frac{-\hbar^2}{2m} \nabla_i^2 + \sum_{\alpha=1}^{A} \frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} + \hat{U}(i), \tag{3.44}$$

but now $\hat{U}(i)$ has the symmetry of the molecule. The precise form of $\hat{U}(i)$ has not yet been specified, but presumably it has an analogous physical role to the atomic potential, namely to describe the average effects of the remaining (N-1) electrons. Of course the ϕ_λ's and ε_λ's are not the atomic orbitals found above, but rather reflect the model energy states of the electrons within the molecule. In fact we shall determine U(i) by the Hartree-Fock variational procedure, as we simultaneously determine the molecular orbitals φ_λ and eigenvalues ε_λ. The orbital index λ now includes the energy ε and spin m_s eigenvalues, as well as symmetry labels identifying the transformation properties of the orbital under the symmetry operations of the group. Symmetry properties are treated in Appendices B and C. The set of eigenfunctions $\{\varphi_\lambda(X)\}$ forms a complete orthonormal set spanning the one-body Hilbert space.

As in the atomic case discussed above, the model eigenfunctions are antisymmetrized products given by

$$\Phi_\Lambda(X_1 \ldots X_N) = \hat{a}(N) \prod_{j=1}^{N} \varphi_{\lambda_j}(X_i) \tag{3.45}$$

and satisfying the eigenvalue equation

$$\hat{\mathcal{H}}_o \Phi_\Lambda = \mathcal{E}_\Lambda \Phi_\Lambda \tag{3.46}$$

with eigenvalues

$$\mathcal{E}_\Lambda = \sum_{j=1}^{N} \varepsilon_{\lambda_j} . \tag{3.47}$$

$\Lambda = \{\lambda_1, \lambda_2, \ldots, \lambda_N\}$ is an ordered N-tuple of orbitals, and the set $\{\Phi_\Lambda\}$ forms a complete orthonormal set which spans the antisymmetric N-electron space. That is to say, we may express the exact eigenfunctions of the true Hamiltonian as a linear combination of the Φ_Λ's:

$$\Psi_\mu = \sum_\Lambda C_{\Lambda\mu} \Phi_\Lambda . \tag{3.48}$$

For while no one Φ_Λ is an eigenfunction of the "true" Hamiltonian $\hat{H}_0$ yet the two complete sets $\{\Phi_\Lambda\}$, the eigenfunctions of the model Hamiltonian $\hat{\mathit{H}}_0$, and $\{\Psi_\mu\}$, the eigenfunctions of the true Hamiltonian $\hat{H}_0$, presumably span the same N-electron space. In somewhat more practical terms our attention will be focused upon the ground state Ψ_0 and low-lying excited states of $\hat{H}_0$. The expansion (3.48) in terms of a complete set is "just" a mathematical exercise. Eventually we hope that a judicious choice of $\hat{\mathit{H}}_0$ will allow us to associate a single member of the model basis $\{\Phi_\Lambda\}$ with a particular sought-for eigenfunction Ψ_μ through the dominance of a certain coefficient in the expansion (3.48). This "judicious" choice of $\hat{\mathit{H}}_0$ comes down immediately to choosing $\hat{h}_0$. In practice this means we are still faced with the task of choosing $\hat{U}(i)$. On the one hand no choice of $\hat{U}(i)$ could lead to a model Hamiltonian $\hat{\mathit{H}}_0$ having the identical spectrum as $\hat{H}_0$, since no single-particle $\hat{U}(i)$ could mimic all the details of the sum of Coulomb electron-electron repulsions. On the other hand, any choice of U(i) yields a model Hamiltonian $\hat{\mathit{H}}_0$ having a complete set of Slater determinants. Therefore, the question remains as to the optimum choice for $\hat{U}(i)$.

We eventually want to consider the problem of determining the $C_{\Lambda\mu}$'s in the expansion (3.48) and the optimum orbitals--and concomitantly the optimum $\hat{U}(i)$--within the framework of a single variational principle. Ultimately we shall arrive at the choice of orbitals according to the Hartree-Fock procedure. In fact we now approach both problems from the viewpoint of the Rayleigh-Ritz variational principle as a unifying theme.

Considerations begin by envisioning that we already have at our disposal a complete set of single-particle functions (orbitals). Never mind for now where we got such a set; later, in fact, the variational formalism itself will show us how to generate such a complete set. Without loss of generality we assume this set of orbitals $\{\varphi_\lambda\}$ is orthonormal in the sense

$$\int dX \; \varphi^*_\lambda(X) \;\; \varphi_{\lambda'}(X) = \delta_{\lambda\lambda'}. \tag{3.49}$$

It follows, then, that the set of all possible antisymmetrized N-tuples of these orbitals spans the antisymmetric N-particle space. That is, as we did above, we construct the Slater determinants

$$\Phi_\Lambda = \hat{a}(N) \prod_{i=1}^{N} \varphi_{\lambda_i}(X_i) \tag{3.50}$$

where each $\Lambda = \{\lambda_1 < \lambda_2 < \ldots < \lambda_N\}$ stands for an ordered N-tuple of orbitals, and stipulate that any antisymmetric wavefunction may be expanded as

$$\chi(X_1,X_2,\ldots,X_N) = \sum_\Lambda C_\Lambda \; \Phi_\Lambda(X_1,X_2,\ldots,X_N). \tag{3.51}$$

To find the expansion coefficients $C_{\Lambda\mu}$ for the sought-for eigenfunctions, we appeal to the Rayleigh-Ritz variational principle which states that, for any normalized trial wave functions χ in the function space,

$$\mathcal{E}(\chi) = \langle\chi|\hat{H}_o|\chi\rangle \geq E_o, \qquad \langle\chi|\chi\rangle = 1. \tag{3.52}$$

That is, the expectation value of $\hat{H}_o$ obtained using any trial wave function χ is never less than the exact ground state eigenvalue E_o. The proof of this theorem is easily demonstrated by expanding the trial wave function χ in terms of the admittedly yet unknown Ψ_μ, the exact eigenfunctions of $\hat{H}_o$. In fact it can be demonstrated that the equality holds if, and only if, the "trial" wave function is the exact ground state eigenvector. We say that the expectation value $<\chi|\hat{H}_o|\chi>$ is an "upper bound" of the ground state eigenvalue. There are some additional consequences which emerge from the Rayleigh-Ritz variational principle which we shall refer to shortly. However, for now the prescription for obtaining the ground state eigenfunction and eigenvalue of $\hat{H}_o$ is clear. We seek to minimize the expectation value

$$E(\chi) = <\sum_{\Lambda} C_{\Lambda}\Phi_{\Lambda}|\hat{H}_o|\sum_{\Lambda'} C_{\Lambda'}\Phi_{\Lambda'}> = \sum_{\Lambda}\sum_{\Lambda'} C^*_{\Lambda} C_{\Lambda'}<\Phi_{\Lambda}|\hat{H}_o|\Phi_{\Lambda'}> \tag{3.53}$$

with the constraint that

$$<\chi|\chi> = \sum_{\Lambda} |C_{\Lambda}|^2 = 1. \tag{3.54}$$

In principle, E is a function of the yet-to-be-found C_{Λ}'s and a functional of the yet-to-be-chosen ϕ_{λ}'s. For now, however, using a specified set of orbitals we consider E as a function of only the C_{Λ}'s and C^*_{Λ}'s

$$E = E(\ldots C_{\Lambda}, C^*_{\Lambda}, \ldots) = \sum_{\Lambda}\sum_{\Lambda'} C^*_{\Lambda}H_{\Lambda\Lambda'}\,C_{\Lambda'} \tag{3.55}$$

with the known "matrix elements"

$$H_{\Lambda\Lambda'} = <\Phi_{\Lambda}|\hat{H}_o|\Phi_{\Lambda'}> \tag{3.56}$$

indexed by a chosen pair of Slater determinants. (Below we shall show how these "matrix elements" may be evaluated in terms of integrals over the space and spin coordinates of the one and two electrons occupying the specified orbitals.)

By varying the coefficients C_Λ subject to the constraint we seek the lowest possible value of the quadratic form in the C_Λ, C^*_Λ's found in (3.53). Incorporating the constraint by Lagrange's technique we have

$$F(|\chi>) = \mathcal{E}(|\chi>) - E\{<\chi|\chi> - 1\}, \tag{3.57}$$

where, at this point, E is the Lagrange multiplier to insure the normalization. Since the C_Λ may be complex numbers we should consider independent variations in the real and the imaginary parts of each C_Λ. Alternatively, we consider C_Λ and C^*_Λ as independent variational parameters. Requiring F in terms of these coefficients to be stationary leads to two sets of linear equations for determining the optimum coefficients:

$$\begin{aligned} \frac{\partial F}{\partial C^*_\Lambda} = 0 \quad &\text{implies} \quad \sum_{\Lambda'} \{H_{\Lambda\Lambda'} - E\delta_{\Lambda\Lambda'}\}C_{\Lambda'} = 0 \quad \text{for all } \Lambda; \\ \frac{\partial F}{\partial C_\Lambda} = 0 \quad &\text{implies} \quad \sum_{\Lambda'} C^*_{\Lambda'}\{H_{\Lambda'\Lambda} - E\delta_{\Lambda'\Lambda}\} = 0 \quad \text{for all } \Lambda. \end{aligned} \tag{3.58}$$

Since the Hamiltonian $\hat{H}_o$ is in fact a Hermitian operator so that $H_{\Lambda\Lambda'} = H^*_{\Lambda'\Lambda}$, one set of equations is simply the complex conjugate of the other. The resulting equations arising from the independent variations can be put in the form of a matrix equation

$$\left[\begin{pmatrix} H_{11} & H_{12} & \cdots \\ H_{21} & H_{22} & \cdots \\ \vdots & \ddots & \\ & H_{\Lambda\Lambda'} \cdots & \\ & \vdots & \end{pmatrix} - E \begin{pmatrix} 1 & 0 & \cdots \\ 0 & 1 & \cdots \\ \vdots & \ddots & \\ & \delta_{\Lambda\Lambda'} \cdots & \\ & \vdots & \end{pmatrix}\right] \underset{\sim}{C} = \underset{\sim}{0}, \tag{3.59}$$

or in somewhat abbreviated form

$$\{\underset{\sim}{H} - E\,\underset{\sim}{1}\}\,\underset{\sim}{C} = \underset{\sim}{0}. \tag{3.60}$$

Indeed, we obtain a matrix eigenvalue problem. In principle, the orbital basis $\{\phi_\lambda\}$ is infinite and so the Slater determinental basis $\{\Phi_\Lambda\}$ is also infinite. Thus, the matrix we deal with

$$\underset{\sim}{H} = [H_{\Lambda\Lambda'} = \langle\Phi_\Lambda|\hat{H}_o|\Phi_{\Lambda'}\rangle] \tag{3.61}$$

is infinite, the rows and columns being labeled by the basis function labels Λ, each of which a definite N-tuple of orbitals $\lambda_1 < \lambda_2 < \ldots < \lambda_N$.

Solving the above matrix eigenvalue equation is in every respect equivalent to finding the eigenfunctions and eigenvalues of the original Schrödinger equation cast in the form of a many-dimensional partial differential equation. In fact, all the stationary states--and not just the ground state--emerge by solving this infinite matrix equation. The formal approach, which one learns in linear algebra for finite matrices and is generalized here to the infinite matrix, is first to find the eigenvalues as the roots of the secular equation

$$\det\{\underset{\sim}{H} - E\underset{\sim}{1}\} = 0. \tag{3.62}$$

This is necessary and sufficient that the matrix equation (3.59) has nontrivial solutions. Once found, these eigenvalues are then inserted, one at a time, into the matrix equation and the set of linear equations solved by the traditional methods. Thus, emerging from the matrix procedure is a set of eigenvalues and corresponding column eigenmatrices to every member of which we attach an index μ enumerating the various solutions of the eigenvalue problem. In particular, Ψ_o the ground state ($\mu = 0$) eigenfunction will be expanded accordingly as

$$\Psi_o(X_1,X_2,\ldots,X_N) = \sum_{\Lambda} C_{\Lambda o}\, \Phi_{\Lambda}(X_1,X_2,\ldots,X_N), \tag{3.63}$$

the index "o" here denoting the ground electronic state.

Above we have pointed out that with a complete set of orbitals a complete (and thus infinite) set of Slater determinants is formed, resulting in recasting the problem of finding the stationary states into one involving infinite matrices. If we had to leave it go at this, no particular advantage would ensue, since diagonalizing infinite matrices is probably every bit as hard as solving partial differential equations. But--and this is a key point--the Rayleigh-Ritz variational principle holds when the "trial function" χ is confined to a smaller function space than that considered above. Indeed the statement $\mathcal{E}(\chi) \geq E_o$ concerns any χ. However, confining χ to a certain subspace is essentially placing more constraints upon it, and so one is simply guaranteed an upper bound to the exact ground state E_o; no longer can the equality be ensured unless, by some extremely good fortune (which never happens), the exact ground state eigenfunction of $\hat{H}_o$ happened to lie completely within the chosen subspace. Picking a subspace in which to use the Rayleigh-Ritz principle usually happens on a practical level as follows: we do not have at our disposal a complete set of orbitals, but rather only a finite set of, say, M orbitals $\{\phi_1,\phi_2,\ldots,\phi_M\}$. Again, for the moment, let us not worry about where we obtained these orbitals, for the formalism will still show us one possible way to generate them. Having only M orbitals we can construct only

$$\mathcal{M} = M!/(M-N)!N! \tag{3.64}$$

determinants which thus span (and in so doing define) our chosen subspace. Having thus limited our considerations to Φ_Λ's within this subspace, we can proceed in the same variational fashion as before. Now, however, our trial wave function is expanded

$$\chi(X_1,X_2,\ldots,X_N) = \sum_{\Lambda=1}^{\mathcal{M}} C_\Lambda \Phi_\Lambda(X_1,X_2,\ldots,X_N) \tag{3.65}$$

and the optimum C_Λ's obtained as solutions to a matrix equation

$$\{\underset{\sim}{H} - E\,\underset{\sim}{1}\}\underset{\sim}{C} = \underset{\sim}{0}; \tag{3.66}$$

this time the matrix $\underset{\sim}{H}$ is $\mathcal{M}\times\mathcal{M}$, and so the diagonalization procedure (i.e., finding the roots of the secular equation and solving the linear equations for the C_Λ's) can be done by electronic computers. The various determinants belong to different "configurations of orbitals" and this procedure is thus called "configuration interaction".

Before closing this chapter--our first on electronic states--we want to state briefly the rules for evaluating the necessary matrix elements $H_{\Lambda\Lambda'}$ which occur in our matrix equation. We again envision an orthonormal set of orbitals and consequently have an orthonormal set of M Slater determinants $\{\Phi_{\Lambda}\}$. A typical matrix element of the Hamiltonian operator which thus occurs is

$$<\Phi_{\Lambda}|\hat{H}_{o}|\Phi_{\Lambda'}> = \int dX_{1} \ldots \int dX_{N} \, [\hat{a}(N) \prod_{i=1}^{N} \varphi_{\lambda_i}(X_i)]^{*}$$

$$\{ \sum_{i=1}^{N} \hat{h}(i) + \sum_{i<j} \hat{v}(i,j)\}[\hat{a}(N) \prod_{j=1}^{N} \varphi_{\lambda'_j}(X_j)] \qquad (3.67)$$

where Λ and Λ' denote two (in general, different) N-tuples of orbitals. We envision that these sets of orbitals are arranged to have maximal coincidence, with the n differing orbitals located in the first n places. For instance, if the two sets of orbitals have $N-1$ orbitals in common, and thus differ in a single orbital, we arrange the sets so that $\lambda_1 \neq \lambda'_1$, but $\lambda_i = \lambda'_i$, $i = 2,3,\ldots,N$. It must be pointed out that beginning with any two arrangements of orbitals Λ and Λ', a reshuffling of the orbital indices can always bring them into such maximal coincidence. However, each corresponding basis function, now relabeled according to this scheme, has the columns of the determinant also rearranged accordingly, and so may differ by (at most) a phase factor of (-1) from the original determinant. The phase factors introduced by the rearranging process must be incorporated into the matrix element $H_{\Lambda\Lambda'}$ itself. Using the fact that $\hat{a}(N)$ the antisymmetrizer is an Hermitian operator which commutes with the Hamiltonian $\hat{H}_o$ (because $\hat{H}_o$ is symmetric in the particle labels) the above matrix element (3.67) can be rewritten

$$\langle\Phi_\Lambda|\hat{H}_o|\Phi_{\Lambda'}\rangle = \int dX_1 \cdots \int dX_N \prod_{i=1}^{N} \varphi^*_{\lambda_i}(X_i)\{\sum_{i=1}^{N} \hat{h}(i) + \sum_{i<j} \hat{v}(i,j)\}$$

$$\{\sum_P (-1)^{\sigma_P} \hat{P}\} \prod_{j=1}^{N} \varphi_{\lambda'_j}(X_j). \tag{3.68}$$

Here we have also used the fact that

$$[\hat{a}(N)]^2 = \sqrt{N!}\, \hat{a}(N) = \sum_P (-1)^{\sigma_P} \hat{P}. \tag{3.69}$$

Let us next then consider the first "one-body" term:

$$\int dX_1 \ldots dX_N\, \varphi^*_{\lambda_1}(X_1)\, \varphi^*_{\lambda_2}(X_2) \cdots \varphi^*_{\lambda_N}(X_N)$$

$$\hat{h}(1)[\sum_P (-1)^{\sigma_P} \hat{P}]\varphi_{\lambda'_1}(X_1)\varphi_{\lambda'_2}(X_2) \cdots \varphi_{\lambda'_N}(X_N). \tag{3.70}$$

Here, the integrations over particle labels 2,3,...,N can be performed before considering the integration over particle 1. In the integrand the function on the left is a simple product of orbitals--in particular the factor involving particles 2,3,...,N is $\varphi^*_{\lambda_2}(X_2)\, \varphi^*_{\lambda_3}(X_3) \cdots \varphi^*_{\lambda_N}(X_N)$--and so because of the orthogonality of the orbitals, particles 2,3,...,N must occur in precisely these same orbitals in the function on the right if the integral is not to vanish. Recalling that we have already "lined up" the orbital sets Λ and Λ' in maximal coincidence, it is clear that only the identity operator (i.e., no permutation of the particle labels) could lead to a nonvanishing result since any permutation (necessarily involving at least two particles, of course) would assuredly produce a mismatch vis' à vis' particles 2,3,...,N between the orbitals on the right and left. Furthermore, only if $\lambda_i = \lambda'_i$, i=2,3,...,N can the integration be nonvanishing, since otherwise, even in the identity permutation, at least one orbital integration factor would be zero. With $\lambda_i = \lambda_i'$ for i= 2,3,...N the first one-body term becomes

$$(\phi_{\lambda_1}|\hat{h}|\phi_{\lambda_1'}) = \int dX\, \phi^*_{\lambda_1}(X)\hat{h}\phi_{\lambda_1'}(X). \tag{3.71}$$

Similar consideration of the other (N-1) "one-body" terms $\hat{h}(2), \hat{h}(3), \ldots, \hat{h}(N)$ leads to the conclusion that

$$\int dX_1\, dX_2 \ldots dX_N [\hat{a}(N) \prod_{i=1}^{N} \phi_{\lambda_i}(X_i)]^* \{\hat{h}(1) + \hat{h}(2) + \ldots + \hat{h}(N)\} [\hat{a}(N) \prod_{j=1}^{N} \phi_{\lambda_j'}(X_j)]$$

$$= \begin{cases} \sum_{i=1}^{N} (\phi_{\lambda_i} | \hat{h} | \phi_{\lambda_i'}), & \lambda_i = \lambda_i',\ i=1,2,\ldots,N \\ (\phi_{\lambda_1} | \hat{h} | \phi_{\lambda_1'}), & \lambda_1 \neq \lambda_1',\ \lambda_i = \lambda_i',\ i=2,\ldots,N \\ 0, & \text{otherwise.} \end{cases} \tag{3.72}$$

In particular, we note that if the Slater determinants Φ_Λ and $\Phi_{\Lambda'}$ differ in more than one orbital, there are no one-body contributions to the matrix element.

In an analogous fashion we consider the first "two-body" term:

$$\int dX_1\, dX_2 \ldots dX_N \prod_{i=1}^{N} \phi^*_{\lambda_i}(X_i)$$

$$\hat{v}(1,2)[\sum_P (-1)^{\sigma_P} \hat{P}]\phi_{\lambda_1'}(X_1)\phi_{\lambda_2'}(X_2) \ldots \phi_{\lambda_N'}(X_N). \tag{3.73}$$

This time, the integrations over particle labels 3,4,...,N can be performed before considering the integrations over particles 1 and 2. The function on the left is the simple product of orbitals, and in particular the factor involving the particles 3,4,...,N is $\varphi^*_{\lambda_3}(X_3)\, \varphi^*_{\lambda_4}(X_4) \ldots \varphi^*_{\lambda_N}(X_N)$. Considerations like those given above are also applicable here. Again the key point to keep in mind is the orthogonality of the orbitals. This time, however, in addition to the identity, the permutation of simply interchanging particle labels 1 and 2 can lead to non-vanishing results since both operations leave particles 3,4,...,N in their original position vis' à vis' the order of the factor on the left. Of course, the integrations over particles 3,4,...,N lead to nonvanishing factors only if $\lambda_i = \lambda'_i$, i=3,4,...,N. Thus, Λ and Λ' can differ at most in two orbitals, otherwise the corresponding matrix element of the two-body terms will assuredly vanish. The result is certainly analogous to the one-body result found above. There are some differences, however. The fact that both the identity and the $(-1)\hat{P}_{12}$ operators lead to non-vanishing results gives rise to two terms, a so-called direct and exchange term, in the evaluation of each such two-body integration. Indeed, assuming that $\lambda_i = \lambda'_i$, for i=3,4,...,N the first "two-body" matrix element considered above becomes simply

$$\int dX_1 \int dX_2\, \varphi^*_{\lambda_1}(X_1)\, \varphi^*_{\lambda_2}(X_2) v(1,2)\, \varphi_{\lambda'_1}(X_1)\, \varphi_{\lambda'_2}(X_2)$$

$$- \int dX_1 \int dX_2\, \varphi^*_{\lambda_1}(X_1) \varphi^*_{\lambda_2}(X_2) \hat{v}(1,2) \varphi_{\lambda'_1}(X_2) \varphi_{\lambda'_2}(X_1). \qquad (3.74)$$

Similar considerations of the other [(N+1)(N-2)/2] "two-body" terms lead to the conclusion that

$$\int dX_1\, dX_2 \ldots dX_N\, (\hat{a}(N) \prod_{i=1}^{N} \varphi_{\lambda_i}(X_i))^* (\sum_{i<j}^{N} \hat{v}(i,j))(\hat{a}(N) \prod_{j=1}^{N} \varphi_{\lambda_j}(X_j))$$

$$\sum_{i<j} <\varphi_{\lambda_i}(1)\, \varphi_{\lambda_j}(2)|\hat{v}_{12}|\, \varphi_{\lambda'_i}(1)\, \varphi_{\lambda'_j}(2)>, \quad \lambda_i = \lambda'_i,\ i=1,2,\ldots,N$$

$$= \quad \sum_{i=2}^{N} <\varphi_{\lambda_1}(1)\, \varphi_{\lambda_i}(2)|\hat{v}_{12}|\, \varphi_{\lambda'_1}(1)\, \varphi_{\lambda'_i}(2)>, \quad \lambda_1 \neq \lambda'_1;\ \lambda_i = \lambda'_i, \qquad (3.75)$$

$$i=2,3,\ldots,N.$$

$$<\varphi_{\lambda_1}(1)\, \varphi_{\lambda_2}(2)|\hat{v}_{12}|\, \varphi_{\lambda'_1}(1)\, \varphi_{\lambda'_2}(2)>, \quad \lambda_1,\lambda_2 \neq \lambda'_1,\lambda'_2;\ \lambda_i = \lambda'_i,$$

$$i=3,4,\ldots,N.$$

$$0, \quad \text{otherwise.}$$

Here, we define the two-body matrix elements

$$<\varphi_{\lambda_a}(1)\, \varphi_{\lambda_b}(2)|\hat{v}_{12}|\varphi_{\lambda_c}(1)\, \varphi_{\lambda_d}(2)> = (\varphi_{\lambda_a}(1)\, \varphi_{\lambda_b}(2)|\hat{v}_{12}|\, \varphi_{\lambda_c}(1)\, \varphi_{\lambda_d}(2))$$

$$-(\varphi_{\lambda_a}(1)\, \varphi_{\lambda_b}(1)|\hat{v}_{12}|\, \varphi_{\lambda_d}(1)\, \varphi_{\lambda_c}(2)) \qquad (3.76)$$

noting the angular brackets include both the direct and exchange two-body integrals while the rounded brackets imply the two-body states are simple direct products of orbitals. This time we note that the matrix element of the sum of two-body interactions vanishes if the Slater determinants differ in more than two orbitals.

These "rules" for the evaluation of the one- and two- body operator matrix elements are sufficient to construct the entire $M \times M$ Hamiltonian matrix. Indeed the past twenty-five or so years of "quantum-chemistry" have led to some very sophisticated "packages" of computer software for tackling these problems. The reader should not think that we have come close to exhausting the details of this subject. On the other hand if he appreciates the steps envisioned in the discussion above, he has at least an insight into the traditional calculations of electronic stationary states. Again, we presumed to have obtained the orbitals--a subject we seem to keep postponing. Let us say, however, that at the "brute force" level of calculations we could always introduce a set of orthonormal orbitals in terms of sets of "well-known" functions, such as the solutions of the hydrogen-like atom. Having said this we now proceed to the promised discussion of generating the orthonormal set of orbitals within the framework of the variational procedure itself.

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CHAPTER IV

THE HARTREE-FOCK METHOD

Not only is the expectation value E of (3.53) a function of the complex coefficients C_Λ and C_Λ^*, but it may also be viewed as a functional of the yet to be determined orbitals, the ϕ_λ's, themselves. Indeed, the Rayleigh-Ritz variational principle still guarantees that as we search through various possible sets of orbitals in constructing our N-electron Slater determinants an upper bound of the lowest eigenvalue of the Hamiltonian $\hat{H}_o$ is provided by each expectation value. The prescription for obtaining the "best" set of orbitals should thus be clear. We perform a functional variation of E with respect to the orbitals in order to minimize the expectation value. We can insure the constraint of orthonormality among the orbitals with the introduction of Lagrange multipliers. Admittedly, the details are terribly complicated in the most general formulation of the procedure, since presumably one could be simultaneously varying both the orbital functions, $\{\phi_\lambda(X)\}$, as well as the linear expansion coefficients $\{C_\Lambda\}$. In general terms, this is the procedure called a "multiconfiguration-self-consistent-field" calculation. We shall rather consider a very special case in which we allow only N orbitals to be considered in the set $\{\phi_\lambda\}$. As an immediate consequence there is only one Slater determinant to be considered, the coefficient of which is determined by the normalization condition to be unity. Thus, only a functional variation in the N orbitals themselves is considered. The resulting procedure is called single determinant Hartree-Fock theory. One final remark is in order: although our explicit considerations begin by focusing only on N orbitals, we are quickly led to a procedure for generating a complete set of orbitals and the corresponding effective potential $\hat{U}(i)$. Thus, all the ideas introduced in Chapter III will be applicable to these so-called Hartree-Fock orbitals. In particular, truncating the complete set of Hartree-Fock orbitals leads to the notion of configuration-interaction among a finite set of model states.

As mentioned above, our derivation of the Hartree-Fock equations will be restricted to the special case of a single Slater determinant. More explicitly, given a system containing N electrons, we envision a set of N yet-to-be-found orbitals $\{\phi_{\lambda_i}\}$, one orbital for each electron, with the stipulation that the orbitals are orthonormal. We shall refer to the N orbitals $\{\phi_{\lambda_i}\}$ as the occupied orbitals and the single Slater determinant which minimizes the expectation value we shall call the Hartree-Fock determinant denoted by

$$\Phi^{HF} = \sqrt{1/N!} \begin{vmatrix} \phi_{\lambda_1}(1) & \phi_{\lambda_2}(1) & \cdots & \phi_{\lambda_N}(1) \\ \phi_{\lambda_1}(2) & \phi_{\lambda_2}(2) & \cdots & \phi_{\lambda_N}(2) \\ \vdots & \vdots & & \vdots \\ \phi_{\lambda_1}(N) & \phi_{\lambda_2}(N) & \cdots & \phi_{\lambda_N}(N) \end{vmatrix} . \qquad (4.1)$$

Each λ stands for a set of quantum numbers, with the subscript i (i=1,2,...,N) delineating the N different sets. Alternatively, the subscript i labels the "place index" (or column index) of the orbital in the Slater determinant. Any such set of orbitals $\{\phi_{\lambda_1}(X), \phi_{\lambda_2}(X), \ldots, \phi_{\lambda_N}(X)\}$ spans an N dimensional subspace in the infinite dimensional single particle Hilbert space. By varying the N orbitals, we are in essence looking for the one subspace which is spanned by the optimum set of orbitals which minimize the expectation value $E(\phi_{\lambda_1}\phi^*_{\lambda_1}, \ldots, \phi_{\lambda_N}\phi^*_{\lambda_N})$. The result of applying the Rayleigh-Ritz variation method to (the set of N orbitals in order to) minimize the expectation value (3.53) leads to a set of coupled integro-differential equations for these orbitals, the so-called Hartree-Fock equations. Φ^{HF} of course spans a one-dimensional subspace of the antisymmetric N-electron Hilbert space. Thus we can view the variational procedure as a search for either the optimum N-dimensional one-particle space or the optimum one-dimensional N-particle space spanned by an antisymmetrized product of N orbitals, i.e., a single Slater determinant.

With the restriction that χ of (3.53) be a single Slater determinand, $\chi \equiv \Phi$, we write

$$E(\phi^*_{\lambda_1}\phi_{\lambda_1} \ldots) = \langle\chi|\hat{H}_o|\chi\rangle = \langle\Phi|\hat{H}_o|\Phi\rangle. \tag{4.2}$$

Now, the notation emphasizes that it is the orbitals themselves which are subject to the variation. Previously, our viewpoint was that the orbitals were given and the expansion coefficients C_Λ's were the sole variational parameters. As mentioned above, had we included more than one determinant in the expansion of χ--that is, if we had introduced more than N yet-to-be-found orbitals--both the expansion coefficients and the orbitals could be subject to the variational procedure.

We have already shown in (3.72) and (3.75) that the expectation value--a diagonal element $H_{\Lambda\Lambda}$--may be written as the sum of one-body and direct and exchange two-body integrals:

$$E(\varphi^*_{\lambda_1}\varphi_{\lambda_1}\cdots\varphi^*_{\lambda_N}\varphi_{\lambda_N}) = \sum_{i=1}^{N}[\int dX_1\varphi^*_{\lambda_i}(X_1)\{(-\hbar^2/2m)\nabla_1^2+\hat{v}(r_1)\}\varphi_{\lambda_i}(X_1)]$$

$$+ \sum_{1\leq i<j\leq N}[\int dX_1 \int dX_2 \varphi^*_{\lambda_i}(X_1)\varphi^*_{\lambda_j}(X_2)\,\frac{e^2}{r_{12}}\,\varphi_{\lambda_i}(X_1)\varphi_{\lambda_j}(X_2)$$

$$- \int dX_1 \int dX_2 \varphi^*_{\lambda_i}(X_1)\varphi^*_{\lambda_j}(X_2)\,\frac{e^2}{r_{12}}\,\varphi_{\lambda_j}(X_1)\varphi_{\lambda_i}(X_2)]. \tag{4.3}$$

Equation (4.3) may be written more concisely in terms of the angular brackets,

$$E(\Phi) = \sum_{i=1}^{N}\langle\varphi_{\lambda_i}(X_1)|\hat{h}|\varphi_{\lambda_i}(X_1)\rangle + \sum_{i<j}\langle\varphi_{\lambda_i}(X_1)\ \varphi_{\lambda_j}(X_2)|\hat{v}_{12}|\varphi_{\lambda_i}(X_1)\varphi_{\lambda_j}(X_2)\rangle. \tag{4.4}$$

The sums are over the orbitals occupied in Φ^{HF}, which of course remain to be found by minimizing this explicit functional of the orbitals subject to the orthonormality conditions. Often the particle labels are eliminated with the order of the orbital's occurence in the brackets denoting the correct label. We can include the orthonormality constraints in the variational procedure by the use of the Lagrange multipliers which we denote by K_{ij}. Thus we define a new functional of the N orbitals $F(\Phi)$ where

$$F(\Phi) = \sum_{i=1}^{N}\langle\varphi_{\lambda_i}(X_1)|\hat{h}|\varphi_{\lambda_j}(X_1)\rangle + \sum_{i<j}\langle\varphi_{\lambda_i}(X_1)\varphi_{\lambda_j}(X_2)|\hat{v}_{12}|\varphi_{\lambda_i}(X_1)\varphi_{\lambda_j}(X_2)\rangle$$

$$+\sum_{i=1}^{N}\sum_{j=1}^{N} K_{ji}\{\langle\varphi_{\lambda_i}|\varphi_{\lambda_j}\rangle - \delta_{\lambda_i\lambda_j}\}. \tag{4.5}$$

F is a "functional" of the N complex functions, φ_{λ_i}--2N real functions, since $\varphi_{\lambda_i} = R_{\lambda_i}(\vec{r},\xi) + iI_{\lambda_i}(\vec{r},\xi)$--and also a function of the N^2 complex numbers K_{ji}--$2N^2$ real numbers, since $K_{ji} = a_{ji} + ib_{ji}$. In principle we are required to carry out the variations with respect to the real and imaginary parts of both the orbitals $\{\varphi_{\lambda_i}\}$ and the Lagrange multiplier K_{ji} independently. Alternatively, we can view F as a functional of the φ_{λ_i}'s and the $\varphi^*_{\lambda_i}$'s, as well as a function of K_{ji}'s and K^*_{ji}'s, and perform the variations with respect to each of these quantities. The optimum orbitals are those which extremize F--those orbitals for which, to first order, arbitrary variations lead to vanishingly small variations in F. The variation in F with respect to $\varphi^*_{\lambda_k}$ is denoted $\delta_{\varphi^*_{\lambda_k}}F$ and is defined by

$$\begin{aligned}\delta_{\varphi^*_{\lambda_k}} F \equiv\ & F(\varphi^*_{\lambda_1},\varphi_{\lambda_1},\ldots,\varphi^*_{\lambda_k} + \delta\varphi^*_{\lambda_k},\ldots,\varphi^*_{\lambda_N},\varphi_{\lambda_N}) \\ & - F(\varphi^*_{\lambda_1},\varphi_{\lambda_1},\ldots,\varphi^*_{\lambda_k},\varphi_{\lambda_k},\ldots,\varphi^*_{\lambda_N},\varphi_{\lambda_N}).\end{aligned} \tag{4.6}$$

That is, in the first term on the right the function $\varphi^*_{\lambda_k}$, as it occurs in (4.5) in the formal definition of F, is replaced by $\varphi^*_{\lambda_k} + \delta\varphi^*_{\lambda_k}$, where $\delta\varphi^*_{\lambda_k}$ is an arbitrary function. We must also carry out the variation with respect to φ_{λ_k} defined similarly to be

$$\begin{aligned}\delta_{\varphi_{\lambda_k}} F =\ & F(\varphi^*_{\lambda_1},\varphi_{\lambda_1},\ldots,\varphi_{\lambda_k} + \delta\varphi_{\lambda_k},\ldots,\varphi^*_{\lambda_N},\varphi_{\lambda_N}) \\ & - F(\varphi^*_{\lambda_1},\varphi_{\lambda_1},\ldots,\varphi^*_{\lambda_k},\varphi_{\lambda_k},\ldots,\varphi^*_{\lambda_N},\varphi_{\lambda_N}).\end{aligned} \tag{4.7}$$

Of course k runs from 1 to N yielding a total of 2N functional variations.

We shall now carry out $\delta_{\varphi^*_{\lambda_k}} F$, the variation in F with respect to a particular $\varphi^*_{\lambda_k}$, explicitly considering the three terms in (4.5). Any term in F independent of the particular orbital $\varphi^*_{\lambda_k}$ is cancelled in forming the difference defining the variation. Thus there remains only a single one-body term

$$\langle\varphi_{\lambda_k}+\delta\varphi_{\lambda_k}|\hat{h}|\varphi_{\lambda_k}\rangle - \langle\varphi_{\lambda_k}|\hat{h}|\varphi_{\lambda_k}\rangle = \langle\delta\varphi_{\lambda_k}|\hat{h}|\varphi_{\lambda_k}\rangle \tag{4.8}$$

and only (N-1) two-body (direct and exchange) terms:

$$\begin{aligned}&\sum_{i=1}^{k-1}[\langle\varphi_{\lambda_i}\{\varphi_{\lambda_k}+\delta\varphi_{\lambda_k}\}|\hat{v}|\varphi_{\lambda_i}\varphi_{\lambda_k}\rangle - \langle\varphi_{\lambda_i}\varphi_{\lambda_k}|\hat{v}|\varphi_{\lambda_i}\varphi_{\lambda_k}\rangle]\\ &+ \sum_{j=k+1}^{N}[\langle\{\varphi_{\lambda_k}+\delta\varphi_{\lambda_k}\}\varphi_{\lambda_j}|\hat{v}|\varphi_{\lambda_k}\varphi_{\lambda_j}\rangle - \langle\{\varphi_{\lambda_k}\varphi_{\lambda_j}\}|\hat{v}|\varphi_{\lambda_k}\varphi_{\lambda_j}\rangle] \qquad (4.9)\\ &= \sum_{i=1}^{k-1}\langle\varphi_{\lambda_i}(X_1)\delta\varphi_{\lambda_k}(X_2)|\hat{v}_{12}|\varphi_{\lambda_i}\varphi_{\lambda_k}\rangle + \sum_{j=k+1}^{N}\langle\delta\varphi_{\lambda_k}(X_1)\varphi_{\lambda_j}(X_2)|\hat{v}|\varphi_{\lambda_k}\varphi_{\lambda_j}\rangle.\end{aligned}$$

The first term of the right hand side of (4.9) may be expressed

$$\sum_{i=1}^{k-1}\langle\delta\varphi_{\lambda_k}(X_1)\varphi_{\lambda_i}(X_2)|\hat{v}_{12}|\varphi_{\lambda_k}(X_1)\varphi_{\lambda_i}(X_2)\rangle, \tag{4.10}$$

since the operator $\hat{v}$ is symmetric with respect to the interchange of particle labels 1 and 2. Furthermore, the summation index i being a dummy summation index may be replaced with the index j; thus Equation

(4.9) takes the more concise form

$$\sum_{\substack{j=1\\ j\neq k}}^{N} \langle \delta\varphi_{\lambda_k}(X_1)\varphi_{\lambda_j}(X_2)|\hat{v}_{12}|\varphi_{\lambda_k}(X_1)\varphi_{\lambda_j}(X_2)\rangle . \tag{4.11}$$

Note that the omitted term $(j\neq k)$ in fact vanishes due to the antisymmetry of the state on the right. This being true we shall simply drop the restriction $(j\neq k)$ in our subsequent expressions. Finally, the third term in the variation takes the form $\delta_{\varphi^*_{\lambda_k}} F$

$$\sum_{j=1}^{N} K_{jk}\{\langle\delta\varphi_{\lambda_k}+\varphi_{\lambda_k}|\varphi_{\lambda_j}\rangle - \langle\varphi_{\lambda_k}|\varphi_{\lambda_j}\rangle\} = \sum_{j=1}^{N} K_{jk}\langle\delta\varphi_{\lambda_k}|\varphi_{\lambda_j}\rangle . \tag{4.12}$$

We now add expressions (4.8), (4.11), and (4.12) to get

$$\delta_{\varphi^*_{\lambda_k}} F = \langle\delta\varphi_{\lambda_k}(X_1)|\hat{h}|\varphi_{\lambda_k}(X_1)\rangle + \sum_{j=1}^{N}\langle\delta\varphi_{\lambda_k}(X_1)\varphi_{\lambda_j}(X_2)|\hat{v}_{12}|\varphi_{\lambda_k}(X_1)\varphi_{\lambda_j}(X_2)\rangle$$

$$+ \sum_{j=1}^{N} K_{jk}\langle\delta\varphi_{\lambda_k}(X_1)|\varphi_{\lambda_j}(X_1)\rangle . \tag{4.13}$$

For F to have a minimum that is, evaluating F using the optimum orbitals, this variation must vanish. In other words, we may find the equations satisfied by the optimum orbitals by setting each $(k=1,2,\ldots,N)$ of these N variations equal to zero. Thus we have

$$\langle\delta\varphi_{\lambda_k}(X_1)|\hat{h}|\varphi_{\lambda_k}(X_1)\rangle + \sum_{j=1}^{N}\langle\delta\varphi_{\lambda_k}(X_1)\varphi_{\lambda_j}(X_2)|\hat{v}_{12}|\varphi_{\lambda_k}(X_1)\varphi_{\lambda_j}(X_2)\rangle$$

$$+ \sum_{j=1}^{N} K_{jk}\langle\delta\varphi_{\lambda_k}(X_1)|\varphi_{\lambda_j}(X_1)\rangle = 0, \quad \text{for } k=1,2,\ldots,N. \tag{4.14}$$

We write (4.14) in detail, noting that the variation $\delta\varphi^{*}_{\lambda_k}(X_1)$ occurs as a factor in all three terms:

$$\int dX_1\ \delta\varphi^{*}_{\lambda_k}(X_1)\{\hat{h}(X_1)\varphi_{\lambda_k}(X_1) + \int dX_2[\sum_{j=1}^{N}\varphi^{*}_{\lambda_j}(X_2)\ \hat{v}_{12}\ \{\varphi_{\lambda_k}(X_1)\varphi_{\lambda_j}(X_2)$$

$$- \varphi_{\lambda_j}(X_1)\varphi_{\lambda_k}(X_2)\}] + \sum_{j=1}^{N} K_{jk}\,\varphi_{\lambda_j}(X_1)\} = 0. \tag{4.15}$$

Since the variation $\delta\ {}^{*}_{\lambda_k}(X_1)$ is arbitrary, the other factor in the integrand must vanish at every point in the configuration space of particle 1. Thus we conclude from (4.15) that

$$[\frac{-\hbar^2}{2m}\nabla_1^2 + \sum_{\alpha=1}^{A}\frac{-Z_\alpha e^2}{|\vec{r}_1 - \vec{R}_\alpha|} + \sum_{j=1}^{N} e^2 \int dX_2 \varphi^{*}_{\lambda_j}(X_2)\frac{\{\hat{1} - \hat{P}_{12}\}}{|\vec{r}_1 - \vec{r}_2|}\varphi_{\lambda_j}(X_2)]\varphi_{\lambda_k}(X_1)$$

$$= - \sum_{j=1}^{N} K_{jk}\varphi_{\lambda_j}(X_1), \qquad k=1,2,\ldots,N. \tag{4.16}$$

Here we have a set of N coupled integro-differential equations. We have written both the direct and exchange terms under one integral, introducing into the Coulomb potential energy the permutation operation $\hat{P}_{12}$. We note that in the exchange term $\hat{P}_{12}$ must operate prior to carrying out the integral over X_2. When the variation of F with respect to the K_{ji} is carried out we simply get the constraint equations

$$<\varphi_{\lambda_i}|\varphi_{\lambda_j}> - \delta_{ij} = 0. \tag{4.17}$$

Moreover, the variation of F with respect to φ_{λ_k} (k=1,2,...,N) (or the K_{ji}) results in the set of equations obtainable from (4.16) (or (4.17)) simply by complex conjugation. This follows from the hermiticity of the one and two-body operators. As a result we need to solve only the above set of equations.

The operator inside the square brackets of (4.16) will be called the Hartree-Fock operator $\hat{h}^{HF}$;

$$\hat{h}^{HF}(1) = [\frac{-\hbar^2}{2m}\nabla_1^2 + \sum_{\alpha=1}^{A} Z_\alpha \frac{e^2}{|\vec{r}_1 - \vec{R}_\alpha|} + \int dX_2 \sum_{j=1}^{N} e^2 \varphi^*_{\lambda_j}(X_2) \frac{\{\hat{1} - \hat{P}_{12}\}}{|\vec{r}_1 - \vec{r}_2|} \varphi_{\lambda_j}(X_2)]$$

$$= \hat{h}(1) + \hat{U}(1). \tag{4.18}$$

The integrations are over particle 2 and thus the operator in brackets operates in particle 1 space. In particular, we now have an explicit statement about the effective potential energy operator:

$$\hat{U}(1) = \int dX_2 \sum_{j=1}^{N} e^2 \varphi^*_{\lambda_j}(X_2) \frac{\{\hat{1} - \hat{P}_{12}\}}{|\vec{r}_1 - \vec{r}_2|} \varphi_{\lambda_j}(X_2). \tag{4.19}$$

In fact, this operator depends on the sought for orbitals and hence is not explicitly known before the problem is solved. Below we will show that the equations must in fact be solved "self-consistently". Moreover, we point out that U(1) is a non-local operator. Its action depends not simply on the evaluation of the function at the point but most generally at all points in particle 1 configuration space. To see this consider an arbitrary function

$$F(X_1) = F(\vec{r}_1, \xi_1). \tag{4.20}$$

Then, the action of $\hat{U}(1)$ on F(1) is

$$\hat{U}(1)F(X_1) = \int dX_2 \sum_{j=1}^{N} e^2 \varphi^*_{\lambda_j}(X_2) \frac{\{\hat{1} - \hat{P}_{12}\}}{|\vec{r}_1 - \vec{r}_2|} \varphi_{\lambda_j}(X_2)F(X_1)$$

$$= \{\int dX_2 \sum_{j=1}^{N} \varphi^*_{\lambda_j}(X_2)\varphi_{\lambda_j}(X_2)\frac{e^2}{r_{12}}\}F(\vec{r}_1,\xi_1)$$

$$- \sum_{j=1}^{N} \{\int dX_2 \varphi^*_{\lambda_j}(X_2) \frac{e^2}{r_{12}} F(\vec{r}_2,\xi_2)\}\varphi_{\lambda_j}(X_1). \tag{4.21}$$

The first term is local--we simply multiply F evaluated at point X_1 by a function of $\vec{r}_1$. In fact, this is the potential energy of Coulomb interaction between an electron (-e) at $\vec{r}_1$ and a charge distribution

$$\rho(\vec{r}_2) = -e \sum_{j=1}^{N} \sum_{\xi_2} |\varphi_{\lambda_j}(X_2)|^2. \tag{4.22}$$

On the other hand, the second term in (4.21) depends not only upon knowing F at $\vec{r}_1\xi_1$, but, because it stands under the integration $\int dX_2$, F must be known at all points in space. $\hat{U}$ is thus said to be a non-local operator. While the first Coulomb term has a classical interpretation (we refer to it as the "direct term" in the Hartree-Fock potential energy operator), the second has a strictly quantum mechanical origin, viz. the antisymmetry of the wave function. This second term is known as the "exchange" potential energy operator.

The left hand side of Equation (4.16) has the Hartree-Fock $\hat{h}^{HF}(1)$ operating upon the kth orbital. However, it is clear that all equations are coupled together through the presence of all the orbitals in the operator $\hat{U}(1)$ as well as in their explicit appearance on the right side of (4.16) through the "off-diagonal" Lagrange multipliers K_{jk}, $j \neq k$. If, as a formality, we could ignore the dependence of $\hat{U}$ on the orbitals, then

(4.16) would resemble an eigenvalue equation if the right hand side were diagonal in the j-k indices. In fact, we shall now show that we can rewrite these equations in such a form

$$\hat{h}^{HF}\phi_{\lambda_k} = \varepsilon_{\lambda_k}\phi_{\lambda_k}, \tag{4.23}$$

the so-called "canonical form" of the Hartree-Fock equations. To this end we multiply (4.16) written for $\phi_{\lambda_m}(X_1)$, that is

$$\{\frac{-\hbar^2}{2m}\nabla_1^2 + \sum_{\alpha=1}^{A} -Z_\alpha e^2/|\vec{r}_1 - \vec{R}_\alpha| + \sum_{j=1}^{m} e^2\int dX_2\phi^*_{\lambda_j}(X_2)\frac{\{\hat{1} - \hat{P}_{12}\}}{r_{12}}\phi_{\lambda_i}\}\phi_{\lambda_m}(X_1)$$

$$= -\sum_{j=1}^{m} K_{jm}\phi_{\lambda_j}(X_1), \tag{4.24}$$

by $\phi^*_{\lambda_n}(X_1)$ and integrate over X_1 to obtain

$$<\phi_{\lambda_n}|\frac{-\hbar^2}{2m}\nabla_1^2 + \sum_{\alpha=1}^{A} -Z_\alpha e^2/|\vec{r}_1 - \vec{R}_\alpha||\phi_{\lambda_m}> + \sum_{j=1}^{N} <\phi_{\lambda_n}\phi_{\lambda_j}|e^2/r_{12}|\phi_{\lambda_m}\phi_{\lambda_j}>$$

$$= -\sum_{j=1}^{m} K_{jm}<\phi_{\lambda_n}|\phi_{\lambda_j}> = -K_{nm}. \tag{4.25}$$

Similarly, starting with (4.16) written for $\phi_{\lambda_n}(X_1)$ and multiplying by $\phi^*_{\lambda_m}(X_1)$ and integrating over particle 1, we find

$$<\phi_{\lambda_m}|\frac{-\hbar^2}{2m}\nabla_1^2 + \sum_{\alpha=1}^{A} -Z_\alpha e^2/|\vec{r}_1 - \vec{R}_\alpha||\phi_{\lambda_n}> + \sum_{j=1}^{m} <\phi_{\lambda_m}\phi_{\lambda_j}|e^2/r_{12}||\phi_{\lambda_n}\phi_{\lambda_j}>$$

$$= -K_{mn}. \tag{4.26}$$

Next we use the fact that the basic one and two body operators are themselves Hermitian, so that

$$<\phi_{\lambda_a}|\frac{-\hbar^2}{2m}\nabla_1^2+\sum_{\alpha=1}^{A}-Z_\alpha\frac{e^2}{|\vec{r}_1-\vec{R}_\alpha|}|\phi_{\lambda_b}> = <\phi_{\lambda_b}|\frac{-h^2}{2m}\nabla_1^2+\sum_{\alpha=1}^{A}-Z_\alpha\frac{e^2}{|\vec{r}_1-\vec{R}_\alpha|}|\phi_{\lambda_a}>^*,$$

and (4.27)

$$<\phi_{\lambda_a}\phi_{\lambda_b}|\frac{e^2}{r_{12}}|\phi_{\lambda_c}\phi_{\lambda_d}> = <\phi_{\lambda_c}\phi_{\lambda_d}|\frac{e^2}{r_{12}}|\phi_{\lambda_a}\phi_{\lambda_b}>^*.$$

Then a term by term comparison of (4.25) and the complex conjugate of (4.26) establishes that the K_{mn}'s are elements of a Hermitian matrix:

$$K_{nm} = K^*_{mn}. \tag{4.28}$$

At this point we pause to note that the Hermitian matrix $\underset{\sim}{K}$ may be brought to diagonal form by a unitary transformation

$$\underset{\sim}{U}\,\underset{\sim}{K}\,\underset{\sim}{U}^\dagger = -\underset{\sim}{\varepsilon} = -\begin{pmatrix} \varepsilon_1 & 0 \ldots & 0 \\ 0 & \varepsilon_2 & \vdots \\ \vdots & \ddots & \\ 0 & \ldots & \varepsilon_N \end{pmatrix}. \tag{4.29}$$

It is this fact which inspires the following unitary transformation among the N-orbitals $\lambda_1, \lambda_2, \ldots, \lambda_N$.

With the precise choice of $\underset{\sim}{U}$ anticipated by the above discussion we define a new set--the canonical set--of Hartree-Fock orbitals $\{\bar{\phi}_a\}$

$$\phi_k = \sum_{a=1}^{N} U_{ak}\bar{\phi}_a \tag{4.30}$$

where

$$\sum_{\ell} U_{a\ell} U^*_{b\ell} = \delta_{ab}. \tag{4.31}$$

Here, the indices $\lambda_i, \lambda_j, \ldots$ will be abbreviated to $i, j, \ldots$. At the same time the indices $a, b, c, \ldots$ will be used for the canonical Hartree-Fock orbitals with the understanding that they too are short-hand notation for corresponding sets of single particle eigenvalues $\mu_a, \mu_b, \mu_c, \ldots$.

We now substitute in (4.16) for the orbitals $\varphi_i, \varphi_j, \ldots, \varphi_m$, according to the transformation (4.30). The k^th^ equation (4.16) becomes

$$\{\hat{h}(1) + \sum_{j=1}^{N} \int dX_2 (\sum_{a=1}^{N} U_{aj}\, \bar{\varphi}_a(X_2))^* (\hat{1} - \hat{P}_{12}) \frac{e^2}{r_{12}} (\sum_{b=1}^{N} U_{bj}\, \bar{\varphi}_b(X_2))\}\{\sum_{c=1}^{N} U_{ck}\, \bar{\varphi}_c(X_1)$$

$$= - \sum_{\ell=1}^{N} K_{\ell k} (\sum_{c=1}^{N} U_{c\ell}\, \bar{\varphi}_c(X_1)), \qquad (k=1,2,\ldots,N). \tag{4.32}$$

By interchanging the order of carrying out the summations Equation (4.32) may be written

$$\{\hat{h}(1) + \sum_{a=1}^{N} \sum_{b=1}^{N} (\sum_{j=1}^{N} U^*_{aj}\, U_{bj}) \int dX_2\, \bar{\varphi}^*_a(X_2) (\hat{1} - \hat{P}_{12}) \frac{e^2}{r_{12}} \bar{\varphi}_b(X_2)\}\{\sum_{c=1}^{N} U_{ck}\, \bar{\varphi}_c(X_1)\}$$

$$= - \sum_{c=1}^{N} (\sum_{\ell=1}^{N} K_{\ell k}\, U_{c\ell}) \bar{\varphi}_c(X_1), \qquad (k=1,2,\ldots,N). \tag{4.33}$$

Since the factor $\sum_{j=1}^{N} U^*_{aj}\, U_{bj}$ is the Kronecker delta δ_{ab}, the result after summing over b is

$$\{\hat{h}(1) + \sum_{a=1}^{N} \int dX_2\, \bar{\varphi}^*_a(X_2) (\hat{1} - \hat{P}_{12}) \frac{e^2}{r_{12}} \bar{\Phi}_a(X_2)\}\{\sum_{c=1}^{N} U_{ck}\, \bar{\varphi}_c(X_1)\}$$

$$= - \sum_{c=1}^{N} (\sum_{\ell=1}^{N} K_{\ell k}\, U_{c\ell})\, \bar{\varphi}_c(X_1), \qquad (k=1,\ldots,N). \tag{4.34}$$

Multiply the kth equation on both sides by U^*_{dk} for any fixed d to find,

$$\{\hat{h}(1) + \sum_{a=1}^{N} e^2 \int dX_2\, \bar{\varphi}_a^*(X_2)\, \frac{(\hat{1} - \hat{P}_{12})}{r_{12}}\, \bar{\varphi}_b(X_2)\}\{\sum_{c=1}^{N} U^*_{dk}\, U_{ck}\, \bar{\varphi}_c(X_1)\}$$

$$= - \sum_{c=1}^{N} (\sum_{\ell=1}^{N} U_{c\ell}\, K_{\ell k}\, U^*_{dk})\, \bar{\varphi}_c(X_1), \qquad (k=1,\ldots,N). \qquad (4.35)$$

Note that the $\hat{h}^{HF}$ operator appearing here in curly brackets is the same for all k (k=1,2,...,N) equations. Thus, writing out the N coupled equations (4.35), one for each k, adding them together and factoring the common factor $\hat{h}^{HF}$ we get

$$\{\hat{h}(1) + \sum_{a=1}^{N} \int dX_2\, \bar{\varphi}_a^*(X_2)(\hat{1} - \hat{P}_{12})\frac{e^2}{r_{12}}\, \bar{\varphi}_a(X_2)\}\{\sum_{c=1}^{N} (\sum_{k=1}^{N} U^*_{dk}\, U_{ck})\, \bar{\varphi}_c(X_1)\}$$

$$= - \sum_{c=1}^{N} \sum_{\ell=1}^{N} (\sum_{k=1}^{N} U_{c\ell}\, U_{\ell k}\, U^*_{dk})\, \bar{\varphi}_c(X_1). \qquad (4.36)$$

Once again we have interchanged the order of performing the summations. The left hand side of (4.36) becomes after the sum over k and c have been performed

$$\{\hat{h}(1) + \sum_{a=1}^{N} e^2 \int dX_2\, \bar{\varphi}_a^*(X_2)\, \frac{(\hat{1} - \hat{P}_{12})}{r_{12}}\, \bar{\varphi}_a(X_2)\}\, \bar{\varphi}_d(X_1).$$

We now choose $\underset{\sim}{U}$ so as to diagonalize $\underset{\sim}{K}$. Noting that $U^*_{dk} = U^{\dagger}_{kd}$ we have

$$\underset{\sim}{U}\, \underset{\sim}{K}\, \underset{\sim}{U}^{+} = -\underset{\sim}{\varepsilon} = - \begin{pmatrix} \varepsilon_1 & \cdots\cdot & \\ \vdots & \varepsilon_2 & \\ \vdots & & \ddots \end{pmatrix} \qquad (4.37)$$

and so the right side of (4.36) becomes, $\varepsilon_d \bar{\phi}_d$. That is, the canonical form of the Hartree-Fock equations is

$$\{\hat{h}(1) + \sum_{a=1}^{N} \int dX_2\, \bar{\phi}_a^*(X_2)\, \frac{e^2}{r_{12}}\, (\hat{1} - \hat{P}_{12})\, \bar{\phi}_a(X_2)\}\, \bar{\phi}_d(X_1)$$

$$= \varepsilon_d\, \bar{\phi}_d(X_1), \quad (d=1,\ldots,N). \tag{4.38}$$

The salient point of this result is that each member of this set of coupled equations for the $\bar{\phi}_a$'s (or more explicitly $\bar{\phi}_{\mu_a}$'s) resembles an eigenvalue problem. Indeed, the set may be written

$$\{\hat{h}(1) + \hat{U}^{HF}(1)\}\, \bar{\phi}_d(X_1) = \varepsilon_d\, \bar{\phi}_d(X_1), \tag{4.39}$$

where the Hartree-Fock potential energy operator is

$$\hat{U}^{HF}(1) = \sum_{a=1}^{N} \int dX_2\, \bar{\phi}_a^*(X_2)\, \frac{e^2}{r_{12}}\, (\hat{1} - \hat{P}_{12})\, \bar{\phi}_a(X_2). \tag{4.40}$$

We say "resembles" an eigenvalue problem, for indeed the yet to be obtained solutions $\bar{\phi}_a$ are needed to define the Hartree-Fock potential energy operator. In this spirit we refer to (4.38) as a "pseudo-eigenvalue" problem. The point remains that in "canonical form" the equations have been "partially decoupled" in the elimination of the off diagonal Lagrange multipliers (K_{jk}) on the right.

The bar notation is rather clumsy. Therefore, having shown the existence of the canonical form, we shall return to our original notation for the Hartree-Fock orbitals--ϕ_{λ_k}--assuming (unless noted to the contrary) that they are in fact solutions of the canonical form of the

Hartree-Fock equations.

Up to this point we have sought only the orbitals comprising the Hartree-Fock determinant Φ^{HF}, that is we sought only the first N "self-consistent" solutions of Equation (4.38). Now, we recognize that as an operator--forget for the moment that it needs the first N solutions of its "own" eigenvalue equation to actually define it--$\hat{h}^{HF}$ has not just N but rather a "complete set" of solutions associated with it. The first N solutions $\varphi_\lambda^1, \varphi_\lambda^2, \ldots, \varphi_\lambda^N$ will be called the "occupied" orbitals,--they are the orbitals used in constructing Φ^{HF}. The remaining orbitals will be called "virtual orbitals" and labeled $\varphi_\lambda^{N+1}, \ldots, \varphi_\lambda^i, \ldots, \varphi_\lambda^j, \ldots$. To clarify this point, we envision the solutions of the Hartree-Fock pseudo-eigenvalue problem

$$\hat{h}^{HF}\,\varphi_\lambda^k = \varepsilon_\lambda^k\,\varphi_\lambda^k, \tag{4.41}$$

as comprising a complete set $\{\varphi_\lambda^1, \varphi_\lambda^2, \ldots, \varphi_\lambda^N, \varphi_\lambda^{N+1}, \ldots, \varphi_\lambda^j, \ldots\}$. The ordinal superscript implies that the sets of single particle quantum numbers λ have been arranged in some well-defined (indeed, countable) order. Typically, we envision orbitals with the lower Hartree-Fock energy eigenvalues preceding the higher ones and degenerate orbitals arranged according to group theoretical classifications. The Hartree-Fock determinant itself is

$$\Phi^{HF}_{\lambda_1\ldots\lambda_N} = \hat{a}(N)\prod_{i=1}^{N}\varphi_\lambda^i(X_i); \tag{4.42}$$

that is, $\varphi_\lambda^i = \varphi_{\lambda_i}$, the ith solution of the Hartree-Fock equations appears in the ith column of the Hartree-Fock determinant. In fact, the distinction between solution index and column index need not be made previously. However, having recognized the existence of a complete set of orbitals there are other (indeed infinitely many) Slater determinants

$$\Phi^{HF}_{\lambda_1 \dots \lambda_N}(X_1, X_2, \dots, X_N) = \hat{a}(N) \prod_{i=1}^{N} \varphi_{\lambda_i}(X_i) \tag{4.43}$$

formed by choosing various N tuples of these orbitals. That is, the subscripts on the λ's index the columns of the Slater determinant, with a given $\Lambda = \{\lambda_1, \lambda_2, \dots, \lambda_N\}$ implying a particular N-tuple of orbitals chosen from the complete set $\{\varphi_{\lambda_1}, \varphi_{\lambda_2}, \dots, \varphi_{\lambda_N}, \varphi_{\lambda_{N+1}}, \dots, \varphi_{\lambda_j}, \dots\}$.

We now turn our attention to solving the Hartree-Fock equations. First we discuss in rather general terms the iterative process by which one tackles this pseudo-eigenvalue problem and then we present the details or practical approach emphasizing known basis orbitals.

To attempt the solution of (4.39) we guess a set of occupied orbitals $\overset{o}{\varphi}_{\lambda_1}, \overset{o}{\varphi}_{\lambda_2}, \dots, \overset{o}{\varphi}_{\lambda_N}$ with which to construct an effective potential $\hat{U}^{(o)}(1)$ according to Equation (4.40). To be sure, our guess undoubtedly will not be the exact sought-for Hartree-Fock solutions--hence, the zero superscript--and thus the $\hat{U}^{(o)}(1)$ so constructed is not the true Hartree-Fock potential energy operator. Nevertheless we use this $\hat{U}^{(o)}(1)$ to construct a known operator

$$\hat{h}^{(1)} = \hat{h} + \hat{U}^{(o)} \tag{4.44}$$

and solve the eigenvalue problem

$$\hat{h}^{(1)} \varphi^{(1)}_{\lambda_k}(X_1) = \varepsilon^{(1)}_{\lambda_k} \varphi^{(1)}_{\lambda_k}(X_1). \tag{4.45}$$

The superscript notation (1) on the operator and its eigensolutions is to remind us that the true Hartree-Fock orbitals have not yet been obtained. These eigenfunctions $\{\phi_{\lambda k}^{(1)}\}$ form a complete set of orbitals, and may be thought a better approximation to the Hartree-Fock orbitals than our original guess. Indeed, we may continue in an iterative fashion to define a (hopefully) better effective potential energy operator $\hat{U}^{(1)}(1)$ using the first solutions $\phi_{\lambda 1}^{(1)}, \phi_{\lambda 2}^{(1)}, \ldots, \phi_{\lambda N}^{(1)}$ according to Equation (4.40) and thereby construct

$$\hat{h}^{(2)} = \hat{h} + \hat{U}^{(1)} \tag{4.46}$$

and seek its eigenfunctions

$$\hat{h}^{(2)} \phi_{\lambda k}^{(2)} = \varepsilon_{\lambda k}^{(2)} \phi_{\lambda k}^{(2)}. \tag{4.47}$$

The iterative procedure is thus clearly defined by solving the (n+1)st order eigenvalue problem

$$\hat{h}^{(n+1)} \phi_{\lambda k}^{(n+1)} = \varepsilon_{\lambda k}^{(n+1)} \phi_{\lambda k}^{(n+1)}, \tag{4.48}$$

where the known operator $\hat{h}^{(n+1)}$ is constructed using the lowest N solutions of the previous iteration:

$$\hat{h}^{(n+1)}(1) = \hat{h}(1) + \hat{U}^{(n)}(1)$$

with

$$\hat{U}^{(n)}(1) = \sum_{j=1}^{N} \int dX_2 \phi_{\lambda j}^{*(n)}(X_2) \frac{e^2}{r_{12}} (\hat{1} - \hat{P}_{12}) \phi_{\lambda j}^{(n)}(X_2) \, . \tag{4.49}$$

The convergence of the procedure may be monitored by examining the changes in the orbitals or more practically the eigenvalues from one iteration to the next. When the changes become small enough--and such a criterion is of course somewhat arbitrary--the procedure is terminated.

Now we shall outline the details of a practical approach for carrying out the iterative procedure indicated above. Indeed, as it stands in wave mechanical language, (4.38) is a very complicated set of equations. While in atoms the coupled integro-differential equations may be reduced by symmetry to a set of coupled one dimensional problems (in the radial coordinate) such a reduction is virtually impossible in the general molecular problem. It then becomes convenient to reformulate the problem in matrix language.

We envision a known set of M orbitals $\{\theta_\alpha(X),\ \alpha=1,2,\ldots,M\}$. This set of orbitals spans an M dimensional subspace of one-electron Hilbert space; that is, $\{\theta_\alpha\}$ is a basis for this M dimensional subspace. In principle M can become arbitrarily large whence the set is complete. In practice, however, M remains finite, and so exact solutions of the Hartree-Fock equations are not obtained. However, even in this case, a set of "self-consistent" matrix equations based on Hartree-Fock theory can be formulated. The "closeness" of these self consistent solutions to the actual Hartree-Fock solutions will depend on the extent (and quality) of the basis set. We will postpone these subtleties for some future time and now simply discuss the matrix formalism per se. Although our notation suggests M remain finite--as, of course, it will in practice--the mathematics presumes we are working with a complete set. We thus expand the sought for Hartree-Fock orbitals in this complete set.

$$\phi(X) = \sum_{\alpha=1}^{M} C_\alpha\ \theta_\alpha(X). \tag{4.50}$$

Here the yet to be found orbitals $\phi(X)$ are expanded in terms of the still unknown C_α's. The various solutions of Equation (4.38)--the ϕ_{λ^k}'s--correspond to different sets of C's--that is, $C_{\alpha\lambda^k}$--which arise in solving the matrix eigenvalue problem which follows. Substituting (4.50) into (4.39) we obtain

$$\hat{h}^{HF}\left(\sum_{\alpha=1}^{M} C_\alpha\ \theta_\alpha(X)\right) = \varepsilon\left(\sum_{\alpha=1}^{M} C_\alpha\ \theta_\alpha(X)\right) \tag{4.51}$$

or

$$\sum_{\alpha=1}^{M} \hat{h}^{HF}\ \theta_\alpha(X)\ C_\alpha = \varepsilon \sum_{\alpha=1}^{M} C_\alpha\ \theta_\alpha(X). \tag{4.52}$$

In the usual fashion we take the scalar product of each side of this equation with each member θ_β, ($\beta=1,2,\ldots,M$) of our basis set to obtain a set of M coupled equations

$$\sum_{\alpha=1}^{M} h^{HF}_{\beta\alpha}\ C_\alpha = \varepsilon \sum_{\alpha=1}^{M} S_{\beta\alpha}\ C_\alpha, \qquad (\beta=1,2,\ldots,M) \tag{4.53}$$

where

$$h^{HF}_{\beta\alpha} = \int dX\ \theta^*_\beta(X)\ \hat{h}^{HF}\ \theta_\alpha(X), \tag{4.54}$$

and

$$S_{\beta\alpha} = \int dX\ \theta^*_\beta(X)\ \theta_\alpha(X). \tag{4.55}$$

Here we have not assumed that the basis functions $\{\theta_\alpha(X)\}$ are orthonormal. This nonorthonormality of the basis functions is the typical case in practice, as the basis function $\theta_\alpha(\vec{r},\xi)$ are often chosen to be atomic orbitals centered on various nuclei throughout the molecule. On the other hand, it is sometimes useful to fashion a priori an orthonormal basis, in which case $S_{\beta\alpha}$ is replaced by the Kroneker delta $\delta_{\beta\alpha}$. The set of M equations (4.53) can be rewritten in matrix form.

$$\left[\begin{pmatrix} h^{HF}_{11} & h^{HF}_{12} & \cdots & h^{HF}_{1M} \\ h^{HF}_{21} & h^{HF}_{22} & \cdots & h^{HF}_{2M} \\ \vdots & \vdots & & \vdots \\ h^{HF}_{M1} & h^{HF}_{M2} & \cdots & h^{HF}_{MM} \end{pmatrix} - \varepsilon \begin{pmatrix} S_{11} & S_{12} & \cdots & S_{1M} \\ S_{21} & S_{22} & \cdots & S_{2M} \\ \vdots & \vdots & & \vdots \\ S_{M1} & S_{M2} & \cdots & S_{MM} \end{pmatrix}\right] \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_M \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

$$(\underset{\sim}{h}^{HF} - \varepsilon \underset{\sim}{S})\underset{\sim}{C} = \underset{\sim}{0}. \tag{4.56}$$

Solving the matrix eigenvalue problem proceeds by first finding the M eigenvalues ε by setting the determinant of the coefficients matrix equal to zero:

$$\left|\begin{pmatrix} h^{HF}_{11} & \cdots & h^{HF}_{1M} \\ \vdots & & \\ h^{HF}_{M1} & \cdots & h^{HF}_{MM} \end{pmatrix} - \varepsilon \begin{pmatrix} S_{11} & \cdots & S_{1M} \\ \vdots & & \\ S_{M1} & \cdots & S_{MM} \end{pmatrix}\right| = 0. \tag{4.57}$$

The M roots labeled ε_{λ^i}, i=1,2,...,M, are substituted one by one back into Equation (4.56) to obtain M sets of coefficients $\{(C_{\alpha\lambda^i}, \alpha=1,2,\ldots, M), i=1,2,\ldots,M\}$ and thus, the M self consistent orbitals

$$\varphi_{\lambda^i}(X) = \sum_{\alpha=1}^{M} C_{\alpha\lambda^i}\, \Theta_\alpha(X), \quad i=1,2,\ldots,M. \tag{4.58}$$

Here again we presume the orbitals are ordered so that $\varepsilon_{\lambda^i} \leq \varepsilon_{\lambda^{i+1}}$, $i=1,2,\ldots,(M-1)$, with the first N solutions corresponding to the occupied Hartree-Fock orbitals.

One notes at this point that the M×M matrix $\underset{\sim}{h}^{HF}$ is not actually known, for the evaluation of the matrix elements depends on the Hartree-Fock potential $\hat{U}$, which in turn depends on the first N Hartree-Fock orbitals. Indeed we have in detail

$$\begin{aligned}
h^{HF}_{\beta\alpha} &= \int dX_1 \; \theta^*_\beta(X_1)\{\hat{h}(1) + \hat{U}(1)\}\theta_\alpha(X_1) \\
&= \int dX_1 \; \theta^*_\beta(X_1)\hat{h}(1)\theta_\alpha(X_1) + \sum_{j=1}^{N} \int dX_1 \int dX_2 \; \theta^*_\beta(X_1)\varphi^*_{\lambda^j}(X_2) \frac{e^2}{r_{12}} (\hat{1} - \hat{P}_{12}) \\
&\qquad \theta_\alpha(X_1)\varphi_{\lambda^j}(X_2) \\
&= \int dX_1 \; \theta^*_\beta(X_1)\hat{h}(1)\theta_\alpha(X_1) + \sum_{j=1}^{N} \int dX_1 \int dX_2 \; \theta^*_\beta(X_1)\{\sum_{\gamma=1}^{M} C^*_{\gamma\lambda^j} \; \theta^*_\gamma(X_2)\} \\
&\qquad \frac{e^2}{r_{12}} (\hat{1} - \hat{P}_{12})\theta_\alpha(X_1)\{\sum_{\delta=1}^{M} C_{\delta\lambda^j} \; \theta_\delta(X_2)\}.
\end{aligned} \tag{4.59}$$

Here we have inserted the expansions for the yet-to-be-found occupied Hartree-Fock orbitals in terms of our basis orbitals. Of course the expansion for the matrix elements $h^{HF}_{\beta\alpha}$ is really only a formal one in that the "first N" solutions $\underset{\sim}{C}_{\lambda^i}$ of the matrix eigenvalue problem are needed to construct the matrix elements themselves. The analogy of this dilema with the previous formulation in terms of the integro-differential equations should be clear, and in fact the tact to be taken in its solution--an iteration procedure--should also be apparent. Before discussing this iteration procedure, however, let us cast the expression for our matrix element $h^{HF}_{\beta\alpha}$ in final form by introducing the density matrix:

$$\rho_{\delta\gamma} \equiv \sum_{j=1}^{N} C_{\delta\lambda_j} C^*_{\gamma\lambda_j} \qquad \delta,\gamma=1,2,\dots,M. \tag{4.60}$$

These density matrix elements form an M×M array whose rows and columns are indexed by the basis orbitals. In terms of these density matrix elements we have (4.59)

$$h^{HF}_{\beta\alpha} = \langle\theta_\beta|\hat{h}(1)|\theta_\alpha\rangle + \sum_{\gamma=1}^{M}\sum_{\delta=1}^{M} \rho_{\delta\gamma}\langle\theta_\beta\theta_\gamma|\frac{e^2}{r_{12}}|\theta_\alpha\theta_\delta\rangle \tag{4.61}$$

The $\rho_{\delta\gamma}$ depend upon the expansion coefficients for the first N Hartree-Fock, i.e., the "occupied", orbitals. It is evident that the matrix pseudo-eigenvalue problem (4.56) must thus be solved self-consistently, in that the matrix $\underset{\sim}{h}^{HF}$ depends through the density matrix $\underset{\sim}{\rho}$ upon its own first N eigenvectors. We proceed in a similar way to solve these equations by using the output of the current iteration in approximating the Hartree-Fock matrix--through the density matrix--for the next iteration.

$$[\underset{\sim}{h}^{(n+1} - \varepsilon^{(n+1)}_{\lambda_i}\underset{\sim}{S}]\underset{\sim}{C}^{(n+1)}_{\lambda_i} = \underset{\sim}{0},$$

where for the (n + 1)st iteration

$$h^{(n+1)}_{\beta\alpha} = \langle\theta_\beta|\hat{h}(1)|\theta_\alpha\rangle + \sum_{\gamma=1}^{M}\sum_{\delta=1}^{M} \rho^{(n)}_{\delta\gamma}\{\langle\theta_\beta\theta_\gamma|\frac{e^2}{r_{12}}|\theta_\alpha\theta_\delta\rangle\} \tag{4.62}$$

with $\underset{\sim}{\rho}^{(n)}$ obtained with solutions of the nth iteration:

$$\rho^{(n)}_{\delta\gamma} = \sum_{j=1}^{N} C^{(n)}_{\delta\lambda_j} C^{*(n)}_{\gamma\lambda_j}.$$

Here n (n=0,1,2,...) keeps track of the order of iteration. One is again, as in solving the integro-differential equation, required to make a zeroth order guess for the occupied orbitals in order to construct $\underset{\sim}{\rho}^{(o)}$. Subsequent iterations then proceed by the above prescription.

We conclude this chapter with a discussion of the N-electron Hartree-Fock energy defined by

$$E^{HF} = <\Phi^{HF}|\hat{H}_o|\Phi^{HF}>, \tag{4.63}$$

the expectation value of the total N-electron Hamiltonian (3.1) using the Slater determinant Φ^{HF} constructed with the first N--the "occupied"--Hartree-Fock orbitals. E^{HF} is of course the optimum of the functional $\mathcal{E}$. Using (3.72) and (3.75) to evaluate one- and two-body matrix elements (in this instance a diagonal matrix element), we find

$$\begin{aligned} E &= \sum_{i=1}^{N} <\varphi_{\lambda^i}|\hat{h}|\varphi_{\lambda^i}> + \sum_{1\leq i<j\leq N} <\varphi_{\lambda^i}\varphi_{\lambda^j}|\frac{e^2}{r_{12}}|\varphi_{\lambda^i}\varphi_{\lambda^j}> \\ &= \sum_{i=1}^{N} <\varphi_{\lambda^i}|\hat{h}|\varphi_{\lambda^i}> + 1/2 \sum_{i=1}^{N} \sum_{j=1}^{N} <\varphi_{\lambda^i}\varphi_{\lambda^j}|\frac{e^2}{r_{12}}|\varphi_{\lambda^i}\varphi_{\lambda^j}>. \end{aligned} \tag{4.64}$$

The two-body term may be written either as a pairwise sum or two independent sums with a factor of 1/2: recall also that the angular bracket denotes both the direct and the exchange contributions to the two-body terms. Thus terms with $\lambda^i = \lambda^j$ vanish.

Now multiplying the Hartree-Fock equation satisfied by the orbital $\varphi_{\lambda^i}(X_1)$

$$\{\hat{h}(X_1) + \sum_{j=1}^{N} \int dX_2\, \mathcal{G}^*_{\lambda j}(X_2)\frac{e^2}{r_{12}}(\hat{1} - \hat{P}_{12})\, \mathcal{G}_{\lambda j}(X_2)\}\, \mathcal{G}_{\lambda i}(X_1) = \varepsilon_{\lambda i}\mathcal{G}_{\lambda i}(X_1) \qquad (4.65)$$

by $\mathcal{G}^*_{\lambda i}(X_1)$ and integrating, we obtain an expression for the Hartree-Fock (one-electron) eigenvalue

$$<\mathcal{G}_{\lambda i}|\hat{h}|\mathcal{G}_{\lambda i}> + \sum_{j=1}^{N} <\mathcal{G}_{\lambda i}\mathcal{G}_{\lambda j}|\frac{e^2}{r_{12}}|\mathcal{G}_{\lambda i}\mathcal{G}_{\lambda j}> = \varepsilon_{\lambda i}. \qquad (4.66)$$

The sum is over all occupied orbitals. Then adding together these results for all the occupied Hartree-Fock orbitals, we get

$$\sum_{i=1}^{N} <\mathcal{G}_{\lambda i}|\hat{h}|\mathcal{G}_{\lambda i}> = \sum_{i=1}^{N} \varepsilon_{\lambda i} - \sum_{i=1}^{N}\sum_{j=1}^{N} <\mathcal{G}_{\lambda i}\mathcal{G}_{\lambda j}|\frac{e^2}{r_{12}}|\mathcal{G}_{\lambda i}\mathcal{G}_{\lambda j}>. \qquad (4.67)$$

Putting this into Equation (4.64) we find an alternative expression for E^{HF}, namely

$$E^{HF} = \sum_{i=1}^{N} \varepsilon_{\lambda i} - 1/2 \sum_{i=1}^{N}\sum_{j=1}^{N} <\mathcal{G}_{\lambda i}\mathcal{G}_{\lambda j}|\frac{e^2}{r_{12}}|\mathcal{G}_{\lambda i}\mathcal{G}_{\lambda j}>. \qquad (4.68)$$

Clearly, the N-electron Hartree-Fock energy is not just the sum of the one-electron Hartree-Fock eigenvalues but is for sure less than this sum, having subtracted positive definite matrix elements. E^{HF} is the optimum approximation of the ground state for the N-electron system described (approximately of course) by a single Slater determinant.

Finally we must mention an important theorem relating the (approximate) calculation of the first ionization potential energy of an N-electron system. By definition, the negative of the ionization potential (I.P.) is given by

$$-(\mathrm{I.P.}) = E_o(N) - E_o(N-1) \tag{4.69}$$

where $E_o(N)$ and $E_o(N-1)$ are the exact ground state electronic eigenvalues. However, we approximate $E_o(N)$ by the Hartree-Fock energy (4.64) and $E_o(N-1)$ by the expectation value of the $(N-1)$ particle Hamiltonian with respect to a Slater determinant comprised of the first $(N-1)$ orbitals obtained in the N-particle problem. Using our diagonal matrix element rules (3.72) and (3.75), this latter expectation value becomes

$$E_o(N-1) = \sum_{i=1}^{N-1} \langle \varphi_{\lambda i}|\hat{h}|\varphi_{\lambda i}\rangle + 1/2 \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} \langle \varphi_{\lambda i} \varphi_{\lambda j}|\frac{e^2}{r_{12}}|\varphi_{\lambda i}\varphi_{\lambda j}\rangle . \tag{4.70}$$

The (approximate) ionization potential is then found by subtracting expression (4.70) from (4.64) taking into account the particle permutation symmetry of the two-body matrix elements. We obtain

$$-(\mathrm{I.P.}) = \langle \varphi_{\lambda N}|\hat{h}|\varphi_{\lambda N}\rangle + \sum_{i=1}^{N} \langle \varphi_{\lambda N}\varphi_{\lambda i}|\frac{e^2}{r_{12}}|\varphi_{\lambda N}\varphi_{\lambda i}\rangle \tag{4.71}$$

where the other terms--those involving only orbitals $\varphi_{\lambda i}$, $\varphi_{\lambda j}$, $i,j < N$--cancel in taking the difference. It is immediately clear that this remainder is, according to (4.66) the Hartree-Fock orbital eigenvalue $\varepsilon_{\lambda N}$. This is Koopman's theorem:

$$-(\mathrm{I.P}) \cong \varepsilon_{\lambda N} . \tag{4.72}$$

In fact a little reflection confirms that an analogous theorem holds for the ionization from any of the Hartree-Fock orbitals of the N-electron species, not just the highest occupied one. However, the modeling of these excited states of the ionized species by single determinants--indeed single determinants with orbitals obtained from the neutral molecule--is at best highly suspect.

The use of Koopman's theorem in the calculation of ionization potentials is, as we said, an approximation. Indeed the ion as well as the neutral molecule itself should be subject to two independent configuration interactions in order to determine their respective ground state energies. In the next chapter we shall take up the details of SCF and CI calculations of the electronic structure of ethane. We close here with the observation that molecular orbital studies (Lathan et al., 1971, p. 1081) of the ethane action do indeed predict ionization states at variance with those anticipated by Koopman's theorem.

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CHAPTER V

THE ELECTRONIC STRUCTURE OF ETHANE

We now apply the formalism we discussed in the previous two chapters to the electronic structure of the ethane molecule (C_2H_6). In so doing we shall illustrate the concepts developed as well as introduce some additional ideas on how electronic structure calculations are carried out in practice. We shall not report any original results, but rather draw heavily upon already published material of different research groups. Much of this discussion will be couched in the language of group theory, a subject with which we deal only in the appendices. Here we shall simply adopt the results (and language) obtained there, where many of the examples pertain specifically to ethane. We proceed with the understanding that this material has been considered by the reader.

Our first concern is to calculate the electronic ground state energy (and eigenfunction) in the equilibrium conformation of the molecule. In principle the ground state potential energy surface may be found, point by point, in a series of calculations as outlined in the previous chapters. In practice, one may find the minimum energy point on the potential energy surface through a combination of well-founded intuition as to the symmetry and geometry, supplemented with some less sophisticated calculations. Once found, the region about the minimum point may be explored in greater depth by more elaborate calculations. In any event we shall begin by focusing upon Hartree-Fock--or, more appropriately, self-consistent-field (SCF)--calculations in D_{3d} symmetry, the so-called "staggared" configuration of the ethane molecule.

The first point to note is the closed-shell nature of the electronic ground state of ethane. We begin with the ansatz that the SCF spin orbitals may be written as the product of a spatial factor and a spin factor

$$\phi_\lambda(\vec{r},\xi) = \Phi_{\ell_\lambda}(\vec{r})\chi_{m_{s_\lambda}}(\xi) \tag{5.1}$$

with the spin function chosen as one or the other of the spin eigenfunctions of $\hat{s}^2$ and $\hat{s}_z$, namely,

$$\chi_{\frac{1}{2}}(\xi) \equiv \alpha(\xi); \; \chi_{-\frac{1}{2}}(\xi) \equiv \beta(\xi). \tag{5.2}$$

Moreover, in this spirit we assume the Hartree-Fock (N=18) determinant can be written in terms of nine "doubly-occupied" spatial orbitals

$$\Phi^{HF}(X_1,X_2,\ldots,X_{18}) = \hat{a}(18) \prod_{j=1}^{18} \phi_{\lambda j}(X_j)$$

$$= \hat{a}(18) \prod_{i=1}^{9} \{\Phi_{\ell^i}(\vec{r}_{2i-1})\alpha(\xi_{2i-1})\Phi_{\ell^i}(\vec{r}_{2i})\beta(\xi_{2i})\}. \tag{5.3}$$

A word on the notation is in order here. λ is a set of single particle quantum numbers delineating the spin-orbital ϕ_λ. ℓ_λ is a subset of these quantum numbers specifying the spatial factor while m_{s_λ} (=1/2,-1/2) specifies the spin factor. The subscript λ on both the ℓ and the m_s indicates the parent set from which each occurs. Of course, the set λ implies a unique set ℓ and a particular m_s, although, clearly neither ℓ nor m_s alone determines λ. The nine spatial orbitals Φ_{ℓ^i}, i=1,2,...,9, in Φ^{HF}

corresponds to the lowest eighteen (at least) doubly degerate spin orbitals $\phi_{\lambda j}$, j=1,2,...,18.

In the traditional terminology of Hartree-Fock theory this ansatz is the "restricted" Hartree-Fock method. The restricted Hartree-Fock method is particularly useful in describing closed shell (singlet) states with the particular symmetry species given by a single Slater determinant. That this is indeed the case for the ground electronic state of ethane will be verified (at least after the fact) by the calculation itself. The salient point to be made, however, is that the restricted Hartree-Fock method leads to further simplifications in the general single determinant method presented in the last chapter. To begin with, the orbital basis functions themselves may be written in the product form

$$\theta_\alpha(X) = \Theta_{a_\alpha}(\vec{r})\chi_{m_{s_\alpha}}(\xi). \tag{5.4}$$

It follows, then, that the matrix elements simplify to

$$(\theta_\beta|\hat{h}|\theta_\alpha) = (\Theta_{b_\beta}|\hat{h}|\Theta_{a_\alpha})\delta_{m_{s_\beta} m_{s_\alpha}} \tag{5.5}$$

where

$$(\Theta_b|\hat{h}|\Theta_a) = \int d\vec{r}\,\Theta_b^*(r)\{\frac{-\hbar^2}{2m}\nabla^2 + \sum_{\alpha=1}^{8}\frac{-Z_\alpha e^2}{|\vec{r}-\vec{R}_\alpha|}\}\Theta_a(r) \tag{5.6}$$

and

$$(\theta_\beta\theta_\gamma|\frac{e^2}{r_{12}}|\theta_\alpha\theta_\delta) = (\Theta_{b_\beta}\Theta_{c_\gamma}|\frac{e^2}{r_{12}}|\Theta_{a_\alpha}\Theta_{d_\delta})\delta_{m_{s_\beta} m_{s_\alpha}}\delta_{m_{s_\gamma} m_{s_\delta}} \tag{5.7}$$

where

$$(\Theta_b\Theta_c|\frac{e^2}{r_{12}}|\Theta_a\Theta_d) \equiv \int d\vec{r}_1 \int d\vec{r}_2\ \Theta_b^*(\vec{r}_1)\Theta_c^*(\vec{r}_2)\frac{e^2}{r_{12}}\ \Theta_a(\vec{r}_1)\Theta_d(\vec{r}_2). \qquad (5.8)$$

The notation is analogous to that introduced above. Moreover, with M spin-orbitals in the basis set there are $m = M/2$ spatial orbitals $\{\Theta_a\}$ in terms of which we may expand

$$\Phi_\ell(\vec{r}) = \sum_{a=1}^{m} C_{a\ell}\ \Theta_a(\vec{r}). \qquad (5.9)$$

Here, the spin-orbital indices λ and α need not be attached; but clearly, the relationship with the previously introduced expansion coefficients in equation (4.50) is that

$$C_{\alpha\lambda} = C_{a_\alpha \ell_\lambda}\ \delta_{m_{s_\alpha} m_{s_\lambda}} = C_{a\ell}\ \delta_{m_{s_\alpha} m_{s_\lambda}}\ . \qquad (5.10)$$

Consistent with the structure for the coefficient matrix, we find the density matrix element

$$\rho_{\gamma\delta} = \sum_{\lambda^j}^{N} C_{\gamma\lambda^j}\ C^*_{\delta\lambda^j} = \sum_{\ell^i}\ \sum_{m_{s_{\lambda^j}}=-\frac{1}{2}}^{\frac{1}{2}} (C_{c\ell^i}\delta_{m_{s_\gamma} m_{s_{\lambda^j}}})(C^*_{d\ell^i}\ \delta_{m_{s_\delta} m_{s_{\lambda^j}}}) \qquad (5.11)$$

$$= \{\sum_{\ell^i} C_{c\ell^i}\ C^*_{d\ell^i}\}\delta_{m_{s_\gamma} m_{s_\delta}} \qquad (5.11)$$

Here the sum over ℓ^i includes all $\frac{N}{2}$ (nine in the ethane example) occupied spatial orbitals in the Hartree-Fock determinant. Using this result for the density matrix elements along with (5.5) and (5.7) we find that the Hartree-Fock matrix itself $\underset{\sim}{h}^{HF}$ is "diagonal" in the spin indices:

$$
\begin{aligned}
(\theta_\beta|\hat{h}^{HF}|\theta_\alpha) &= (\theta_\beta|\hat{h}|\theta_\alpha) + \sum_{\gamma\delta} \rho_{\delta\gamma}\{(\theta_\beta\theta_\gamma|\frac{e^2}{r_{12}}|\theta_\alpha\theta_\delta) - (\theta_\beta\theta_\gamma|\frac{e^2}{r_{12}}|\theta_\delta\theta_\alpha)\} \\
&= (\Theta_b|\hat{h}|\Theta_a)\delta_{m_{s_\beta} m_{s_\alpha}} + \sum_{c=1}^{m}\sum_{d=1}^{m}\sum_{m_{s_\delta}=-\frac{1}{2}}^{\frac{1}{2}}\sum_{m_{s_\gamma}=-\frac{1}{2}}^{\frac{1}{2}} [(\sum_{\ell i} C_{d\ell i} C^*_{c\ell i})\delta_{m_{s_\gamma} m_{s_\delta}} \qquad (5.12) \\
&\quad \{(\Theta_b\Theta_c|\frac{e^2}{r_{12}}|\Theta_a\Theta_d)\delta_{m_{s_\beta} m_{s_\alpha}}\delta_{m_{s_\gamma} m_{s_\delta}} - (\Theta_b\Theta_c|\frac{e^2}{r_{12}}|\Theta_d\Theta_a)\delta_{m_{s_\beta} m_{s_\delta}}\delta_{m_{s_\gamma} m_{s_\alpha}}\}] \\
&= ((\Theta_b|\hat{h}|\Theta_a) + \sum_{c=1}^{m}\sum_{d=1}^{m}[(\sum_{\ell i} C_{d\ell i} C^*_{c\ell i})\{2(\Theta_b\Theta_c|\frac{e^2}{r_{12}}|\Theta_a\Theta_d) \\
&\quad - (\Theta_b\Theta_c|\frac{e^2}{r_{12}}|\Theta_d\Theta_a)\}])\delta_{m_{s_\beta} m_{s_\alpha}} \\
&= ((\Theta_b|\hat{h}|\Theta_a) + \sum_{c=1}^{m}\sum_{d=1}^{m}[P_{dc}\{(\Theta_b\Theta_c|\frac{e^2}{r_{12}}|\Theta_a\Theta_d) - \frac{1}{2}(\Theta_b\Theta_c|\frac{e^2}{r_{12}}|\Theta_d\Theta_a)\}])\delta_{m_{s_\beta} m_{s_\alpha}} .
\end{aligned}
$$

Here, the spatial orbitals define a density matrix with elements in terms of the expansion coefficients in (5.9):

$$P_{dc} = 2\sum_{\ell i} C_{d\ell i} C^*_{c\ell i}. \qquad (5.13)$$

The factor of 2 arises naturally because of the double occupancy of the spatial orbitals. We remind the reader that the sums are indeed over the $\frac{N}{2}$ occupied spatial orbitals.

As a consequence of these properties the entire restricted Hartree-Fock procedure can be recast in terms of the spatial orbitals alone, bearing in mind that in constructing the N-electron determinants the appropriate spin factor α or β must be attached to each spatial orbital. To be specific, with the elements of the m×m matrices

$$H^{HF}_{ba} = [(\Theta_b|\hat{h}|\Theta_a) + \sum_{c=1}^{m}\sum_{d=1}^{m} P_{dc}\{(\Theta_b\Theta_c|\frac{e^2}{r_{12}}|\Theta_a\Theta_d) - \frac{1}{2}(\Theta_b\Theta_c|\frac{e^2}{r_{12}}|\Theta_d\Theta_a)\}] \qquad (5.14)$$

and

$$S_{ba} = (\Theta_b|\Theta_a) = \int d\vec{r}\; \Theta^*_b(\vec{r})\; \Theta_a(\vec{r}) \qquad (5.15)$$

we must solve the pseudo (matrix) eigenvalue problem

$$[\underset{\sim}{H}^{HF} - \varepsilon_\ell \underset{\sim}{S}]\underset{\sim}{C}_\ell = \underset{\sim}{0} \qquad (5.16)$$

self-consistently with the spatial orbital density matrix

$$\underset{\sim}{P} = (P_{dc} = 2\sum_{\ell_i} C_{d\ell_i}\, C^*_{c\ell_i}). \qquad (5.17)$$

Once again the self-consistent solution may be reached iteratively, with the nth order density matrix used to construct the (n+1)st order approximation to $\underset{\sim}{H}^{HF}$. In practice the eigenvalues ε_ℓ along with the column matrices $\underset{\sim}{C}_\ell$ must be monitored from one iteration to the next. When the change is less than some acceptable convergence criteria the iterative procedure is terminated. The scope of the problem is thus reduced markedly.

In the particular case of ethane we shall use for the atomic orbital basis the m (=16) spatial orbitals centered on the two carbon and the six hydrogen atoms and denoted by

$$\{\Theta_{1sC_1},\Theta_{2sC_1},\Theta_{2p_xC_1},\Theta_{2p_yC_1},\Theta_{2p_zC_1},\Theta_{1sC_2},\Theta_{2sC_2},\Theta_{2p_xC_2},\Theta_{2p_yC_2},\Theta_{2p_zC_2},$$
$$\Theta_{1sH_1},\Theta_{1sH_2},\Theta_{1sH_3},\Theta_{1sH_4},\Theta_{1sH_5},\Theta_{1sH_6}\}.$$

The indicated self-consistency problem involves 16×16 matrices $\underset{\sim}{H}^{HF}$, $\underset{\sim}{S}$, and $\underset{\sim}{P}$. With N=18, solving this problem leads to nine occupied spatial orbitals needed to construct $\underset{\sim}{P}$ in accord with (5.17) and therefore seven virtual spatial orbitals remain. As shown in an appendix these SCF spatial orbitals transform as basis functions for various rows of the irreducible representation of the molecular symmetry group D_{3d}. In principle, the solution index ℓ will include the eigenvalue of the one-electron Hartree-Fock operator, as well as indices to identify the row and irreducible representation to which this spatial Hartree-Fock orbital belongs. In practice, ℓ simply includes, besides the irreducible representation and row, the occurence label of such a symmetry. As usual, we order the orbitals according to the increasing value of the single-particle energy eigenvalue ε_{ℓ^i}. Thus, the first nine orbitals are needed to construct Φ^{HF}.

Although a detailed discussion of various kinds of spatial orbitals is given in Appendix A, a word or two about the atomic orbital basis functions is in order here. As the notation suggests, the atomic functions are centered on one or the other of the eight nuclei in the ethane molecule. More generally, basis functions might be placed anywhere in space, since what is desired is an adequate representation of a "complete set" of spatial functions. Indeed, such basis sets of "floating" (i.e., not associated with a particular nucleus) orbitals are now routinely used, but we shall not consider them. Specifically, our basis set is limited to 1s (n=1, l=0, m=0) orbitals on each of the six hydrogen nuclei along with 1s and 2s and $2p_x$, $2p_y$, and $2p_z$ orbitals on both of the carbon nuclei. For an orbital Φ_a centered at $\vec{R}_a$ we write

$$\Phi_a(\vec{r}_a) = N \begin{Bmatrix} 1 \\ x_a \\ y_a \\ z_a \end{Bmatrix} R_{n_a \ell_a}(r_a) \tag{5.18}$$

for the s ($\ell_a = 0$) and the various p ($\ell_a = 1$) orbitals respectively. Here N is a normalization factor, and with

$$\vec{r}_a = \vec{r} - \vec{R}_a \tag{5.19}$$

x_a, y_a, and z_a are its components. $R_{n_a \ell_a}(r_a)$ is a function of only the magnitude of $\vec{r}_a$ and typically it is expanded either as a linear combination of Slater type orbitals (STO's)

$$R_{n_a \ell_a}(r_a) \equiv \sum_{i=1}^{N_a} \beta_{ia}\, e^{-\gamma_{ia} r_a} \tag{5.20}$$

or alternatively as a linear combination of Gaussian type orbitals (GTO's)

$$R_{n_a \ell_a}(r_a) \equiv \sum_{i=1}^{N'_a} \beta'_{ia}\, e^{-\gamma'_{ia} r_a^2}. \tag{5.21}$$

We shall refer to the STO's or the GTO's as the "primitive" basis functions. The linear coefficients--the β_{ia} (or β'_{ia})--and the non-linear parameters--the γ_{ia} (or γ'_{ia})--may be determined for each size basis set--N_a (or N'_a)--by a variational calculation on the atoms themselves. Each type of primitive function has its own advantages and disadvantages in carrying out electronic structure calculations. Further details as to the choice and use of these orbitals would, at present, only distract from our mainline of thought, the molecular calculations. Suffice it to say that a bibliography lists many of the frequently used tables of atomic orbitals (Cook, 1974).

We emphasize the point made earlier that the restricted Hartree-Fock problem, embodied in (5.14) and (5.16), centers on iterating on the density matrix (5.17) defined over the spatial orbitals. Indeed, with a given basis set of atomic spatial orbitals the one- and two- electron integrals

$$(\Theta_b|\hat{h}|\Theta_a) = \int d\vec{r}\ \Theta_b^*(\vec{r}_b)\{\frac{-\hbar^2}{2m}\nabla^2 + \sum_{\alpha=1}^{A}\frac{-Z_\alpha e^2}{|\vec{r}-\vec{R}_\alpha|}\}\Theta_a(\vec{r}_a) \tag{5.22}$$

and

$$(\Theta_b\Theta_c|\frac{e^2}{r_{12}}|\Theta_a\Theta_d) = \int d\vec{r}_1 \int d\vec{r}_2 \Theta_b^*(\vec{r}_{1b})\Theta_c^*(\vec{r}_{2c})\frac{e^2}{r_{12}}\ \Theta_a(\vec{r}_{1a})\Theta_d(\vec{r}_{2d}), \tag{5.23}$$

where, for example, $\vec{r}_{1a} = \vec{r}_1 - \vec{R}_a$, are fixed numbers to be evaluated once and for all in the course of the problem. To begin the iteration process one must simply make an initial guess at the density matrix, or alternatively, the column matrices $\underset{\sim}{C}_\ell$ for the nine occupied orbitals. Without some previous experience this may indeed prove to be a practical difficulty in terms of the atomic orbitals discussed so far here. Surely, the source of this difficulty is the "open shall" character of the carbon atom and the attendant ambiguities in intuitively expressing the bonding of the carbon electrons within the ethane molecule.

These ambiguities may begin to be resolved with the introduction of another atomic orbital basis set in which the valence orbitals centered on the carbon nuclei are "prepared" for the formation of chemical bonds. This preparation, called hybridization, mixes the 2s and the $2p_x$, $2p_y$, $2p_z$ orbitals on each of the carbon atoms so that the probability density distribution--and thus the charge density--of the resulting hybridized orbitals is directed toward the adjacent atoms. In this instance, we desire four valence atomic orbitals on each of the carbon atoms to be directed toward the four vertices of the tetrahedron defined by three adjacent hydrogens and the other carbon atom (See Figure 5.1). The bonding angles are thus determined by geometry. As shown in Appendix A, the hybrid orbitals centered on either carbon atom may be expanded in terms of the $\Theta_{2s}, \Theta_{2p_x}, \Theta_{2p_y}, \Theta_{2p_z}$ orbitals to obtain the atomic hybridized orbitals. For example, the atomic hybrids centered on carbon atom C_2 are found to be

$$\Theta_{C_2C_1} = A\Theta_{2sC_2} + B\Theta_{2p_zC_2} \tag{5.24}$$

$$\Theta_{C_2H_1} = \frac{B}{\sqrt{3}}\Theta_{2sC_2} + \sqrt{2/3}\,\Theta_{2p_yC_2} - \frac{A}{\sqrt{3}}\Theta_{2p_zC_2} \tag{5.25}$$

$$\Theta_{C_2H_2} = \frac{B}{\sqrt{3}}\Theta_{2sC_2} - \frac{1}{\sqrt{2}}\Theta_{2p_xC_2} - \frac{1}{\sqrt{6}}\Theta_{2p_yC_2} - \frac{A}{\sqrt{3}}\Theta_{2p_zC_2} \tag{5.26}$$

$$\Theta_{C_2H_3} = \frac{B}{\sqrt{3}}\Theta_{2sC_2} + \frac{1}{\sqrt{2}}\Theta_{2p_xC_2} - \frac{1}{\sqrt{6}}\Theta_{2p_yC_2} - \frac{A}{\sqrt{3}}\Theta_{2p_zC_2} \tag{5.27}$$

where

$$A = \sqrt{2}\cot\alpha, \quad B = (1 - 2\cot^2\alpha)^{\frac{1}{2}}, \quad \alpha = 109°.$$

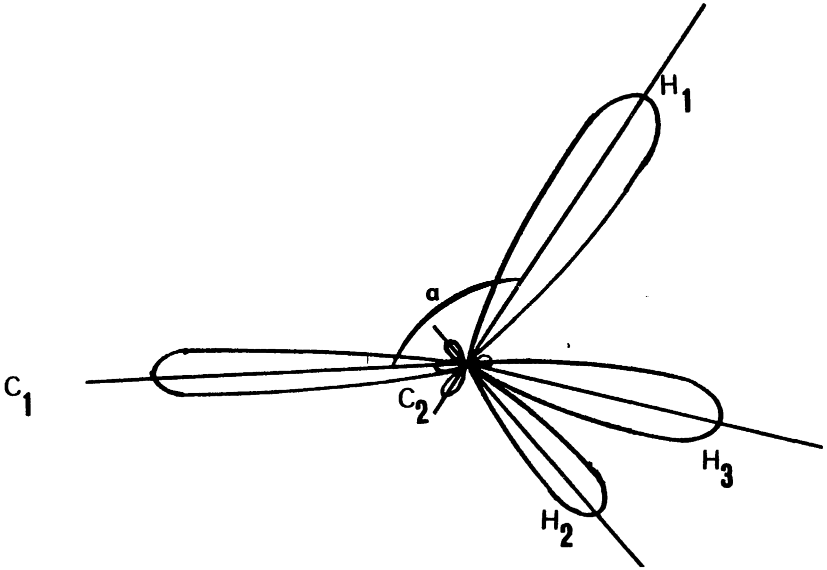

Figure 5.1. Tetrahedron Defined by Three Adjacent Hydrogens and the Carbon Atom

It is important to realize that the transformation is simply a unitary transformation (i.e., a rotation) in a four-dimensional subspace of one-particle Hilbert space. Both sets of four orthonormal basis functions span the same four dimensional subspace of one-particle Hilbert space. This set of atomic hybrid orbitals (explicitly shown in Appendix A)

$$\{\Theta_{1sC_1},\Theta_{1sC_2},\Theta_{C_1C_2},\Theta_{C_1H_4},\Theta_{C_1H_5},\Theta_{C_1H_6},\Theta_{C_2C_1},\Theta_{C_2H_1},\Theta_{C_2H_2},\Theta_{C_2H_3},\Theta_{1sH_1},$$
$$\Theta_{1sH_2},\Theta_{1sH_3},\Theta_{1sH_4},\Theta_{1sH_5},\Theta_{1sH_6}\}$$

may be used as a second atomic orbital basis to carry out the SCF problem.

However, the real value of this set lies in the formation of yet another basis set which intuitively reflects the notions of chemical bonds. Thus as also shown in Appendix A, we form "bonding" and antibonding" orbitals by taking linear combinations of these "directed" valence orbitals with those orbitals located on the atoms toward which they point. For instance, the unnormalized bonding orbitals between the two carbon atoms and between carbon atom C2 and hydrogen atom H1 are respectively $\chi^b_{C_1C_2} = \Theta_{C_1C_2} + \Theta_{C_2C_1}$ and $\chi^b_{C_2H_1} = \Theta_{C_2H_1} + \Theta_{1sH_1}$. The corresponding antibonding orbital have the plus replaced with a minus sign. The bonding and antibonding orbitals are therefore not atomic orbitals, but rather combinations of atomic orbitals from adjacent atoms. A bonding orbital builds up charge density in the region between the two adjacent atoms while the antibonding orbital depletes charge density in this region. We shall denote the bonding/antibonding orbital basis functions by χ's rather than Θ's to emphasize they are in fact superpositions of atomic orbitals from different centers. These bonding and antibonding orbitals (explicitly given in Appendix A) constitute a third set of spatial orbital basis functions

$$\{\Theta_{1sC_1},\Theta_{1sC_2},\chi^b_{C_1H_4},\chi^b_{C_1H_5},\chi^b_{C_1H_6},\chi^b_{C_2H_1},\chi^b_{C_2H_2},\chi^b_{C_2H_3},\chi^b_{C_1C_2},\chi^a_{C_1H_4},\chi^a_{C_1H_5},$$
$$\chi^a_{C_1H_6},\chi^a_{C_2H_1},\chi^a_{C_2H_2},\chi^a_{C_2H_3},\chi^a_{C_1C_2}\}.$$

Once again, therefore, we have a set of $m = 16$ spatial orbital basis functions to carry the SCF procedure iteratively. The point to be made here is that an initial guess of the occupied orbitals would choose the double occupation of the two 1s "core" orbitals on the carbon atoms along with the seven bonding orbitals formed above.

$$\{\Theta_{1sC_1}\ \Theta_{1sC_2}\ \chi^b_{C_1H_4}\ \chi^b_{C_1H_5}\ \chi^b_{C_1H_6}\ \chi^b_{C_2H_1}\ \chi^b_{C_2H_2}\ \chi^b_{C_2H_3}\ \chi^b_{C_1C_2}\}.$$

These orbitals are not the SCF functions but simply an initial guess. To be sure we expect the antibonding orbitals to "mix" with the bonding orbitals through the Hartree-Fock Hamiltonian in the iteration procedure.

In both the original atomic orbital bases as well as the bonding/antibonding orbital basis one may anticipate all the elements of the matrix $\underset{\sim}{H}^{HF}$ to be nonzero. In terms of group theoretical concepts all three bases span reducible, rather than irreducible, representations. However, to take advantage of the symmetry ideas discussed in the Appendices B and C, we introduce a fourth basis of sixteen spatial orbitals to carry out the SCF calculation. Beginning with the original set of atomic orbitals, we employ the projection operator techniques (formulated in the Appendix B) to construct the sixteen symmetry adapted functions which belong to (or, "transform as") specific rows of certain irreducible representations of the symmetry group of the molecule. At the minimum energy configuration of the ground state potential energy surface of ethane the symmetry group is D_{3d}. The details of this group and its irreducible representations can be found in Appendix C. In particular, the sixteen symmetry adapted functions (explicitly given in Appendix C) arranged according to rows of the irreducible representations are labeled

$$\{\chi_{1a_{1g}}, \chi_{1a_{2u}}, \chi_{2a_{1g}}, \chi_{2a_{2u}}, \chi_{3a_{1g}}, \chi_{3a_{2u}}, \chi_{1e_g1}, \chi_{1e_g2}, \chi_{1e_u1}, \chi_{1e_u2}, \chi_{4a_{1g}}, \chi_{4a_{2u}}, \chi_{2e_g1}, \chi_{2e_g2}, \chi_{2e_u1}, \chi_{2e_u2}\}.$$

These symmetry adapted basis functions are not themselves atomic orbitals, but each is a linear combination of atomic orbitals centered on the various atoms in the molecule. Again χ, rather than Θ, is used to denote such a linear combination.

In this indexing scheme, $\chi_{\nu\mu i}$ is the νth ($\nu=1,2,\ldots,d_\mu$) occurence of a function which transforms as the ith row ($i=1,2,\ldots,n_\mu$) of the μth irreducible representation. For an irreducible representation of dimensionality n_μ there are $(n_\mu - 1)$ partners for a given $\chi_{\nu\mu i}$ transforming, together with this function, among themselves under all the operations of the symmetry group. When there is more than a single occurrence ($d_\mu > 1$) of a given irreducible representation, there are an infinite number of ways of choosing the set of symmetry functions. Each set spans the same d_μ-dimensional subspace $S_{\mu i}$ which is indexed by the particular row of the particular irreducible representation.

Most importantly, the Hartree-Fock operator is invariant under all the operations of the symmetry group

$$\hat{O}_R \hat{h}^{HF} \hat{O}_R^{-1} = \hat{h}^{HF}. \tag{5.28}$$

As shown in Appendix B, all matrix elements of $\hat{h}^{HF}$ between symmetry adapted basis functions belonging to different subspaces $S_{\mu i}$, $S_{\mu' i'}$ vanish. That is,

$$<\chi_{\nu\mu i}|\hat{h}^{HF}|\chi_{\nu'\mu' i'}> = H^{HF}_{\nu\nu'}(\mu)\delta_{\mu\mu'}\delta_{ii'}. \tag{5.29}$$

Indeed, the $d_\mu \times d_\mu$ block $\underset{\sim}{H}^{HF}(\mu)$ indexed by the basis functions is repeated n_μ times, once for each row i (i=1,2,...,n_μ) of the μth irreducible representation.

In the particular problem of ethane in D_{3d} symmetry, the six symmetry representations (a_{1g},a_{2u},$e_g 1$,$e_g 2$,$e_u 1$,$e_u 2$) divide our chosen sixteen-dimensional orbital space into six subspaces ($S_{a_{1g}}$,$S_{a_{2u}}$,$S_{e_g 1}$, $S_{e_g 2}$,$S_{e_u 1}$,$S_{e_u 2}$). The dimensionalities of these subspaces ($d_{\mu i} \equiv d_\mu$, all i=1,2,...,n_μ) are $d_{a_{1g}}$=4, $d_{a_{2u}}$=4, d_{e_g}=2, and d_{e_u}=2. The a_{2g} and a_{1u} symmetries have no occurrences with our particular limited basis set. The resulting "block diagonal" structure of $\underset{\sim}{H}^{HF}$ is shown in Figure 5.2.

The implications of this block diagonal structure are both formal and practical. In the first instance, it is clear that the SCF orbitals themselves are to be labeled according to the irreducible representation scheme. Indeed, each set of SCF spatial quantum numbers Nμi also consists of an occurrence label N and a row and irreducible representation label. As a practical result of the block diagonal form, $\underset{\sim}{H}^{HF}$ may

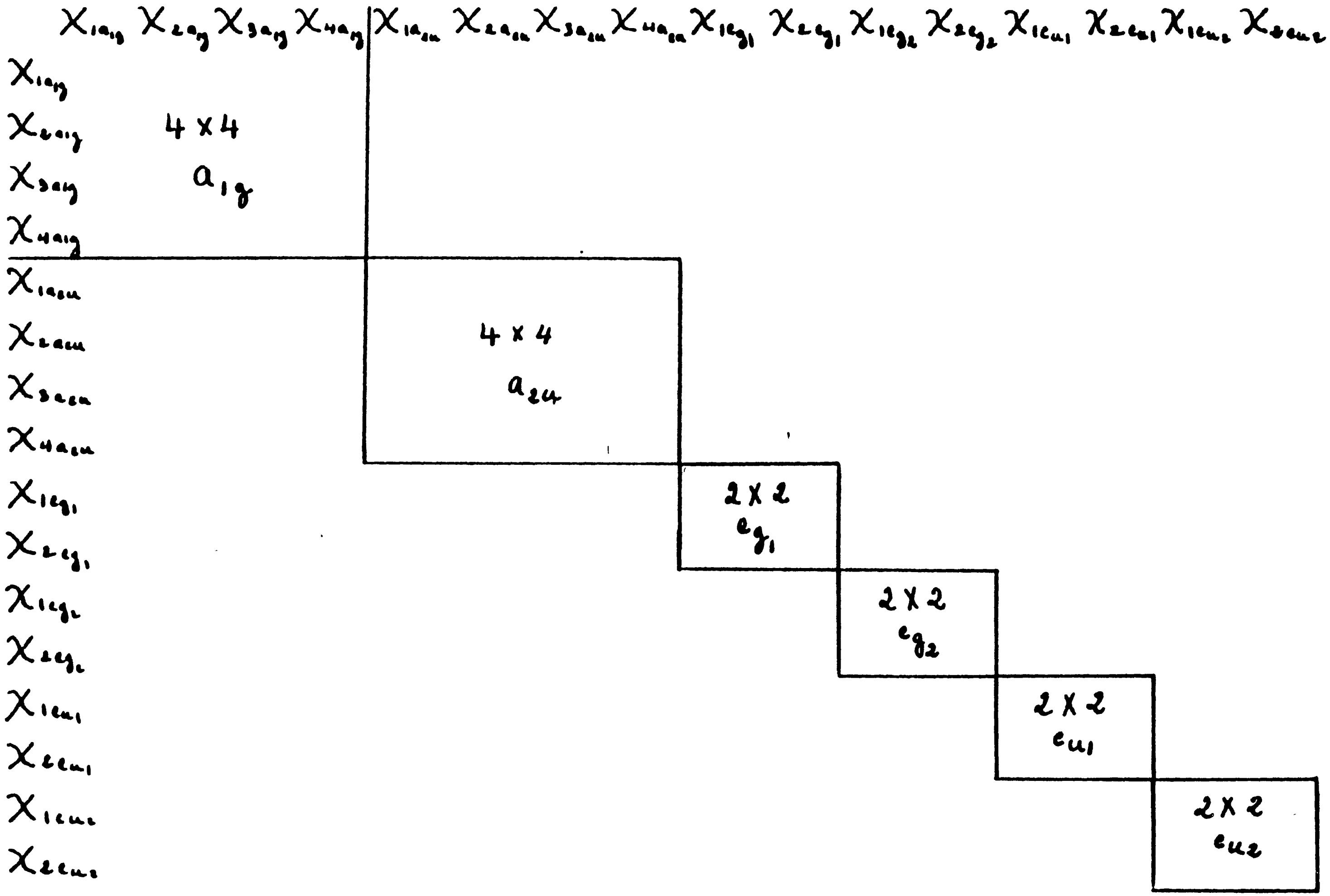

Figure 5.2. The "Block Diagonal" Structure of $\underset{\sim}{H}^{HF}$

be diagonalized block by block. Thus each secular equation is much smaller than in the original atomic orbital basis. Not only is $\underset{\sim}{H}^{HF}$ block diagonal, but the blocks which are distinguished by simply belonging to different rows of the same irreducible representation are identical. Thus, the diagonalization need not be repeated for different subspaces characterized only by different rows. As a consequence, the eigenvalues $\varepsilon_{N\mu}$ and the expansion coefficients $C_{\nu\mu;N\mu}$ are not dependent upon the row index i. N simply orders the roots $\varepsilon_{N\mu} < \varepsilon_{(N+1)\mu}$ within a specific irreducible representation μ. Like ν, N runs from 1 to dμ; for $n_\mu > 1$, we speak of the orbital degeneracy of the SCF solutions. Specifically we have for each N and μ a set of n_μ SCF solutions

$$\Phi_{N\mu i} = \sum_{\nu=1}^{d_\mu} C_{\nu\mu;N\mu}\chi_{\nu\mu i}(\vec{r}), \tag{5.30}$$

indexed by i ($i=1,2,\ldots,n_\mu$) which in fact are a set of partners for the (Nth occurrence of the) μth irreducible representation. Clearly the density matrix (5.17) also must have the same block diagonal form as $\underset{\sim}{H}^{HF}$ in the symmetry adapted basis. (It must be noted, however, that the entire matrix is needed to construct each block of $\underset{\sim}{H}^{HF}$.)

The ground state Hartree-Fock function for ethane is the Slater determinant

$$\Phi^{HF}(X_1,X_2,\ldots,X_{18}) = \hat{a}(18)$$

$$\{\Phi_{1a_{1g}}(\vec{r}_1)\alpha(\xi_1)\Phi_{1a_{1g}}(\vec{r}_2)\beta(\xi_2)\Phi_{1a_{2u}}(\vec{r}_3)\alpha(\xi_3)\Phi_{1a_{2u}}(\vec{r}_4)\beta(\xi_4)$$

$$\Phi_{2a_{1g}}(\vec{r}_5)\alpha(\xi_5)\Phi_{2a_{1g}}(\vec{r}_6)\beta(\xi_6)\Phi_{2a_{2u}}(\vec{r}_7)\alpha(\xi_7)\Phi_{2a_{2u}}(\vec{r}_8)\beta(\xi_8)$$

$$\Phi_{1e_u1}(\vec{r}_9)\alpha(\xi_9)\Phi_{1e_u1}(\vec{r}_{10})\beta(\xi_{10})\Phi_{1e_u2}(\vec{r}_{11})\alpha(\xi_{11})\Phi_{1e_u2}(\vec{r}_{12})\beta(\xi_{12})$$

$$\Phi_{3a_{1g}}(\vec{r}_{13})\alpha(\xi_{13})\Phi_{3a_{1g}}(\vec{r}_{14})\beta(\xi_{14})$$

$$\Phi_{1e_g1}(\vec{r}_{15})\alpha(\xi_{15})\Phi_{1e_g1}(\vec{r}_{16})\beta(\xi_{16})\Phi_{1e_g2}(\vec{r}_{17})\alpha(\xi_{17})\Phi_{1e_g2}(\vec{r}_{18})\beta(\xi_{18})\} \quad (5.31)$$

Here, for example, $\Phi_{3a_{1g}}$ is the SCF orbital for the third occurrence (i.e., the third lowest root) within the a_{1g} subspace. Similarly Φ_{1e_u2} is the first occurrence of the SCF orbital in the subspace characterized as the second row of the e_u irreducible representation. (In the first example, no row index need be included on $\Phi_{3a_{1g}}$ since a_{1g} is in fact a one dimensional irreducible representation; of course, all three indices, $N = 1$ occurrence, $\mu = e_u$ irreducible representation, and row $i = 2$ appear appropriately on Φ_{1e_u2}.) The column-wise arrangement of the orbitals in Φ^{HF} follows the energy ordering scheme. Indeed, we have included Buenker and Peyerimhoff's (1975) lowest eleven orbital energies $\varepsilon_{N\mu}$'s in Table VI. The spatial orbitals Φ_{1e_u1} and Φ_{1e_u2} are "orbitally degenerate" in that they have the same SCF eigenvalue ε_{1e_u}. Φ_{1e_g1} and Φ_{1e_g2} are also orbitally degenerate. Of course, in accordance with our "restricted" Hartree-Fock ansatz each of the spatial orbitals is associated with two spin orbitals. Thus there are, for example, four spin orbitals appearing in Φ^{HF} which correspond to the energy ε_{1e_g}.

Indicating the occupancy of the degenerate spin orbitals by superscripts, we label the Hartree-Fock "configuration"

$$(1a_{1g})^2(1a_{2u})^2(2a_{1g})^2(2a_{2u})^2(1e_u)^4(3a_{1g})^2(1e_g)^4[^1A_{1g}].$$

TABLE VI

BUENKER AND PEYERIMHOFF'S LOWEST ELEVEN SCF ENERGIES

Orbital	Energy (Hartree)*
Occupied	
$\varepsilon_{1a_{1g}}$	-11.19882
$\varepsilon_{1a_{2g}}$	-11.19824
$\varepsilon_{2a_{1g}}$	-1.01277
$\varepsilon_{2a_{2u}}$	-0.83364
ε_{1e_u}	-0.59292
$\varepsilon_{3a_{1g}}$	-0.48876
ε_{1e_g}	-0.47624
Virtual	
$\varepsilon_{4a_{1g}}$	0.04503
$\varepsilon_{3a_{2u}}$	0.04659
ε_{2e_u}	0.04652
$\varepsilon_{4a_{2u}}$	0.31096

*1 Hartree = 27.21 ev

The 18 electron function Φ^{HF} transforms under the symmetry operations of D_{3d} according to the A_{1g} irreducible representation. (Note that capital letters (e.g., A_{1g}) denote the irreducible representations to which the N electron state belongs while lower case letters (e.g., a_{1g}) denote the symmetry properties of the orbitals.) In addition Φ^{HF} is an eigenfunction of the 18-particle spin operator $\hat{S}^2$ where

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 , \tag{5.32}$$

$$\hat{\vec{S}} = \sum_{i=1}^{18} \hat{\vec{S}}_i , \tag{5.33}$$

with the eigenvalues $S(S+1)\hbar^2 = 0\ (0+1)\hbar^2 = 0$. Thus, with S=0 and multiplicity $2S+1 = 1$, we speak of a "singlet" state (Multiplicity = 1).

Although we have exhibited four different bases--atomic, atomic hybrids, bonding/antibonding, and symmetry adapted--and discussed some of the features of each, we must now hasten to add that all the matrix elements must ultimately be expressed in terms of the primitive STO's or GTO's of Equations (5.20) and (5.21) used in expanding the original atomic orbitals. Consequently the final numerical results are independent of which basis we choose to carry out the SCF iteration solution. Of course, the numerical results do depend upon the "extent" and "quality" of the atomic orbital basis set. A larger finite dimensional space--more atomic orbitals--presumably better approximates the entire one-particle Hilbert space. In addition, for a given type of atomic orbital basis, the number of primitive functions employed (and, of course, the choice of the linear and non-linear parameters) determines exactly which finite dimensional space is spanned. Typically, each atomic orbital is expanded as a linear combination of two or three STO's, whence we speak of "double or triple zeta" type accuracy. Generally, more GTO's than STO's are required to produce results of the same numerical accuracy, since the STO's better mimic the behavior of atomic radial wavefunctions.

The Hartree-Fock solution is, of course, not the exact electronic ground state, but only the best (energy-wise) approximation with the restriction to a single Slater determinant. Those properties of the electronic system which depend on a more sophisticated wavefunction than the Hartree-Fock approximation affords are called "correlation effects". In particular, the residual energy difference between the exact non-relativistic energy eigenvalue and the Hartree-Fock energy is called the correlation energy:

$$E_{cor}(R) = E(R) - E^{HF}(R). \tag{5.34}$$

In computing the potential energy surface the correlation energy contributions may, in general, be expected to be very important. For as our consideration moves from one configuration space point R to another point R'--say in the calculation of ethane's rotational energy barrier--the most significant parameter is the <u>energy difference</u>

$$E(R') - E(R) = \{E^{HF}(R') - E^{HF}(R)\} + \{E_{cor}(R') - E_{cor}(R)\}. \tag{5.35}$$

While it is true that, at a given point R, E^{HF} is of much greater magnitude than E_{cor}, the required energy differences appearing in the two terms of (5.35) may, in fact, be comparable. In general, then, one should investigate the possibility of substantial influences of the correlation effects on such properties as force constants and binding energies. On the other hand, even if each correlation energy terms $E_{cor}(R)$ and $E_{cor}(R')$ were not negligible in the absolute sense of the total electronic energy contribution, it may be that the energy difference $\{E_{cor}(R') - E_{cor}(R)\}$ is small due to a more or less constant (R independent) correlation energy. In fact, it is this latter situation which obtains most often for closed shell electronic states, as in the case of the ground state of ethane. For instance Clementi and Popkie (1968) obtain a Hartree-Fock value of .00511 a.u. for the rotational barrier (with geometry optimization of the C-C bond), and estimate that the inclusion of correlation effects gives only a slightly different result for the barrier of .00515 a.u. as reported in Table I.

A second problem in which the electronic correlation effects loom important is the electronic excitation of the molecule. Here, we shall consider only "vertical" electronic excitation by which we mean the nuclear coordinates are 'frozen' in place. In such a model of molecular excitation, the point in "configuration space" of the nuclei does not change on the time scale of electronic excitation and so the excitation energy is simply the difference (solid arrow) between the two electronic potential energy surfaces at (see Figure 5.3) that given nuclear configuration. More realistically, one must also take into account the quantum numbers depicting the states of nuclear motion on these two respective surfaces, say in the context of the Born-Oppenheimer approximation. Thus, on a different electronic potential energy surface a new set of quantum numbers must depict the new vibrational state of the molecule. A more accurate approximation of the excitation energy takes these

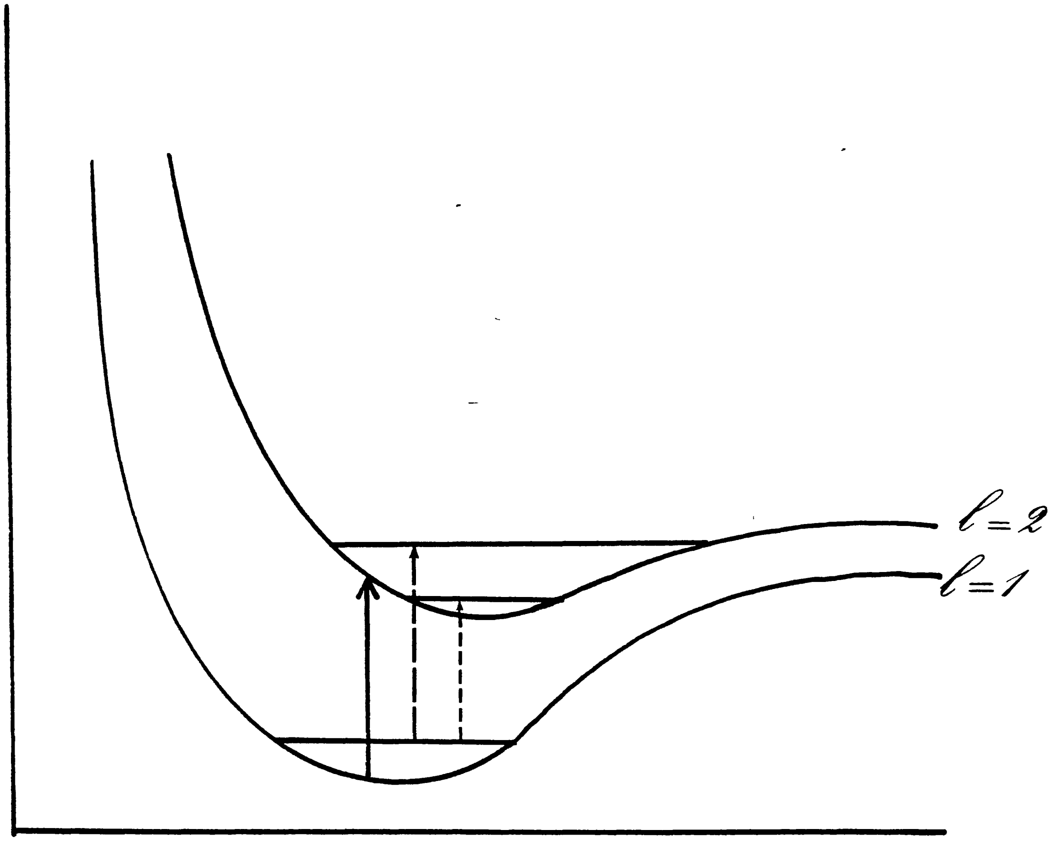

Figure 5.3. The Electronic Excitation Energy

vibration energies into account as depicted by the broken arrows in Figure 5.3. Be that as it may we must consider finding approximate excited electronic state energies as well as the ground state energy as accurately as possible. But in computing excitation energies it is once again <u>energy differences</u> which play the key role.

We shall wind up our discussion of electronic structure calculations by considering configuration interaction (CI) in the structure of ethane. We shall thereby illustrate some general points in the specific example. Among these are first and foremost the idea that the Hartree-Fock states--and those excited "model states" obtained by replacing the "occupied" by "virtual" orbitals--are not the exact eigenstates of the electronic Hamiltonian. However, an essential concept behind the discussion is that the exact eigenstates can be expanded as linear combinations of the complete set of "model states" with the mixing coefficients determined by diagonalizing the matrix representing the exact Hamiltonian in the basis model states as described at the end of Chapter IV. The implication of the term "model states" is that each such state corresponds to one of the true physical eigenstates (in the spirit of the independent particle model) while at the same time serving to correct the shortcomings of the model in its mathematical role as an element of a complete set (basis) of expansion functions. In fact for those states involving the "virtual excitation" of many orbitals the correspondence with actual physical eigenstates of the true Hamiltonian is almost surely lost. Nevertheless, the mathematical completeness of such a set persists and its use as an expansion set remains.

Thus in addition to incorporating the correlation effects of the electronic ground state, the configuration interaction method also yields the excited states in the diagonalization of the CI matrix. As outlined at the end of Chapter IV, however, the practical limitations of computations necessitate truncating the complete set to a finite set spanning some finite-dimensional N-electron subspace. It is intuitively clear that the larger the space of the model function the more accurate will be the approximate answers, both for the ground state and for the excited states. On the other hand, reason must prevail in finding the size of the model space and consequently some selection process must be introduced. We must hasten to add, however, that with modern computing technologies and programs very large calculations--some involving 10^5 determinants--are done routinely on moderately large molecules.

The model states may be constructed by first choosing a set of determinants, say L of them, obtained by replacing one or more of the orbitals occupied in Φ^{HF} by virtual orbitals. The finite dimensional model space typically is spanned by the Hartree-Fock state and those additional states obtained by replacing one or two of the valence orbitals in Φ^{HF} by the low-lying virtual orbitals, since in fact it is usually the low-lying excited states in which we are interested. Most often the determinants so obtained through these virtual excitations are not "symmetry adapted"--that is they are not eigenstates of $\hat{S}^2$ and $\hat{S}_z$ and do not transform as basis functions for irreducible representations of the symmetry group. Indeed, one must in general take linear combinations of these Slater determinants in order to form such symmetry adapted functions. Although this is not necessary from the point of view of the dynamics--the determinants span the same space as the symmetry adapted functions constructed with them--the introduction of symmetry at the outset is, just like in the Hartree-Fock problem, a convenient tool not only in classifying the model states but also in reducing the size of the matrix to be diagonalized.

Before proceeding with our example we will introduce some general notation to describe the determinants obtained by these virtual excitations. In general terms with

$$\Phi^{HF} = \hat{a}(N)\prod_{i=1}^{N}\phi_{\lambda^i}(X_i) = 1/\sqrt{N!}\begin{vmatrix} \phi_{\lambda^1}(X_1) & \phi_{\lambda^2}(X_1) & \cdots & \phi_{\lambda^N}(X_1) \\ \phi_{\lambda^1}(X_2) & \phi_{\lambda^2}(X_2) & \cdots & \phi_{\lambda^N}(X_2) \\ \vdots & \vdots & & \vdots \\ \phi_{\lambda^1}(X_N) & \phi_{\lambda^2}(X_N) & \cdots & \phi_{\lambda^N}(X_N) \end{vmatrix} \qquad (5.36)$$

we write the "excited determinants" as

$$\Delta^{\mu_{i_1}\mu_{i_2}\cdots\mu_{i_n}}_{\lambda^{i_1}\lambda^{i_2}\cdots\lambda^{i_n}} = 1/\sqrt{N!}\begin{vmatrix} \phi_{\lambda^1}(X_1) & \cdots & \phi_{\mu_{i_1}}(X_1) & \cdots & \phi_{\mu_{i_n}}(X_1) & \cdots & \phi_{\lambda^N}(X_1) \\ \vdots & & \vdots & & \vdots & & \vdots \\ \phi_{\lambda^1}(X_N) & \cdots & \phi_{\mu_{i_1}}(X_N) & \cdots & \phi_{\mu_{i_n}}(X_N) & \cdots & \phi_{\lambda^N}(X_N) \end{vmatrix} \qquad (5.37)$$

with $\lambda^{i_1}, \lambda^{i_2}, \ldots, \lambda^{i_n}$ a set of occupied Hartree-Fock orbitals (occupying columns $i_1, i_2, \ldots, i_n$ respectively in Φ^{HF}) which have been replaced by the virtual orbitals $\mu_{i_1}, \mu_{i_2}, \ldots, \mu_{i_n}$ in determinant Φ^{HF}; $\lambda^{i_1} \equiv \lambda_{i_1}$, the solution ordering index--the superscript--equals the place ordering index--the subscript--within each determinant. $\{\mu_{i_1}, \mu_{i_2}, \ldots, \mu_{i_n}\}$ is an ordered n-tuple of orbitals chosen from the set $\{\lambda^{N+1}, \ldots, \lambda^{M}\}$. Although for a complete set of orbitals we envision $M \to \infty$, here we admit M is in fact finite. There are then a total of $\mathcal{M} = \frac{M!}{N!(M-N)!}$ determinants which could be constructed with these M orbitals, and so a choice of L of them as stated above (where generally $L \ll M$) surely involves definite selection criteria.

To illustrate these and other ideas in the calculation of ethane in D_{3d} symmetry we examine the list in Table I of the occupied and (some of the) virtual orbitals obtained by Buenker and Peyerimhoff (1975). The Hartree-Fock state is given by (5.31). In somewhat abbreviated notation we write this

$$\Phi^{HF} = \hat{a}\{[\text{core}]\phi_{3a_{1g}\alpha}\phi_{3a_{1g}\beta}\phi_{1e_g 1\alpha}\phi_{1e_g 1\beta}\phi_{1e_g 2\alpha}\phi_{1e_g 2\beta}\}. \tag{5.38}$$

The rational for including all six explicitly shown orbitals as valence is the "near degeneracy" ($\varepsilon_{1e_g} - \varepsilon_{3a_{1g}} \approx 0.34\text{eV}$) in the Hartree-Fock spectrum. Consider the five determinants obtained by the indicated replacements from the Hartree-Fock determinant

$$\begin{aligned} \Delta_I &= \Delta_{3a_{1g}\alpha}^{4a_{1g}\alpha} & \Delta_{IV} &= \Delta_{3a_{1g}\beta}^{4a_{1g}\beta} \\ \Delta_{II} &= \Delta_{3a_{1g}\alpha}^{4a_{1g}\beta} & \Delta_V &= \Delta_{3a_{1g}\alpha\, 3a_{1g}\beta}^{4a_{1g}\alpha\, 4a_{1g}\beta} \\ \Delta_{III} &= \Delta_{3a_{1g}\beta}^{4a_{1g}\alpha} \end{aligned} \tag{5.39}$$

Here we have also relabeled these five determinants with Roman numerals to avoid the extended notation. Clearly, the first four determinants involve a single virtual excitation while the fifth involves a double virtual excitation. Note also, for instance, that Δ_I and Δ_{IV} differ from one another in two orbitals. These determinants are not in general eigenstates of $\hat{S}^2$, although in this instance, they all transform according to the A_{1g} irreducible representation. As indicated above, however, such eigenstates may be formed by simple linear combinations of the Slater determinants. The construction of the symmetry adapted states from the Slater determinants is well developed and practiced part of group theory (Clebsch-Gordan Algebra) familiar in quantum chemical calculations. In our present example the five excited symmetry adapted model states are

$$\begin{aligned}
\Phi_{I} &= \frac{1}{\sqrt{2}}[\Delta_{I} + \Delta_{IV}] = \Phi(\text{core})(3a_{1g})(4a_{1g})(1e_{g})^{4}[{}^{1}A_{1g}] \\
\Phi_{II} &= \Delta_{V} = \Phi(\text{core})(4a_{1g})^{2}(1e_{g})^{4}[{}^{1}A_{1g}] \\
\Phi_{III} &= \frac{1}{\sqrt{2}}[\Delta_{I} - \Delta_{IV}] = \Phi(\text{core})(3a_{1g})(4a_{1g})(e_{g})^{2}[{}^{3}A_{1g} \quad M_{s}=0] \\
\Phi_{IV} &= \Delta_{III} = \Phi(\text{core})(3a_{1g})(4a_{1g})(1e_{g})^{4}[{}^{3}A_{1g} \quad M_{s}=1] \\
\Phi_{V} &= \Delta_{II} = \Phi(\text{core})(3a_{1g})(4a_{1g})(1e_{g})^{4}[{}^{3}A_{1g} \quad M_{s}=-1].
\end{aligned} \tag{5.40}$$

Here we used the expanded notation as well as the more suscinct Roman numerals to label our symmetry adapted model states. A word about the expanded notation is in order. Each model state is labeled by the configuration label--i.e., the occupancy of the spin orbitals of various symmetries used to construct the state--as well as the specific quantum numbers--i.e., the shorthand for the eigenvalues--labeling the particular symmetry species, the particular row, as well as the eigenvalues of

$\hat{S}^z$ and $\hat{S}_z$. In this spirit the Hartree-Fock state is designated $\Phi(\mathrm{core})(3a_{1g})^2(1e_g)^4[{}^1A_{1g}]$. Including the Hartree-Fock configuration itself a total of three configurations

$$(\mathrm{core})(3a_{1g})^2(1e_g)^4,\ (\mathrm{core})(3a_{1g})(4a_{1g})(1e_g)^4 \text{ and } (\mathrm{core})(4a_{1g})^2(1e_g)^4 \tag{5.41}$$

are represented by these six model states.

Thus we have a six dimensional model space with the structure of the CI matrix indicated in Figure 5.4. In particular, the block diagonal structure of the matrix results from the use of symmetry adapted functions. For example, since

$$[\hat{S}^2 , \hat{H}_0] = \hat{0} \tag{5.42}$$

we obtain

$$\begin{aligned}&<\Phi_{II}({}^1A_{1g})|\hat{S}^2\hat{H}_0 - \hat{H}_0\hat{S}^2|\Phi_{III}({}^3A_{1g})> = \\ &[0(0+1)\hbar^2 - 1(1+1)\hbar^2]\ <\Phi_I({}^1A_{1g})|\hat{H}_0|\Phi_{III}({}^3A_{1g})> = 0\end{aligned} \tag{5.43}$$

with the implication that

$$<\Phi_{II}({}^1A_{1g})|\hat{H}_0|\Phi_{III}({}^3A_{1g})> = 0. \tag{5.44}$$

Thus the 6×6 CI matrix is block diagonal, with the largest block being simply 3×3 as shown in Figure 5.5. Let us examine this 3×3 ${}^1A_{1g}$ block in a little more detail. Each of these matrix elements may be obtained

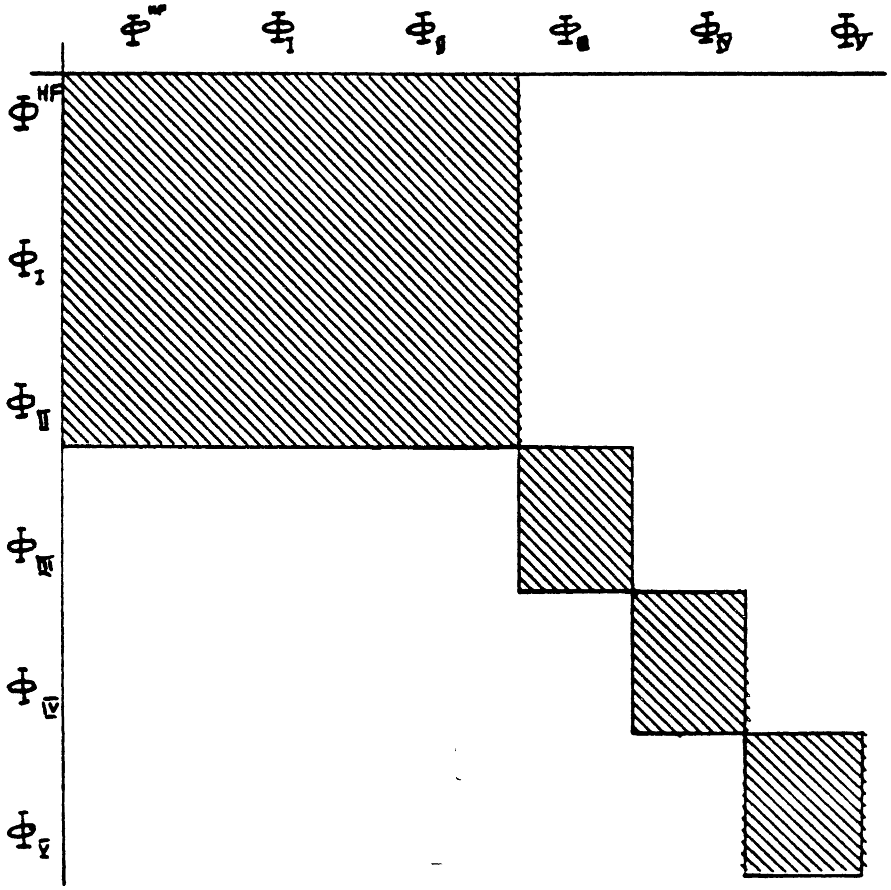

Figure 5.4. The Structure of the CI Matrix a Six-Dimensional Space

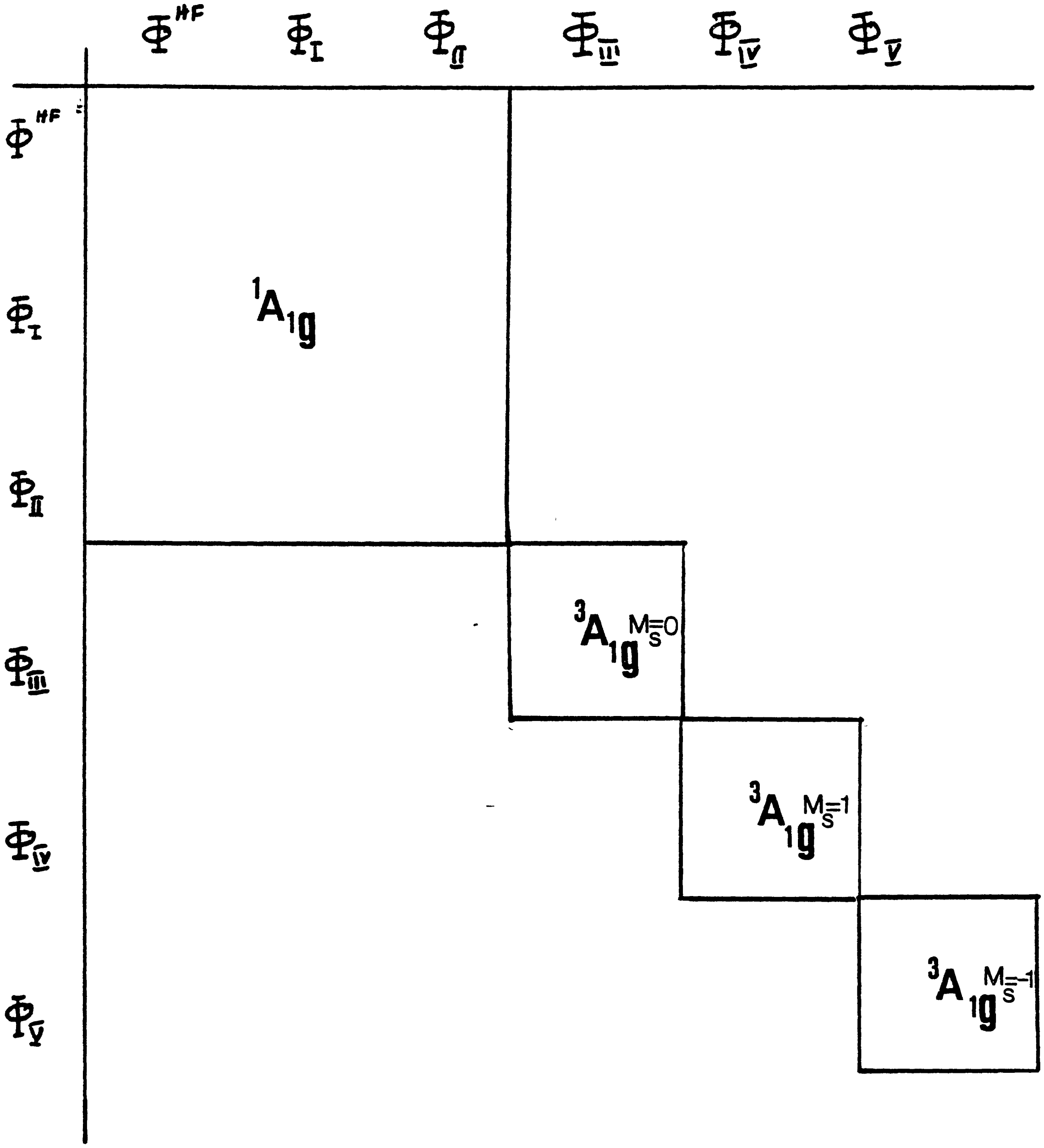

Figure 5.5. Blockdiagonal CI Matrix

as the sum of matrix elements between Slater determinants. For example the diagonal element $<\Phi_I|\hat{H}_o|\Phi_I>$ may be written

$$<\Phi_I|\hat{H}_o|\Phi_I> = \frac{1}{2}\{<\Delta_I|\hat{H}_o|\Delta_I> + <\Delta_I|\hat{H}_o|\Delta_{IV}>$$

$$+ <\Delta_{IV}|\hat{H}_o|\Delta_I> + <\Delta_{IV}|\hat{H}_o|\Delta_{IV}>\} \qquad (5.45)$$

and formulas (3.72) and (3.75) applied to each of the four terms. Of course, with Δ_I and Δ_{IV} differing in two orbitals $<\Delta_{IV}|\hat{H}_o|\Delta_I> = <\Delta_I|\hat{H}_o|\Delta_{IV}>^*$ becomes simply

$$< 3a_{1g}\alpha\ 4a_{1g}\beta|\frac{e^2}{r_{12}}|\ 4a_{1g}\alpha\ 3a_{1g}\beta > = < 4a_{1g}\alpha\ 3a_{1g}\beta|\frac{e^2}{r_{12}}|\ 3a_{1g}\alpha\ 4a_{1g}\beta >^*$$

As a second example, we consider,

$$<\Phi^{HF}|\hat{H}_o|\Phi_I> = 1/\sqrt{2}\{<\Phi^{HF}|\hat{H}_o|\Delta_I> + <\Phi^{HF}|\hat{H}_o|\Delta_{IV}>\}. \qquad (5.46)$$

Here, however, we digress to consider Brillouin's theorem which shows that in fact this matrix element--and indeed all matrix elements between the Hartree-Fock determinant and any determinant depicted as a single virtual excitation from the Hartree-Fock determinant--vanishes.

We consider the matrix $<\Phi^{HF}|\hat{H}_o|\Delta^{p_1}_{\lambda i}>$ where, in $\Delta^{p_1}_{\lambda i}$, orbital $\phi_{\lambda i}$, occupied in Φ^{HF} is replaced by the virtual orbital ϕ_{p_1}. $\hat{H}_o$ is given by (3.1), the sum of one and two-body operators, and thus using (3.72) and (3.75) the matrix element is

$$\langle \Phi^{HF}|\hat{H}|\Delta_{\lambda^i}^{p_1}\rangle = \langle \phi_{\lambda^i}|\hat{h}|\phi_{p_1}\rangle + \sum_{\substack{j=1\\ j\neq i}}^{N} \langle \phi_{\lambda^i}\phi_{\lambda^j}|\frac{e^2}{r_{12}}|\phi_{p_1}\phi_{\lambda^j}\rangle . \tag{5.47}$$

The sum is over orbitals common to both Φ^{HF} and $\Delta_{\lambda^i}^{p_1}$, that is over all occupied orbitals ϕ_{λ^j}, except λ^i. However, including this term in the sum changes nothing since the direct and the exchange terms cancel in $\langle \phi_{\lambda^i}\phi_{\lambda^i}|\frac{e^2}{r_{12}}|\phi_{p_1}\phi_{\lambda^i}\rangle$. Thus the result becomes

$$\langle \phi_{\lambda^i}|\{\hat{h} + \sum_{j=1}^{N} \int dX_2 \phi^*_{\lambda^j}(X_2)\frac{e^2}{r_{12}}(\hat{1} - \hat{P}_{12})\phi_{\lambda^j}(X_2)\}|\phi_{p_1}\rangle . \tag{5.48}$$

But the one-electron operator in curly brackets is recognized as the Hartree-Fock operator, $\hat{h}^{HF}$. Therefore, since the orbitals are eigenfunctions of this operator this matrix element reduces to

$$\langle \phi_{\lambda^i}|\hat{h}^{HF}|\phi_{p_1}\rangle = \varepsilon_{p_1}\langle \phi_{\lambda^i}|\phi_{p_1}\rangle = 0 , \tag{5.49}$$

where the final result follows from the orthogonality of the Hartree-Fock eigenfunctions. The actual structure of the 3×3 block is shown in Figure 5.6.

In addition to those above, four states of ${}^1E_u$ symmetry may be constructed, each as linear combinations of two determinants involving single excitations from the Hartree-Fock determinant. The first pair involve $1e_g \longrightarrow 3a_{2u}$ orbital excitations while the second pair involve $3a_{1g} \longrightarrow 2e_u$ excitations. Each pair are a set of partners transforming as the first or second row of the E_u irreducible representation. Following the configuration and multiplicity is the designation of the irreducible representation and the particular row (1) or (2). Explicitly we write

$$
\begin{array}{c|c|c|c}
 & \Phi^{HF} & \Phi_{I} & \Phi_{II} \\
\hline
\Phi^{HF} & A & 0 & X^{*} \\
\hline
\Phi_{I} & 0 & B & Y^{*} \\
\hline
\Phi_{II} & X & Y & C \\
\hline
\end{array}
$$

Figure 5.6. The Structure of the 3×3 Block

$$\Phi_{VI} = \frac{1}{\sqrt{2}}\{\Delta_{1e_g 1\beta}^{3a_{2u}\beta} + \Delta_{1e_g 1\alpha}^{3a_{2u}\alpha}\} = \Phi(\text{core})(3a_{1g})^2(1e_g)^3(3a_{2u})[{}^1E_u(1)]$$

$$\Phi_{VII} = \frac{1}{\sqrt{2}}\{\Delta_{1e_g 2\beta}^{3a_{2u}\beta} + \Delta_{1e_g 2\alpha}^{3a_{2u}\alpha}\} = \Phi(\text{core})(3a_{1g})^2(1e_g)^3(3a_{2u})[{}^1E_u(2)] \tag{5.50}$$

$$\Phi_{VIII} = \frac{1}{\sqrt{2}}\{\Delta_{3a_{1g}\beta}^{2e_u 1\beta} + \Delta_{3a_{1g}\alpha}^{2e_u 1\alpha}\} = \Phi(\text{core})(3a_{1g})(2e_u)(1e_g)^4[{}^1E_u(1)]$$

$$\Phi_{IX} = \frac{1}{\sqrt{2}}\{\Delta_{3a_{1g}\beta}^{2e_u 2\beta} + \Delta_{3a_{1g}\alpha}^{2e_u 2\alpha}\} = \Phi(\text{core})(3a_{1g})(2e_u)(1e_g)^4[{}^1E_u(2)].$$

Again we note by group theory arguments that the matrix elements between states transforming as different rows of even the same irreducible representation vanish. Thus the entire 10×10 CI matrix has the block diagonal form in Figure 5.7. Thus, the configuration interaction calculation envisioned here is based upon the ten dimensional "model space" which is subdivided and classified according to certain rows of certain irreducible representations. The approximate electronic states are found by diagonalizing this matrix, which clearly, can be accomplished block by block. For instance, the ground state is now labeled

$$\Psi(1\ {}^1A_{1g}) = C_o\Phi^{HF} + C_I\Phi_I + C_{II}\Phi_{II}. \tag{5.51}$$

The designation $1\ {}^1A_{1g}$ no longer strictly includes a configuration label for the electronic state, since as indicated in (5.51) the ground state is a linear superposition of ${}^1A_{1g}$ model states belonging to three different configurations. Indeed, this is the origin of the term "configuration interaction." Nevertheless, whenever the Hartree-Fock model state dominates in that $C_o > C_I$ and $C_o > C_{II}$ we still often associate the

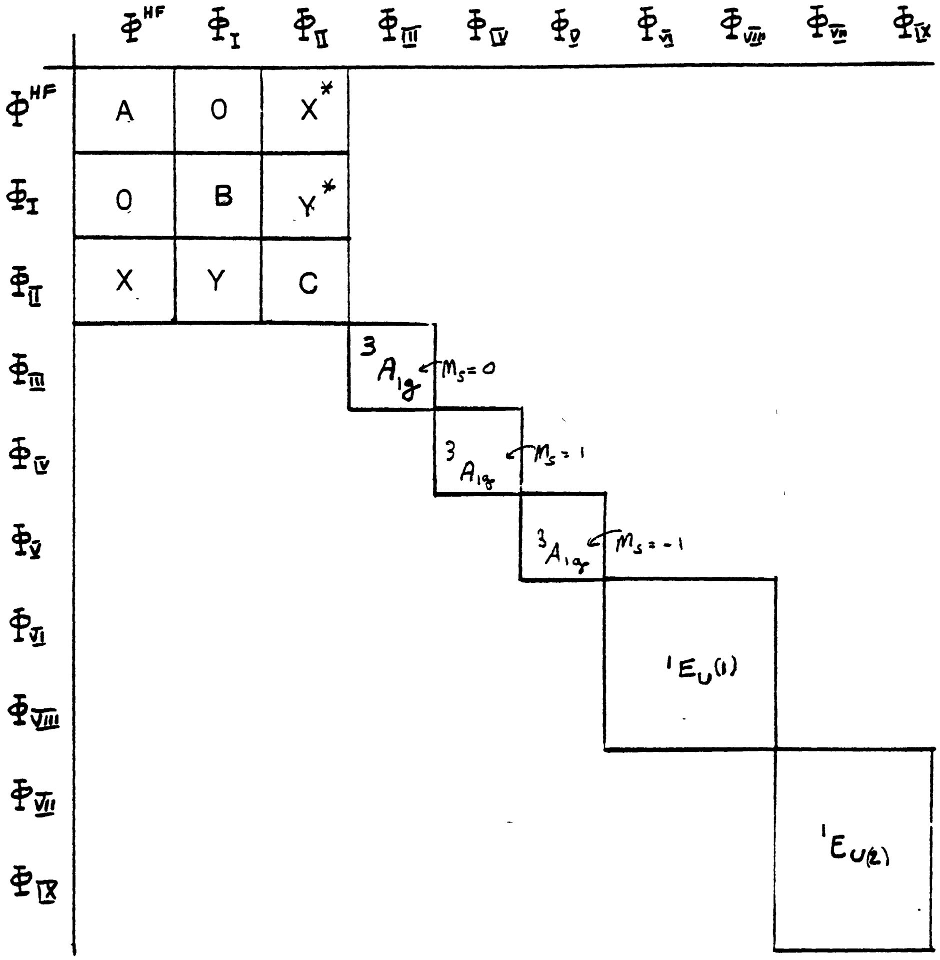

Figure 5.7. The Entire CI 10×10 Blockdiagonal Matrix

[core]$(3a_{1g})^2(1e_g)^4$ configuration with the approximate ground electronic state.

In addition to the ground state we obtain two excited states belonging to $^1A_{1g}$ symmetry. These states also are written as linear combinations of the three model basis states. Indeed, "diagonalizing" the 3×3 block is finding that particular basis in the 3-dimensional $^1A_{1g}$ model space in which the "new" basis states do not couple to one another through the Hamiltonian. These states which diagonalize the 3×3 matrix are, of course, not the exact eigenstates of the true electronic Hamiltonian, but rather, are eigenstates of that Hamiltonian projected onto this three dimensional model space. Equivalently it would require the infinite dimensional $^1A_{1g}$ subspace spanned by symmetry adapted model states belonging to an infinite number of configurations to represent completely the true Hamiltonian, and thus only by diagonalizing this infinite matrix could the exact eigenvalues--including the exact ground state eigenvalue--be found. Clearly, as mentioned previously, increasing the size of the model space should lead to better approximations of the eigenfunctions and eigenvalues.

The excited electronic states may be reached by the absorption of the electromagnetic radiation (i.e., photons). A detailed discussion of these processes and the quantum predictions of the probabilities of their taking place is beyond the scope of our discussion. We must mention, however, that the prominent features in the electronic excitation of ethane focus upon an electromagnetic transition from the $^1A_{1g}$ ground state to a state of ^1E_u symmetry. Such is in fact an "allowed electric dipole" transition, and the quantum calculations predict its occurrence with relatively large probability. What is required by such a calculation are the eigenfunctions and eigenvalues of the initial and final electronic states of the molecule. Indeed, one should calculate the electronic eigenfunctions and eigenvalues for all the nuclear configurations. Then one may determine the vibrational states on the upper and lower potential energy surface and do the transition integral. In a more modest approach--the vertical excitation approximation--the transition energy is just the difference in the eigenvalues of the two stationary electronic states at fixed nuclear coordinates.

Having found--at least approximately--the ground state energy and wavefunction by diagonalizing the 3×3 block, we must also approximate the excited ${}^1E_u$ states involved in the transition by diagonalizing the corresponding 2×2 (${}^1E_u$) blocks. There are two 2×2 blocks, the first with both model functions Φ_{VI} and Φ_{VIII} belonging to the first row of the ${}^1E_u$ representation and the second with both model functions Φ_{VII} and Φ_{IX} belonging to the second row of the ${}^1E_u$ representation. There are two approximate eigenstates labeled $1\,{}^1E_u$ and $2\,{}^1E_u$ obtained upon diagonalizing the 2×2 matrix for each of the two rows. Indeed, these excited eigenstates fall into two sets of doubly degenerate partners, $\{\Psi(1^1E_u(1)), \Psi(1^1E_u(2))\}$ spanning one occurrence and $\{\psi(2^1E_u(1), \Psi(2^1E_u(2))\}$ spanning another occurrence of E_u. That is, once again "configuration interaction" produces for each ψ a linear superposition of the model basis functions

$$\Psi(1^1E_u(1)) = A\Phi_{VI} + A'\Phi_{VIII}$$

$$\Psi(1^1E_u(2)) = A\Phi_{VII} + A'\Phi_{IX}$$

$$\Psi(2^1E_u(1)) = B\Phi_{VI} + B'\Phi_{VIII} \tag{5.49}$$

$$\Psi(2^1E_u(2)) = B\Phi_{VII} + B'\Phi_{IX}.$$

In the same spirit as before, however, one of the coefficients of the model functions may dominate and the configuration label--which most rigorously may be attached only to the Φ's--may be used also to identify the Ψ's. On the other hand it is possible that the model states "mix" with one another with more or less equal amplitudes in expanding the approximate eigenfunctions. In such a case the configuration label would be inappropriate as a label for the Ψ. This appears to be the case for the two ^1E_u states obtained in diagonalizing the 2×2 matrix (Buenker and Peyerimhoff (1975)). Thus, we set aside the configuration label and simply in fact identify the "lower" ^1E_u state and the "higher" ^1E_u state as 1^1E_u and 2^1E_u respectively.

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CHAPTER VI

CONCLUDING REMARKS

Our focus on the Hartree-Fock theory must be put into perspective. For instance, molecular quantum mechanics in principle requires going beyond the independent particle description of electronic states. Certainly, we have alluded to these "correlation effects" in Chapter V where we discussed the limited configuration interaction techniques. Suffice it to say here that in recent years other techniques, e.g. many-body perturbation theory, have been successfully applied to study correlation effects. In addition to these considerations, we have not touched on the problems concerning the response of molecules to external fields. For example, one must be able to compute the various electrical and magnetic moments of an isolated molecule in its various stationary states from the molecular wavefunctions. Also using such stationary state wave functions we may predict the probabilities of transitions when the molecule is subjected to external electromagnetic fields.

The problem of calculating electromagnetic transition probabilities is surely one involving time-dependent quantum mechanics. We have only briefly discussed this topic in Chapter I. This fascinating subject can be cast into many different formal guises; it may cover everything from "pictures" of quantum mechanics and time-dependent perturbation theory to the elegant techniques of Green's functions. Other time-dependent phenomena, such as tunneling, are also recognized as playing an important role in our understanding of nature. The point to be made here is simply that investigations of such phenomena must go beyond the stationary state description pursued in this thesis.

In this same vein, we must also realize that the "systems" with which we deal in practice are not isolated single molecules. On the contrary the typical subjects of experiment say in a biochemical laboratory is indeed a macroscopic system whose initial quantum state is known only incompletely. Thus, the apparatus of quantum statistical mechanics must be brought to bear upon such problems. Quantum statistical mechanics is built upon the foundation of quantum mechanics, but proceeds to include also the laws of statistics as it is realized that many different microscopic quantum states may correspond to our admittedly less detailed macroscopic knowledge of the system. In effect quantum statistical mechanics is a way of computing averages over the various possible quantum microstates of the system. The elegant formulation of quantum statistical mechanics is usually cast in the language of density operations. Again the point is simply to appreciate how limited the scope of this thesis has been.

Finally, we could not close without recalling the fact that all scientific undertakings are predicated on the belief that quantum theory--i.e., quantum mechanics, quantum electrodynamics, quantum statistical mechanics--is both correct and sufficiently complete insofar as explaining macroscopic chemical and physical phenomena. To be sure it has been experiment which has led us to these laws, sifting the truths--the theories which "work"--from the fictions--the ideas which have been disproven by subsequent detailed experiment. It may well be, of course, that our present theories of matter are just an "asymptotic approximation" to some deeper, more revealing truths. This, in fact, is just our present view of classical physics--mechanics, electromagnetics, statistical mechanics--vis' à vis' Twentieth Century quantum theory. Perhaps the best lesson we can learn from Nineteenth Century physics is a certain sense of openness toward what Twenty-first Century science may bring.

APPENDIX A

ORBITALS

The concept of orbitals occurs again and again in our discussion. Thus we feel an overall view of the basic ideas would be helpful. From the outset let us confine our remarks to the electronic structure problem.

Although our interest focuses on many-electron states, the construction of these states as the product of one-electron functions--indeed the antisymmetrized product of such functions--is important in model building. Thus the first point to be made about orbitals is that they are indeed one-electron functions,

$$\psi = \psi(\vec{r},\xi) = \psi(X). \tag{A.1}$$

The orbital ψ is defined over the four-dimensional configuration space whose points are labeled by the three variables x,y,z (or in spherical coordinates r, θ, ϕ) locating the position in ordinary three dimensional space and the spin coordinate ξ a discrete index taking on just two values. The "direction" in spin space (picturesquely denoted up or down) corresponds to the eigenvalue of an operator denoting the component of spin along the axis of quantization. More precisely there are three components of the vector spin operator

$$\hat{\vec{s}} = \hat{s}_x \hat{i} + \hat{s}_y \hat{j} + \hat{s}_z \hat{k} \tag{A.2}$$

with which we can form a set of two commuting observables, say

$$\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 \tag{A.3}$$

and

$$\hat{s}_n = \hat{n}\cdot\hat{\vec{s}} \tag{A.4}$$

where $\hat{n}$ is a unit vector indicating the arbitrarily chosen direction of quantization. Without loss of generality we take $\hat{n} = \hat{k}$, so that $\hat{s}^2$ and $\hat{s}_z$ form the set of commuting observables. Empirically it is found that electrons have only two spin eigenstates and thus we write

$$\hat{s}^2\{C_{m_s}(\vec{r})\chi_{m_s}^{1/2}(\xi)\} = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\{C_{m_s}(\vec{r})\chi_{m_s}^{1/2}(\xi)\} \tag{A.5}$$

$$\hat{s}_z\{C_{m_s}(\vec{r})\chi_{m_s}^{1/2}(\xi)\} = m_s\hbar\{C_{m_s}(\vec{r})\chi_{m_s}^{1/2}(\xi)\}, \quad m_s = \pm\frac{1}{2}. \tag{A.6}$$

The "constant" $C_{m_s}(\vec{r})$ is of course not determined by the eigenvalue problem in spin space. The "constant" is independent of the spin coordinate ξ but may depend on $\vec{r}$.

We introduce the two orthonormal basis vectors, frequently denoted α and β, and satisfying

$$\begin{aligned} \hat{s}^2\alpha &= \frac{1}{2}(\frac{1}{2}+1)\hbar^2\alpha, \quad \hat{s}_z\alpha = \frac{\hbar}{2}\alpha \\ \hat{s}^2\beta &= \frac{1}{2}(\frac{1}{2}+1)\hbar^2\beta, \quad \hat{s}_z\beta = -\frac{\hbar}{2}\beta. \end{aligned} \tag{A.7}$$

The components $\alpha(\xi) \equiv \langle\xi|\alpha\rangle$ and $\beta(\xi) \equiv \langle\xi|\beta\rangle$, with $\xi = \uparrow,\downarrow$ are taken as

$$\begin{aligned} \alpha(\uparrow) &= \beta(\downarrow) = 1 \\ \alpha(\downarrow) &= \beta(\uparrow) = 0, \end{aligned} \tag{A.8}$$

and the inner products may thus be computed as

$$\begin{aligned} \langle\alpha|\alpha\rangle &= \sum_{\xi}\langle\xi|\alpha\rangle^{*}\langle\xi|\alpha\rangle = 1\cdot1 + 0\cdot0 = 1 \\ \langle\alpha|\beta\rangle &= \sum_{\xi}\langle\xi|\alpha\rangle^{*}\langle\xi|\beta\rangle = 1\cdot0 + 0\cdot1 = 0 \\ \langle\beta|\alpha\rangle &= \sum_{\xi}\langle\xi|\beta\rangle^{*}\langle\xi|\alpha\rangle = 0\cdot1 + 1\cdot0 = 0 \\ \langle\beta|\beta\rangle &= \sum_{\xi}\langle\xi|\beta\rangle^{*}\langle\xi|\beta\rangle = 0\cdot0 + 1\cdot1 = 1. \end{aligned} \tag{A.9}$$

Below we will find it convenient to let

$$\chi^{1/2}_{1/2}(\xi) = \alpha(\xi) \quad \text{and} \quad \chi^{1/2}_{-1/2}(\xi) = \beta(\xi). \tag{A.10}$$

The most general form for the spin orbital is then

$$\psi(\vec{r},\xi) = \psi_{\uparrow}(\vec{r})\alpha(\xi) + \psi_{\downarrow}(\vec{r})\beta(\xi) \tag{A.11}$$

where the two functions $\psi_{\uparrow}(\vec{r})$ and $\psi_{\downarrow}(\vec{r})$ depend only upon the spatial coordinates. The differential probability

$$|\psi(\vec{r},\xi)|^2\,dx\,dy\,dz = \psi^*(\vec{r},\xi)\psi(\vec{r},\xi)\,dx\,dy\,dz \qquad (A.12)$$

is the likelihood that a particle "occupying orbital ψ" will be found in the volume element dx dy dz located at (x,y,z) with spin coordinate ξ. Of course, in an N particle system one must first determine the yet a priori probability of finding the particle occupying orbital ψ. This may in fact be done, though the details are beyond the scope of the present work. However, it is essential to remember that it is impossible to distinguish which of the N electrons occupies orbital $\psi(\vec{r},\xi)$. In an orbital model, such as Hartree Fock in which one electron is assigned to each of N different spin orbitals, one immediately has the a priori probability orbital assignment to be unity. Clearly, the antisymmetry requirement on the N electron wavefunction reflects the indistinguishability of the electrons and the inability to identify any particular electron with orbital $\psi(\vec{r},\xi)$.

In constructing a basis of orbitals it is often convenient to consider those spin orbitals whose probability amplitude factors into the product of a spatial orbital times a spin function,

$$\boldsymbol{\theta}_\alpha = \Theta_a(\vec{r})\chi_{m_s}(\xi). \qquad (A.13)$$

The orbital index α involves m_s ($= \pm\frac{1}{2}$) and a label a needed to enumerate the elements of a complete set of spatial orbitals. As indicated above the most general spin orbital can still be expanded as a linear superposition of such basis functions accordingly as

$$\psi(\vec{r},\xi) = \sum_a \sum_{m_s} C_{am_s} \Theta_a(\vec{r})\chi_{m_s}(\xi)$$

$$= (\sum_a C_{a\frac{1}{2}} \Theta_a(\vec{r}))\alpha(\xi) + (\sum_a C_{a-\frac{1}{2}} \Theta_a(\vec{r}))\beta(\xi). \quad (A.14)$$

In terms of our previous conclusion in Equation (A.11) we have that

$$\psi_\uparrow(\vec{r}) = \sum_a C_{a\frac{1}{2}} \Theta_a(\vec{r})$$
$$\psi_\downarrow(\vec{r}) = \sum_a C_{a-\frac{1}{2}} \Theta_a(\vec{r}). \quad (A.15)$$

Clearly, in general $\psi(\vec{r},\xi)$ does not factor into the product of a space and spin factor. Thus, as postulated in the restricted Hartree Fock theory, the form of the SCF orbital as the product of a spatial and spin function is indeed an additional constraint beyond the restriction to a single determinant requirement.

Often the spatial factor itself is an eigenfunction of a set of commuting observables which depend only on the position and momentum operators of a single particle. For atomic orbitals these are taken as $\hat{\ell}^2$ and $\hat{\ell}_z$, the square of orbital angular momentum and the z- component of orbital angular momentum, and $\hat{h}_o$ the single particle (effective) Hamiltonian (Merzbacher, 1970, pp. 172-190). The set of eigenfunctions

$$\hat{h}_o \Theta_{\varepsilon\ell m}(\vec{r}) = \varepsilon\Theta_{\varepsilon\ell m}(\vec{r}) \quad (A.16)$$

$$\hat{\ell}^2 \Theta_{\varepsilon\ell m}(\vec{r}) = \ell(\ell+1)\hbar^2 \Theta_{\varepsilon\ell m}(\vec{r}), \quad \ell = 1,2,\ldots \quad (A.17)$$

$$\hat{\ell}_z \Theta_{\varepsilon\ell m}(\vec{r}) = m\hbar \Theta_{\varepsilon\ell m}(\vec{r}), \quad -\ell \leq m \leq \ell \quad (A.18)$$

is presumably complete, in that $\psi_{\downarrow}(\vec{r})$ and $\psi_{\downarrow}(\vec{r})$ may be expanded as in (A.15). These atomic spatial orbitals are generally complex functions of the form

$$\Theta_{\varepsilon\ell m}(\vec{r}) = R_{\varepsilon\ell}(r) Y_{\ell}^{m}(\theta,\phi) \tag{A.19}$$

where the spherical harmonics

$$Y_{\ell}^{m}(\theta,\phi) = \left[\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}\right]^{\frac{1}{2}} P_{\ell}^{|m|}(\cos\theta)\, e^{im\phi} \tag{A.20}$$

arise quite generally in the separation of variables method applied to the central field problem. On the other hand the so-called radial wavefunction depends on the details incorporated into the central effective potential $\hat{U}$ found in (3.11).

Throughout the discussion we have focused on the ethane molecule, so here let us consider specifically the orbitals on one of the carbon atoms in ethane. The probability density of the spatial orbitals

$$\Theta_{2s_0}(\vec{r}),\ \Theta_{2p_1}(\vec{r}),\ \Theta_{2p_0}(\vec{r}),\ \Theta_{2p_{-1}}(\vec{r}) \tag{A.21}$$

may be schematically indicated by the shading (density of dots) as indicated in Figures A.1a through A.1c. (In these figures, we present the density distributions--the absolute squares of the functions--for the 2s and 2p ($m = -1,0,+1$) orbitals using the radial wavefunctions for hydrogen.) Clearly the $|\Theta_{2p_1}|^2$ and $|\Theta_{2p_{-1}}|^2$ are the same function. The 2s orbital probability density distribution ($\sim[1-\frac{1}{2}\alpha r]^2 e^{-\alpha r}$) is spherically symmetric, while $2p_0$ orbital ($\sim r^2\, e^{-\alpha r} \cos^2\theta$) has its largest density

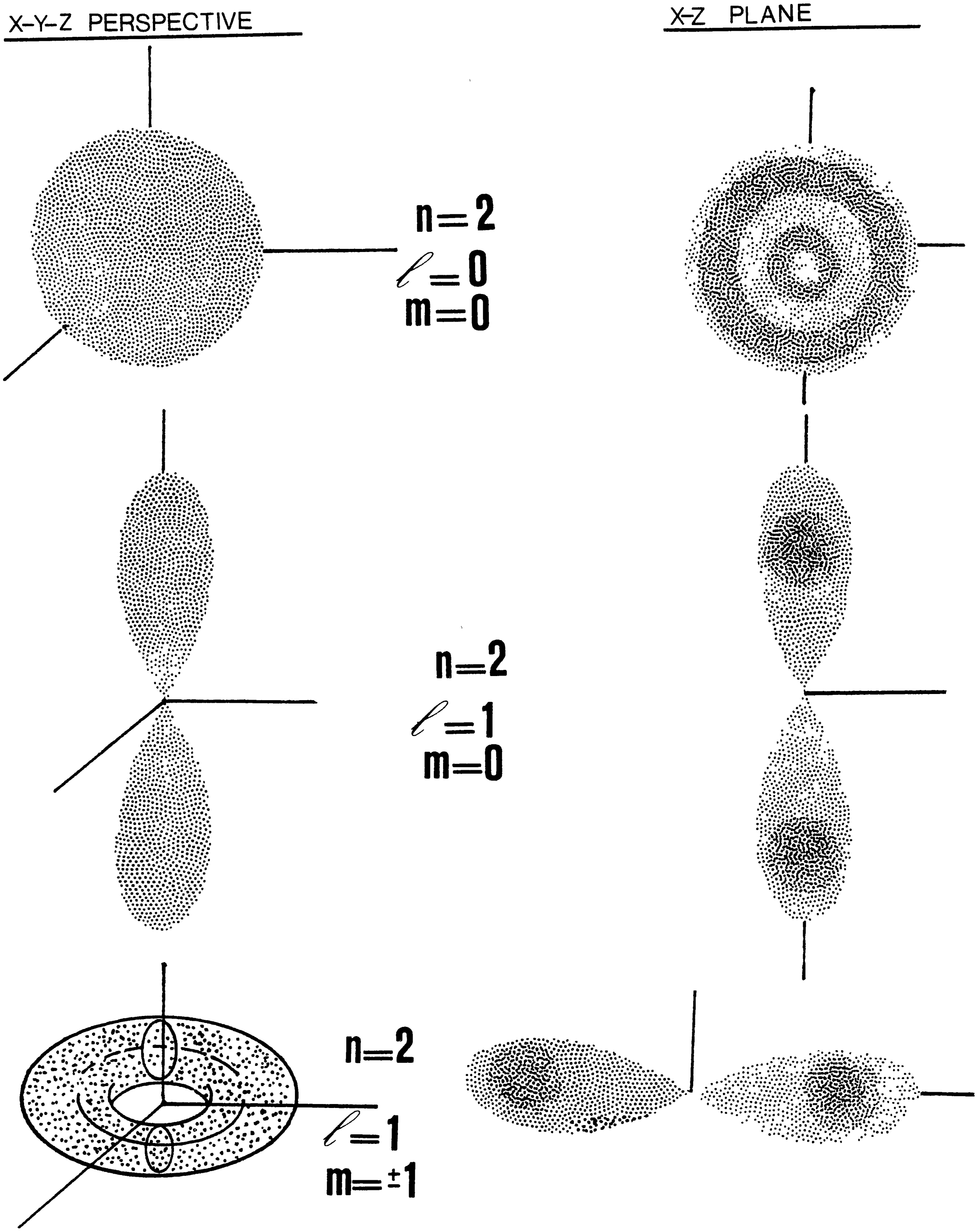

Figure A.1. Representation of the Probability Density for Different Sets of Quantum Numbers at points along the z-axis and the 2p (m = -1) and 2p (m = +1) orbitals ($\sim r^2 e^{-\alpha r} \sin^2 \theta$) assume the largest densities at points in the xy plane. Although the azimuthal angle ϕ appears in the orbitals themselves the probability densities are in fact azimuthally symmetric.

We can also form directed real orbitals by taking linear combinations of the complex 2p orbitals. Specifically we have

$$\Theta_{2p_x}(\vec{r}) = \frac{1}{\sqrt{2}} [\Theta_{2p_1} - \Theta_{2p_{-1}}] = R_{21}(r) \frac{x}{\sqrt{4\pi}}$$

$$\Theta_{2p_y}(\vec{r}) = \frac{1}{\sqrt{2}} [\Theta_{2p_1} + \Theta_{2p_{-1}}] = R_{21}(r) \frac{y}{\sqrt{4\pi}} \tag{A.22}$$

$$\Theta_{2p_z}(\vec{r}) = \Theta_{2p_0} = R_{21}(r) \frac{z}{\sqrt{\pi}} .$$

We have plotted these probability densities of these "cartesian" p orbitals in Figure A.2. These p orbitals are eigenfunctions of $\hat{\ell}^2$ and $\hat{h}$ but not eigenfunctions of $\hat{\ell}_z$ (in fact, Θ_{2p_z} is still an eigenfunction of $\hat{\ell}_z$). However, this second set of p orbitals clearly has the property of density maxima lying along the coordinate axes. This is our first indication of "preparing" linear combinations of atomic orbitals for chemical bonding. The procedure--called hybridization--is most useful in making connections with the intuitive notions of valency in the spirit of atomic fragments sharing localized charges with other atoms in forming chemical bonds. Both sets of four orbitals $\{\Theta_{2s_0}, \Theta_{2p_1}, \Theta_{2p_0}, \Theta_{2p_{-1}}\}$ and $\{\Theta_{2s}, \Theta_{2p_x}, \Theta_{2p_y}, \Theta_{2p_z}\}$ form an orthonormal basis for the same four dimensional function space. That is,

$$\int d\vec{r}\, \Theta_a^*(\vec{r})\, \Theta_b(\vec{r}) = \delta_{ab} \tag{A.23}$$

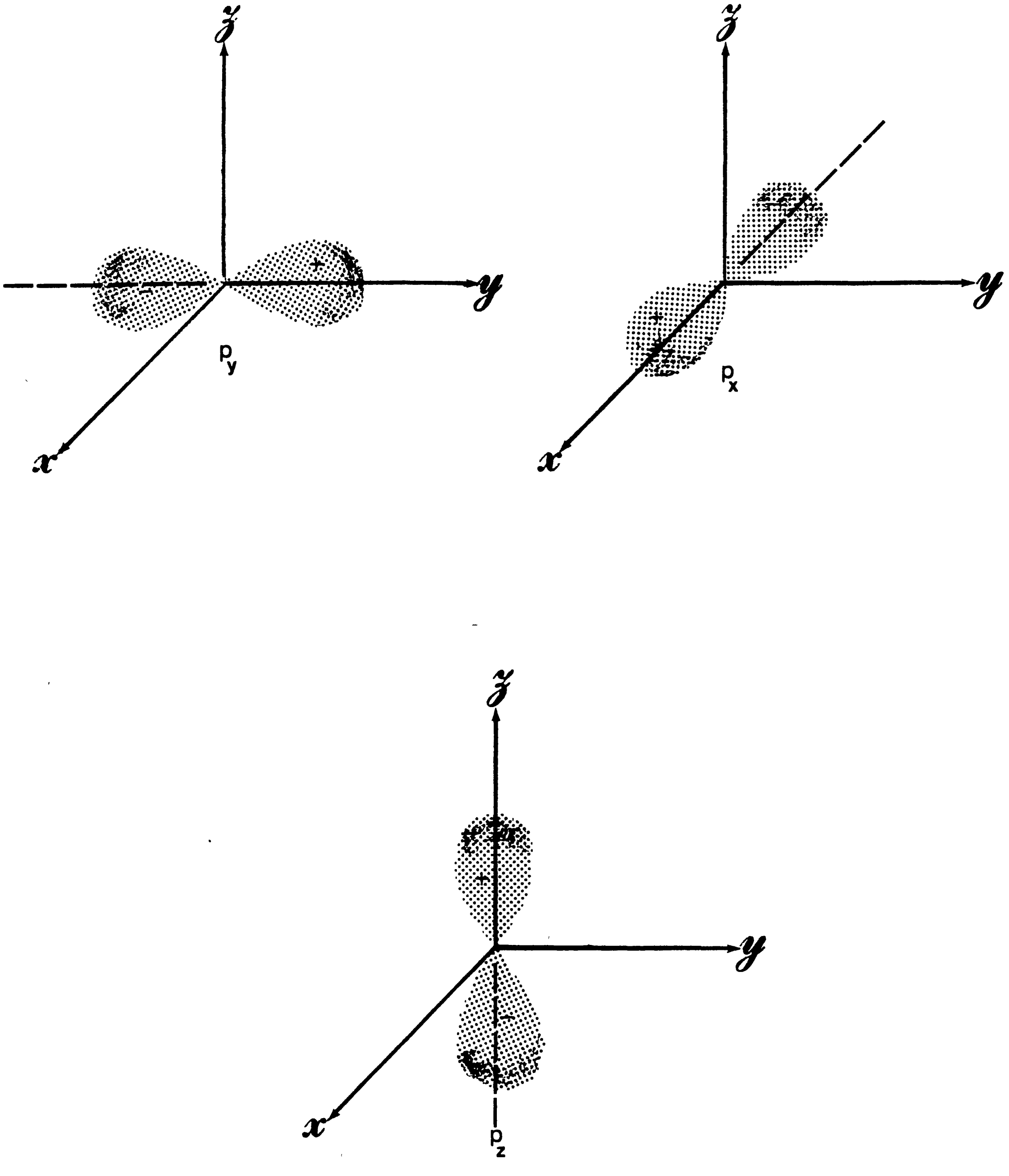

Figure A.2. Probability Distributions of p Orbitals

where

$$a,b \equiv \{2s_0,2p_1,2p_0,2p_{-1}\} \tag{A.24}$$

or

$$a,b \equiv \{2s_0,2p_x,2p_y,2p_z\}. \tag{A.25}$$

In fact there are an infinite number of bases for this same four dimensional vector space. Each of the elements of any of the other bases may be expressed as linear combinations of either the basis $\{\Theta_{2s},\Theta_{2p_1},\Theta_{2p_0},\Theta_{2p_{-1}}\}$ or the $\{\Theta_{2p_s},\Theta_{2p_x},\Theta_{2p_y},\Theta_{2p_z}\}$ basis. The possibility arises that the absolute square of the linear combination of these orbitals in Hilbert space may have various directional character in ordinary three dimensional space. These "directional" properties of the atomic orbitals--the fact that the density maxima are attained along specific directions in space--is determined by the linear coefficients in their expansion in terms of, say, $\{\Theta_{2s},\Theta_{2p_x},\Theta_{2p_y},\Theta_{2p_z}\}$. In turn, the geometrical arrangement of the adjacent atoms will determine what directional character should be chosen for these orbitals in the spirit of redistributing atomic charge density to facilitate chemical bonding. This so-called hybridization is a convenient intuitive starting point in selecting a basis set of spatial orbitals for molecular calculations. We shall illustrate this with our example of the ethane molecule.

In considering the ethane molecule in the staggered geometry we include the 1s orbitals on each of the six hydrogen nuclei and $1s,2s,2p_x$, $2p_y,2p_z$ on each of the two carbon nuclei. The coordinate system used--including the local coordinate axes on each carbon atom--and the numbering scheme for the atoms is shown in Figure A.3. This scheme is used throughout this thesis. The orbital lobe scheme is indicated also in this figure. Using the model of Sovers et al. (1968) (but changing the notation to fit with the present choice of axes and site labels) we construct the hybrid combinations of 2s and 2p valence orbitals on C_1 to point toward the adjacent atoms, H_4, H_5, H_6 and C_2 respectively as shown in Figure A.4. The arbitrary phase factors have been chosen so that the (real) positive lobes are directed toward the adjacent atoms. In their work, the hybrid centered on carbon atom C_1 and directed toward carbon atom C_2 is shown to be

$$\Theta_{C_1C_2} = -\sqrt{2}\cot\alpha\ \Theta_{2s_{C_1}} + (1-2\cot^2\alpha)^{\frac{1}{2}}\ \Theta_{2p_{zC_1}} \tag{A.26}$$

while that hybrid centered on C_1 and directed toward H_6 is

$$\Theta_{C_1H_6} = [\tfrac{1}{3}(1-2\cot^2\alpha)]^{\frac{1}{2}}\ \Theta_{2s_{C_1}} - \sqrt{\tfrac{2}{3}}\,[\Theta_{2p_{yC_1}} - \cot\alpha\ \Theta_{2p_{zC_1}}]. \tag{A.27}$$

The expansion coefficients are given in terms of the CCH angle α which for ethane is 109°. (Note that $\cot(109°) = -0.3443$.) The two remaining hybrids on C_1 as well as the four counterparts on C_2 may be generated by applying symmetry operators to the two orbitals given above. (We discuss some of the basic notions of group theory in the next two appendices.) Here we note, more or less intuitively, that

$$\Theta_{C_1H_4} = \hat{O}_{C_3}\ \Theta_{C_1H_6} \tag{A.28}$$

$$\Theta_{C_1H_5} = \hat{O}_{C_3}\ \Theta_{C_1H_4} = \hat{O}_{C_3^2}\ \Theta_{C_1H_6}. \tag{A.29}$$

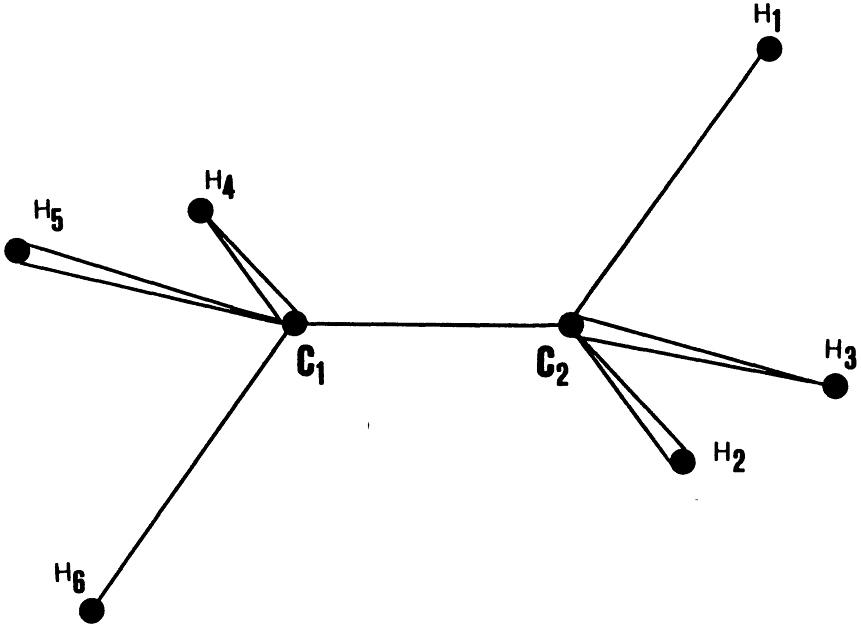

Figure A.3. Numbering Scheme for Atoms in Ethane

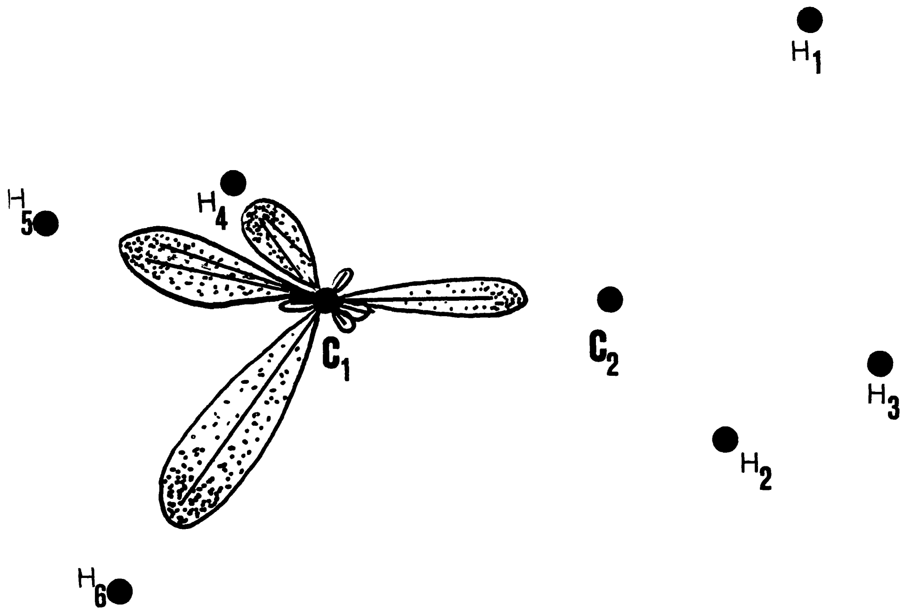

Figure A.4. Hybrid Orbital Densities

$\hat{O}_{C_3}$ is an operator on functions defined in space corresponding to a counter-clockwise rotation of $\frac{2\pi}{3}$ about the carbon-carbon axis. (C_3 is a rotation of $\frac{2\pi}{3}$ about this axis and has nothing to do with a non-existent third carbon nucleus.) The probability densities for these four hybrid orbitals centered on carbon atom C_1 are shown in Figure A.4. Similarly, the hybrid orbitals on C_2 may be found by applying $\hat{O}_{S_6}$ to the corresponding orbitals

$$\Theta_{C_2C_1} = \hat{O}_{S_6}\ \Theta_{C_1C_2} \tag{A.30}$$

$$\Theta_{C_2H_1} = \hat{O}_{S_6}\ \Theta_{C_1H_4} \tag{A.31}$$

$$\Theta_{C_2H_2} = \hat{O}_{S_6}\ \Theta_{C_1H_5} \tag{A.32}$$

$$\Theta_{C_2H_3} = \hat{O}_{S_6}\ \Theta_{C_1H_6}. \tag{A.33}$$

Here, $\hat{O}_{S_6}$ is the so-called "rotation-reflection" operator, where after rotating through angle $\frac{2\pi}{6}$ a reflection in the midplane perpendicular to the carbon-carbon axis is performed. Explicitly, we find for the eight hybrid atomic orbitals--four on each carbon nucleus--the following functions

$$\Theta_{C_1H_6} = [\tfrac{1}{3}(1 - 2\cot^2\alpha)]^{\frac{1}{2}}\ \Theta_{2sC_1} + \sqrt{\tfrac{2}{3}}\ [-\Theta_{2p_yC_1} + \cot\alpha\ \Theta_{2p_zC_1}] \tag{A.34}$$

$$\Theta_{C_1C_2} = -\sqrt{2}\cot\alpha\ \Theta_{2sC_1} + (1 - 2\cot^2\alpha)^{\frac{1}{2}}\ \Theta_{2p_zC_1} \tag{A.35}$$

$$\Theta_{C_1H_5} = O_{C_3}\ \Theta_{C_1H_4} = [\tfrac{1}{3}(1 - 2\cot^2\alpha)]^{1/2}\ \Theta_{2sC_1} + \sqrt{\tfrac{2}{3}}\ [-\tfrac{\sqrt{3}}{2}\ \Theta_{2p_xC_1} + \tfrac{1}{2}\Theta_{2p_yC_1} + \cot\alpha\ \Theta_{2p_zC_1}] \tag{A.36}$$

$$\Theta_{C_1H_4} = O_{C_3}\ \Theta_{C_1H_6} = [\tfrac{1}{3}(1 - 2\cot^2\alpha)]^{1/2}\ \Theta_{2sC_1} + \sqrt{\tfrac{2}{3}}\ [-(-\tfrac{\sqrt{3}}{2}\ \Theta_{2p_xC_1} - \tfrac{1}{2}\Theta_{2p_yC_1}) + \cot\alpha\ \Theta_{2p_zC_1}] \tag{A.37}$$

$$\Theta_{C_2C_1} = \hat{O}_{S_6}\ \Theta_{C_1C_2} = -\sqrt{2}\ \cot\alpha\ \Theta_{2sC_2} + (1 - 2\cot^2\alpha)^{1/2}\ [-\Theta_{2p_zC_2}] \tag{A.38}$$

$$\begin{aligned}\Theta_{C_2H_1} = \hat{O}_{S_6}\ \Theta_{C_1H_4} &= [\tfrac{1}{3}(1 - 2\cot^2\alpha)]^{1/2}\ \Theta_{2sC_2} + \tfrac{\sqrt{3}}{2}\ [\tfrac{\sqrt{3}}{2}(\tfrac{1}{2}\Theta_{2p_xC_2} + \tfrac{\sqrt{3}}{2}\ \Theta_{2p_yC_2}) \\ &\quad + \tfrac{1}{2}(-\tfrac{\sqrt{3}}{2}\ \Theta_{2p_xC_2} + \tfrac{1}{2}\Theta_{2p_yC_2}) + \cot\alpha\ (-\Theta_{2p_zC_2})] \\ &= [\tfrac{1}{3}(1 - 2\cot^2\ )]^{1/2}\ \Theta_{2sC_1} + \sqrt{\tfrac{2}{3}}\ [\Theta_{2p_yC_2} - \cot\alpha\ \Theta_{2p_zC_2}]\end{aligned} \tag{A.39}$$

$$\begin{aligned}\Theta_{C_2H_2} = \hat{O}_{S_6}\ \Theta_{C_1H_5} &= [\tfrac{1}{3}(1 - 2\cot^2\alpha)]^{1/2}\ \Theta_{2sC_2} + \sqrt{\tfrac{2}{3}}\ [-\tfrac{\sqrt{3}}{2}(\tfrac{1}{2}\Theta_{2p_xC_2} + \tfrac{\sqrt{3}}{2}\Theta_{2p_yC_2}) \\ &\quad + \tfrac{1}{2}(-\tfrac{\sqrt{3}}{2}\ \Theta_{2p_xC_2} + \tfrac{1}{2}\Theta_{2p_yC_2}) + \cot\alpha\ (-\Theta_{2p_zC_2})] \\ &= [\tfrac{1}{3}(1 - 2\cot^2\alpha)]^{1/2}\ \Theta_{2sC_2} + \sqrt{\tfrac{2}{3}}\ [-\tfrac{\sqrt{3}}{2}\ \Theta_{2p_xC_2} - \tfrac{1}{2}\Theta_{2p_yC_2} - \cot\alpha\ \Theta_{2p_zC_2}]\end{aligned} \tag{A.40}$$

$$\begin{aligned}\Theta_{C_2H_3} = \hat{O}_{S_6}\ \Theta_{C_1H_6} &= [\tfrac{1}{3}(1 - 2\cot^2\alpha)]^{1/2}\ \Theta_{2sC_2} + \sqrt{\tfrac{2}{3}}\ [(-1)(-\tfrac{\sqrt{3}}{2}\ \Theta_{2p_xC_2} \\ &\quad + \tfrac{1}{2}\Theta_{2p_yC_2}) + \cot\alpha\ (-\Theta_{2p_zC_2})].\end{aligned} \tag{A.41}$$

The atomic valence hybrid orbitals $\{\Theta_{C_1C_2}, \Theta_{C_1H_4}, \Theta_{C_1H_5}, \Theta_{C_1H_6}\}$ centered on C_1 form an orthonormal basis spanning the same four dimensional subspace as do $\{\Theta_{2sC_1}, \Theta_{2p_1C_1}, \Theta_{2p_0C_1}, \Theta_{2p_{-1}C_1}\}$ and $\{\Theta_{2sC_1}, \Theta_{2p_xC_1}, \Theta_{2p_yC_1}, \Theta_{2p_zC_1}\}$. Two atomic spatial orbitals centered on different atoms are, in general, not orthogonal.

All three basis sets considered so far are strictly atomic orbitals --that is, each orbital is centered on a carbon or a hydrogen atom in the ethane molecule. In Chapter V we shall use these spatial atomic orbital basis sets. To be explicit the three bases sets each with a total of sixteen spatial orbitals are:

1. $[\Theta_{1sC_1}, \Theta_{2sC_1}, \Theta_{2p_1C_1}, \Theta_{2p_0C_1}, \Theta_{2p_{-1}C_1}, \Theta_{1sC_2}, \Theta_{2sC_2}, \Theta_{2p_1C_2}, \Theta_{2p_0C_2}, \Theta_{2p_{-1}C_2},$
   $\Theta_{1sH_1}, \Theta_{1sH_2}, \Theta_{1sH_3}, \Theta_{1sH_4}, \Theta_{1sH_5}, \Theta_{1sH_6}];$

2. $[\Theta_{1sC_1}, \Theta_{1sC_1}, \Theta_{2p_xC_1}, \Theta_{2p_yC_1}, \Theta_{2p_zC_1}, \Theta_{1sC_2}, \Theta_{2sC_2}, \Theta_{2p_xC_2}, \Theta_{2p_yC_2}, \Theta_{2p_zC_2},$
   $\Theta_{1sH_1}, \Theta_{1sH_2}, \Theta_{1sH_3}, \Theta_{1sH_4}, \Theta_{1sH_5}, \Theta_{1sH_6}]$

3. $[\Theta_{1sC_1}, \Theta_{1sC_2}, \Theta_{C_1C_2}, \Theta_{C_1H_4}, \Theta_{C_1H_5}, \Theta_{C_1H_6}, \Theta_{C_2C_1}, \Theta_{C_2H_1}; \Theta_{C_2H_2}, \Theta_{C_2H_3}, \Theta_{1sH_1},$
   $\Theta_{1sH_2}, \Theta_{1sH_3}, \Theta_{1sH_4}, \Theta_{1sH_5}, \Theta_{1sH_6}].$

It is important to remember that all three of these atomic orbital basis sets span the same 16-dimensional function space. Thus mathematically none is preferable over any other. On the other hand, as we shall now see the hybrid basis offers a physically intuitive starting point for constructing orbitals for the molecular environment.

A fourth basis set of orbitals, a set including so-called bonding and antibonding orbitals may be formed by taking linear combinations of the atomic valence hybridized orbitals on adjacent atoms. In this instance we have in addition to the two 1s orbitals on each of the carbon atoms the following set of seven bonding (b) and seven antibonding (a) orbitals:

$$\chi^{b/a}_{C_1C_2} = N^{b/a}_{C_1C_2}[\Theta_{C_1C_2} \pm \Theta_{C_2C_1}] \tag{A.42}$$

$$\chi^{b/a}_{C_2H_1} = N^{b/a}_{C_2H_1}[\Theta_{C_2H_1} \pm \Theta_{1sH_1}] \tag{A.43}$$

$$\chi^{b/a}_{C_2H_2} = N^{b/a}_{C_2H_2}[\Theta_{C_2H_2} \pm \Theta_{1sH_2}] \tag{A.44}$$

$$\chi^{b/a}_{C_2H_3} = N^{b/a}_{C_2H_3}[\Theta_{C_2H_3} \pm \Theta_{1sH_3}] \tag{A.45}$$

$$\chi^{b/a}_{C_1H_4} = N^{b/a}_{C_1H_4}[\Theta_{C_1H_4} \pm \Theta_{1sH_4}] \tag{A.46}$$

$$\chi^{b/a}_{C_1H_5} = N^{b/a}_{C_1H_5}[\Theta_{C_1H_5} \pm \Theta_{1sH_5}] \tag{A.47}$$

$$\chi^{b/a}_{C_1H_6} = N^{b/a}_{C_1H_6}[\Theta_{C_1H_6} \pm \Theta_{1sH_6}]. \tag{A.48}$$

We use the χ's (rather than Θ's) for the bonding/antibonding orbitals to emphasize that they can not be associated with a single atomic center. Here, the normalization factor $N^{b/a}_{AB}$ for the bonding (b) and antibonding (a) orbitals is

$$N_{AB}^{b/a} = [2(1 \pm S_{AB})]^{-\frac{1}{2}} \tag{A.49}$$

where the overlap integral

$$S_{AB} = \int d\vec{r}\ \Theta_A^*(\vec{r})\ \Theta_B(\vec{r}) \tag{A.50}$$

pertains to the atomic orbitals Θ_A and Θ_B. In the bonding orbitals the "+" insures a build up of electronic charge density in the region between the two atomic centers. In the antibonding orbitals, on the other hand, the "-" guarantees that there is a depletion of charge in this region.

Thus, there is a fourth set of orbitals spanning the original 16-dimensional function space

$$4.\quad [\Theta_{1sC_1}\ \Theta_{1sC_2}, \chi^b_{C_1C_2}, \chi^b_{C_2H_1}, \chi^b_{C_2H_2}, \chi^b_{C_2H_3}, \chi^b_{C_1H_4}, \chi^b_{C_1H_5}, \chi^b_{C_1H_6}, \chi^a_{C_1C_2}, \chi^a_{C_2H_1},$$
$$\chi^a_{C_2H_2}, \chi^a_{C_2H_3}, \chi^a_{C_1H_4}, \chi^a_{C_1H_5}, \chi^a_{C_1H_6}].$$

In addition to the double occupancy of both 1s spatial orbitals on each of the two carbon atoms the double occupancy of the bonding spatial orbitals--i.e., associating each with both an α and a β spin function--provides a "zeroth order" description for the ground electronic state of the ethane molecule,

$$\Phi(X_1,X_2,\ldots,X_{18}) = \hat{a}(18)[\Theta_{1sC_1}(\vec{r}_1)\alpha(\xi_1)\ \Theta_{1sC_1}(\vec{r}_2)\beta(\xi_2)\ \Theta_{1sC_2}(\vec{r}_3)\alpha(\xi_3)$$
$$\Theta_{1sC_2}(\vec{r}_4)\beta(\xi_4)\ \chi^b_{C_1C_2}(\vec{r}_5)\alpha(\xi_5)\ \chi^b_{C_1C_2}(\vec{r}_6)\beta(\xi_6)\ \chi^b_{C_2H_1}(\vec{r}_7)\alpha(\xi_7)\ \chi^b_{C_2H_1}(\vec{r}_8)\beta(\xi_8)$$

$$\chi^{b}_{C_2H_2}(\vec{r}_9)\alpha(\xi_9)\ \chi^{b}_{C_2H_2}(\vec{r}_{10})\beta(\xi_{10})\ \chi^{b}_{C_2H_3}(\vec{r}_{11})\alpha(\xi_{11})\ \chi^{b}_{C_2H_3}(\vec{r}_{12})\beta(\xi_{12})$$

$$\chi^{b}_{C_1H_4}(\vec{r}_{13})\alpha(\xi_{13})\ \chi^{b}_{C_1H_4}(\vec{r}_{14})\beta(\xi_{14})\ \chi^{b}_{C_1H_5}(\vec{r}_{15})\alpha(\xi_{15})\ \chi^{b}_{C_1H_5}(\vec{r}_{16})\beta(\xi_{16})$$

$$\chi^{b}_{C_1H_6}(\vec{r}_{17})\alpha(\xi_{17})\ \chi^{b}_{C_1H_6}(\vec{r}_{18})\beta(\xi_{18})].$$

More importantly, these basis sets of spatials orbitals are the starting point for carrying out the self consistent field procedure outlined in Chapter V to completion. Alternatively, one may at the very outset bypass the Hartree-Fock calculation and simply carry out a configuration interaction procedure using any one of the basis sets of spin orbitals--spatial orbitals multiplied by α or β spin functions--discussed here. In the next two appendices we discuss yet another set of spatial orbitals the so-called symmetry adapted spatial orbitals.

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APPENDIX B

GROUP THEORY AND GROUP REPRESENTATIONS

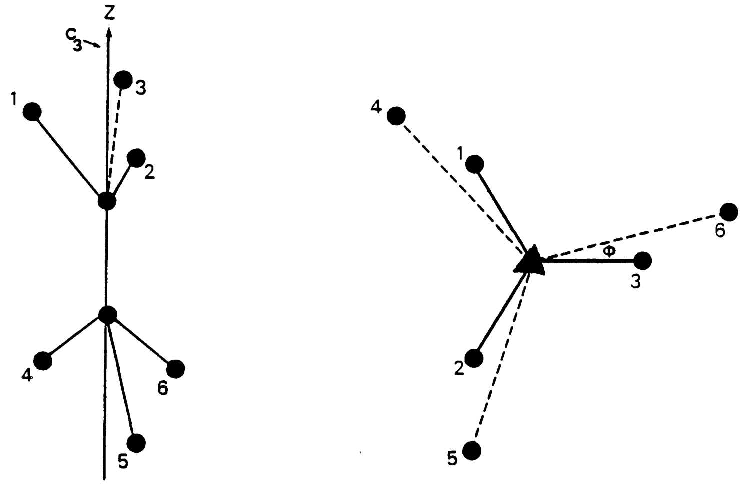
The symmetry of molecules plays an important role in the classification of their energy levels and stationary states. Furthermore, symmetry is related to the problem of finding the vibration spectrum and the transition selection rules. For example, in Chapter V group theory proves useful in the theory of electronic spectra because the Hartree-Fock matrix can be written as the direct sum of lower dimensionality matrices, i.e., the matrix representation of the Hartree-Fock Hamiltonian can be put in block diagonal form. To diagonalize the $m \times m$ matrix, we end up diagonalizing separately the smaller diagonal blocks. We must point out that the problem of finding the eigenvalues can be done without the use of group theory; however, group theory makes "things easier".

In this appendix we present the basic tools for dealing with symmetry groups and group representations to help us find the so-called symmetry adapted bases orbitals in our electronic structure calculations. These functions will be used as one of the bases for one-particle Hilbert space. The Hartree-Fock matrix representation written in the symmetry adapted basis which labels the rows and the columns gives the block-diagonal form mentioned earlier.

The symmetry of a molecule is described by all distance preserving operations on points in real, three dimensional space, which bring the molecule into coincidence with itself. We shall speak of a "symmetry operation" for the present as a transformation (or mapping) of the points in space onto themselves. Similarly, by "symmetry element" we mean a particular set of points (e.g., a single point, a line of points, or a plane of points) which are unaffected by a symmetry operation. We will postpone until later in this appendix the mathematical niceties implied by these concepts. As we shall see in more detail shortly, these symmetry operations correspond to transformations (in Hilbert space) which will leave the Hamiltonian operator invariant. The system "looks the same" to the electron after the operation. The distance preserving operations for finite molecules (as will be the case in our discussion) involve rotations about given axes through specific angles, mirror reflections in planes, and inversions through the center of symmetry, as well as products of these operations, such as rotation-reflections. All axes of rotation and all planes of reflection have at least one point in common, the center of symmetry, which is mapped into itself under all symmetry operations. These points, lines, and planes are the symmetry elements. A very good reference for a deeper insight into the concepts of symmetry is Chapter Two of Hamermesh (1964). We will presume much of the formal development of group theory and simply use the occasion to illustrate some of the concepts in regard to the ethane molecule.

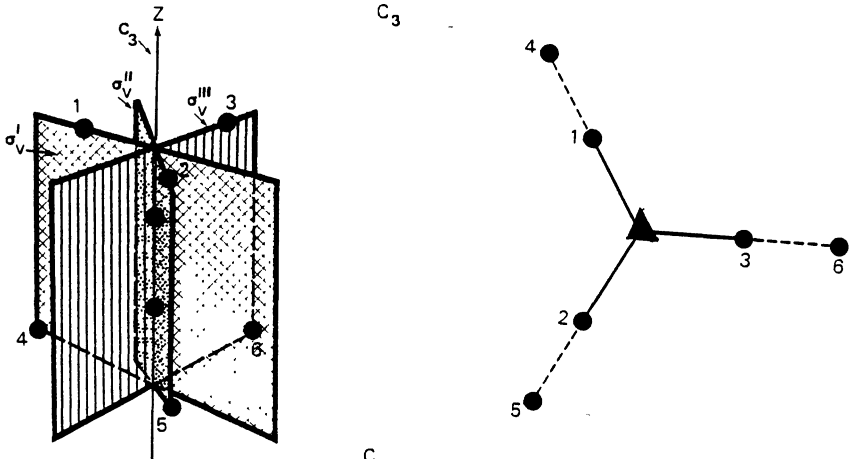
An atom consists of N electrons moving in the field of a fixed positively charged nucleus. Under the symmetry operations the Hamiltonian operator for the electrons is invariant, in the sense that the system "looks the same" after the transformation. A more precise statement of this invariance must await the mathematical development given below. The symmetry operations which leave the atomic Hamiltonian invariant include all rotations about any axis passing through the nucleus, reflections in any plane containing the nucleus, all inversions through the nucleus as well as all products of these operations. All these operations leave the nucleus unchanged. Clearly, there is an indenumerable set of symmetry operations for an atom. When we compare two geometrical figures such as a fixed nucleus and the nuclear framework of an ethane molecule, we may intuitively conclude that the atom possesses a higher order of symmetry, since there is only a finite number of transformations in space which bring the nuclear framework of the ethane molecule into coincidence with itself.

Associated with symmetry is an algebra with we shall explore in some detail through examples restricted to six geometrical arrangements of ethane (among the infinite possibilities). The molecule can be pictured as two "inside-out" umbrella-like structures of hydrogen atoms joined by the carbon-carbon bond. In our cases each set of hydrogen atoms form an equilateral triangle lying in a plane perpendicular to the C-C axis. In general the two umbrellas may have sets of spokes of different lengths and may be oriented at an arbitrary angle relative to one another. The six geometrical cases are presented in Figure B.1 with each case presented in two perspectives; one a three dimensional perspective and the other a two dimensional projection looking along the C-C bond. We shall use this two dimensional figure extensively throughout this appendix. Each of these six geometrical arrangements corresponds to a different "group" of symmetry operations. That is, there are different sets of symmetry operations which bring the molecule into coincidence with itself for each of the five different geometries. To be sure, these five different groups have some common elements, but they do in fact differ from one another in the remaining elements. Accordingly, the five symmetry



(a)

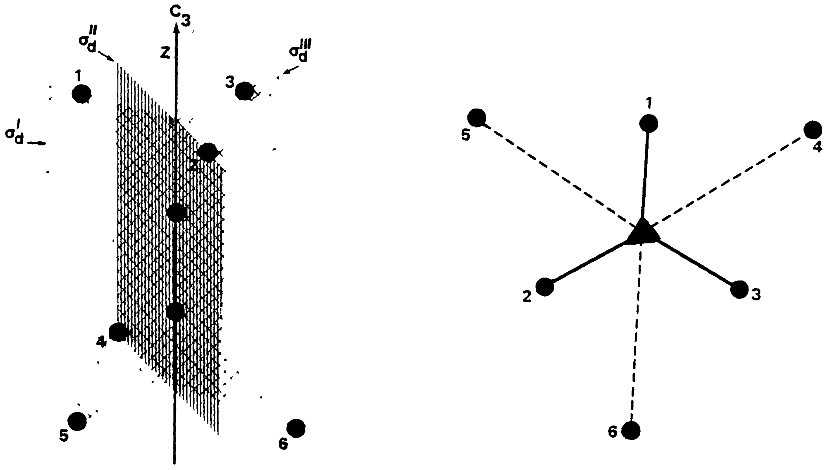
C_3



(b)

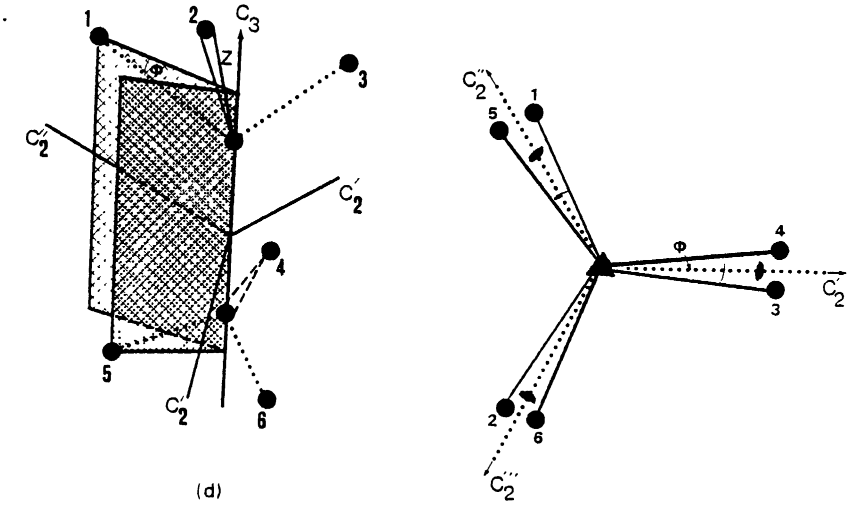
C_{3v}

Figure B.1. The Point Groups C_3, C_{3v}, D_3, D_{3d} and D_{3h}



(c)

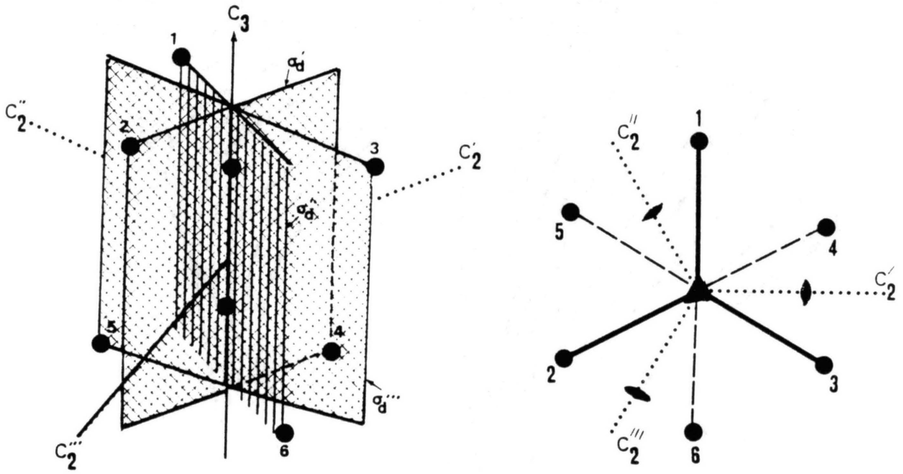
C3v



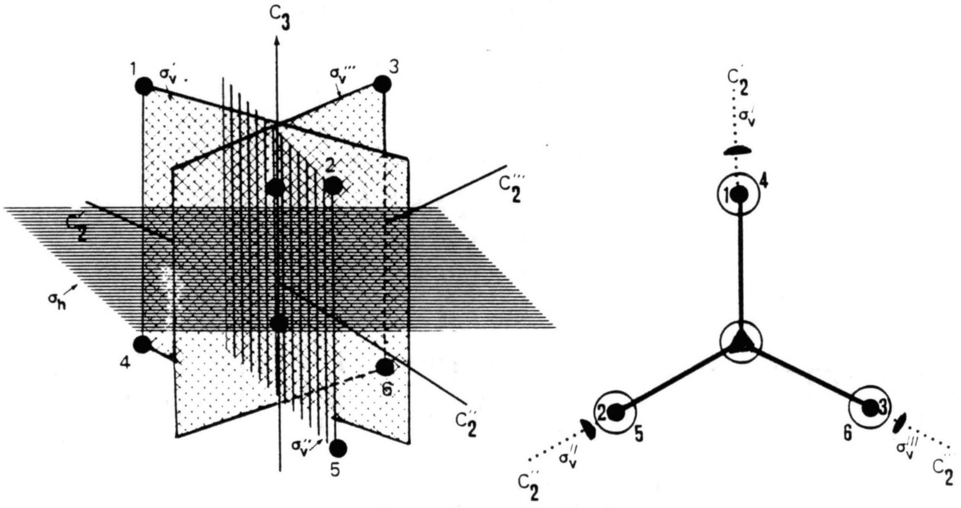
(d)

D3

Figure B.1. (Continued)



(e) D_{3d}



(f) D_{3h}

Figure B.1. (Continued)

groups are denoted $\{C_3, C_{3v}, D_3, D_{3d}$, and $D_{3h}\}$. Let us choose the C-C bond as the z-axis of a right handed coordinate system and the point midway between the C-C atoms as the origin of the coordinate system "O" for all the forms in Figure B.1.

We shall proceed with our analysis of the ethane molecule by systematically introducing more and more symmetry elements beginning with the least symmetrical form of Figure B.1a. We begin by having the two sets of three hydrogen atoms form equilateral triangles in planes perpendicular to the z-axis. However, as Figure B.1a shows, the H-C bond lengths are different for each umbrella and the umbrella spokes are oriented at arbitrary dihedral angle ϕ. Consequently, only three symmetry operations, $\{C_3, C_3^2, C_3^3 = I\}$ bring the molecule into coincidence with itself. C_3 is a rotation of $\frac{2\pi}{3}$ about the z-axis. We shall henceforth · call the z-axis the principal (threefold or C_3) axis and use the triangle symbol - ▲ - to denote this fact in the figures. The symmetry group for this geometrical form of ethane is thus denoted C_3. If now one set of hydrogens is rotated so as to make the dihedral angle $\phi = 0$ (Figure B.1b) or $\phi = \frac{\pi}{3}$ (Figure B.1e) then there are additional symmetry operations which bring the molecule into coincidence with itself, namely reflections in planes denoted σ_v', σ_v'', σ_v'''. Each of these planes contains the two carbon atoms as well as two hydrogen atoms. In Figure B.1b each of the hydrogen atoms is on the same side of the C-C bond (cis configuration) while in Figure B.1c each of the hydrogen atoms is on the opposite side of the C-C bond (trans configuration). Starting with the general C_3 symmetry depicted in Figure B.1a we obtain the D_3 form, shown in figure B.1d (the D stands for dihedral) by allowing all the six bonds to assume the same length. Thus, we adjoin three two-fold rotation symmetry axes perpendicular to the principal axis, rotations about which through π and 2π bring the molecule into coincidence with itself. These are denoted by C_2', C_2'', and C_2'''. (The elipse symbol is used to indicate a two fold axis.)

Two special cases emerge from D_3, one when the two umbrellas are oriented at $\phi = \frac{\pi}{3}$ relative to each other (the staggered case) and another when the two umbrellas are at $\phi = 0$ relative to each other (the eclipsed case). Both special cases possess a higher order of symmetry than D_3. In the staggered case D_{3d} shown in Figure B.1e we have, in addition to the symmetry elements defining D_3, three diagonal reflection planes denoted by σ_d', σ_d'', and σ_d''', each plane contains the principal (C_3) axis and two hydrogens diagonally opposite one another along their adjoining line through the origin. Each reflection plane σ_d bisects the angle between adjacent two-fold rotation axes (see Figure B.1e) and contains two diagonally opposite (trans) hydrogen atoms. The symmetry operations in D_{3d} include, in addition to those in D_3, the reflections in the three σ_d planes, rotation-reflections S_6 and S_6', and inversion i through the origin of symmetry. In the eclipsed case D_{3h}, shown in Figure B.1f we have, in addition to the symmetry elements defining D_3, three vertical reflection planes denoted by σ_v', σ_v'', σ_v'''. Each plane contains the principal (C_3) axis and two hydrogen atoms, one eclipsing the other as viewed along the z-axis. Also, a horizontal reflection plane σ_h, perpendicular to the principal axis is included. Each reflection plane σ_v contains a two-fold rotation axis (see Figure B.1f) and two eclipsing (cis) hydrogen atoms. The symmetry operations in D_{3h} include, in addition to those six in D_3, the reflections in the three σ_v planes, the reflection σ_h and rotation-reflections S_3 and S_3'. In passing, we note that the symmetry groups D_{3d} and D_{3h} could also be obtained as special cases of the two C_{3v} examples noted in Figures B.1b and B.1c respectively as the two sets of C-H bond lengths are made equal.

Having presented the six geometrical forms of the ethane molecule, we now introduce the concept of a group, a subgroup of a group, and classes of group operations. We shall refer to axes of rotation, planes of reflection, and the point of inversion as "symmetry elements". Likewise, we shall call the transformations on the points in space into themselves "group operations". (It should be noted that the operations of the symmetry group are those which bring the ethane molecule into coincidence with itself; however, the group operations are upon all spatial points not simply the nuclei.) Following long-standing tradition, we shall denote both the symmetry elements and the corresponding "group operations" by the same symbol. Thus to summarize our notation:

1. The counterclockwise rotations of $\frac{2}{3}\pi$, $\frac{4}{3}\pi$, and 2π will be denoted by $\{C_3$, C_3^2, and $I\}$ respectively.
2. The notation used to indicate the set of the three vertical planes in D_{3d} $\{\sigma_d'$, σ_d'', and $\sigma_d'''\}$ will also serve to indicate the operations of reflection in these planes. Similarly, the vertical planes in D_{3h} $\{\sigma_v'$, σ_v'', and $\sigma_v'''\}$ will serve to indicate the operations of reflection in these planes.
3. In the same spirit we shall use the notation σ_h to indicate the operation of reflection in the σ_h plane.
4. The operation which takes a point P to its image along a line passing through the origin "O" is called the inversion operation and is denoted by i.
5. The combined operation resulting from reflecting in the σ_h plane

followed by a counterclockwise rotation $\frac{2}{3}\pi$ (or vice versa) will be denoted by S_3; that resulting from the combined operation of a counterclockwise rotation of $\frac{4}{3}\pi$ followed by a reflection in the plane σ_h will be denoted by S_3'. Note that S_3 and S_3' are called rotation reflection operations.

6. The rotation reflection operations in D_{3d} are

$$S_6 = C_6\sigma_h \tag{B.1}$$

and

$$S_6' = C_6^5\sigma_h. \tag{B.2}$$

Note, however, this does not imply the existence of a separate σ_h operation and a C_6 (or C_6^5) operation in D_{3d}. On the other hand, σ_h and C_3 do exist as separate symmetry operations in D_{3h} together with S_3 and S_3'.

7. We shall use the notation C_2', C_2'', and C_2''' to denote both the axes of two-fold rotations as well as the operations of rotation of π counterclockwise about the two-fold axes.

We see that with each geometry of ethane presented in Figure B.1 there are a finite number of symmetry elements and operations. In Table VII we present each of the geometrical forms of ethane along with the symmetry elements and operations which are affiliated with it.

A symmetry operation associates each point ρ in space with an image point P'. The operation I, called the identity, maps each point into itself. Other operations generally map each given point into a different (image) point, but those points on a symmetry element are mapped into themselves under the corresponding operations. Two symmetry operations can be "multiplied" by applying them in sequence upon the points in space;

that is, if R and R' are two group operations, then the "product" RR' is performed upon a general point P by first applying R' upon P to get the image point P' and then applying R on P' to get another image point P". There always exists a single operation which maps P into P".

TABLE VII

GEOMETRICAL FORMS OF ETHANE

Symmetry	Elements	Operations
C_3	$[C_3]$	$\{I,C_3,C_3^2\}$
C_{3v}	$[C_3,\sigma_v',\sigma_v'',\sigma_v''']$	$\{I,C_3,C_3^2,\sigma_v',\sigma_v'',\sigma_v'''\}$
D_3	$[C_3,C_2',C_2'',C_2''']$	$\{I,C_3,C_3^2,C_2',C_2'',C_2'''\}$
D_{3d}	$[C_3,C_2',C_2'',C_2''',$	$\{I,C_3,C_3^2,C_2',C_2'',C_2'''$
	$0,\sigma_d',\sigma_d'',\sigma_d''']$	$i,S_6,S_6',\sigma_d',\sigma_d'',\sigma_d'''\}$
D_{3h}	$[C_3,C_2',C_2'',C_2''',$	$\{I,C_3,C_3^2,C_2',C_2'',C_2''',$
	$\sigma_h,\sigma_v',\sigma_v'',\sigma_v''']$	$\sigma_h,\sigma_v',\sigma_v'',\sigma_v''',S_3,S_3'\}$

To illustrate the procedure of multiplication of symmetry operations, we construct a "multiplication" table for the three symmetry operations of C_3. This is shown in Table VIII. The three operations are used to label the rows and columns in a specific chosen order starting with the identity operation. The table entries are the product operations R'R where R is the column operation and R' the row operation.

TABLE VIII

MULTIPLICATION TABLE FOR THE GROUP C_3

C_3	I	C_3	C_3^2
I	I	C_3	C_3^2
C_3	C_3	C_3^2	I
C_3^2	C_3^2	I	C_3

Multiplication table for the symmetry operations C_3 on ethane shown in Figure B.1a.

An investigation of Table VIII reveals the following:

1. Each row and each column contain all the symmetry operations. The set of operations is said to be closed under this law of multiplication.
2. Corresponding to each operation R labeling a row (or column) there is a unique operation S in some column (or row) such that their product yields the identity

$$RS = SR = I. \tag{B.3}$$

   That is, each element has a unique inverse.
3. Finally one can easily show that the product of the operations is associative: $R(ST) = (RS)T$.

The set of symmetry operations with these multiplication properties, closure, a unique inverse, and associativity, is said to form a group. We refer to the three symmetry operations in Table VIII as the symmetry group C_3 of order $g = 3$, that is, having three operations. The operations in Table VIII commute; the order in which they are performed is immaterial. When all the elements do commute we say the group is abelian or commutative. However, as we shall soon see, group operations in general are non-commutative.

In the same spirit we present the "multiplication tables" for the groups C_{3v}, D_3, D_{3d}, and D_{3h} in Tables IX, X, XI, and XII respectively. A careful investigation of Table XI for D_{3d} shows that the order of multiplication does matter, the group is non-commutative. For example, the resulting operation $(C_3 \sigma_d')$ is σ_d'', while the reverse order of operations $(\sigma_d' C_3)$ is σ_d'''. We also note that the upper left-hand corner of Table XI with row and column labels $\{I, C_3, C_3^2\}$ is none other than the multiplication table for the group C_3. When a subset of the elements of a given group forms a group, we have a subgroup. Thus we see that, in addition to the subgroup C_3, the group D_{3d} also has a subgroup of order six having elements $\{I, C_3, C_3^2, C_2', C_2'', C_2'''\}$ which we recognize as D_3. Finally, nine other subgroups of D_{3d} are: $\{I\}, \{I, C_2'\}, \{I, C_2''\}, \{I, C_2'''\}, \{I, i\}, \{I, \sigma_d'\}, \{I, \sigma_d''\}, \{I, \sigma_d'''\}, \{I, C_3, C_3^2, \sigma_d', \sigma_d'', \sigma_d'''\}$.

A very important and useful concept in group theory is that of conjugate operations in a group. The group operation A is said to be the conjugate of another group operation B if there is an operation X in the group such that XAX^{-1} equals B. Those elements of a group which are conjugate to one another are said to form a class. The operations of a group can, therefore, be divided into classes, and each group operation appears in one and only one class. For an abelian group, since $XAX^{-1} = A$, each element is in a class by itself. More generally if two group operations are each conjugate to a third, then they are conjugate to each other. For example, the elements of the group D_{3d} can be divided into six classes

1. $\{I\}$, since $R^{-1}IR = I$, all $R \in G$.
2. $\{i\}$, since $R^{-1}iR = i$, all $R \in G$.
3. $\{C_3, C_3^2\}$, since $C_2' \; C_3 \; C_2' = C_3^2$.
4. $\{S_6, S_6'\}$, since $C_2' \; S_6 \; C_2' = S_6'$.
5. $\{C_2', C_2'', C_2'''\}$, since $\sigma_d''' \; C_2' \; \sigma_d''' = C_2''$, and $\sigma_d'' \; C_2''' \; \sigma_d'' = C_2'$.
6. $\{\sigma_d', \sigma_d'', \sigma_d'''\}$, since $C_3 \; \sigma_d' \; C_3^2 = \sigma_d'''$ and $C_3^2 \; \sigma_d'' \; C_3 = \sigma_d'''$.

Note that $C_2' = C_2'^{-1}$, $C_2'' = C_2''^{-1}$, $C_2''' = C_2'''^{-1}$, $\sigma_d' = \sigma_d'^{-1}$, $\sigma_d'' = \sigma_d''^{-1}$, $\sigma_d''' = \sigma_d'''^{-1}$, and $C_3^2 = C_3^{-1}$.

TABLE IX

MULTIPLICATION TABLE FOR THE POINT GROUP C_{3v}

C_{3v}	I	C_3	C_3^2	σ_v'	σ_v''	σ_v'''
I	I	C_3	C_3^2	σ_v'	σ_v''	σ_v'''
C_3	C_3	C_3^2	I	σ_v'''	σ_v'	σ_v''
C_3^2	C_3^2	I	C_3	σ_v''	σ_v'''	σ_v'
σ_v'	σ_v'	σ_v''	σ_v'''	I	C_3	C_3^2
σ_v''	σ_v''	σ_v'''	σ_v'	C_3^2	I	C_3
σ_v'''	σ_v'''	σ_v'	σ_v''	C_3	C_3^2	I

TABLE X

MULTIPLICATION TABLE FOR THE POINT GROUP D_3

D_3	I	C_3	C_3^2	C_2'	C_2''	C_2'''
I	I	C_3	C_3^2	C_2'	C_2''	C_2'''
C_3	C_3	C_3^2	I	C_2'''	C_2'	C_2''
C_3^2	C_3^2	I	C_3	C_2''	C_2'''	C_2'
C_2'	C_2'	C_2''	C_2'''	I	C_3	C_3^2
C_2''	C_2''	C_2'''	C_2'	C_3^2	I	C_3
C_2'''	C_2'''	C_2'	C_2''	C_3	C_3^2	I

TABLE XI

MULTIPLICATION TABLE FOR THE POINT GROUP D_{3d}

D_{3d}	I	C_3	C_3^2	C_2'	C_2''	C_2'''	i	S_6	S_6'	σ_d'	σ_d''	σ_d'''
I	I	C_3	C_3^2	C_2'	C_2''	C_2'''	i	S_6	S_6'	σ_d'	σ_d''	σ_d'''
C_3	C_3	C_3^2	I	C_2'''	C_2'	C_2''	S_6'	i	S_6	σ_d''	σ_d'''	σ_d'
C_3^2	C_3^2	I	C_3	C_2''	C_2'''	C_2'	S_6	S_6'	i	σ_d'''	σ_d'	σ_d''
C_2'	C_2'	C_2''	C_2'''	I	C_3	C_3^2	σ_d''	σ_d'''	σ_d'	S_6'	i	S_6
C_2''	C_2''	C_2'''	C_2'	C_3^2	I	C_3	σ_d'	σ_d''	σ_i'''	i	S_6	S_6'
C_2'''	C_2'''	C_2'	C_2''	C_3	C_3^2	I	σ_d'''	σ_d'	σ_d''	S_6	S_6'	i
i	i	S_6'	S_6	σ_d''	σ_d'	σ_d'''	I	C_3^2	C_3	C_2''	C_2'	C_2'''
S_6	S_6	I	S_6'	σ_d'	σ_d'''	σ_d''	C_3^2	C_3	I	C_2'''	C_2''	C_2'
S_6'	S_6'	S_6	i	σ_d'''	σ_d''	σ_d'	C_3	I	C_3^2	C_2'	C_2'''	C_2''
σ_d'	σ_d'	σ_d'''	σ_d''	S_6	i	S_6'	C_2''	C_2'	C_2'''	I	C_3^2	C_3
σ_d''	σ_d''	σ_d'	σ_d'''	i	S_6'	S_6	C_2'	C_2'''	C_2''	C_3	I	C_3^2
σ_d'''	σ_d'''	σ_d''	σ_d'	S_6'	S_6	i	C_2'''	C_2''	C_2'	C_3^2	C_3	I

TABLE XII

MULTIPLICATION TABLE FOR THE POINT GROUP D_{3h}

D_{3h}	I	C_3	C_3^2	C_2'	C_2''	C_2'''	σ_h	S_3	S_3'	σ_v'	σ_v''	σ_v'''
I	I	C_3	C_3^2	C_2'	C_2''	C_2'''	σ_h	S_3	S_3'	σ_v'	σ_v''	σ_v'''
C_3	C_3	C_3^2	I	C_2'''	C_2'	C_2''	S_3	S_3'	σ_h	σ_v'''	σ_v'	σ_v''
C_3^2	C_3^2	I	C_3	C_2''	C_2'''	C_2'	S_3'	σ_h	S_3	σ_v''	σ_v'''	σ_v'
C_2'	C_2'	σ_h	C_2'''	I	C_3	σ_v''	σ_v'''	σ_v'	C_3^2	S_3	S_3'	C_2''
C_2''	C_2''	S_3'	S_3	C_3^2	I	σ_v'''	σ_v'	σ_v''	C_3	σ_h	C_2'	C_2'''
C_2'''	C_2'''	C_2'	C_2''	σ_v'''	C_3^2	I	σ_v''	C_3	σ_v'	S_3'	σ_h	S_3
σ_h	σ_h	S_3	S_3'	C_3	σ_v'	C_3^2	I	σ_v'''	σ_v''	C_2''	C_2'''	C_2'
S_3	S_3	C_2'''	σ_h	σ_v''	σ_v'''	σ_v'	C_3	C_3^2	I	C_2'	C_2''	S_3'
S_3'	S_3'	C_2''	C_2'	σ_v'	σ_v''	C_3	C_3^2	I	σ_v'''	C_2'''	S_3	σ_h
σ_v'	σ_v'	σ_v''	σ_v'''	S_3'	σ_h	S_3	C_2''	C_2'''	C_2'	I	C_3	C_3^2
σ_v''	σ_v''	σ_v'''	σ_v'	S_3	S_3'	σ_h	C_2'''	C_2'	C_2''	C_3^2	I	C_3
σ_v'''	σ_v'''	σ_v'	σ_v''	σ_h	S_3	S_3'	C_2'	C_2''	C_2'''	C_3	C_3^2	I

As was done for the group D_{3d}, an investigation of Table XII reveals that the group D_{3h} has as subgroups the groups C_3, D_3 and C_{3v}. In addition there are seven other subgroups of order 2. The group D_{3h} can be subdivided into six classes:

$$\{I\},\{\sigma_h\},\{C_3,C_3^2\},\{C_2',C_2'',C_2'''\},\{S_3,S_3'\}, \text{ and } \{\sigma_v',\sigma_v''\ \sigma_v'''\}.$$

Having presented the fundamental concepts of group theory which will be useful to us as we shall soon see, we turn our attention to the topic of group representations with the eventual aim of finding the symmetry adapted basis functions for the D_3, D_{3d}, and D_{3h} symmetries of ethane.

Group Representations

We shall begin our discussion of group representations by showing how to describe the transformations of spatial points under group operations. Suppose that we have a vector $\vec{r}$ drawn from a chosen fixed origin "0" to the point P. Associated with each point P in three-dimensional space is a unique vector $\vec{r}$. The group operation $\hat{R}$ maps each point P into another point P' (We shall place carets over the operations in order to distinguish them from the matrices introduced below which are underlined by tildes.),

$$\vec{r} = \hat{R}\vec{r}. \tag{B.4}$$

For a molecule we locate the origin at the center of symmetry: that is, $\hat{R}$ is limited to rotations about axes through "0", and reflections in planes containing "0" and rotation-reflections, all of which map the origin "0" into itself. Thus, the origin is always a point included on all symmetry elements.

If we let $\hat{e}_1$, $\hat{e}_2$, and $\hat{e}_3$ be an orthonormal basis for a three dimensional Cartesian coordinate space, then the vector $\vec{r}$ may be written

$$\vec{r} = \sum_{i=1}^{3} x_i\hat{e}_i. \tag{B.5a}$$

Equivalently, the coordinates of the point P, that is the components of the vector $\vec{r}$, are given by the dot products

$$x_i = \hat{e}_i\cdot\vec{r}, \qquad i = 1,2,3. \tag{B.5b}$$

Next we apply to the vector $\vec{r}$ the operation $\hat{R}$ which associates a new vector $\vec{r}'$ with $\vec{r}$. Thus,

$$\vec{r}' = \hat{R}\vec{r} = \hat{R}(\sum_{i=1}^{3} x_i\hat{e}_i) = \sum_{i=1}^{3} x_i\hat{R}\hat{e}_i = \sum_{i=1}^{3} x_i\hat{e}_i'. \tag{B.6}$$

Equation (B.6) states that the coordinates of $\vec{r}'$ with respect to the basis $\{\hat{R}\hat{e}_i \equiv \hat{e}_i'\}$ are the same as the coordinates of $\vec{r}$ with respect to the basis $\{\hat{e}_i\}$. Such a perspective focuses upon the "rotation" of the basis vectors. However, an alternative viewpoint lets us focus on the transformation of coordinates of the two vectors $\vec{r}$ and $\vec{r}'$ expressed in the basis $\{\hat{e}_i\}$. The vectors $\hat{e}_i'$ being linear combinations of the vectors $\hat{e}_i$ may be written

$$\hat{R}\hat{e}_i = \hat{e}_i' = \sum_{j=1}^{3} R_{ji}\hat{e}_j, \qquad i = 1,2,3, \tag{B.7}$$

where, according to (B.5b), the transformation coefficients are

$$R_{ji} = \hat{e}_j \cdot \hat{R}\hat{e}_i. \tag{B.8}$$

Then, Equation (B.6) becomes

$$\vec{r}\,' = \sum_{i=1}^{3} x_i \Big(\sum_{j=1}^{3} R_{ji}\hat{e}_j \Big). \tag{B.9}$$

If we interchange the order of the sums, we express the transformation of the spatial points

$$\vec{r}\,' = \sum_{j=1}^{3} \Big(\sum_{i=1}^{3} R_{ji}x_i \Big)\hat{e}_j. \tag{B.10}$$

The quantity in brackets relates the coordinates of points $\vec{r}$ and $\vec{r}\,'$ expressed in the same basis $\{\hat{e}_i\}$ and may be written

$$x_j' = \sum_{i=1}^{3} R_{ji}x_i, \qquad j = 1,2,3. \tag{B.11}$$

We note that this is matrix multiplication. Thus, every group operation $\hat{R}$ corresponds to a 3×3 matrix $\underset{\sim}{R}$ with elements $R_{ji} = \hat{e}_j \cdot \hat{R}\hat{e}_i$. Clearly, the matrix $\underset{\sim}{R}$ depends both on the operator $\hat{R}$ and the choice of the orthonormal basis.

The set of 3×3 matrices $\{\underset{\sim}{R}\}$ is said to form a representation of the group. That is, if

$$\hat{R}\hat{S} = \hat{T}, \tag{B.12}$$

then

$$\vec{r}\,'' = \hat{T}\vec{r} = \hat{R}\vec{r}\,' = \hat{R}(\hat{S}\vec{r}) \tag{B.13}$$

with

$$x''_k = \sum_{i=1}^{3} T_{ki} x_i . \tag{B.14a}$$

In terms of the separate operations we have

$$x'_j = \sum_{i=1}^{3} S_{ji}\, x_i , \tag{B.14b}$$

and

$$x''_k = \sum_{j=1}^{3} R_{kj} x'_j = \sum_{j=1}^{3} \sum_{i=1}^{3} R_{kj}\, S_{ji}\, x_i = \sum_{i=1}^{3} \{ \sum_{j=1}^{3} R_{kj}\, S_{ji} \} x_i . \tag{B.14c}$$

The coordinate transformations must hold for all points in space. Comparing (B.14a) with (B.14c) we conclude that the matrix corresponding to the product of operations $\hat{R}\hat{S}$ is the matrix product $\underset{\sim}{R}\underset{\sim}{S}$. That is, we find

$$T_{ki} = \sum_{j=1}^{3} R_{kj}\, S_{ji} \tag{B.15}$$

or, in matrix language

$$\underset{\sim}{T} = \underset{\sim}{R}\underset{\sim}{S} . \tag{B.15a}$$

The fact that $\hat{R}$ preserves the length of a vector (i.e., the distances of P and P' from the origin are the same) implies that $\underset{\sim}{R}$ is an orthogonal matrix

$$\underset{\sim}{R}^T \underset{\sim}{R} = \underset{\sim}{I} . \tag{B.16}$$

Next we associate with each operation $\hat{R}$ on the points in space a linear operator $\hat{O}_R$ on the function space $\{f(\vec{r})\}$ such that for any given function $f(\vec{r})$,

$$\hat{0}_R f(\vec{r}) = f(\hat{R}^{-1}\vec{r}) \equiv g(\vec{r}). \tag{B.17a}$$

Here $f(\vec{r})$ is a function defined over the points $\vec{r}$ in three dimensional space. $\hat{0}_R$ is thus a mapping of the function space onto itself. Above $\hat{0}_R$ maps f into g. This definition (B.17) can be extended to functions defined over the configuration space of many particles. Thus

$$\hat{0}_R f(\vec{r}_1,\vec{r}_2) = f(\hat{R}^{-1}\vec{r}_1,\hat{R}^{-1}\vec{r}_2) \equiv g(\vec{r}_1,\vec{r}_2). \tag{B.17b}$$

Here, the six dimensional configuration space has points labeled $(\vec{r}_1,\vec{r}_2)$ with the subscripts denoting the particle labels. The set of linear operators $\hat{0}_R$ obtained as $\hat{R}$ ranges over the group of point transformations does itself form a group. Indeed, if

$$\hat{T} = \hat{R}\hat{S}, \tag{B.18a}$$

then it may be shown from the definition (B.17) that

$$\hat{0}_T = \hat{0}_R\hat{0}_S. \tag{B.18b}$$

Indeed, we shall use the same language in referring to $\{\hat{0}_R\}$ as we do for $\{\hat{R}\}$.

If we have a set of functions $(f_1,f_2,\ldots,f_n)$, such that the result of applying any $\hat{0}_R$ to each function f may be written

$$\hat{0}_R f_i(\vec{r}) = \sum_{j=1}^{n} D_{ji}(R) f_j(\vec{r}), \qquad i=1,2,\ldots,n, \tag{B.19}$$

then the set of functions spans a representation for the group. That is analogously to the basis $\{\hat{e}_i\}$, we now have the functions $\{f_i\}$ serving as a basis for the function space. The coefficients $D_{ji}(R)$ for a given R may be collected into an n×n matrix:

$$\underset{\sim}{D}(R) = \begin{pmatrix} D_{11} & D_{12} & \cdots & D_{1n} \\ D_{21} & D_{22} & \cdots & D_{2n} \\ \vdots & \vdots & & \vdots \\ D_{n1} & D_{n2} & \cdots & D_{nn} \end{pmatrix}. \tag{B.20}$$

Here, we recognize that the ith column (with rows labeled $j = 1,2,\ldots,n$) contains the coefficients in the expansion of $\hat{O}_R f_i$ in terms of the "basis" set $\{f_1, f_2, \ldots, f_n\}$. Generating such a set of functions--they are often called a set of partners--is an essential problem in group theory. More often than not, however, such a set naturally appears in terms of atomic orbitals (or products of atomic orbitals) in considering electronic structure problems. Repeating the same procedure for each group operation $\hat{R}$ we obtain a set of g matrices, each similar in form to (B.20). Thus, each group operation $\hat{O}_R$ has a matrix associated with it; however, the same matrix may represent two or more operations. This set of n×n matrices is also said to form a representation for the group. The matrix multiplication yields the same structure as the group multiplication table. That is, if $\hat{O}_R$ and $\hat{O}_S$ are operations which belong to the group then, analogously to the 3×3 coordinate transformation matrices considered above, we have

$$\underset{\sim}{D}(RS) = \underset{\sim}{D}(R) \cdot \underset{\sim}{D}(S). \tag{B.21}$$

In particular,

$$\underset{\sim}{D}(R^{-1}) = [\underset{\sim}{D}(R)]^{-1}, \tag{B.22}$$

and,

$$\underset{\sim}{D}(I) = \underset{\sim}{I}. \tag{B.23}$$

Among the important properties of these matrix representations is the notion of trace or character defined as the sum of the diagonal elements:

$$\chi(R) = \mathrm{Tr}\,\underset{\sim}{D}(R) = \sum_{i=1}^{n} D_{ii}(R). \tag{B.24}$$

Among other properties it follows that $\chi(RS) = \chi(SR)$. This may easily be shown from matrix algebra. In particular, from (B.24) and the notion of class we have that if

$$\underset{\sim}{R} = \underset{\sim}{T}^{-1}\,\underset{\sim}{S}\,\underset{\sim}{T}, \tag{B.25}$$

then

$$\chi(R) = \chi(S). \tag{B.26}$$

All elements in the same class have the same character.

If we are dealing with more than one representation, as we usually are, we may distinguish the various representations by Roman numeral superscripts $D^{I}_{ji}(R)$. For instance, we may have a set of ℓ functions $(f^{I}_{1}, f^{I}_{2}, \ldots, f^{I}_{\ell})$ where

$$\hat{O}_R\ f_i^I = \sum_{j=1}^{\ell} D_{ji}^I(R)\ f_j^I, \qquad i = 1,\ldots,\ell, \tag{B.27}$$

and thus a set of $\ell\times\ell$ representation matrices $\{\underset{\sim}{D}^I(R)\}$. Also there may be another set of m functions $(f_1^{II}, f_2^{II}, \ldots, f_m^{II})$, linearly independent of $(f_1^I, f_2^I, \ldots, f_\ell^I)$, such that

$$\hat{O}_R\ f_i^{II} = \sum_{j=1}^{m} D_{ji}^{II}(R)\ f_j^{II}, \qquad i = 1,2,\ldots,m \tag{B.28}$$

and so a set of $m\times m$ matrices $\{\underset{\sim}{D}^{II}(R)\}$. The two sets of functions may be merged into a single set of $(\ell + m) \equiv n$ functions f_k, $k=1,2,\ldots n$ such that

$$f_k = f_k^I, \qquad k \leq \ell, \tag{B.29}$$

$$f_k = f_{k-\ell}^{II}, \qquad k \geq \ell + 1, \ldots, \ell + m. \tag{B.30}$$

Then we may obtain an $(\ell+m)\times(\ell+m)$ matrix representation which is composed of both representations $\underset{\sim}{D}^I(R)$ and $\underset{\sim}{D}^{II}(R)$. Written in matrix form

$$\underset{\sim}{\mathcal{D}}(R) = \begin{array}{cc} \left(\begin{array}{c|c} \underset{\sim}{D}^I(R) & \underset{\sim}{0} \\ \hline \underset{\sim}{0} & \underset{\sim}{D}^{II}(R) \end{array}\right) & \begin{array}{l} \ell \text{ rows} \\ m \text{ rows} \end{array} \\ \begin{array}{cc} \ell \text{ columns} & m \text{ columns} \end{array} & \end{array} . \tag{B.31}$$

For $i \leq \ell$

$$\hat{O}_R f_i = D_{1i}^I(R) f_1 + D_{2i}^I(R) f_2 + \ldots + D_{\ell i}^I(R) f_\ell + 0\cdot f_{\ell+1} + \ldots + 0\cdot f_{\ell+m} \tag{B.32}$$

and for $\ell < i \leq \ell+m$

$$\hat{O}_R f_i = 0 \cdot f_1 + 0 \cdot f_2 + \ldots + 0 \cdot f_\ell + D^{II}_{1i-\ell} f_{\ell+1} + D^{II}_{2i-\ell} f_{\ell+2} + \ldots + D^{II}_{mi-\ell} f_{\ell+m} \tag{B.33}$$

The representation $\{\underset{\sim}{\mathcal{D}}(R)\}$ thus obtained is said to be a reducible representation because it is composed of two other representations. On the other hand given another set of n×n matrices $\underset{\sim}{\mathcal{D}}(R)$ representing the group, this set may also be reducible. That is given

$$\hat{O}_R f_i = \sum_{j=1}^{n} D_{ji}(R)\, f_j \tag{B.34}$$

we may be able to find two disjoint sets of functions $\{g'_1,\ldots,g'_\ell\}$ and $\{g''_1,\ldots,g''_m\}$, with $n = \ell+m$ and

$$g'_i = \sum_{k=1}^{n} a_{ik}\, f_k, \qquad i = 1,\ldots,\ell, \tag{B.35a}$$

and

$$g''_j = \sum_{k=1}^{n} b_{jk}\, f_k, \qquad j = 1,\ldots,m, \tag{B.35b}$$

such that under the group operations, each function transforms as a linear combination of functions in the same set. That is,

$$\hat{O}_R g'_i = \sum_{j=1}^{\ell} D'_{ji}(R)\, g'_j, \qquad i = 1,2,\ldots,\ell \tag{B.36a}$$

and

$$\hat{O}_R g''_i = \sum_{j=1}^{m} D''_{ji}(R)\, g''_j, \qquad i = 1,2,\ldots,m. \tag{B.36b}$$

for all operations $\hat{0}_R$. If we relabel the functions

$$g_i = g_i', \quad i = 1,2,\ldots,\ell \tag{B.37a}$$

$$g_{\ell+j} = g_j'', \quad j = 1,2,\ldots,m \tag{B.37b}$$

then the set of n functions $\{g_i, i = 1,\ldots,n\}$ transforms as

$$\hat{0}_R g_i = \sum_{j=1}^{n} \mathcal{D}_{ji}(R)\, g_j, \quad i = 1,2,\ldots,n \tag{B.38}$$

which have a structure analogous to (B.32) and (B.33). Equivalently we have that all the n×n matrices have the "block diagonal" form:

$$\underset{\sim}{\mathcal{D}}(R) = \begin{array}{cc} \left(\begin{array}{c|c} \underset{\sim}{D}'(R) & \underset{\sim}{0} \\ \hline \underset{\sim}{0} & \underset{\sim}{D}''(R) \end{array}\right) & \begin{array}{l} \ell \text{ rows} \\ m \text{ rows} \end{array} \\ \begin{array}{cc} \ell \text{ columns} & m \text{ columns} \end{array} & \end{array} .$$

In turn, either or both of these sets may be able to be subdivided into smaller disjoint subsets with the representation matrices assuming the block diagonal form. If we can not divide a set of functions into two disjoint subsets, the representation is said to be irreducible; that is, it cannot be written as a direct sum of two or more representations with the off-diagonal matrices being zero. Although the general definition of irreducibility is somewhat less restrictive, the block diagonal form can be assured for finite point group representations. The Hartree-Fock or self consistent field solution molecular orbitals will be basis functions for irreducible representations.

To illustrate these ideas, we shall generate a representation for the point group D_3 shown in Table X. (In the next appendix we shall consider the point groups D_{3d} and D_{3h}.) We choose six spherically symmetric functions $f_k(\vec{r})$ centered at the six hydrogen atoms of the ethane molecule as shown in Figure B.1d. To be specific, let

$$f_k(\vec{r}) = Ne^{-\xi|\vec{r} - \vec{R}_\alpha|}; \qquad \alpha = 1,2,\ldots,6. \tag{B.39}$$

The "orbital centers" $\vec{R}_\alpha$

$$\vec{R}_\alpha = \sum_{i=1}^{3} (X_\alpha)_i \hat{e}_i \tag{B.40}$$

are parameters in the functions $f_k(\vec{r})$, but they also correspond, of course, to (fixed) points in three dimensional space. Formally, we apply the definition

$$\begin{aligned} \hat{0}_R f_k(\vec{r}) &= f_k(\hat{R}^{-1}\vec{r}) = Ne^{-\xi|\hat{R}^{-1}\vec{r} - \vec{R}_\alpha|} \\ &= g_k(\vec{r}) = Ne^{-\xi|\vec{r}\,' - \vec{R}_\alpha|}, \end{aligned} \tag{B.41}$$

where

$$\hat{R}^{-1}\vec{r} = \vec{r}\,' = \sum_{j=1}^{3} \sum_{i=1}^{3} R^{-1}_{ji}\, x_i\, \hat{e}_j. \tag{B.42}$$

Here we note that $\hat{R}^{-1}$ operates upon $\vec{r}$ only according to the definition of $\hat{0}_R$, but the fact that $\vec{R}_\alpha$ refers to spatial points allows us to rewrite the exponent. It is easily shown that

$$|(\vec{r}\,' - \vec{R}\,)| = |\{\hat{R}^{-1}(\vec{r} - \hat{R}\,\vec{R}_\alpha)\}| = |(\vec{r} - \vec{R}_{\alpha'}| \tag{B.43}$$

where

$$\vec{R}_{\alpha'} = \hat{R}\,\vec{R}_\alpha = \sum_{j=1}^{3} R_{ji}(X_\alpha)_i\,\hat{e}_j . \tag{B.44}$$

But $\vec{R}_{\alpha'}$ is just one of the other (depending specifically on $\hat{R}$) of the hydrogen centers in ethane. Thus $\hat{0}_R$ maps f_k into orbital $f_{k'}$, the spherically symmetric orbital centered at $\vec{R}_{\alpha'}$. We could continue in this fashion to find the "new centers" $\vec{R}_{\alpha'}$ under all operations $\hat{0}_R$ using expression (B.43). Alternatively we can use intuition to see how the functions behave under $\hat{0}_R$, as each orbital under $\hat{0}_R$ becomes one or the other orbitals on a different site. The function $g_k(\vec{r}) \equiv \hat{0}_R f_k(\vec{r})$ can be expanded as a linear combination of f_i $(i = 1,2,\ldots,6)$. Indeed under these operations one function simply maps into another. Using Equation (B.19),

$$\hat{0}_I\; f_1(\vec{r}) = 1\cdot f_1 + 0\cdot f_2 + 0\cdot f_3 + 0\cdot f_4 + 0\cdot f_5 + 0\cdot f_6 \tag{B.45}$$

and similarly for the functions $f_2,\ldots,f_6$. That is, all the coefficients will be zero except for the function acted on by $\hat{0}_I$. We shall use the following notation to label the rows and columns of matrix representations: we label the rows of the matrix $\underset{\sim}{D}(R)$ with the bases functions $f_i(\vec{r})$ and the columns with the transformed functions $[\hat{0}_R\; f_i(\vec{r})]$. Thus the matrix $\underset{\sim}{D}(I)$ for D_3 is written

$$\underset{\sim}{D}(I) = \begin{array}{c} \\ f_1 \\ f_2 \\ f_3 \\ f_4 \\ f_5 \\ f_6 \end{array} \begin{array}{c} \begin{array}{cccccc} \hat{0}_I f_1 & \hat{0}_I f_2 & \hat{0}_I f_3 & \hat{0}_I f_4 & \hat{0}_I f_5 & \hat{0}_I f_6 \end{array} \\ \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \end{array} . \qquad (B.46)$$

Similarly, under $\hat{0}_{C_3}$, f_1 goes to f_2, f_2 to f_3, and f_3 to f_1; while f_4 goes to f_5, f_5 t0 f_6, and f_6 to f_4. Thus, the matrix $\underset{\sim}{D}(C_3)$ is

$$\underset{\sim}{D}(C_3) = \begin{array}{c} \\ f_1 \\ f_2 \\ f_3 \\ f_4 \\ f_5 \\ f_6 \end{array} \begin{array}{c} \begin{array}{cccccc} \hat{0}_{C_3} f_1 & \hat{0}_{C_3} f_2 & \hat{0}_{C_3} f_3 & \hat{0}_{C_3} f_4 & \hat{0}_{C_3} f_5 & \hat{0}_{C_3} f_6 \end{array} \\ \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \end{array} . \qquad (B.47)$$

Similarly, we operate on the functions f_i $(i = 1,2,\ldots,6)$ using $\hat{0}_{C_3^2}, 0_{C_2'}$, $\hat{0}_{C_2''}$, and $\hat{0}_{C_2'''}$ to generate the matrices for these group operations. The remaining four 6×6 matrices are listed below. This set of six matrices forms a matrix representation for the point group D_3. This matrix representation is in fact reducible to the direct sum of irreducible representations in the sense discussed above. Equivalently, the set of six functions $\{f_i\}$ spans a reducible subspace. In Appendix C we shall show how to form linear combinations of these functions spanning irreducible representations.

$$\underset{\sim}{D}(C_3^2) = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

$$\underset{\sim}{D}(C_2') = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\underset{\sim}{D}(C_2'') = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

$$\underset{\sim}{D}(C_2''') = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

We now concentrate on the physical significance of group operations. The symmetry properties of the physical system determine which transformations leave the Hamiltonian invariant. That is to say, given a Hamiltonian operator $\hat{H}$, if

$$\hat{H} = \hat{0}_R \hat{H} \hat{0}_R^{-1} \tag{B.48}$$

the Hamiltonian $\hat{H}$ is said to be invariant under the operation $\hat{0}_R$ which is then included in the group of symmetry operators. Physically, we may envision "transforming" the function space before and after operating with $\hat{H}$ and finding the same result as operating with $\hat{H}$ directly on any function f. This corresponds to "transforming" the molecule and finding it impossible to tell the difference between the "before" and "after" case.

Using the concept of invariance we investigate the symmetry properties of the eigenfunctions of $\hat{H}$. We shall find that the degenerate eigenfunctions are a set of partners spanning an irreducible representations of the symmetry group. That is, they all transform among themselves under all the operations $\hat{0}_R$ and no proper subset of them can be found which transforms simply among themselves. To see this, we begin with the eigenvalue problem

$$\hat{H}\, \Psi_{n,\nu} = E_n \Psi_{n,\nu} \qquad \nu = 1,2,\ldots,\ell \tag{B.49}$$

where the index n enumerates the successive energy levels and the index ν runs over a maximal set of linearly independent eigenfunctions belonging to a given energy level E_n. That is for a given n, we have a set of linearly independent eigenfunctions $(\Psi_{n,1},\Psi_{n,2},\ldots,\Psi_{n,\ell})$ corresponding to the eigenvalue E_n; any arbitrary linear combination of the functions in this set is also an eigenfunction of the Hamiltonian $\hat{H}$, and there exists no other eigenstate of $\hat{H}$ corresponding to E_n other than some linear combination of the eigenfunctions in the set. Therefore the set of linearly independent functions $\{\Psi_{n,\nu}\}$ spans a (finite) ℓ-dimensional subspace. We speak of this subspace as ℓ-fold degenerate.

Suppose that $\hat{0}_R$ is applied to both sides of the eigenvalue Equation (B.49); then

$$\hat{0}_R \hat{H} \Psi_{n,\nu} = \hat{0}_R E_n \Psi_{n,\nu}. \tag{B.50}$$

Next by inserting the identity operator $\hat{0}_R^{-1}\ \hat{0}_R = \hat{0}_I$ to the right of $\hat{H}$ we obtain

$$\hat{0}_R \hat{H} \hat{0}_R^{-1} \hat{0}_R \Psi_{n,\nu} = \hat{0}_R E_n \Psi_{n,\nu}. \tag{B.51}$$

If the Hamiltonian $\hat{H}$ is invariant under the operations $\hat{0}_R$ of the group, we get

$$\hat{H} \hat{0}_R \Psi_{n,\nu} = E_n \hat{0}_R \Psi_{n,\nu}. \tag{B.52}$$

That is the transformed function $\hat{0}_R \Psi_{n,\nu}$ is also an eigenfunction of $\hat{H}$ having the same eigenvalue E_n. This implies that with $\{\Psi_{n,\nu},\ \nu = 1,2,\ldots,\ell\}$ a maximal set of eigenfunctions, the "new" eigenfunction $\hat{0}_R \Psi_{n,\nu}$ may be written

$$\hat{0}_R \Psi_{n,\nu} = \sum_{\mu=1}^{\ell} C_{\mu\nu} \Psi_{n,\mu} \tag{B.53}$$

because linear combinations of $\{\Psi_{n,\nu}\}$ are the only eigenstates of $\hat{H}$ having eigenvalue E_n. Thus, according to (B.53) the set of eigenfunctions $\{\Psi_{n,\nu}\}$ forms a basis for representation of the group. It is generally assumed that, as we consider all group operations, all ℓ functions $\{\Psi_{n,\nu}\}$ must enter the expansions. Thus the representation is irreducible.

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APPENDIX C

SYMMETRY ADAPTED FUNCTIONS FOR THE SYMMETRY GROUPS D_3, D_{3d}, AND D_{3h}

In order to find the symmetry adapted electronic orbitals for ethane having D_3 type symmetry, we adopt a notation which is better suited to the molecule; thus, we shall relabel the spherically symmetric basis function $f_i(r)$ introduced in Appendix B and centered at each of the hydrogen sites by atomic orbital quantum number $1sH_1, 1sH_2, \ldots, 1sH_6$ respectively. In addition to the 1s hydrogen orbitals we shall also include atomic orbitals (1s,2s,2p) on each of the two carbon atoms. These orbitals introduced in Appendix A will be shown to span reducible representations of the symmetry group. (Indeed, we have already done this in Appendix B for the six hydrogen orbitals.) Quite generally, we can envision the one-electron space spanned by a set of atomic orbitals, subsets of which span reducible representations of the symmetry group. Note that here the term "span" is used in both the formal vector space sense implying a complete set, and also in the group theoretical sense of the elements of the subsets transforming as partners. As we have seen in Appendix B, each reducible representation can be decomposed into a finite number of irreducible representations, the basis functions for which will be found to be linear combinations of the atomic orbitals. In general terms, the process upon which we are about to embark can be thought of as a restructuring of the basis functions of the one electron space so as to transform according to specific irreducible representations.

In Table XIII we write the six matrices for each of the four different reducible representations. The sixteen basis functions for these reducible representations fall into five subsets: ($1sH_1$,$1sH_2$,$1sH_3$,$1sH_4$, $1sH_5$,$1sH_6$) (a six dimensional representation); ($1sC_1$,$1sC_2$) and ($2sC_1$, $2sC_2$), two occurences of a two-dimensional reducible representation; ($2p_zC_1$,$2p_zC_2$) a second two-dimensional reducible representation; and ($2p_xC_1$,$2p_yC_1$,$2p_xC_2$,$2p_yC_2$) a four dimensional reducible representation. Note that both the ($1sC_1$,$1sC_2$) and ($2sC_1$,$2sC_2$) transform in the same fashion under all six operations of D_3. Although from a symmetry point of view we speak of both bases as spanning the same (reducible in this instance) representation, the two sets clearly span different subspaces in Hilbert space. In fact, a given symmetry type may occur many times over (i.e., an infinite number of times) in an infinite-dimensional Hilbert space. However, as indicated in our discussion of electronic structure, calculations are usually based upon truncating the actual Hilbert space to a finite dimensional space. Still we must expect a given symmetry type to "occur" more than once. The "reduction" of reducible representations proceeds quite generally without reference to the atomic orbital details.

First, we need to find the irreducible representations for the point group D_3. Once we have found the irreducible representations, we consider the above reducible representation and ask ourselves the following questions:

1. Which irreducible representations for D_3 occur in the reducible representations?

TABLE XIII

REDUCIBLE REPRESENTATIONS OF D_3 SPANNED BY THE 16 ATOMIC ORBITAL BASIS FUNCTIONS LISTED AT THE RIGHT

Two-Dimensional Reducible Representation Spanned by: $\{\Theta_{1sC_1},\Theta_{1sC_2}\}$ or $\{\Theta_{2sC_1},\Theta_{2sC_2}\}$

$$\underset{\sim}{D}(R):\quad I = \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix};\quad C_3 = \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix};\quad C_3^2 = \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix};$$

$$C_2' = \begin{pmatrix}0 & 1\\1 & 0\end{pmatrix};\quad C_2'' = \begin{pmatrix}0 & 1\\1 & 0\end{pmatrix};\quad C_2''' = \begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}.$$

A Second Two-Dimensional Reducible Representation Spanned by: $\{\Theta_{2p_zC_1},\Theta_{2p_zC_2}\}$

$$\underset{\sim}{D}(R):\quad I = \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix};\quad C_3 = \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix};\quad C_3^2 = \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix};$$

$$C_2' = \begin{pmatrix}0 & -1\\-1 & 0\end{pmatrix};\quad C_2'' = \begin{pmatrix}0 & -1\\-1 & 0\end{pmatrix};\quad C_2''' = \begin{pmatrix}0 & -1\\-1 & 0\end{pmatrix}.$$

A Four-Dimensional Reducible Representation Spanned by: $\{\Theta_{2p_xC_1},\Theta_{2p_yC_1},\Theta_{2p_xC_2},\Theta_{2p_yC_2}\}$

$$\underset{\sim}{D}(R):\quad I = \begin{pmatrix}1 & 0 & 0 & 0\\0 & 1 & 0 & 0\\0 & 0 & 1 & 0\\0 & 0 & 0 & 1\end{pmatrix};\quad C_3 = \begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0\\0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2}\\0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix};$$

TABLE XIII (Continued)

$$C_3^2 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}; \quad C_2' = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix};$$

$$C_2'' = \begin{pmatrix} 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \end{pmatrix}; \quad C_2''' = \begin{pmatrix} 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \end{pmatrix}.$$

A Six-Dimensional Reducible Representation Spanned by:
$\{\Theta_{1sH_1}, \Theta_{1sH_2}, \Theta_{1sH_3}, \Theta_{1sH_4}, \Theta_{1sH_5}, \Theta_{1sH_6}\}$

$$\underset{\sim}{D}(R): \qquad I = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix};$$

TABLE XIII (Continued)

$$C_3 = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}; \quad C_3^2 = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix};$$

$$C_2' = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}; \quad C_2'' = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix};$$

$$C_2''' = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

2. Of those that do occur, how many times does each irreducible representation occur?
3. If we have a two dimensional irreducible representation, how do we go about finding the partner functions; that is, the pair of symmetry adapted functions that transform among themselves under $\hat{O}_R$.

The reduction of a representation proceeds by using the results of the orthogonality theorems (Hamermesh, 1964, pp. 101-104). Specifically, a_μ, the number of times the μth irreducible representation occurs in a given representation is

$$\begin{aligned} a_\mu &= \frac{1}{g} \sum_R \chi^{(\mu)*}(R)\ \chi(R) \\ &= \frac{1}{g} \sum_i m_i\ \chi_i^{(\mu)*}\ \chi_i. \end{aligned} \tag{C.1}$$

Here $\{\chi^{(\mu)*}(R)\}$ and $\{\chi(R)\}$ are the sets of characters of the group elements for the μth irreducible representation and the reducible represen-taion respectively. The second expression in (C.1) in which m_i is the number of group elements in class i recognizes that the characters of all elements in the same class are equal in a given representation. Thus, in order to answer the first question we need the so-called character table of the irreducible representations, as well as the characters for the reducible matrices.

Character tables for the irreducible representations may be found in any group theory text. These tables [see for example Jaffee, 1965] also include sets of basis functions--or basis vectors--spanning the irreducible representations. In Table XIV we have the character table for the point group D_3. The group D_3 has three irreducible representations, two one-dimensional denoted a_1 and a_2 and one two-dimensional, e. In passing we note that the theorem relating these dimensionalities with the order of the group

$$g = \sum_i n_i^2 \tag{C.2}$$

is satisfied with

$$g = 6,\ n_{a_1} = 1,\ n_{a_2} = 1,\ n_e = 2. \tag{C.3}$$

TABLE XIV

CHARACTER TABLE FOR THE GROUP D_3

D_3	$\{I\}$	$\{C_3, C_3^2\}$	$\{C_2', C_2'', C_2'''\}$
a_1	1	1	1
a_2	1	1	-1
e	2	-1	0

Although questions 1 and 2, concerning the reductions of these representations may be answered from the character tables, certain problems like the construction of the symmetry adapted partners posed in question 3 require the irreducible representation matrices themselves--not simply their characters.

Since a_1 is a one-dimensional representation of D_3 the characters are the matrices for the one-dimensional irreducible representation.

Thus we get our one dimensional irreducible representation "matrices" directly from the character table. The same argument holds for the one-dimensional irreducible representation a_2 of Table XIV.

To obtain the matrices for the two dimensional irreducible representation e we find from the character table that the basis vectors spanning e are $\hat{e}_1$ and $\hat{e}_2$; $\hat{e}_1$ and $\hat{e}_2$ can be any pair of vectors spanning the mid-plane perpendicular to the three-fold axis of rotation. We obtain the transformation matrices by applying the six group operations to the orthonormal basis $\hat{e}_1 \equiv \hat{e}_x$ and $\hat{e}_2 \equiv \hat{e}_y$ shown in Figure C.1. As discussed in Appendix B the point transformations may be expressed as coordinate (matrix) transformations once the transformations of the basis vectors $\hat{e}_x$, $\hat{e}_y$ under all the operations are found. Indeed, we have

$$\hat{R}\hat{e}_x = (\hat{e}_x \cdot \hat{R}\hat{e}_x)\hat{e}_x + (\hat{e}_y \cdot \hat{R}\hat{e}_x)\hat{e}_y$$

and (C.4)

$$\hat{R}\hat{e}_y = (\hat{e}_x \cdot \hat{R}\hat{e}_y)\hat{e}_x + (\hat{e}_y \cdot \hat{R}\hat{e}_y)\hat{e}_y .$$

The 2×2 matrices may then be found by evaluating the dot products

$$R_{ij} = (\hat{e}_i \cdot \hat{R}\hat{e}_j) \qquad i,j = 1,2, \tag{C.5}$$

using our intuition to carry out the group operations. The resulting six 2×2 matrices are found in Table XV. It should be noted that had we chosen a different pair of orthonormal basis vectors, another set of six matrices would be obtained, related to those found here by an orthogonal transformation

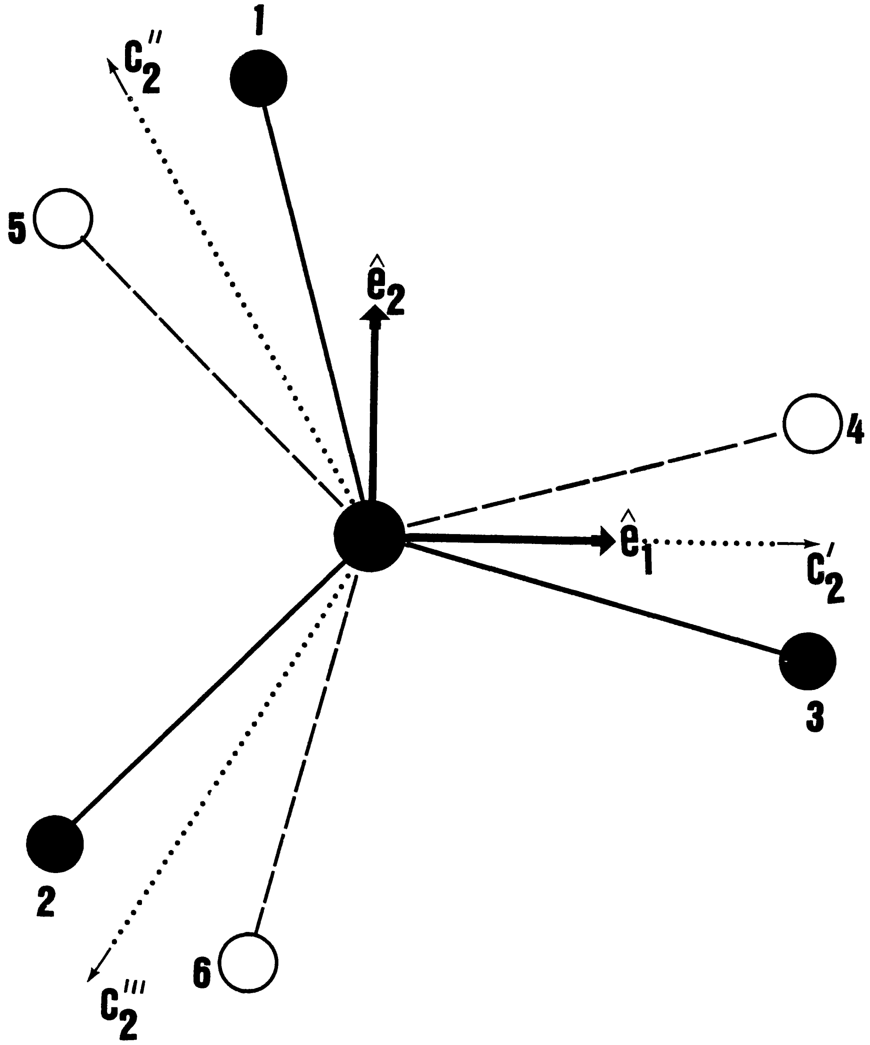

Figure C.1. The Point Group D_3 in Two-Dimensional Perspective Showing the Bases $\hat{e}_1$ and $\hat{e}_2$

$$\underset{\sim}{D}'(R) = \underset{\sim}{O}^{T}\,\underset{\sim}{D}(R)\,\underset{\sim}{O}. \qquad \text{(C.6)}$$

We say that the two sets of matrices {D(R)} and {D'(R)} are equivalent. If the two bases are not orthonormal, then the two sets of matrices are still equivalent, being related by the more general similarity transformation. However, we need distinguish only between inequivalent irreducible representations. Thus in Table XV we present the three sets of six matrices--two inequivalent sets of 1×1 matrices and one (of the infinitely many equivalent) set of 2×2 matrices for the irreducible representations of D_3.

TABLE XV

IRREDUCIBLE REPRESENTATION FOR D_3

---

a_1: $\underset{\sim}{D}(I)=1;\underset{\sim}{D}(C_3)=(1);\underset{\sim}{D}(C_3^2)=(1);\underset{\sim}{D}(C_2')=(1);\underset{\sim}{D}(C_2'')=(1);\underset{\sim}{D}(C_2''')=(1).$

a_2: $\underset{\sim}{D}(I)=(1);\underset{\sim}{D}(C_3)=(1);\underset{\sim}{D}(C_3^2)=(1);\underset{\sim}{D}(C_2')=(-1);\underset{\sim}{D}(C_2'')=(-1);\underset{\sim}{D}(C_2''')=(-1).$

$$e:\quad \underset{\sim}{D}(I)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix};\ \underset{\sim}{D}(C_3)=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_3^2)=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};$$

$$\underset{\sim}{D}(C_2')=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix};\ \underset{\sim}{D}(C_2'')=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & 1/2\end{pmatrix};\ \underset{\sim}{D}(C_2''')=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & 1/2\end{pmatrix}.$$

We now derive the symmetry adapted basis for the point group D_3.

We shall begin by finding the symmetry adapted basis for the space spanned by the two orbitals Θ_{1sC_1} and Θ_{1sC_2}. Using Equation (C.1) and the characters found from Table XIII (for the two-dimensional reducible representation spanned by Θ_{1sC_1} and Θ_{1sC_2}) and Table XIV (for the irreducible representations) we obtain how often each irreducible representation occurs in the two dimensional reducible representation. Thus the a_1 irreducible representation occurs once:

$$n_{a_1} = \frac{1}{6}[1\times 2 + 1\times 2 + 1\times 2] = 1. \tag{C.7}$$

Similarly, the irreducible representation a_2 occurs once and the irreducible representations e does not occur. Thus, there is a transformation $\underset{\sim}{S}$ bringing each of the matrices of the two-dimensional reducible representation $\underset{\sim}{D}(R)$ into (block) diagonal form

$$\underset{\sim}{S}\ \underset{\sim}{D}(R)\ \underset{\sim}{S}^{-1} = \left(\begin{array}{c|c} \underset{\sim}{D}^{(a_1)}(R) & \underset{\sim}{0} \\ \hline \underset{\sim}{0} & \underset{\sim}{D}^{(a_2)}(R) \end{array}\right). \tag{C.8}$$

In order to obtain a symmetry adapted function (e.g., a basis function for the ith row of the μth irreducible representation), we apply the projection operator (Hamermesh, 1964, pp. 68-114)

$$\hat{P}^{\mu}_{i} = \frac{n_{\mu}}{g} \sum_{R} D^{(\mu)*}_{ii}(R)\ \hat{O}_{R} \tag{C.9}$$

to Θ_{1sC_1} or Θ_{1sC_2}. As pointed out earlier, the matrix elements (in this case, the diagonal elements)--and not simply the trace--are required to find the symmetry adapted functions. To be specific, the projection operator for the first row of a_1 (in this case there is only one row) is

$$\hat{P}_1^{a_1} = \frac{1}{6}\{1\cdot\hat{O}I + 1\cdot\hat{O}C_3 + 1\cdot\hat{O}C_3^2 + 1\cdot\hat{O}C_2' + 1\cdot\hat{O}C_2'' + 1\cdot\hat{O}C_2'''\}. \qquad (C.10)$$

The symmetry adapted function as a linear combination of the orbitals $\{\Theta_{1sC_1}, \Theta_{1sC_2}\}$ is found by simply applying $\hat{P}_1^{a_1}$ to either of the two basis functions. Thus

$$\hat{P}_1^{a_1}\,\Theta_{1sC_1} = \frac{1}{2}(\Theta_{1sC_1} + \Theta_{1sC_2}). \qquad (C.11)$$

We shall use the notation $\chi_{n\mu i}$ for the symmetry adapted basis functions, where n is the nth occurence of the ith row of the μth irreducible representation. Thus (C.11) may be written

$$\chi_{1a_1} = \frac{1}{2}(\Theta_{1sC_1} + \Theta_{1sC_2}), \qquad (C.12)$$

where the row index has been deleted in this case because we only have one row in a_1. Similarly the projection operator

$$\hat{P}_1^{a_2} = \frac{1}{6}[\hat{O}_I + \hat{O}_{C_3} + \hat{O}_{C_3^2} - \hat{O}_{C_2'} - \hat{O}_{C_2''} - \hat{O}_{C_2'''}] \qquad (C.13)$$

when applied to Θ_{1sC_1} gives a symmetry adapted function for a_2

$$\chi_{1a_2} = \frac{1}{2}\{\Theta_{1sC_1} - \Theta_{1sC_2}\}\ . \qquad (C.14)$$

Next we consider the Θ_{2sC_1} and Θ_{2sC_2} orbitals on both carbons. These two "2s" orbitals transform in the same fashion as the "1s" orbitals and so the reduction into symmetry adapted basis functions proceeds in the same way yielding the same irreducible representations. Of course the "2s" orbitals are linearly independent of the "1s" orbitals, and thus we speak of the second occurences of the a_1 and a_2 irreducible representations. As mentioned above, we can envision subdividing the one particle function space into such subspaces classified by a particular row i of a particular irreducible representation μ and spanned by the set $\{\chi_{n\mu i}\}$ where n runs over the various occurences. Thus

$$\chi_{2a_1} = \frac{1}{2}\{\Theta_{2sC_1} + \Theta_{2sC_2}\}$$

and (C.15)

$$\chi_{2a_2} = \frac{1}{2}\{\Theta_{2sC_1} - \Theta_{2sC_2}\}.$$

In a similar way we obtain the two symmetry adapted functions for the subspace spanned by $\{\Theta_{2p_zC_1},\Theta_{2p_zC_2}\}$. The symmetry adapted functions belong to the third occurences of a_1 and a_2 irreducible representations:

$$\chi_{3a_1} = \frac{1}{2}\{\Theta_{2p_zC_1} - \Theta_{2p_zC_2}\}$$

and (C.16)

$$\chi_{3a_2} = \frac{1}{2}\{\Theta_{2p_zC_1} + \Theta_{2p_zC_2}\}.$$

We now consider the four-dimensional reducible representation spanned by $\{\Theta_{2p_xC_1},\Theta_{2p_yC_1},\Theta_{2p_xC_2},\Theta_{2p_yC_2}\}$. This time irreducible representations a_1 and a_2 do not occur, but the two-dimensional irreducible representation e occurs twice in the four-dimensional reducible representation.

Thus we need to find four linearly independent symmetry adapted basis functions each being a linear combination of $\{\Theta_{2p_xC_1}, \Theta_{2p_yC_1}, \Theta_{2p_xC_2}, \Theta_{2p_yC_2}\}$. In particular we seek two pairs of partners. For occurences greater than one, there is no unique resolution into symmetry adapted basis functions. This is done by applying the projection operator

$$\hat{P}^e_1 = \frac{n_\mu}{g} \sum_R D^{(e)*}_{11}(R)\, \hat{O}_R$$

$$= \frac{2}{6}[1\hat{O}_E - \frac{1}{2}\hat{O}_{C_3} - \frac{1}{2}\hat{O}_{C_3^2} + \hat{O}_{C_2'} - \frac{1}{2}\hat{O}_{C_2''} - \frac{1}{2}\hat{O}_{C_2'''}] \tag{C.17}$$

to the basis function $\Theta_{2p_xC_1}$ in order to get the symmetry adapted function

$$\chi_{1e1} = \hat{P}^E_1\, \Theta_{2p_xC_1} = \frac{1}{2}[\Theta_{2p_xC_1} + \Theta_{2p_xC_2}]. \tag{C.18}$$

Since e has two rows, we need to obtain the partner of χ_{1e1} denoted by χ_{1e2}. To accomplish this, we apply the partner operator to χ_{1e1}. That is, in general the ℓth partner of the kth function of the μ irreducible representation is given by (Hamermesh, 1964, p. 112)

$$f^{(\mu)}_\ell = \frac{n_\mu}{g} \sum_R D^{(\mu)*}_{\ell k}(R)\, \hat{O}_R\, f^{(\mu)}_k = \hat{P}^{(\mu)}_{\ell k}\, f^\mu_k. \tag{C.19}$$

Here,

$$\hat{P}^{(\mu)}_{\ell k} = \frac{n_\mu}{g} \sum_R D^{(\mu)*}_{\ell k}(R)\hat{O}_R \tag{C.20}$$

is the partner operator. Again we note the presence of the off-diagonal elements of the representation matrices in constructing these operators. Thus, in this particular instance

$$\chi_{1e2} = \frac{2}{6} \sum_R D_{21}^{(e)*} (R) \ \hat{O}_R \ \chi_{1e1}$$

$$= \frac{1}{3} \sum_R D_{21}^{(e)*} \ \hat{O}_R [\frac{1}{2}(\Theta_{2P_xC_1} + \Theta_{2P_xC_2})]$$

$$= \frac{1}{3}[0 \cdot \hat{O}_I + \frac{\sqrt{3}}{2} \cdot \hat{O}_{C_3} - \frac{\sqrt{3}}{2} \cdot \hat{O}_{C_3^2} + 0 \cdot \hat{O}_{C_2'} - \frac{\sqrt{3}}{2} \cdot \hat{O}_{C_2''} + \frac{\sqrt{3}}{2} \cdot \hat{O}_{C_2'''}]$$

$$[\frac{1}{2}(\Theta_{2p_xC_1} + \Theta_{2p_xC_2})]$$

$$= \frac{1}{2}[\Theta_{2p_yC_1} + \Theta_{2p_yC_2}]. \qquad \text{(C.21)}$$

Since e occurs twice, we repeat the procedure starting with the projection operator on the orbital $\Theta_{2p_yC_1}$ and in this instance obtain a symmetry adapted function which is linearly independent of both χ_{1e1} and χ_{1e2}. If, however, the application of the projection operator on the basis function $\Theta_{P_yC_1}$ had produced χ_{1e1}, then the application of this projection operator on one of the remaining two functions will certainly give a function which is linearly independent of χ_{1e1} since we know that there are in fact two occurences of (the pair of partners in) e. We shall denote the symmetry adapted function and its partner for the second occurence of e in the four-dimensional reducible representation by χ_{2e1} and χ_{2e2}. Thus, applying $\hat{P}_1^e$ to $\Theta_{2p_yC_1}$ we obtain

$$\chi_{2e1} = \frac{1}{2}\{\Theta_{2P_yC_1} - \Theta_{2P_yC_2}\} \qquad \text{(C.22)}$$

and then applying $\hat{P}_{21}^e$ to this result, we obtain its partner

$$\chi_{2e2} = \frac{1}{2}\{\Theta_{2P_xC_1} - \Theta_{2P_xC_2}\}. \qquad (C.23)$$

Lastly we obtain the six symmetry adapted functions spanning the space of the six hydrogen orbitals in Table XIII. Applying formula (C.1) and the character Tables in XIII and XIV, we find that a_1 and a_2 each occur once and e occurs twice in the six-dimensional reducible representation. We use the same approach of applying the projection and partner operators as we did for the four dimensional reducible representation. These operators have already appeared in previous equations. We use the six 6×6 matrices describing the transformations of the hydrogen orbitals to carry out the results. The six symmetry adapted functions are presented in Table XVI. This ends our detailed reduction of the 16 dimensional space in D_3 symmetry.

TABLE XVI

THE SIX SYMMETRY ADAPTED FUNCTIONS FOR THE POINT GROUP D_3

$$\chi_{4a_1} = \frac{1}{6}[\Theta_{1sH_1} + \Theta_{1sH_2} + \Theta_{1sH_3} + \Theta_{1sH_4} + \Theta_{1sH_5} + \Theta_{1sH_6}]$$

$$\chi_{4a_2} = \frac{1}{6}[\Theta_{1sH_1} + \Theta_{1sH_2} + \Theta_{1sH_3} - \Theta_{1sH_4} - \Theta_{1sH_5} - \Theta_{1sH_6}]$$

$$\chi_{3e1} = \frac{1}{6}[2\Theta_{1sH_1} - \Theta_{1sH_2} - \Theta_{1sH_3} - \Theta_{1sH_4} - \Theta_{1sH_5} + 2\Theta_{1sH_6}]$$

$$\chi_{3e2} = \frac{\sqrt{3}}{6}[\Theta_{1sH_2} - \Theta_{1sH_3} + \Theta_{1sH_4} - \Theta_{1sH_5}]$$

$$\chi_{4e1} = \frac{1}{6}[-\Theta_{1sH_1} + 2\Theta_{1sH_2} - \Theta_{1sH_3} - \Theta_{1sH_4} + 2\Theta_{1sH_5} - \Theta_{1sH_6}]$$

$$\chi_{4e2} = \frac{\sqrt{3}}{6}[-\Theta_{1sH_1} + \Theta_{1sH_3} - \Theta_{1sH_4} + \Theta_{1sH_6}]$$

We consider now the point groups D_{3d}. We write the character table (Table XVII). When a point group contains the inversion i, an irreducible representation is subscripted by g (gerade) if the basis functions are even functions $(f(\vec{r}) = +f(-\vec{r}))$ with respect to inversion and by u (ungerade) if they are odd functions $(f(\vec{r}) = -f(-\vec{r}))$ with respect to inversion. The matrices for the two-dimensional irreducible representations e_g and e_u for D_{3d} are presented in Table XVIII. (Of course, a set of one-dimensional matrices may be obtained from the character table itself.) In Table XIX we give the matrices for the reducible representations of D_{3d} spanned by the various subsets of atomic orbitals. The coordinate system and symmetry operations are those shown in Figure B1.e. Finally the sixteen symmetry adapted functions for D_{3d} are presented in Table XX.

TABLE XVII

CHARACTER TABLE FOR THE POINT GROUP D_{3d}

D_{3d}	$\{I\}$	$\{2S_6\}$	$\{2C_3\}$	$\{i\}$	$\{3C_2'\text{'s}\}$	$\{3\sigma_d'\text{'s}\}$
a_{1g}	+1	+1	+1	+1	+1	+1
a_{1u}	+1	-1	+1	-1	+1	-1
a_{2g}	+1	+1	+1	+1	-1	-1
a_{2u}	+1	-1	+1	-1	-1	+1
e_g	+2	-1	-1	+2	0	0
e_u	+2	+1	-1	-2	0	0

TABLE XVIII

THE TWO-DIMENSIONAL IRREDUCIBLE REPRESENTATIONS FOR THE POINT GROUP D_{3d}

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e_g irreducible representation

$$\underset{\sim}{D}(I)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix};\ \underset{\sim}{D}(C_3)=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_3^2)=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_2')=\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix};$$

$$\underset{\sim}{D}(C_2'')=\begin{pmatrix}1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_2''')=\begin{pmatrix}1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(S_6)=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};$$

$$\underset{\sim}{D}(S_6')=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(i)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix};\ \underset{\sim}{D}(\sigma_d')=\begin{pmatrix}1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(\sigma_d'')=\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix};$$

$$\underset{\sim}{D}(\sigma_d''')=\begin{pmatrix}1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix}.$$

e_u irreducible representation

$$\underset{\sim}{D}(I)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix};\ \underset{\sim}{D}(C_3)=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_3^2)=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_2')=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix};$$

$$\underset{\sim}{D}(C_2'')=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & 1/2\end{pmatrix};\ \underset{\sim}{D}(C_2''')=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & 1/2\end{pmatrix};\ \underset{\sim}{D}(S_6)=\begin{pmatrix}1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & 1/2\end{pmatrix};$$

$$\underset{\sim}{D}(S_6')=\begin{pmatrix}1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & 1/2\end{pmatrix};\ \underset{\sim}{D}(i)=\begin{pmatrix}-1 & 0\\ 0 & -1\end{pmatrix};\ \underset{\sim}{D}(\sigma_d')=\begin{pmatrix}1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};$$

$$\underset{\sim}{D}(\sigma_d'')=\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix};\ \underset{\sim}{D}(\sigma_d''')=\begin{pmatrix}1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix}.$$

TABLE XIX

REDUCIBLE REPRESENTATIONS OF D_{3d} SPANNED BY THE 16 ATOMIC ORBITAL BASIS FUNCTIONS LISTED AT THE RIGHT

Two-Dimensional Reducible Representations Spanned by:
$\{\Theta_{1sC_1},\Theta_{1sC_2}\}$ or $\{\Theta_{2sC_1},\Theta_{2sC_2}\}$

$$\underset{\sim}{D}(R):\quad I=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; C_3=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; C_3^2=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; C_2'=\begin{pmatrix}0&1\\1&0\end{pmatrix};$$

$$C_2''=\begin{pmatrix}0&1\\1&0\end{pmatrix};\; C_2'''=\begin{pmatrix}0&1\\1&0\end{pmatrix};\; S_6=\begin{pmatrix}0&1\\1&0\end{pmatrix};\; S_6'=\begin{pmatrix}0&1\\1&0\end{pmatrix};$$

$$\sigma_d'=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; \sigma_d''=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; \sigma_d'''=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; i=\begin{pmatrix}0&1\\1&0\end{pmatrix}.$$

A Second Two-Dimensional Reducible Representation Spanned by:
$\{\Theta_{2p_zC_1},\Theta_{2p_zC_2}\}$

$$\underset{\sim}{D}(R):\quad I=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; C_3=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; C_3^2=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; C_2'=\begin{pmatrix}0&-1\\-1&0\end{pmatrix};$$

$$C_2''=\begin{pmatrix}0&-1\\-1&0\end{pmatrix};\; C_2'''=\begin{pmatrix}0&-1\\-1&0\end{pmatrix};\; S_6=\begin{pmatrix}0&-1\\-1&0\end{pmatrix};\; S_6'=\begin{pmatrix}0&-1\\-1&0\end{pmatrix};$$

$$\sigma_d'=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; \sigma_d''=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; \sigma_d'''=\begin{pmatrix}1&0\\0&1\end{pmatrix};\; i=\begin{pmatrix}0&-1\\-1&0\end{pmatrix}.$$

A Four-Dimensional Reducible Representation Spanned by:
$\{\Theta_{2p_xC_1},\Theta_{2p_yC_1},\Theta_{2p_xC_2},\Theta_{2p_yC_2}\}$

$$\underset{\sim}{D}(R):\quad I=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix};\; C_3=\begin{pmatrix}-1/2&-\sqrt{3}/2&0&0\\ \sqrt{3}/2&-1/2&0&0\\0&0&-1/2&-\sqrt{3}/2\\0&0&\sqrt{3}/2&-1/2\end{pmatrix};$$

TABLE XIX (Continued)

$$C_3^2=\begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 & 0 \\ 0 & 0 & -1/2 & \sqrt{3}/2 \\ 0 & 0 & -\sqrt{3}/2 & -1/2 \end{pmatrix}; \quad C_2'=\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix};$$

$$C_2''=\begin{pmatrix} 0 & 0 & -1/2 & -\sqrt{3}/2 \\ 0 & 0 & -\sqrt{3}/2 & 1/2 \\ -1/2 & -\sqrt{3}/2 & 0 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 & 0 \end{pmatrix}; \quad C_2'''=\begin{pmatrix} 0 & 0 & -1/2 & \sqrt{3}/2 \\ 0 & 0 & \sqrt{3}/2 & 1/2 \\ -1/2 & \sqrt{3}/2 & 0 & 0 \\ \sqrt{3}/2 & 1/2 & 0 & 0 \end{pmatrix};$$

$$S_6=\begin{pmatrix} 0 & 0 & 1/2 & -\sqrt{3}/2 \\ 0 & 0 & \sqrt{3}/2 & 1/2 \\ 1/2 & -\sqrt{3}/2 & 0 & 0 \\ \sqrt{3}/2 & 1/2 & 0 & 0 \end{pmatrix}; \quad S_6'=\begin{pmatrix} 0 & 0 & 1/2 & \sqrt{3}/2 \\ 0 & 0 & -\sqrt{3}/2 & 1/2 \\ 1/2 & \sqrt{3}/2 & 0 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 & 0 \end{pmatrix};$$

$$\sigma_d'=\begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 & 0 \\ \sqrt{3}/2 & -1/2 & 0 & 0 \\ 0 & 0 & 1/2 & \sqrt{3}/2 \\ 0 & 0 & \sqrt{3}/2 & -1/2 \end{pmatrix}; \quad \sigma_d''=\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix};$$

$$\sigma_d'''=\begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 & 0 \\ 0 & 0 & 1/2 & -\sqrt{3}/2 \\ 0 & 0 & -\sqrt{3}/2 & -1/2 \end{pmatrix}; \quad i=\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}.$$

TABLE XIX (Continued)

A Six-Dimensional Reducible Representation Spanned by: $\{\Theta_{1sH_1}, \Theta_{1sH_2}$ $\Theta_{1sH_3}, \Theta_{1sH_4}, \Theta_{1sH_5}, \Theta_{1sH_6}\}$

$$\underset{\sim}{D}(R):\quad I=\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix};\quad C_3=\begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix};$$

$$C_3^2=\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix};\quad C_2'=\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix};$$

$$C_2''=\begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix};\quad C_2'''=\begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix};$$

$$S_6=\begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}\quad S_6'=\begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix};$$

TABLE XIX (Continued)

$$\sigma'_d = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}; \quad \sigma''_d = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix};$$

$$\sigma'''_d = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}; \quad i = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

TABLE XX

SYMMETRY ADAPTED BASES FUNCTIONS FOR THE POINT GROUP D_{3d}

$$\chi_{1a_{1g}} = \frac{1}{2}(\Theta_{1sC_1} + \Theta_{1sC_2})$$

$$\chi_{1a_{2u}} = \frac{1}{2}(\Theta_{1sC_1} - \Theta_{1sC_2})$$

$$\chi_{2a_{1g}} = \frac{1}{2}(\Theta_{2sC_1} + \Theta_{2sC_2})$$

$$\chi_{2a_{2u}} = \frac{1}{2}(\Theta_{2sC_1} - \Theta_{2sC_2})$$

$$\chi_{3a_{1g}} = \frac{1}{2}(\Theta_{2p_zC_1} - \Theta_{2p_zC_2})$$

$$\chi_{3a_{2u}} = \frac{1}{2}(\Theta_{2p_zC_1} + \Theta_{2p_zC_2})$$

$$\left\{\begin{aligned} \chi_{1e_g1} &= \frac{1}{2}[\Theta_{2p_xC_1} - \Theta_{2p_xC_2}] \\ \chi_{1e_g2} &= \frac{1}{2}[\Theta_{2p_yC_1} - \Theta_{2p_yC_2}] \end{aligned}\right.$$

$$\left\{\begin{aligned} \chi_{1e_u1} &= \frac{1}{2}[\Theta_{2p_xC_1} + \Theta_{2p_xC_2}] \\ \chi_{1e_u2} &= \frac{1}{2}[\Theta_{2p_yC_1} + \Theta_{2p_yC_2}] \end{aligned}\right.$$

$$\chi_{4a_{1g}} = \frac{1}{6}[\Theta_{1sH_1} + \Theta_{1sH_2} + \Theta_{1sH_3} + \Theta_{1sH_4} + \Theta_{1sH_5} + \Theta_{1sH_6}]$$

$$\chi_{4a_{2u}} = \frac{1}{6}[\Theta_{1sH_1} + \Theta_{1sH_2} + \Theta_{s1H_3} - \Theta_{1sH_4} - \Theta_{1sH_5} - \Theta_{1sH_6}]$$

$$\left\{\begin{aligned} \chi_{2e_g1} &= \frac{1}{4}[\Theta_{1sH_2} - \Theta_{1sH_3} + \Theta_{1sH_4} - \Theta_{1sH_5}] \\ \chi_{2e_g2} &= \frac{-\sqrt{3}}{12}[2\Theta_{1sH_1} - \Theta_{1sH_2} - \Theta_{1sH_3} - \Theta_{1sH_4} - \Theta_{1sH_5} + 2\Theta_{1sH_6}] \end{aligned}\right.$$

$$\left\{\begin{aligned} \chi_{2e_u1} &= \frac{1}{4}[\Theta_{1sH_2} - \Theta_{1sH_3} - \Theta_{1sH_4} + \Theta_{1sH_5}] \\ \chi_{2e_u2} &= \frac{-\sqrt{3}}{12}[2\Theta_{1sH_1} - \Theta_{1sH_2} - \Theta_{1sH_3} + \Theta_{1sH_4} + \Theta_{1sH_5} - 2\Theta_{1sH_6}] \end{aligned}\right.$$

We repeat this same procedure for the symmetry group D_{3h}. This time, however, the coordinate system and symmetry operations are those found in Figure B.1f. The characters are given in Table XXI, while the matrices for the two-dimensional irreducible representations e' and e" are given in Table XXII. The irreducible representation matrices for the sixteen atomic orbitals are given in Table XXIII. Finally in Table XXIV we present the symmetry adapted orbitals for D_{3h}.

TABLE XXI

CHARACTER TABLE FOR THE POINT GROUP D_{3h}

D_{3h}	{I}	{2C_3's}	{3C_2's}	{σ_h}	{2S_3's}	{3σ_v''s}
a_1'	+1	+1	+1	+1	+1	+1
a_1''	+1	+1	+1	-1	-1	-1
a_2'	+1	+1	-1	+1	+1	-1
a_2''	+1	+1	-1	-1	-1	+1
e'	+2	-1	0	+2	-1	0
e"	+2	-1	0	-2	+1	0

TABLE XXII

TWO-DIMENSIONAL IRREDUCIBLE REPRESENTATIONS FOR THE POINT GROUP D_{3h}

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e' Irreducible Representations

$$\underset{\sim}{D}(I)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix};\ \underset{\sim}{D}(C_3)=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_3^2)=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_2')=\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix};$$

$$\underset{\sim}{D}(C_2'')=\begin{pmatrix}1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_2''')=\begin{pmatrix}1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(S_3)=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};$$

$$\underset{\sim}{D}(S_3')=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(\sigma_h)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix};\ \underset{\sim}{D}(\sigma_v')=\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix};$$

$$\underset{\sim}{D}(\sigma_v'')=\begin{pmatrix}1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(\sigma_v''')=\begin{pmatrix}1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix}.$$

e" Irreducible Representation

$$\underset{\sim}{D}(I)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix};\ \underset{\sim}{D}(C_3)=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_3^2)=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(C_2')=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix};$$

$$\underset{\sim}{D}(C_2'')=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & 1/2\end{pmatrix};\ \underset{\sim}{D}(C_2''')=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & 1/2\end{pmatrix};\ \underset{\sim}{D}(S_3)=\begin{pmatrix}1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & 1/2\end{pmatrix};$$

$$\underset{\sim}{D}(S_3')=\begin{pmatrix}1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & 1/2\end{pmatrix};\ \underset{\sim}{D}(\sigma_h)=\begin{pmatrix}-1 & 0\\ 0 & -1\end{pmatrix};\ \underset{\sim}{D}(\sigma_v')=\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix};$$

$$\underset{\sim}{D}(\sigma_v'')=\begin{pmatrix}1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \underset{\sim}{D}(\sigma_v''')=\begin{pmatrix}1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix}.$$

TABLE XXIII

REDUCIBLE RE ESENTATIONS OF D_{3h} SPANNED BY THE
16 AT IC ORBITAL BASIS FUNCTIONS
LISTED AT THE RIGHT

Two-Dimensional Reducibl Representation Spanned by:
$\{\Theta_{1sC_1},\Theta_{1sC_2}\}$ or $\{\Theta_{2sC_1},$ $sC_2\}$

$$\underset{\sim}{D}(R): \quad I = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}; \quad {}_3 = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}; \quad C_3^2 = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix};$$

$$C_2' = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}; \quad {}''_2 = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}; \quad C_2''' = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix};$$

$$\sigma_h = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}; \quad {}_3 = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}; \quad S_3' = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix};$$

$$\sigma_v' = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}; \quad {}''_v = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}; \quad \sigma_v''' = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}.$$

A Second Two-Dimensional educible Representation Spanned by:
$\{\Theta_{2p_zC_1},\Theta_{2p_zC_2}\}$

$$\underset{\sim}{D}(R): \quad I = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}; \quad {}_3 = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}; \quad C_3^2 = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix};$$

$$C_2' = \begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix}; \quad {}''_2 = \begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix}; \quad C_2''' = \begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix};$$

$$\sigma_h = \begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix}; \quad {}_3 = \begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix}; \quad S_3' = \begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix};$$

TABLE XXIII (Continued)

$$\sigma_v' = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \; ; \; \sigma_v'' = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \; ; \; \sigma_v''' = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} .$$

A Four-Dimensional Reducible Representation Spanned by:
$\{\Theta_{2p_x C_1}, \Theta_{2p_y C_1}, \Theta_{2p_x C_2}, \Theta_{2p_y C_2}\}$

$$\underset{\sim}{D}(R): \quad I = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} ; \quad C_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} ;$$

$$C_3^2 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} ; \quad C_2' = \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} ;$$

$$C_2'' = \begin{pmatrix} 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \end{pmatrix} ; \quad C_2''' = \begin{pmatrix} 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \\ \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \end{pmatrix} ;$$

$$\sigma_h = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} ; \quad S_3 = \begin{pmatrix} 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \end{pmatrix} ;$$

TABLE XXIII (Continued)

$$S_3' = \begin{pmatrix} 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \end{pmatrix}; \quad \sigma_v' = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix};$$

$$\sigma_v'' = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}; \quad \sigma_v''' = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}.$$

A Six-Dimensional Reducible Representation Spanned by:
$\{\Theta_{1sH_1}, \Theta_{1sH_2}, \Theta_{1sH_3}, \Theta_{1sH_4}, \Theta_{1sH_5}, \Theta_{1sH_6}\}$

$$I = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}; \quad C_3 = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix};$$

$$C_3^2 = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}; \quad C_2' = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix};$$

TABLE XXIII (Continued)

$$C_2'' = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}; \quad C_2''' = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix};$$

$$\sigma_h = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}; \quad S_3 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix};$$

$$S_3' = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}; \quad \sigma_v' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix};$$

$$\sigma_v'' = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}; \quad \sigma_v''' = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}.$$

TABLE XXIV

SYMMETRY ADAPTED BASES FUNCTIONS FOR THE POINT GROUP D_{3h}

$$\chi_{1a'_1} = \frac{1}{2}[\Theta_{1sC_1} + \Theta_{1sC_2}]$$

$$\chi_{1a''_2} = \frac{1}{2}[\Theta_{1sC_1} - \Theta_{1sC_2}]$$

$$\chi_{2a'_1} = \frac{1}{2}[\Theta_{2sC_1} + \Theta_{2sC_2}]$$

$$\chi_{2a''_2} = \frac{1}{2}[\Theta_{2sC_1} - \Theta_{2sC_2}]$$

$$\chi_{3a'_1} = \frac{1}{2}[\Theta_{2p_zC_1} - \Theta_{2p_zC_2}]$$

$$\chi_{3a''_2} = \frac{1}{2}[\Theta_{2p_zC_1} + \Theta_{2p_zC_2}]$$

$$\left\{\begin{aligned} \chi_{1e'1} &= \frac{1}{2}[\Theta_{2p_xC_1} + \Theta_{2p_xC_2}] \\ \chi_{1e'2} &= \frac{1}{2}[\Theta_{2p_yC_1} + \Theta_{2p_yC_2}] \end{aligned}\right.$$

$$\left\{\begin{aligned} \chi_{1e''1} &= \frac{1}{2}[\Theta_{2p_xC_1} - \Theta_{2p_xC_2}] \\ \chi_{1e''2} &= \frac{1}{2}[\Theta_{2p_yC_1} - \Theta_{2p_yC_2}] \end{aligned}\right.$$

$$\chi_{4a'_1} = \frac{1}{6}[\Theta_{1sH_1} + \Theta_{1sH_2} + \Theta_{1sH_3} + \Theta_{1sH_4} + \Theta_{1sH_5} + \Theta_{1sH_6}]$$

$$\chi_{4a''_2} = \frac{1}{6}[\Theta_{1sH_1} + \Theta_{1sH_2} + \Theta_{1sH_3} - \Theta_{1sH_4} - \Theta_{1sH_5} - \Theta_{1sH_6}]$$

$$\left\{\begin{aligned} \chi_{2e'1} &= \frac{1}{4}[\Theta_{1sH_2} - \Theta_{1sH_3} + \Theta_{1sH_5} - \Theta_{1sH_6}] \\ \chi_{2e'2} &= \frac{-\sqrt{3}}{12}[2\Theta_{1sH_1} - \Theta_{1sH_2} - \Theta_{1sH_3} + 2\Theta_{1sH_4} - \Theta_{1sH_5} - \Theta_{1sH_6}] \end{aligned}\right.$$

$$\left\{\begin{aligned} \chi_{2e''1} &= \frac{1}{4}[\Theta_{1sH_2} - \Theta_{1sH_3} - \Theta_{1sH_5} + \Theta_{1sH_6}] \\ \chi_{2e''2} &= \frac{-\sqrt{3}}{12}[2\Theta_{1sH_1} - \Theta_{1sH_2} - \Theta_{1sH_3} - 2\Theta_{1sH_4} + \Theta_{1sH_5} + \Theta_{1sH_6}] \end{aligned}\right.$$

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VITA 2

Evangelos Theodore Skoumbourdis

Candidate for the Degree of

Doctor of Education

Thesis: AN INTRODUCTION TO THE ELECTRONIC STRUCTURE OF MOLECULES

Major Field: Higher Education/Physics

Biographical:

Personal Data: Born in Nazareth, Israel, April 4, 1945, the son of Dr. and Lady T. C. Skoumbourdis.

Education: Received B.Sc. in Mathematics, June, 1970; received B.Sc. in Physics, August, 1972; received M.Sc. in Mathematics, August, 1974, from Tennessee Technological University; received M.Sc. in Physics, December, 1982, from Oklahoma State University. Completed requirements for Doctor of Education degree at Oklahoma State University, May, 1985.