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DEVELOPMENT OF THE ONE-CENTER EXPANSION METHOD COUPLED WITH MODEL POTENTIALS FOR MOLECULAR WAVEFUNCTIONS

by

ALEX R. TINDIMUBONA

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled DEVELOPMENT OF THE ONE-CENTER EXPANSION METHOD COUPLED WITH MODEL POTENTIALS FOR MOLECULAR WAVEFUNCTIONS submitted by ALEX R. TINDIMUBONA in partial fulfilment of the requirements for the degree of Doctor of Philosphy.

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M. D

R Moccia
(External Examiner)

Date July 25th, 1979

To the African extended family, in partial fulfilment of great expectations. In particular, to the memory of my brother, Sebastian Tibategyeza and my mother's brother, Daniel Kaamaguubwa, for whom the wait was too long.

Hide nothing from the masses of our people.
Tell no lies. Mask no difficulties, mistakes,
failures. Claim no easy victories.

Amilcar Cabral

ABSTRACT

This thesis presents a development of the One-Center Expansion (OCE) method in a way which extends its use to molecules with heavy off-center nuclei, a prospect previously beyond reach. This extension is achieved through the use of model potentials (MP) to approximate the tightly bound core orbitals, which remain virtually unchanged from atom to molecule and do not contribute to bonding. The remaining diffuse valence charge distribution, which determines many of the physical and chemical properties of the molecule, is then rather easy to simulate using the One-Center Expansion method.

The formulation of the method is described. New molecular integrals arising from the coupling of the One-Center Expansion method and the model potential approximation are evaluated to a high degree of accuracy. Successful results are reported for H_2O, H_2S and N_2. The valence electron distributions and orbital energies are in good agreement with those obtained from more complete calculations.

The method combines the effort-saving qualities of both the OCE and MP procedures, resulting in a potentially useful package for further chemical applications.

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INTRODUCTION

A. Preamble

The fundamental, microscopic understanding of chemistry, its processes and reactions, requires a detailed and if possible quantitative knowledge of the properties of atoms, molecules and their interactions. Atomic and molecular properties of chemical interest are governed by the details of their electronic structures and nuclear arrangements.

There are two important methods which permit us to obtain this detailed information, one experimental (spectroscopy), the other theoretical (quantum mechanics). Spectroscopy, with its many variants, has yielded a great deal of such information. In quantum mechanics, it is assumed that chemical systems can be completely represented by mathematical functions. The purpose of quantum-mechanical calculations as applied to chemistry is to find these functions, which are called "eigenfunctions" or "wavefunctions" of the atom, molecule, or assemblage of atoms and/or molecules being investigated. Thus insofar as quantum mechanics is correct, chemical questions can be reduced to problems in applied mathematics. The framework of quantum mechanics has been established for the last 50 years. In 1929 Dirac was able to write:

> "The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore

> of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."[1]

With the advent of large-scale computers in the last twenty years, increasingly sophisticated computational methods have been developed which give results approaching chemical accuracy. However, these methods get prohibitively expensive, and the search for cheaper methods continues. It is in this spirit that this thesis attempts to develop a One-Center Expansion (OCE) method [2,3] coupled with model potentials (MP) [4], in a way that extends the applicability of the former to molecules with heavy off-center nuclei, a prospect previously beyond reach.

B. One-Center Expansion Method

1. History

The problem of constructing electronic wavefunctions for molecules has been attacked in several ways. The most usual method entails the use of atomic orbitals centered on all atomic nuclei (LCAO) [5,6]. This method has conceptual simplicity, being in line with chemical intuition: a molecule is made by combination of atoms, so too a molecular orbital should be made from a (linear) combination of atomic orbitals (LCAO). It converges well to the Hartree-Fock (HF) limit as basis sets get larger.

The only difficulty with it, but an essential difficulty, is that it requires the evaluation of many difficult multicenter molecular integrals. This is a tedious process, especially for Slater-type orbitals (STO) on several, non-collinear centers. This bottleneck has indeed led to the virtual abandonment of STOs in favour of Gaussian-type orbitals (GTO) in molecular calculations, which result in more tractable integrals, although they are inferior to STOs in the description of molecular electron distributions.

It was in search of a device to avoid these difficult integrals [7] that the one-center expansion method was developed. In this method, an attempt is made to simulate the total wavefunction using functions centered at one convenient point in space. Conceptually, this method is not so direct, especially for the ground state. Also, it converges poorly, requiring many more terms than LCAO to achieve a given accuracy. But it has the advantage that the integrals are simple, especially as the two-electron integrals are all one-center, as are the one-electron integrals except nuclear attraction, which are up to two-center. It can also take advantage of formulations which have been developed for atoms.

Single-center ideas have been developing since the early days of quantum chemistry [3]. In 1928, Finkelstein and Horowitz [8] approximated the ground state wavefunction of H_2 as a product of two hydrogen-like orbitals centered at the mid-point. Since then, this and many other molecules have been tackled, with some success. The method saw extensive investigation in the decade or so following 1955, during which time more than 100 papers on it appeared, culminating in two important reviews [2,3].

The work using the method may be divided into two classes:

(i) Those workers who were searching for an exact OCE wavefunction and good predictions of the energy [9]. These workers encountered the fundamental drawback of the method: the difficulty in adequately describing the wavefunction in the immediate vicinity of the off-center nuclei, where the compact charge-concentration is difficult to generate from another point, even with many terms.

Figure 1.1 illustrates this difficulty for the ground state $1\sigma_g$ wavefunction of H_2^+ along the internuclear axis [10]. One nucleus sits at $z=-1.0$, the other at $z=+1.0$, and the origin for the one-center expansion is at $z=0$. The dashed curves are the results [9b] of expansions using STOs of number and symmetry-type indicated. The function 2s+1d+1g+1i has converged quite well to the wavefunction of Cohen and Coulson [9a], which contains the same symmetry types with numerical radial functions, but both wavefunctions are a poor fit to the accurate function of Bates et al [11] in the immediate vicinity of the nucleus at $z=1.0$.

This disparity, or "off-center cusp problem", is smallest when the off-center nuclei are smallest (H), but becomes prohibitive for heavier off-center nuclei. In particular, it is completely impossible to expand the inner shells on one atom in terms of STOs centered at another point. Thus the method was inherently restricted to molecules with no non-hydrogen off-center nuclei: H_n^{k+}, or central hydrides AH_n^{k+} with the expansion center at the heavy nucleus A.

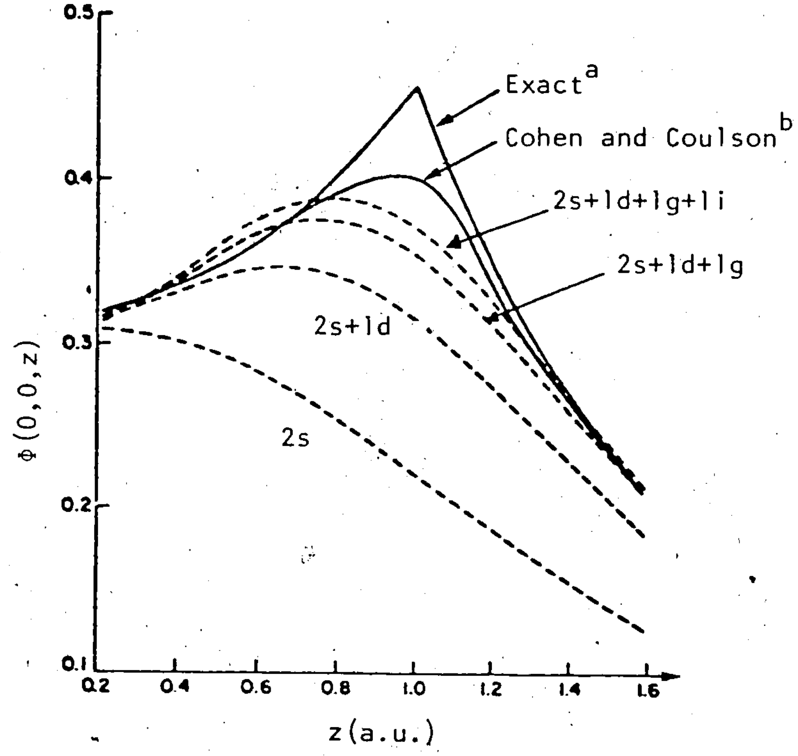


FIG. 1.1. Comparison of OCE wavefunctions for H_2+ along the internuclear axis. From ref.10, p.59.

[a] Ref.11

[b] Ref.9a

ii) The other group of workers chose simple wavefunctions and attempted to calculate properties of molecules which are determined more by the general shape of the wavefunction, rather than by its detailed shape in a particular region of space. Perhaps the greatest encouragement for the method came from the work of Moccia [12]. Approximating the wavefunction as a single Slater determinant, and using Roothaan's SCF procedure with all basis functions located at a common center, he was able to calculate bond distances, angles, dipole moments, ionisation potentials (orbital energies) and molecular energies for a whole range of molecules to a high degree of accuracy.

After 1967, however, the method relatively died down due to disappointment over its slow convergence, its need for high-n, high-l orbitals, and its poor prospects for extension to molecules with heavier off-center nuclei. Another factor in its relative demise seems to have been the advent of GTOs and virtual abandonment of STOs for molecular calculations.

2. Demand for OCE wavefunctions

The utility of the method has been established in several areas besides the calculation of ground states for hydrides. Recent literature reports of applications in diverse areas demonstrate the continuing demand for OCE wavefunctions. The method is proving suitable in the determination of excited states [13], where the average distance of the electrons from the nuclei is much greater than the internuclear separation, and where the magnitude of the wavefunction close to the nuclei is small. In particular, electrons in Rydberg orbitals are so far that they "see" a "united-atom" potential [14].

In the study of atom-atom collisions, the problem of such a collision may be reconstituted as one of determining the potential energy curves, wavefunctions and MO correlation diagrams of the corresponding quasi-molecule [15]. The OCE wavefunction is found to be the best at short internuclear distances, where the situation is almost united-atom, and LCAO deteriorates as linear dependencies develop among functions based on different centers. Possibility of extension to atom-molecule or molecule-molecule collisions is conceivable.

In the study of molecular photoelectron (ESCA) intensities and angular distributions, the calculated quantity is the photoionisation cross-section. The primary ingredients are the wavefunctions of the initial and residual ionised states. The OCE formulation simplifies the problem appreciably. Iwata and Nagakura [16a] have used Moccia's [12] OCE wavefunctions for NH_3, H_2O, H_2S and CH_4; Chapman [16b] has used the Hayes-Parr [9e] wavefunction for H_2.

In the study of electron-scattering by molecules, the problem is to work out the static interaction potentials between the projectile electron and the target molecule. This calls for a single-center wavefunction if the calculations are to be tractable. Burke and coworkers [17] have used the Harris-Michels [18,19] method of transforming an LCAO wavefunction into a "single-center" one for N_2, H_2O, H_2CO, and SF_6. These workers lament the poor convergence of the technique, which results in expensive calculations. The same idea finds use in Tobin and Hinze's [20] recent numerical multiconfigurational SCF scheme. It is possible that a straightforward Moccia-type OCE wavefunction might be better.

Finally Combs [21] has suggested that molecular wavefunctions can be constructed through combination of wavefunctions of molecular fragments, which could be of OCE variety.

These are the reasons why we have undertaken a revival of the One-Center Expansion method by trying to extend it to molecules with heavy off-center nuclei, a prospect previously beyond reach.

3. Extension to molecules with heavy off-center nuclei

This is achieved through the use of model potentials to approximate the compact core orbitals of the off-center nuclei, which, as we saw above, cannot be expanded by the OCE method. Once this burden on OCE is removed, the remaining, diffuse valence charge distribution is then easy to simulate.

The quest to solve the off-center cusp problem, and thus improve the wavefunction at the off-center nuclei, has seen attention before. Bishop [2] suggested the addition of orbitals which exist only near and are centered at the off-center nuclei. These orbitals would be of small enough range so that they do not overlap. He suggested that the two-center integrals between them and the OCE basis functions would be so small that they could be evaluated numerically. He reported satisfactory results for H_2^+.

The same idea may be seen in the "three-center" basis sets for diatomic molecules at short internuclear distances [15], whereby united-atom basis functions are centered at the mid-point to represent the diffuse outer MOs, while the tightly bound core MOs are expanded in terms of basis functions situated at the nuclear positions. However, the introduction of many two-center, two-electron integrals may defeat the whole purpose of single-center calculations. In contrast, we shall show that using model potentials introduces only two-center one-electron integrals which are not only fewer in number, but, in principle, easier to solve. This should represent a considerable economy of computational effort.

Another method which has been tried for solving the off-center cusp problem is that of Conroy [22]. In this method, a shape factor is built into the expression for the total wavefunction, of a form specifically to kill singularities at the off-center nuclei. The resulting equations are complicated, requiring numerical integration. The method has not seen application beyond H_2, H_3, H_4 and their positive ions.

4. Model Potentials

Here we give a few words of introduction to the concept of model potentials. For many years, chemists and physicists have realised that the chemical and physical properties of atoms and molecules are determined mainly by only the few outer "valence" electrons, the "core" taking little part. Thus, in describing the nature of the chemical bond, one needs to focus attention only on the outer few electrons of each atom. This concept of separability of an atomic or molecular system into "relevant" and "unimportant" regions also appears in other cases, for example σ and π electrons in conjugated systems, and functional groups in organic chemistry.

It would be desirable to set up a quantum-mechanical framework whereby the states of the "relevant" part may be evaluated accurately, but without explicit concern for the "unimportant" part.

This is precisely the goal of the pseudo- or model potential. It does so by approximating the effects of the "unimportant" part on the "relevant" part. The mathematical set-up is rather tricky, and only in the last five or six years has the potential accuracy and practicality of the method for molecular applications become apparent, leading to a surge of interest in the technique. A recent review details the use of pseudopotentials in molecular calculations to date [4]. The method is being investigated in several laboratories, including ours, and this author believes that when fully understood and made to work properly, it will take its place beside, if not altogether transcend, the semi-empirical methods.

One of the most promising formulations of the model potential, proposed by Bonifacic and Huzinaga [23], is chosen here for incorporation into the OCE-MP method.

C. Structure of thesis

This thesis describes the formulation of our method, coupling the OCE method to the model potential (MP) approximation, to give what we call the OCE-MP algorithm. First, some of the theoretical background necessary for studying problems in quantum chemistry is presented in Chapter II. The hierarchy of standard approximations commonly assumed in the electronic theory of molecules is discussed. The place occupied by the OCE method in this hierarchy is pinpointed. An attempt is also made to trace the linkage between quantum mechanical calculations and the chemical information which may be extracted from them.

Chapter III furnishes more direct background to our method by examining the concept of the model potential approximation. The essential features of the method are outlined, and then the model potential formulation of Bonifacic and Huzinaga [23] is singled out for special review. The saving qualities of the method are emphasised.

Chapter IV presents the formulation of the OCE-MP algorithm. It sets down the formal set of equations that must be solved, and launches the computational strategy and tactics adopted in this work. The calibration of model potentials is described, the integrals arising from the coupling of OCE to MP are identified, and most of them are solvable by common methods [6b, 12d]. However, there are some new integrals, whose explicit solution could not be found in the literature. We have developed a method to solve them to a high degree of accuracy. It is based on the Fourier Convolution method [24, 25, 26]. The derivation and application of this method is highly technical, and so Chapter V and the appendices have been set aside for this task.

Chapter VI gives the results of application of the OCE-MP method to real molecules. Successful results are given for H_2O, H_2S, and N_2. The valence electron distributions and orbital energies are found to be in good agreement with those obtained from more complete calculations. A serious problem of basis set redundancy [12] was encountered, which slowed progress in extensive applications. Nevertheless, the outlook for the method is promising, as it combines the saving qualities of both the OCE and MP procedures, resulting in a potentially useful package for further chemical applications.

CHAPTER II

THEORETICAL BACKGROUND AND METHODS

A. Hierarchy of Approximations

In this chapter the hierarchy of approximations used in this work is presented. It may be summarised as follows, proceeding from the general to the particular.

i) Schroedinger Equation: Non-relativistic Hamiltonian; Time-independent (stationary states, molecular structure); Clamped nuclei; Electronic Schroedinger equation.

ii) Variational Method: The best wavefunction is that which gives the lowest total energy.

iii) Orbital Model: Each electron is assigned to a separate one-electron wavefunction (Orbital).

iv) Hartree-Fock SCF: Total wavefunction is a Slater determinant of orbitals; best orbitals are determined by an SCF iterative solution of coupled integrodifferential equations.

v) Hartree-Fock-Roothaan Method: Search for analytical orbitals by finite expansion of them in terms of known analytical basis functions. Expansion coefficients become the variational parameters to be determined by SCF.

vi) One-Center Expansion Method: A device to avoid difficult multicenter integrals; all expansion basis functions located at one convenient point in space.

vii) Model Potential Approximation: Chemically "relevant" valence region determined accurately, "unimportant" core regions treated approximately.

The discussion in this chapter covers the standard, basic approximations i)-v) commonly used in quantum chemistry and assumed in this work. The one-center expansion method is introduced superficially. The model potential approximation is discussed in Chapter 3, and in Chapter 4, we show how it is coupled to the OCE method to produce the OCE-MP algorithm.

B. The Schroedinger Equation

The primary task in the electronic theory of molecules is to find solutions to the time-independent Schroedinger equation [27]

$$H\Psi = E\Psi \qquad (2\text{-}1)$$

which is taken as the master equation. H is the Hamiltonian operator for the system under investigation. For a system of M nuclei and N electrons, the Hamiltonian operator is

$$H = T_n + T_e + V_{ne} + V_{ee} + V_{nn} , \qquad (2\text{-}2)$$

comprising the nuclear and electronic kinetic energy operators, and the electron-nuclear attraction, electron-electron repulsion and nuclear-nuclear repulsion potentials. Neglecting relativistic effects and assuming that the only forces acting between particles are Coulombic, the Hamiltonian operator in c.g.s. Gaussian units is

$$H = -\sum_{\alpha}^{M} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 - \sum_{i}^{N} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{\alpha}^{M} \sum_{i}^{N} \frac{Z e^2}{|\underset{\sim}{R}_\alpha - \underset{\sim}{r}_i|} + \sum_{i>j}^{N} \sum^{N} \frac{e^2}{|\underset{\sim}{r}_i - \underset{\sim}{r}_j|} + \sum_{\alpha>\beta}^{M} \sum^{M} \frac{Z_\alpha Z_\beta e^2}{|\underset{\sim}{R}_\alpha - \underset{\sim}{R}_\beta|} . \qquad (2\text{-}3)$$

and in atomic units,

$$H = -\sum_{\alpha}^{M} \frac{1}{2M_\alpha} \nabla_\alpha^2 - \sum_{i}^{N} \frac{1}{2} \nabla_i^2 - \sum_{\alpha}^{M} \sum_{i}^{N} \frac{Z_\alpha}{r_{\alpha i}} + + \sum_{i>j}^{N} \sum^{N} \frac{1}{r_{ij}} + \sum_{\alpha>\beta}^{M} \sum^{M} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \tag{2-4}$$

Ψ is the wavefunction which describes the distribution or configuration of the particles in the system:

$$\Psi \equiv \Psi(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots, \underset{\sim}{r}_N; \underset{\sim}{R}_1, \underset{\sim}{R}_2, \ldots, \underset{\sim}{R}_M) \tag{2-5}$$

and E is the allowed energy of the system in state Ψ.

It is seen from (2-1) and (2-4) that the Schroedinger equation is both a second-order partial <u>differential equation</u> and an <u>eigenvalue problem</u>. Thus it would seem that in the framework of quantum mechanics, chemical questions can be reduced to problems in applied mathematics.

For nearly all systems, equation (2-1) is very difficult to solve, and for the past 50 years or so quantum chemists have been concerned with alleviating the mathematical problem. In order to obtain information of chemical value from the theory, a series of further approximations of varying severity is usually made. The following sections are concerned with some of the major approximations.

C. Clamped Nuclei or Born-Oppenheimer Approximation [28]

This approximation rests upon the physical picture that the massive nuclei (m/M_α is usually in the range $10^{-3} - 10^{-4}$) move very slowly compared to the electrons. To a first approximation then, the motion of the electrons may be separated out and treated as if the nuclei were fixed in space. Born and Oppenheimer showed that solutions to (2-1) may be approximated by first solving the wave-equation for fixed nuclear positions (K.E. of nuclei excluded), thus obtaining the electronic energy for particular arrangements of the nuclei. This electronic energy can then be used as the potential energy for the wavefunction involving the nuclei alone.

The electronic portion of the motion is represented at each nuclear configuration by an electronic Schroedinger equation

$$H^e \Psi^e = E^e \Psi^e \tag{2-6}$$

where

$$H^e = - \sum_i \frac{1}{2} \nabla_i^2 + V \tag{2-7}$$

$$V = - \sum_i^N \sum_\alpha^M \frac{Z_\alpha}{r_{i\alpha}} + \sum_{i>j}^N \frac{1}{r_{ij}} + \sum_{\alpha>\beta}^M \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \tag{2-8}$$

$$\Psi^e \equiv \Psi^e(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots, \underset{\sim}{r}_N; \underset{\sim}{R}_1, \underset{\sim}{R}_2, \ldots, \underset{\sim}{R}_M) \tag{2-9}$$

where this means that Ψ^e is a function of $\{\underset{\sim}{r}_i\}$ as dynamical variables, but contains $\{\underset{\sim}{R}_\alpha\}$ as parameters since it is defined at each nuclear configuration. Similarly

$$E^e = E^e(\underset{\sim}{R}_1, \underset{\sim}{R}_2, \ldots, \underset{\sim}{R}_M) \tag{2-10}$$

The total wavefunction is taken as a product of Ψ^e and a nuclear wavefunction which depends only on the nuclear coordinates.

$$\Psi = \Psi^e(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots, \underset{\sim}{r}_N; \underset{\sim}{R}_1, \underset{\sim}{R}_2, \ldots, \underset{\sim}{R}_M) \cdot \Psi^n(\underset{\sim}{R}_1, \underset{\sim}{R}_2, \ldots, \underset{\sim}{R}_M) \; . \tag{2-11}$$

Substituting this in (2-1) gives

$$[-\sum_{\alpha}^{M} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^{2} + H^{e}]\ \Psi^{e}\Psi^{n} = E\Psi^{e}\Psi^{n} \tag{2-12a}$$

or

$$[-\sum_{\alpha}^{M} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^{2} - \sum_{i}^{N} \frac{1}{2m} \nabla_{i} + V]\ \Psi^{e}\Psi^{n} = E\Psi^{e}\Psi^{n} \quad . \tag{2-12b}$$

Now, from (2-9),

$$\nabla_{i}^{2}\ \Psi^{e}\Psi^{n} = \Psi^{n}\ \nabla_{i}^{2}\ \Psi^{e} \tag{2-13}$$

but

$$\begin{aligned} \nabla_{\alpha}^{2}\ \Psi^{e}\Psi^{n} &= \nabla_{\alpha}(\Psi^{e}\nabla_{\alpha}\Psi^{n} + \Psi^{n}\nabla_{\alpha}\Psi^{e}) \\ &= \Psi^{e}\nabla_{\alpha}^{2}\Psi^{n} + \Psi^{n}\nabla_{\alpha}^{2}\Psi^{e} + 2\nabla_{\alpha}\Psi^{e}\cdot\nabla_{\alpha}\Psi^{n} \quad . \end{aligned} \tag{2-14}$$

If the electronic part Ψ^{e} does not change very much as nuclei move, the last two terms of (2-14) may be neglected, i.e., we assume

$$\nabla_{\alpha}\Psi^{e} \simeq \nabla_{\alpha}^{2}\Psi^{e} \simeq 0 \quad . \tag{2-15}$$

Born and Oppenheimer showed formally that the neglect of Ψ^{e} dependence on $\{\underset{\sim}{R}_{\alpha}\}$ is justified so long as not too high vibrational and rotational modes are excited. Under these conditions, (2-12a) becomes

$$[-\sum_{\alpha}^{M} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^{2} + E^{e}]\ \Psi^{e}\Psi^{n} = E\Psi^{e}\Psi^{n} \tag{2-16}$$

from which Ψ^{e} may be cancelled, giving an approximate Schroedinger equation for nuclear motion.

$$[-\sum_{\alpha} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^{2} + E^{e}]\ \Psi^{n} = E\Psi^{n} \quad . \tag{2-17}$$

This equation says the states of nuclear motion can be obtained from a Schroedinger equation whose potential is provided by the energy of the electronic charge cloud. The potential E^{e} is called the adiabatic potential, and defines a potential energy surface spanning the space of the nuclear coordinates.

Calculated potential energy surfaces, whose concept is a direct result of the Born-Oppenheimer approximation, yield encouraging results on equilibrium geometries, force constants, anharmonicity and binding or dissociation energies. They are being used in discussing spectroscopy, kinetics and reaction mechanisms [29].

In the Born-Oppenheimer approximation, then, the problem reduces to one of finding solutions, at each nuclear configuration, to the electronic Schroedinger equation (2-6), from which we henceforth drop the superscript and write:

$$H\,\Psi = E\,\Psi \tag{2-18a}$$

$$H = -\sum_i \frac{1}{2}\Delta_i - \sum_{\alpha,i}^{M,N} \frac{Z_\alpha}{r_{i\alpha}} + \sum_{i>j}^{N} \frac{1}{r_{ij}} + \sum_{\alpha>\beta}^{M} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \;. \tag{2-18b}$$

D. The Variational Method

The electronic Schroedinger equation has been solved exactly only for one-electron systems, for which a coordinate system can be found in which the problem is separable. In H-like atoms it is the spherical polar [57] and in H_2^+-like molecules it is the elliptical coordinate system.[11] For all other systems, approximate methods must be sought. Nearly all current electronic structure calculations are based on the Variational Principle, whose outline follows:

1. Variational Theorem:

The energy of a system in its k^{th} state is expressed from (2-18) as

$$E_k = \langle \Psi_k \,|H|\, \Psi_k \rangle$$

$$= \frac{\int \Psi_k^* H \Psi_k \, d\tau}{\int \Psi_k^* \cdot \Psi_k \, d\tau} \qquad (2\text{-}19)$$

where $d\tau$ signifies integration over all space. We assume that

i) there exists a complete set of exact solutions to (2-18) with the eigenvalues ordered in increasing value

$$E_o \leq E_1 \leq E_2 \leq \ldots \leq E_\infty \quad . \qquad (2\text{-}20)$$

The lowest eigenvalue E_0 is usually called the ground state of the system.

ii) The exact eigenvalues form a complete orthonormal set

$$\int \Psi_k^* \Psi_\ell \, d\tau = \delta_{k\ell} \qquad (2\text{-}21)$$

where $\delta_{k\ell}$ is the Kronecker delta.

Let Φ be any approximate, trial wavefunction chosen in any convenient manner using chemical, physical or mathematical intuition or experience. Its energy functional E is defined as

$$E[\Phi] = \frac{\int \Phi^* H \Phi \, d\tau}{\int \Phi^* \Phi \, d\tau}$$

$$= \frac{\langle \Phi \,|H|\, \Phi \rangle}{\langle \Phi \,|\, \Phi \rangle} \quad . \qquad (2\text{-}22)$$

The variational theorem states that

$$E \geq E_0 \ , \ \text{with equality only if} \quad \Phi = \Psi_0 \ . \tag{2-23}$$

Proof. The assumption of completeness allows the expansion of Φ in terms of the $\{\Psi_k\}$.

$$\Phi = \sum_{k=o}^{\infty} c_k \ \Psi_k \tag{2-24}$$

where $\{c_k\}$ are, in general, complex. Then (2-22) gives

$$E[\Phi] = \frac{\int (\sum_k c_k^* \Psi_k^*) H (\sum_\ell c_\ell \Psi_\ell) d\tau}{\int (\sum_k c_k \Psi_k)^* (\sum_\ell c_\ell \Psi_\ell) d\tau}$$

$$= \frac{\sum_k \sum_\ell c_k^* c_\ell E_k \ \delta_{k\ell}}{\sum_k \sum_\ell c_k^* c_\ell \ \delta_{k\ell}}$$

$$= \frac{E_0 |c_0|^2 + E_1 |c_1|^2 + E_2 |c_2|^2 + \ldots}{\sum_k |c_k|^2} \ . \tag{2-25}$$

Keeping in mind that from (2-20), $E_k \geq E_0$, we get

$$E[\Phi] \geq \frac{E_0 (|c_0|^2 + |c_1|^2 + |c_2|^2 + \ldots)}{\sum_k |c_k|^2} = E_0 \tag{2-26}$$

which completes the proof.

Thus, if we start with an arbitrary trial function, its energy functional (expectation value) is always an upper bound to the true ground-state energy of the system in question.

Calculations within the framework of the variational method are usually performed by choosing a trial wavefunction of a desired form, which depends on certain parameters. The parameters are then varied so as to minimise the energy functional and thus obtain the best possible wavefunction of the chosen form.

2. Schroedinger Equation as an Euler Equation of Motion

The variational principle applied to equation (2-22) demands that for an arbitrary variation in Φ,

$$\Phi \longrightarrow \Phi + \delta\Phi \tag{2-26a}$$

$$\Phi^{*} \longrightarrow \Phi^{*} + \delta\Phi^{*} \tag{2-26b}$$

the energy functional $E[\Phi]$ remains stationary (or extremum), i.e.,

$$\delta E = 0 \quad . \tag{2-27}$$

Assuming $E[\Phi]$ is a constant so that it can be incorporated into the integral, (2-22) can be rewritten as

$$\int \Phi^{*}(H-E[\Phi])\Phi \, d\tau = 0 \quad ..$$

After the variation (2-22) and (2-26) give

$$\begin{aligned} \delta E = & \int(\Phi^{*}+\delta\Phi^{*})(H-E[\Phi])(\Phi+\delta\Phi)d\tau - \int\Phi^{*}(H-E[\Phi])\Phi \, d\tau = 0 \\ = & \int\delta\Phi^{*}(H-E[\Phi])\Phi d\tau + \int \Phi^{*}(H-E[\Phi])\Phi \, d\tau \\ & + \int\delta\Phi^{*}(H-E[\Phi])\delta\Phi \, d\tau \quad . \end{aligned} \tag{2-28}$$

The last term is of order $[(\delta\Phi)^{2}]$ any may be neglected. The Hermitian property of the Hamiltonian is exploited, i.e.,

$$\begin{aligned} \int \Phi^{*} H\delta\Phi \, d\tau &= \int(H^{*}\Phi^{*})\delta\Phi \, d\tau \\ &= \int\delta\Phi \, H^{*}\Phi^{*} \, d\tau \end{aligned} \tag{2-29}$$

to give

$$\int \delta\Phi^{*}(H-E[\Phi]\Phi d\tau + \int \delta\Phi(H^{*}-E^{*}[\Phi])\Phi^{*} d\tau = 0 \quad . \tag{2-30}$$

Since $\delta\Phi$ and $\delta\Phi^{*}$ are completely arbitrary, the other factors in the integrands must vanish separately, giving the Euler equations:

$$H\Phi = E[\Phi]\cdot\Phi \tag{2-31a}$$

$$H^{*}\Phi^{*} = E^{*}[\Phi]\cdot\Phi^{*} \tag{2-31b}$$

The similarity with a Schroedinger equation is apparent.

Thus Schroedinger's equation provides the basis for modern quantum mechanics, in which it plays the same role as the equations established by Newton, Lagrange and Hamilton play in classical mechanics.

There is no guarantee that the energy obtained by the variational method is an absolute minimum. The method only demands that E be stationary with respect to the permitted variation of Φ, so it could be trapped at a local maximum, minimum or saddle point. It is generally believed that for most physical systems the energy surfaces are simple and a true minimum will be obtained, but exceptions exist.

3. Variation with Linear Constraints

The problem of "deriving" the Schroedinger equation from the variational integral hinged on the arbitrary variation of Φ. Usually, however, there is the constraint that Φ must remain normalised throughout the variation, and thus cannot vary arbitrarily. This is equivalent to demanding

$$\delta J = 0 \tag{2-32a}$$

where

$$J[\Phi] = \int \Phi^* H \Phi \, d\tau \qquad (2\text{-}32b)$$

with variations

$$\Phi \longrightarrow \Phi + \delta\Phi \quad , \qquad (2\text{-}32c)$$

$$\Phi^* \longrightarrow \Phi^* + \delta\Phi^* \qquad (2\text{-}32d)$$

under the constraint (normalisation)

$$\int \Phi^* \Phi \, d\tau = 1 \quad \text{or} \quad \left(\int \Phi^* \Phi \, d\tau - 1\right) = 0 \quad . \qquad (2\text{-}32e)$$

We form a new functional to be made stationary:

$$I[\Phi] = \int \Phi^* H \Phi \, d\tau - \epsilon\left(\int \Phi^* \Phi \, d\tau - 1\right) \quad . \qquad (2\text{-}33a)$$

We demand that

$$\delta I = 0 \qquad (2\text{-}33b)$$

with <u>arbitrary</u> $\delta\Phi$, $\delta\Phi^*$. This is then a valid procedure for variation since arbitrary variation has been reinstated. The number ϵ is called the Lagrangian multiplier, to be determined in some manner.

E. Orbital Approximation and the Hartree-Fock Method

In its general form as formulated by Roothaan, [5,6] the Hartree-Fock SCF method is truly a forbidding jungle. Many writers have succumbed to the temptation of merely reproducing it from Roothaan's monumental papers. In this section, we have chosen instead to discuss the simplest example to which it is applicable, namely the ground state of the Helium atom, in a way which makes the essential features of the method transparent. At the end, we summarise by giving the generalised equations as usually used.

1. Concept of orbitals. Example of He atom

For systems of more than one electron, the wavefunction Ψ (or Φ) is complicated because of the sheer number of coordinates to be considered. The Helium atom will suffice to illustrate this difficulty. The electronic Schroedinger equation is

$$H\Phi(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = E\,\Phi(\underset{\sim}{r}_1, \underset{\sim}{r}_2) \qquad (2\text{-}34)$$

where

$$H = h(1) + h(2) + \frac{1}{r_{12}} \qquad (2\text{-}35)$$

and

$$h(1) = -\frac{1}{2}\Delta_1 - Z/r_1 \qquad (2\text{-}36)$$

$$h(2) = -\frac{1}{2}\Delta_2 - Z/r_2 \qquad (2\text{-}37)$$

are the one-electron Hamiltonians. The wavefunction may be written as:

$$\begin{aligned}\Phi(\underset{\sim}{r}_1, \underset{\sim}{r}_2) &\equiv \Phi(x_1,y_1,z_1,x_2.y_2,z_2)\\ &\equiv (r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) \qquad (2\text{-}38)\end{aligned}$$

in Cartesian and spherical polar coordinates respectively. Thus Φ for two electrons is a wave in a six-dimensional space. Since real space is only three-dimensional, Φ is an abstract quantity.

The numerical results obtained for Φ would be unwieldy. Suppose we wanted values of Φ for 20 values of each of the coordinates. The number of such values is $20^6 = 64 \times 10^6$. Suppose 8 such values are written on a line and a computer printout page carries 64 lines. It would take 1.25×10^5 pages of output, which is ridiculous. For tractable results, then, the number of coordinates must be reduced. Separation of Φ into a product of one-electron functions thus seems a necessary simplification:

$$\Phi(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = \phi(\underset{\sim}{r}_1)\phi(\underset{\sim}{r}_2) \quad . \tag{2-39}$$

It partially reintroduces a 3-dimensional wave concept, which is easier to picture. This separation is based on the assumption that as $\frac{1}{r_{12}} \to 0$ the electrons move independently.

By substituting (2-39) into (2-34) and neglecting the $\frac{1}{r_{12}}$ term, we can confirm that each ϕ satisfies its own Schroedinger equation:

$$(-\frac{1}{2}\Delta_i - \frac{Z}{r_i})\phi(\underset{\sim}{r}_i) = E_i\phi(\underset{\sim}{r}_i) \qquad i = 1,2 \tag{2-40}$$

with the usual hydrogenic solutions (see Chapter 3) for example,

$$\phi_{1s}(r_1) \sim (\frac{Z^3}{\pi})^{\frac{1}{2}} e^{-Zr_1} \tag{2-41}$$

$$\phi_{1s}(r_2) \sim (\frac{Z^3}{\pi})^{\frac{1}{2}} e^{-Zr_2} \tag{2-42}$$

$$E_{1s} = -\frac{1}{2}Z^2 \tag{2-43}$$

This is what has led to the common notion that this is an "independent-particle" model. From (2-40)-(2-43) a sensible guess at the form of the wavefunction for the ground state is an exponential

$$\Phi(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = (\frac{\zeta^3}{\pi})\, e^{-\zeta r_1}\, e^{-\zeta r_2} \tag{2-44}$$

with ζ as the parameter to be optimised through a variation principle. This form has an energy according to (2-22) of:

$$E(\zeta) = \frac{\int \Phi^* H \Phi \, d\tau}{\int \Phi^* \Phi \, d\tau} = \zeta^2 - 2Z\zeta + \frac{5}{8}\zeta \quad . \tag{2-45}$$

and demanding

$$\frac{dE}{d\zeta} = 0 \tag{2-46}$$

yields

$$\zeta_{opt} = Z - \frac{5}{16} \tag{2-47}$$

$$E(\zeta_{opt}) = -(Z - \frac{5}{16})^2 \ . \tag{2-48}$$

The result for He with $Z = 2$ is

$$\zeta_{opt} = 1.6875 \tag{2-49a}$$

$$E(\zeta_{opt}) = -2.8476563 \text{ a.u.} \ , \tag{2.49b}$$

not bad compared to the true experimental value obtained from Moore's tables [31] by adding the ionisation potentials corresponding to the successive stripping of the He atom:

$$-(24.58 + 54.38) = -78.96 \text{ eV} = -2.90187 \text{ a.u.} \tag{2-50}$$

2. Hartree-Fock SCF Method for Helium

In the method of Hartree and Fock, the goal is to find the optimal functional form of ϕ without fixing it a priori.

Variation of the type given in Section C3 can be applied to this system to give the equations of motion.

If ϕ is contrained to be normalised, i.e.,

$$\int \phi^* \phi \, d\tau = 1 \tag{2-51}$$

then Φ is also normalised, and this is the constraint on the variation:

$$\int \Phi^* \Phi \, d\tau = 1 \tag{2-52}$$

From (2-32b) and (2-35),

$$J[\Phi] = \int \Phi^{*} H \Phi \, d\tau$$

$$= \int \phi^{*}(1)\phi^{*}(2)[h(1)+h(2) + \frac{1}{r_{12}}]\phi(1)\phi(2) \, d\tau_1 \, d\tau_2$$

$$= J[\phi, \phi^{*}] \quad . \qquad (2\text{-}53)$$

Using the Lagrange Multiplier method, the new functional is

$$I[\phi,\phi^{*}] = J[\phi,\phi^{*}] - 2\epsilon(\int \phi^{*}(1)\phi(1)d\tau_1 - 1)$$

$$= 2\int \phi^{*}(1)h(1)\phi(1)d\tau \quad ,$$

$$+ \iint \phi^{*}(1)\phi^{*}(2) \frac{1}{r_{12}} \phi(1)\phi(2)d\tau_1 \, d\tau_2$$

$$- 2\epsilon(\int \phi^{*}(1)\phi(1) - 1) \quad . \qquad (2\text{-}54)$$

Applying arbitrary variations in ϕ and ϕ^{*}, we demand

$$\delta I = I[\phi+\delta\phi,\phi^{*}+\delta\phi^{*}] - I[\phi,\phi^{*}] = 0 \quad . \qquad (2\text{-}55)$$

Using the Hermitian property of h, i.e.,

$$\int \phi^{*} h \delta\phi d\tau = \int \delta\phi^{*} \cdot h^{*} \phi^{*} \, d\tau \qquad (2\text{-}56)$$

we get

$$\delta I = 2\int \delta\phi^{*}(1)\{[h(1)+\int d\tau_2 \frac{\phi^{*}(2)\phi(2)}{r_{12}} - \epsilon]\phi(1)\} \, d\tau_1$$

$$+ 2\int \delta\phi(1)\{[h^{*}(1)+\int d\tau_2 \frac{\phi^{*}(2)\phi(2)}{r_{12}} - \epsilon]\phi^{*}(1)\}d\tau_1 \equiv 0 \quad . \qquad (2\text{-}57)$$

Because $\delta\phi$, $\delta\phi^{*}$ are completely arbitrary, the items in the curly brackets must vanish separately:

$$[h(1) + \int d\tau_2 \frac{\phi^{*}(2)\phi(2)}{r_{12}} - \epsilon]\phi(1) = 0 \qquad (2\text{-}58a)$$

$$[h^{*}(1) + \int d\tau_2 \frac{\phi^{*}(2)\phi(2)}{r_{12}} - \epsilon]\phi^{*}(1) = 0 \quad . \qquad (2\text{-}58b)$$

These are the famous Hartree-Fock equations, written for electron number 1. Interchanging labels results in the HF equation for electron 2. Only if the Lagrange multiplier ϵ is Hermitian, i.e.,

$$\epsilon^* = \epsilon \tag{2-59}$$

do the two equations have the same content and any one of them (say the first) will suffice. The full significance of this Hermitian condition has only recently been exposed [32].

Hartree and Fock set out to solve equations (2-58) for the optimum functional form of ϕ, without fixing it beforehand. The equations are pseudo-eigenvalue problems

$$F\phi(1) = \epsilon\phi(1) \tag{2-60a}$$

where

$$F = h(1) + \int d\tau_2 \frac{\phi^*(2)\phi(2)}{r_{12}} \tag{2-60b}$$

is called the Fock operator. The term pseudo-eigenvalue arises because to define the operator, we need to know ϕ, yet ϕ is what we are looking for. This suggests that the only solution is an iterative one:

i) choose or guess $\phi^{(0)}$

ii) construct F using $\phi^{(0)}$. Numerical integration is usually used.

iii) solve resulting eigenvalue problem (2-60a) for new $\phi^{(1)}$

iv) if $\phi^{(1)} = \phi^{(0)}$, stop. If not, go to ii), replacing $\phi^{(0)}$ by $\phi^{(1)}$.

Thus continue, building the sequence

$$\phi^{(0)}, \phi^{(1)}, \ldots, \phi^{(n)}, \phi^{(n+1)} .$$

Convergence occurs when $\phi^{(n)}$ and $\phi^{(n+1)}$ are so close to each other that we are willing to accept the error of their difference.

The final answer is a so-called self-consistent field wavefunction. The term SCF results from the fact that looked at as a Schroedinger equation for electron 1, equation (2-60a) shows that this electron moves in the potential of the nucleus, shielded by the average potential of the other electron's charge cloud as represented by the integral term in (2-60b). The energy of the Helium atom as represented by this optimum orbital is $E_{opt}[\Phi] = -2.8616800$ a.u.

3. Indistinguishability of Particles

In all the above sections, it is assumed that both electrons occupy functions of the same form. For example,

$$\begin{aligned}\Phi(\mathbf{r}_1,\mathbf{r}_2) &= \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2) \\ &= e^{-\zeta r_1} e^{-\zeta r_2} , \quad \text{same } \zeta \quad . \qquad (2\text{-}61)\end{aligned}$$

This is justified on the philosophical grounds that the two electrons are identical, and there is no reason to assume they behave differently.

Thus, interchanging the electrons should not change the physical content of the wavefunction, for example the electron density. In the most general form, we can say interchanging the electrons merely introduces a phase factor:

$$\Phi(\mathbf{r}_2,\mathbf{r}_1) = e^{i\alpha}\Phi(\mathbf{r}_1,\mathbf{r}_2) \qquad (2\text{-}62)$$

where $e^{i\alpha}$ is some phase factor, a complex number to be determined in the following manner. Suppose another interchange is carried out. We get

$$\Phi(\mathbf{r}_1,\mathbf{r}_2) = e^{i\alpha}\Phi(\mathbf{r}_2,\mathbf{r}_1) = e^{2i\alpha}\Phi(\mathbf{r}_1,\mathbf{r}_2) \quad . \qquad (2\text{-}63)$$

Therefore

$$e^{2i\alpha} = 1 \qquad \text{or} \qquad e^{i\alpha} = \pm 1 \quad . \tag{2-64}$$

Thus the theorem of indistinguishability can be stated as

$$\Phi(\underset{\sim}{r}_2,\underset{\sim}{r}_1) = \pm\, \Phi(\underset{\sim}{r}_1,\underset{\sim}{r}_2) \tag{2-65}$$

and defines two types of wavefunction: the symmetric one which remains unchanged upon interchange of electrons, and the antisymmetric one which changes sign.

4. Spin and the Pauli Exclusion Principle

Electrons have intrinsic spin which cannot be neglected. Thus the spin coordinate is usually included for most calculations.

$$\begin{aligned} \Phi &\equiv \Phi(\underset{\sim}{r}_1, \sigma_1, \underset{\sim}{r}_2, \sigma_2) \\ &= \Phi_{He}(1, 2) \quad . \end{aligned} \tag{2-66}$$

The Pauli Exclusion Principle states that no two electrons can have the same set of quantum numbers, if the calculation results are to agree with experiment. Thus the interchange of the labels (coordinates) of any two electrons must change the wavefunction, and this means only the antisymmetric form of eqn (2-65) is allowed.

It is usual to assume the absence of spin-orbit coupling so that Φ is separable into space and spin functions

$$\Phi(1,2) = \phi(r_1,r_2)\Theta(\sigma_1,\sigma_2) \quad . \tag{2-67}$$

Also, it is found that the spin function for each electron takes two orthogonal forms designated as α and β. The possible forms of Θ are then

$$\alpha(1)\alpha(2) \quad ,$$

$$\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \alpha(2)\beta(1)\} \quad ,$$

$$\beta(1)\beta(2) \quad , \tag{2-68}$$

and

$$\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\} \quad .$$

The first 3 are symmetric, the fourth antisymmetric. In order to satisfy the Pauli principle, the symmetric space part (agreeing with space indistinguishability) must be combined with the antisymmetric spin part to produce an antisymmetric total wavefunction

$$\Phi_{He}(1,2) = \frac{1}{\sqrt{2}}\{\phi_{1s}(1)\alpha(1)\alpha_{1s}(2)\beta(2) - \phi_{1s}(1)\beta(1)\phi_{1s}(2)\alpha(2)\} \tag{2-69}$$

and

$$\Phi_{He}(1,2) = -\Phi_{He}(2,1) \quad . \tag{2-70}$$

For more electrons things can get really tricky, as a brief look at Lithium with 3 electrons shows. Suppose again the space part is taken as **a** symmetric product of similar functions.

$$\Phi(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3) = \phi_{1s}(\underset{\sim}{r}_1)\phi_{1s}(\underset{\sim}{r}_2)\phi_{1s}(\underset{\sim}{r}_3) \quad , \tag{2-71}$$

which agrees with the indistinguishability condition. Several problems arise

i) We have to use an antisymmetric spin function constructed from a product of 3 spins, e.g., $\alpha(\sigma_1)\beta(\sigma_2)\alpha(\sigma_3)$ etc. The point is that it is impossible to construct an antisymmetric spin function with more than 2 functions. Thus the space part must change, and a new space function, the usual 2s, singly occupied, is introduced. The result is the configuration Li $1s^2 2s$. Only then can an antisymmetric Φ be constructed. The 2s electron is mostly spread outside the $1s^2$

space.

ii) It can be shown that the wave function of (2-71) violates the variation principle. Suppose we use the approximate exponential functional form, as in the case of He above:

$$\phi(\underset{\sim}{r}) = (\zeta^3/\pi)^{\frac{1}{2}} e^{-\zeta r} \tag{2-72}$$

and solve

$$H(1,2,3)\Phi(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3) = E\Phi(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3) \tag{2-73}$$

with

$$H(1,2,3) = h(1) + h(2) + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \tag{2-74}$$

$$h(i) = -\frac{1}{2}\Delta_i - Z/r_i \ , \qquad i = 1,2,3 \ . \tag{2-75}$$

Analysis similar to that done on He in equation (2-45) give

$$E(\zeta) = 3\ (\frac{\zeta^2}{2} - Z\zeta + \frac{5}{8}\zeta) \ . \tag{2-76}$$

This give the optimum $\zeta = \zeta_0$ at which

$$\frac{dE(\zeta)}{d\zeta} = 0 \tag{2-77}$$

as

$$\zeta_0 = Z - \frac{5}{8} \tag{2-78}$$

with

$$E(\zeta_0) = -\frac{3}{2}(Z - \frac{5}{8})^2 \ . \tag{2-79}$$

With $Z = 3$ for Li, we get

$$\zeta_0 = 2.375 \tag{2-80}$$

$$E(\zeta_0) = -8.46094 \text{ a.u.} = -230.222 \text{ eV} \ . \tag{2-81}$$

This is much lower than the true experimental value obtained from Moore's tables [31] by adding the first, second and third ionisation potentials corresponding to the successive stripping of the Li atom:

$$-(5.39 + 75.64 + 122.45)\text{eV} = -203.5 \text{ eV} = -7.47887 \text{ a.u.} \qquad (2\text{-}82)$$

iii) A word may be said about atomic sizes. The orbital of equation (2-72) is an exponential which dies faster than that of H, $e^{-1.0r}$. The size of Li atom would thus be very small compared to H. Larger atoms with such product functions would be correspondingly smaller and smaller, disappearing to tiny points, a situation contrary to reality.

Thus it would appear that it is the Pauli Principle which holds the material of the universe in place, preventing it from collapsing.

5. Slater Determinant

Slater was the first to realise that the determinant is an apt way of expressing these wavefunctions formally, in a way which satisfies all the implications of the Pauli Principle [34]. In Slater's parlance, (2-69) becomes

$$\Phi_{He}(1,2) = (2!)^{-\frac{1}{2}} \sum_{p} \epsilon_{p} P \, \phi_{1s}(1)\alpha(1)\phi_{1s}(2)\beta(2) \qquad (2\text{-}83a)$$

where

$$A_s = (2!)^{-\frac{1}{2}} \sum_{p} \epsilon_{p} P \qquad (2\text{-}83b)$$

is called the antisymmetriser for 2 particles. P are the 2! permutations; $\epsilon_p = (-1)^{n_p}$ is called the signature of permutation P where n_p is the number of interchanges in the permutation. This translates into determinant shorthand as:

$$\Phi_{He}(1,2) = (2!)^{-\frac{1}{2}} \begin{vmatrix} \phi_{1s}(1)\alpha(1)\,\phi_{1s}(1)\beta(1) \\ \phi_{1s}(2)\alpha(2)\,\phi_{1s}(2)\beta(2) \end{vmatrix}$$

$$\equiv (2!)^{-\frac{1}{2}} \det\{\phi_{1s}(1)\alpha(1)\phi_{1s}(2)\beta(2)\}$$

$$\equiv (2!)^{-\frac{1}{2}} \mid \phi_{1s}(1)\ \bar{\phi}_{1s}(2) \mid . \qquad (2\text{-}84)$$

Similarly for Li atom; we have one version of the wavefunction as

$$\Phi_{Li}(1,2,3) = (3!)^{-\frac{1}{2}} \begin{vmatrix} \phi_{1s}(1)\alpha(1)\,\phi_{1s}(1)\beta(1)\,\phi_{2s}(1)\alpha(1) \\ \phi_{1s}(2)\alpha(2)\,\phi_{1s}(2)\beta(2)\,\phi_{2s}(2)\alpha(2) \\ \phi_{1s}(3)\alpha(3)\,\phi_{1s}(3)\beta(3)\,\phi_{2s}(3)\alpha(3) \end{vmatrix} . \qquad (2\text{-}85)$$

i) If the electron label in 2 rows or columns is the same, this is equivalent to 2 electrons occupying the same quantum state, and the determinant vanishes.

ii) Interchanging two rows or columns (electrons) changes the sign of the determinant.

6. Summary and General HF Form

a. Wavefunction as Slater Determinant for N Electrons

$$\Phi = A_s \psi_1(\xi_1)\psi_2(\xi_2)\ \dots\ \psi_N(\xi_N) \qquad (2\text{-}86)$$

where

$$\psi_k(\xi) = \begin{cases} \phi_k(\underset{\sim}{r})\alpha(\sigma) \\ \phi_k(\underset{\sim}{r})\beta(\sigma) \end{cases} . \qquad (2\text{-}87)$$

$\psi_k(\xi)$ are called Molecular Spin Orbitals (MSO), and the form (2-86) is called the spin-unrestricted form. $\phi_k(\underset{\sim}{r})$ are the usual molecular orbitals (MO). The spin-restricted form of Φ is usually used:

$$\Phi = A_s\ \phi_1^\alpha(1)\ \alpha(1)\phi_2^\alpha(2)\ \alpha(2)\ \ldots\ \phi_p^\alpha(p)\ \alpha(p)$$

$$\times\ \phi_1^\beta(p+1)\ \beta(p+1)\phi_2^\beta(p+2)\ \beta(p+2)\ \ldots\ \phi_q^\beta(N)\ \beta(N) \qquad (2\text{-}88)$$

where

$$p + q = N \qquad (2\text{-}89)$$

$$\psi_i(\xi) = \phi_i^\beta(\underset{\sim}{r})\ \alpha(\sigma) \quad i = 1,\ldots,p \qquad (2\text{-}90)$$

$$\psi_{p+i}(\xi) = \phi_i^\beta(\underset{\sim}{r})\ \beta(\sigma) \quad i = 1,\ldots,q \qquad (2\text{-}91)$$

<u>Closed Shell</u>: A closed shell structure is defined as an antisymmetrised product in which all MOs are doubly occupied, and each shell, i.e., set of degenerate MOs is completely filled. Thus Be $1s^2\ 2s^2$ is a closed-shell, but C $1s^2\ 2s^2\ 2p^2$ is open-shell. For a closed-shell,

$$p = q = n\ , \qquad N = 2n \qquad (2\text{-}92)$$

and

$$\Phi = [(2n)!]^{-\frac{1}{2}}\,|\phi_1(1)\alpha(1)\phi_1(2)\beta(2)\ldots\phi_n(2n-1)\alpha(2n-1)\phi_n(2n)\beta(2n)| \qquad (2\text{-}93)$$

b. Energy Expression

With the Hamiltonian of eqn (2-4), this form of the wavefunction results into an energy expression which is a sum over orbitals:

$$E = \langle\Phi|H|\Phi\rangle$$

$$= 2\sum_{i=1}^{n} H_i + \sum_i^n \sum_j^n (2J_{ij} - K_{ij}) \qquad (2\text{-}94)$$

where

$$H_i = \int \phi_i^*\ h\ \phi_i\ dv$$

$$= \int \phi_i^*\ (-\tfrac{1}{2}\Delta - \sum_\alpha^M \frac{Z}{r_\alpha})\phi_i\ dv \qquad (2\text{-}95)$$

$$J_{ij} = \iint \phi_i^*(1)\phi_j^*(2)\left(\frac{1}{r_{12}}\right)\phi_i(1)\phi_j(1)dv_1dv_2$$

$$= [\phi_i\phi_i|\phi_j\phi_j] \quad (2\text{-}96)$$

$$K_{ij} = \iint \phi_i^*(1)\phi_j^*(2)\left(\frac{1}{r_{12}}\right)\phi_i(2)\phi_j(1)dv_1dv_2$$

$$= [\phi_i\phi_j|\phi_j\phi_i] \quad . \quad (2\text{-}97)$$

c. Hartree-Fock Equation

Carrying out variation on E by carrying out variations on the orbitals under orthogonality constraints, and defining potentials J_j and K_j by

$$J_j(1)\phi(1) = \int \frac{\phi_j^*(2)\phi_j(2)}{r_{12}} dv_2\cdot\phi(1) \quad (2\text{-}98)$$

$$K_j(1)\phi(1) = \int \frac{\phi_j^*(2)\phi(2)}{r_{12}} dv_2\cdot\phi_j(1) \quad (2\text{-}99)$$

the Hartree-Fock equations to be solved by SCF are

$$F\phi_i = \sum_j \phi_j \epsilon_{ji} \quad . \quad (2\text{-}100)$$

The Lagrangian **multiplier** matrix $\{\epsilon_{ij}\}$ is Hermitian:

$$\epsilon_{ji} = \epsilon_{ij}^* \quad . \quad (2\text{-}101)$$

Usually a unitary transformation is applied to this matrix to make it diagonal. The result of this transformation which leaves F and Φ invariant is **the** <u>canonical</u> <u>form</u> of the Hartree-Fock equations,

$$F\phi_i' = \epsilon_i\phi_i' \quad (2\text{-}102)$$

where

$$F = h + \sum_j (2J_j - K_j) \quad (2\text{-}103)$$

is called the Fock operator.

The canonical form corresponds to the usual chemical picture of shell structure, i.e., each electron pair put in an individual MO with a specific orbital energy of its own.

F. Hartree-Fock-Roothaan Finite Expansion Method [5,6]

1. Introduction

The HF integro-differential equations have been solved to a high degree of accuracy by numerical integration for many electron atoms [35] and small diatomics. [36] However, prospects for extension to larger molecules look bleak, even with the next generation of computers. There is also the unattractive feature of numerical methods, namely that the HF orbitals come out as numerical tables, which are unwieldy to use as basis functions for molecular calculations. Thus for some time to come, quantum chemists will have to live with the approximate expansion method of Roothaan.

Historically, Roothaan's method came from the idea of the LCAO-MO method. For example in Huckel's treatment of benzene, the MOs are expanded in terms of the actual free-atom p_z orbitals on each carbon. Thus LCAO can be a starting point for studying Roothaan. But it can be misleading especially as the method is used in atoms. A better way is to proceed as follows:

Again we take the He atom. In the above sections, we took $\Phi = \phi(\underset{\sim}{r}_1)\phi(\underset{\sim}{r}_2)$ and tried to solve HF equations in order to determine the best, optimal shape of ϕ, without a priori assigning the shape, in order to minimise $E = \langle\Phi|H|\Phi\rangle$.

Roothaan's idea is to expand ϕ in terms of a given number m of known analytical (basis) functions, and if the expansion is long enough, a good approximation to ϕ should result. The task is then to determine by variation the set of expansion coefficients for which the energy of the corresponding Slater determinant reaches its minimum.

For the Helium ϕ_{1s}, Roothaan used

$$\phi_{1s} = c_1 e^{-\zeta_1 r} + c_2 e^{-\zeta_2 r} + \ldots + c_n e^{-\zeta_n r} \qquad (2\text{-}104)$$

The basis functions are all 1s "Slater-Type orbitals" and are not orthogonal. This was a strange choice, contrary to the prevailing theoretical belief that expansion must be in terms of a complete, orthogonal basis set, and that a non-orthogonal basis would require prohibitively many terms. Roothaan's surprising finding was that very few terms are needed to get gratifyingly close to the HF result. In the He case as few as 5 terms give $E = -2.8616799$ a.u., compared with accurate value $E_{HF} = -2.8616800$ a.u.[37]. Even one term is not too bad, as we saw in Section 1. And in fact, an orthogonal basis does not give such a compact expansion. Thus non-orthogonality seems to be a necessary feature of the method.

Since Roothaan's paper, the expansion method has come a long way, and nowadays "near - HF" results calculated by this method are standard fare [38,39]. Besides STOs, other types of basis functions have been proposed and used [40], the most popular being the GTOs [40b,c]. Whatever the basis set, the Roothaan procedure most commonly used is as summarised below.

2. General Form of Roothaan's Method

Each MO or AO e.g., ϕ_{1s}, ϕ_{2s} in N atom or $\phi_{1\sigma g}$, $\phi_{1\sigma u}$ in N_2, is expressed as a linear combination of basis functions $\{\chi_p\}$.

$$\phi_i = \sum_{p=1}^{m} \chi_p c_{pi} , \qquad i = 1,\ldots,n \tag{2-105}$$

$m \geq n$, usually $m > n$. $\{\chi_p\}$ are normalised:

$$\int \chi_p^* \chi_p \, dv = 1 \tag{2-106}$$

but in general not orthogonal

$$\int \chi_p^* \chi_q \, dv = S_{pq} \neq 0 \quad \text{in general} \quad (p \neq q) \quad . \tag{2-107}$$

It is helpful to introduce matrix notation. Defining

$$\underset{\sim}{\chi} = [\chi_1, \chi_2, \ldots, \chi_m] \tag{2-108}$$

$$\underset{\sim}{c}_i = \begin{bmatrix} c_{1i} \\ c_{2i} \\ c_{3i} \\ \cdot \\ \cdot \\ \cdot \\ c_{mi} \end{bmatrix} \tag{2-109}$$

and

$$\underset{\sim}{c} = \begin{bmatrix} c_{11} & c_{12} & \cdots & c_{1n} \\ c_{21} & c_{22} & \cdots & c_{2n} \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ c_{m1} & c_{m2} & \cdots & c_{mn} \end{bmatrix} , \tag{2-110}$$

we may write

$$\phi_i = \chi\, \underset{\sim}{c}_i \qquad i = 1,\ldots,n \qquad m \geq n \tag{2-111}$$

and

$$\begin{aligned} \underset{\sim}{\phi} &= [\phi_1,\phi_2,\ldots,\phi_n] \\ &= \underset{\sim}{\chi}\, \underset{\sim}{c} \end{aligned} \tag{2-112}$$

As in Section E we consider the closed shell case and again the energy expression is the same as that given in equations (2-94)-(2-99) for the Hartree-Fock method.

Introducing the Roothaan expansion gives the HF structure in terms of the basis functions. We need new summations (with arbitrary summation indices)

$$\phi_i^* = \sum_{p=1}^{m} \chi_p^*\, c_{pi}^* \tag{2-113}$$

$$\phi_i = \sum_{q=1}^{m} \chi_q\, c_{qi} \tag{2-114}$$

$$\phi_j^* = \sum_{r=1}^{m} \chi_r^*\, c_{rj}^* \tag{2-115}$$

$$\phi_j = \sum_{s=1}^{m} \chi_s\, c_{sj} \tag{2-16}$$

to get

$$H_i = \sum_{p}^{m} \sum_{q}^{m} c_{pi}^* \langle \chi_p | h | \chi_q \rangle\, c_{qi} \tag{2-117}$$

$$J_{ij} = \sum_{pq}^{m} \sum_{rs}^{m} c_{pi}^*\, c_{qi}\, [\chi_p \chi_q | \chi_r \chi_s]\, c_{rj}^*\, c_{sj} \tag{2-118}$$

$$K_{ij} = \sum_{pq}^{m} \sum_{rs}^{m} c_{pi}^*\, c_{qi}\, [\chi_p \chi_s | \chi_r \chi_q]\, c_{rj}^*\, c_{sj} \;. \tag{2-119}$$

MO orthonormality is still needed:

$$\langle\phi_i \mid \phi_j\rangle = \delta_{ij} = \sum_{pq}^{m} c_{pi}^{*}\langle\chi_p \mid \chi_p\rangle\, c_{qj} \qquad (2\text{-}120)$$

$$E = 2 \sum_{i}^{n} \sum_{pq}^{m} c_{pi}^{*} \langle\chi_p|h|\chi_q\rangle\, c_{qi}$$

$$+ \sum_{ij}^{n} \sum_{pq}^{m} \sum_{rs}^{m} c_{pi}^{*}\, c_{qi}\, \{2[\chi_p\chi_q|\chi_r\chi_s]-[\chi_p\chi_s|\chi_r\chi_q]\}\cdot c_{rj}^{*}\, c_{sj} \,. \qquad (2\text{-}121)$$

The functional to be made stationary as in eqn (2-54) is now

$$I = E - 2 \sum_{ij}^{n} \epsilon_{ji} \,(\sum_{pq} c_{pi}^{*} \langle\chi_p|\chi_q\rangle\, c_{qj} - \delta_{ij}) \;; \qquad (2\text{-}122)$$

the $\{c_{pi}\}$ are now the variational parameters. We demand

$$\delta I = 0 \qquad (2\text{-}123)$$

under arbitrary variations

$$c_{pi}^{*} \longrightarrow c_{pi}^{*} + \delta c_{pi}^{*} \qquad (2\text{-}124)$$

etc., to get

$$\sum_{q}^{m} [\langle\chi_p|h|\chi_q\rangle + \sum_{rs}^{m} P_{pq,rs}\, (2 \sum_{j}^{m} c_{rj}^{*}\, c_{sj})]c_{qi}$$

$$= \sum_{j}^{n} \epsilon_{ji} \sum_{q}^{m} \langle\chi_p|\chi_q\rangle\, c_{qj} \qquad (2\text{-}125)$$

where

$$P_{pq,rs} = [\chi_p\chi_q|\chi_r\chi_s] - \frac{1}{2}\, [\chi_p\chi_s|\chi_r\chi_q] \qquad (2\text{-}126)$$

defines the two-electron "supermatrix", a kind of matrix whose 4 indices come in pairs, defining "super-rows" and "super-columns", with the Hermitian condition

$$\epsilon^{*}_{ji} = \epsilon_{ij} \quad . \tag{2-127}$$

Also defined is the density matrix, by

$$D_{rs} = 2 \sum_{j}^{n} c^{*}_{rj} \, c_{sj} \quad . \tag{2-128}$$

and the one-electron matrix

$$h_{pq} = \langle \chi_p | h | \chi_p \rangle \quad . \tag{2-129}$$

The Fock matrix is then

$$\underset{\sim}{F} = \underset{\sim}{h} + \underset{\sim}{P}\,\underset{\sim}{D} \tag{2-130}$$

where

$$(\underset{\sim}{P}\,\underset{\sim}{D})_{pq} = \sum_{rs} P_{pq,rs} \cdot D_{rs} \quad . \tag{2-131}$$

Then (2-125) becomes

$$\sum_{q}^{m} F_{pq} \, c_{qi} = \sum_{j}^{n} \left(\sum_{q}^{m} S_{pq} \, c_{qj} \right) \epsilon_{ji} \tag{2-132}$$

or

$$\underset{\sim}{F} \, \underset{\sim}{c}_i = \sum_{j} \underset{\sim}{S} \, \underset{\sim}{c}_j \, \epsilon_{ji} \tag{2-133}$$

or

$$\underset{\sim}{F} \, \underset{\sim}{c} = \underset{\sim}{S} \, \underset{\sim}{c} \, \underset{\sim}{\epsilon} \tag{2-134}$$

which is the Roothaan-Hartree-Fock equation.

This equation is a pseudo-eigenvalue problem, since the evaluation of $\underset{\sim}{F}$ operator requires knowledge of $\underset{\sim}{c}$, which the equation is supposed to determine. So it is solvable by SCF procedure. Usually also, the RHF equation is reduced to "canonical form" by a unitary transformation on $\underset{\sim}{\epsilon}$, to give

$$\underset{\sim}{\epsilon}' = \underset{\sim}{u}^{-1} \underset{\sim}{\epsilon} \underset{\sim}{u} \qquad (2\text{-}135)$$

where $\underset{\sim}{\epsilon}' = \epsilon_i \underset{\sim}{1}$ is diagonal. Then (2-134) takes the form

$$\underset{\sim}{F} \underset{\sim}{c}_i = \epsilon_i \underset{\sim}{S} \underset{\sim}{c}_i \qquad (2\text{-}136)$$

This is still not quite an eigenvalue problem, and there remains the diagonalisation of $\underset{\sim}{S}$ to reduce to

$$\underset{\sim}{F} \underset{\sim}{c}_i = \epsilon_i \underset{\sim}{c}_i \qquad i = 1,\ldots,m \qquad (2\text{-}137)$$

or

$$(\underset{\sim}{F} - \epsilon_i \underset{\sim}{1})\underset{\sim}{c}_i = 0 \qquad (2\text{-}138)$$

the secular equation.

The sequential steps for obtaining solutions to the Schroedinger equation in the Hartree-Fock-Roothaan approximation may be summarised as follows:

i) choose a basis set $\{\chi_p\}$ for each ϕ_i

ii) compute molecular integrals $\underset{\sim}{S}$, $\underset{\sim}{h}$ and $\underset{\sim}{P}$

iii) guess or estimate an initial electron distribution, i.e., initial vectors or $\underset{\sim}{c}^{OLD}$ matrix

iv) form density matrix $\underset{\sim}{D}$

v) form Fock matrix $\underset{\sim}{F}$ with equation (2-130)

vi) solve the Hartree-Fock-Roothaan equation (2-134). This needs diagonalisation of $\underset{\sim}{S}$ to give (2-137) and then of $\underset{\sim}{F}$, to give orbital energies and a new set of vectors or $\underset{\sim}{c}^{NEW}$ matrix.

vii) if this c^{NEW} is tolerably close to that in iii), stop. If not, go to iii) and replace $\underset{\sim}{c}^{OLD}$ with $\underset{\sim}{c}^{NEW}$.

3. The One-Center Expansion Method

In atoms, it is natural to place all basis functions $\{\chi_p\}$ of equation (2-105) on the atomic center. In molecules too, the most usual procedure has been to locate the basis functions on atomic centers, and is still loosely called LCAO. This method

i) is conceptually simple, because it is a straightforward way of constructing one-electron functions (MOs, $\{\phi_i\}$), which extend over the whole molecule. It is also in line with the chemical concept that molecules are made through the coming together of atoms, so molecular orbitals should also be constructed by (linear) combination of atomic orbitals.

ii) converges well towards the HF limit as the basis sets get larger.

The only difficulty with it, but an essential difficulty, is that it requires the evaluation of many difficult integrals involving atomic orbitals on two, three or four centers. To date this is the biggest bottleneck in molecular calculations, especially the two-electron integrals over STOs on more than two non-collinear centers. It has led to the virtual abandonment of STOs in favour of GTOs which, although inferior in describing electron distribution in many electron systems, result in more tractable integrals.

It was in search of a device to avoid these difficult multi-center integrals [7] that the One-Center Expansion method was developed. In this method, an attempt is made to simulate the total wavefunction using orbitals $\{\chi_p\}$ centered at one convenient point in space [41]. All the two-electron integrals are then one-center, as are the one-electron ones except the nuclear attraction integrals which are at most two-center. They are all easy to solve [12d]. The rest of the procedure is exactly the same as outlined in Section F2.

Conceptually, the OCE method is not so direct, especially for the ground state. It converges slowly, so that many more terms are required in the wavefunction to achieve a given accuracy than in LCAO. Nevertheless the simplicity of the integrals means that complicated functions can be handled easily, and atomic formulations can be taken advantage of even in molecules.

The essential drawback of the method is the difficulty in adequately describing the wavefunction in the immediate vicinity of the off-center nuclei, where the compact charge concentration is difficult to generate with functions at another point, even with many terms (see. Figure 1.1). In particular, it is completely impossible to expand inner shells on one atom in terms of STOs centered at another point.

This off-center cusp problem is smallest when the off-center nuclei are hydrogens, but becomes prohibitive for heavier nuclei. Thus the method was inherently restricted to hydrides (H_n or AH_n) with at most one heavy atom, which had to be taken as the expansion center.

In Chapter 4 we show how the One-Center Expansion method can be extended to evaluate electronic wavefunctions for molecules with non-hydrogen off-center nuclei, a prospect previously beyond reach. This extension is achieved through the use of model potentials to approximate the tightly bound core orbitals. The remaining, diffuse valence charge distribution is then rather easy to simulate using the One-Center Expansion method.

G. "Chemical" Properties of Hartree-Fock Wavefunctions

1. Introduction

As we develop the procedures for handling the numerical quantities involved in the "orbital model Schroedinger equation", we shall seem very far from the Schroedinger equation as a partial differential equation, and still further away from the chemical basis of the mathematics. But at various stages chemical intuition will be brought to bear on the mathematical forms and models to be used. In this section, we explore some of the information of chemical value which can be gleaned from HF theory.

Because of its mathematical structure, the Hartree-Fock or MO method provides a powerful model world which seems very similar to the real one, and is suitable for the qualitative discussion of molecular structures, chemical bonding, changes in chemical bonds and the excited electronic states of molecules.

Quantitatively, however, the record of Hartree-Fock calculations in mimicking experimental results to "chemical accuracy" has been less than outstanding.

The main strengths of the method, and also its weaknesses, lie in the orbital approximation on which it is based. Further features result from the kinds of approximations introduced in the solution of the Hartree-Fock equations, such as expansion basis set choices and approximations in the evaluation of integrals. In this section we try to discuss only the properties of accurate HFR wavefunctions which are near the HF limit.

2. Hartree-Fock Binding or Dissociation Energies

The HF ground-state dissociation energy is defined as the difference between the sum of the HF energies of the separated ground-state atoms and the HF energy of the molecule at its (computed) equilibrium geometry:

$$D_e = \sum_{\text{atom}} E_{HF}\,(\text{atom}) - E_{HF}\,(\text{molecule}) \tag{2-139}$$

It should be positive if the molecule is to exist.

Binding energies are useful in determining enthalpies of reaction, important quantities in discussion of chemical equilibria and mechanisms. HF binding energies are generally poor, smaller than experimental values by up to 30-40%. In some notorious cases, notably F_2 and MgO, the negative HF values predict no binding for the molecules, contrary to experiment. The reason for such glaring errors is that the binding energies are very small compared to the total energies (of the order of several percent) which must be subtracted. The intrinsic numerical errors associated with the subtraction of nearly equal quantities are added to the errors of calculating the total energies themselves.

These poor results have dramatised the basic deficiency of the orbital model, which is well known as the electron correlation energy problem, and is discussed next.

3. Electron Correlation Energy

In Section D, the two electrons in helium are assumed to occupy functions of the same form, as in equation (2-61). It is then conceivable that they could be at the same point in space, where the functions take the same value. Such a result is contrary to reality, since the repulsion potential $\frac{1}{r_{12}}$ between them becomes infinite in that case. A function which keeps the electrons apart in some manner or correlates their motions would be expected to be a better wavefunction and to yield a lower variational energy. Coulson has found such a function:

$$\Phi = N[e^{-\zeta_a r_1} e^{-\zeta_b r_2} + e^{-\zeta_a r_2} e^{-\zeta_b r_1}] \times \text{spin apart} \qquad (2\text{-}140)$$

where N is a normalisation factor. This wavefunction has been symmetrised to maintain indistinguishability of electrons, and the spin part is as in Section D. Its energy is $E = -2.876$ a.u. with $\zeta_a = 1.19$, $\zeta_b = 2.18$ compared to the Hartree-Fock limit of $E = -2.862$ a.u.

In the HF formulation for more than two electrons, electrons of parallel spins are correlated through the exchange potential terms which result from the Pauli principle; but those with opposing spins are not, and they could still occupy the same orbitals. If a proper account of electronic interactions is to be made, the motion of all the electrons must be correlated so that the position of one depends on the instantaneous position, rather than on the average position of the other.

Hartree-Fock total energies are thus the best possible in the orbital approximation of the wavefunction Φ, but not the best eigenvalues of the non-relativistic Schroedinger equation. The difference is usually defined [42] as the correlation energy:

$$E_{\text{correl}} = E_{\text{HF}} - E_{\substack{\text{exact}\\ \text{non-rel}}} \qquad (2\text{-}141)$$

The correlation energy can be of the order of several percent of the total energy, and is therefore very important, especially in problems of molecular binding since binding energies are of the same order of magnitude. It also changes between different states, so must be treated with care.

Various schemes have been devised to recoup the correlation energy lost by HF method.

One scheme due to Hylleraas [43a] is to explicitly include the interelectronic distances r_{12} as a variable in the wavefunction, and this yields the experimental energy. This in effect renounces the orbital picture. However, it quickly results in integrals which are very tedious to solve, and so has not been widely applied.

The most popular and successful methods, also apparently first discussed by Hylleraas [43b] are based on superposition of configurations which are Slater determinants constructed from HF orbitals. These are configuration interaction and multiconfiguration SCF methods. In effect, each configuration added affords each electron more scope for moving about, lowering the energy further. Again in these configuration superposition methods, chemical concepts such as electron pairs based on the orbital model become somewhat blurred.

4. Hartree-Fock Potential Curves and Surfaces

Potential energy surfaces are plots of the variation of the energy of a particular electronic state with the nuclear configuration of the nuclei.

We saw in Section C that the concept of potential energy surfaces plays an important role in theoretical chemistry:

i) Indeed the very structure or geometry of a molecule is defined as the equilibrium nuclear configuration at which the potential energy surface reaches a minimum. Where this minimum occurs and the shape of the surface about this point are used to determine spectroscopic constants (vibrational and rotational).

ii) The asymptotic behaviour at large inter-nuclear distances gives information on the dissociative behaviour of the molecule: what products are given in what states when the molecule dissociates? -- or conversely, what states of what entities come together to form the molecule? Which bonds are broken or formed?

iii) Bumps in the energy surface becomes interpreted as energy barriers. How well single-configuration HF potential energy surfaces mimic experimental band spectroscopic data therefore becomes an interesting question. Hurley [10] has analysed the theoretical potential surfaces (curves) for a number of diatomics and found that spectroscopic constants R_e, ω_e, $\omega_e x_e$ and α_e are quite well reproduced. The equilibrium distances R_e are generally less than 5% shorter than experimental ones. The shapes of the HF potential energy surfaces are found to be too steep, resulting in slightly too large values for ω_e.

But the dissociative behaviour of nearly all diatomics based on single configuration HF theory breaks down, as the surfaces tend to the wrong dissociation limits. Hurley concludes that HF wavefunctions are not good enough for interpreting the energetics of any chemical reaction involving the breaking or formation of a covalent bond. The culprit is correlation energy again, which may change drastically in such reactions.

Energy barriers to internal rotation, such as the rotational barrier between staggered and eclipsed geometries of C_2H_6 and the umbrella inversion barrier of NH_3 are found to be in good agreement with experiment.

Hurley concludes that for closed shell polyatomic molecules, HF calculations yield quite accurate molecular geometries, vibration frequencies and energy barriers to internal rotation.

5. Electron Binding Energies and Koopmans' Theorem

a. Concepts in Chemical Structure

The following are some of the concepts whose analysis is possible in terms of Hartree-Fock orbital energies:

i) Electron binding energies are the basis of the aufbau principle of building up atomic and molecular electronic structure, as it is taught in freshman chemistry [44]. The orbitals are ordered in increasing energy and filled up one by one according to some familiar rules.

ii) Ionisation potentials and electron affinities of atoms are important in determining the nature of their chemical bonds.

iii) Photo-electron spectroscopy (ESCA) has in recent years become a powerful analytical tool for the determination and interpretation of molecular structure [45]. It is concerned with the experimental study of both valence and inner-shell binding energies, which are found to be characteristic of each atom and its environment and so may be used in detection of particular atoms in mixtures.

In HF theory, the ionisation (binding) or excitation energies of an electron may be calculated by two methods, ΔSCF and Koopmans' Theorem.

b. ΔSCF Method

This is a straightforward method. Set up and solve separately the HF problem for both the initial state and the final state (after a particular electron has undergone the transition). The difference in the energies of the two states must be the proper binding energy of the electron affected, e.g., first ionisation potential of O is

$$\text{I.P.} = E_{tot}(O, {}^3P) - E_{tot}()^{+}, {}^4S) \quad . \qquad (2\text{-}142)$$

This can get rather cumbersome, as many states may need to be calculated.

c. Koopmans' Theorem [46]

According to this theorem, it is possible to estimate ionisation energies in one shot, i.e., by solving for the initial state only and looking at the orbital energies. A popular version of the theorem states: "Minus the Hartree-Fock orbital energy of an electron is approximately equal to its ionisation (binding) energy".

What Koopmans actually derived was more general. Although he dealt with spin-unrestricted HF theory (using equation (2-86)), we can demonstrate the features of his derivation in the restricted form of Roothaan for a closed shell. The assumptions are:

i) The ground state is given as in equations (2-93) and (2-94), in <u>any</u> representation $\{\phi_i\}$, canonical or not.

ii) The ionised state corresponding to removal of one electron from MO ϕ_i (assumed non-degenerate), may be represented by the same Slater determinant except that one function is missing:

$$\Phi_{i^-} = [(2n)!]^{-\frac{1}{2}} \det[\phi_1(1)\bar{\phi}_1(2) \ldots \phi_{i-1}(2i-3)\bar{\phi}_{i-1}(2i-2)\left\{\begin{matrix}\phi_i(2i-1)\\ \bar{\phi}_i(2i-1)\end{matrix}\right\}$$

$$\times\phi_{i+1}(2i+1)\bar{\phi}_{i+1}(2i+2)\ldots\phi_n(2n-1)\bar{\phi}_n(2n)] \ . \qquad (2\text{-}143)$$

The new Hamiltonian is

$$H_{2n-1} = \sum_{\mu=1}^{2n-1} h(\mu) + \sum_{\mu>\nu}^{2n-1} \frac{1}{r_{\mu\nu}} \ . \qquad (2\text{-}144)$$

The energy of this doublet state is

$$E({}^2\Phi_{i-}) = \langle\Phi_{i-}|H_{2n-1}|\Phi_{i-}\rangle \ . \qquad (2\text{-}145)$$

Analysis similar to that involved in (2-94) produces

$$\begin{aligned} E({}^2\Phi_{i-}) &= 2\sum_{j\neq i}^{n} H_j + H_i + \sum_{j\neq i}^{n}\sum_{k\neq i}^{n}(2J_{jk}-K_{jk}) + \sum_{j\neq i}^{n}(2J_{ij}-K_{ij}) \\ &= 2\sum_{j}^{n} H_j + \sum_{j,k}^{n}(2J_{ij}-K_{jk}) - H_i - \sum_{j}^{n}(2J_{ij}-K_{ij}) \\ &= E_0(\Phi) - H_i - \sum_{j}^{n}(2J_{ij}-K_{ij}) \ . \end{aligned} \qquad (2\text{-}146)$$

In this approximation, the energy required for removing one of the electrons in ϕ_i is

$$\begin{aligned} E({}^2\Phi_{i-}) - E_0(\Phi) &= - H_i - \sum_{j}^{n}(2J_{ij}-K_{ij}) \\ &= -\int\phi_i^*\{H - \sum_{j}^{n}(2J_i-K_j)\}\phi_i \, dv \\ &= -\langle\phi_i|F|\phi_i\rangle \\ &= -\epsilon_{ji} \ . \end{aligned} \qquad (2\text{-}147)$$

ϵ_{ii} is the general Lagrange multiplier of equation (2-100). If canonical orbitals are chosen, then $-\epsilon_i$ is taken as the estimate of the ionisation potential. But this choice would be rather arbitrary. Koopmans tried to put this choosing business on a variational footing. He sought to determine the best choice of ϕ_i which makes the energy of the ionised state

$$<\Phi_{i-}|H_{2n-1}|\Phi_{i-}> = E_0 - <\phi_i|F|\phi_i> \tag{2-148}$$

stationary, by allowing the ϕ_i to vary under the orthonormality constraint

$$<\phi_i|\phi_i> = 1 \quad . \tag{2-148a}$$

Now, any ϕ_i can be expanded in terms of the canonical orbital set $\{\phi_j'\}$, since the two sets are connected by a unitary transformation:

$$\phi_i = \sum_{j=1}^{n} c_j \phi_j' \quad . \tag{2-149}$$

$\{c_j\}$ may then become the variational paramaters, and $\{\phi_i\}$ are varying only within the occupied (Hartree-Fock) subspace of 2n electrons. The normalisation constraint becomes

$$<\phi_i|\phi_i> = 1 = \sum_j c_j^* c_j \tag{2-150}$$

and also

$$<\phi_i|F|\phi_i = \sum_j^n c_j^* c_j \epsilon_j \quad . \tag{2-151}$$

Variation under constraints is done as usual by the Lagrangian multiplier method; the functional we try to minimise is then

$$I = E_0 - \sum_j^n c_j^* c_j \epsilon_j + \lambda(\sum_j^n c_j^* c_j - 1) \quad . \tag{2-152}$$

where λ are Lagrangian multipliers. This is a linear variation problem We make I stationary with respect to each coefficient (and its complex conjugate)

$$\frac{dI}{dc_p} = 0 \tag{2-152a}$$

$$\frac{dI}{dc_p^*} = 0 \tag{2-152b}$$

leading to two sets of homogenous linear equations

$$(\lambda - \epsilon_p) c_p = 0 \quad , \qquad p = 1,\ldots,n \tag{2-153a}$$

$$(\lambda - \epsilon_p) c_p^* = 0 \quad , \qquad p = 1,\ldots,n \quad . \tag{2-153b}$$

For non-trivial solutions, the determinant in

$$\begin{bmatrix} \epsilon_1-\lambda & & & 0 \\ & \epsilon_2-\lambda & & \\ & & \ddots & \\ 0 & & & \epsilon_n-\lambda \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = 0 \tag{2-154}$$

must vanish, i.e.,

$$(\epsilon_1-\lambda)\ (\epsilon_2-\lambda)\ \ldots\ (\epsilon_n-\lambda) = 0 \quad . \tag{2-155}$$

There are n roots

$$\lambda = \epsilon_i \quad , \qquad i = 1,\ldots,n \tag{2-156}$$

representing n stationary values of the functional I. ϵ_n is the smallest root. Koopmans looked at each particular root $\lambda = \epsilon_i$. For this, the secular equations (2-153 a, b):

$$c_p = 0 \qquad p \neq i \tag{2-157a}$$

and

$$c_i = 1 \tag{2-157b}$$

from normalization, giving

$$I = E_0 - \epsilon_i \tag{2-158}$$

From (2-149)

$$\phi_i = \phi_i' \,, \tag{2-159}$$

meaning the canonical orbital is the one which makes $\langle\phi_{i-}|H_{2n-1}|\phi_{i-}\rangle$ stationary, with value

$$\langle\phi_{i-}|H_{2n-1}|\epsilon_{i-}\rangle = E_0 - \epsilon_i \,. \tag{2-160}$$

Thus a statement of Koopmans' theorem may go [46b] "Minus the eigenvalues $(-\epsilon_i)$ of the canonical HF equations provides a good estimate of the ionisation potentials of an atom or molecule". But one can go further and ask for the LOWEST stationary value of I. Clearly, this occurs when $\lambda = \epsilon_n$, since E_0 is negative, giving

$$I = E_0 - \epsilon_n \,. \tag{2-161}$$

The choice $\lambda = \epsilon_n$ automatically chooses $i = n$ in (2-149), i.e., $\phi_i = \phi_n'$. Remembering that E_0 is negative, the minimum energy of the ionised state is

$$\langle\phi_{i-}|H_{2n-1}|\phi_{i-}\rangle = E_0 - \epsilon_n \,. \tag{2-162}$$

Thus, the highest occupied molecular orbital (HOMO) ϕ_n' does give the best approximation to forming an ionised state and $-\epsilon_n$ gives the best estimate of the first ionisation energy of the system within the Hartree-Fock subspace of 2n electrons.

Koopmans hinted at a similar analysis for the electron affinity, i.e., addition of an electron into a virtual orbital x. The energy of the ion is then

$$\langle\phi_{x+}|H_{2n+1}|\phi_{x+}\rangle = E_0 + \langle\phi_x|F|\phi_x\rangle \ . \qquad (2\text{-}163)$$

And this quantity is also best minimised when x is the lowest unoccupied MO (LUMO).

Koopmans' theorem is usually invoked for the interpretation of photoelectron spectra. Hartree-Fock orbital energies usually give, by Koopmans' theorem, ionisation potentials which are larger than the experimental values. Typical errors range from 1-10%. In some cases such an error is sufficient to produce reversed ordering of levels which are close to each other, as in the notorious case of the $3\sigma_g$ and $1\pi_u$ levels of N_2.

The errors in Koopmans IPs are due to the failure to allow for relaxation of the orbitals after ionisation. Such relaxation can only be captured by using the true stationary values of $\langle\phi_{i-}|H_{2n-1}|\phi_{i-}\rangle$ in the full functional space for (2n-1) electrons, that is by separate calculations. That is why ΔSCF IP's are usually closer to the experimental values [47a].

6. Molecular Symmetry in HF Theory

The marriage of group theory to quantum mechanics, especially at the orbital level, results in many attractive features which explain many chemical concepts. Group theory is a mathematical tool which allows the use of symmetry properties to be made in an exact and complete manner [48]. It provides a powerful means of simplifying the problem of finding the electronic wavefunctions. It also provides a direct linkage to the language of spectroscopy, dealing with spectral transitions between states and their selection rules.

A knowledge of the symmetry properties of MOs has led to breakthroughs in the prediction of shapes of molecules, the kinds of reactions they may undergo, and the mechanisms of these reactions. Indeed ideas like Walsh's Rules, Jahn-Teller Effects, Woodward-Hoffmann Rules, Wigner-Witmer Rules, Fukui's Frontier Orbitals (HOMO-LUMO) and Pearson's Symmetry Rules, have now become classic in the discussion of molecular structure and chemical reaction [49].

a. Symmetry Properties of the Total Wavefunction

It all starts with the Hamiltonian of equation (2-18b), which is invariant under the operations of the point group of the molecule, i.e., under operations which interchange like nuclei to produce an indistinguishable configuration. It follows that the exact wavefunction(s) of a particular electronic state k as given in equation (2-18a) belong(s) to an irreducible representation of the symmetry group. The wavefunctions of various states can be classified according to the symmetry species to which they belong.

Roothaan [5] proved the gratifying result that Hartree-Fock wavefunctions have similar properties to the exact ones. For a closed-shell ground state, the HF wavefunction given as in equation (2-93), belongs to the identical representation of the molecular point group, i.e., it is a singlet and totally symmetric, ^1S for atoms and $^1\Sigma^+$ for molecules. Other HF states can be similarly classified.

One implication of this result is that statements may be made *a priori* about which HF states may interact and which spectroscopic transitions are allowed under some stimulus or perturbation. Selection rules are based on the theorem that a transition or interaction between states i and j, caused by a perturbation or operator P is allowed only if the transition integral or matrix element

$$P_{ij} = \int \Psi_i \, P \, \Psi_j \, d\tau \tag{2-164}$$

is non-zero. The intensity of the transition is proportional to P_{ij}. P may be electric or magnetic multipoles, polarisability tensors, or the Hamiltonian operator, etc.

Theorem: According to group theory, the integral (2-164) vanishes unless the direct product of Ψ_i, P and Ψ_j contains the totally symmetric representation. This is so only if the direct product of two entities contains the representation of the third. In the case of a totally symmetric operator such as H, the integral is non-zero only if Ψ_i and Ψ_j belong to the same irreducible representation.

All this gives rise to the powerful Brillouin's theorem [47b], which is used in perturbation theory, in assessing the accuracy of one-electron properties calculated using HF wavefunctions, and in determining which configurations may be superposed in multi-configuration techniques.

b. Symmetry Properties of MOs

The Fock operator of equation (2-103) is also invariant under the operations of the molecular point group. Its eigenfunctions, namely the HF MOs even in the expansion form, may therefore be grouped in sets each of which forms the basis for an irreducible representation of the point group. This gives a convenient recipe for choosing expansion basis functions. More will be said about this in Chapter 6.

The theorem in Section **a** may then be applied to the MOs themselves. For a symmetric operator M such as those arising in H-F-R procedure,

$$<\phi_i|M|\phi_j> = 0 \qquad (2\text{-}165)$$

$$<\chi_p|M|\chi_q> = 0 \qquad (2\text{-}166)$$

if ϕ_i and ϕ_j or χ_p and χ_q belong to different irreducible representations. This means that we know beforehand that these integrals vanish identically, so no need to waste time calculating them. In Roothaan's expansion method, it also means that all matrices of formulas (2-130)-(2-138) may be reduced to simpler block diagonal forms to be dealt with separately. This is a considerable simplification. Hybridisation is also a concept that can come naturally out of such considerations.

c. MOs, Geometry and Reaction

Mechanisms of reactions can be derived, and even activation energies estimated, by watching the correlation of MOs as atoms or molecules come together or apart. This is done under strict symmetry constraints such as non-crossing rules and conservation of symmetry. Similarly, shapes of simple molecules have been deduced by noting what happens to MOs as the geometry is changed smoothly. A new era of mechanistic theory based on Hartree-Fock calculations may be in the making.

CHAPTER III

THE MODEL POTENTIAL APPROXIMATION

A. Introduction

For many years, chemists and physicists have realised that the chemical and physical properties of atoms are mainly determined by only the few outer "valence" electrons, the "core" taking little part. Indeed, Mendeleyev's concept of the Periodic Table was derived from this idea [50]. Thus he arranged his Table in such a way that elements in the same column (group)

i) have similar chemical properties (e.g., the alkali elements form similar Halide compounds, for example HCℓ, NaCℓ, KCℓ)

ii) have similar electronic spectra (e.g., it is well known that the spectra of the alkaline-earth atoms Be, Mg, Ca, Sr and Ba are essentially 2-electron spectra).

In describing the nature of the chemical bond, then, one needs to focus attention only upon the few outer electrons of each atom. This is the basis of G.N. Lewis' beautiful system of chemical bonding. In this scheme, the driving force is the desire of each atom to attain a "noble-gas" electron configuration, usually an "octet" in its outermost shell, by gaining, losing or sharing valence electrons.

This concept of separability of an atomic or molecular system into "relevant" and "unimportant" regions has long been a part of chemical intuition, and appears in other cases, e.g.

i) σ and π electrons in conjugated systems

ii) functional groups in organic chemistry

iii) "valence" and "core" regions in spatially separated but interacting systems, e.g., a molecule or a metal. The "valence" electrons move throughout the system, while the "core" electrons are considered localised.

However, for ab initio quantum mechanical calculations of atomic and molecular properties, all the electrons of the atom must be included. In order to find the motions or states of the valence electrons, one needs to know the wavefunctions of all the core electrons. This is because the nuclear charge is partially screened by the surrounding core electrons, and also the valence electron wavefunctions must be orthogonal to the core functions.

The goal of the model or pseudo-potential has been to make it possible to determine the quantum mechanical states of the "relevant" region ACCURATELY, without explicit concern for the "unimportant" region. This requires the replacement of the "unimportant" part by some effective potential.

The first attempts were made in 1935 by Hellman [51] and Gombas [52] to approximate, for example, the ten core-electrons of sodium $[1s^2, 2s^2, 2p^6]3s^1$ by an appropriate effective potential, thus reducing an 11-electron problem to a 1-electron problem. Since then, the method of pseudo-potentials has been used in solid state physics [53] and in the application of quantum mechanics to atomic and molecular problems [54]. But in the last five or six years, there has been a resurgence of interest in the method, as its potential accuracy and practicality have become more apparent [4]. It is not unreasonable to predict that when fully understood and made to work properly the model potential method will take its place beside, if not transcend, semi-empirical methods in the near future.

As was realised by the earliest workers, the effective potential must account for two effects of the inner-electron cloud:

i) electrostatic shielding of the nucleus

ii) the repulsive effect due to Pauli exclusion: roughly, this is an orthogonality requirement between the core and valence orbitals, which "holds up" the valence shells and prevents their possible variational collapse into the core region.

However, there is no unique solution to such a problem. So a number of compelting approaches ahve been suggested and used, with some success, to achieve the same purpose. They fall into two classes:

i) Semi-empirical [51, 52, 55]. These adjust the parameters of the effective potential to match some experimental data, for example excitation or ionisation energies.

ii) Non-empirical or "semi-<u>ab initio</u>" [56]

These theoretically based methods calibrate the effective potential to mimic the results of standard <u>ab initio</u> calculations.

B. Semi-Empirical Potentials

Hellman investigated the following question: [55a] What kind of potential field does the single valence electron of an atom such as sodium, if the valence wavefunction is a nodeless (Slater-type) orbital ϕ_0? He suggested a simple static positive repulsive potential in addition to the Coulomb attraction of the shielded nucleus:

$$V_H = -\frac{(Z-n_c)}{r} + A\,\frac{e^{-2kr}}{r} \qquad (3\text{-}1)$$

where n_c is the number of core electrons, Z the atomic number; and A and K are parameters to be determined semi-empirically in the following way: The Schroedinger equation for the valence electron is

$$H_v \phi_0 = E \phi_0 \tag{3-2}$$

or

$$\{ -\frac{1}{2}\Delta - \frac{Z-n_c}{r} + A\,\frac{e^{-2kr}}{r} \}\phi_0 = E\,\phi_0 \tag{3-3}$$

where

$$\phi_0(\underset{\sim}{r}) = R_{n\ell}(r)\; Y_{\ell m}(\theta,\phi) \quad . \tag{3-4}$$

$R_{n\ell}$ is a hydrogen-like radial function and $Y_{\ell m}(\theta,\phi)$ are the normalised spherical harmonics. For the ground state, the first excited P state, and the first excited S state, we may put

$$R_{1s} = e^{-\epsilon r} \tag{3-5}$$

$$R_{2p} = r\, e^{-\omega r} \tag{3-6}$$

$$R_{2s} = [1 - \frac{1}{3}(\epsilon+\eta)]e^{-\eta r} \tag{3-7}$$

where ϵ, ω, η are variational parameters. With these functions we calculate the minimum of the energy expression

$$\begin{aligned} E &= <\phi_0|H_v|\phi_0>/<\phi_0|\phi_0> \\ &= [\int\phi_0^*\{-\frac{1}{2}\Delta - \frac{Z-n_c}{r} + A\,\frac{e^{-2kr}}{r}\}\phi_0 dv]\,/(\int\phi_0^*\phi_0 dv) \quad . \end{aligned} \tag{3-8}$$

There are five constants to be caluclated A, K, ϵ, ω, η. These are determined under the requirements that the energy minimum E_{1s} calculated with (3-8) should agree exactly with the experimental values; and for the two excited states, the minimum E_{2s} and E_{2p} calculated with (3-6) and (3-7) should approximate the experimental value as closely as possible.

Since then, more general forms of the Hellmann potential in eqn (3-1) have been used, with fits to a larger number of experimental excitation energies [55].

C. Semi-*Ab Initio* Potentials

1. Introduction

Phillips and Kleinman,[53a] in their treatment of the solid state, were the first to put pseudo-potentials on a firm theoretical basis. They derived a theoretical pseudo-potential form based on Hartree-Fock theory for a single valence electron outside a closed shell core.

Like Hellmann and Gombas, they sought a radially "smooth", i.e., nodeless, valence pseudo-wavefunction with the correct orbital energy, an approach which was of great relevance to the theory of solids, especially metals. According to Hartree-Fock theory, the true valence wavefunction must be orthogonal to all the core wavefunctions. The manipulation of this requirement is the key to their success.

The Phillips-Kleinman idea has been formally generalised to systems with many valence electrons [54] and forms the basis for the majority of effective potentials which have been proposed to date. The hall-mark of the method is that it searches *a priori* for a radially smooth or nodeless pseudo-valence orbital.

A different school of thought has proposed effective potentials in which the exact "noded" valence orbital can be obtained, but with the option of deleting the nodes if necessary [23, 56b].

In this section, we shall not try to give a rigorous derivation of the model potential method. Instead, we shall attempt to demonstrate the essential features and justification of the precedure by considering some examples.

2. Excited State of a Hydrogen-Like Atom

For a one-electron atom, the problem is exactly solvable [57]. The Schroedinger equation is simply

$$(-\frac{1}{2}\Delta - Z/r)\phi_i(r) = E_i\ \phi_i(r) \qquad (3\text{-}9)$$

where the parameter Z is not restricted to integer values. Introducing spherical polar coordinates (r,θ,ϕ), the kinetic energy (Laplacian) operator takes the form

$$\begin{aligned}\Delta &= \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2}\Lambda \\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda \qquad (3\text{-}10)\end{aligned}$$

where

$$\Lambda = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\theta^2}\ . \qquad (3\text{-}11)$$

In this coordinate system, separation of variables is possible into radial and angular components:

$$\phi(r,\theta,\phi) = R(r)\ Y(\theta,\phi) \tag{3-12}$$

where $Y(\theta,\phi)$ satisfy the eigenvalue equation

$$\Lambda\, Y_{\ell m}(\theta,\phi) = -\ell(\ell+1)\ Y_{\ell m}(\theta,\phi)\ , \qquad \ell = 0,1,2,3,\ldots \tag{3-13}$$

and

$$Y_{\ell m}(\theta,\phi) = (-1)^{(m+|m|)/2}\left[\frac{2\ell+1}{2\pi}\cdot\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2} P^{|m|}(\cos\,\phi)\,e^{im\phi}$$

$$m = 0,\ \pm\,1,\ \pm\,2,\ \ldots,\ \pm\,(\ell-1),\ \pm\,\ell\ . \tag{3-14}$$

The radial equation is then, for a bound state $(E < 0)$,

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} + \frac{(\ell+1)}{2r^2} - \frac{Z}{r}\right] R_{n\ell}(r) = E_n R_{n\ell}(r) \tag{3-15}$$

with

$$E_n = -\frac{1}{2}\frac{Z^2}{n^2}\ , \qquad n = 1,2,3,\ldots \tag{3-16}$$

and

$$R_{n\ell}(r) = \frac{1}{(2\ell+1)!}\left[\frac{(n+\ell)!}{(n-\ell-1)!\,2n}\right]^{1/2}\left(\frac{2Z}{n}\right)^{3/2} e^{-\frac{Z}{n}r}\left(\frac{2Zr}{n}\right)^{\ell}$$

$$\times\ F\left(-n+\ell+1,\ 2\ell+2;\ \frac{2Zr}{n}\right) \tag{3-17}$$

where

$$F(a,c;x) = 1 + \frac{a}{c}\frac{x}{1!} + \frac{a(a+1)}{c(c+1)}\frac{x^2}{2!} + \ldots\ , \tag{3-18}$$

are confluent hypergeometric functions. The lowest solutions are of the form

$$\phi_{1s} \sim e^{-Zr} \tag{3-19}$$

$$\phi_{2s} \sim (1-(Z/2)r)e^{-(Z/2)r} \qquad (3\text{-}20)$$

$$\phi_{2p} \sim re^{-(Z/2)r} . \qquad (3\text{-}21)$$

The ground state ϕ_{1s} is radially nodeless, as is the ϕ_{2p}, while ϕ_{2s} has one radial node. The three are mutually orthogonal. Also from (3-16), it is seen that in the one-electron atom, the 2s and 2p orbitals are accidentally degenerate, a situation not seen in many-electron systems.

The question addressed in the model potential procedure is: What kind of Hamiltonian must we construct to obtain the 2s orbital as the lowest solution, if the 1s orbital is known exactly? Clearly, it must be different from the Hamiltonian of equation (3-9), whose lowest solution is always ϕ_{1s}. New terms must be added, whose work is to unseat the 1s level from this position and shift it elsewhere or eliminate it altogether. We examine two model terms which can do this job.

a) Core projection operators [23,53a]

Consider a model Hamiltonian of the form

$$H_{vm} = -\frac{1}{2}\Delta - \frac{Z}{r} + B|\phi_{1s}><\phi_{1s}| \qquad (3\text{-}22)$$

where

$$|\phi_{1s}><\phi_{1s}|f> = \phi_{1s} \int d\tau\, \phi_{1s}^{*}(\underset{\sim}{r})f(\underset{\sim}{r}) \qquad (3\text{-}23)$$

defines a projection operator and B is some constant factor. The model Hamiltonian has the following properties:

i) ϕ_{2s} is indeed a solution, with energy E_{2s}.

Proof:

$$H_{vm}|\phi_{2s}> = \{-\frac{1}{2}\Delta - \frac{Z}{r} + B|\phi_{1s}><\phi_{1s}|\}|\phi_{2s}>$$

$$= \{-\frac{1}{2}\Delta - \frac{Z}{r}\}|\phi_{2s}> + B|\phi_{1s}><\phi_{1s}|\phi_{2s}> \quad . \tag{3-24}$$

But

$$<\phi_{1s}|\phi_{2s}> = 0 \tag{3-25}$$

from orthogonality condition.

$$\therefore \quad H_{vm}|\phi_{2s}> = \{-\frac{1}{2}\Delta - \frac{Z}{r}\}|\phi_{2s}> \tag{3-26}$$

and by (3-9)

$$H_{vm}|\phi_{2s}> = E_{2s}|\phi_{2s}> \quad . \tag{3-27}$$

Thus the model Hamiltonian can produce the 2s (or 2p) orbital exactly.

ii) What H_{vm} does to ϕ_{1s} is a different matter. Using (3-22), we get

$$H_{vm}|\phi_{1s}> = \{-\frac{1}{2}\Delta - \frac{Z}{r}\}|\phi_{1s}> + B|\phi_{1s}><\phi_{1s}|\phi_{1s}>$$

$$= E_{1s}|\phi_{1s}> + B|\phi_{1s}>$$

$$= (E_{1s} + B)|\phi_{1s}> \quad . \tag{3-28}$$

Thus $|\phi_{1s}>$ is also an exact eigen solution to H_{vm}, except that its eigenvalue is <u>shifted</u> by B.

iii) Arbitrariness - As shown in ii) above, the ϕ_{1s} can be obtained exactly (as to shape). However, its orbital energy can be shifted artifically to anywhere we like, by changing the value of B.

This arbitrariness has been exploited in various ways [58]. Here we show how its manipulation results into either a Phillips-Kleinman pseudopotential [53a] or a Bonifacic-Huzinaga model potential [23] as special cases.

iv) Phillips-Kleinman pseudopotential [53a]. In (3-22), put

$$B = E_{2s} - E_{1s} \; ; \tag{3-29}$$

to give the Phillips-Kleinman model Hamiltonian

$$H_{vm}^{PK} = -\frac{1}{2}\Delta - \frac{Z}{r} + (E_{2s}-E_{1s})|\phi_{1s}><\phi_{1s}| \quad . \tag{3-30}$$

The result is that the 1s level is tucked exactly into the 2s level, so that they are degenerate:

$$H_{vm}^{PK}|\phi_{1s}> = E_{2s}|\phi_{1s}> \tag{3-31a}$$

$$H_{vm}^{PK}|\phi_{2s}> = E_{2s}|\phi_{2s}> \quad . \tag{3-31b}$$

Therefore <u>any</u> linear combination of these functions is also an eigenfunction with same eigenvalue:

$$H_{vm}^{PK}|\chi_{2s}> = E_{2s}|\chi_{2s}> \tag{3-31c}$$

where

$$\chi_{2s} = C_1\,\phi_{1s} + C_2\,\phi_{2s} \quad . \tag{3-31d}$$

Thus one may say that the arbitrariness has been moved from the orbital energy of the 1s to the orbital shape of the 2s, but it has not been removed. In the PK scheme and its descendants this arbitrariness is used to construct a nodeless χ_{2s} orbital by judiciously admixing some of the 1s in order to remove the inner nodes wholly or in part.

v) Bonifacic-Huzinaga Scheme [23]. In (3-22) put

$$B = x|E_{1s}| \tag{3-32}$$

where

$$x \geq 1.0 .$$

This shifts the 1s level very high into the virtual manifold, so that the electron is discouraged from ever occupying it. The lowest energy is the E_{2s}, and uniqueness is maintained in the 2s orbital. If the inner node is not wanted, it is removed in other ways, as we see in a later section.

b. Centrifugal Potentials [56a]

One may ask: If we want a radially nodeless excited orbital, why not aim for the 2p orbital which has the same energy as the 2s? Our model Hamiltonian must then contain a term which suppresses the 1s and 2s orbitals, and selects the 2p as the lowest solution.

The way to do this is illuminated by a look at the radial equation (3-15). The 1s and 2s orbitals are solutions to the differential equation with $\ell = 0$:

$$(-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{Z}{r})\ R(r) = ER(r) \tag{3-33}$$

while the 2p is the lowest solution to the $\ell = 1$ version:

$$(-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} + \frac{1}{r^2} - \frac{Z}{r})\ R(r) = ER(r) \tag{3-34}$$

This suggests that if we construct a new Hamiltonian with a repulsive term added,

$$H_{vm} = -\frac{1}{2}\Delta - \frac{Z}{r} + \frac{1}{r^2} \qquad (3\text{-}35)$$

its eigenvalue equation

$$\hat{H}_{vm}\,\phi = E\phi \qquad (3\text{-}36)$$

will have a radial component which looks like this:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{Z}{r} + \frac{\ell(\ell+1)}{2r^2} + \frac{1}{r^2}\right] R'_{n\ell}(r) = ER'_{n\ell}(r)\ . \qquad (3\text{-}37)$$

Putting $\ell = 0$ eliminates the term in $\ell(\ell+1)$, makes (3-37) the same as (3-34). The lowest solution (R'_{10}) then has the radial part of the 2p, but the angular part $(\ell = 0)$ of an s orbital. This is precisely what a 2s Slater Type Orbital has, and we could have arrived at the model Hamiltonian (3-35) by asking "Which differential equation do STOs satisfy?" Huzinaga has shown [40c] that a normalised STO

$$\psi_s = (n_s, \ell, m, \zeta_s, \frac{Z}{n_s}) = R_{n_s}(r)\, Y_{\ell m}(\theta,\phi) \qquad (3\text{-}38)$$

where

$$R_{n_s}(r) = (2n_s)!^{-\frac{1}{2}}\,(2Z/n_s)^{n_s+\frac{1}{2}}\, r^{n_s-1}\, e^{-(Z/n_s)r} \qquad (3\text{-}39)$$

and the parameter Z is not restricted to integer values, satisfies the equation

$$H_s\,\psi_s = E\psi_s \qquad (3\text{-}40)$$

where

$$H_s = -\frac{1}{2}\Delta - (Z/r) - \frac{1}{2r^2}\left[\ell(\ell+1) - n_s(n_s-1)\right] \qquad (3\text{-}41)$$

$$E = -\frac{1}{2}(Z/n_s)^2 \quad . \tag{3-42}$$

The first term of the "additional potential"

$$-\frac{1}{2r^2}\,[\ell(\ell+1) - n_s(n_s-1)] \tag{3-43}$$

cancels out the angular part of the kinetic energy operator when the polar coordinate system is introduced. Thus the radial component of H_s is

$$-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{Z}{r} + \frac{n_s(n_s-1)}{2r^2} \tag{3-44}$$

which, for a 2s STO with $n_s = 2$, is the same as the operator in equation (3-34). The repulsive term in r^2 dominates at short r.

Unfortunately the static repulsive potential in (3-37) or (3-44) is not sufficient, as it says nothing about the angular dependence of the solution. This is incorporated by introducing an angular momentum projection operator:

$$H_{vm} = -\frac{1}{2}\Delta - \frac{Z}{r} + \frac{1}{r^2}\,|\ell\rangle\langle\ell| \tag{3-45}$$

where in this case $\ell = 0$. This ensures that the solution is s-type, and in general selects spherical harmonics of a given ℓ value.

These ideas underlie all those model potential schemes which use a static repulsive potential with angular momentum projection [4,56a]

$$H_{vm} = -\frac{1}{2}\Delta - \frac{Z}{r} + \sum_{\ell}^{\ell\,\max} V_\ell(r)\,|\ell\rangle\langle\ell| \tag{3-46a}$$

or incorporating the $-\frac{Z}{r}$ term in $V_\ell(r)$,

$$H_{vm} = -\frac{1}{2}\Delta - \sum_{\ell}^{\ell\,\max} V_\ell(r)\,|\ell\rangle\langle\ell| \tag{3-46b}$$

where ℓ max is the maximum ℓ in all lower states. $V_\ell(r)$ is different for each ℓ, and in general it is calibrated to be attractive in the outer region, repulsive in the inner region of the atom.

3. Electrostatic Shielding Due to Core Electrons

In paragraph two, we have considered the problem of an electron in a higher level, but with no inner electrons to complicate matters. The static attraction potential was then that of the bare nucleus, $-\frac{Z}{r}$. The case of valence electron outside a closed shell can be considered as a simple extension to the one-electron case, affecting only this attraction term.

Consider a Li atom, $Z = 3$. It is known that even a valence electron penetrates the core region to some extent. Close to the nucleus, it should see the full, bare nuclear potential, $-\frac{3}{r}$, and far away it sees the completely shielded potential $-\frac{1}{r}$. The tradition has been to add terms to the bare nuclear potential which reflect this smooth transition, in order to reproduce the correct valence orbital energies and shapes. Figure 3.1 shows how the model potential might look, in the similar case of Be atom.

Typically [4,23,56a], the static attractive term is of the form

$$V_m(r) = -\frac{(Z-n_c)}{r} - \sum_j A_j\, r^{n_j} \frac{e^{-\alpha_j r}}{r} \quad (-47)$$

where n_c is number of core electrons, and A_j, α_j are parameters of the model to be calibrated.

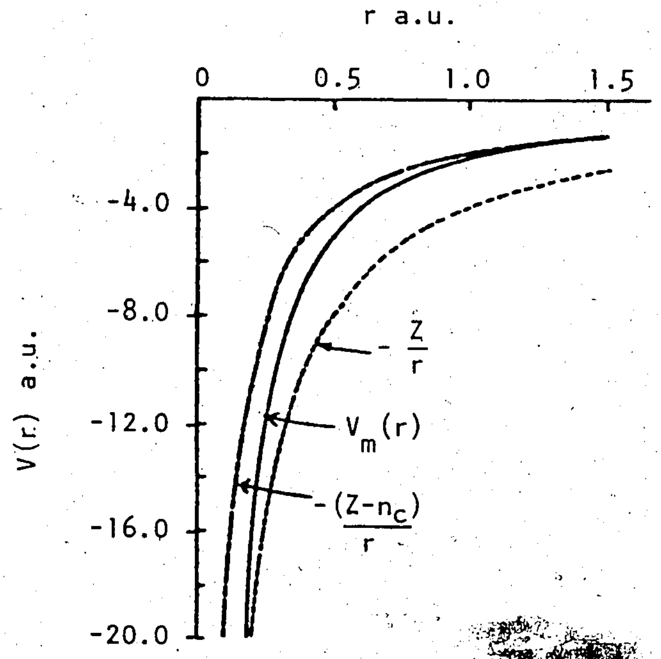


FIG. 3.1 Model potential as a smooth intermediate between bare and fully shielded nuclear potentials. Be case $Z=4$, $n_c=2$.

It may be tempting to think that the adjustment of the static potential above would be sufficient to produce the desired 2s orbital without the repulsive terms of Section 2. But a simple illustration will dispel this misconception.

In the case of Lithium atom, the correct 2s HF orbital energy is [38] $E_{2s}^{Li} = -0.19632$ a.u. Suppose we assume complete core shielding of the 2s electron and solve the one-electron problem of equation (3-9) with $Z = 1$. The resulting orbital energy as given by (3-13) will be that of a hydrogen 1s orbital, i.e., $E_{1s} = -0.5$ a.u. And with no shielding, i.e., $Z = 3$, equation (3-13) gives $E_{1s} = -4.5$ a.u. Both these values are clearly lower than the required value, and are indeed pseudo - 1s orbital energies. They illustrate the so-called collapse of the valence orbital into the core region. It is the job of the repulsion terms of Section 2 to prevent this collapse by enforcing some kind of Pauli principle. Indeed, even the repulsive static potentials of equation (3-30) were not complete till an ℓ-dependent projection operator was introduced.

4. Extension to Many Valence-Electron Systems

In addition to experiencing the static and Pauli Principle interactions of the core, each valence electron will interact with the other valence electrons in the usual manner. The model Hamiltonian for valence electrons may then be written as

$$H_{vm} = \sum_{i=1}^{nv} [-\frac{1}{2}\Delta_i + V_m(i)] + \sum_{i>j}^{nv} \frac{1}{r_{ij}} \qquad (3\text{-}48)$$

where $V_m(i)$ is the effective core potential containing the static core shielding potential and the repulsive effect due to the Pauli exclusion principle.

In summary, all pseudo- or model potential schemes which have been proposed essentially fall into three basic categories defined by the form of $V_m(i)$:

i) Core projection with degeneracy [59], giving a pseudo valence orbital,

$$V_m = V(r) + \sum_c (\epsilon_r - \epsilon_c)|\phi_c\rangle\langle\phi_c| \quad . \tag{3-49}$$

ii) Core projection without degeneracy [23,56b]. Exact valence orbital if necessary,

$$V_m = V(r) + \sum_c B|\phi_c\rangle\langle\phi_c| \quad . \tag{3-50}$$

In i) and ii) $V(r)$ is purely attractive static potential.

iii) Repulsive static potentials with angular momentum projection[56a] Smooth pseudo valence orbital,

$$V_m = \sum_{\ell}^{\ell\, max} V_\ell(r)|\ell\rangle\langle\ell| \quad . \tag{3-51}$$

As we have seen, model potentials are aimed at economisation of molecular calculations. But first, they must be calibrated in atomic calculations. The parameters of the model potentials are usually adjusted so as to reproduce the valence orbital energies and shapes as closely as possible. This is taken to mean that the model potentials so obtained have then simulated the effect of the core satisfactorily. The calibrated model potentials are then transferred to molecular calculations.

D. Bonifacic-Huzinaga Model Potential Method

We give a cursory review of the model potential method described by Bonifacic and Huzinaga [23], in a form relevant to this work.

The Bonifacic-Huzinaga model potential developed rather naturally from the group's work on coupling and projection operator techniques in Hartree-Fock theory, and on the theory of separability in many electron systems [58].

1. Atomic System

We consider an atomic system with n_c core and n_v valence electrons. The conditions under which the core and valence electron distributions may be determined separately are as follows:

a. Separable Total Wavefunction: The total wavefunction may be written as an antisymmetrised product

$$\Phi = MA_p [\Phi_c \Phi_v] \tag{3-52}$$

where the core and valence wavefunctions

$$\Phi_c \equiv \Phi_c(1,2,\ldots,n_c) \tag{3-53}$$

$$\Phi_v \equiv \Phi_v(n_c+1,\ n_c+2,\ \ldots,\ n_c+n_v) \tag{3-54}$$

are both antisymmetrised and normalised. M is the normalisation constant for Φ, and A_p the partial antisymmetriser bridging Φ_c and Φ_v, to ensure that Φ is antisymmetric under exchange of core electrons with valence electrons. Φ may then be written as

$$\Phi = \left[\frac{(n_c+n_v)!}{n_c!\; n_v!}\right]^{-\frac{1}{2}} \sum_{P_{cv}} (-1)^{p_{cv}} P_{cv}[\Phi_c\ \Phi_v] \qquad (3\text{-}55)$$

where the summation is over all the $(n_c+n_v)!/(n_c!\ n_v!)$ distinct permutations P_{cv} of core electrons 1, 2, ..., n_c with valence electrons $n_c+1, \ldots, n_c+n_v$.

b. Strong Orthogonality Condition: Φ_v and Φ_c are assumed to satisfy the strong orthogonality condition:

$$\int \Phi_c^*(1,i,j,\ldots)\Phi_v(1,k,\ell,\ldots)d\tau_1 = 0 \ . \qquad (3\text{-}56)$$

This condition demands integration over only one electron, while the usual orthogonality condition involves integration over all electrons involved.

The total Hamiltonian may be written as

$$\begin{aligned} H = & \sum_{k=1}^{n_c} \left(-\frac{1}{2}\Delta_k - \frac{Z}{r_k}\right) + \sum_{k>\ell}^{n_c}\sum \frac{1}{r_{k\ell}} && \text{core} \\ & + \sum_{i=n_c+1}^{n_c+n_v} \left(-\frac{1}{2}\Delta_i - \frac{Z}{r}\right) + \sum_{i>j=n_c+1}^{n_c+n_v}\sum \frac{1}{r_{ij}} && \text{valence} \\ & + \sum_{k=1}^{n_c} \sum_{i=n_c+1}^{n_c+n_v} \frac{1}{r_{ik}} && \text{interaction} \end{aligned} \qquad (3\text{-}57)$$

Under these conditions of separability, the total energy may generally be written as

$$\begin{aligned} E &= \langle \Phi |H| \Phi \rangle \\ &= \langle \Phi_v |H_v| \Phi_v \rangle + E_c \ . \end{aligned} \qquad (3\text{-}58)$$

Illuminating steps towards the proof of this form have been given by Lykos and Parr [60].

c. Closed-Shell Core: Explicit forms of H_v and E_c depend on the form of Φ_c. In this work, we assume Φ_c to be an ordinary Slater determinant of a doubly occupied Hartree-Fock type closed shell:

$$\Phi_c = [\frac{1}{n_c!}]^{\frac{1}{2}} \det [\phi_1^c(1)\alpha(1)\phi_1^c(2)\beta(2) \times \times \phi^c_{n_c/2}(n_c-1)\alpha(n_c-1)\phi^c_{n_c/2}(n_c)\beta(n_c)] \quad . \qquad (3\text{-}59)$$

Then H_v and E_c take the forms

$$H_v = \sum_i^{n_v} (-\frac{1}{2}\Delta_i - \frac{Z}{r_i}) + \sum_k^{n_c/2}\sum_\ell (2J_k^c - K_k^c) + \sum_i^{n_v}\sum_j \frac{1}{r_{ij}} \qquad (3\text{-}60)$$

$$E_c = 2\sum_k^{n_c/2} H_k^c + \sum_k^{n_c/2}\sum_\ell (2J^c_{k,\ell} - K^c_{k,\ell}) \qquad (3\text{-}61)$$

with obvious definitions of the various familiar quantities (see Chapter 2, Section E.6). The form of E_c is the same as if the core stood alone without valence electrons: the core-valence interactions have been incorporated into valence term.

Note: A single determinant closed shell core is not the only possibility of course. Φ_c could be open or multiconfigurational, but the expressions for H_v and E_c would be more complicated.

d. Frozen-Core Approximation: To obtain the best value of the total energy E, we need to apply the variation principle to equation (3-58), i.e., to vary Φ_c and Φ_v. The frozen core approximation means we assume the core orbitals $\{\phi_k^c, k = 1,\ldots,n_c/2\}$ are known, and we keep them constant throughout the variation procedure, but maintain the strong orthogonality condition.

The problem of finding E and Φ then reduces to that of varying only Φ_v to minimise $< \phi_v |H_v| \phi_v >$, since E_c is constant with the frozen core.

e. Form of Φ_v, Strong Orthogonality Revisited: In the present work, we assign a Hartree-Fock type wavefunction (not necessarily closed shell) also to Φ_v as a functional of a set of valence orbitals $\{\phi_k^v\}$. Then, the strong orthogonality condition (3-56) can usually be resolved into a set of orthogonality conditions between the two sets of orbital sets $\{\phi_k^c\}$ and $\{\phi_k^v\}$, in addition to those among valence electrons.

$$< \phi_k^c \,|\, \phi_\ell^v > = 0 \qquad \text{all} \quad k,\ell \tag{3-62a}$$

$$< \phi^v \,|\, \phi_m^v > = \delta_{\ell m} . \tag{3-62b}$$

As is well known, these conditions or constraints may be incorporated as additional terms into the variational treatment of Φ_v by the use of Lagrangian multipliers λ_{ki} as in Chapter 2. When this is done, these conditions resurface as projection operators in the one-electron term for the valence electrons:

$$h(i) = \sum_i^{n_v} [- \frac{1}{2} \Delta_i - \frac{Z}{r_i} + \sum_k^{n_c/2} (2J_k^c(i) - K_k^c(i)) + \\ + \sum_k^{n_c/2} B_k^c \,|\, \phi_k^c(i)><\phi_k^c(i) \,|\,] \tag{3-63}$$

where B_k^c are numerical constants originating from the Lagrangian multipliers.

We demonstrate how the projection operators arise in the case of a closed-shell Φ_v [4]. The expression for the energy of the valence electrons is then, as in (2-94)

$$E_v = < \Phi_v |H_v| \Phi_v >$$

$$= 2 \sum_i^{n_v/} (h_i + U_i^{core}) + \sum_i^{n_v/2} \sum_j (2J_{ij}^v - K_{ij}^v) \qquad (3\text{-}64)$$

where

$$U_i^{core} = \sum_k^{n_c/2} (2J_{ki}^c - K_{ki}^c) \ . \qquad (3\text{-}65)$$

Under the variation procedure, with the constraints (3-62), the eigenvalue problem may be written as in (2-100)

$$F \phi_i^v = \sum_j^{n_v/2} \phi_j^v \epsilon_{ji} + \sum_k^{n_c/2} \phi_k^c \lambda_{ki} \qquad (3\text{-}66)$$

where

$$F = h + \sum_k^{n_c/2} (2J_k^c - K_k^c) + \sum_i^{n_v/2} (2J_i^v - K_i^v) \ . \qquad (3\text{-}67)$$

The eigenvalue matrix can be diagonalised by a unitary transformation among the set $\{\phi_i^v\}$, to give

$$F \phi_i^v = \epsilon_i \phi_i^v + \sum_k^{n_c/2} \lambda_{ki} \phi_k^c \ . \qquad (3\text{-}68)$$

The usual coupling operator methods are invoked. Multiplying (3-68) by $\langle\phi_j^c|$ and integrating we see for an arbitrary j,

$$\langle\phi_j^c|F|\phi_i^v\rangle = \langle\phi_j^c|\epsilon_i|\phi_i^v\rangle + \sum_k \langle\phi_j^c|\lambda_{ki}|\phi_k^c\rangle$$

$$= 0 + \lambda_{ji} \tag{3-69}$$

or

$$\langle\phi_k^c|F|\phi_i^v\rangle = \lambda_{ki} \tag{3-70}$$

since j is arbitrary. Substituting this in (3-68) gives

$$F|\phi_i^v\rangle = \epsilon_i|\phi_i^v\rangle + \sum_k^{n_c/2} |\phi_k^c\rangle\langle\phi_k^c|F|\phi_i^v\rangle$$

or

$$[F - \sum_k^{n_c/2} |\phi_k^c\rangle\langle\phi_k^c|F]\phi_i^v = \epsilon_i\ \phi_i^v \quad . \tag{3-71}$$

This further simplifies to give an effective Fock operator

$$F_v = F - \sum_k^{n_c/2} \epsilon_k^c|\phi_k^c\rangle\langle\phi_k^c| \tag{3-72}$$

on condition that

$$|\phi_k^c\rangle\langle\phi_k^c|F = F|\phi_k^c\rangle\langle\phi_k^c| \quad . \tag{3-73}$$

This condition is possible only if the core orbitals are eigenfunctions of the valence Fock operator, i.e.,

$$F|\phi_k^c\rangle = \epsilon_k^c|\phi_k^c\rangle \quad . \tag{3-74}$$

This is true in this case of a closed shell valence wavefunction, and in spin-unrestricted HF theory, but only approximately so in open-shell cases [23a]. To cover both these situations, an adjustable parameter B_k^c is used in (3-72), resulting in (3-63).

The proper valence Hamiltonian to be used is then

$$H_v = \sum_i^{n_v} \left[\left(-\frac{1}{2}\Delta_i - \frac{Z}{r_i}\right) \sum_k^{n_c/2} (2J_k^c - K_k^c) + \sum^{n_c/2} B_k^c |\phi_k^c\rangle\langle\phi_k^c| \right] + \sum_{i>j}^{n_v} \sum_j \frac{1}{r_{ij}} \quad . \tag{3-75}$$

f. Model Hamiltonian: If the Hamiltonian of (3-75) is used directly, two-electron integrals arising from the non-local integral potentials

$$\sum_k^{n_c/2} (2J_k^c - K_k^c) \tag{3-76}$$

must be calculated. In atoms, these pose no substantial trouble, but in molecules they could get expensive. Bonifacic and Huzinaga noted that for s core orbitals the potentials J_k^c and K_k^c are spherically symmetric as operators with suggestive forms, also found by Roothaan [61]. For example if the (1s) core is described approximately by a single 1s - STO,

$$\phi_{1s} \sim e^{-\zeta r} \tag{3-77}$$

then J_{1s} can be expressed as

$$J_{1s} = \int \phi_{1s}^2(2) \frac{1}{r_{21}} dv_2$$

$$= \int e^{-2\zeta r_2} \cdot \frac{1}{r_{21}} dv_2$$

$$= \frac{1}{r_1}\,[1 - (1 + \zeta r_1)e^{-2\zeta r_1}] \quad . \tag{3-78}$$

Thus

$$-\frac{Z}{r} + 2J_{1s} = -\frac{(Z-2)}{r} - \frac{2}{r}\,e^{-2\zeta r} - \frac{2\ re^{-2\zeta r}}{r} \quad . \tag{3-79}$$

For orbitals of higher angular momentum, summation over all components is needed to produce a spherically symmetric potential, e.g.,

$$(J^c_{px} + J^c_{py} + J^c_{pz}) \tag{3-80}$$

and

$$(K^c_{px} + K^c_{py} + K^c_{pz}) \tag{3-81}$$

are spherically symmetric, with results similar to (3-79), with the exchange contribution is much smaller than the Coulomb potential [62]. This suggested that these potentials could be replaced by properly-parametrised static local potential functions, thus replacing many two electron integrals with fewer one-electron integrals, a considerable saving in computational effort. The resulting model Hamiltonian is

$$H_{vm} = \sum_i^{n_v} \Big[-\frac{1}{2}\Delta_i + V_m(r_i) + \sum_k^{n_c/2} B^c_k|\phi^c_k(i)\rangle\langle\phi^c_k(i)|\Big] + \sum_{i>j}^{n_v} \frac{1}{r_{ij}} \quad . \tag{3-82}$$

where $V_m(r_i)$ is a spherical static local potential. In the present work we use "STO-screened" forms of $V_m(r_i)$:

$$V_m(r_i) = -\frac{(Z-n_c)}{r}\left(1+\sum_{j=1}^{n_t} A_j\, r_i^{n_j}\, e^{-\alpha_j r_i}\right) \qquad (3\text{-}83)$$

where n_t is the number of terms in the model potential. A_j, α_j and B_k^c are parameters of the model to be determined. We shall describe the calibration of these parameters in detail in Chapter 4. Here we mention that the procedure involves doing an atomic HF-R valence calculation, and adjusting the parameters so as to reproduce the correct valence orbital energies and shapes as closely as possible. Bonifacic and Huzinaga found that they could calibrate model potentials with truncated valence basis sets in which the core contribution was deleted. Thus $\{\phi_k^v\}$ may be the accurate ones or smoothed-out ones as needed.

2. Molecular System

Let us consider a molecular system containing N atoms with individual closed shell core regions numbered c1, c2, ..., cl, ... cN. The l th core contains n_{cl} electrons and the valence region of the whole molecular system contains n_v electrons which shape up the bonding characteristics of the molecular system.

We assume that the total wavefunction is of the form

$$\Phi = M\, A_p[\Phi_{c1}\, \Phi_{c2} \cdots \Phi_{cN}\, \Phi_v] \quad . \qquad (3\text{-}84)$$

As in the atomic case, the orbital sets corresponding to the grouping in Φ may be designated by $\{\phi_k^{c1}\}$, $\{\phi_k^{c2}\}$, ...,$\{\phi_k^{cN}\}$, $\{\phi_k^v\}$. If we assume the following orthogonality conditions:

$$<\phi_i^v|\phi_j^v> = \delta_{ij} \quad , \qquad (3\text{-}85a)$$

$$<\phi_i^{cI}|\phi_j^v> = 0 \quad , \qquad I = 1,2,\ldots,N \qquad (3\text{-}85b)$$

$$<\phi_j^{cI}|\phi_j^{cJ}> = \delta_{ij}\delta_{IJ} \quad , \qquad I,J = 1,\ldots,N \qquad (3\text{-}85c)$$

then the total energy of the system may be written as

$$E = <\Phi_v|H_v|\Phi_v> + \sum_I^N E_{cI} + \sum_{I>}^N \sum_J^N E_{cI,cJ} \quad . \qquad (3\text{-}86)$$

The Hamiltonian H_v for the valence electrons of the molecule may be written as

$$H_v = \sum_i^{n_v} \left(-\frac{1}{2}\Delta_i - \sum_I^N \frac{1}{r_{Ii}}\right) + \sum_I^N \sum_k^{n_{cI}/2} (2J_k^{cI} - K_k^{cI}) + \sum_{i>}^{n_v} \sum_j \frac{1}{r_{ij}} \qquad (3\text{-}87)$$

and the core energy E_{cI} is given as

$$E_{cI} = 2\sum_k^{n_{cI}/2} H_k^{cI} + \sum_k^{n_{cI}/2} \sum_\ell (2J_{k,\ell}^{cI} - K_{k,\ell}^{cI}) \quad . \qquad (3\text{-}88)$$

The term $E_{cI,cJ}$ represents the interaction between the two ionic cores cI and cJ. In the present work we use the approximation

$$E_{cI,cJ} \simeq \frac{(ZI-n_{cI})(ZJ-n_{cJ})}{R_{IJ}} \qquad (3\text{-}89)$$

which amounts to assuming a complete shielding of the nuclear charge by the core electron cloud.

The transition from the Hamiltonian H_v to the corresponding model Hamiltonian may be accomplished in a similar manner to the atomic case:

$$H_{vm} = \sum_{i=1}^{n_v} [- \frac{1}{2} \Delta_i + \sum_{I}^{N} (V_m^{cI}(r_{Ii}) + \sum^{n_{cI}/2} B_k^{cI} | \phi_k^{cI}(i) >< \phi_k^{cI}(i) |)] + \sum_{i > j}^{n_v} \sum \frac{1}{r_{ij}} . \quad (3\text{-}90)$$

The model potential part

$$V_m^{cI}(r_{Ii}) + \sum^{n_{cI}/2} B_k^{cI} | \phi_k^{cI} >< \phi_k^{cI} | \qquad (3\text{-}91)$$

is to be brought in from calibratory work on the free atoms. In this sense, H_{vm} for the molecular system does not involve any parameter adjustment.

3. Valence Basis Sets for ϕ_v

With the model Hamiltonian of equation (3-90) and ϕ_v as defined in Section 2e above, Bonifacic and Huzinaga go ahead to determine the Hartree-Fock-Roothaan molecular valence orbitals $\{\phi_k^v\}$. The truncated atomic basis sets such as those described in 1f are of a size appreciably smaller than the ones which are required to expand the space including the innermost part of the atoms. They present themselves as economical and effective expansion basis sets for the construction of $\{\phi_k^v\}$. The resulting significant reduction in the size of the basis set together with the reduction in the total number of electrons to be included in the molecular calculation results in a substantial economy of computational effort. We shall see in Chapter 4 that in this work we proceed slightly differently.

CHAPTER IV

FORMULATION OF THE OCE-MP METHOD

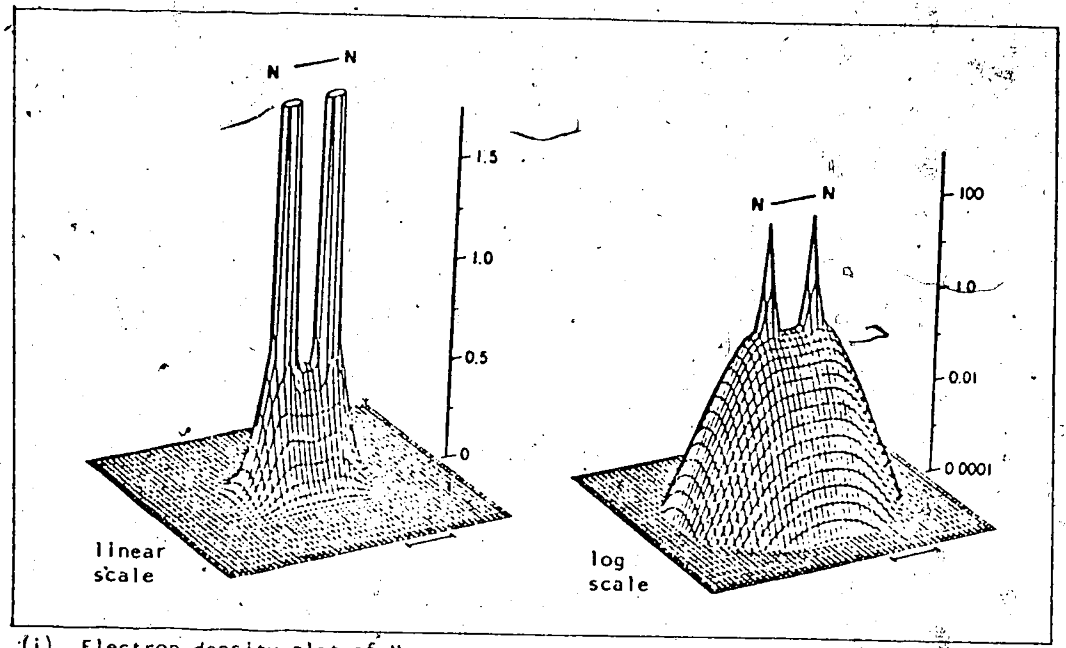
A. Introduction

This is the chapter in which the central idea of this thesis is developed. It is shown that the One-Center Expansion (OCE) method can be extended to calculate electronic wavefunctions for molecules with non-hydrogen off center nuclei, a prospect previously beyond reach. This extension is to be achieved through the use of model potentials (MP) to approximate the tightly bound core orbitals. The remaining diffuse valence charge distribution should then be rather easy to simulate using the One-Center Expansion method.

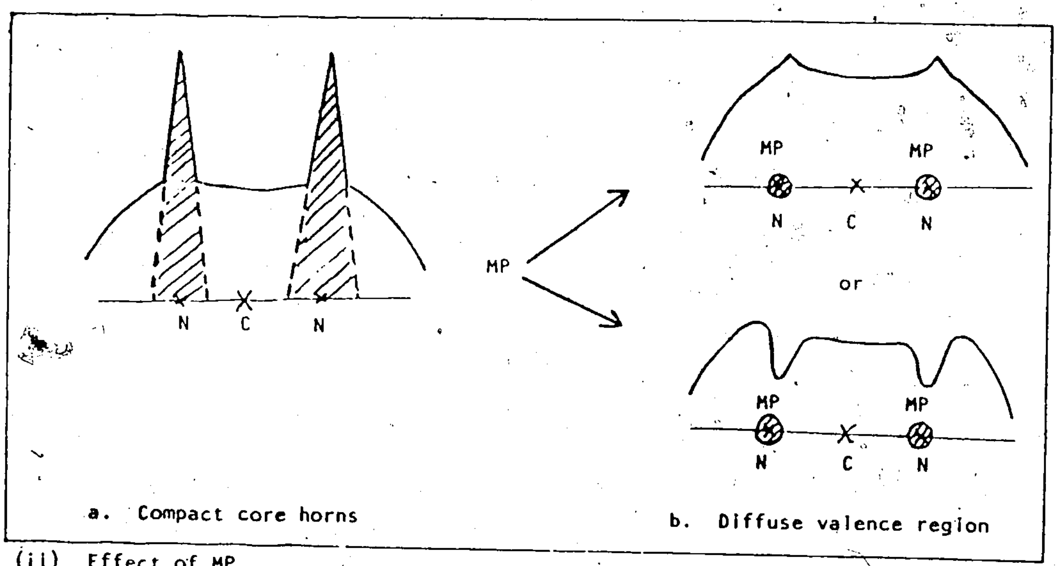
The explicit formulation of the coupling of these two techniques to give the OCE-MP algorithm is presented; and the practical computational strategies and tactics for solving the resulting equations are launched.

B. The Idea

The central idea of the OCE-MP method can be illustrated by ~~an~~ examination of the electron density plot of N_2 molecule [63] shown in Figure 4.1. The compact horns sticking out at the nuclear positions are composed mostly of the very low-lying core MOs $1\sigma_g$ and $1\sigma_u$, ($\epsilon = -15.65$ a.u. SZ). These in turn are dominated by the plus and minus combinations of the nitrogen 1s, ($\epsilon = -15.59$ a.u. SZ) atomic orbitals.



(i) Electron density plot of N_2.



a. Compact core horns

b. Diffuse valence region

(ii) Effect of MP.

FIG. 4.1. OCE-MP: The Idea.

As is widely accepted, these core orbitals which typically are 10 times deeper than valence orbitals, do not contribute heavily to the bonding characteristics of the N_2 molecule, remaining virtually unchanged upon bond formation. Table 4.1 compares Clementi's SZ atomic orbital energies [38] with the core MOs of Ransil [64] and shows that the changes in core orbital energies upon diatomic bond formation are indeed small. Yet, in a variationally-driven OCE calculation with the expansion center at the molecular mid-point, most of the terms would be taken up in trying, unsuccessfully, to reproduce these horns, since they contain the bulk of the total energy (for N_2, E_{core} = -89.4 a.u. SZ, 82% of the total) [65]. Thus an OCE calculation would indeed give very poor results.

Now suppose the core region is replaced by appropriate model potentials. This would remove the burden of core orbitals from OCE. The remaining, diffuse valence charge distribution (Figure 4.1) should then be easy to simulate using OCE.

Thus, our OCE-MP calculations are of the "all-valence-electron" variety, an approach which is currently being systematically investigated in several laboratories and which holds great promise for the practical study of molecular structure.

C. The Recipe

1. Ingredients

We now collect together the formal set of equations which are the basic ingredients of the OCE-MP method for molecular calculations:

TABLE 4.1. SZ Orbital Energies for Low-Lying AOs and MOs in Selected First Row Diatomics.

Atom	$-\varepsilon_{1s}$[a]	Diatomic	$-\varepsilon_{1\sigma_{g,u}}$[b]	% change AO → MO
Li	2.46	Li_2	2.44	0.8
		LiH	2.43	1.2
Be	4.72	Be_2	4.71	0.2
B	7.68	BH	7.66	0.3
C	11.30	C_2	11.34	0.4
N	15.59	N_2	15.65	0.4
F	26.30	F_2	26.36	0.2
		HF	26.27	0.1

[a] Values taken from ref [38].

[b] "Best limited LCAO" values of Ransil, Ref. [64].

a. Schroedinger Equation: set up for valence electrons only

$$H_{vm}\,\Phi_v = E_v\,\Phi_v \quad . \tag{4-1}$$

b. Bonifacic-Huzinaga Model Hamiltonian:

$$H_{vm} = \sum_i^{n_v} [-\frac{1}{2}\Delta_i + \sum_l^N (V_m(r_{li}) + \sum_k^{n_{Cl}/2} B_k^{Cl}|\phi_k^{Cl}(i)\rangle\langle\phi_k^{Cl}(i)|)] + \sum_{i>j}^{n_v}\sum \frac{1}{r_{ij}} \tag{4-2}$$

$$V_m(r_{li}) = [-(z_l - n_{Cl})/r_{li}](1 + \sum_j^{n_t} A_j\, r^{n_j}\, e^{-\alpha_j r_{li}}) \quad , \tag{4-3}$$

with model parameters A_j, α_j, n_j, n_t, B_k^{Cl} to be determined by atomic calibration.

c. QCE Valence Wavefunction (closed-shell):

$$\phi_v = [\frac{1}{n_v!}]^{\frac{1}{2}} \det \; \phi_1^v(1)\alpha(1)\phi_1(2)\beta(2) \ldots \phi_{n_v/2}(n_v-1) \times$$

$$\times\; \alpha(n_v-1)\phi_{n_v/2}(n_v)\beta(n_v)\,] \tag{4-4}$$

$$\phi_i^v = \sum_p \chi_p\, c_{pi} \tag{4-5}$$

χ_p are STOs all at one center, and c_{pi} to be determined by SCF procedure.

A word of explanation is in order here. In the usual LCAO-MP application to molecular systems, such as that of Bonifacic and Huzinaga, it is not only the model potentials which are brought in from the work on atomic calibration. With each model potential is associated a set of valence (atomic) orbitals. These (or their expansion basis functions) are used for the construction of the molecular valence orbitals $\{\phi_k^v\}$, as we saw in Chapter 3. Thus, although drastically reduced in number, multicenter integrals still persist, since these basis functions are centered at the various nuclei.

In the present OCE-MP formation, only the model potentials, but not th[illegible]responding atomic valence orbitals, are brought in. The molecular [illegible]lence orbitals $\{\phi_k^v\}$, representing the total molecular valence space, are then constructed using basis functions situated at one convenient point in space. In this way, difficult multicenter integrals are avoided. For, as we shall see, all the two-electron integrals in OCE-MP are of the one-center type, just as in OCE method.

d. Total Molecular Energy:

$$E = \langle\Phi_v|H_{vm}|\Phi_v\rangle + \sum_{I}^{N} E_{CI} + \sum_{I}^{N}\sum_{J}^{N} E_{CI,CJ} \tag{4-6}$$

$$E_{CI} = 2\sum_{k}^{n_{CI}/2} H_k^{I} + \sum_{k}^{n_{CI}/2}\sum_{\ell} (2J_{k,\ell}^{CI} - K_{k,\ell}^{CI}) \tag{4-7}$$

$$E_{CI,CJ} \simeq \frac{(C_I - n_{CI})(C_J - n_{CJ})}{R_{IJ}} . \tag{4-8}$$

Formula (4-8) gives the approximate repulsion energy between the two ionic cores CI, CJ. It amounts to assuming a complete shielding of the nuclear charge by the core electron charge cloud.

2. General Computational Strategy

The biggest task is to calculate

$$E_v = <\phi_v|H_{vm}|\phi_v> \qquad (4\text{-}9)$$

We have tried to break the procedure into modules which can be developed and tested separately, then hooked up logically for a complete run, i.e., for the SCF solution of the corresponding Roothaan's equations. Here F is still defined as in equation (2-103), with $n = n_v$ and the one-electron operator

$$h(i) = -\frac{1}{2}\Delta_i + \sum_{I}^{N} (V_m(r_{Ii}) + \sum_{k}^{n_{CI}/2} B_k^{CI} <\phi_k^{CI}(i)><\phi_k^{CI}(i)|) . \qquad (4\text{-}10)$$

The strategy is summarised below:

a. <u>Integral Package</u>: To prepare methods for solving all types of integrals arising from the coupling of OCE and MP methods.

b. <u>Model Potentials</u>: To calibrate STO-MP version for atoms.

c. <u>SCF Procedure</u>: This is the driving mechanism of the whole process. It handles matrix and supermatrix organisation, receiving, storing and retrieving integrals properly; matrix manipulation routines for addition, multiplication of matrices; matrix diagonalisations, eigenvectors and eigenvalues; iterative procedures; optimisation of exponents, etc.

d. Hook-Up and Testing: Valence basis set developments; dependence of results on model potentials, basis sets; scope of utility-molecular properties.

D. Matrix Elements of the Model Hamiltonian

1. Classification

In this work, all the basis functions $\{\chi_p\}$ are centered at one point. We designate this expansion center as A, and write the general functions as χ_p^a, χ_q^a, χ_r^a, χ_s^a, ... The model potentials on the other hand may sit at any other point B. With these functions, the following types of matrix elements may arise in the solution of Roothaan's equations with the model Hamiltonian:

a. Overlap Integrals:

$$< \chi_p^a \mid \chi_q^a > . \tag{4-11}$$

b. Kinetic Energy Integrals:

$$< \chi_p^a \mid -\frac{1}{2}\Delta \mid \chi_q^a > . \tag{4-12}$$

Thus the overlap and Kinetic energy terms are all one-center.

c. Static Model Potential Integrals:

$$< \chi_p^a \mid V_m^b(r_b) \mid \chi_q^a > . \tag{4-13}$$

This can be one-center $(A = B)$ or two-center $(A \neq B)$, and can be further broken down into

i) Nuclear attraction (Coulomb potential)

$$<\chi_p^a|-(Z_b-n_b)/r_b|\phi_q^a> \quad . \tag{4-14}$$

ii) Yukawa-type potential $n_j = 0$

$$< \chi_p^a \left| \frac{A_j e^{-\alpha_j r_b}}{r_b} \right| \chi_q^a > \quad . \tag{4-15}$$

iii) s-STO or Huzinaga potential

$$< \chi_p^a | A_j r_b^{n_j-1} e^{-\alpha_j r_b} | \chi_q^a > \quad , \quad n_j = 1,2,3,... \quad . \tag{4-16}$$

d. Non-Local Projection Operator Integrals:

$$< \chi_p^a | \sum_k B_k^b |\phi_k^b><\phi_k^b| \chi_q^a > \quad . \tag{4-17}$$

These integrals are to be treated with caution. $\{\phi_k^b\}$ are the frozen atomic orbitals, which have as usual been expressed as linear combinations of basis functions $\{\chi_p^b\}$. We may say in Dirac notation,

$$|\phi_k^b> = | \sum_s \chi_s^b c_{sk}> = \sum_s | \chi_s^b> c_{sk} \tag{4-18}$$

and

$$< \phi_k^b| = < \sum_t c_{tk} \chi_t^b | = \sum_t c_{tk}^* <\chi_t^b| \quad . \tag{4-19}$$

Then the integral in (4-17) becomes

$$\sum_k B_k^b \langle \chi_p^a | \sum_s c_{sk} \chi_s^b \rangle \langle \sum_t c_{tk} \chi_t^b | \chi_q^a \rangle$$

$$= \sum_k \sum_s \sum_t B_k^b c_{sk} c_{tk}^* \langle \chi_p^a | \chi_s^b \rangle \langle \chi_t^b | \chi_q^a \rangle \quad . \qquad (4\text{-}20)$$

The definition of the projection operator (eqn (3-23)) means this expression reduces to summation of products of one- or two-center overlap integrals

$$\langle \chi_p^a \mid \chi_s^b \rangle \qquad (4\text{-}21)$$

and

$$\langle \chi_t^b \mid \chi_q^a \rangle = \langle \chi_q^a \mid \chi_t^b \rangle \quad . \qquad (4\text{-}22)$$

e. Two-Electron Integrals:

i) Coulomb

$$[\chi_p^a \chi_q^a \mid \chi_r^a \chi_s^a] \quad . \qquad (4\text{-}23)$$

ii) Exchange

$$[\chi_p^a \chi_s^a \mid \chi_r^a \chi_q^a] \quad . \qquad (4\text{-}24)$$

Thus all two-electron integrals in OCE-MP are one-center and this is the effort-saving quality of the method.

3. Methods of Evaluation

In this work all integrals are calculated over STOs with real spherical harmonics as defined by Roothaan [61]:

$$\chi = (n,\ell,m,\zeta) = N_n(\zeta)\, r^{n-1}\, e^{-\zeta r}\, S_{\ell m}(\theta,\phi) \qquad (4\text{-}25)$$

where

$$\vec{N}_n(\zeta) = (2\zeta)^{n+\frac{1}{2}}/[(2n)!]^{\frac{1}{2}} \qquad (4\text{-}26)$$

is the radial normalisation factor, and $S_{\ell m}(\theta,\phi)$ are the normalised real spherical harmonics. The full definition of these functions is given in Chapter 5.

Except for those arising from the static model potentials, all the integrals enumerated above are well known, and methods for their solution abound in the literature. The one-center overlap, kinetic energy and nuclear attraction integrals are identical to the corresponding integrals for the atomic case, and are given by Roothaan and Bagus [6b]. The two-center overlap and nuclear attraction integrals have also been solved for a number of cases [12d,61,66].

For the static potentials no explicit and accurate solutions could be found in the literature. These integrals may be divided into two categories:

a. <u>One-Center MP Integrals</u>: We find that the one-center versions can easily be transformed into common "atomic" forms and so solved using the familiar techniques of Roothaan and Bagus.

i) One-center nuclear attraction may be solved as such, or transformed into a pseudo-overlap integral:

$$<(n_p,\ell_p,m_p,\zeta_p)_a|\frac{1}{r_a}|(n_q,\ell_q,m_q,\zeta_q)_a>$$

$$= <("n_p-1",\ell_p,m_p,\zeta_p)_a|(n_q,\ell_q,m_q,\zeta_q)_a>$$

$$= <(n_p,\ell_p,m_p,\zeta_p)_a|("n_q-1",\ell_q,m_q,\zeta_q)_a> \qquad (4\text{-}27)$$

where the quotation marks mean only the power of r and/or the exponent changes, but the normalisation factor remains as $N_n(\zeta)$.

ii) Similarly the Yukawa-type integral can be rewritten in pseudo-overlap form:

$$<(n_p,\ell_p,m_p,\zeta_p)_a|A_j\frac{e^{-\alpha_j r_a}}{r_a}|(n_q,\ell_q,m_q,\zeta_q)_a>$$

$$= A_j<("n_p-1",\ell_p,m_p,"\zeta_p+\alpha_j")_a|(n_q,\ell_q,m_q,\zeta_q)_a>$$

$$= A_j<("n_p-1",\ell_p,m_p,\zeta_p)_a|(n_q,\ell_q,m_q,"\zeta_q+\alpha_j")_a>$$

$$= A_j<(n_p,\ell_p,m_p,"\zeta_p+\alpha_j")_a|("n_q-1",\ell_q,m_q,\zeta_q)_a>$$

$$= A_j<(n_p,\ell_p,m_p,\zeta_p)_a|("n_q-1",\ell_q,m_q,"\zeta_q+\alpha_j")_a> \qquad (4\text{-}28)$$

or (especially in the case n_p or $n_q = 1$) as a pseudo-nuclear attraction integral

$$<(n_p,\ell_p,m_p,"\zeta_p+\alpha_j")_a|\frac{1}{r_a}|(n_q,\ell_q,m_q,\zeta_q)_a>$$

$$= A_j<(n_p,\ell_p,m_p,\zeta_p)_a|\frac{1}{r_a}|(n_q,\ell_q,m_q,"\zeta_q+\alpha_j")_a \quad . \qquad (4\text{-}29)$$

iii) Similarly, the one-center integrals over s-STO potentials reduce to pseudo-overlaps:

$$\begin{aligned}&<(n_p,\ell_p,m_p,\zeta_p)_a|A_j\ r_a^{n_j-1}\ e^{-\alpha_j r_a}|(n_q,\ell_q,m_q,\zeta_q)_a>\\ &\quad = A_j<(\text{"}n_p+n_j-1\text{"},\ell_p,m_p,\text{"}\zeta_p+\alpha_j\text{"})_a|(n_q,\ell_q,m_q,\zeta_q)_a>\\ &\quad = A_j<(n_p,\ell_p,m_p,\zeta_p)_a|(\text{"}n_q+n_j-1\text{"},\ell_q,m_q,\text{"}\zeta_q+\alpha_j\text{"})_a> \text{ etc } \ldots \quad (4\text{-}30)\end{aligned}$$

b. Two-Center Integrals: Thinking mainly of molecules with first-row off-center atoms whose core is $[1s^2]$ only, we first coded a program to calculate two-center overlaps between s and $\ell\sigma$ orbitals ($m = 0$), based on the method of Ruedenberg et al [66].

This was superceded when we evolved a unified method for the exact solution of all the two-center integrals arising in OCE-MP, including two-center overlap. It is based on the Fourier Convolution Theorem [24-26]. In this work, the scheme originally developed by Harris and Michels [24] for two-center two-electron Coulomb integrals is modified to evaluate two-center one-electron integrals, be they overlap or attraction integrals. As the evaluation of these integrals is a highly technical matter, a whole Chapter 5 and a number of appendices have been devoted to the derivation and application of the Fourier Convolution technique.

E. Atomic Calibration of Model Potentials

1. STO-Screened Model Potentials

In this work we have used the "STO-Screened" model potentials of Bonifacic and Huzinaga [23], which are suitable for use with our STO basis.

For first-row atoms the model potentials calibrated by those workers were used. The static part has $n_t = 2$, $n_1 = 0$ and $n_2 = 1$, or in our shorthand, MP(0,1), so that

$$V_m(r) = -\frac{(Z-2)}{r}(1 + A_1 e^{-\alpha_1 r} + A_2 re^{-\alpha_2 r}) \quad . \qquad (4\text{-}31)$$

$n_c/2 = 1$, so that the core projection operator term is

$$B_{1s}|\phi_{1s}><\phi_{1s}| \quad , \qquad (4\text{-}32)$$

and the valence configuration $2s^m\ 2p^n$.

It is interesting to note that this core-valence separation is justified on the chemical grounds that the 2s and 2p orbitals are definitely together in the valence, and are used in such ideas as hybridisation. Physically too, the separation is reasonable because the core orbital energy lies much deeper (10 times) than the valence orbital energies. But mathematically this separation is not the only one possible. For example no mathematical problems would arise if in nitrogen we separated [$1s^2\ 2s^2$] as closed-shell core and $2p^3$ as valence.

For second-row atoms, the valence space is $3s^m\ 3p^n$ and we have chosen a three-term ($n_t = 3$) model potential MP(0,1,1):

$$V_m(r) = -\frac{(Z-10)}{r}(1 + a_1 e^{-\alpha_1 r} + A_2 re^{-\alpha_2 r}\ A_3 re^{-\alpha_3 r}) \qquad (4\text{-}33)$$

$n_c/2 = 5$ and the projection operator is

$$B_{1s}|\phi_{1s}><\phi_{1s}| + B_{2s}|\phi_{2s}><\phi_{2s}| + B_{2p}\{|\phi_{2px}><\phi_{2px}| + + |\phi_{2py}><\phi_{2py}| + |\phi_{2pz}><\phi_{2pz}|\} \quad (4\text{-}34)$$

For the first-row of transition metals, we decided on model potentials of the form MP(0,1,2):

$$V_m(r) = -\frac{(Z-18)}{r}(1 + A_1 e^{-\alpha_1 r} + A_2 r e^{-\alpha_2 r} + A_3 r e^{-\alpha_3 r}) \ . \quad (4\text{-}35)$$

We tested MP(0,1,1) similar to that of Bonifacic and Huzinaga for Vanadium but were not satisfied with the results. However, it is likely that with harder pushing, it too could give acceptable results.

The projection operator is

$$B_{1s}|\phi_{1s}><\phi_{1s}| + B_{2s}|\phi_{2s}><\phi_{2s}| + B_{3s}|\phi_{3s}><\phi_{3s}| \ . \quad (4\text{-}36)$$

Missing are the terms

$$B_{2p}|\phi_{2p}><\phi_{2p}| + B_{3p}|\phi_{3p}><\phi_{3p}| \ , \quad (4\text{-}37)$$

or actually six terms corresponding to the x, y, z p orbitals. The reason is because we take the electronic configuration as $4s^2\ 3d^n$ or $4s\ 3d^n$. In atoms, both s and d orbitals in the valence shell are automatically orthogonal to p orbitals in the core. In molecules, however, the missing terms must be included since the valence-shell orbitals on one atomic site are generally not orthogonal to inner-core orbitals on another site. In such cases there is in principle no way of determining the B_{2p}, B_{3p} parameters except perhaps by considering excited states of the atom. Bonifacic and Huzinaga have recommended

$B_{2p} = 2|\epsilon_{2p}|$ and $B_{3p} = 2|\epsilon_{3p}|$ for all sizes of basis sets.

2. Calibration Procedure

This involved solving the SCF problem using the model Hamiltonian and adjusting the parameters $\{A_j\}$, $\{\alpha_j\}$, $\{B_k\}$ until the valence orbital energies and shapes agreed with reference ones satisfactorily. The adjustment of the parameters was incorporated into a general Roothaan STO-SCF atomic program capable of handling closed and open shells. Written by Huzinaga, it is modelled on the Roothaan-Bagus method. The test of accuracy used is that square deviation summed over the valence orbitals

$$D = \sum_i (\epsilon_i^{ref} - \epsilon_i)^2 \tag{4-38}$$

is minimised by varying each parameter individually. Our procedure is rather pedestrian in conception but almost fully automatic in implementation.

i) Choose core and valence basis set. We followed Bonifacic and Huzinaga in using the Double zeta basis sets of Clementi and Roetti and truncating them in a similar manner.

ii) Guess a set of $\{A_j\}$, $\{\alpha_j\}$ and $\{B_k\}$ parameters and appropriate step sizes for each parameter. Mostly this was done by experience; for transition metals, definite trends were found so that the final parameter set for one calculation could be used as initial values for the next, whether from one basis set to another in one atom, or from one atom to the next.

iii) Carry out the valence SCF procedure using the model Hamiltonian. This involves solving one-center integrals such as those in Section 3a. Determine orbital energies and a D estimate.

vi) Optimise a new parameter individually. Let the initial value of this parameter be x_0. Change the parameter by step-size h and use iii) to obtain a new deviation D_1. If $D_0 < D_1$, step backwards twice in x, and obtain D_2. If, on the other hand $D_0 > D_1$, step forwards to get (x_2, D_2).

v) If the sequence D_0, D_1, D_2, appropriately renamed in increasing x_0, x_1, x_2, goes through a minimum, i.e., $D_0 > D_1 < D_2$, we go to vi). If not, i.e., if the sequence is monotonic, we try one more step as described in iii) and iv) to search for this minimum. If a minimum is detected, i.e., $D_0 > D_1 > D_2 < D_3$, we go to vi) with the last three points renamed D_0, D_1, D_2. If not, we go to iii) to optimise the next parameter keeping the last x value. Thus for each parameter we try only four points to search for a minimum before we quit. This is to ensure that one parameter does not take over and dominate and distort the total picture.

vi) The sequence D_0, D_1, D_2 which goes through a minimum is fitted with a second-degree interpolating polynomial

$$f(x) = a_0 + a_1 x + a_2 x^2 \qquad (4\text{-}39)$$

The minimum of this quadratic is determined in the following manner: First, the constants a_0, a_1, and a_2 are determined by requiring the interpolating function to pass through all three points $\{x_i, D_i, i = 0,1,2\}$:

$$D_i = f(x_i) = a_0 + a_1x_i + a_2x_i^2 \;, \quad i = 0,1,2 \;. \tag{4-40}$$

Solving the set of three simultaneous equations and substituting the resulting values of $\{a_i\}$ in (4-39) leads to

$$f(x) = \frac{(x-x_1)(x-x_2)D_0}{(x_0-x_1)(x_0-x_2)} + \frac{(x-x_0)(x-x_2)D_1}{(x_1-x_0)(x_1-x_2)} + \frac{(x-x_0)(x-x_1)D_2}{(x_2-x_0)(x_2-x_1)} \;. \tag{4-41}$$

The minimum occurs when

$$\frac{df(x)}{dx} = 0 \tag{4-42}$$

or

$$\frac{[2x-(x_1+x_2)]D_0}{2h^2} - \frac{[2x-(x_0+x_2)]\cdot 2D_1}{2h^2} + \frac{[2x-(x_0+x_1)]D_2}{2h^2} = 0 \tag{4-43}$$

where

$$h = x_1 - x_0 = x_2 - x_1 \tag{4-44}$$

is the step size. Rewriting (4-43) with x_1 as reference point yields

$$2x[D_0-2D_1+D_2] = 2x_1[D_0-2D_1+D_2] + h(D_0-D_2) \;,$$

or

$$x = x_1 + \Delta x \tag{4-45}$$

where

$$x = \frac{h(D_0-D_2)}{2(D_0-2D_1+D_2)} \;. \tag{4-46}$$

One sweep ends when all parameters have been optimised in turn. We found that in general, about 20 sweeps at step size $h \simeq 10\%$ of the parameter, followed by another 20 at $h \simeq 1\%$ of the parameter, was sufficient to reproduce all valence orbital energies to four or five significant figures. The results are given in Tables 4.2 - 4.6.

One of the parameters may be determined by physical considerations as discussed in Section 3 of Chapter 3. At very small r, the static potential approaches

$$\frac{-(Z-n_c)}{r}(1 + A_1) \quad . \tag{4-47}$$

Then in turn, it should be that

$$\frac{-(Z-n_c)}{r}(1 + A_1) \simeq -\frac{Z}{r} \tag{4-48a}$$

or

$$(Z - n_c)(1 + A_1) \simeq Z \tag{4-48b}$$

because an electron should see the whole nuclear charge when it comes very close to a bare nucleus. This relation was used to fix A_1 as

$$A_1 = \frac{Z}{Z-n_c} - 1 \tag{4-49}$$

which was not varied any further.

The B_k parameters were also not assiduously optimised, but were fixed at $m \times$ absolute value of core orbital energy ϵ_k, with $m = 2.0$, 1.5 or 1.0. We found that the B values appreciably affect the valence orbital shapes as a comparison of the largest expansion

TABLE 4.2 Parameters for (6s/2d) STO basis, MP(0,1,2)[a,b]

Atom	Term	Z*	A_1	A_2	A_3	α_1	α_2	α_3	B_1	B_2	B_3
Sc	^2D	3	6.0	10.4411	0.3355	5.5814	3.1080	1.5261	331.7869	38.1495	5.1243
Ti	^3F	4	4.5	8.6803	0.2958	6.1289	3.3587	1.6216	366.5291	42.8276	5.7303
V	^4F	5	3.6	7.7903	0.2445	6.6258	3.6310	1.6670	402.9848	47.7231	6.3426
Cr	^7S	6	3.0	7.5250	0.2086	7.4250	3.9000	1.6645	440.7110	52.3428	6.4972
Cr	^5D	6	3.0	6.9760	0.2007	7.2040	3.9000	1.6967	441.1583	52.8429	6.9663
Mn	^6S	7	2.5714	6.9050	0.1545	8.0471	4.1300	1.6733	481.0366	58.1743	7.5934
Fe	^5D	8	2.25	6.6329	0.1182	8.7600	4.3700	1.6576	522.7053	63.8106	8.2848
Co	^4F	9	2.0	6.5014	0.0867	9.5055	4.6240	1.5920	566.0792	69.6603	8.9804
Ni	^3F	10	1.8	6.4794	0.0618	10.3099	4.8900	1.5017	611.1751	75.7419	9.6922
Cu	^2S	11	1.6364	7.1060	0.0463	11.3699	5.2023	1.3667	657.4564	81.4591	9.8541
Cu	^2D	11	1.6364	7.1060	0.0509	10.3323	5.1003	1.4344	657.9936	82.0567	10.4211
Zn	^1S	12	1.5	7.3052	0.0567	10.9462	5.6860	1.5048	706.5201	88.5906	11.1583

[a] $B=2.0|\varepsilon|$

[b] A_1 estimated from equation (4-49)

TABLE 4.3 Parameters for (4s/2d) STO Basis, MP(0,1,2)[a]

Atom	Term	A_1	A_2	A_3	α_1	α_2	α_3
Sc	^2D	6.0	10.1911	0.3763	6.0309	3.1000	1.3759
Ti	^3F	4.5	8.1461	0.3374	6.2476	3.3587	1.4560
V	^4F	3.6	7.3719	0.2363	6.4707	3.6537	1.4283
Cr	^7S	3.0	7.0926	0.1950	6.6270	3.9700	1.4330
Cr	^5D	3.0	6.5784	0.1994	6.6923	3.9700	1.4568
Mn	^6S	2.5714	6.4891	0.1759	6.4010	4.3376	1.4698
Fe	^5D	2.25	6.4043	0.1553	6.4000	4.7200	1.4800
Co	^4F	2.0	6.5506	0.1354	6.4000	5.1330	1.4759
Ni	^3F	1.8	6.8200	0.1284	6.4000	5.5790	1.5000
Cu	^2S	1.6364	7.5854	0.1376	5.9200	5.9903	1.5200
Cu	^2D	1.6364	7.8463	0.1346	5.9200	6.0758	1.5350
Zn	^1S	1.5	6.6298	0.1459	6.7981	6.1820	1.6698

[a] $B=2.0|\epsilon|$

TABLE 4.4 Parameters for (3s/2d) STO Basis, MP(0,1,2)[a]

Atom	Term	A_1	A_2	A_3	α_1	α_2	α_3
Sc	^2D	6.0	9.5903	0.4343	6.4190	3.1000	1.3343
Ti	^3F	4.5	7.6309	0.3603	6.2932	3.3587	1.4030
V	^4F	3.6	6.9383	0.2410	6.3490	3.6593	1.3647
Cr	^7S	3.0	6.7228	0.2043	6.6190	3.9878	1.3725
Cr	^5D	3.0	6.1746	0.1965	6.3838	4.0000	1.3794
Mn	^6S	2.5714	5.5221	0.1621	5.4055	4.4216	1.3657
Fe	^5D	2.25	4.0323	0.1565	5.1930	4.5133	1.4140
Co	^4F	2.0	2.8187	0.1564	4.9788	4.5600	1.4768
Ni	^3F	1.8	2.0179	0.1465	4.8658	4.6896	1.5113
Cu	^2S	1.6364	1.5642	0.1507	4.7062	4.7800	1.5586
Cu	^2D	1.6364	1.5794	0.1489	4.4638	4.7800	1.5597
Zn	^1S	1.5	1.1796	0.1501	4.7870	5.2898	1.6320

[a] $B=2.0|\epsilon|$

TABLE 4.5 . Parameters for (2s/2d) STO Basis, MP(0,1,2)[a]

Atom	Term	A_1	A_2	A_3	α_1	α_2	α_3	B_{1s}	B_{2s}	B_{3s}
Sc	^2D	6.0	10.9444	0.4564	6.1688	3.1880	1.5034	165.8935	19.0748	2.5622
Ti	^3F	4.5	9.2594	0.3482	6.8425	3.4427	1.5640	183.2646	21.4238	2.8651
V	^4F	3.6	8.2974	0.2866	7.3461	3.7218	1.6160	201.4924	23.8616	3.1713
Cr	^7S	3.0	7.2830	0.2830	7.5379	3.8976	1.7973	220.3555	26.1714	3.2486
Cr	^5D	3.0	6.7182	0.2933	7.6943	3.8976	1.7842	220.5791	26.4215	3.4832
Mn	^6S	2.57143	5.9323	0.3341	7.4843	4.0900	1.9330	240.5183	29.0872	3.7967
Fe	^5D	2.25	5.1995	0.3501	7.5000	4.2900	2.0726	261.3526	31.9053	4.1424
Co	^4F	2.0	4.6431	0.3692	7.5100	4.5000	2.2000	283.0396	34.8301	4.4902
Ni	^3F	1.8	4.3074	0.3924	7.5200	4.7200	2.3300	305.5876	37.8709	4.8461
Cu	^2S	1.6364	3.9698	0.4199	7.5300	4.9500	2.4700	328.7282	40.7296	4.9271
Cu	^2D	1.6364	4.0173	0.5077	6.9653	4.8722	2.4870	328.9968	41.0284	5.2106
Zn	^1S	1.5	3.5424	0.4604	8.0121	5.0900	2.6520	353.2601	44.2953	5.5792

[a] $B=1.0|\varepsilon|$

TABLE 4.6 Orbital Exponents, Coefficients and Energies for First Row of Transition Elements - (a)-(ℓ)

(a) Scandium $K(2)L(8)M(8)4s^2 3d^1$, ^2D, MP(0,1,2)

STO	Exponents	Full H-F-R (8s/2d) coefficients	MODEL POTENTIAL H-F-R Coefficients (6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	22.0770	-0.00294				
1s	15.76440	-0.03176				
2s	10.10970	-0.02337	0.10732			
2s	7.76457	0.15078	-0.17468			
3s	3.92714	-0.22341	0.12275	0.15009		
3s	2.70064	-0.07919	0.14308	-0.39451	-0.14988	
4s	1.53840	0.51722	-0.50596	0.59347	0.34936	0.34626
4s	0.91407	0.58703	-0.61306	0.57799	0.74967	0.71635
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	4.22244	0.35922	0.35114	0.27862	0.20310	0.28903
3d	1.74647	0.76601	0.77239	0.82724	0.87982	0.81963
	Valence orbital energies in a.u.					
	ε(4s)	-0.20824	-0.20831	-0.20805	-0.20801	-0.20800
	ε(3d)	-0.33810	-0.33805	-0.33815	-0.33815	-0.33816

(b) Titanium $K(2)L(8)M(8)4s^2 3d^2$, ^3F, MP(0,1,2)

STO	Exponents	Full H-F-R (8s/2d) coefficients	MODEL POTENTIAL H-F-R Coefficients (6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	23.00460	-0.00354				
1s	16.3272	-0.03133				
2s	11.02380	-0.02283	0.09574			
2s	8.25215	0.14951	-0.16152			
3s	4.14661	-0.23197	0.13020	0.13144		
3s	2.79906	-0.06145	0.12854	-0.37173	-0.15472	
4s	1.61853	0.51724	-0.51204	0.60045	0.38316	0.36826
4s	0.94889	0.58740	-0.60919	0.57489	0.72586	0.69943
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	4.67000	0.36461	0.35758	0.29700	0.24428	0.30922
3d	1.98614	0.75561	0.76129	0.81025	0.84728	0.79923
	Valence orbital energies in a.u.					
	ε(4s)	-0.21807	-0.21817	-0.21808	-0.21796	-0.21792
	ε(3d)	-0.43184	-0.43178	-0.43180	-0.43184	-0.43187

(c) Vanadium K(2)L(8)M(8)$4s^2 3d^3$, ^4F, MP(0,1,2)

STO	Exponents	Full H-F-R (8s/2d) coefficients	MODEL POTENTIAL H-F-R Coefficients			
			(6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	24.00780	-0.00391				
1s	16.92690	-0.03091				
2s	11.81230	-0.02311	0.09003			
2s	8.72824	0.14398	-0.15449			
3s	4.39565	-0.23094	0.13034	0.11922		
3s	2.94007	-0.05400	0.11943	-0.34744	-0.15033	
4s	1.69734	0.51328	-0.50626	0.58019	0.38108	0.37942
4s	0.98281	0.59195	-0.61503	0.59144	0.72908	0.69217
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	5.05186	0.37378	0.37616	0.33750	0.30315	0.33506
3d	2.17279	0.74564	0.74369	0.77494	0.80171	0.77687
	Valence orbital energies in a.u.					
	$\varepsilon(4s)$	-0.22698	-0.22704	-0.22708	-0.22709	-0.22709
	$\varepsilon(3d)$	-0.49698	-0.49693	-0.49690	-0.49689	-0.49690

(d) Chromium K(2)L(8)M(8)$4s^1 3d^5$, ^7S, MP(0,1,2)

STO	Exponents	Full H-F-R (8s/2d) coefficients	MODEL POTENTIAL H-F-R Coefficients			
			(6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	24.98800	-0.00347				
1s	17.51200	-0.02869				
2s	11.63200	-0.02945	-0.10706			
2s	9.16411	0.14584	0.16611			
3s	4.72727	-0.20226	-0.11803	0.09097		
3s	3.13745	-0.05242	-0.09666	-0.27323	-0.12578	
4s	1.74438	0.45362	0.43405	0.47732	0.33860	0.38432
4s	0.96230	0.65446	0.68251	0.67375	0.76665	0.69940
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	5.13843	0.40714	0.41269	0.40458	0.36340	0.39003
3d	2.07723	0.73242	0.72782	0.73453	0.76768	0.74642
	Valence orbital energies in a.u.					
	$\varepsilon(4s)$	-0.20772	-0.20764	-0.20781	-0.20768	-0.20763
	$\varepsilon(3d)$	-0.33930	-0.33929	-0.33921	-0.33927	-0.33929

(e) **Chromium** K(2)L(8)M(8)$4s^2 3d^4$, ^5D, MP(0,1,2)

STO	Exponents	Full H-F-R (8s/2d) coefficients	MODEL POTENTIAL H-F-R Coefficients (6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	24.99790	-0.00449				
1s	17.40750	-0.03030				
2s	12.66540	-0.02208	0.08053			
2s	9.19252	0.14648	-0.14157			
3s	4.64782	-0.22770	0.12160	0.11057		
3s	3.09125	-0.04889	0.11731	-0.32659	-0.14378	
4s	1.77218	0.50946	-0.50041	0.56343	0.37698	0.39856
4s	1.01451	0.59636	-0.62165	0.60404	0.73298	0.67745
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	5.40992	0.38301	0.36371	0.34404	0.32421	0.31398
3d	2.34014	0.73672	0.75263	0.76852	0.78425	0.79224
	Valence orbital energies in a.u.					
	$\epsilon(4s)$	-0.23523	-0.23500	-0.23512	-0.23512	-0.23503
	$\epsilon(3d)$	-0.55218	-0.55224	-0.55220	-0.55220	-0.55221

(f) **Manganese** K(2)L(8)M(8)$4s^2 3d^5$-^6S, MP(0,1,2)

STO	Exponents	Full H-F-R (8s/2d) coefficients	MODEL POTENTIAL H-F-R Coefficients (6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	26.03260	-0.00382				
1s	18.36130	-0.03038				
2s	12.94970	-0.02688	-0.09284			
2s	9.66930	0.14980	0.15397			
3s	4.94055	-0.21814	-0.11761	0.10447		
3s	3.29090	-0.05134	-0.11277	-0.30406	-0.13528	
4s	1.84488	0.50463	0.48803	0.53306	0.35746	0.40927
4s	1.04408	0.60238	0.63243	0.62560	0.74822	0.67046
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	5.76739	0.38984	0.39595	0.43206	0.45304	0.35648
3d	2.50969	0.72965	0.72450	0.69344	0.67488	0.75722
	Valence orbital energies in a.u.					
	$\epsilon(4s)$	-0.24262	-0.24265	-0.24273	-0.24250	-0.24265
	$\epsilon(3d)$	-0.61762	-0.61759	-0.61752	-0.61765	-0.61757

(g) Iron K(2)L(8)M(8)$4s^2 3d^6$, ^5D, MP(0,1,2)

STO	Exponents	Full H-F-R (8s/2d) coefficients	MODEL POTENTIAL H-F-R Coefficients			
			(6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	27.03350	-0.00392				
1s	29.01040	-0.03027				
2s	13.51700	-0.02829	0.09110			
2s	10.13050	0.15090	-0.15187			
3s	5.21660	-0.21377	0.11698	0.10244		
3s	3.47616	-0.05096	0.10772	-0.29209	-0.12768	
4s	1.92517	0.50156	-0.47973	0.51434	0.35053	0.41648
4s	1.07742	0.60709	-0.64046	0.64072	0.75404	0.66666
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	6.06828	0.40379	0.41437	0.48182	0.45934	0.37677
3d	2.61836	0.71984	0.71082	0.65102	0.67139	0.74246
	Valence orbital energies in a.u.					
	ε(4s)	-0.25129	-0.25112	-0.25131	-0.25132	-0.25106
	ε(3d)	-0.61788	-0.61794	-0.61763	-0.61782	-0.61790

(h) Cobalt K(2)L(8)M(8)$4s^2 3d^7$, ^4F, MP(0,1,2)

STO	Exponents	Full H-F-R (8s/2d) coefficients	MODEL POTENTIAL H-F-R Coefficients			
			(6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	28.03440	-0.00394				
1s	19.67470	-0.03008				
2s	14.03660	-0.02990	-0.09210			
2s	10.58910	0.15176	0.15183			
3s	5.50254	-0.20743	-0.11169	0.09924		
3s	3.67136	-0.05214	-0.10563	-0.27740	-0.12193	
4s	2.00140	0.49765	0.46866	0.49102	0.34756	0.42264
4s	1.10841	0.61250	0.65116	0.65880	0.75660	0.66369
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	6.38612	0.41333	0.43054	0.53220	0.46349	0.39309
3d	2.74495	0.71262	0.69778	0.60471	0.66865	0.72975
	Valence orbital energies in a.u.					
	ε(4s)	-0.25907	-0.25904	-0.25921	-0.25918	-0.25908
	ε(3d)	-0.63869	-0.63866	-0.63856	-0.63859	-0.63868

(I) Nickel $K(2)L(8)M(8)4s^23d^8$, ^3F, MP(0,1,2)

STO	Exponents	Full H-F-R (8s/2d) coefficients	MODEL POTENTIAL H-F-R Coefficients (6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	29.03620	-0.00389				
1s	20.35820	-0.02991				
2s	14.50890	-0.03189	-0.09397			
2s	11.04660	0.15289	-0.15254			
3s	5.79629	-0.20048	-0.10593	0.09646		
3s	3.87206	-0.05423	-0.10377	-0.26416	-0.11573	
4s	2.07712	0.49292	0.45472	0.46972	0.33966	0.42493
4s	1.13888	0.61875	0.66434	0.67536	0.76316	0.66420
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	6.70551	0.42120	0.44715	0.57761	0.46986	0.40838
3d	2.87381	0.70658	0.68395	0.56077	0.66366	0.71754
	Valence orbital energies in a.u.					
	ε(4s)	-0.26640	-0.26643	-0.26644	-0.26647	-0.26639
	ε(3d)	-0.66185	-0.66173	-0.66157	-0.66177	-0.66150

(J) Copper $K(2)L(8)M(8)4s^13d^{10}$, ^2S, MP(0,1,2)

STO	Exponents	Full H-F-R (8s/2d) coefficients	MODEL POTENTIAL H-F-R Coefficients (6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	30.00890	-0.00333				
1s	21.03960	-0.02322				
2s	14.46680	-0.03356	-0.08712			
2s	11.44970	0.13085	0.13328			
3s	6.19332	-0.15333	-0.07957	0.06436		
3s	4.06469	-0.04224	-0.07278	-0.17534	-0.08387	
4s	2.00757	0.41432	0.36078	0.35294	0.29560	0.37799
4s	1.03682	0.69833	0.74918	0.76681	0.80230	0.72145
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	6.79466	0.44729	0.51269	0.69693	0.50948	0.44636
3d	2.76527	0.69683	0.63811	0.44717	0.64109	0.69762
	Valence orbital energies in a.u.					
	ε(4s)	-0.21805	-0.21805	-0.21813	-0.21807	-0.21776
	ε(3d)	-0.40408	-0.40408	-0.40400	-0.40407	-0.40368

(k) Copper $K(2)L(8)M(8)4s^2 3d^9$, ^2D, MP(0,1,2)

STO	Exponents	Full H-F-R	MODEL POTENTIAL H-F-R Coefficients			
		(8s/2d) coefficients	(6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	30.03790	-0.00381				
1s	21.04960	-0.02971				
2s	14.95750	-0.03408	-0.10134			
2s	11.50220	0.15417	0.16226			
3s	6.09683	-0.19338	-0.11052	0.09314		
3s	4.07634	-0.05662	-0.09395	-0.24980	-0.11091	
4s	2.15090	0.48850	0.43313	0.44219	0.33019	0.42363
4s	1.16808	0.62466	0.68276	0.69699	0.77117	0.66791
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	7.02531	0.42787	0.54547	0.71053	0.54661	0.48909
3d	3.00372	0.70140	0.59331	0.41727	0.59220	0.64674
	Valence orbital energies in a.u.					
	$\epsilon(4s)$	-0.27338	-0.27332	-0.27358	-0.27338	-0.27350
	$\epsilon(3d)$	-0.68608	-0.68600	-0.68591	-0.68607	-0.68599

(l) Zinc $K(2)L(8)M(8)4s^2 3d^{10}$, ^1S, MP(0,1,2)

STO	Exponents	Full H-F-R	MODEL POTENTIAL H-F-R Coefficients			
		(8s/2d) coefficients	(6s/2d) basis	(4s/2d) basis	(3s/2d) basis	(2s/2d) basis
		(4s)	(4s)	(4s)	(4s)	(4s)
1s	31.00410	-0.00387				
1s	21.53360	-0.02963				
2s	15.27860	-0.03517	-0.10088			
2s	11.90690	0.15497	0.15839			
3s	6.42595	-0.18484	-0.09469	0.09300		
3s	4.29540	-0.06080	-0.09970	-0.24566	-0.10436	
4s	2.22120	0.48426	0.42562	0.45091	0.32835	0.43418
4s	1.19514	0.63036	0.69110	0.68901	0.77261	0.66071
		(3d)	(3d)	(3d)	(3d)	(3d)
3d	7.34928	0.43305	0.51838	0.60039	0.48197	0.41554
3d	3.13941	0.69712	0.61961	0.53845	0.65351	0.71222
	Valence orbital energies in a.u.					
	$\epsilon(4s)$	-0.27973	-0.27979	-0.27971	-0.27973	-0.27983
	$\epsilon(3d)$	-0.71910	-0.71892	-0.71907	-0.71910	-0.71901

TABLE 4.7 Orbital Exponents, Coefficients, Energies and Model Potential Parameters for Sulphur

Sulphur K(2)L(8)$3S^2 2P^4$, 3P, MP(0,1,1).

STO	Exponents (DZ)	Full HFR 6S/4P basis coefficients	MODEL POTENTIAL H-F-R (6S/4P) basis $B=2.0\lvert\varepsilon\rvert$	(6S/4P) basis $B=1.5\lvert\varepsilon\rvert$
		(3s)	(3s)	(3s)
1S	17.07720	0.00074	0.00562	-0.00131
1S	12.69440	0.10897	0.06550	0.07011
2S	6.72875	-0.03080	0.12894	0.09934
2S	5.24284	-0.37678	-0.48306	-0.44321
3S	2.66221	0.59902	0.58983	0.60481
3S	1.68771	0.52459	0.54791	0.53040
		(3p)	(3p)	(3p)
2P	9.51251	-0.05241	-0.01372	-0.01593
2P	5.12050	-0.22012	-0.20189	-0.18798
3P	2.33793	0.53768	0.49988	0.52291
3P	1.33331	0.56153	0.60065	0.57807
	Valence orbital energies in a.u.			
	(3s)	-0.87897	-0.87894	-0.87896
	(3p)	-0.43694	-0.43698	-0.43697

Model Potential Parameters for Sulphur

Basis Set	A_1	A_2	A_3	α_1	α_2	α_3	B_1	B_2	B_3
6S/4P	1.6667	3.6002	0.4332	9.1447	6.0316	2.6742	184.0022[a]	18.0032	13.3624
6S/4P	1.6667	4.0664	0.4176	9.5677	5.6226	2.8882	138.0017[b]	13.5046	10.0218

[a] $B=2.0\lvert\varepsilon\rvert$

[b] $B=1.5\lvert\varepsilon\rvert$

coefficients shows. Especially for less extravagant basis sets, smaller B values gave better fits, larger B values tending to push orbitals out.

A crude explanation for this imvolves the projection term $B_k^c|\phi_k^c\rangle\langle\phi_k^c|$. This is a repulsive term since any overlap of the valence orbital with a core orbital increases the total energy, working against the variation principle. If B_k^c is large, only very little overlap is safe and the orbital is pushed out, while for a smaller B_k^c the valence orbital may shift further inwards for the same gain in total energy.

3. Basis Set Dependency of Model Potentials

In the Bonifacic-Huzinaga formulation of the model potential method, the parameters depend on the basis sets chosen for the calibration. One obvious dependence is in the projection operator terms, which are to be constructed with some <u>specific</u> core orbitals. They represent how well the core orbital shapes and energies are known. For example, it is conceivable that SZ accuracy in the core orbitals would produce a different model potential from that produced by DZ or HF quality in the core. In addition and independently, the valence basis set chosen for calibration affects the model parameters, as it does the shape of the associated pseudo-valence wavefunctions. This basis-set-dependency is common to all model potentials, even though some claims to the contrary have been found in the literature [56a].

Model potentials are primarily constructed for use in molecular calculations, atomic calculations being calibratory in nature.

The basis set dependency usually means that the same accuracy must be maintained in molecular calculation as was used in the calibration. But the flexibility in basis sets may be exploited to construct valence orbitals which are suitable for specific purposes [65].

In this work, we chose model potentials calibrated at DZ accuracy in both the core and valence, a choice which is both economical and close to HF accuracy in most cases.

F. Molecular SCF Computer Program

The SCF calculations are based on a One-Center Expansion program written by Y. Hatano, T. Nomura and K. Tanaka of Hokkaido University and modified by Y. Hatano at Nagoya University, Japan. Originally written in single precision FORTRAN for the FACOM 230-75 computer, it was translated by the present author into the IBM dialect of FORTRAN, modified and run at double precision on the University of Alberta's AMDAHL 470V/6 computer. The modified version is available from the author.

The program is written as an aggregate of many options, each of which performs a specific function and calls a set of subroutines for the purpose. The program makes extensive use of magnetic tapes for the storage and retrieval of intermediate results or data, thus providing an extension to the memory capacity necessary for SCF calculations. We illustrate the general structure of the program by considering the simplest SCF calculation on H_2O, without geometry or orbital exponent optimisation. The sequence of options is:

* MTOPEN opens all magnetic tape files to be used

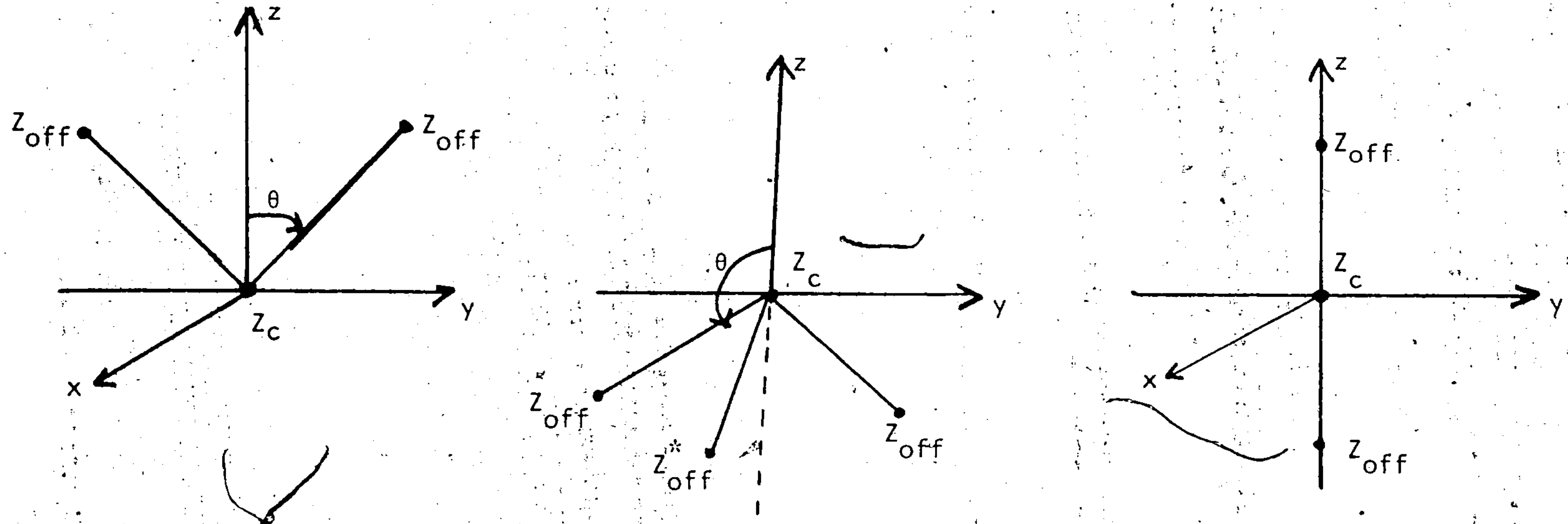
* HEAD allows input of headings and titles

* BASE	reads in basis functions and symmetries
* INTEGRAL	calculates all one-center integrals: overlap, kinetic energy one-center nuclear attraction and two-electron integrals
* OFFCENTER	calculates the offcenter nuclear attraction integrals and nuclear-nuclear repulsion terms
* SCF	solves the Roothaan equations and outputs the SCF results.
* STOP	closes files and terminates the job.

There are many other options.

Clearly, our modification was necessary in *INTEGRAL and/or *OFFCENTER, since we may have model potentials sitting at the expansion center and/or the offcenter nuclei. We did this by adding new options *MPEC and *MPOFF, whose subroutines incorporate model potential terms, but are organised in the same manner as those in *INTEGRAL and *OFFCENTER. Thus they calculate the new OCE-MP integrals without changing the basic organisation of the program, nor its internal alarms, flags, convergence and divergence thresholds. In this way the program is modified to handle all cases covered by Hatano's program, plus cases where the model potential sits at the expansion center, at the off-center locations, or both.

In order to take full advantage of symmetry, [12d] Hatano's program is written specifically for closed-shell hydrides AH_2 of C_{2v} symmetry, or AH_3 of C_{3v} symmetry. As shown in Figure 4.2, the coordinate system chosen is such that the molecular axis is the z-axis bisecting the bond angle in case of C_{2v}, and the expansion center at the heavy central atom A. The C_{2v} molecule lies in the y-z plane. The basis functions corresponding to the different



i) $C_{2v}(D_{\infty h})$ ii) $C_{3v}(D_{3h})$ iii) $C_{\infty v}$ or Illegal $D_{\infty h}$

Fig. 4. 2. Coordinates for C_{2v}, C_{3v} and $D_{\infty h}$

*atom in xz plane

irreducible representations may then be classified according to their spherical harmonics. Table 4.8 summarises the classification of symmetries encountered, in our own notation.

The dimensions imposed on the arrays allow the program to handle up to 25 basis functions per symmetry species, for a grand total of 50 functions per molecule. The STO quantum numbers are limited to n an integer up to 25 and ℓ up to 7, which are considered sufficient for most applications.

As shown in Figure 4.2, the program can handle $D_{\infty h}$ and D_{3h} symmetry when $\theta = 90^{\circ}$. We had set our sights on N_2 as the test case for the development of the OCE-MP method, and soon realised the problems involved in putting the N atoms on the y-axis. One problem is that basis function not normally considered in $D_{\infty h}$ symmetry have to be included, e.g., d_{+2} in σ_g (A_1) symmetry, thus restricting the calculation to an essentially smaller basis.

The other immediate problem was that, with model potentials at the offcenter position, rotational coordinate transformation would be needed for the integrals, a feature we did not have initially and which we consider extraneous complication in the development. This feature is not explicitly present in Hatano's program, since their offcenter nuclear attraction integrals are apparently calculated by the method of expanding $\frac{1}{r_b}$ in terms of spherical harmonics and then using Wigner 3j-symbols.

We therefore instead explored the possibility of "tricking" the program to handle molecules with atoms situated on the z-axis, in

Table 4.8: Symmetry Classification of Basis Functions for C_{2v} and C_{3v} Groups

C_{2v}

Symmetry Label	Spherical Harmonic
1 (A_1)	$S_{\ell,0}$, $S_{\ell,+(2+2k)}$
2 (B_1)	$S_{\ell,-(1+2k)}$
3 (B_2)	$S_{\ell,+(1+2k)}$
4 (A_2)	$S_{\ell,-(2+2k)}$

C_{3v}

Symmetry Label	Spherical Harmonic
1 (A_1)	$S_{\ell,0}$, $S_{\ell,+(3+3k)}$
2 (E_x)	$S_{\ell,-(1+3k)}$
3 (E_y)	$S_{\ell,+(1+3k)}$
4 (A_2)	$S_{\ell,-(3+3k)}$

$k = 0,1,2,3, \ldots$

which case the integrals are as developed in Chapter 5 without rotational coordinate transformation. Slight modifications were needed in the *OFFCENTER or *MPOFF routines of our program.

The modified program was tested on linear H_2O with Moccia's bases [12c], along both the y- and z-axes. The results, were identical showing the proper π-like (π_x-π or π_x-π_y) degeneracy characteristics. The program was also tested on the C_{2v} molecule HF with Moccia's basis, and yielded exactly the same results as Moccia's. The program was now ready for N_2.

We have subsequently incorporated the rational coordinate transforamtion feature, since it cannot be avoided in non-linear molecules such as SO_2.

CHAPTER V

CONVOLUTION METHODS FOR NEW MOLECULAR INTEGRALS

A. Introduction

In Chapter 4, we saw that the coupling of the One-Center Expansion (OCE) method to the STO - Screened Model Potential (MP) approximation produces new types of molecular integrals, whose specific solutions could not be found in the literature. We saw that the one-center versions of these integrals are easily transformed into common atomic forms and so solved using familiar techniques. The two-center integrals, on the other hand, require more elaborate procedures.

In this chapter, the Fourier Convolution Method is adapted to solve all the two-center integrals that arise in the OCE-MP algorithm. The principles of the method are defined and previous usage of the method is reviewed. Then, application to OCE-MP integrals is followed through carefully and in detail, and numerical results are presented at the end.

The Fourier Convolution method is, in principle, an exact method, the only approximations coming possibly from tolerances imposed by numerical computational procedures. The results are thus expected, and indeed are found, to be indistinguishable from the most accurate available, in those cases where comparisons are possible.

Several useful off-shoots to the method became apparent in the course of the derivation, and these are recorded in later sections of the chapter. Notable are the various novel uses to which our Clebsch-Gordan coefficients are put, and a new convolution scheme suggested for solving one-center overlap and electron-repulsion integrals.

B. Fourier Convolution Method

As proposed by Prosser and Blanchard [26] this method states that a one-electron, two-center integral of the form

$$I(\underset{\sim}{R}) = \int f(\underset{\sim}{r}_a)g(\underset{\sim}{r}_b)d\underset{\sim}{\tau} \tag{5-1}$$

where (see Figure 5.1) $\underset{\sim}{r}_a$, $\underset{\sim}{r}_b$, $\underset{\sim}{R}$ are the sides of a vector triangle and $d\underset{\sim}{\tau}$ is the volume element, can be recovered through the Fourier Convolution theorem as

$$I(\underset{\sim}{R}) = A_p \int_{\underset{\sim}{k}\text{-space}} F(\underset{\sim}{k})G(\underset{\sim}{k})e^{-i\underset{\sim}{k}\,\underset{\sim}{R}}\,d\underset{\sim}{k} \tag{5-2}$$

where $F(\underset{\sim}{k})$ and $G(\underset{\sim}{k})$ are the Fourier Transforms [68] of $f(\underset{\sim}{r})$ and $g(\underset{\sim}{r})$ respectively:

$$F(\underset{\sim}{k}) \equiv f^T(\underset{\sim}{k}) = (2\pi)^{-\frac{3}{2}} \int_{\underset{\sim}{r}\text{-space}} e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} f(\underset{\sim}{r})d\underset{\sim}{r} \tag{5-3a}$$

$$G(\underset{\sim}{k}) \equiv g^T(\underset{\sim}{k}) = (2\pi)^{-\frac{3}{2}} \int_{\underset{\sim}{r}\text{-space}} e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} g(\underset{\sim}{r})d\underset{\sim}{r} \tag{5-3b}$$

and A_p is some constant related to the parity of $g(\underset{\sim}{r}_b)$, i.e., to whether or not g changes sign when $\underset{\sim}{r}_b$ does.

<u>Proof of Claim</u> (After Prosser and Blanchard)

The claim is that equation (5-1) and (5-2) are equivalent.

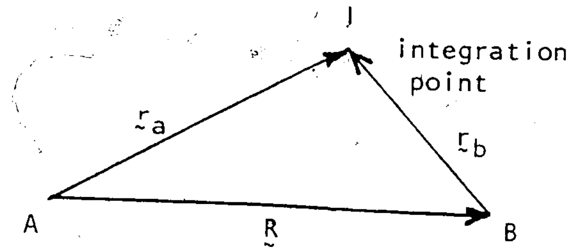


Figure 5.1 Two-Center Coordinates for One-Electron Convolution Method

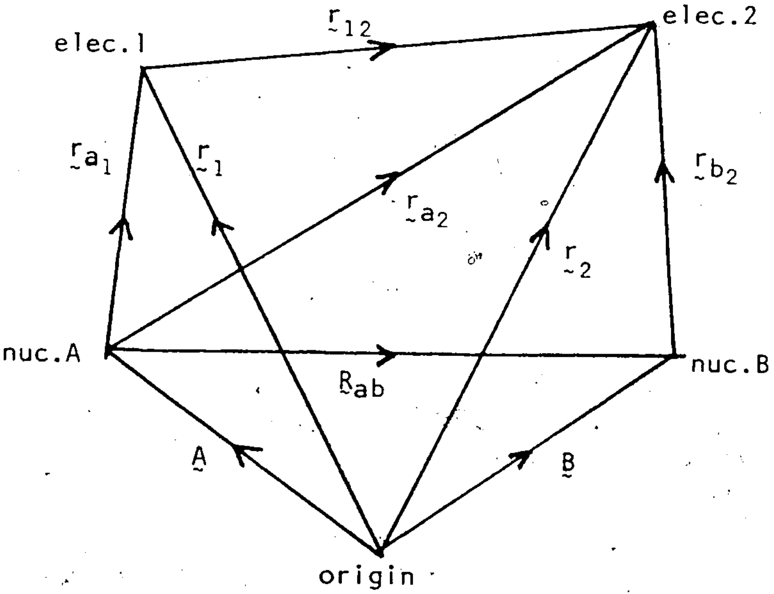


Figure 5.2 Two-Center Coordinates for Two-Electron Convolution Methods

Step 1. From Figure 5.1, $\underset{\sim}{r}_b = \underset{\sim}{r}_a - \underset{\sim}{R}$. Equation (5-1) can then be rewritten as

$$I(\underset{\sim}{R}) = \int f(\underset{\sim}{r}_a) g(\underset{\sim}{r}_a - \underset{\sim}{R})\, d\underset{\sim}{r}_a \tag{5-4}$$

which is called the "convolution" or "folding" of the function g with the function f.

Step 2. Lemma (Fourier Convolution theorem [69]): The Fourier transform of the convolution of two functions is the product of the Fourier transforms of those two functions. Thus the Fourier transform of $I(\underset{\sim}{R})$,

$$I^T(\underset{\sim}{k}) \equiv (2\pi)^{-\frac{3}{2}} \int_{\underset{\sim}{k}} I(\underset{\sim}{R})\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}}\, d\underset{\sim}{R} \tag{5-5}$$

is given by

$$I^T(\underset{\sim}{k}) = F(\underset{\sim}{k}) G(\underset{\sim}{k}) \tag{5-6}$$

where $F(\underset{\sim}{k})$ and $G(\underset{\sim}{k})$ are the transforms in (5-3).

Proof of Lemma.

$$\begin{aligned} I^T(\underset{\sim}{k}) &= (2\pi)^{-\frac{3}{2}} \int I(\underset{\sim}{R})\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}}\, d\underset{\sim}{R} \\ &= (2\pi)^{-\frac{3}{2}} \int_{\underset{\sim}{R}} \int_{\underset{\sim}{r}_1} f(\underset{\sim}{r}_a) g(\underset{\sim}{r}_a - \underset{\sim}{R})\, d\underset{\sim}{r}_a\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}}\, d\underset{\sim}{R} \\ &= (2\pi)^{-\frac{3}{2}} A_p \int_{\underset{\sim}{R}} \int_{\underset{\sim}{r}_1} f(\underset{\sim}{r}_a) g(\underset{\sim}{R} - \underset{\sim}{r}_a)\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}} \cdot e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}_a} \cdot e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}_a}\, d\underset{\sim}{r}_a\, d\underset{\sim}{R} \\ &= (2\pi)^{-\frac{3}{2}} A_p\, (2\pi)^{\frac{3}{2}} \int_{\underset{\sim}{R}} F(\underset{\sim}{R})\, g(\underset{\sim}{R} - \underset{\sim}{r}_a)\, e^{i(\underset{\sim}{R} - \underset{\sim}{r}_a)}\, d\underset{\sim}{R}\ . \end{aligned} \tag{5-7}$$

Since in this form $\underset{\sim}{r}_a$ is independent

$$d\underset{\sim}{R} = d(\underset{\sim}{R} - \underset{\sim}{r}_a) \qquad (5\text{-}8)$$

$$\therefore I^T(k) = A_p \int_{\underset{\sim}{R}} F(\underset{\sim}{k}) g(\underset{\sim}{R}-\underset{\sim}{r}_a) e^{i\underset{\sim}{k}\cdot(\underset{\sim}{R}-\underset{\sim}{r}_a)} d(\underset{\sim}{R}-\underset{\sim}{r}_a)$$

$$= A_p \; F(\underset{\sim}{k}) G(\underset{\sim}{k}) \cdot (2\pi)^{\frac{3}{2}} \qquad (5\text{-}9)$$

where A_p is defined by the parity equation

$$g(\underset{\sim}{r}_a - \underset{\sim}{R}) = A_p \; g(\underset{\sim}{R} - \underset{\sim}{r}_a) \qquad (5\text{-}9a)$$

and expresses the parity of g.

Step 3. We use the Fourier Inversion Integral (Inverse Fourier Transform) associated with (5-5):

$$I(\underset{\sim}{R}) = (2\pi)^{-\frac{3}{2}} \int_{\underset{\sim}{k}} I^T(\underset{\sim}{k}) \; e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}} \, d\underset{\sim}{k} \;. \qquad (5\text{-}5a)$$

Substituting (5-9) in (5-5a) immediately leads to (5-2):

$$I(\underset{\sim}{R}) = A_p \int F(\underset{\sim}{k}) \; G(\underset{\sim}{k}) \; e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}} \, d\underset{\sim}{k} \qquad \text{Q.E.D.} \qquad (5\text{-}2)$$

Alternative Proof. It is possible to prove the equivalence of equations (5-1) and (5-2) without directly using the Fourier Convolution Theorem:

Step 1. Form Convolution eqn (5-4)

Step 2. Define the Inverse Fourier Transforms [68] of eqn (5-3a) and (5-3b):

$$f(\mathbf{r}) = (2\pi)^{-\frac{3}{2}} \int_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} F(\mathbf{k})\, d\mathbf{k} \qquad (5\text{-}10a)$$

$$g(\mathbf{r}) = (2\pi)^{-\frac{3}{2}} \int_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} G(\mathbf{k})\, d\mathbf{k} \qquad (5\text{-}10b)$$

Define the parity operator A_p:

$$g(\mathbf{R} - \mathbf{r}_a) = A_p\, g(\mathbf{r}_a - \mathbf{R}) \qquad (5\text{-}9a)$$

<u>Step 3</u>. Substituting all these into (5-4) to get:

$$\begin{aligned} I(\mathbf{R}) &= \int_{\mathbf{r}_1} f(\mathbf{r}_a)\, g(\mathbf{r}_a - \mathbf{R})\, d\mathbf{r}_a \\ &= A_p \int_{\mathbf{r}_1} f(\mathbf{r}_a)\, g(\mathbf{R} - \mathbf{r}_a)\, d\mathbf{r}_a \; . \end{aligned}$$

Use (5-10a) and (5-10b) with $\mathbf{r} = \mathbf{R} - \mathbf{r}_a$:

$$\begin{aligned} I(R) &= A_p \int_{\mathbf{r}_a} f(\mathbf{r}_a)\, d\mathbf{r}_a \; (2\pi)^{-\frac{3}{2}} \int_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{r}_a)}\, G(\mathbf{k})\, d\mathbf{k} \\ &= A_p (2\pi)^{-\frac{3}{2}} \int_{\mathbf{k}} \int_{\mathbf{r}_a} f(\mathbf{r}_a)\, e^{i\mathbf{k}\cdot\mathbf{r}_a}\, d\mathbf{r}_a\, G(\mathbf{k})\, d\mathbf{k} \\ &= A_p (2\pi)^{-\frac{3}{2}} \int_{\mathbf{k}} (2\pi)^{\frac{3}{2}} F(\mathbf{k})\; G(\mathbf{k})\; d\mathbf{k} \end{aligned}$$

$$I(\mathbf{R}) = A_p \int_{\mathbf{k}} F(\mathbf{k}) G(\mathbf{k})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k} \quad . \qquad \text{Q.E.D.} \qquad (5\text{-}2)$$

The Fourier Convolution Method allows the transformation of the two-center integral (5-1) or its 2-centric convolution (5-4) into a <u>one-center</u> Fourier integral (5-2), which is, in principle, a considerable simplification. However, in general, the method requires the evaluation of three integrals, namely $F(k)$, $G(k)$ of equations (5-3a) and (5-3b) and the final integral of equation (5-2). This is not a trivial matter, and can be cumbersome or even impossible in some cases. For f and g Slater type orbitals, these integrals are easily calculated, making the method convenient and essentially exact.

C. Review of Previous Usage of FC Method

The Fourier Convolution Method is very versatile and has been put to a variety of uses by various workers.

1. Two-Center One-Electron Integrals

Prosser and Blanchard [66] have used it to evaluate one-electron two-center integrals arising from molecular orbital analysis of Ramsey's formula for the NMR screening constants. These are of the type

$$I(\underset{\sim}{R}) = \int \phi_a^*(\underset{\sim}{r}_a) f(\underset{\sim}{r}_b) \phi_b(\underset{\sim}{r}_b)\, d\underset{\sim}{r}_b \qquad (5\text{-}11)$$

where $f(r_b)$ is a scalar function of distance from center b, only, which is incorporated in the corresponding Fourier transform for center b:

$$G(\underset{\sim}{k}) = \int_{\underset{\sim}{k}\text{-space}} e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}_b} f(\underset{\sim}{r}_b)\phi_b(\underset{\sim}{r}_b)\, d\underset{\sim}{k} \quad . \qquad (5\text{-}12)$$

In their case the function was

$$f(r_b) = r_b^{-3} \quad . \qquad (5\text{-}12a)$$

Geller [70a] used FC to calculate 2-center overlap integrals for Slater type orbitals of non-integer principal quantum numers n, in calculations on the hydrogen molecule-ion. Later he applied the method to both the two-center and one-center one-electron integrals over products of Slater-type orbitals on one center, and an operator involving "solid spherical harmonics" [functions of the type $r^{-n-1} P_n^m (\cos \phi) \cos m\phi$] on the other center [25]. These integrals are needed in the evaluation of electromagnetic interactions and are essentially of the form

$$\int [N,L,M]_a \frac{r_b^{N'} P_{L'}^{M'} (\cos\theta_b)}{r_b^{L'+1}} \left\{ \begin{array}{c} \cos |M'|\phi \\ \sin |M'|\phi \end{array} \right\} d\tau \tag{5-13}$$

where $[N,L,M]$ are basic charge distributions as defined by Roothaan. Geller's scheme can also handle, as a special case, two-center nuclear attraction integrals of the type

$$\int \chi_a \chi_a' \frac{1}{r_b} d\tau \rightarrow \int [NLM]_a \, r_b^{-1} \, d\tau \tag{5-14}$$

about which more will be said in a later section. Filter and Steinborn [71] have recently evaluated one-electron type convolution integrals over functions of the form

$$B_{\nu,L}^{M}(\underset{\sim}{r}) = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} r^{L+\nu} K_\nu(r) \, Y_L^M (\theta,\phi) \tag{5-15}$$

where $K_\nu(r)$ are modified Bessel Functions of the second kind and $Y_L^M(\theta,\phi)$ are the usual spherical harmonics. The authors show how these "reduced Bessel functions" $B_{\nu,L}^M$ can be used in approximating multicenter molecular integrals, depending essentially upon an expansion of STOs in terms of the "reduced Bessel functions" $B_{\nu,L}^M$. However, it should be noted that in view of the present state of the art, such an expansion has to perform competitively vis-a-vis the Gaussian expansions. It remains to be seen how successful this method will be.

2. Two-Center Two-Electron Integrals.

The Fourier Convolution Theorem has been used by several workers to solve double integrals of the form

$$C = \iint_{\underset{\sim}{r}\text{-space}} f(\underset{\sim}{r}_{a1})\, g(\underset{\sim}{r}_{b2})\, h(\underset{\sim}{r}_{12})\, d\underset{\sim}{r}_1\, d\underset{\sim}{r}_2 \tag{5-16}$$

where $\underset{\sim}{r}_{a1}$, $\underset{\sim}{r}_{b2}$, are electron nuclear distances and $\underset{\sim}{r}_{12} = \begin{cases} \underset{\sim}{r}_2 - \underset{\sim}{r}_1 \\ \underset{\sim}{r}_{2a} - \underset{\sim}{r}_{1a} \end{cases}$ is interelectronic distance (Figure 5.2). The integral C is reconstituted through Fourier Convolution ideas as [24]

$$C = A_p \int_{\underset{\sim}{k}\text{-space}} f^T(\underset{\sim}{k})\, g^T(\underset{\sim}{k})\, h^T(\underset{\sim}{k})\, d\underset{\sim}{k} \quad . \tag{5-17}$$

This transformation is achieved through a rather simple trick.

Introduce the inverse Fourier transform representation for $h(\underset{\sim}{r}_{12})$:

$$\begin{aligned} h(\underset{\sim}{r}_{12}) &= h(\underset{\sim}{r}_{2a} - \underset{\sim}{r}_{1a}) \\ &= (2\pi)^{-\frac{3}{2}} \int_{\underset{\sim}{k}\text{-space}} h^T(\underset{\sim}{k})\, e^{-i\underset{\sim}{k}\cdot(\underset{\sim}{r}_{2a}-\underset{\sim}{r}_{1a})}\, d\underset{\sim}{k} \\ &= (2\pi)^{-\frac{3}{2}} \int_{\underset{\sim}{k}\text{-space}} h^T(\underset{\sim}{k})\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}_{1a}}\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}_{2a}}\, d\underset{\sim}{k} \quad . \end{aligned} \tag{5-18}$$

We use the following vector relations, which are extentions to the one-electron case.

$$\underset{\sim}{r}_{2b} = \underset{\sim}{r}_{2a} - \underset{\sim}{R} \;, \qquad \text{where} \qquad \underset{\sim}{R} = \underset{\sim}{B} - \underset{\sim}{A} \quad .$$

So the parity equation equivalent to (5-9a) is

$$g(\underset{\sim}{r}_{2b}) = g(\underset{\sim}{r}_{2a}-\underset{\sim}{R}) = A_p\, g(\underset{\sim}{R}-\underset{\sim}{r}_{2a}) \quad . \qquad (5\text{-}19)$$

Also

$$\underset{\sim}{r}_1 = \underset{\sim}{A} + \underset{\sim}{r}_{1a} \quad \text{so} \quad d\underset{\sim}{r}_1 = d\underset{\sim}{r}_{1a} \ , \qquad \underset{\sim}{A} \ \text{fixed} \ ,$$

$$\underset{\sim}{r}_2 = \underset{\sim}{B} + \underset{\sim}{r}_{2b} \quad \text{so} \quad d\underset{\sim}{r}_2 = d\underset{\sim}{r}_{2b} = d\underset{\sim}{r}_{2a} \ , \qquad \underset{\sim}{B} \ \text{fixed.}$$

Substituting (5-18) and (5-19) in (5-16) gives

$$C = A_p \iint f(\underset{\sim}{r}_{1a}) g(\underset{\sim}{R}-\underset{\sim}{r}_{2a})\ (2\pi)^{-\frac{3}{2}} \int_{\underset{\sim}{k}} h^T(\underset{\sim}{k}) e^{i\underset{\sim}{k}\, \underset{\sim}{r}_{1a}} e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}_{2a}}\, d\underset{\sim}{r}_1 d\underset{\sim}{r}_2$$

$$= A_p\ (2\pi)^{-\frac{3}{2}} \int_{\underset{\sim}{k}} h^T(\underset{\sim}{k}) d\underset{\sim}{k} \int f(\underset{\sim}{r}_{1a}) e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}_{1a}}\, d\underset{\sim}{r}_1 \ \times$$

$$\times \int g(\underset{\sim}{R}-\underset{\sim}{R}_{2a})\ e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}_{2a}}\, d\underset{\sim}{r}_2 \quad .$$

Using the relations (5-3a) and (5-3b), the following results:

$$C = A_p\ (2\pi)^{-\frac{3}{2}} \int_{\underset{\sim}{k}} d\underset{\sim}{k}\ h^T(\underset{\sim}{k})\ (2\pi)^{\frac{3}{2}} f^T(\underset{\sim}{k}) \ \times$$

$$\times \int g(\underset{\sim}{R}-\underset{\sim}{r}_{2a})\ e^{i\underset{\sim}{k}\cdot(\underset{\sim}{R}-\underset{\sim}{r}_{2a})}\ e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}}\, d\underset{\sim}{r}_{2a}$$

$$= A_p\ (2\pi)^{\frac{3}{2}} \int d\underset{\sim}{k}\ h^T(\underset{\sim}{k}) f^T(\underset{\sim}{k}) g^T(\underset{\sim}{k})\ e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}} \qquad (5\text{-}20)$$

where now

$$g^T(\underset{\sim}{k}) = (2\pi)^{-\frac{3}{2}} \int g(\underset{\sim}{R}-\underset{\sim}{r}_{2a})\ e^{i\underset{\sim}{k}\cdot(\underset{\sim}{R}-\underset{\sim}{r}_{a2})}\, dr_{2a} \qquad (5\text{-}20a)$$

The two-electron integral then is solved by finding the three Fourier transforms and solving the integral of eqn (5-20).

A major drawback of this method for molecular integrals is that it can handle only Coulomb-type integrals of the form

$$C(\underset{\sim}{R}) = \iint \chi_a^p(1)\chi_a^q(1) \frac{1}{|\underset{\sim}{r}_1-\underset{\sim}{r}_2|} \chi_b^r(2)\chi_b^s(2)\, d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \qquad (5\text{-}21)$$

i.e., where the charge distribution of each electron is one-centric. This reduces by Roothaan [61] decomposition to integrals between basic charge distributions.

$$C(\underset{\sim}{R}) = \int_{\underset{\sim}{r}_1} \int_{\underset{\sim}{r}_2} \Omega_a(1) \cdot \frac{1}{|\underset{\sim}{r}_1-\underset{\sim}{r}_2|} \Omega_b(2)\, d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \qquad (5\text{-}22)$$

where Ω_a and Ω_b are equivalent to f and g, and $h(\underset{\sim}{r}_{12}) = \frac{1}{|\underset{\sim}{r}_1-\underset{\sim}{r}_2|}$ is the electron repulsion potential. The method cannot handle exchange-type integrals:

$$C(R) = \iint \chi_a^p(1)\chi_b^q(1) \cdot \frac{1}{|\underset{\sim}{r}_1-\underset{\sim}{r}_2|} \cdot \chi_a^r(2)\chi_b^s(2)\, d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \qquad (5\text{-}23)$$

which demands the evaluation of 2-centric charge distributions.

Geller [70b] has used the method to evaluate two-center coulomb-type integrals with

$$h(\underset{\sim}{r}_{12}) = \frac{1}{r_{12}} \qquad \text{(pure Coulombic)}$$

and

$$h(\underset{\sim}{r}_{12}) = \begin{cases} r_{12}^{-3}\, P_2(\cos\theta_{12}) \\ \text{or} \\ r_{12}^{-3}\, P_2^2(\cos\theta_{12}) \cos 2\phi_{12} \,. \end{cases} \qquad (5\text{-}24)$$

These two-particle potential operators arise in the analysis of zero-field splitting in molecules [70c]. Geller's derivations usually involve the use of Condon-Shortley coefficients and spherical Bessel functions. Perhaps the most obvious characteristic of his derivations is that they reduce to a lengthy list of special final formulas for each combination of orbitals or basic charge distributions, rather than one final general formula.

A slightly different procedure is that of Harris and Michels for two-center Coulomb Electron replusion integrals. They use a different type of vector coupling coefficients, and exploit a number of recurrence procedures to obtain a unified final expression. Their method, as adapted in this work, is discussed in detail in Section C of this chapter.

3. One-Center Integrals: A Limiting Case as $R \to 0$?

Geller [25,70b] noticed that the one-center one-electron and two-electron integrals can be formulated as a special case of the two-center general formulas. For example, by letting $R = 0$ in equations (5-16) and (5-20), centers A and B fuse together and the subscripts a and b can be dropped. The resulting integral is

$$J = \iint f(\underset{\sim}{r}_1)g(\underset{\sim}{r}_2)h(\underset{\sim}{r}_{12})d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \tag{5-25}$$

which can be recovered through Fourier Convolution as

$$J = A_p(2\pi)^{\frac{3}{2}} \int f^T(\underset{\sim}{k})g^T(\underset{\sim}{k})h^T(\underset{\sim}{k})d\underset{\sim}{k} \quad . \tag{5-26}$$

The efficacy of this route to one-center integrals has not been put to numerical testing, the probable reason being the existence of the authoritative and well-established Laplace expansion method for $\frac{1}{r_{12}}$ as used by Roothaan.

4. Three- and Four-Center Integrals

Ruedenberg [72] has derived the convolution integrals to be solved in the case of multicenter two-electron integrals. His method hinges on the manipulation of the Fourier transform of the 2-electron interaction potential. He writes the Fourier inversion formula (5-18) as

$$h(r_{12}) = (2\pi)^{-\frac{3}{2}} \int d\mathbf{k}\, h^T(\mathbf{k})\, e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}$$

where $r_{12} = |\mathbf{r}_1-\mathbf{r}_2|$, and defines new variables

$$\begin{aligned} &\mathbf{s}_1 = \mathbf{r}_1 - \mathbf{A}, \quad \mathbf{s}_2 = -(\mathbf{r}_2 - \mathbf{B}) \\ &\mathbf{s}_3 = -\mathbf{R} \qquad \text{(see Figure 5.2)} \end{aligned} \tag{5-27}$$

It is clear that

$$\mathbf{r}_1 - \mathbf{r}_2 = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 \quad . \tag{5-28}$$

Thus he can write

$$h(r_{12}) = (2\pi)^{-\frac{3}{2}} \int d\mathbf{k}\, h^T(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{s}_1}\, e^{i\mathbf{k}\cdot\mathbf{s}_2}\, e^{i\mathbf{k}\cdot\mathbf{s}_3} \quad . \tag{5-29}$$

Applying the plane wave expansion

$$e^{i\mathbf{ks}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} J_\ell(\mathbf{ks})\, Y_{\ell m}(\theta,\phi)\, Y_{\ell m}(u,v) \tag{5-30}$$

where $s = (s,\theta,\phi)$ and $k = (k,u,v)$, to each term, and carrying on, he is able to recover a Coulomb-type integral

$$J = \int dv_1 \int dv_2\, \omega'(1)\omega''(2)/r_{12} \tag{5-31}$$

as

$$J = \sum_{\ell m} C(\ell m)\, Y_{\ell_3 m_3}(\theta_3,\phi_3)\, F_{\ell m}(s_3) \tag{5-32}$$

where

$$F_{\ell\bar{m}}(s_3) = \left(\frac{16}{\pi}\right) i^{\ell_1+\ell_2+\ell_3} \int_0^{\infty} dk\, F'_{\ell_1 m_1}(k)\, F''_{\ell_2 m_2}(k)\, j_{\ell_3}(ks_3) \tag{5-33}$$

and

$$F'_{\ell_1 m_1}(k) = \iiint dv_1\, Y_{\ell_1 m_1}(\theta_1 \phi_1)\, j_{\ell_1}(ks_1)\omega'(s_1) \tag{5-34}$$

$$F''_{\ell_2 m_2}(k) = \iiint dv_2\, Y_{\ell_2 m_2}(\theta_2 \phi_2)\, j_{\ell_2}(ks_2)\omega''(s_2) \tag{5-35}$$

$C(\ell m)$ is a vector coupling coefficient

$$C(\ell m) = 2\pi^2 \iint d\phi\, \sin\phi\, d\phi\, Y^*_{\ell_1 m_1}(\theta,\phi) Y^*_{\ell_2 m_2}(\theta,\phi) Y^*_{\ell_3 m_3}(\theta,\phi)\ . \tag{5-36}$$

For three- and four-center integrals, he says the ω's in (5-31) could be two-centric charge distributions

$$\begin{aligned} \omega' &= \chi_a\, \chi_c \\ \omega'' &= \chi_b\, \chi_d \end{aligned} \tag{5-37}$$

The actual evaluation of the 3 integrals (5-33), (5-34) and (5-35) is not a trivial matter, and can pose difficulties. Ruedenberg did not offer any clues as to how they might be evaluated, and no follow-up for actual numerical implementation of this method could be found in the literature. We believe this to be a reflection of scepticism toward the applicability of Ruedenberg's scheme.

5. Other Uses of Fourier Convolution Method

Consider the integral (see Figure 5.1)

$$\int \chi_a^p(1)\ \chi_a^q(1) \cdot \frac{1}{r_b}\ d\underset{\sim}{r}_1\ .$$

This is the potential generated at point B by the charge distribution $\chi_a^p(1)\chi_a^q(1)$ at point 1, in analogy to electrostatic attraction of two point charges. For a charge distribution, it is necessary to integrate over all the space of electron 1 to simulate a point charge. Similarly a two-electron integral of the form (5-22) can be rewritten as

$$C = \int d\underset{\sim}{r}_2\ \Omega_b(2) \int d\underset{\sim}{r}_1\ \Omega_a(1)\ \frac{1}{|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|} \quad . \tag{5-38}$$

Integration over the coordinates of electron 1 amounts to calculating the potential of the corresponding charge distribution at electron 2, i.e.,

$$\begin{aligned} U_a(r_2,\theta_2,\phi_2) &= \int \Omega_a(1) \cdot \frac{1}{r_{12}}\, dr_1 \\ &= \iiint [N,L,M]_a(r_1,\theta_1,\phi_1)\ \frac{1}{r_{12}} \cdot r_1^2 dr_1 \\ &\qquad \sin\theta_1 d\theta_1\ d\phi_1 \end{aligned} \tag{5-39}$$

is the potential for electron 2 due to the charge distribution of electron 1. Roothaan has used these ideas to evaluate two-center two-electron Coulomb integrals [61].

Ruedenberg, O-ohata and Wilson [66] regarded the Coulomb integral slightly differently. They observed that when written as

$$C(\underset{\sim}{R}) = \int d\underset{\sim}{r}_1\ [\int d\underset{\sim}{r}_2\ \Omega_a(1)\Omega_b(a)] \cdot \frac{1}{r_{12}} \tag{5-40}$$

the integral can be regarded as the potential arising from a source defined by the overlap integral between charge disbtributions f and g

$$S(\underset{\sim}{R}) = \int d\underset{\sim}{r}\ f(\underset{\sim}{r}_a)\ g(\underset{\sim}{r}_b) \quad . \tag{5-41}$$

This led them to consider the Poisson equation

$$\Delta_R\ C(\underset{\sim}{R}) = -4\pi\ S(\underset{\sim}{R}) \tag{5-42}$$

and its inverse

$$C(\underset{\sim}{R}) = \int dV'\ S(\underset{\sim}{R}')/|\underset{\sim}{R}-\underset{\sim}{R}'| \tag{5-43}$$

as valid.

The proof of these two equations was carried out by the Fourier convolution method:

$$S(\underset{\sim}{R}) = \int d\underset{\sim}{k}\ f^T(\underset{\sim}{k})\ g^T(\underset{\sim}{k})\ e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}}$$

as above, and

$$C(\underset{\sim}{R}) = 4\pi \int f^T(\underset{\sim}{k})\ g^T(\underset{\sim}{k})\ |\underset{\sim}{k}|^{-2}\ e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}} \tag{5-44}$$

since

$$h^T(\underset{\sim}{k}) = 4\pi\ |\underset{\sim}{k}|^{-2}$$

when

$$h(\underset{\sim}{r}_{12}) = h(|\underset{\sim}{r}_1-\underset{\sim}{r}_2|) = \frac{1}{|\underset{\sim}{r}_1-\underset{\sim}{r}_2|} \quad .$$

Differentiating (5-44) with respect to $\underset{\sim}{R}$ twice under the integral sign gives (by Liebnitz Rule)

$$\begin{aligned}\Delta_R\ C(\underset{\sim}{R}) &= 4\pi \int (-ik)^2|\underset{\sim}{k}|^{-2}\ f^T(\underset{\sim}{k})\ g^T(\underset{\sim}{k})\ e^{-i\underset{\sim}{k}}\quad d\underset{\sim}{k}\\ &= -4\pi\ S(\underset{\sim}{R})\end{aligned}$$

Expression (5-43) was used to calculate the Coulomb integral, building on their experience in calculation of overlap integrals (5-41).

Silverstone [73] found a clever use for the Fourier Convolution Method: to evaluate the coefficients in the expansion of a function of the form

$$\Psi(\underset{\sim}{r}) = f(\underset{\sim}{r})\ Y_L^M(\theta,\phi) \quad , \tag{5-45}$$

where $Y_L^M(\theta,\phi)$ is a spherical harmonic, in terms of spherical harmonics and radial functions whose coordinates are measured from an arbitrary point in space, vector $\underset{\sim}{R}$ away. The expression for this expansion is

$$\Psi(\underset{\sim}{r}-\underset{\sim}{R}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} V(\ell,m;L,M;\underset{\sim}{r},\underset{\sim}{R})\, Y_\ell^m(\theta,\phi) \quad . \tag{5-46}$$

As usual, the coefficients V can be obtained by multiplying both sides by $Y_\ell^{m*}(\theta,\phi)$ and integrating over the solid angle. Invoking orthogonality of spherical harmonics gives

$$V(\ell,m;L,M;\underset{\sim}{r},\underset{\sim}{R}) = \int_0^{2\pi}\int_0^{\pi} \sin\theta\ d\theta\ d\phi\ Y_\ell^{m*}(\theta,\phi)\Psi(r-R) \quad . \tag{5-47}$$

In order to obtain parity with a 3-dimensional Fourier Convolution integral, Silverstone introduces a Dirac delta-function-type "radial function" $r^{-2}\delta(r'-r)$, in order to validate integration over all space, for

$$\int r^2\ dr \cdot r^{-2}\delta(r-r') = 1 \quad . \tag{5-48}$$

Thus the coefficient is given by

$$V(\ell,m;L,M;\underset{\sim}{r},\underset{\sim}{R}) = \int d\underset{\sim}{r}'\ \phi^*(\underset{\sim}{r}')\Psi(\underset{\sim}{r}'-\underset{\sim}{R}) \tag{5-49}$$

where now

$$\phi(\underset{\sim}{r}') = r^{-2}\ \delta(r-r')\ Y_\ell^m(\theta,\phi) \quad . \tag{5-50}$$

Eqn. (5-49) is clearly in convolution form, c.f., equation (5-4), and thus amenable to the use of Fourier Convolution methods. He used this to obtain expansions of STOs

$$\Psi(\underset{\sim}{r}) = N \cdot r^{n-1}\ e^{-\zeta r}\ \ Y_L^M(\theta,\phi) \tag{5-50a}$$

parallel to those of Barnett and Coulson[74] and Harris and Michels [19]. Blakemore and co-workers [75] have used the Fourier Convolution theorem to solve molecular integrals involving Green's functions. In their methods, the primary ingredient is their variational principle, which is formulated using the functional

$$\eta = \frac{\iint \omega^*(1)\ V(1)\ G(1,2)\ V(2)\omega(2)\ d\underset{\sim}{r}_1\ d\underset{\sim}{r}_2}{\int \omega^*\ V\ \omega\ dx} \tag{5-51}$$

where

$$V(r) = -\left(\frac{1}{r_a} + \frac{1}{r_b}\right) \qquad \text{(potential engergy)} \tag{5-52}$$

$$\omega(r) = e^{-c\lambda}\ , \qquad \text{a trial function} \tag{5-53}$$

$$\lambda = (\underset{\sim}{r}_a + \underset{\sim}{r}_b)/\underset{\sim}{R} \tag{5-54}$$

$$G(1,2) = -\frac{1}{2\pi\underset{\sim}{r}_{12}}\ e^{-k\underset{\sim}{r}_{12}} \tag{5-55}$$

where $r_{12}=|\underset{\sim}{r}_2-\underset{\sim}{r}_1|$ and

$$w = \frac{1}{2}k^2 - \frac{1}{R} \tag{5-56}$$

is the total energy.

The double integral in eqn (5-51) is simply of standard form (5-16) for the use of Fourier Convolution. Writing $G(r_1,r_2,k)$ in Fourier transform form,

$$G(\underset{\sim}{r}_1,\underset{\sim}{r}_2,k) = -\frac{1}{4\pi^3}\int e^{-is\cdot(\underset{\sim}{r}_1-\underset{\sim}{r}_2)}(s^2+k^2)^{-1}\,ds \tag{5-57}$$

gives immediately

$$I = \iint \omega^*(1)\,V(1)G(1,2)V(2)\omega(2)\;d\underset{\sim}{r}_1\,d\underset{\sim}{r}_2$$

$$= -\frac{1}{4\pi^3}\int |F(\underset{\sim}{s})|^2\,(s^2+k^2)^{-1}\,d\underset{\sim}{s} \tag{5-58}$$

where

$$F(\underset{\sim}{s}) = \int \omega^*(\underset{\sim}{r})\;V(\underset{\sim}{r})\;e^{-i\underset{\sim}{s}\,\underset{\sim}{r}}\,d\underset{\sim}{r}\quad . \tag{5-58}$$

D. Application to OCE-MP Integrals

1. The Scope

In this work, the Fourier Convolution scheme of Harris and Michels [24] is modified to evaluate integrals which can be represented in generalised two-center overlap form:

$$I(\underset{\sim}{R}) = \int (n_1,\ell_1,m_1,\delta_1)^*_a\,(n_2,\ell_2,m_2,\delta_2)_b\;d\tau$$

$$= \langle (n_1,\ell_1,m_1,\delta_1)_a|(n_2,\ell_2,m_2,\delta_2)_b\rangle\quad . \tag{5-60}$$

Here, (n,ℓ,m,δ) is a loosely defined Slater-type function written in the form

$$(n,\ell,m,\delta) = N_{n\ell m}\, r^{n}\, e^{-\delta r}\, P_{\ell}^{|m|}(\cos\theta) \begin{Bmatrix} \cos|m|\phi \\ \cos|m|\phi \end{Bmatrix} \qquad (5\text{-}61)$$

where $N_{n\ell m}$ is the overall radial and angular normalisation factor. This function is adapted from Roothaan's definition of STOs with real spherical harmonics:

$$(n,\ell,m,\delta) = \frac{(2\delta)^{n+3/2}}{[(2n+2)!]^{1/2}}\, r^{n}\, e^{-\delta r}\, s_{\ell m}(\theta,\phi) \qquad (5\text{-}62)$$

where $s_{\ell m}(\theta,\phi)$ are normalised real spherical harmonics defined by

$$S_{\ell 0}(\theta,\phi) = Y_{\ell 0}(\theta,\phi)$$

$$= \left[\frac{2\ell+1}{4\pi}\right]^{1/2} P_{\ell}(\cos\theta) \qquad (5\text{-}63)$$

$$S_{\ell,+|m|}(\theta,\phi) = \frac{1}{\sqrt{2}}\{Y_{\ell,-|m|}(\theta,\phi) + Y_{\ell,|m|}(\theta,\phi)\}$$

$$= \left[\frac{2\ell+1}{2\pi}\cdot\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2} P_{\ell}^{|m|}(\cos\theta)\cos|m|\phi \qquad (5\text{-}64)$$

$$S_{\ell,-|m|}(\theta,\phi) = \frac{i}{\sqrt{2}}\{Y_{\ell,-|m|}(\theta,\phi) - Y_{\ell,+|m|}(\theta,\phi)\}$$

$$= \left[\frac{2\ell+1}{2\pi}\cdot\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2} P_{\ell}^{|m|}(\cos\theta)\sin|m|\phi \qquad (5\text{-}65)$$

where $Y_{\ell m}(\theta,\phi)$ are the usual complex spherical harmonics [76]. Notice that the power of r in equations (5-61), (5-62) is slightly different from the usual one. n is any integer such that $-1 \leq n \leq \infty$.

This formulation can handle the following kinds of integrals:

a. Two-Center Overlap Between STOs

$$<(n_1,\ell_1,m_1,\delta_1)_a|(n_2,\ell_2,m_2,\delta_2)_b> \qquad (5\text{-}67)$$

Here $n = 0$ for 1s, 1 for 2s, 2p and so on; and

$$N^{STO}_{n\ell m} = \frac{(2\delta)^{n+3/2}}{[(2n+2)!]^{1/2}}\left[\frac{2\ell+1}{2\pi}\ \frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2}(1+\delta_{m,0})^{-\frac{1}{2}} \qquad (5\text{-}67a)$$

and δ_{m0} is a Kronecker delta. These integrals arise from the projection operator part of the model potential as seen in Chapter 4.

b. Two-Center Nuclear Attraction Integrals

$$<\chi^b_a|\frac{1}{r_b}|\chi^q_a> \qquad (5\text{-}68)$$

can be reconstituted into a overlap form through a Roothaan-type decomposition of the one-center charge distribution:

$$<\chi^p_a|\frac{1}{r_b}|\chi^q_a> \sim \sum_{L,M} B_{LM} <[N,L,M,\bar{\delta}]_a|\frac{1}{r_b}>$$

$$= \sum_{L,M} B_{LM} <[N,L,M,\bar{\delta}]_a|(-1,0,0,0)_b> \qquad (5\text{-}68a)$$

where

$$\bar{\delta} = \delta^p_a + \delta^q_a \qquad (5\text{-}69)$$

$$N_{NLM} = \frac{(\delta)^{-N+2_2L}}{(n+L+1)!}\cdot\left(\frac{2L+1}{4\pi}\right)^{1/2}\left[\frac{2L+1}{2\pi}\cdot\frac{(L-|M|)!}{(L+|M|)!}\right]^{1/2}\cdot(1+\delta_{M0})^{-\frac{1}{2}} \qquad (5\text{-}70)$$

and the Coulomb potential $\frac{1}{r_b}$ is denoted in STO form as

$$(-1,0,0,0) = N^{NUC} \cdot r^{-1} e^{-0r} \cdot P_0^0(\cos\theta) \qquad (5\text{-}71)$$

where

$$N^{NUC} = 1 \quad . \qquad (5\text{-}72)$$

c. Two-Center Electrostatic Model Potential Integrals

These similarly reduce to

$$\sum_{L,M} B_{LM} \quad \langle [NLM\bar{\delta}]_a | (r^n e^{-\delta r})_b \rangle \qquad (5\text{-}73)$$

where $n = -1,0,1,2,3,\ldots$.

i) The case $n = -1$ is the Yukawa-type potential,

$$\frac{e^{-\delta r}}{r} \sim (-1,0,0,\delta) \qquad (5\text{-}74a)$$

$$N^{YUK} = 1 \quad . \qquad (5\text{-}74b)$$

ii) The case $n = 0,1,2,\ldots$ gives the "s-STO-type" potential or Huzinaga Potential

$$r^n e^{-\delta r} \sim (n,0,0,\delta) \quad . \qquad (5\text{-}75)$$

$$N^{HUZ} = 1 \quad . \qquad (5\text{-}76)$$

d. Two-Center Nuclear Attraction Integrals of the Type

$$I = \int \chi_a \cdot \frac{1}{r_b} \chi_b \, d\tau \quad . \qquad (5\text{-}77)$$

Thease can be rewritten as overlap integrals:

$$I = \langle (n_1, \ell_1, m_1, \delta_1)_a | (\text{''}n_2 - 1\text{''}, \ell_2, m_2, \delta_2)_b \rangle \qquad (5\text{-}78)$$

where $\text{''}n_2 - 1\text{''}$ means the power of r in (5-61) is equal to $n_2 - 1$, but that the n in the normalisation factor is still n_2. These integrals do not arise in the OCE-MP method, but it is of interest to note that this method can solve them.

It is thus seen that a unified method has been found to solve, in principle, all the two-center integrals that arise in our OCE-MP Scheme. The ability of this method to solve exactly the attraction integrals with a Yukawa potential (Type C.j.) initially attracted us to the method.

2. Further Definitions and Conventions

a. Coordinate System

The coordinate system adopted in this work is the one with all axes parallel and the polar or z-axes aligned along the internuclear axis in the same direction, as shown in Figure 5.3. Thus

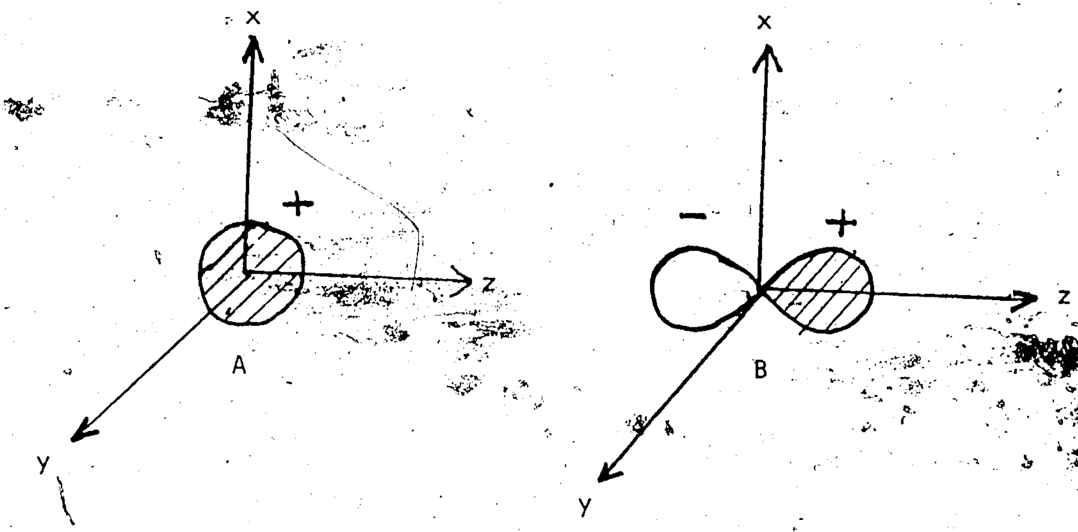


Fig. 5.3. Coordinate system Convention for STOs.

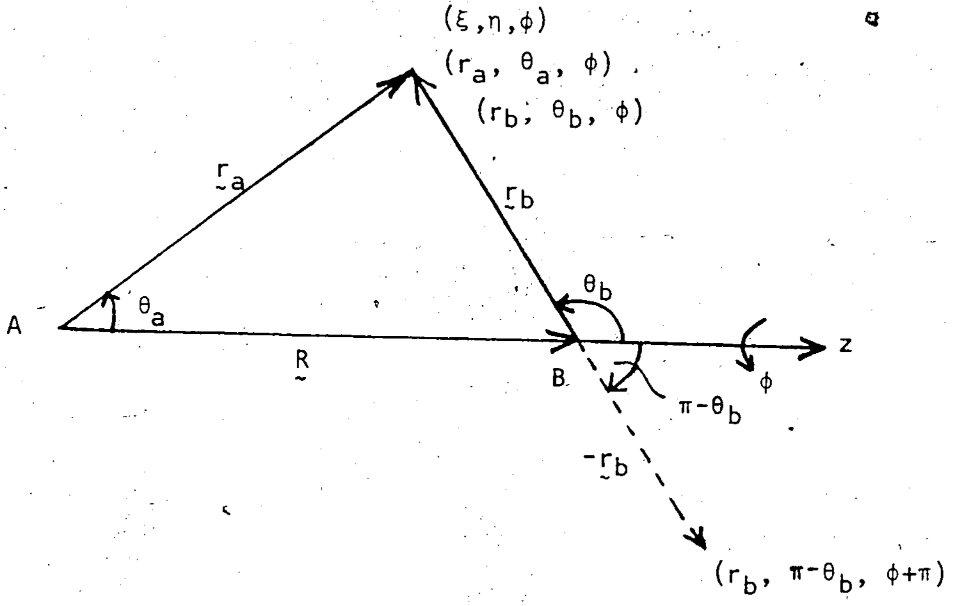


Fig. 5.4. Spheroidal Coordinate system

$\xi=(r_a + r_b)/R, \eta=(r_a - r_b)/R, \phi = \phi_a = \phi_b$

according to this system,

$$\langle S_a | P_{z_b} \rangle \quad \text{is negative}$$

while

$$\langle P_{z_a} | S_b \rangle \quad \text{is positive} .$$

b. Theorem (Roothaan [61])

$$I = \int (n_1,\ell_1,m_1,\delta_1)_a | (n_2,\ell_2,m_2,\delta_2)_b \, d\tau$$

$$= \delta_{m_1 m_2} \cdot \int (n_1,\ell_1,m_1,\delta_1)_a \, (n_2,\ell_2,m_1,\delta_2)_b \, d\tau \quad . \qquad (5\text{-}79)$$

In words, the generalised two-center overlap integral vanishes unless the magnetic quantum numbers of the two functions are the same.

<u>Proof</u>: For this proof (see Figure 5.4), we may, as Roothaan did, adopt the probate spheroidal coordinate (or elliptical coordinates) system in which the integral is separable:

$$(r,\theta,\phi) \rightarrow (\xi,\eta,\phi) \qquad (5\text{-}80)$$

where

$$\xi = (r_a+r_b)/R , \quad \eta = (r_a-r_b)/R , \quad \phi = \phi_a = \phi_b \qquad (5\text{-}81)$$

$$\cos\theta_a = (1+\xi\eta)/(\xi+\eta) , \quad \cos\theta_b = (1-\xi\eta)/(\xi-\eta) \quad . \qquad (5\text{-}82)$$

The Cosine Rule gives also

$$\sin\theta_a = [(\xi^2-1)(1-\eta^2)]^{\frac{1}{2}} / (\xi+\eta) \qquad (5\text{-}83)$$

$$\sin \theta_b = [(\xi^2-1)(1-\eta^2)]^{\frac{1}{2}} (\xi-\eta) \quad . \tag{5-84}$$

For volume integration in these coordinates, the volume element is

$$d\tau = \left(\frac{R}{2}\right)^3 (\xi^2-\eta^2)\ d\xi\ d\eta\ d\phi \tag{5-85}$$

where the integration limits are

$$\begin{array}{lll} 0 \text{ to } 2\pi & \text{for} & \phi \\ -1 \text{ to } 1 & \text{for} & \eta \\ 1 \text{ to } \infty & \text{for} & \xi \ . \end{array}$$

The significant thing is that the component which is involved in the ϕ integration in (5-79) does not change upon coordinate transformation. It is

$$I_\phi = \int_0^{2\pi} \begin{Bmatrix} \cos\ |m_1|\phi & m_1 \geq 0 \\ \sin\ |m_1|\phi & m_1 < 0 \end{Bmatrix} \cdot \begin{Bmatrix} \cos\ |m_2|\phi & m_2 \geq 0 \\ \sin\ |m_2|\phi & m_2 < 0 \end{Bmatrix} d\phi \ . \tag{5-86}$$

It gives rise to many combinations. A typical one, with $|m_1| \neq |m_2|$; m_1, $m_2 \geq 0$,

$$\begin{aligned} I_\phi &= \int_0^{2\pi} \cos\ |m_1|\phi \cdot \cos\ |m_2|\phi\ d\phi \\ &= \frac{1}{2} \int_0^{2\pi} [\cos\ (|m_1|+|m_2|)\phi + \cos\ (|m_1|-|m_2|)\phi] d\phi \\ &= \frac{1}{2} [\sin\ (|m_1|+|m_2|)\phi + \cos\ (|m_1|-|m_2|)\phi]_0^{2\pi} = 0 \end{aligned} \tag{5-87a}$$

But if $|m_1| = |m_2|$, the integral becomes

$$\frac{1}{2}\int_0^{2\pi} [\cos 2|m_1|\phi+1]d\phi = \pi \quad , \tag{5-87b}$$

$m_1, m_2 > 0$ and if $m_1 = m_2 = 0$, the integral reduces to 2π. Similarly for all the other combinations, it will be found that the integral vanishes unless $m_1 = 2$. Therefore, without any loss of generality the integral to be solved by Fourier convolution method can by written right from the beginning as

$$I(\underset{\sim}{R}) = \int_{\underset{\sim}{r}\text{ space}} (n_1,\ell_1,m_1,\delta_1)_a (n_2,\ell_2,m_1,\delta_2)_b \, d\tau$$

$$= A_p \int_{\underset{\sim}{k}\text{-space}} (n_1,\ell_1,m_1,\delta_1)_a^T (n_2,\ell_2,m_1,\delta_2)_b^T \cdot e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}} \, d\underset{\sim}{k} \tag{5-88}$$

which is just a form of eqns (5-1) and (5-2).

c. On Parity, or How to Determine A_p

From Figure 5.1 or 5.4, it is clear that

$$\underset{\sim}{r}_b = \underset{\sim}{r}_a - \underset{\sim}{R} \ .$$

So invoking (5-9a) yields

$$g(\underset{\sim}{r}_b) = g(\underset{\sim}{r}_a - \underset{\sim}{R}) = A_p \, g(\underset{\sim}{R} - \underset{\sim}{r}_a)$$

$$g(\underset{\sim}{r}_b) = A_p \, \overline{g(-\underset{\sim}{r}_b)} \quad . \tag{5.89}$$

It is this equation that we must solve explicitly for A_p, in the case of g as Slater-type orbitals.

From (5-66)

$$g(\underset{\sim}{r}_b) = N_{n_2,\ell_2,m_1} \; r_b^{n_2} e^{-\delta_2 r_b} P_{l_2}^{|m_1|}(\cos\theta_b) \begin{Bmatrix} \cos|m_1|\phi & m_1 \geq 0 \\ \sin|m_1|\phi & m_1 \leq 0 \end{Bmatrix} \quad . \tag{5-90}$$

According to the convention shown in Figure 5.4, the transformation

$$\underset{\sim}{r}_b \rightarrow -\underset{\sim}{r}_b \tag{5-91a}$$

is equivalent to

$$(\underset{\sim}{r}_b, \theta_b, \phi) \rightarrow (r_b, \pi-\theta_b, \phi+\pi) \quad . \tag{5-91b}$$

This becomes clear if we remember that in spherical polar coordinates, θ is always measured from the positive z-axis, and must satisfy $0 \leq \theta \leq \pi$. This eliminates $(\theta_b+\pi)$, but not $(\phi+\pi)$ which is legal, as it satisfies $0 \leq \phi \leq 2\pi$.

An alternative method to obtain the transformation is to go back to Cartesian coordinates, in which the transformation (5-91a) is recognised as

$$(x,y,z) \rightarrow (-x,-y,-z) \quad . \tag{5-91c}$$

Using the relations

$$\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \quad . \end{aligned} \tag{5-92}$$

We see that $z \rightarrow -z$ implies

$$\cos\theta \longrightarrow -\cos\theta = \cos\theta' \quad .$$

If both $0 \leq \theta \leq \pi$ and $0 \leq \theta' \leq \pi$ have to hold, the choice $\theta' = \pi-\theta$ cannot be avoided. Similarly for $\phi \longrightarrow \phi' = \phi+\pi$. All this gives

$$g(-\underset{\sim}{r}_b) = N_{n_2\ell_2 m_1}\, r_b^{n_2}\, e^{-\delta_2 r_b}\, P_{\ell_2}^{|m_1|}\,(\cos(\pi-\theta_b)) \left\{\begin{array}{l} \cos\,[|m_1|(\phi+\pi)] \\ \sin\,[|m_1|(\phi+\pi)] \end{array}\right\} \begin{array}{l} m_1 \geq 0 \\ m_1 < 0 \end{array} \quad . \qquad (5\text{-}93)$$

Now,

$$\cos(\pi-\theta_b) = -\cos\theta_b$$

and

$$\left\{\begin{array}{l} \cos\,(|m_1|\phi+|m_1|\pi) \\ \sin\,(|m_1|\phi+|m_1|\pi) \end{array}\right\} = \left\{\begin{array}{l} \cos|m_1|\phi\,\cos|m_1|\pi - \sin|m_1|\phi\,\sin|m_1|\pi \\ \sin|m_1|\phi\,\cos|m_1|\pi + \cos|m_1|\phi\,\sin|m_1|\pi \end{array}\right\}$$

$$= (-1)^{|m_1|} \left\{\begin{array}{l} \cos|m_1|\phi \\ \sin|m_1|\phi \end{array}\right\} \begin{array}{l} m_1 \geq 0 \\ m_1 < 0 \end{array} \qquad (5\text{-}94)$$

which gives

$$g(-\underset{\sim}{r}_b) = N_{n_2\ell_2 m_1}\, r_b^{n_2}\, e^{-\delta_2 r_b}\, P_{\ell_2}^{|m_1|}\,(-\cos\theta_b)(-1)^{|m_1|} \left\{\begin{array}{l} \cos|m_1|\phi \\ \sin|m_1|\phi \end{array}\right\} \begin{array}{l} m_1 \geq 0 \\ m_1 < 0 \end{array} \quad . \qquad (5\text{-}95)$$

We invoke the parity of associated Legendre functions. (See Appendix A.)

$$P_\ell^m(-x) = (-1)^{\ell+m} P_\ell^m(x) \tag{5-96}$$

and compare eqns (5-95) and (5-90) under this substitution, to get

$$g(-\underset{\sim}{r}_b) = (-1)^{\ell_2} g(\underset{\sim}{r}_b) \ , \quad \text{or} \quad A_p = (-1)^{\ell_2} \ . \tag{5-97}$$

Then

$$I(\underset{\sim}{R}) = (-1)^{\ell_2} \int_{\underset{\sim}{k}} (n_1\ell_1m_1\delta_1)_a^T \, (n_2\ell_2m_1\delta_2)_b^T \ \cdot$$
$$\cdot \, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}} \, d\underset{\sim}{k} \tag{5-98}$$

where superscript T indicates Fourier transform and $\underset{\sim}{k} \equiv (k,u,v)$ is the transform variable.

The task that remains is to obtain explicit expressions for the Fourier transforms $(n_1\ell_1m_1\delta_1)_a^T$ and $(n_2\ell_2m_1\delta_2)_b^T$, then solve the Fourier inversion integral (5-98).

3. Fourier Transforms of Slater Type Orbitals

The method used to derive these transforms closely follows that of Geller [25], a route which, we believe, was taken also by Harris and Michels.

From (5-3),

$$(n_1\ell_1m_1\delta_1)_a^T = (2\pi)^{-\frac{3}{2}} \int e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}_a} (n_1\ell_1m_1\delta_1)_a \, d\underset{\sim}{r}_a \ . \tag{5-99}$$

We make use of the spherical coordinate expansion of a plane wave

$$e^{\underline{+}ik\cdot r} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (\underline{+}i)^\ell \, j_\ell(kr) \, Y_{\ell m}(\theta,\phi) \, Y_{\ell m}^*(u,v) \tag{5-100}$$

where $j_\ell(x)$ is a spherical Bessel function; $\underset{\sim}{r} \equiv (r,\theta,\phi)$; and $\underset{\sim}{k} \equiv (k,u,v)$; ℓ and m are summation indices. This expression is written in terms of complex spherical harmonics $Y_{\ell m}(\theta,\phi)$. In terms of real spherical harmonics, the situation is slightly more complicated, but it can be gleaned from (5-100).

We note that from (5-65), the complex conjugate is

$$Y^*_{\ell m}(u,v) = (-1)^m \left[\frac{2\ell+1}{4\pi}\,\frac{(\ell-m)!}{(\ell+m)!}\right]^{\frac{1}{2}} P^m_\ell\,(\cos u)\; e^{-imv} \quad . \qquad (5\text{-}101)$$

So the plane wave expansion (5-100) becomes

$$e^{\underline{+}i\underset{\sim}{k}\cdot\underset{\sim}{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (\underline{+}\ i)\ \ j_\ell(kr)\ \frac{2\ell+1}{4\pi}\ \frac{(\ell-m)!}{(\ell+m)!}\ \cdot$$

$$\cdot\ P^m_\ell\ (\cos\ \theta)\ P^m_\ell\ (\ \cos\ u)\cdot e^{im(\phi-v)}$$

$$= \sum_{\ell=0}^{\infty} (\underline{+}\ i)^\ell (2\ell+1)\ j_\ell(kr) \sum_{m=-\ell}^{\ell} \frac{(\ell-m)!}{(\ell+m)!}\ P^m_\ell\ (\cos\ \theta)\ \cdot$$

$$\cdot\ P^m_\ell\ (\cos\ u)\cdot\{\cos\ [m(\phi-v)] + i\ \sin\ [m(\phi-v)]\}\ . \qquad (5\text{-}102)$$

Now let $x = (\phi-v)$, note $\cos mx = \cos (-mx)$; and $\sin mx = -\sin (-xm)$, $\sin 0 = 0$. So in the summation over m, the sine term disappears completely, while the cosine term appears twice except for $m = 0$, when it appears once. We follow Geller in writing all this as:

$$e^{\underline{+}i\underset{\sim}{k}\cdot\underset{\sim}{r}} = \sum_{\ell=0}^{\infty} (2\ell+1)(\underline{+}\ i)^\ell\ j_\ell(kr) \sum_{m=0}^{\ell} (2-\delta_{m0}) \cdot \frac{(\ell-m)!}{(\ell+m)!}\ \times$$

$$\times\ P^m_\ell\ (\cos\ \theta)\ P^m_\ell\ (\cos\ u)\cdot \cos\ [m(\phi-v)] \qquad (5\text{-}103)$$

or

$$e^{\pm i \underset{\sim}{k} \cdot \underset{\sim}{r}} = \sum_{\ell=0}^{\infty} (2\ell+1)(\pm i)^{\ell}\, j_{\ell}(kr) \cdot \{P_{\ell}(\cos\theta)P_{\ell}(\cos u) +$$

$$+ 2\sum_{m=1}^{\ell} \frac{(\ell-m)!}{(\ell+m)!} P_{\ell}^{m}(\cos\theta)\cdot P_{\ell}^{m}(\cos u)\cdot \cos[m(\phi-v)]\} \,. \quad (5\text{-}104)$$

Note now that the summation index m is non-negative, i.e., $m = |m| \geq 0$. Explicitly the Fourier transformation (5-99) for an STO becomes

$$(n_1\ell_1 m_1 \delta_1)_a^T = (2\pi)^{-\frac{3}{2}} \cdot N_{n_1\ell_1 m_1} \cdot \sum_{\ell=0}^{\infty} (2\ell+1)(\pm i)^{\ell} \cdot$$

$$\times \sum_{m=0}^{\ell} \epsilon_m \frac{(\ell-m)!}{(\ell+m)!} P_{\ell}^{m}(\cos u) \cdot$$

$$\times \int_0^{\infty} r_a^{n_1} e^{-\delta_1 r_a} j_{\ell}(kr_a) \cdot r_a^2\, dr_a \cdot$$

$$\times \int_0^{\pi} P_{\ell_1}^{|m_1|}(\cos\theta_a)\, P_{\ell}^{m}(\cos\theta_a) \sin\theta_a\, d\theta_a$$

$$\times \int_0^{2\pi} \left\{ \begin{array}{l} \cos|m_1|\phi_a \\ \sin|m_1|\phi_a \end{array} \right\} \cdot \cos[m(\phi_a - v)]\, d\phi_a \quad (5\text{-}105)$$

where

$$\epsilon = 2 - \delta_{m0} \,. \quad (5\text{-}105a)$$

Integration over ϕ_a determines m to be equal to $|m_1|$:

$$I_{\phi} = \int_0^{2\pi} \left\{ \begin{array}{l} \cos|m_1|\phi_a \\ \sin|m_1|\phi_a \end{array} \right\} \cos[m(\phi_a - v)]d\phi_a =$$

$$= \frac{1}{2}\int_0^{2\pi} \left\{ \begin{array}{l} \cos\ |m_1|\phi_a \\ \sin\ |m_1|\phi_a \end{array} \right\} \times$$

$$\times[\cos\ m\phi_a\ \cos\ mv + \sin\ m\phi_a\ \sin\ mv]d\phi_a \ . \qquad (5\text{-}106)$$

The following statements are true about this integral I_ϕ:

i) all mixed (cos-sin) products make it vanish (annihilate it);

ii) so do all products with $m \neq |m_1|$, just as in (5-87a) above;

iii) for $m = |m_1| \neq 0$, the integral is merely equal to 2π - eqn (5-87b);

iv) for $m = |m_1| = 0$, it is equal to

$$\frac{2\pi}{2} \left\{ \begin{array}{l} \cos\ |m_1|v \\ \sin\ |m_1|v \end{array} \right\} .$$

Therefore,

v) it can be rewritten as

$$I_\phi = \frac{2}{\epsilon_m} \left\{ \begin{array}{l} \cos\ |m_1|v \\ \sin\ |m_1|v \end{array} \right\} \delta_{m,|m_1|} \ . \qquad (5\text{-}107)$$

With $m = |m_1|$, now the integral over θ_a selects ℓ to be equal to ℓ_1, only. This is a statement of the orthogonality relation for Associated Legendre functions.

$$I_{\phi_a} = \int_0^\pi P_{\ell_1}^{|m_1|}(\cos\ \theta_a) \cdot P_\ell^{|m_1|}(\cos\ \theta_a)\ \sin\ \theta_a\ d\theta_a$$

$$= \left(\frac{2}{2\ell+1}\right) \cdot \frac{(\ell+|m_1|)!}{(\ell-|m_1|)!} \cdot \delta_{\ell\ell_1} \ . \qquad (5\text{-}108)$$

Combining (5-105), (5-107) and (5-108), we get

$$(n_1 \ell_1 m_1 \delta_1)_a^T = (2\pi)^{-\frac{3}{2}} N_{n_1\ell_1 m_1} \cdot (2\ell_1+1) \quad i^{\ell_1} \cdot \epsilon_{|m_1|} \times$$

$$\times \frac{(\ell_1-|m_1|)!}{(\ell_1+|m_1|)!} \quad P_{\ell_1}^{|m_1|} \cdot (\cos u) \times$$

$$\times \int_0^\infty r_a^{n_1+2} \, e^{-\delta_1 r_a} \, j_{\ell_1}(kr_a) \, dr_a \times$$

$$\times \frac{2}{2\ell_1+1} \quad \frac{(\ell+|m_1|)!}{(\ell-|m_1|)!} \quad \frac{2\pi}{\epsilon_{|m_1|}} \cdot \left\{ \begin{array}{l} \cos |m_1| v \\ \sin |m_1| v \end{array} \right\}$$

or

$$(n_1\ell_1 m_1\delta_1)_a^T = \frac{4\pi}{(2\pi)^{3/2}} \cdot N_{n_1\ell_1 m_1} \cdot i^{\ell_1} \cdot P_{\ell_1}^{|m_1|} \quad (\cos u) \times$$

$$\times \quad (n_1\ell_1\delta_1)_a^T \left\{ \begin{array}{l} \cos |m_1| v \\ \sin |m_1| v \end{array} \right\} \qquad (5\text{-}109)$$

where

$$(n\ell\delta)^T = \int_0^\infty r^{n+2} \, e^{-\delta r} \, j_\ell(kr) dr \qquad (5\text{-}110)$$

is some kind of one-dimensional Fourier Transform. (See Appendix C.) Similarly, by replacing the subscript a with b in all that has transpired in this section, the Fourier transform for the STO at B becomes

$$(n_2\ell_2 m_1\delta_2)_b^T = \frac{4\pi}{(2\pi)^{3/2}} \cdot i^{\ell_2} \quad P_{\ell_2}^{|m_1|} \quad (\cos u) \times$$

$$\times (n_2\ell_2\delta_2)_b^T \left\{ \begin{array}{l} \cos |m_1| v \\ \sin |m_1| v \end{array} \right\} . \qquad (5\text{-}111)$$

4. Fourier Inversion Integral (5-98)

After substitution of the STO Fourier transforms, integral (5-98) takes the following shape:

$$I(\underset{\sim}{R}) = N_{n_1 \ell_1 m_1} \cdot N_{n_2 \ell_2 m_1} \cdot (-1)^{\ell_2} \cdot i^{\ell_1+\ell_2} \left[\frac{4\pi}{(2\pi)^{3/2}} \right]^2 \times$$

$$\times \int_{\underset{\sim}{k}} d\underset{\sim}{k}\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}} \cdot (n_1 \ell_1 \delta_1)_a^T \, (n_2 \ell_2 \delta_2)_b^T \cdot P_{\ell_1}^{|m_1|} (\cos u)$$

$$\times P_{\ell_2}^{|m_1|} (\cos u) \cdot \left\{ \begin{matrix} \cos |m_1| v \\ \sin |m_1| v \end{matrix} \right\} \cdot \left\{ \begin{matrix} \cos |m_1| v \\ \sin |m_1| v \end{matrix} \right\} . \qquad (5\text{-}112)$$

Again the plane wave expansion (5-100) is applied to $e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}}$, where $\underset{\sim}{R} \equiv (R, \theta_R, \phi_R)$, giving

$$I(R) = N_{n_1 \ell_1 m_1} \cdot N_{n_2 \ell_2 m_1} \cdot (-1)^{\ell_2} \, i^{\ell_1+\ell_2} \left[\frac{4\pi}{(2\pi)^{3/2}} \right]^2$$

$$\times \sum_{L=0}^{\infty} (2L+1)(-i)^L \sum_{M=0}^{L} \epsilon_M \frac{(L-M)!}{(L+M)!} \cdot P_L^M (\cos \theta_R)$$

$$\times \int_{k=0}^{\infty} (n_1 \ell_1 \delta_1)_a^T \, (n_2 \ell_2 \delta_2)_b^T \, j_L(kR) \cdot k^2 \, dk$$

$$\times \int_0^{\pi} P_L^M (\cos u) \cdot P_{\ell_1}^{|m_1|} (\cos u) \cdot P_{\ell_2}^{|m_1|} (\cos u) \cdot \sin u du \times$$

$$\times \int_0^{2\pi} \cos M(\phi_R - v) \cdot \left\{ \begin{matrix} \cos |m_1| v \\ \sin |m_1| v \end{matrix} \right\} \cdot \left\{ \begin{matrix} \cos |m_1| v \\ \sin |m_1| v \end{matrix} \right\} dv \; . \qquad (5\text{-}113)$$

Again angular integration over v annihilates all the values of M except $M = 0$. This rather surprising result can be shown in the following way: The integral over v reduces to such terms as:

$$I_v = \int_0^{2\pi} [\cos M\phi_R \ \cos Mv - \sin M\phi_R \ \sin Mv] \times \times \frac{1}{2} \left\{ \begin{array}{c} 1 + \cos 2|m_1|v \\ \cos 2|m_1|v - 1 \\ \sin 2|m_1|v \end{array} \right\} dv \quad . \tag{5-114}$$

For reasons detailed above, the term most likely to survive after integration is the 1 in the curly brackets. To do so it must not combine with any cos or sin term with $M \neq 0$. Thus the integral vanishes unless $M = 0$. For this value of M, the integral has the value $\frac{2\pi}{\epsilon_{|m_1|}}$, since if $|m_1| = 0$, the whole integral becomes 2 anyway. So we write it as

$$I_v = \frac{2\pi}{\epsilon_{|m_1|}} \quad \delta_{M,0} \tag{5-115}$$

where ϵ is defined as in eqn (5-105a).

This value of $M = 0$ ties in conveniently with another transformation we make in order to simplify the integration over u. This is the decomposition of a product of Legendre functions into a linear combination of new Legendre functions. We write this in the form

$$P_\ell^m(x) \ P_{\ell'}^{m'}(x) = \sum_j C_{j\ell\ell'}^{mm'} \ P_j^{m-m'}(x) \quad , \tag{5-116}$$

where the combination coefficients $C_{j\ell\ell'}^{mm'}$ are some kind of Clebsch-Gordan coefficients. The methods used to generate these angular momentum vector coupling coefficients are discussed in Appendix A.

There is a slight, but important, difference between our definition and that of Harris and Michels. Their formula was defined with complex spherical harmonics in mind, and springs also from their interpretation of Roothaan's theorem. For complex orbitals, they are obliged to write the integral in (5-60) as

$$\begin{aligned} \langle \chi_a | \chi_b \rangle &= \int (n_1\ell_1m_1\delta_1)_a\ (n_2\ell_2m_2\delta_2)_b^*\ d\tau \\ &= \langle (n_1\ell_1m_1\delta_1)_a | (n_2\ell_2m_2\ _2)_b \end{aligned} \qquad (5\text{-}117)$$

(see (5-65). By Roothaan's theorem, the integral is then

$$\langle \chi_a | \chi_b \rangle = \delta_{m_1,-m_2} \int (n_1\ell_1m_1\delta_1)_a\ (n_2\ell_2{-m_1}\delta_2)_b\ d\tau\ . \qquad (5\text{-}118)$$

They are then forced to adopt the decomposition

$$P_{\ell_1}^{m_1}(x)\ P_{\ell_2}^{m_2}(x) = \sum_j C_{j\ell_1\ell_2}^{m_1m_2}\ P_j^{m_1+m_2}(x) \quad , \qquad (5\text{-}119)$$

so that in their whole analysis, they have

$$P_{\ell_1}^{m_1}(x)\ P_{\ell_2}^{-m_1}(x) = \sum_j C_{j\ell_1\ell_2}^{m_1,-m_1}\ P_j^0 \quad . \qquad (5\text{-}120)$$

When our decomposition formula (5-116) is inserted into (5-113), the integral over u becomes

$$I_u = \int_0^\pi P_L^0\ (\cos\ u) \cdot \sum_j C_{j\ell_1\ell_2}^{|m_1|,|m_1|}\ P_j^0\ (\cos\ u) \cdot \sin u\ du =$$

$$= \sum_j C^{|m_1|,|m_1|}_{j\ell_1\ell_2} \int_0^\pi P^0_L(\cos u)\ P^0_j\ (\cos u) \cdot \sin u\ du\ ,$$

which by the orthonormality relation (5-108) fixes $L = j$, making the integral

$$I_u = \sum_L C^{|m_1|,|m_1|}_{L\ell_1\ell_2} \cdot \frac{2}{2L+1}\ . \qquad (5\text{-}121)$$

Substituting for I_v and I_u in (5-113) and using the relation $(-1)^{\ell_2} = (i)^{-2\ell_2}$, we get

$$\begin{aligned} I(\underset{\sim}{R}) &= N_{n_1\ell_1m_1} \cdot N_{n_2\ell_2m_1} \cdot \frac{16\pi^2}{8\pi^3} \cdot \frac{4\pi}{\epsilon_{|m_1|}} \times \\ &\times \sum_L i^{\ell_1-\ell_2-L} \cdot C^{|m_1|,|m_1|}_{L\ell_1\ell_2} \times \\ &\times \int_0^\infty (n_1\ell_1\delta_1)^T (n_2\ell_2\delta_2)^T\ j_L(kR)k^2\ dk \\ &= N_{n_1\ell_1m_1} \cdot N_{n_2\ell_2m_1} \cdot \sum_L A^{m_1}_{L\ell_1\ell_2} \\ &\times \frac{2}{\pi} \int_0^\infty j_L(kR)(n_1\ell_1\delta_1)^T (n_2\ell_2\delta_2)^T\ k^2\ dk \end{aligned} \qquad (5\text{-}122)$$

where

$$A^{m_1}_{L\ell_1\ell_2} = \frac{4\pi}{\epsilon_{|m_1|}} \cdot i^{\ell_1-\ell_2-L} \cdot C^{|m_1|,|m_1|}_{L\ell_1\ell_2}\ . \qquad (5\text{-}123)$$

Notice the striking similarity of the integral in (5-122) to that of

Harris and Michels (see equations (5-16) to (5-20). The only difference is the factor $4\pi k^2$ here, which in their case is eliminated by the Fourier transform of the electron-repulsion potential:

$$h^T(k) = (\frac{1}{r_{12}})^T = 4\pi k^{-2} \quad .$$

It is also essentially the result obtained by Geller.

The next task is to obtain explicit expressions for the transforms $(n,\ell,\delta)^T$. One method for this is due to Geller [25], who derived a general formula for the explicit representation:

$$(n\ell\delta)^T = \frac{2^\ell \; \ell!(n-\ell+1)! \; \delta^{n-\ell+1} k^\ell}{(k^2+\delta^2)^{n+2}} \leq \sum_{s=0}^{\frac{1}{2}(n+\ell+1)} (-1)^s \binom{n+\ell+2}{2s+2\ell+1}\binom{s+\ell}{s} (\frac{k}{\delta})^{2s} \quad . \qquad (5\text{-}124)$$

Geller states that this formula can be proved by mathematical induction.

A more transparent method was that of Harris and Michels. In this method, the transforms $(n,\ell,\delta)^T$ are generated recursively, using recurrence relations obtained by applying either partial integrations or Bessel function identities to eqn (5-110). Some of these recurrence relations are derived in Appendix C.

From the recurrence relations and using mathematical induction, it can be seen that the $(n,\ell,\delta)^T$ have the general form:

$$(n,\ell,\delta)^T = k^\ell \sum_{i \geq \frac{1}{2}(n+\ell+3)}^{n+2} B_{n\ell i}(\delta)(k^2+\delta^2)^{-i} \quad . \qquad (5\text{-}125)$$

Proof by Induction: From equation (C-23), (5-125) is definitely true for $n = -1$, $\ell = 0$. It is true also for $n = \ell-1$, all ℓ, as (C-20a) shows. As usual with induction proofs, we assume (5-125) to be true for everything up to $(n-1,\ell,\delta)^T$ and try to show that it is true for $(n,\ell,\delta)^T$. For this the recurrence relation (C-15) is used.

$$(n\ell\delta)^T = \frac{(2n+2)\delta}{(k^2+\delta^2)}(n-1,\ell,\delta)^T - \frac{(n-\ell)(n+\ell+1)}{(k^2+\delta^2)}(n-2,\ell,\delta)^T$$

$$= \frac{(2n+2)\delta}{(k^2+\delta^2)} k^\ell \sum_{i\geq\frac{1}{2}(n-1+\ell+3)}^{n-1+2} B_{n-1,\ell,i}(\delta)(k^2+\delta^2)$$

$$\sum_{i\geq\frac{1}{2}(n-2+\ell+3)}^{n-2+2} B_{n-2,\ell,i}(\delta)(k^2+\delta^2)^{-i}$$

$$= k^\ell \left\{ \sum_{i\geq\frac{1}{2}(n+\ell+2)}^{n+1} (2n+2)\delta\, B_{n-1,\ell,i}(\delta)(k^2+\delta^2)^{-(i+1)} \quad \text{I} \right.$$

$$\left. - \sum_{i\geq\frac{1}{2}(n+\ell+1)}^{n} (n-\ell)(n+\ell+1) B_{n-2,\ell,i}(\delta)(k^2+\delta^2)^{-(i+1)} \quad \text{II} \right\}.$$

We create a new index $j = i+1$, so that $i = j-1$,

$$(n,\ell,\delta)^T = k \left\{ \sum_{j\geq\frac{1}{2}(n+\ell+2)+1}^{n+2} (2n+2)\delta\, B_{n-1,\ell,j-1}(\delta)(k^2+\delta^2)^{-j} \right.$$

$$\left. - \sum_{j\geq\frac{1}{2}(n+\ell+1)+1}^{(n-1)(n+\ell+1)} B_{n-2,\ell,j-1}(\delta)(k^2+\delta^2)^{-j} \right\} \tag{5-126}$$

Clearly, the lowest value of j is

$$[\tfrac{1}{2}\ (n+\ell+1)+1] = [\tfrac{1}{2}\ (n+\ell+3)]$$

and the highest is n+2. Thus without loss of generality we can write

$$(n,\ell,\delta)^T = k^\ell \sum_{j\geq\frac{1}{2}(n+\ell+3)}^{n+2} B_{n\ell j}(\delta)(k^2+\delta^2)^{-j} \quad , \tag{5-127}$$

where, in general, $B_{n\ell j}(\delta)$ is made up of terms from both I and II in (5-126):

$$B_{n\ell j}(\delta) = (2n+2)\delta B_{n-1,\ell,j-1} - (n-\ell)(n+\ell+1)B_{n-2,\ell,j-1}(\delta) \quad .$$

j is just an index, so we can use i instead. This is in fact an anticipation of a later recurrence relation (C-33)!

The functions $B_{n\ell i}(\delta)$ may be generated from the recursion relations

$$B_{-101} = 1 \tag{5-128}$$

$$B_{-1,\ell,\ell+1} = 2\ell \cdot B_{\ell-2,\ell-1}, \tag{5-129}$$

$$B_{\ell,\ell,\ell+2} = (2\ell+2)\delta\ B_{\ell-1,\ell,\ell+1} \tag{5-130}$$

$$B_{n\ell i} = 2(n+1)\delta\ B_{n-1,\ell,i-1} - (n-\ell)(n+\ell+1)B_{n-2,\ell,i-1} \quad . \tag{5-131}$$

Equations (5-28) to (5-131) are consequences of the recurrence relations derived in Appendix C.

Note the difference between our equations (5-130) and (5-131) and the corresponding ones of Harris and Michels, (their equations (67) and (68)) which we believe to contain misprints.

Substitution of eqn (5-127) for $(n_1,\ell_1,\delta_1)^T$ and $(n_2,\ell_2,\delta_2)^T$ into eqn (5-122) leads to

$$I(R) = N_{n_1\ell_1m_1} \cdot N_{n_2\ell_2m_1} \sum_L \sum_{i_1} \sum_{i_2} A^{m_1}_{L\ell_1\ell_2} \cdot B_{n_1\ell_1i_1}(\delta_1) \times$$

$$\times B_{n_2\ell_2i_2}(\delta_2) \frac{2}{\pi} \int_0 \frac{j_L(kR)\, k^{\ell_1+\ell_2} k^2 \, dk}{(k^2+\delta_1^2)^{i_1} (k^2+\delta_2^2)^{i_2}} \quad . \tag{5-132}$$

We put $k^{\ell_1+\ell_2+2}$ in the form k^{L+2j} by letting

$$L+2j = 2+\ell_1+\ell_2$$

$$j = \frac{1}{2}(2+\ell_1+\ell_2-L) \quad . \tag{5-133}$$

So (5-132) becomes finally,

$$I(R) = N_{n_1\ell_1m_1} \cdot N_{n_2\ell_2m_1} \sum_L \sum_{i_1} \sum_{i_2} A^{m_1}_{L\ell_1\ell_2} \cdot B_{n_1\ell_1i_1}(\delta) \times$$

$$\times B_{n_2\ell_2i_2}(\delta_2)\, W^{L,\frac{1}{2}(2+\ell_1+\ell_2-L)}_{i_1,i_2}(\delta_1,\delta_2,R) \tag{5-134}$$

where

$$W^{L,j}_{i_1i_2}(\delta_1,\delta_2,R) = \frac{2}{\pi} \int_0^\infty \frac{k^{L+2j}\, j_L(kR)\,dk}{(k^2+\delta_1^2)^{i_1}(k^2+\delta_2^2)^{i_2}} \quad . \tag{5-135}$$

The summation limits are

$$\frac{1}{2}(n+\ell+3) \leq i \leq n+2 \qquad \text{in steps of } 1$$

and

$$|\ell_1 - \ell_2| \leq L \leq \ell_1 + \ell_2 \quad \text{in steps of } 2 \,. \tag{5-136}$$

Equation (5-134) is of a particularly convenient form, because it is separable into distinct arrays $A^{m_1}_{L\ell_1\ell_2}$, $B_{n\ell i}(\delta)$, and $W^{L,j}_{i_1,\ell_2}(\delta_1,\delta_2,R)$, which can be prepared and checked independently, and then combined together in an aggregate sum.

5. Generation of $W^{Lj}_{i_1,i_2}(\delta_1,\delta_2,R)$ Integrals of Spherical Bessel Functions

The remaining problem is the evaluation of eqn (5-135). Here again, advantage is taken of recursive methods and properties of spherical Bessel functions.

Using the identity

$$k^2/(k^2+\delta^2) = 1 - \delta^2/(k^2+\delta^2) \tag{5-137}$$

(5-135) immediately gives

$$\delta_1^2 \, W^{L,j}_{i_1 i_2} = W^{L,j}_{i_1-1,i_2} - W^{L,j+1}_{i_1,i_2} \tag{5-138}$$

and

$$\delta_2^2 \, W^{L,j}_{i_1,i_2} = W^{L,j}_{i_1,i_2-1} - W^{L,j+1}_{i_1,i_2} \,. \tag{5-139}$$

Proof: From (5-135),

$$\delta_1^2\, W^{L,j}_{i_1,i_2} = \frac{2}{\pi} \int_0 \frac{k^{L+2j}\, j_L(kR)\delta_1^2}{(k^2+\delta_1^2)^{i_1}(k^2+\delta_2^2)^{i_2}}\, dk$$

$$= \frac{2}{\pi} \int_0^\infty \frac{\delta_1^2}{(k^2+\delta_1^2)} \cdot \frac{k^{L+2j}\, j_L(kR)}{(k^2+\delta_1^2)^{i_1-1}(k^2+\delta_2^2)^{i_2}}\, dk \quad . \tag{5-140}$$

Now apply (5-137) with $\delta = \delta_1$:

$$\delta_1^2\, W^{L,j}_{i_1,i_2} = \frac{2}{\pi} \int_0^\infty \left[\frac{j_L(kR)\, k^{L+2j}}{(k^2+\delta_1^2)^{i_1-1}(k^2+\delta_2)^{i_2}} - j_L(kR) \times \right.$$

$$\left. \times \frac{k^{L+2(j+1)}}{(k^2+\delta_1^2)^{i_1}(k^2+\delta_2^2)^{i_2}} \right] dk$$

which is precisely (5-138). Similarly using (5-137) with $\delta = \delta_2$ gives (5-139). Using the recurrence relation (B-7) for j_L,

$$\frac{2L+1}{R}\, j_L(kR) = k[j_{L+1}(kR) + j_{L-1}(kR)] \tag{5-141}$$

and putting it into (5-135) we obtain

$$\left(\frac{2L+1}{R}\right) W^{L,j}_{i_1 i_2} = W^{L+1,j}_{i_1 i_2} + W^{L-1,j+1}_{i_1 i_2} \quad . \tag{5-142}$$

Subtracting (5-138) from (5-139) gives

$$(\delta_2^2 - \delta_1^2)\, W^{L,j}_{i_1 i_2} = W^{L,j}_{i_1,i_2-1} - W^{L,j}_{i_1-1,i_2} \quad . \tag{5-143}$$

In (5-138) put L → L-1 to give

$$W^{L-1,j+1}_{i_1,i_2} = W^{L-1,j}_{i_1-1,i_2} - \delta_1^2 W^{L,j}_{i_1 i_2} .$$

When this is substituted into (5-142) it yields

$$W^{L+1,j}_{i_1,i_2} = \left(\frac{2L+1}{R}\right) W^{L,j}_{i_1 i_2} - W^{L-1,j}_{i_1-1,i_2} + \delta_1^2 W^{L-1,j}_{i_1 i_2} \tag{5-144}$$

If instead (5-139) is used, we obtain

$$W^{L+1,j}_{i_1 i_2} = \left(\frac{2L+1}{R}\right) W^{L,j}_{i_1 i_2} - W^{L-1,j}_{i_1,i_2-1} + \delta_2^2 W^{L-1,j}_{i_1 i_2} . \tag{5-145}$$

Further useful relations follow. In certain cases the $W^{L,j}_{i_1 i_2}$ may be evaluated by direct quadrature. In particular,

$$W^{00}_{1,0} = \frac{2}{\pi} \int_0^\infty \frac{k^0 \; j_0(kR)}{(k^2+\delta_1^2)^1} \, dk$$

$$= \frac{2}{\pi} \int_0^\infty \frac{\sin kR \, dk}{kR(k^2+\delta_1^2)} \tag{5-146a}$$

$$= \frac{1}{\delta_1^2 R} \left(1 - e^{-\delta_1 R}\right) . \tag{5-146b}$$

Proof of (5-146b) The integral in (5-146b) can be converted to standard or proven forms by use of partial fraction analysis. First we write it as

$$W^{00}_{10} = \frac{2\pi}{\pi 2R} \int_0^\infty \frac{\sin kR}{k(k^2+\delta_1^2)} \, dk .$$

According to partial fraction analysis, we can write

$$\frac{1}{k(k^2+\delta_1^2)} = \frac{A}{k} + \frac{Bk}{(k^2+\delta_1^2)} .$$

$$= \frac{A(k^2+\delta_1^2) + Bk^2}{k(k^2+\delta^2)} .$$

Examining the terms associated with the powers of k in the numerators of both sides, we find

$k^2 : A + B = 0$

$k^1 : \quad -$

$k^0 : A\,\delta_1^2 = 1$

which give $A = \frac{1}{\delta_1^2}$, $B = -\frac{1}{\delta_1^2}$. So in (5-146a) we get

$$W_{10}^{00} = \frac{2\pi}{\pi 2R} \int_0^\infty \frac{\sin k\,R}{\delta_1^2\,k}\,dk - \int_0^\infty \frac{k \sin kR}{\delta_1^2 (k^2 + {}_1^2)}\,dk .$$

Using Formula 621 of Handbook of Chemistry and Physics and Hildebrand, this integral becomes

$$W_{10}^{00} = \frac{1}{R}\,\delta_1^2\,\frac{\pi}{2} - \frac{\pi}{2} e^{-\delta_1 R}$$

which is (5-146b). Similarly

$$W_{10}^{00} = \frac{1}{\delta_2^2\,R}\,(1 - e^{-\delta_2 R}) . \qquad (5\text{-}146c)$$

We found it more satisfying and enlightening to prove this integral from first principles using the Method of Residues but chose not to present the lengthy proof in this thesis.

Similarly,

$$W_{01}^{00} = \frac{1}{\delta_2^2 R} \left(1 - e^{-\delta_2 R}\right) . \tag{5-147}$$

We also note the important result

$$W_{i_1,0}^{L,1} = \frac{2}{\pi} \int_0^\infty \frac{k^{L+2} \, j_L(kR)}{(k^2+\delta_1^2)^{i_1}} \, dk$$

using (B-2), this becomes

$$= \left(\frac{2}{\pi R}\right)^{\frac{1}{2}} \int_0^\infty \frac{k^{L+3/2} J_{L+1/2}(kR)}{(k^2+\delta_1^2)^{i_1}} \, dk$$

and using (B-14)

$$= \frac{\text{[illegible]}}{(i_2-1)!} \left(\frac{R}{2\delta_2}\right)^{i_2-1} \left(\frac{2}{\pi\delta_2 R}\right)^{\frac{1}{2}} K_{i_2-L-3/2}(\delta_1 R) \tag{5-148}$$

and similarly

$$W_{0,i_2}^{L,1} = \frac{\delta_2^{L+1}}{(i_2-1)!} \left(\frac{R}{2\delta_2}\right)^{i_2-1} \left(\frac{2}{\pi\delta_2 R}\right)^{\frac{1}{2}} K_{i_2-L-3/2}(\delta_2 R) . \tag{5-149}$$

The Bessel functions J and K appearing here are defined in Appendix B.

Even the very starting function W_{00}^{00} is not trivial:

$$W_{00}^{00} = \frac{2}{\pi} \int_0^\infty \frac{k^0 \, j_0(kR)}{1 \cdot 1} \, dk$$

$$= \frac{1}{R} . \tag{5-150}$$

Proof: Using the definition of j_u , i.e., eqn (B-1), we get

$$W^{00}_{00} = \frac{2}{\pi} \int_0^\infty J_{1/2}(kR)\left(\frac{}{2kR}\right)^{\frac{1}{2}} \frac{d(kR)}{R}$$

$$= \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \cdot \frac{1}{R} \int_0^\infty J_{1/2}(t)\, t^{-\frac{1}{2}}\, dt \qquad (5\text{-}150)$$

where $t = kR$. Using the standard integral (B-13), with $\mu = -\frac{1}{2}$, $\nu = \frac{1}{2}$ so that the conditions $\mu+\nu = 0 > -1$ $\mu = -\frac{1}{2} < \frac{1}{2}$, are satisfied, we get

$$W^{00}_{00} = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \cdot \frac{1}{R} \cdot \frac{2^{-\frac{1}{2}}\Gamma(\frac{1}{2})}{(1)}$$

$$= \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \cdot \frac{1}{R} \cdot \left(\frac{\pi}{2}\right)^{\frac{1}{2}} = \frac{1}{R} \quad . \qquad \text{Q.E.D.}$$

when reconstituted in equation (B-1),

$$W^{00}_{00} = \frac{2}{\pi R} \int_0^\infty \frac{\sin kR}{k}\, dk \quad , \qquad (5\text{-}142)$$

it is a standard integral (eq., Handbook of Chemistry and Physics Formula 621), which gives

$$W^{00}_{00} = \frac{2}{\pi R} \cdot \frac{\pi}{2} = \frac{1}{R} \quad ,$$

and holds only for $R > 0$.

A possible proof of this standard integral is of course through the method of Residues (Hildebrand, p. 559).

Our procedure for generating the $W^{L,j}_{i_1,i_2}$ consists of three parts:

<u>Part 1</u>: Prepare $W^{00}_{i_1,i_2}$, $W^{10}_{i_1,i_2}$ for a sufficient range of i_1, i_2 (determined by eqn (5-125) to be $\frac{1}{2}(n+\ell+3) \leq i \leq n+2$).

<u>Part 2</u>: Using eqns (5-144) or (5-145), advance L to get

$$W^{L,0}_{i_1,i_2} \quad \text{up to} \quad L = \ell_1 + \ell_2 \ .$$

<u>Part 3</u>: Raise j if necessary with (5-138) or (5-139) giving $W^{L,j}_{i_1,i_2}$.

Part 1 is the most problematic, and it turns out that three alternative schemes are needed for different combinations of δ_1 and δ_2.

<u>Case 1</u>: δ_1 "far from" δ_2 or δ_1/δ_2 "not too near unity" (see later for meaning).

In this case, forward use of (5-143) is a numerically satisfactory way to obtain $W^{L,j}_{i_1,i_2}$ from $W^{L,j}_{i_1,i_2-1}$ and $W^{L,j}_{i_1-1,i_2}$ because there is no subtraction of nearly equal numbers which would result in loss of significant figures/precision, especially for higher i_1 and i_2 values. Then the scheme is as follows:

i) Prepare W^{00}_{00} (by eqn (5-150)), W^{00}_{10} and W^{00}_{01} (eqn (5-146)).

ii) Next, prepare $W^{01}_{i_1,0}$, W^{01}_{0,i_2} which are special cases of eqns (5-148) and (5-149):

$$W^{01}_{i,0} = \delta_1 \left(\frac{R}{2\delta_1}\right)^{i_1-1} \frac{k_{i_1-2}}{(i_1-1)!} (\delta_1 R) \ , \quad \text{all} \quad i_1 \qquad (5\text{-}153)$$

$$W^{01}_{0,i_1} = \delta_2 \left(\frac{R}{2_2}\right)^{i_2-1} \frac{k_{i_2-2}}{(i_2-1)!} (\delta_2 R), \quad \text{all} \quad i_2 \qquad (5\text{-}154)$$

where k_i are calculated by methods described in Appendix B; especially see eqn (B-16). iii) Using eqns (5-138) and (5-139), $W^{00}_{i_1,0}$, W^{00}_{0,i_2} can be generated in the following way:

$$W^{00}_{i_1,0} = \delta_1^{-2} \left(W^{00}_{i_1-1,0} - W^{01}_{i_1,0}\right), \quad \text{all} \quad i_1 \qquad (5\text{-}155)$$

$$W^{00}_{0,i_2} = \delta_2^{-2} \left(W^{00}_{0,i_2-1} - W^{01}_{0,i_2}\right), \quad \text{all} \quad i_2 \; . \qquad (5\text{-}156)$$

iv) With $L = -1$, eqns (5-148) and (5-149), or (B-16) yields

$$W^{-1,1}_{i_1,0} = \left(\frac{R}{2\delta_1}\right)^{i_1-1} k_{i_1-1} (\delta_1 R), \quad \text{all} \quad i_1 \qquad (5\text{-}157)$$

$$W^{-1,1}_{0,i_2} = \left(\frac{R}{2\delta_2}\right)^{i_2-1} k_{i_2-1} (\delta_2 R), \quad \text{all} \quad i_2 \; . \qquad (5\text{-}158)$$

v) $W^{10}_{i_1,0}$ and W^{10}_{0,i_2} are obtained from (5-142) as:

$$W^{10}_{i_1,0} = R^{-1} W^{00}_{i_1,0} - W^{-1,1}_{i_1,0} \qquad (5\text{-}159)$$

$$W^{01}_{0,i_2} = R^{-1} W^{00}_{0,i_2} - W^{-1,1}_{0,i_2} \; . \qquad (5\text{-}160)$$

vi) Apply (5-143) to generate all of $W^{00}_{i_1,i_2}$ and $W^{10}_{i_1,i_2}$ (Figure 5.5).

vii) Go to Part 2.

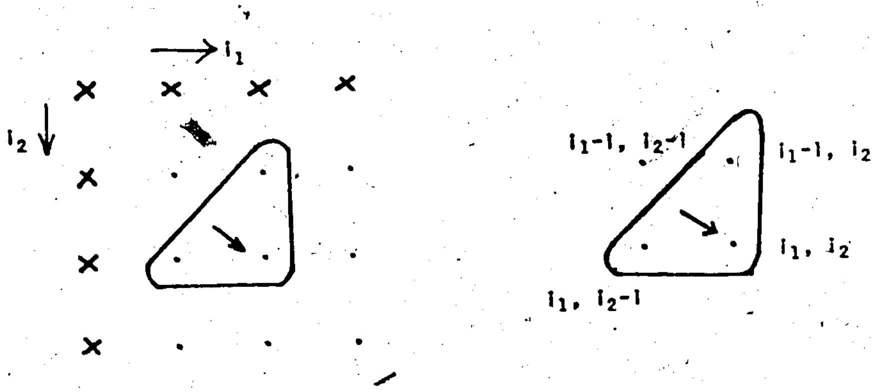


Fig. 5.5. Equation (5-143)

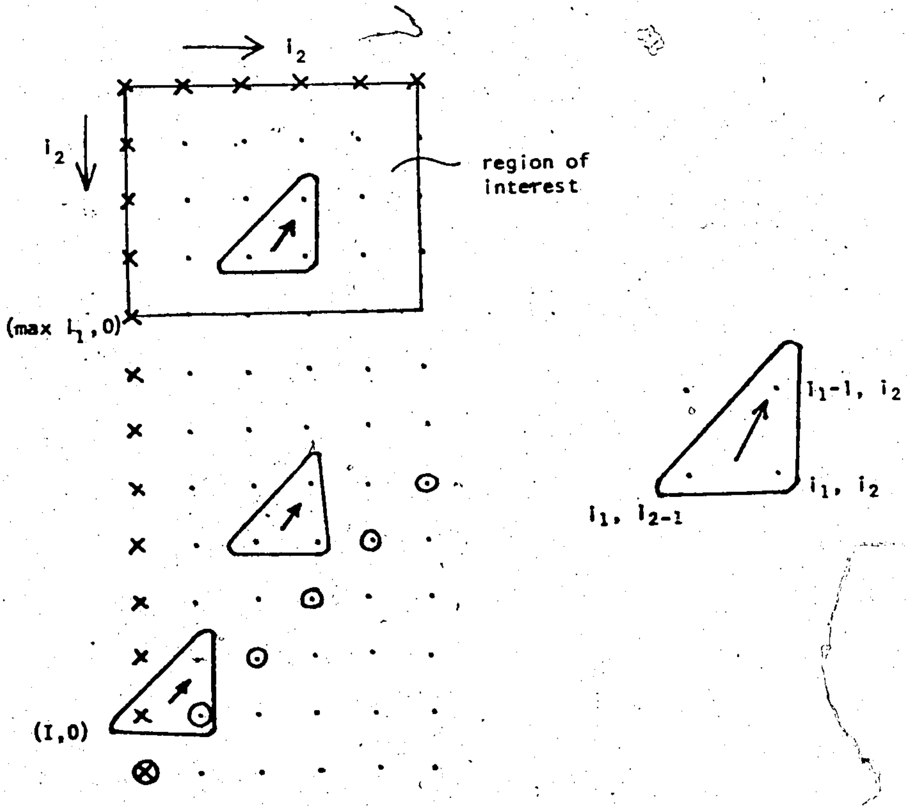


Fig. 5.6 Equation (5-161)

Case 2: δ_1/δ_2 "near, but not quite equal to unity".

In this case forward use of (5-143) becomes unsatisfactory, because then

$$W^{L,j}_{i_1-1,i_2} - W^{L,j}_{i_1,i_2-1} \simeq 0 \cdot W^{L,j}_{i_1,i_2}$$

or

$$W^{L,j}_{i_1-1,i_2} \simeq W^{L,j}_{i_1,i_2-1}$$

and subtraction of these leads to loss of precision. "Backward" use of (5-143) is called for, i.e., going down the index i_1 to zero

$$\begin{aligned} W^{L,j}_{i_1-1,i_2} &= W^{L,j}_{i_1,i_2-1} - (\delta_2^2 - \delta_1^2)\, W^{L,j}_{i_1,i_2} \\ &= W^{L,j}_{i_1,i_2-1} + (\delta_1^2 - \delta_2^2)\, W^{L,j}_{i_1,i_2} \end{aligned} \qquad (5\text{-}161)$$

This scheme will work provided $W^{L,j}_{i_1,i_2}$ are available for the maximum relevant i_1 value. Figure 5.6 shows how this problem is tackled. The scheme is as follows:

i) Use steps i) to v) of Case 1 to prepare $W^{00}_{i_1,0}$, W^{00}_{0,i_2}, $W^{10}_{i_1,0}$, W^{10}_{0,i_2}, this time for $i_1 = 0, 1, \ldots, I$, where $I > \max(i_2)$ is some big number to be determined by experimentation.

ii) Assign zeros to all the elements $(I-i_2, i_2+1)$:

$$W^{00}_{I-i_2,i_2-1} = 0 = W^{10}_{I-i_2,i_2+1} \qquad (5\text{-}162)$$

An alternative to this is to assign very small numbers to the elements (I, i_2), $i_2 = 0,1,\ldots,i_2 \max$; e.g.,

$$W^{L,j}_{I,i_2} = 10^{-(45 + i_2)} \qquad (5\text{-}163)$$

iii) Apply eqn (5-143) in the form (5-161) to obtain all $W^{00}_{i_1,i_2}$ and $W^{10}_{i_1,i_2}$.

iv) Go to Part 2 to raise L and J.

Note 1: Justification for approximation ii), and determination of I.

Equation (5-161) can always be arranged in such a way that its right hand side represents addition of numbers of the same sign, leading to successive gain in significant figures and thus accuracy. Successive attenuation of (5-161) in this way will cause an alternation of any error in the initial $W^{Lj}_{i_1,i_2}$, and the numbers get increasingly better. So if we start with I "sufficiently large", by the time i_1 has reduced to the area of interest (see Figure 5.6) the values of $W^{L,j}_{i_1,i_2}$ should be of acceptable accuracy. The value of I was determined by experimentation. We chose, for geometrical reasons, I of the form

$$I = i_1 \max + n \cdot i_2 \max \qquad (5\text{-}164)$$

and set out to determine the best (minimal) n. For a given n, we implemented the scheme i) - iii), and compared the values of W^{00}_{0,i_2} , W^{10}_{0,i_2} obtained from it after scaling (see below), against those accurate ones from iii) and v). An alternative is to start with high n, reduce the n and watch the point at which results start becoming detectably different. It was found that for $n \geq 3$, satisfactory accuracy was obtained (8 significant figures or better).

Note 2: Scaling - In this procedure, where arbitrary values are given to some initial functions, the normalisation of the functions is also arbitrary. This is illustrated as follows: Suppose the assigned value is a factor N times the actual value, which we do not know. Recurrence relations will not remove this factor. Thus the resulting values must be scaled by an appropriately determined constant dependent on some accurately known function. Thus

$$(W^{L,j}_{i_1,i_2})^{FINAL} = (W^{L,j}_{i_1,i_2})^{BACK} \frac{W_{KNOWN}}{W_{BACK}} \quad . \tag{5-165}$$

In our case we used W^{00}_{01}, and W^{10}_{01} (respectively), which we assumed to be known accurately from (5-147) and (5-160). Thus

$$(W^{00}_{i_1,i_2})^{FINAL} = (W^{0,0}_{i_1,i_2})^{BACK} \cdot \frac{(W^{00}_{01})^{KNOWN}}{(W^{00}_{01})^{BACK}} \tag{5-166}$$

and

$$(W^{10}_{i_1,i_2})^{FINAL} = (W^{10}_{i_1,i_2})^{BACK} \cdot \frac{(W^{01}_{01})^{KNOWN}}{(W^{10}_{01})^{BACK}} \quad . \tag{5-167}$$

Note 3: How far is "far" and how near is "near". The definition of "far" and "near" was worked out as follows:

We make the assumption that whereas the "forward" use of eqn (5-143) is stable only when δ_1 is "far" from δ_2, its "backward" use (5-161) is stable all the time for sufficiently high l. Thus, as δ_1 and δ_2 get farther and farther away from each other, the results of the forward usage should become more and more like those of the backward usage. So for different values of threshold relative difference

$$\epsilon = \left| \frac{\delta_1 - \delta_2}{\delta_1} \right| ,$$

we performed both the FAR and NEAR (high l, $n = 8$) schemes and examined the results for differences. It was found that for $\epsilon \lesssim 1\%$, differences were detectable in the two schemes. Thus we define "FAR" (Case 1) as

$$\epsilon = \left| \frac{\delta_1 - \delta_2}{\delta_1} \right| \geq 1\% \qquad (5\text{-}168)$$

and accordingly, (conversely) "NEAR" as

$$\epsilon = \left| \frac{\delta_1 - \delta_2}{\delta_1} \right| < 1\% \ . \qquad (5\text{-}169)$$

Case 3: $\delta_1 = \delta_2$ - The procedure of Case 2 - δ_1 "near" δ_2 is acceptable, but unnecessarily complicated. Instead, advantage can be taken of the identities:

$$W^{L,j}_{i_1,i_2}(\delta_1,\delta_1,R) = W^{L,j}_{i_1+i_2,0}(\delta_1,\delta_1,R) = W^{L,j}_{0,i_1+i_2}(\delta_1,\delta_1,R) \ . \qquad (5\text{-}170)$$

The scheme is then as follows:

i) Prepare $W^{00}_{i,0}$, $W^{10}_{i,0}$ for $i = 0,1,\ldots (i_1 \max + i_2 \max)$, using i) - v) of Case 1.

ii) Eqn (5-170) immediately gives $W^{00}_{i_1,i_2}$, $W^{10}_{i_1,i_2}$.

iii) Go to Part 2 to raise L and j.

6. Decomposition of Single-Center Charge Distributions

The two-center attraction integrals of Section 1b and 1c can be written in the form

$$I = \int \chi_a(1)\chi_a'(1) \cdot \Omega_b \, d\tau \tag{5-171}$$

where

$$\Omega_b = \begin{cases} \dfrac{1}{r_b} & \text{(nuclear attraction)} \\ \dfrac{e^{-\alpha r_b}}{r_b} & \text{(Yukawa potential)} \\ r_b^n \, e^{-\alpha r_b} & \text{("s-STO" (Huzinaga) potential)} \end{cases} . \tag{5-172}$$

And they can be interpreted, following Roothaan [61], as electrostatic interactions between charge distributions $(\chi\chi')_a$ and Ω_b on the two-centers A and B, respectively. Thus for example, the case $\Omega_b = \frac{1}{r_b}$ represents the interaction of a point charge (z = 1) on center B with the charge distribution $(\chi\chi')_a$ on center A. The potential $\Omega_b = e^{-\alpha r_b}/r_b$ is similar to that one postulated by Yukawa for the mesonic field between a neutron and a photon in atomic and nuclear physics. In the case of the Huzinaga model potential, this and the s-STO forms result from the averaging of the potential of the core electron cloud upon the valence cloud, as shown in Chapter 3.

In this section we are concerned mainly with the representation of the charge distribution $(\chi\chi')_a$.

In Roothaan's notation, such a charge distribution has, apart from a numerical factor, the form

$$(\chi\chi')_a \sim r^{n+n'-2}\, e^{-2\bar{\zeta}r}\, S_{\ell m}(\theta,\phi)\, S_{\ell' m'}(\theta,\phi) \qquad (5\text{-}173)$$

with

$$\bar{\zeta} = \frac{1}{2}(\zeta + \zeta') \ . \qquad (5\text{-}173a)$$

The product $S_{\ell m}(\theta,\phi)\, S_{\ell' m'}(\theta,\phi)$ can always be expressed as a finite linear combination of spherical harmonics:

$$S_{\ell m}(\theta,\phi) S_{\ell' m'}(\theta,\phi) = \sum_{L=|\ell-\ell'|}^{\ell+\ell'} \sum_{M=-L}^{L} A_{LM} S_{LM}(\theta,\phi) \qquad (5\text{-}174)$$

where the rules of angular momentum coupling and orthogonality reign supreme. This means that not all terms in the sum necessarily servive. As is usual in such cases, the coefficients can in principle always be determined by integration of a three-product:

$$A_{LM} = N \cdot \int S_{\ell m}(\theta,\phi) S_{\ell' m'}(\theta,\phi) S_{LM}(\theta,\phi)\, d\omega \qquad (5\text{-}174a)$$

where N is a constant born out of normalisation, and $d\omega = \sin\theta\, d\theta\, d\phi$ is the solid angle, with limits of integration being as usual 0 to π for θ and 0 to 2π for ϕ.

Roothaan uses (5-174) to justify the decomposition of the charge distribution as a linear combination of basic charge distributions

$$(n\ell m\zeta)_a (n'\ell'm'\zeta)_a = \sum_L \sum_M B_{LM} [N,L,M,2\bar{\zeta}] \tag{5-175}$$

$$[NLM,2\bar{\zeta}] = \left(\frac{2L+1}{2\pi}\right)^{\frac{1}{2}} \frac{2^L (2\bar{\zeta})^{N+2}}{(N+L+1)!} r^{N-1} e^{-2\bar{\zeta}r} S_{LM}(\theta,\phi) \tag{5-176}$$

and B_{LM} are to be determined.

At a large distance $[N,L,M,2\bar{\zeta}]$ acts like a multipole of order 2^L and magnitude $\bar{\zeta}^{-L}$.

Except for their unusual normalisation factors these basic charge distributions look like STOs (equation (5-62)) and can be treated in the same manner with respect to Fourier convolution. The problem then reduces to the evaluation of the coefficients A_{LM} or B_{LM}. Roothaan does not show how he obtained his coefficients, and he deals with only up to p orbitals. A coherent scheme for the determination of these coefficients is needed to extend the analysis to higher n and higher ℓ orbitals. Two possible methods are apparent to us:

a) By going back to the definition of the real spherical harmonics in terms of the complex ones (equations (5-63) - (5-65)), then using the addition theorem for these

$$Y_{\ell_1 m_1}(\theta,\phi) Y_{\ell_2 m_2}(\theta,\phi) = \sum_{\ell m} \left[\frac{(2\ell_1+1)(2\ell_2+1)(2\ell+1)}{4\pi} \right]^{\frac{1}{2}}$$

$$\begin{pmatrix} \ell_1 & \ell_2 & \ell \\ m_1 & m_2 & m \end{pmatrix} Y^*_{\ell m}(\theta,\phi) \begin{pmatrix} \ell_1 & \ell_2 & \ell \\ 0 & 0 & 0 \end{pmatrix} \tag{5-177}$$

Then for example, since

$$S_{\ell_1|m_1|}S_{\ell_2|m_2|} = \frac{1}{2}\{Y_{\ell_1-|m_1|}+Y_{\ell_1|m_1|}\}\{Y_{\ell_2-|m_2|}+Y_{\ell_2|m_2|}\}$$

$$= \frac{1}{2}[Y_{\ell_1-|m_1|}Y_{\ell_2-|m_2|}+Y_{\ell_1-|m_1|}Y_{\ell_2|m_2|}$$

$$+Y_{\ell_1|m_1|}Y_{\ell_2-|m_2|}+Y_{\ell_1|m_1|}Y_{\ell_2|m_2|}] \,. \qquad (5\text{-}178)$$

Using (5-178) and manipulating the Wigner - 3-j symbols

$$\begin{pmatrix} \ell_1 & \ell_2 & \ell \\ m_1 & m_2 & m \end{pmatrix}$$

equation (12) of Roothaan [61] should result, upon conversion back to real spherical harmonics.

b) By using the real spherical harmonics directly, and deriving each individual formula directly, exploiting the properties of Legendre functions in a pedestrian manner. An example will illuminate this line of thought and action [81]:

$$(np\pi)(n'p\pi) \quad \underset{\sim}{\overset{\text{angular}}{\text{part}}} \quad P_1^1(\cos\theta)\cdot\cos\phi\cdot P_1^1(\cos\theta)\cos\phi$$

$$= \quad P_1^1\cdot P_1^1\cdot\frac{1}{2}(1+\cos 2\phi) \quad . \qquad (5\text{-}179)$$

The $\cos 2\phi$ part, in order to become a complete spherical harmonic, must be associated with a Legendre function of order 2, i.e., P_L^2, where L is to be determined. In this case $L = 1+1 = 2$ is the only plausible value of L. Thus we must express, for this term,

$$P_1^1 \, P_1^1 = C_{22} \, P_2^2 \quad , \tag{5-180}$$

and using the explicit expressions,

$$P_1^1(x) = (1-x^2)^{\frac{1}{2}} \quad , \qquad P_2^2 = 3(1-x^2) \tag{5-181}$$

we find that $C_{22} = \frac{1}{3}$.

Similarly the term 1 in the bracket of equation (5-179) suggests

$$P_1^1 \, P_1^1 = C_{00} \, P_0^0 + C_{20} \, P_2^0 \tag{5-182}$$

or

$$(1-x^2) = C_{00} \cdot 1 + C_{20} \cdot \frac{1}{2} (3x^2-1) \tag{5-183}$$

or

$$C_{22} = \frac{1}{3} \, , \quad C_{20} = -\frac{2}{3} \, , \quad C_{00} = \frac{2}{3} \quad . \tag{5-184}$$

These three coefficients clearly express not only the terms which survive, but are intimately related to the actual coefficients B_{LM} in (5-175). This can be tedious and fraught with arithmetical errors.

The recognition of this possible scheme b), which we have reason to suspect was the path taken by Roothaan , has led us to a promising third method:

c) By exploiting our formula (5-116) to the hilt, we have achieved an apparently straightforward generalisation of Roothaan's prodedure which is susceptible to computer generation of the coefficients. It also involves no major new programming effort, since it uses routine already developed for other parts of the integral package.

We write the product of spherical harmonics explicitly:

$$S_{\ell m}(\theta,\phi)S_{\ell' m'}(\theta,\phi) = N_{\ell m} \cdot N_{\ell' m'} \cdot P_{\ell}^{|m|}(\cos\theta) \cdot P_{\ell'}^{|m'|}(\cos\theta)$$

$$\times \begin{Bmatrix} \cos|m|\phi \\ \\ \sin|m|\phi \end{Bmatrix} \begin{Bmatrix} \cos|m'|\phi \\ \\ \sin|m'|\phi \end{Bmatrix} \qquad (5\text{-}185)$$

where

$$N_{\ell m} = \left[\frac{2\ell+1}{2\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{\frac{1}{2}} \cdot (1+\delta_{m0})^{-\frac{1}{2}} \qquad (5\text{-}185\text{a})$$

is the angular normalisation factor. The various combinations of ϕ parts result in slightly different terms upon expansion. These terms can be divided into distinct cases;

i) m , $m' \geq 0$

$$\cos|m|\phi \cdot \cos|m'|\phi = \frac{1}{2}[\cos(|m|+|m'|)\phi + \cos(|m|-|m'|)\phi] \qquad (5\text{-}186)$$

ii) $m \geq 0$, $m' < 0$

$$\cos|m|\phi \cdot \sin|m'|\phi = \frac{1}{2}[\sin(|m|+|m'|)\phi - \sin(|m|-|m'|)\phi] \qquad (5\text{-}187)$$

iii) $m < 0$, $m' \geq 0$

$$\sin|m|\phi \cdot \cos|m'|\phi = \frac{1}{2}[\sin(|m|+|m'|)\phi + \sin(|m|-|m'|)\phi] \qquad (5\text{-}188)$$

iv) $m < 0, \quad m' < 0$

$$\sin |m|\phi \cdot \sin |m'|\phi = \frac{1}{2} [- \cos (|m|+|m'|)\phi + \cos (|m|-|m'|)\phi] . \qquad (5\text{-}189)$$

Take Case i, which is a good representative of the analysis

$$S_{\ell m}(\theta,\phi)S_{\ell' m'}(\theta,\phi) = N_{\ell m} \cdot N_{\ell' m'} \cdot P_{\ell}^{|m|} (\cos \phi) P_{\ell'}^{|m'|}(\cos\phi) \times \frac{1}{2} \{\cos (|m|-|m'|)\phi + \cos (|m|+|m'|)\phi\} , \qquad (5\text{-}190)$$

corresponding to the two cos terms, we use the arguments of Method b), above to expand the Legendre function product in two ways, using eqn (5-116):

$$P_{\ell}^{|m|} (\cos \theta) P_{\ell'}^{|m'|} (\cos \theta) = \sum_{j=\max(|\ell-\ell'|,|m|-|m'|)}^{\ell+\ell'} \times C_{j\ell\ell'}^{|m|,|m'|} P_j^{|m|-|m'|} (\cos \theta) . \qquad (5\text{-}191)$$

since $P_{\ell'}^{|m'|} = P_{\ell'}^{-|m'|}$ shown by definitions in Appendix A, the following equation is also true,

$$P_{\ell}^{|m|} (\cos \theta) P_{\ell'}^{|m'|} (\cos \theta) = \sum_{k=\max(|\ell-\ell'|,|m|+|m'|)}^{\ell+\ell'} \times C_{k\ell\ell'}^{|m|,-|m'|} P_k^{|m|+|m'|} (\cos \theta) . \qquad (5\text{-}192)$$

So (5-190) becomes

$$S_{\ell m}S_{\ell' m'} = N_{\ell m}N_{\ell' m'} \cdot \frac{1}{2}\Big[\sum_j C_{j\ell\ell'}^{|m|,|m'|} \cdot P_j^{|m|-|m'|}(\cos\theta)\cdot$$

$$\cdot\cos(|m|-|m'|)\phi + \sum_k C_{k\ell\ell'}^{|m|-|m'|} \cdot P_k^{|m|+|m'|}(\cos\theta)\cdot$$

$$\cdot\cos(|m|+|m'|)\phi\Big] \quad . \qquad (5\text{-}193)$$

We define the new spherical harmonics:

$$S_{j|M_D|} = N_{j,M_D}\, P_j^{M_D}(\cos\theta)\begin{Bmatrix}\cos|M_D|\phi\\ \sin|M_D|\phi\end{Bmatrix} \qquad (5\text{-}194)$$

and

$$S_{k|M_S|} = N_{k,M_S}\, P_k^{M_S}(\cos\theta)\begin{Bmatrix}\cos|M_S|\phi\\ \sin|M_S|\phi\end{Bmatrix} \qquad (5\text{-}195)$$

where

$$M_D = |m| - |m'| \qquad (5\text{-}196)$$

$$M_S = |m| + |m'| \qquad (5\text{-}197)$$

which when substituted in (5-193) give

$$S_{\ell m}S_{\ell' m'} = N_{\ell m}N_{\ell' m'} \cdot \frac{1}{2}\Big[\sum_j C_{j\ell\ell'}^{|m|,|m'|} \cdot \frac{1}{N_j M_D} \cdot S_{j,|M_D|}$$

$$+ \sum_k C_{k\ell\ell'}^{|m|,-|m'|} \cdot \frac{S_{k,|M_S|}}{N_{k,|M_S|}}\Big] \quad . \qquad (5\text{-}198)$$

We can introduce the radial parts of the charge distributions to try and get at the final expression for eqn (5-175).

$$\chi\,\chi = (n,\ell,|m|,\zeta)(n',\ell',|m'|,\zeta')$$

$$= \frac{(2\zeta)^{n+\frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}}\; r^{n-1}\, e^{-\zeta r}\, S_{\ell m}(\theta,\phi) \cdot \frac{(2\zeta')^{n'+\frac{1}{2}}}{[(2n')!]^{\frac{1}{2}}} \cdot r^{n'-1}\, e^{-\zeta' r}$$

$$\cdot\, S_{\ell' m'}(\theta,\phi) \qquad (5\text{-}199)$$

Defining

$$\tau = (\zeta-\zeta')/(\zeta+\zeta') \quad ,$$

$$\bar{\zeta} = \frac{1}{2}(\zeta + \zeta') \qquad (5\text{-}200)$$

we find

$$(1+\tau) = \frac{\zeta+\zeta'+\zeta-\zeta'}{(\zeta+\zeta')} = \frac{2\zeta}{(\zeta+\zeta')}$$

and

$$(1-\tau) = \frac{2\zeta'}{(\zeta+\zeta')}$$

so

$$(2\zeta)^{n+\frac{1}{2}} = [(1+\tau)(\zeta+\zeta')]^{n+\frac{1}{2}} \qquad (5\text{-}201)$$

$$(2\zeta')^{n+\frac{1}{2}} = [(1+\tau)(\zeta+\zeta')]^{n'+\frac{1}{2}} \qquad (5\text{-}202)$$

giving

$$(2\zeta)^{n+\frac{1}{2}}\,(2\zeta)^{n'+\frac{1}{2}} = (1+\tau)^{n+\frac{1}{2}}(1-\tau)^{n'+\frac{1}{2}} \cdot (\zeta+\zeta')^{n+n+1} \quad . \qquad (5\text{-}203)$$

Thus (5-199) becomes

$$(n,\ell,|m|,\zeta)(n',\ell',|m'|,\zeta') = \frac{(1+\tau)^{n+\frac{1}{2}}(1-\tau)^{n'+\frac{1}{2}}}{[(2n)!\,(2n')!]^{\frac{1}{2}}} \times$$

$$\times\ (2\bar{\zeta})^{N+2}\, e^{-(\zeta+\zeta')r} \cdot S_{\ell m}(\theta,\phi) \cdot S_{\ell' m'}(\theta,\phi) \quad . \qquad (5\text{-}204)$$

We substitute (5-198) into this (5-204) and observe from (5-176) that

$$(2\bar{\zeta})^{N+2}\, r^{N-1}\, e^{-2\bar{\zeta}r}\, S_{LM}(\theta,\phi) = [N,L,M,2\bar{\zeta}] \times$$

$$\times \left(\frac{4}{2L+1}\right)^{\frac{1}{2}} \cdot \frac{(N+L+1)!}{2L} \qquad (5\text{-}205)$$

to give

$$(n,\ell,|m|,\zeta)(n',\ell',|m'|,\zeta') = \frac{(1+\tau)^{n+\frac{1}{2}}(1-\tau)^{n'+\frac{1}{2}}}{[(2n)!\,(2n')!]^{\frac{1}{2}}} \times$$

$$\times\ N_{\ell m} \cdot N_{\ell' m'} \cdot \frac{1}{2} \{ \sum_{j} C^{|m|,|m'|}_{j\ell\ell'} \cdot \left(\frac{4\pi}{2j+1}\right)^{\frac{1}{2}} \cdot \frac{(N+j+1)!}{2^{j}\, N_{j,M_D}} \times$$

$$\times\ [N,j,|M_D|,2\bar{\zeta}] + \sum_{k} C^{|m|,-|m'|}_{k\ell\ell'} \left(\frac{4\pi}{2k+1}\right)^{\frac{1}{2}} \times$$

$$\times\ \frac{(N+k+1)!}{2^{k}\cdot N_{k,M_S}} \cdot [N,k,|M_S|,2\bar{\zeta}] \quad . \qquad (5\text{-}206)$$

where the limits on j and k are still as imposed (5-91) and (5-192).

Case ii), $m \geq 0$, $m' < 0$ is very similar.

$$(n,\ell,|m|,\zeta)(n',\ell',-|m'|,\zeta) = \frac{(1+\tau)^{n+\frac{1}{2}}(1-\tau)^{n'+\frac{1}{2}}}{[(2n)!\,(2n')!]^{\frac{1}{2}}} \times$$

$$N_{\ell m} \cdot N_{\ell' m'} \frac{1}{2} \{ - \sum_{j} C^{|m|,|m'|}_{j\ell\ell'} \cdot (\frac{4\pi}{2j+1})^{\frac{1}{2}} \cdot \frac{(N+j+1)!}{2^{j} N_{k,M_S}} \times$$

$$\times [N,k,-|M_S|,2\bar{\zeta}]\} . \qquad (5\text{-}207)$$

Case iii). $m < 0$, $m' \geq 0$

$$(n,\ell,-|m|,\zeta)(n',\ell',|m'|,\zeta') = \frac{(1+\tau)^{n+\frac{1}{2}} (1-\tau)^{n'+\frac{1}{2}}}{[(2n)!\ (2n')!]^{\frac{1}{2}}} \times$$

$$\times \frac{1}{2} \{ \sum_{j} C^{|m|,|m'|}_{j\ell\ell'} (\frac{4\pi}{2j+1})^{\frac{1}{2}} \frac{(N+j+1)!}{2^{k} N_{k,M_D}} \cdot [N,j,-|M_D|,2\bar{\zeta}]$$

$$+ \sum_{k} C^{|m|,|m'|}_{k\ell\ell'} (\frac{4\pi}{2j+1})^{\frac{1}{2}} \frac{(N+k+1)!}{2^{k} N_{k,M_S}} [N,k,-|M_S|,2\bar{\zeta}]\} . \qquad (5\text{-}208)$$

Case iv). $m,m' < 0$

$$(n,\ell,-|m|,\zeta)(n',\ell',-|m'|,\zeta') = \frac{(1+\tau)^{n+\frac{1}{2}} (1-\tau)^{n'+\frac{1}{2}}}{[(2n)!\ (2n')!]^{\frac{1}{2}}} \times$$

$$\times N_{\ell m} \cdot N_{\ell' m'} \cdot \frac{1}{2} \{ \sum_{j} C^{|m|,|m'|}_{j\ell\ell'} \cdot (\frac{4}{2j+1})^{\frac{1}{2}} \cdot \frac{(N+j+1)!}{2^{j} N_{j,M_D}} \times$$

$$\times [N,j,|M_D|,2\bar{\zeta}] - \sum_{k} C^{|m|,|m'|}_{k\ell\ell'} (\frac{4\pi}{2k+1})^{\frac{1}{2}}$$

$$\cdot \frac{(N+k+1)!}{2^{k} N_{k,M_S}} \cdot [N,k,|M_S|,2\bar{\zeta}]\} . \qquad (5\text{-}209)$$

These four cases cover the whole gamut of possibilities.

Note 1: In any combination of m, m', the terms in M_D and M_S do not necessarily both appear. E. g. in $(n,1,-1,\zeta)(n',1,1,\zeta)$: $M_D = |1| - |1| = 0$, and because of (5-194) $[N,j,-0,2\bar{\zeta}]$ is not defined. So this term must disappear from the expression, leaving the $M_S = |1| + |1| = 2$ term $[N,k,-|2|,2\bar{\zeta}]$, which in Roothaan's parlance [61] is a $\bar{\Delta}$-type term, to survive.

Note 2: Accordin[illegible]o Roothaan's theorem [61] (eqn (5-79)), the only term which contribute to the two-center attraction integrals are the σ-type ($M = 0$) charge distributions. Evidently (by inspection and Note 1) these arise only from the special cases of i), and iv) when $m = m' = \pm|m|$, but no where else. In these cases the charge distributions look as follows:

$$(n,\ell,\pm|m|,\zeta)(n',\ell',\pm|m|,\zeta') = \frac{(1+\tau)^{n+\frac{1}{2}}(1-\tau)^{n'+\frac{1}{2}}}{[(2n)!\,(2n')!]^{\frac{1}{2}}} N_{\ell m}\cdot N_{\ell' m} \times$$

$$\times \frac{1}{2}\left\{\sum_{L=|\ell-\ell'|}^{\ell+\ell',2} C^{|m|,|m|}_{L\ell\ell'} \left(\frac{4\pi}{2L+1}\right)^{\frac{1}{2}} \frac{(N+L+1)!}{2L} \left(\frac{4\pi}{2L+1}\right)^{\frac{1}{2}} \times\right.$$

$$\times [N,L,0,2\bar{\zeta}] \pm \sum_k C^{|m|,-|m|}_{k\ell\ell'} \left(\frac{4\pi}{2k+1}\right)^{\frac{1}{2}} \times$$

$$\times \frac{(N+k+1)!}{2^k N_{k,M_S}} [N,k,2|m|,2\bar{\zeta}] \quad, \tag{5-210}$$

where it is understood that the pair $(+|m|, -|m|)$ is disallowed. For our attraction integrals, only the term in $[N,L,0,2\bar{\zeta}]$ need be programmed in fact. The case $m = m' = 0$ means $M_D = M_S$; in this case the official M_D term only can be used again with little modification. Therefore for the purposes of two-center attraction integrals the effective decomposition to be programmed is

$$(n,\ell,m,\zeta)(n',\ell',m,\zeta') = \frac{(1+\tau)^{n+\frac{1}{2}}(1-\tau)^{n'+\frac{1}{2}}}{\left[(2n)!\,(2n')!\right]^{\frac{1}{2}}} N_{\ell m}\cdot N_{\ell' m}\times$$

$$\times \sum_{L=\ell-\ell'}^{\ell+\ell'} \frac{1}{2-\delta_{m0}}\, C^{|m|,|m|}_{L\ell\ell'}\left(\frac{4\pi}{2L+1}\right)\cdot\frac{(N+L+1)!}{2^{L}}[N,L,0,2\bar{\zeta}] \;. \quad (5\text{-}211)$$

It is the $[N,L,0,2\bar{\zeta}]$ that, after the appropriate transformation $N \rightarrow N+1$, $2\bar{\zeta} \rightarrow \delta$, are plugged into the generalised overlap scheme represented by eqn (5-60).

7. Two-Center Nuclear Attraction: A Special Case: $\Omega_b = \frac{1}{r_b}$

It became clear late in the analysis that two-center nuclear attraction integrals of the type represented in eqn (5-68) could not be solved accurately by a Harris-Michels type scheme. The reason is that a few of the vital formulas require division by δ^2, an illegal manoeuver if $\delta = 0$. Indeed, the scheme for generating the $W^{Lj}_{i_p,i_2}(\delta_1,\delta_2,R)$ blows up if any of δ_1, δ_2, R becomes zero. A few tests revealed that the integrals could be obtained approximately (to 4 or 5 significant figures) by giving δ a small but non-zero value. It was found that the minimum value of δ achievable was $\sim 10^{-5}$, before computer overflow problems started to interfere in the scheme.

For an accurate determination, a diversion was made according to Geller's method [25], where this nuclear attraction integral appears as a special case of in eqn (5-13), the "quantum numbers" for the solid spherical harmonic being $N' = 0$, $L' = 0$, $M' = 0$.

The method of Geller is very similar to that of Harris and Michels. The difference is essentially that the Fourier transform of the solid spherical harmonic, being different from that of an STO, leads to slightly different routes.

For a solid spherical harmonic, the Fourier transform is defined as

$$G_b = (N',L',M')_b^T = \int e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}_b}\, r_b^{N'}\, P_L^{|M'|}(\cos\theta_b) \times$$

$$\times \begin{Bmatrix} \cos|M'|\phi_b \\ \sin|M'|\phi_b \end{Bmatrix} r_b^{L'+1}\, d\underset{\sim}{r}_b \ . \qquad (5\text{-}212)$$

The plane wave expansion (5-100) is used, and the integration over ϕ_b and θ_b readily performed (see eqns (5-106) - (5-108)). This leaves a single integral over the radial variable r_b in the form

$$G_b = 4\pi i^{L'}\, P_{L'}^{M'}(\cos u) \begin{Bmatrix} \cos|M'|v \\ \sin|M'|v \end{Bmatrix} \int_0^\infty r_b^{N'-L+1} \times$$

$$\times\; j_{L'}(kr_b)\,dr_b \qquad (5\text{-}213)$$

which is analogous to (5-109) and (5-110), except of course that the exponential term in δ is missing. The integral in (5-215) is easily evaluated. We use the standard integral (B-13) with

$$\mu = N'-L' + \frac{1}{2}\,, \qquad \nu = L' + \frac{1}{2}\ . \qquad (5\text{-}214)$$

Using the definition of our Bessel functions in (B-1), we get

$$j_{L'}(kr) = \left(\frac{\pi}{2kr}\right)^{\frac{1}{2}} J_{L' + \frac{1}{2}}(kr) \qquad (5\text{-}215)$$

$$r = \frac{kr}{k}\,, \qquad dr = \frac{d(kr)}{k}\,. \qquad (5\text{-}216)$$

So,

$$\int_0^\infty r^{N'-L'+1}\, j_{L'}(kr)dr = \int_0^\infty \left(\frac{kr}{k}\right)^{N'-L'+1} J_{L' + \frac{1}{2}}(kr)$$

$$\times \left(\frac{\pi}{2(kr)}\right)^{\frac{1}{2}} \times \frac{d(kr)}{k}$$

$$= \left(\frac{\pi}{2}\right)^{\frac{1}{2}} \int_0^\infty \frac{t^{N'-L'+1-(1/2)}}{k^{N'-L'+1}\cdot k}\; J_{L'+(1/2)}(t)\, dt \qquad (5\text{-}217)$$

where $t = kr$. The integral becomes equal to

$$\left(\frac{\pi}{2}\right)^{\frac{1}{2}} k^{L'-N'-2} \cdot \frac{2^{N'-L'+(1/2)}\;\Gamma(1+(1/2)N'}{\Gamma(L - \frac{N'}{2} + \frac{1}{2})}$$

$$= k^{L'-N'-2}\; \frac{\Gamma(1/2)\;\Gamma(1+(1/2)N'}{2^{L'-N'}\;\Gamma(L + \frac{1}{2} + \frac{N'}{2})} \qquad (5\text{-}218)$$

where $\Gamma(1/2) = \pi^{(1/2)}$. Thus the transform of the solid spherical harmonic is

$$G_b = (N',L',M') = 2\pi i^{L'}\; B(L',N') \cdot k^{L'-N'-2} \;\times$$

$$\times\; P_L^{|M'|}(\cos\, u) \begin{Bmatrix} \cos\, |M'|v \\ \sin\, |M'|v \end{Bmatrix} \qquad (5\text{-}219)$$

where

$$B(L',N') = \frac{\Gamma(1/2)\ \Gamma(1+(1/2)N')}{2^{L'-N'}\ \Gamma(L+\frac{1}{2}-\frac{N'}{2})} \quad . \tag{5-220}$$

Note that the integral in (5-213) in fact only exists for $L' > N' > -2$, because of the conditions of (B-13). For $M < \frac{1}{2}$ implies $N' - L' + \frac{1}{2} < \frac{1}{2}$ or $N' < -L' < 0$ or $L' > N'$; and $\mu+\nu > -1 \Longrightarrow B'+1 > -1 \Longrightarrow N' > -2$. So $L' > N' > -2$. This condition is not such a deadly limitation to the scope of the method, which still covers many cases of interest.

Geller substitutes the Fourier transfroms back into (5-98), and expands $e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}}$, eqn (5-100), just like us. He chooses to go by way of the Condon-Shortley coefficients, and his final formula (analogous to our (5-134)) is

$$\begin{aligned} I = {} & \delta_{M,\pm|M'|}(1 \pm \delta_{M',0})\,[(2(H\ \delta_{M'0}))]^{-(1/2)}\,(2\bar{\zeta})^{L'+1-N'} \\ & \times\ (2L+1)^{-(1/2)}\ D(L',M',N') \\ & \times \sum_{r=0}^{L_<} (-1)^r\ (2L+2L'+1-4r) \\ & \times\ c^{L+L'-2r}\ (L,|M'|;L',|M'|) \\ & \times\ F_{p,N,L}\ (L'-2r,2r-N) \end{aligned} \tag{5-221}$$

where

$$\begin{aligned} D(L',M',N') = {} & B(L',N')(2L'+1)^{-(1/2)} \\ & \times [(L'+|M'|)!/(L'-|M'|)!]^{(1/2)} \quad , \end{aligned} \tag{5-222}$$

L = the smaller of L and L' ;

the upper signs are associated with $\cos|M'|\phi$, and the lower signs with $\sin|M'|\phi$; $C^k(\ell_i,m_i;\ell_j,m_j)$ are the Condon-Shortley coefficients; and

$$F_{\rho,N,L}(k,t) = \frac{2^{2L+1}\ (N-L)!\ (2L+1)}{(N+L+1)!} \sum_{s=0}^{[\frac{1}{2}(N-L)]} (-1)^s \begin{pmatrix} N+L+1 \\ 2s+2L+1 \end{pmatrix} \times$$

$$\times \frac{(s+L)!}{s!} \int_0^\infty \frac{x^{2s+L+k+t}\ j_{\ell+k}(x)}{(1+x^2)^{N+1}}\,dx \qquad (5\text{-}223)$$

where

$$\rho = 2\bar{\zeta} R \quad . \qquad (5\text{-}224)$$

This $F_{\rho,N,L}^{(k,t)}$ of course quite related to our $W_{i,i_2}^{L,j}$ in eqn (5-135), but its treatment is slightly different. Geller chooses to generate these functions by use of the recursive relations

$$F_{\rho,N,L}(k+1,t) = [(L+k)/\rho]F_{\rho,N,L}(k,t) - (\frac{\partial}{\partial\rho})\ F_{\rho,N,L}(\ ,t) \qquad (5\text{-}225)$$

$$F_{\rho,N,L}(k-1,t+2) = [(L+k+1)/\rho]F_{\rho,N,L}(k,t) + (\frac{\partial}{\partial\rho})\ F_{\rho,N,L}(k,t) \qquad (5\text{-}226)$$

which are based on known identities for spherical Bessel functions, and a starting formula for each value of N'.

For the case $N' = 0$, all terms can be generated from eqns (5-225) and (5-226), and

$$F_{\rho,N,L}(0,0) = 2^L[\rho^{-L-1}\ \gamma(N+L+2,\rho) + \rho^L\Gamma(N-L+1,\rho)]/(N+L+1)! \qquad (5\text{-}227)$$

where $\gamma(m,n)$ and $\Gamma(m,n)$ are Incomplete Gamma Functions defined by

$$\Gamma(m,n) = \int_n^\infty e^{-t}\ t^{m-1}\ dt \qquad (5\text{-}228)$$

$$\gamma(m,n) = \int_0^n e^{-t}\ t^{m-1}\ dt$$

$$= \Gamma(m) - \Gamma(m,n) \qquad (5\text{-}229)$$

where

$$\Gamma(m) = \int_0^\infty e^{-t}\ t^{m-1}\ dt \qquad (5\text{-}230)$$

is the usual gamma function. γ and Γ therefore satisfy

$$\gamma(N+1,\rho) = N!\ [1 - e^{\rho}\ e_N(\rho)] \qquad (5\text{-}231)$$

$$\Gamma(N+1,\rho) = N!\ e^{-\rho}\ e_N(\rho) \qquad (5\text{-}232)$$

where

$$e_N(\rho) = \sum_{k=0}^{N}\ \rho_k/k! \qquad (5\text{-}233)$$

is a truncated exponential.

Under these substitutions, the nuclear attraction integral reduces to a surprisingly simple form:

$$\int\ [N,L,M]_a\ r_b^{-1}\ d\tau = \delta_{M,0}\cdot 2\bar{\zeta}\ \cdot\ F_{\rho,N,L}(0,0)\ . \qquad (5\text{-}234)$$

The δ_{M0} of course comes from Roothaan's theorem, $F_{\rho,N,L}(0,0)$ are easily evaluated from equations (5-227) - (5-233).

8. Rotational Coordinate Transformations

In previous sections, we have seen that the two-center integrals are derived for a specific coordinate system (Figure 5.3) which affects the terms that contribute to the integrals. See for example, the discussion of formula (5-210). The integrals can be used directly in cases where all centers are collinear along the z-axis. In bent molecules, or in cases where considerations of group theory dictate that atomic centers are situated elsewhere, the integrals must be adjusted for this non-alignment of axes. This adjustment is what is called rotational coordinate transformation. By this transformation, functions previously defined in one coordinate system are expressed in terms of similar functions defined in another coordinate system.

In this work, the main problem associated with rotational coordinate transforamtions is the effect of the transformation upon the spherical harmonics the radial parts remaining unchanged. Let (θ,ϕ) be angular coordinates in some Cartesian system and (θ',ϕ') be the corresponding coordinates in another Cartesian system.

It is well-known that any Cartesian system can be transformed into any other Cartesian system by means of three successive rotations performed in a specific sequence. The angles in the rotations are called Euler angles $(\alpha\ \beta\ \gamma)$ [82]. There is no unanimity about the definition of Euler angles in the literature, and here we define them in a way which later makes our work easier. The sequence is

i) Rotate clock-wise by α $(0 \leq \alpha \leq 2\pi)$ about z-axis: $(r,\theta,\phi) \equiv (x,y,z) \xrightarrow{\alpha} (x',y',z)$.

ii) Rotate clock-wise by β $(0 \leq \beta < \pi)$ about the new x-axis: $(x',y',z) \xrightarrow{\beta} (x',y'',z'')$.

iii) Rotate clock-wise by γ $(0 \leq \gamma < 2\pi)$ about the newest z-axis: $(x',y'',z'') \xrightarrow{\gamma} (x''',y''',z'') \equiv (r,\theta',\phi')$.

Expressing the old spherical harmonics in terms of the new,

$$Y_{\ell m}(\theta,\phi) = \sum_{\sigma=-\ell}^{\ell} D_{\ell}^{m\sigma}(\alpha\beta\gamma)\, Y_{\ell\sigma}(\theta',\phi') \tag{5-235}$$

where

$$D_{\ell}^{m\sigma}(\alpha\beta\gamma) = e^{im\alpha} \cdot d_{m\sigma}^{\ell}(\cos\beta) \cdot e^{im\gamma} \tag{5-236}$$

the problem becomes one of evaluating the $D_{\ell}^{m\sigma}(\alpha\beta\gamma)$ or $d_{m\sigma}^{\ell}(\cos\beta)$. Harris and Michels, [24] and also Edmonds, [76] have detailed recursion methods for generating these coefficients.

We have tried to get away without generating all of them, by finding out which coefficients are needed in the treatment of a specific group of molecules, those with first row off-center atoms.

In this case, functions on the off-center atom are all sperically symmetric, including the 1s core projection operator. So, as seen in equation (5-210), only the $\sigma = 0$ term in (5-235) will contribute to the two-center integrals. This term has a very simple form: it is merely a spherical harmonic over the Euler angles

$$D_{\ell}^{m0}(\alpha\beta\gamma) = (-1)^{m} \left(\frac{4\pi}{2\ell+1}\right)^{\frac{1}{2}} Y_{\ell m}(\beta\alpha) \quad . \tag{5-237}$$

It is necessary in this work to convert the formulation to our kind of real spherical harmonics. We may rewrite (5-235) in two forms:

$$Y_{\ell|m|}(\theta,\phi) = D_{\ell}^{|m|0}\, Y_{\ell 0}(\theta',\phi') + \sum_{\sigma=1}^{\ell} \{D_{\ell}^{|m|,-\sigma} Y_{\ell\ -\sigma}(\theta',\phi')\} + D_{\ell}^{|m|,\sigma}\, Y_{\ell\sigma}(\theta',\phi') \tag{5-237a}$$

and

$$Y_{\ell,-|m|}(\theta,\phi) = D_{\ell}^{-|m|,0}\, Y_{\ell 0}(\theta',\phi') + \sum_{\sigma=1}^{\ell} \{D_{\ell}^{-|m|,-\sigma}\, Y_{\ell,-\sigma} + D^{-|m|,\sigma}\, Y_{\ell\sigma}\} \quad . \tag{5.238}$$

We neglect the terms with $\sigma \neq 0$ as we use equations (5-63) - (5-65) to manufacture real spherical harmonics:

$$S_{\ell 0}(\theta,\phi) \simeq \left(\frac{4\pi}{2\ell+1}\right)^{\frac{1}{2}} S_{\ell 0}(\beta\alpha)\, S_{\ell 0}(\theta',\phi') \tag{5-239}$$

$$S_{00}(\theta,\phi) \simeq S_{00}(\theta',\phi') \tag{5-240}$$

$$\begin{aligned} S_{\ell,|m|}(\theta,\phi) &\simeq \frac{1}{\sqrt{2}} \left(\frac{4\pi}{2\ell+1}\right)^{\frac{1}{2}} \{(-1)^{-|m|}\, Y_{\ell,-|m|}(\beta\alpha) \\ &\quad + (-1)^{|m|}\, Y_{\ell,|m|}(\beta\alpha)\}\ S_{\ell 0}(\theta',\phi') \\ &\simeq \left(\frac{4\pi}{2\ell+1}\right)^{\frac{1}{2}} (-1)^{|m|}\, S_{\ell,|m|}(\beta\alpha)\, S_{\ell 0}(\theta',\phi') \end{aligned} \tag{5-241}$$

and

$$S_{\ell,-|m|}(\theta,\phi) \simeq \left(\frac{4\pi}{2\ell+1}\right)^{\frac{1}{2}} (-1)^{|m|}\ S_{\ell,-|m|}(\beta\alpha)\ S_{\ell 0}(\theta',\phi') \quad . \qquad (5\text{-}242)$$

Combining these formulas and introducing Legendre functions, we see that the transformation takes the form

$$S_{\ell,\pm|m|}(\theta,\phi) = (-1)^{|m|}\left[\frac{2(\ell-|m|)!}{(\ell+|m|)!}\right]^{\frac{1}{2}} (1+\delta_{M0})^{-\frac{1}{2}} \times P_{\ell}^{|m|}(\cos\beta) \times \begin{Bmatrix}\cos|m|\alpha \\ \sin|m|\alpha\end{Bmatrix} S_{\ell 0}(\theta',\phi') \quad . \qquad (5\text{-}243)$$

An overlap integral of the type given in eqns (5-67) can be recovered under the transformation as

$$\langle(n_1\ell_1 \pm m_1\delta_1)_a|(n_2\ell_2 m_2\delta_2)_b\rangle$$

$$= (-1)^{|m_1|}\left[\frac{2(\ell-|m_1|)!}{(\ell+|m_1|)!}\right]^{\frac{1}{2}} (1+\delta_{m_1 0})^{-\frac{1}{2}} P_{\ell}^{|m_1|}(\cos\beta)$$

$$\times \begin{Bmatrix}\cos|m_1|\alpha \\ \sin|m_1|\alpha\end{Bmatrix} \times \langle(n_1\ell_1 0\delta_1)_a|(n_2\ell_2 m_2\delta_2)_b\rangle \qquad (5\text{-}244)$$

where it is understood that the function at B is spherically symmetric and is not affected by rotation of coordinates.

For the other integrals in OCE-MP all the basic charge distributions arising in eqns (5-206) - (5-209), and not just the $[N,L,0,2\bar{\zeta}]$, have a chance of contributing terms under the rotation. Again in the special case of first-row off-center atoms, the only modification needed is to replace the general basic charge distributions and thus

$$[N,L,\pm M,2\bar{\zeta}]_{(r,\theta,\phi)} = (-1)^{|M|}(1+\delta_{M0})^{-\frac{1}{2}} \left[\frac{2(L-|M|)!}{(L+|M|)!}\right]^{\frac{1}{2}} \times$$

$$\times\, P_L^{|M|}(\cos\,\beta) \begin{Bmatrix} \cos\,|M|\alpha \\ \sin\,|M|\alpha \end{Bmatrix} [N,L,0,2^{-}]_{(r,\theta',\phi')} \; . \quad (5.245)$$

A further simplification arises in the case of $C_{2v}(D_{\infty h})$ symmetry. Here, the Euler angles are $(\alpha\beta\gamma) = (0\beta 0)$ where $\beta = \theta$, the half bond-angle of Figure 4.2. Because $\alpha = 0$, the terms in $\sin\,|m|\,\alpha$ in equations (5-244) and (5-245) vanish. Thus under rotational coordinate transformation, orbitals or charge distributions with negative m quantum number do not contribute to off-center integrals. This is as it should be, since these behave like x and are not affected by a rotation in the y-z plane.

9. Test Results

a. For two-center nuclear (Coulomb) attraction and overlap integrals, the results were identical with the reference values calculated by the ALCHEMY program [83] to at least nine significant figures, the output field used, for all orbitals tested (up to 4f).

b. For Yukawa-type and S-STO potentials, the results were tested by two methods.

i) We compare our results to those which we calculated using Huzinaga's method of expanding an STO in terms of GTOs [40c] and then calcualting the resulting GTO integrals by familiar methods [84]. Thus for example a general three-center STO integral

$$< \chi_a | e^{-\alpha r_c} | \chi'_b >$$

is converted into Gaussian form

$$< \sum_i C^a_i e^{-\alpha_i r^2_a} \mid \sum_j C^c_j e^{-\alpha_j r^2_c} \mid \sum_k C^b_k e^{-\alpha_k r^2_b} > .$$

Huzinaga has coded a program to evaluate overlap Coulomb attraction and some of the model potential integrals arising in this work. Comparison of results from the expansion method and our Fourier Convolution technique is shown in Tables 5.1-3. It is to be noted that, in principle, our method is an accurate one, while the expansion method is approximate. The comparison is thus to assure ourselves that no gross factors have been missed in the derivation, not to get an exact measure of accuracy.

ii) The method was further tested indirectly, by investigating the limiting behaviour of some of the integrals. We tested the hypothesis that as the α-parameter tends to zero, the Yukawa-type and ls-STO integrals tend to two-center Coulomb and one-center overlap respectively:

$$\lim_{\alpha \to 0} <\chi_a | \frac{e^{-\alpha r_b}}{r_b} | \chi'_a> = <\chi_a | \frac{1}{r_b} | \chi'_a>$$

$$\lim_{\alpha \to 0} <\chi_a | e^{-\alpha r_b} | \chi'_a> = <\chi_a | \chi'_a> .$$

We reduced α gradually and found that at $\alpha \simeq 10^{-5}$, agreement with ALCHEMY values for two-center nuclear attraction and one-center overlap

TABLE 5.1 Two-center overlap Integrals over STOs

Orbital pair	Exponents ζ_a	ζ_b	R_{ab}	OVERLAP This work	ALCHEMY[a]	GTO-Expn[b]	R.O.W.[c]
$(1S_a\|1S_b)$	14.413	1.35	3.2	3.078839(-3)[d]	3.078839(-3)	3.078187(-3)	3.078839(-3)
$(1S_a\|2P\sigma_b)$	14.413	1.80	3.2	-6.469020(-3)	-6.469020(-3)	-6.46820(-3)	-6.46902(-3)
$(1S_a\|3d\sigma_b)$	14.413	2.40	3.2	7.065464(-3)	7.065464(-3)	7.06305(-3)	7.06546(-3)
$(2S_a\|1S_b)$	4.902	1.35	3.2	3.025995(-2)	3.025995(-2)	3.02712(-2)	3.025995(-2)
$(2S_a\|2P\sigma_b)$	3.50	1.80	3.2	-6.251656(-2)	-6.251656(-2)	-6.25193(-2)	-6.251656(-2)
$(4d\sigma_a\|2P\sigma_b)$	3.60	1.80	3.2	-1.468297(-1)	-1.468297(-1)	-1.46836(-1)	
$(2P\pi_a\|2P\pi_b)$	8.636	1.80	3.2	2.076778(-3)	2.076778(-3)	2.07727(-3)	
$(4f\pi_a\|3d\pi_b)$	4.00	2.40	3.2	-8.760785(-2)	-8.760785(-2)	-8.75634(-2)	
$(4d\pi_a\|2P\pi_b)$	3.60	1.80	3.2	7.838377(-2)	7.838377(-2)	7.836265(-2)	
$(2P\sigma_a\|3d\sigma_b)$	8.636	2.40	5.2	3.404487(-4)	3.404487(-4)	3.39053(-4)	
$(4f\delta_a\|3d\sigma_b)$	4.00	2.40	5.2	7.713656(-3)	7.713656(-3)	7.70948(-3)	
$(4f\sigma_a\|1S_b)$	4.00	1.35	5.2	3.065936(-3)	3.065936(-3)	3.05090(-3)	
$(4d\pi_a\|2P\pi_b)$	3.60	1.80	5.2	3.961842(-3)	3.961842(-3)	3.95178(-3)	
$(4f\pi_a\|3d\pi_b)$	4.00	2.40	5.2	-3.584961(-3)	-3.584961(-3)	-3.57178(-3)	

[a] Reference 83.

[b] Calculated by present author after reference 40.c.

[c] Calculated by present author after reference 66.

[d] Number in parenthesis indicates power of 10.

Table 5.2: Two-Center Nuclear Attraction Integrals $<\chi_a|\frac{1}{r_b}|\chi_a'>$

Orbital Pair	Exponents δ_1	δ_1	R_{ab}	Nuclear Attraction This Work	ALCHEMY[a]	GTO-Expn[b]
$(1s_a\|1s_a)$	14.413	14.413	3.2	3.125000(-1)	3.125000(-1)	3.12501 (-1)
			5.2	1.923077(-1)	1.923077(-1)	1.923085(-1)
$(1s_a\|2s_a)$	14.413	8.513	3.2	2.819750(-1)	2.819750(-1)	2.81976 (-1)
			5.2	8.121950(-2)	8.121950(-2)	8.121822(-2)
$(3d\sigma_a\|2d\sigma_a)$	3.60	3.60	3.2	3.235137(-1)	3.235137(-1)	3.235137(-1)
			5.2	1.946437(-1)	1.946437(-1)	1.946437(-1)
$(3d\pi_a\|3d\pi_a)$	3.60	3.60	3.2	3.161449(-1)	3.161449(-1)	3.161449(-1)
			5.2	1.933113(-1)	1.933113(-1)	1.933113(-1)
$(4f\pi_a\|4f\pi_a)$	4.0	4.0	3.2	3.209255(-1)	3.209255(-1)	3.209239(-1)
			5.2	1.943170(-1)	1.943170(-1)	1.943161(-1)

[a] Reference [83]

[b] Calculated by present author, after reference [40c]

Table 5.3: Yukawa-Type and Is-STO Integrals

STO			Yukawa	$\alpha = 1.0$	Is-STO	$\alpha = 1.0$
Pair	Exponents	R_{ab}	This Work	GTO-Expn[a]	This Work	GTO-Expn[a]
$(1s_a\|1s_a)$	14.413	3.2	0.12769 (-1)	0.12768 (-1)	0.40799(-1)	0.40785(-1)
		5.2	0.10634 (-2)	0.10632 (-2)	0.55247(-2)	0.55237(-2)
$(1s_a\|2s_a)$	14.413	3.2	0.11538 (-1)	0.11537 (-1)	0.36833(-1)	0.36829(-1)
	8.513[b]	5.2	0.96090 (-3)	0.96072 (-3)	0.49894(-2)	0.49884(-2)
$(3d\sigma_a\|3d\sigma_a)$	3.6	3.2	0.19483 (-1)	0.19484 (-1)	0.49622(-1)	0.49623(-1)
		5.2	0.15116 (-2)	0.15116 (-2)	0.69421(-2)	0.69422(-2)
$(3d\pi_a\|3d\pi_a)$	3.6	3.2	0.16280 (-1)	0.16280 (-1)	0.90835(-2)	0.90837(-2)
		5.2	0.13517 (-2)	0.13516 (-2)	0.12899(-1)	0.12899(-1)
$(4f\pi_a\|4f\pi_a)$	4.0	3.2	0.18992 (-2)	0.18992 (-2)	0.97788(-1)	0.97790(-1)
		5.2	0.15319 (-2)	0.15319 (-2)	0.14005(-1)	0.14005(-1)

[a] Calculations by present author using Huzinaga program, reference [40c]

[b] Exponent for 2s

Table 5.4: Limiting Behaviour of OCE-MP Integrals

STO Pair	Exponents	R_{ab}	YUKAWA $\alpha = 10^{-5}$	Two-Center Nuc. AT.[a]	1s-STO $\alpha = 10^{-5}$	One-Center Overlap[a]
$(1s_a\|1s_a)$	14.413	3.2	0.31249	0.31250	1.00004	1.0
		5.2	0.19230	0.19231	1.0003	1.0
$(1s_a\|2s_a)$	14.413	3.2	0.28197	0.28198	0.90206	0.90232
	8.513[b]	5.2	0.17351	0.17352	0.90206	0.90232
$(3d\sigma_a\|3d\sigma_a)$	3.6	3.2	0.32350	0.32351	0.99989	1.0
		5.2	0.19463	0.19464	0.99824	1.0
$(3d\pi_a\|3d\pi_a)$	3.6	3.2	0.31613	0.31614	1.00024	1.0
		5.2	0.19330	0.19331	1.00066	1.0
$(4f\pi_a\|4f\pi_a)$	4.0	3.2	0.32092	0.32093	1.00000	1.0
		5.2	0.19432	0.19432	1.00000	1.0

[a] ALCHEMY results, reference [83]

[b] Exponent for 2s

was up to four significant figures, as shown in Table 5.4. For smaller values of α, overflow problems started to interfere with the Fourier Convolution scheme.

We are therefore satisfied that our scheme generates all the two-center integrals needed in OCE-MP to a high degree of accuracy.

E. One-Center Integrals by Fourier Convolution Methods

We have explored the possibility of using the HM scheme to solve both one-electron and two-electron integrals of the one-center type.

For the two-electron Coulomb and Exchange integrals, the formula (5-26), proposed by Geller, can be used as a starting point. Or one can merely put $R = 0$ in eqn (5-61) of HM and proceed as in Section C above. The results will be similar to those we are going to derive in the one-electron case, as suggested in the note accompanying equations (5-122) and (5-123).

1. Generalised One-Center Overlap

Put $R = 0$ in the Fourier inversion integral (5-98) or (5-112), to get

$$I(R=0) = N_{n_1 \ell_1 m_1} N_{n_2 \ell_2 m} (-1)^{\ell_2} i^{\ell_1+\ell_2} \left[\frac{4\pi}{(2\pi)^{3/2}} \right] \times$$

$$\times \int (n_1 \ell_1 \delta_1)^T (n_2 \ell_2 \delta_2)^T P_{\ell}^{|m_1|} (\cos u) P_{\ell 1}^{|m_2|} (\cos u) \times$$

$$\times \left\{ \begin{matrix} \cos |m_1| v \\ \sin |m_1| v \end{matrix} \right\} \left\{ \begin{matrix} \cos |m_2| v \\ \sin |m_2| v \end{matrix} \right\} d\underset{\sim}{k} \qquad (5\text{-}246)$$

As before, integration over v fixes $m_1 = m_2$ and gives $\frac{2\pi}{\epsilon_m} \delta_{m_1,m_2}$ where $m = m_1 = m_2$.

The integration over u is an orthogonality relation of associated Legendre functions, and it fixes $\ell = \ell_1 = \ell_2$ as in eqn (5-108) which is not surprising, when compared with the atomic case.

We go through the analysis of the Fourier transforms $(n\ell\delta)^T$, as in equations (5-124) - (5-131), to find that the equation analogous to (5-132) is

$$I = N_{n_1\ell_1 m} \; N_{n_2\ell_2 m} \sum_{i_1} \sum_{i_2} \frac{4\pi}{\epsilon_m} \cdot \frac{\pi}{2} \frac{(\ell+|m|)!}{(2\;+1)(\ell-|m|)!} B_{n_1\ell i_1}(\delta_1) \times$$

$$\times B_{n_2\ell i_2}(\delta_2) \times \int_0^\infty \frac{k^{2\ell} \cdot k^2 \, dk}{(k^2+\delta_1^2)^{i_1} (k^2+\delta_2^2)^{i_2}} \quad . \tag{5-247}$$

The problem then reduces to one of obtaining the integral

$$T^{\ell}_{i_1 i_2}(\delta_1,\delta_2) = \int_0^\infty \frac{k^{2\ell} \cdot dk}{(k^2+\delta_1^2)^{i_1} (k^2+\delta_2^2)^{i_2}} \tag{5-248}$$

so that the final formula is

$$I = N_{n_1\ell m} N_{n_2\ell m} \sum_{i_1} \sum_{i_2} \frac{4\pi}{\epsilon_m} \cdot \frac{\pi}{2} \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!} B_{n_1\ell i_1}(\delta_1) \times$$

$$\times B_{n_2\ell i_2}(\delta_2) \; T^{\ell+1}_{i_1,i_2}(\delta_1,\delta_2) \quad , \tag{5-249}$$

for the one-electron integral.

2. One-Center Two-Electron Integral

The corresponding one for the one-center two-electron integral is

$$C = N_{n_1 m} N_{n_2 m} \sum_{i_1} \sum_{i_2} \frac{4\pi}{\epsilon_m} \cdot \frac{\pi}{2} \cdot 4\pi \sqrt{\frac{(\ell+|m|)!}{(\ell-|m|)!}} \times$$

$$\times \; B_{n_1 \ell i_1}(\delta_1) \, B_{n_2 \ell i_2}(\delta_2) \, T_{i_1 i_2}(\delta_1, \delta_2) \quad . \qquad (5\text{-}250)$$

3. Generation of Auxilliary Functions

For the solution of equation (5-248), we draw heavily on the HM experience.

Using the identity (5-137), we see immediately that

$$T_{i_1 i_2} = \int_0^\infty \frac{k^{2\ell-2} \cdot k^2 \, dk}{(k^2+\delta_1^2)^{i_1} (k^2+\delta_2^2)^{i_2}}$$

$$= \int_0^\infty \frac{k^{2(\ell-1)}}{(k^2+\delta_1^2)^{i_1-1} (k^2+\delta_2^2)^{i_2}} \left\{ 1 - \frac{\delta_1^2}{(k^2+\delta_1^2)} \right\} dk$$

or

$$T^{\ell}_{i_1,i_2} = T^{\ell-1}_{i_1-1,i_2} - \delta_1^2 \, T^{\ell-1}_{i_1 i_2} \quad . \qquad (5\text{-}251)$$

Similarly, using $\delta = \delta_2$,

$$T^{\ell}_{i_1,i_2} = T^{\ell-1}_{i_1,i_2} - {}^{2}_{2} \, T^{\ell-1}_{i_1,i_2} \quad . \qquad (5\text{-}252)$$

We subtract (5-252) from (5-251) to get

$$(\delta_2^2 - \delta_1^2)T^{\ell}_{i_1,i_2} = T^{\ell}_{i_1,i_2-1} - T^{\ell}_{i_1-1,i_2} \quad . \tag{5-253}$$

The recipe can again be divided into three parts.

<u>Part 1</u>: obtain $T^0_{i_1 0}$, T^0_{0,i_2} for all i_1, i_2.

<u>Part 2</u>: Generate $T^0_{i_1,i_2}$, using (5-253).

<u>Part 3</u>: Raise index ℓ using (5-251) or (5-252), all of which mimic our work in Section C, but much more simply. <u>Part 1</u>: To generate $T^0_{0i_2}$, $T^0_{i_1 0}$, we found an apt standard integral (Handbook of Physics and Chemistry, [77] Formula 615):

$$\int_0^{\infty} \frac{x^a}{(m+x^b)^c}\, dx = \frac{m^{\left[\frac{a+b}{c} - c\right]}}{b} \cdot \frac{\Gamma(\frac{a+1}{b})\ \Gamma(c - \frac{a+1}{b})}{\Gamma(c)} \tag{5-254}$$

under the conditions

$$a > -1, \quad b > 0, \quad m > 0, \quad c > \frac{a+1}{b} \quad . \tag{5-255}$$

For us (5-237) gives, $a = 0 > -1$, $b = 2 > 0$, $m = \delta^2 > 0$ (thus nuclear attraction may again give problems), $c = i > \frac{1}{b} = \frac{1}{2}$ always.

We get

$$T^0_{i_1 0} = \int_0^{\infty} \frac{1}{(k^2+\delta_1^2)^{i_1}}\, dk = \frac{(\delta_1^2)^{(\frac{1}{2} - i_1)}}{2} \ \frac{\Gamma(\frac{1}{2})\ \Gamma(i_1 - \frac{1}{2})}{\Gamma(i_1)} \tag{5-256}$$

and

$$T_{0i_2} = \frac{(\delta_2^2)^{\frac{1}{2} - i_2}}{2} \cdot \frac{\Gamma(\frac{1}{2})\ \Gamma(i_2 - \frac{1}{2})}{\Gamma(i_2)} \quad . \tag{5-257}$$

Also, the lowest gives

$$T_{10}^{0} = \frac{\pi}{2\delta_1} \tag{5-258}$$

$$T_{01}^{0} = \frac{\pi}{2\delta_2} \; . \tag{5-259}$$

Part 2: With our experience, we use the analysis outlined in Section C for the different cases:

Case 1: δ_1 "far" from δ_2 .

Case 2: δ_1 "near" to δ_2 but not equal.

Case 3: δ_1 equal δ_2.

Part 3 is nothing really new.

We have yet to check, code and test the performance this scheme for one-center integrals but it looks promising.

CHAPTER VI

MOLECULAR CALCULATIONS: RESULTS AND DISCUSSION

A. One-Center Basis Sets

Once the molecular SCF computer program has been put together and tested on known molecules to make sure that it calculates the things expected of it, the problem of molecular calculations basically reduces to one of basis set development. How to choose basis sets ($\{x_p\}$ of formula (2-105)) which will properly span the space in question (in our case, the molecular valence region) is a far from trivial task, and takes experience to master. It is easier in some cases than in others. Ultimately, any basis set reflects the prejudices of its creator, giving rise to such tongue-in-cheek terminology as "LCMBF" (linear combination of my basis functions).

In this chapter, we shall discuss the development of valence basis sets in order of increasing difficulty, although this may not be the order in which we developed them. We start with central hydrides AH_n with model potentials at the expansion center, and then go on to the N_2 case in which the model potentials sit at the off-center nuclei. The problems involved in applications of the OCE-MP method to more complicated molecules will become apparent as we progress.

B. Central Hydrides H_2O and H_2S

1. Basis Sets

The least ambitious test of the OCE-MP method is its application to the central hydride molecules AH_n with the model potential and expansion center coincident at the central heavy atom. Here, the development of the valence basis set is governed by the same considerations as those involved in the development of the full one-center basis in the first place.

As seen from Moccia's work, [12] the deeper-lying MO's retain almost completely the character of the atomic orbitals of the heavy central atom. The H atoms introduce small perturbations in the outer AOs, which are more involved in the bonding characteristics of the molecule. It is natural, therefore, to take the basis for the heavy atom as a starting point for the molecular calculation, and then add valence functions of proper symmetry to build up the molecular eigenspace. Thus for H_2O, the ground-state configuration

$$1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 1b_1^2\ ,\quad {}^1A_1$$

may be approximated by

$$[1s^2]\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 1b_1^2\ ,\quad {}^1A_1$$

where the 1s refers to the oxygen atom. In Moccia's calculation, even the valence orbitals are dominated in coefficients by oxygen atomic functions, and one may indeed detect a crude correspondence between the MO's and atomic STOs with orbital exponents which are rather close to the SZ values for the oxygen atom:

$$2a_1 \sim 2s,\quad 3a_1 \sim 2p_0,\quad 1b_1 \sim 2p_{-1}\ \text{and}\ 1b_2 \sim 2p_{+1}\ .$$

Similarly for the H_2S ground-state configuration

$$1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 1b_1^2\ 4a_1^2\ 2b_2^2\ 5a_1^2\ 2b_1^2\ ,\quad {}^1A_1$$

It can be seen from Moccia's calculation that the $1a_1$ and $2a_1$ orbitals display an almost perfectly spherical symmetry, while the $3a_1$, $1b_1$ and $1b_2$ appear to be quasi-degenerate and closely resemble the sulphur $2p_{x,y,z}$ atomic orbitals (SZ $\zeta = 5.99$, $\epsilon = -6.44$ a.u.). Thus, the H_2S ground-state configuration may be fairly well approximated by

$$[1s^2\ 2s^2\ 2p_{-1}^2\ 2p_0^2\ 2p_{+1}^2]\ 4a_1^2\ 2b_2^2\ 5a_1^2\ 2b_1^2\ ,\quad {}^1A_1$$

where 1s, 2s, 2p refer to the sulphur. Again, it is clear that $4a_1 \sim 3s$, $5a_1 \sim 3p_0$, $2b_1 \sim 2p_{+1}$, $2b_2 \sim 3p_{-1}$.

From the above analysis it appears reasonable to assume that if one takes the basis sets of Moccia as a starting point and replaces the core - MO's with atomic model potentials, the results should approach those of Moccia. In this work, this is the idea we set out to test. We started with Moccia's basis sets and geometry and tried to modify the valence basis in accordance with our model potential approximation, so as to improve the valence orbitals. We tried three types of basis set:

i) Moccia's basis without any change, including the core-like basis functions.

ii) A truncated Moccia basis in which core-like STOs have been removed from i).

iii) A modified Mocca basis in which core-like STOs are reintroduced, but now carry the DZ exponents coming from the model potential calibration.

2. Results

a. H_2O

The results for H_2O are collected in Tables 6.1 - 6.4. Table 6.1 shows the results of the three basis sets used, along side those from selected sources in the literature: [45, 85, 86]. Basis sets i) - iii) all give higher orbital energies for $2a_1$ than Moccia's with the truncated basis value highest. At the same time, the $1b_2$ orbital energies are lowered beyond that of Moccia. The $3a_1$ and $1b_1$ orbitals do not seem to be affected by the introduction of the model potential. It appears that if a good value of the $2a_1$ orbital energy is desired, core-like STO's must be included in the molecule. But the calculation is insensitive to whether these core-like functions are those of Moccia or those from the model potential calibration.

Now for comparison with results from more complete calculations and experiment. Although the geometries used are slightly different, our results appear within quite the acceptable regions. Notable is the recent pseudo-potential calculation of Barthelat et al, [86] in which a SZ basis is used on all the three atoms. Their pseudo-potentials are determined to DZ accuracy in the core and valence regions. The molecular calculation starts out with SZ STOs, then expands these in terms of three GTO's so as to simplify the multi-center molecular integrals. Aside from the $2a_1$ value, their orbital energies are further from those of more complete calculations than ours, probably due to the approximations in their integrals, or because of incompatibility between their valence basis

TABLE 6.1. H_2O Valence Orbital Energies

	This work OCE-MP STO Basis Sets i)	ii)	iii)	Mocciaa[a] OCE STO	Neumann[b] GTO "Near HF"	Barthelat[c] STO-MP SZ	Siegbahn[d] Exptal ESCA
R_{O-H}(a.u.)	1.8140	1.8140	1.8140	1.8140	1.80	1.8085	1.8132
HÔH(deg)	106.57	106.57	106.57	106.57	105	104.52	104.52
E_{tot}(a.u.)	-75.35[e]	-74.90	-75.35	-75.92	-76.06	-75.71	-76.481
εval.							
$2a_1^2$	-1.21	-1.02	-1.21	-1.33	-1.35	-1.27	-1.18
$3a_1^2$	-0.56	-0.56	-0.56	-0.56	-0.58	-0.45	-0.54
$1b_1^2$	-0.51	-0.55	-0.51	-0.50	-0.51	-0.39	-0.46
$1b_2^2$	-0.70	-0.74	-0.70	-0.68	-0.72	-0.62	-0.68

[a] Ref. 12.

[b] Ref. 85.

[c] Ref. 86.

[d] Ref. 45.

[e] For model potential calculation, E_{tot} is obtained from formulas (4-6) - (4-8).

TABLE 6.2. H_2O Valence Basis Set i)

#	STO (nlm)	Exponents	$2a_1^2$	$3a_1^2$	$1b_1^2$	$1b_2^2$
1	1s	12.60	0.0428	-0.0180		
2	1s	7.45	-0.1918	0.0735		
3	2s	2.20	0.8986	-0.3574		
4	2s	3.24	-0.0960	0.0169		
5	2s	1.28	0.1942	0.0773		
6	$2p_0$	1.51	0.2366	0.7461		
7	$2p_0$	2.44	-0.0050	0.0914		
8	$2p_0$	3.92	0.0310	0.1915		
9	$3d_0$	1.60	0.0097	0.0603		
10	$3d_0$	2.40	0.0027	0.0041		
11	$3d_2$	1.60	0.0797	0.0756		
12	$3d_2$	2.40	0.0073	-0.0126		
13	$4f_0$	1.95	-0.0303	-0.0150		
14	$4f_2$	1.95	0.0659	0.0575		
15	$2p_{-1}$	1.51			-0.6913	
16	$2p_{-1}$	2.44			-0.1884	
17	$2p_{-1}$	3.92			-0.1940	
18	$3d_{-1}$	1.60			-0.0561	
19	$3d_{-1}$	2.40			-0.0041	
20	$4f_{-1}$	1.95			-0.0094	
21	$4f_{-3}$	1.95			-0.0270	
22	$2p_1$	1.51				-0.8532
23	$2p_1$	2.44				0.0050
24	$2p_1$	3.92				-0.1862
25	$3d_1$	1.60				-0.2518
26	$3d_1$	2.40				0.0165
27	$4f_1$	1.95				-0.0454
28	$4f_3$	1.95				-0.0637
Orbital Energy (a.u.)			-1.2101	-0.5560	-0.5061	-0.6979

TABLE 6.3. H_2O Valence Basis Set ii)

#	STO (nlm)	Exponents	$2a_1^2$	$3a_1^2$	$1b_1^2$	$1b_2^2$
1	2s	2.20	-1.2856	0.6791		
2	2s	3.24	0.6224	-0.3143		
3	2s	1.28	-0.1459	0.0066		
4	$2p_0$	1.51	-0.3725	-0.6214		
5	$2p_0$	2.44	0.0023	-0.1733		
6	$2p_0$	3.92	-0.0659	-0.1799		
7	$3d_0$	1.60	-0.0182	-0.0575		
8	$3d_0$	2.40	-0.0037	-0.0039		
9	$3d_2$	1.60	-0.1122	-0.0265		
10	$3d_2$	2.40	-0.0009	0.0031		
11	$4f_0$	1.95	0.0377	0.0029		
12	$4f_2$	1.95	-0.0849	-0.0314		
13	$2p_{-1}$	1.51			-0.6469	
14	$2p_{-1}$	2.44			-0.2321	
15	$2p_{-1}$	3.92			-0.1953	
16	$3d_{-1}$	1.60			-0.0543	
17	$3d_{-1}$	2.40			-0.0045	
18	$4f_{-1}$	1.95			-0.0091	
19	$4f_{-3}$	1.95			-0.0259	
20	$2p_1$	1.51				-0.8174
21	$2p_1$	2.44				-0.0354
22	$2p_1$	3.92				-0.1864
23	$3d_1$	1.60				-0.2387
24	$3d_1$	2.40				0.0114
25	$4f_1$	1.95				-0.0437
26	$4f_3$	1.95				-0.0617
Orbital Energy (a.u.)			-1.0222	-0.5608	-0.5512	-0.7371

TABLE 6.4 H_2O Valence Basis Set iii)

#	STO (nlm)	Exponents	$2a_1^2$	$3a_1^2$	$1b_1^2$	$1b_2^2$
1	1s	9.47	-0.0965	-0.0467		
2	1s	6.84	-0.2714	0.1148		
3	2s	2.69	0.3509	-0.2244		
4	2s	1.68	0.6766	-0.0684		
5	$2p_0$	1.51	0.2380	0.7426		
6	$2p_0$	2.44	-0.0059	0.0970		
7	$2p_0$	3.92	0.0316	0.1903		
8	$3d_0$	1.60	0.0098	0.0604		
9	$3d_0$	2.40	0.0027	0.0040		
10	$3d_2$	1.60	0.0805	0.0733		
11	$3d_2$	2.40	0.0068	-0.0112		
12	$4f_0$	1.95	-0.0304	-0.0149		
13	$4f_2$	1.95	0.0660	0.0571		
14	$2p_{-1}$	1.51			-0.6919	
15	$2p_{-1}$	2.44			-0.1878	
16	$2p_{-1}$	3.92			-0.1940	
17	$3d_{-1}$	1.60			-0.0564	
18	$3d_{-1}$	2.40			-0.0038	
19	$4f_{-1}$	1.95			-0.0094	
20	$4f_{-3}$	1.95			-0.0271	
21	$2p_{+1}$	1.51				-0.8536
22	$2p_{+1}$	2.44				0.0053
23	$2p_{+1}$	3.92				-0.1862
24	$3d_{+1}$	1.60				-0.2518
25	$3d_{+1}$	2.40				0.0166
26	$4f_{+1}$	1.95				-0.0454
27	$4f_{+3}$	1.95				-0.0637
Orbital Energy (a.u.)			-1.2134	-0.5589	-0.5085	-0.7002

sets and calibrated atomic pseudo-potentials.

Tables 6.2 - 6.4 give the details of the three basis sets. The expansion coefficients of the three highest orbitals are very similar, suggesting that the profiles of these valence molecular orbitals do not change much as the basis sets are changed, although we have not drawn the profiles to compare more conclusively.

b. H_2S

The results for H_2S are collected in Tables 6.5 - 6.6. Table 6.5 compares the results of the three basis sets with results from selected literature sources [45, 86, 87]. The trends in the valence orbitals are rather similar to those found in H_2O. The $4a_1$ orbital is raised by the introduction of the model potential. Truncation raises $4a_1$ further, while deepening the rest of the orbitals. Using Moccia's core-like basis functions (1s, 2s, 2p) gives virtually the same result as using the DZ ones from model potential calibration, although we found that including the DZ 3s - STO lowered the $4a_1$ orbital appreciably (Table 6.6).

In comparison with other calculations, our OCE-MP results are in the accepted ranges. But it must be emphasised that our calculations are tied to those of Moccia, and carry with them any flaws inherent in the latter. For example, Moccia notes that because of limitations in his program, he was forced to use the same size of basis set for both H_2O and H_2S, although H_2S has eight more electrons. In a variational optimisation, most of the terms will tend to be pulled into the description of the deep-lying core, leaving the valence region relatively starved. This meant that the valence orbitals

TABLE 6.5. H_2S Valence orbital energies

	This work OCE-MP STO Basis Sets			Moccia[a] OCE STO	Rothenberg[b] GTO "Near HF"	Barthelat[c] STO-MP	Siegbahn[d] Exptal ESCA
	i)	ii)	iii)				
R_{S-H}(a.u.)	2.5090	2.5090	2.5090	2.5090	2.5096	2.5096	2.5096
$H\hat{S}H$(deg)	89.4	89.4	89.4	89.4	92.2	92.2	92.2
E_{tot}(a.u.)	-397.79[e]	-397.19[e]	-397.92[e]	-397.59	-398.69	-398.60[e]	-400.81
ε val.							
$4a_1^2$	-0.90	-0.85	-0.93	-0.94	-0.99	-0.97	-0.81
$5a_1^2$	-0.46	-0.47	-0.45	-0.45	-0.50	-0.45	-0.49
$2b_1^2$	-0.35	-0.38	-0.34	-0.35	-0.38	-0.35	-0.38
$2b_1^2$	-0.55	-0.59	-0.54	-0.53	-0.59	-0.56	-0.55

[a] Ref. 12.c.

[b] Ref. 87.

[c] Ref. 86.

[d] Ref. 45.

[e] See footnote e, Table 6.1

TABLE 6.6. H_2S Valence Basis Set III)

#	STO (nlm)	Exponents	$2a_1^2$	$3a_1^2$	$1b_1^2$	$1b_2^2$
1	1s	17.08	-0.0899	-0.0340		
2	1s	12.69	0.1334	0.0504		
3	2s	6.73	-0.0604	0.0020		
4	2s	5.24	-0.1110	-0.0820		
5	3s	2.66	0.1283	0.1256		
6	3s	1.69	0.9923	0.3433		
7	4s	1.57	-0.1370	-0.1895		
8	$3d_0$	1.40	0.0538	-0.0719		
9	$4d_0$	1.40	0.0050	-0.0446		
10	$3d_2$	1.40	0.0893	-0.0782		
11	$4d_2$	1.40	0.0034	-0.0501		
12	$2p_0$	9.51	0.0037	-0.0122		
13	$2p_0$	5.12	-0.0246	0.0928		
14	$3p_0$	1.56	0.2254	-0.9328		
15	$4p_0$	1.56	0.0324	-0.0164		
16	$4f_0$	1.25	-0.0191	0.0061		
17	$4f_2$	1.25	0.0825	-0.1030		
18	$3d_{-1}$	1.40			-0.0359	
19	$4d_{-1}$	1.40			-0.0267	
20	$2p_{-1}$	9.51			-0.0136	
21	$2p_{-1}$	5.12			0.1038	
22	$3p_{-1}$	1.56			-1.0813	
23	$4p_{-1}$	1.56			0.0740	
24	$4f_{-1}$	1.25			-0.0243	
25	$4f_{-3}$	1.25			-0.0350	
26	$3d_1$	1.40				-0.2874
27	$4d_1$	1.40				-0.1237
28	$2p_1$	9.51				-0.0118
29	$2p_1$	5.12				0.0879
30	$3p_1$	1.56				-0.8635
31	$4p_1$	1.56				-0.0518
32	$4f_1$	1.25				-0.1407
33	$4f_3$	1.25				-0.0734
Orbital Energy (a.u.)			-0.9280	-0.4527	-0.3412	-0.5375

of H_2S would be inherently poorer than those of H_2O. This feature remains in our calculation.

However, in the use of model potentials, an interesting situation arises. The molecular valence regions of both H_2O and H_2S contain the same number of electrons, and so the use of equal basis sets would be justified. But these basis sets would have to be optimised anew in presence of the model potentials.

C. Heavy Off-Center Nuclei: N_2 Molecule

1. Basis Set Build-Up

The nitrogen molecule represents our first true test of the OCE-MP method, since it has heavy, non-hydrogen off-center nuclei. In such a molecule, where the off-center nuclei cannot be said to be a small perturbation on some central problem, a starting basis set is not as immediately obvious as in the central hydrides. Indeed this can be considered the case in even such a relatively simple molecule as H_2.

The electrons in a diatomic feel a potential which is deformed considerably from spherical symmetry along the molecular axis, and this is reflected in the shapes of the molecular orbitals. The challenge is to determine, from scratch, a combination of basis functions which interfere in the proper manner to reproduce the features of the MOs. In understanding this problem, the MO diagrams of Streitwieser and Owens [63] were helpful. For example, the $1\sigma_g$ MO of H_2 exhibits the contours of a sphere, perhaps slightly squashed into an ellipsoid, but with small peaks at the nuclear positions (see Figure 6.1). This may be well simulated by a combination of an s-STO and a dσ-STO which eats out part of the s and enhances the peaks at the nuclear positions. Indeed, in his one-center calculation on H_2 molecule, Huzinaga [88] obtained in STO-approximation for this orbital as

$$1\sigma_g = 0.6614319 \{(1s;\ 1.0) + 0.5126091\ (4s;\ 3.0) + 0.2707095\ (4d\sigma;\ 3.0)\}\ .$$

The numbers after the semi-colons are the orbital exponents, and together with the quantum number n they express the peaking properties of the STO radial functions. Note that a 1s STO is necessary to produce a non-zero charge distribution at the mid-point, since all other STOs vanish at the origin. Indeed from the coefficients, the 1s is the dominant component in the MO.

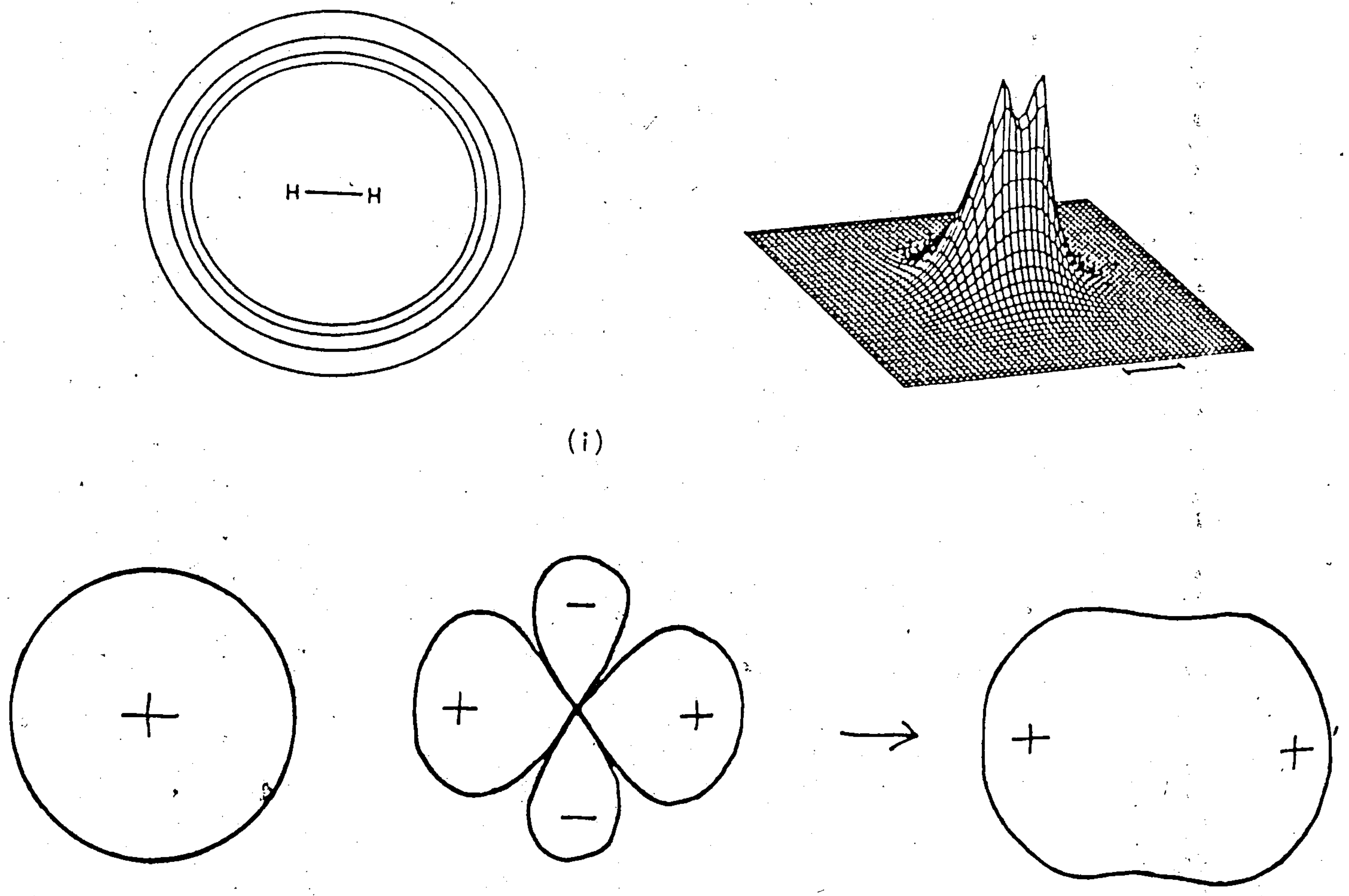
The situation in larger molecules is more complicated. There are several orbitals, with more detailed structure. These must be shaped up at the same time, keeping the basis sets sufficiently flexible and balanced in order to produce the proper total molecular picture. Inflexible or inadequate basis sets can result in wrong ordering of orbitals due to the artificial dominance of one orbital over the others.

The N_2 ground-state configuration

$$[1\sigma_g^2\ 1\sigma_u^2]2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_{u,x,y}^4\ , \qquad {}^1\Sigma_g^+$$

may be approximated by

$$[1s_a^2\ 1s_b^2]\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_{u,x,y}^4\ , \qquad {}^1\Sigma_g^+\ .$$



(i)

(ii)

FIG. 6.1. (i) Schematic of H_2 $1\sigma_g$ MO^a and
(ii) its OCE approximation.

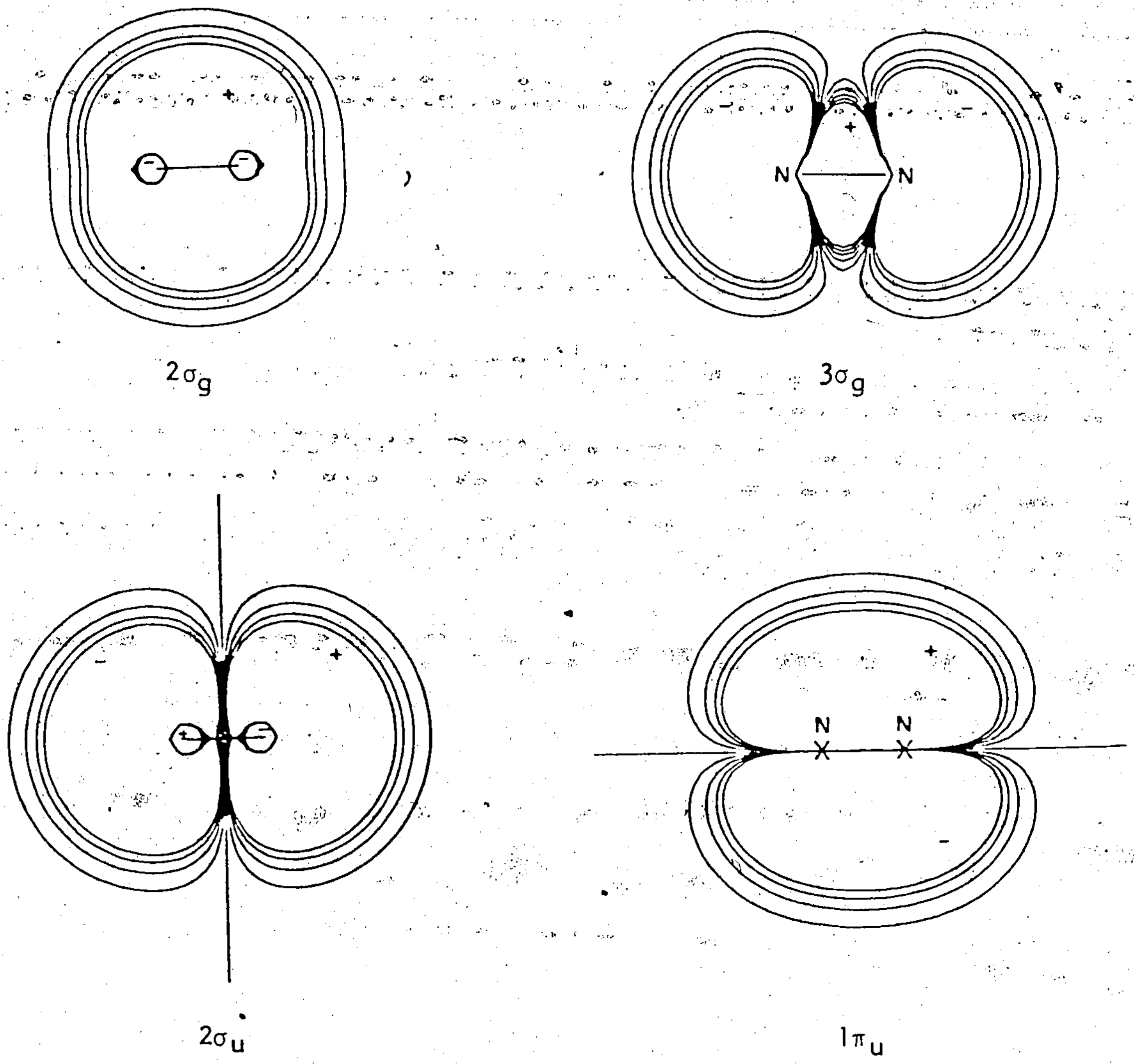
^{a}From ref. 63.

The core ls orbitals are replaced by model potentials and the valence MOs simulated by OCE basis functions. Let us examine the shapes of MOs to be simulated. Again from Streitwieser and Owens we reproduce the diagrams (Figures 6.2).

It may be seen that apart from the sharp negative peaks at the nuclear positions, $2\sigma_g$ is positive and almost spherically symmetric about the mid-point. The $2\sigma_u$ looks like a p_z orbital, aside from the opposite sign spikes at the nuclei. $3\sigma_g$ vaguely resembles a $d\sigma$ orbital and $2\sigma_u$ resembles a p_x or p_y orbital at the mid-point. Of course, the model potential is expected to remove the sharp peaks and then OCE functions should easily simulate the diffuse parts of the MOs. Clearly, the ideas of Huzinaga [88] could be applied here.

The N_2 basis set was developed for one inter-nuclear separation, the often-quoted experimental distance of $R = 2.068$ a.u. The way our program was set up allowed us to develop a basis set which is simplified considerably from that dictated by group theory for the C_{2v} symmetry: The basis functions for σ_g symmetry carry even ℓ, $m = 0$; for σ_u, it is odd ℓ, $m = 0$; for $1\pi_{ux}$, odd ℓ, $m = -1$; and for $1\pi_{uy}$, odd ℓ, $m = +1$.

After many abortive attempts, we started out with a skeleton basis set of nine STOs up to $\ell = 2$: one 1s (1.0), one 2s (1.0) and one $3d_0$ (2.0) for σ_g symmetry; one $2p_0$ (1.0) and one $3p_0$ (1.0) for σ_u symmetry; two $2p_{\underline{+}1}$ (1.5, 1.0) for the $1\pi_u$ symmetries. The exponents (in brackets) were chosen so as to make the STOs have radial peaks in predetermined regions. This is easily done by differentiation of the radial part



$2\sigma_g$ $3\sigma_g$

$2\sigma_u$ $1\pi_u$

Contours at 0.0, 0.004, 0.008, 0.012 and 0.016

FIG. 6.2 Contour diagrams of N_2 valence MOs, from ref. 63.

$$R_{n\ell}(r) = r^{n-1}\, e^{-\zeta r} \qquad (6\text{-}1)$$

which has a maximum when

$$\zeta = \frac{n-1}{r} \;. \qquad (6\text{-}2)$$

This does not apply to a 1s STO. Alternatively one can use the radial distribution function

$$r^2 R_{n\ell}^2(r) = r^{2n}\, e^{-2\zeta r} \;. \qquad (6\text{-}3)$$

This has a maximum when

$$\zeta = \frac{n}{r} \;. \qquad (6\text{-}4)$$

It seems then that the relation

$$\zeta = \frac{n-\delta}{r} , \quad 0 \le \delta \le 1 \qquad (6\text{-}5)$$

is a good way of guessing the region of effectiveness of an STO, or, conversely, of tailoring an exponent to cover a required region.

The electronic energy E_v of this early basis was high (-26.2 a.u. compared to -31.6 a.u. as estimated by Formula (4-6)), and the orbital energies were horrible, ordered wrongly with $1\pi_u$ too deep. But the salient features were there. The orbital exponents were then optimised by hand, one by one, to try and lower the energy and improve the ordering. Not much could be done with such a starved basis set, and the picture did not change much after a lot of adjustment.

The basis set was then fleshed out by adding one or two functions at a time. At each stage the exponent of the new function was changed a few times manually and not too assiduously. The ℓ quantum numbers were generally kept small and the n values were also kept close to the smallest value allowed for each ℓ $(n = \ell+1)$, in order to keep some arrays in the integral routines small. Thus our basis set has only one function for each symmetry for which $\ell \geq 4$, and $\ell = 5$ is the largest value.

Graphical checking of MO profiles was performed at various stages, to compare values along the internuclear axis with those calculated from the results of Ransil [64] and McWilliams and Huzinaga, [65] in order to get an idea about which regions needed more attention.

In this manner a final basis set was arrived at, comprising nine σ_g, nine σ_u, eight π_{ux} and eight π_{uy} basis functions. It took numerous attempts, many of them futile, because the interaction of several STOs is too intricate to guess beforehand. Besides, we came up against a serious redundancy problem, which is discussed in Section 3, after the results are presented.

2. Results and Discussion

a. Valence Orbital Energies

Our best results for the N_2 molecule are given in Tables 6.7 - 6.8 and Figures 6.3 - 6.8. Table 6.7 and Figure 6.3 show our results in comparison with those from ESCA measurements [45] and more complete calculations [65, 89]. Our total energy is about 2.5 a.u. higher than the rest, but it still represents a respectable 97.6% of HF energy. The orbital energies are found in quite the acceptable ranges.

TABLE 6.7. N_2 Valence Orbital Energies

	EXPT. (ESCA) Siegbahn[a]	NEAR-HF (STO) Cade[b]	OCE-MP ~~(STO)~~ This Work	4-31G (GTO-MP) McWilliams[c]	MINIM. (STO) Ransil[d]
R (a.u.)		2.068	2.068	2.068	2.068
Tot. Energy		-108.99	-106.4	-108.86	-108.63
$2\sigma_g^2$	-1.37	-1.47	-1.46	-1.52	-1.42
$2\sigma_u^2$	-0.68	-0.77	-0.72	-0.77	-0.71
$3\sigma_g^2$	-0.57	-0.63	-0.67	-0.63	-0.56
$1\pi_{ux,y}^4$	-0.62	-0.61	-0.65	-0.62	-0.54

[a] Ref. 45

[b] Ref. 89

[c] Ref. 65

[d] Ref. 64

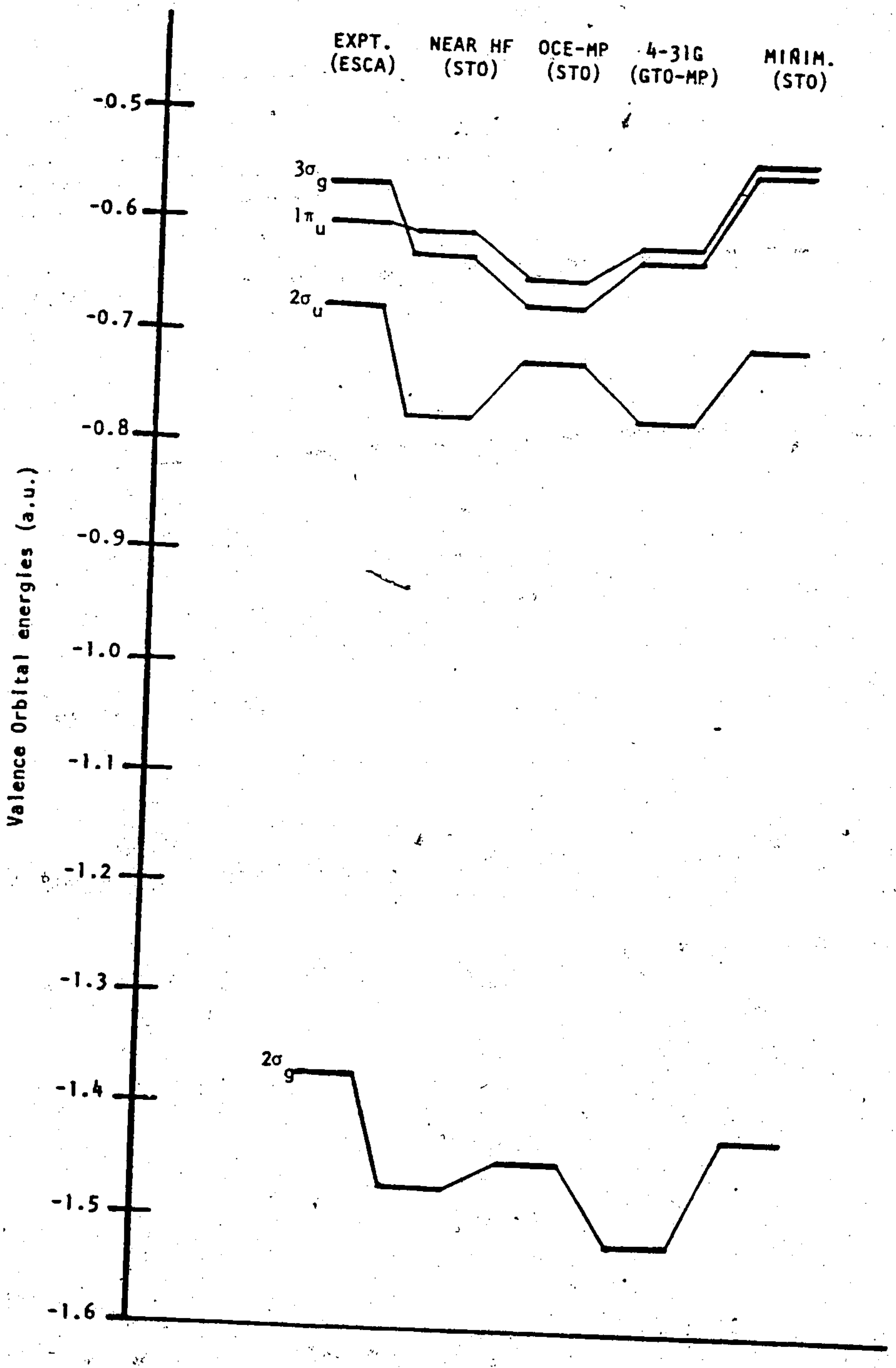


FIG. 6.3 N_2 Valence orbital energies

Our highest orbitals are slightly deeper than the rest, but their ordering is parallel to that in all the other calculations, including the near - HF result. N_2 is one of those cases in which the HF ordering of outer orbitals is the reverse of the experimental ordering, as we saw in Chapter 2. Comparison with the calculation of McWilliams and Huzinaga [65] is interesting. These workers have incorporated a GTO-screened Bonifacic-Huzinaga model potential into a two-center calculation with an adapted Pople 4-31G basis set. Their $2\sigma_g$ orbital is the deepest in the set, while the other orbitals are close to Hartree-Fock. On the other hand our $2\sigma_g$ orbital is closer to the HF value, while the outer orbitals are deeper. There seems to be a trade-off when electrons correlate themselves among energy levels, and it can go either way.

b. Composition of Valence Orbitals

Table 6.8 shows ~~the OCE-MP~~ basis set and the expansion coefficients for the valence MOs. First, it may be noted that the exponents of STOs with the same ℓ but belonging to different symmetries are not kept equal as Moccia did, except in the π_u symmetries which are known to be degenerate. This enhances the flexibility of the basis. Of course, the reason Moccia fixed them as equal was so that, for example, degeneracy of the π_z-like orbital with a π_x would appear naturally when a C_{2v} molecule was straightened into $D_{\infty h}$ form. Secondly since we used a C_{2v} program, the σ_g and σ_u symmetries of $D_{\infty h}$ had to be treated as one, namely A_1. This represents a limitation on the number of basis functions that could be added to each symmetry, since the matrices became very large.

TABLE 6.8: N_2 Valence Basis Set

#	STO (nlm)	Exponents Z	$2\sigma_g^2$	$3\sigma_g^2$	$2\sigma_u^2$	$1\pi_{ux}^2$	$1\pi_{uy}^2$
1	1s	2.0	-0.4112	-0.1972			
2	2s	2.0	-0.3267	0.4992			
3	$3d_0$	7.6	0.0348	0.0754			
4	3s	1.1	-0.0222	0.6170			
5	$3d_0$	2.2	0.1293	1.2593			
6	4s	6.0	-0.2233	-0.3936			
7	$4d_0$	6.0	-0.1473	-0.3670			
8	$6d_0$	5.0	0.2676	-0.7080			
9	$5g_0$	3.0	0.1965	0.0280			
10	$2p_0$	1.3			-0.0398		
11	$3p_0$	1.3			0.3031		
12	$4p_0$	3.9			-0.4095		
13	$4f_0$	2.6			0.1488		
14	$4p_0$	2.6			1.2003		
15	$6p_0$	5.2			-0.2529		
16	$6f_0$	3.9			0.3104		
17	$6f_0$	5.2			-0.3762		
18	$6h_0$	5.2			-0.0522		
19	$2p_{+1}$	0.5				-0.0360	
20	$3p_{+1}$	1.0				-0.1416	
21	$4f_{+1}$	1.0				-0.1987	
22	$4p_{+1}$	2.0				-0.1810	
23	$4f_{+1}$	2.0				-0.5815	
24	$6p_{+1}$	4.0				-0.6630	
25	$6f_{+1}$	2.0				0.4809	
26	$6h_{+1}$	5.0				-0.0642	
27	$2p_{-1}$	0.5					-0.0360
28	$3p_{-1}$	1.0					-0.1416
29	$4f_{-1}$	1.0					-0.1987
30	$4p_{-1}$	2.0					-0.1810
31	$4f_{-1}$	2.0					-0.5815
32	$6p_{-1}$	4.0					-0.6630
33	$6f_{-1}$	2.0					0.4809
34	$6h_{-1}$	5.0					-0.0642
Orbital energies:			-1.4588	-0.6670	-0.7180	-0.6507	-0.6507

The largest coefficients in the $2\sigma_g$ orbital belong to the 1s (2.0), 2s (2.0) and $6d_0$ (5.0) STOs, with 4s (6.0) a close fourth. The numbers in brackets are orbital exponents. The dominance of one STO is more pronounced in $3\sigma_g$ and $2\sigma_u$. $3\sigma_g$ is dominated by $3d_0$ (2.2), followed by $6d_0$ (5.0) STO; $2\sigma_g$ is mostly $4p_0$ (2.6). $1\pi_u$ is mainly dominated by a $6p_{\pm 1}$ (4.0), $4f_{\pm 1}$ (2.0) and $6f_{\pm 1}$ (2.0) STOs.

These compositions show striking resemblances to those based on the concept of the "semi-united atom", as discussed by Huzinaga [90] and Mulliken. [91]. These practitioners noticed that the nature and arrangement of the outer electronic energy levels of N_2 resemble those of the Mg atom ($Z = 12$) instead of the united atom Si ($Z = 14$), and sought a correspondence between the 10 electrons in the N_2 valence configuration $2\sigma_g^2$ $2\sigma_u^2$ $1\pi_u^4$ $3\sigma_g^2$ with those in the Mg configuration $2s^2$ $2p^6$ $3s^2$ or $3d^2$. Huzinaga [90] carried out numerical calculations to test this correlation. He prepared a set of atomic orbitals $1s_c$, $2s_c$, $2p\pi_c$, $3s_c$, $3d\sigma_c$, etc., with adjustable exponents ζ_c, of a hypothetical atom seated at the midpoint of the N_2 molecule. He calculated overlap integrals between these STOs and the two-center MOs of Ransil as functions of ζ_c. He found overlaps approaching unity for the pairs ($2\sigma_g$, $1s_c$; 1.2), ($2\sigma_g$, $3s_c$; 2.0), ($2\sigma_u$, $2p\sigma_c$; 1.1), ($2\sigma_u$, $3p\sigma_c$; 1.8), ($2\sigma_g$, $3d\sigma_c$; 1.7), ($3\sigma_g$, $2s_c$; 0.8) and ($1\pi_u$, $2p\pi_c$; 1.0). The numbers after the semi-colons are the orbital exponents of the STOs as estimated by us from his graphs. It turns out that they are actually not all that close to the SZ exponents of Mg ($\zeta_{1s} = 11.6$, $\zeta_{2s} = 3.7$ and $\zeta_{3s} = 1.1$). Nevertheless the hint was strong [91] that the valence MOs of N_2, may be well approximated by united-atom STOs with suitably adjusted ζ values: $2\sigma_g$ by $1s_c$ or $2s_c$ with some admixture of $3d\sigma_c$; $2\sigma_u$ by $2p\sigma_c$; $1\pi_u$ by $2p\pi_c$; and $3\sigma_g$ by $3d\sigma_c$ with some admixture of $2s_c$.

Our calculation may be considered to represent the first variational test, although unintended and therefore loose, of the concept of the semi-united atom. The compositions Huzinaga postulated for the N_2 orbitals are less detailed than those obtained here, but they certainly reveal the salient features.

c. MO Profiles Along Bond Axis

Table 6.9 and Figures 6.4 - 6.6 show the profiles (values in atomic units), of our σ MOs along the interOnuclear axis, in comparison with values calculated from Ransil [64] and from McWilliams and Huzinaga [65]. In the figures, the nuclear positions are at RA = 0 a.u. and RA = 2.068 a.u., but only one-half of the picture is drawn, the other half being a mirror image or an inversion through the mid-point. The OCE-MP origin is at the molecular mid-point, quite close to the origin for the graphs (RA = 1.0 a.u.).

Figure 6.6 shows the $2\sigma_g$ profiles. In the bonding region, the OCE-MP (⊡) and GTO-MP(x) start out lower than the min- 0(▲). There is a kink at the mid-point for OCE-MP, no doubt arising from the 1s-STO contribution. A small local maximum occurs near here too, as if the basis is struggling to shape a flat curve, which indeed it is. Both OCE-MP and GTO-MP then rise and cross the bond axis extremely close to the nuclear position, whereas the min-STO crosses earlier and has a high maximum here. After that OCE-MP and GTO-MP go through a maximum, but unlike GTO-MP, OCE-MP does not recover quickly enough to mimic the

TABLE 6.9 N_2 Behaviour of σ orbitals along internuclear axis

	$2\sigma_g$			$3\sigma_g$			$2\sigma_u$		
r	OCE-MP	min-STO[a]	GTO-MP[b]	OCE-MP	min-STO[a]	GTO-MP[b]	OCE-MP	min-STO[a]	GTO-MP[b]
1.0	-0.6604	-0.4270	-0.4773	0.3056	0.3056	0.3060	-0.019	0.0038	0.0040
1.1	-0.5891	-0.4267	-0.4778	0.2073	0.3057	0.3071	0.0030	-0.0072	-0.0077
1.2	-0.5370	-0.4248	-0.4810	0.1621	0.3063	0.3143	0.0138	-0.0173	-0.0184
1.4	-0.5651	-0.4075	-0.4873	0.3191	0.3086	0.3378	0.0806	-0.0260	-0.0318
1.6	-0.4474	-0.3321	-0.4652	0.3387	0.3122	0.3569	0.1682	0.0117	0.0212
1.8	-0.2198	-0.5803	-0.3355	0.2067	0.3360	0.3493	0.1830	0.2112	0.0570
1.9	-0.1118	0.2740	-0.1971	0.1232	0.3826	0.2788	0.1517	0.4765	-0.1002
2.0	-0.0224	0.8915	-0.0311	0.0418	0.4958	0.1202	0.0998	0.9925	0.0942
2.1	0.0453	1.2752	0.1031	-0.0322	0.4536	-0.1010	0.0352	1.2296	0.0139
2.2	0.0921	0.6224	0.1555	-0.0962	0.2822	-0.3074	-0.0338	0.4550	-0.1165
2.4	0.1354	0.1219	0.0754	-0.1900	-0.3456	-0.4879	-0.1585	-0.1795	-0.3287
2.5	0.1392	0.0381	0.2954	-0.2203	-0.4121	-0.4932	-0.2058	-0.2900	-0.3697
2.6	0.1359	-0.0026	0.0035	-0.2405	-0.4378	-0.4792	-0.2407	-0.3391	-0.3797
2.8	0.1174	-0.0286	-0.0183	-0.2557	-0.4230	-0.4229	-0.2745	-0.3475	-0.3524
3.0	0.0936	-0.0294	-0.0266	-0.2462	-0.3691	-0.3493	-0.2702	-0.3074	-0.2999
3.2	0.0712	-0.0247	-0.0251	-0.2220	-0.3052	-0.2811	-0.2431	-0.2549	-0.2437
3.6	0.0380	-0.0147	-0.0143	-0.1603	-0.1902	-0.1764	-0.1671	-0.1589	-0.1497
4.0	0.0189	-0.0082	-0.0100	-0.1062	-0.1102	-0.1053	-0.1021	-0.0920	-0.0881
4.4	0.0088	-0.0044	-0.0078	-0.0683	-0.0611	-0.0631	-0.0594	-0.0509	-0.0522
4.8	0.0038	-0.0023	-0.0051	-0.0440	-0.0328	-0.0388	-0.0343	-0.0274	-0.0312

[a] Calculated by present author from reference [64]

[b] Calculated by present author from reference [65]

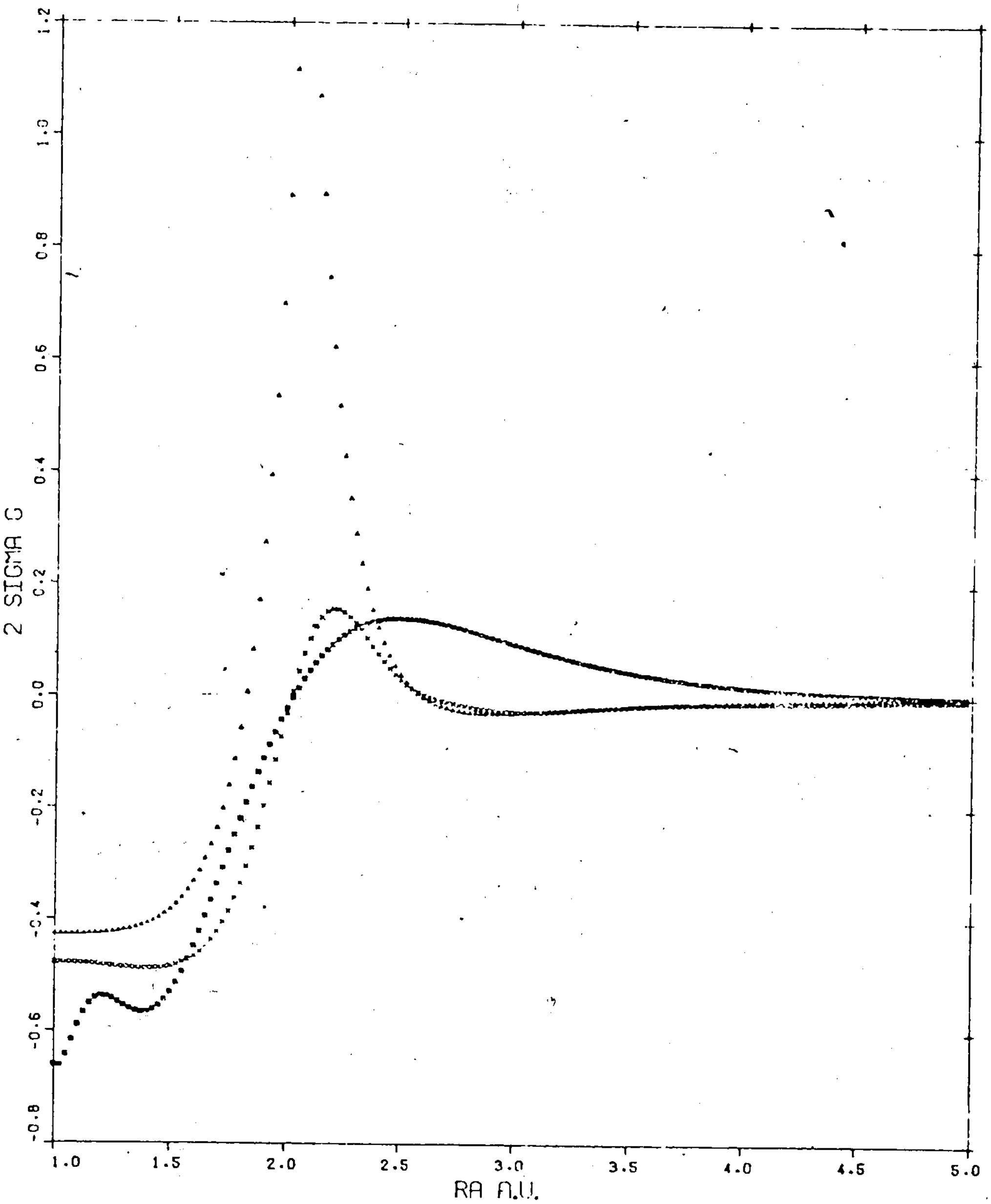


Fig. 6.4 N_2 MO PROFILES ALONG INTERNUCLEAR AXIS: $2\sigma_g$

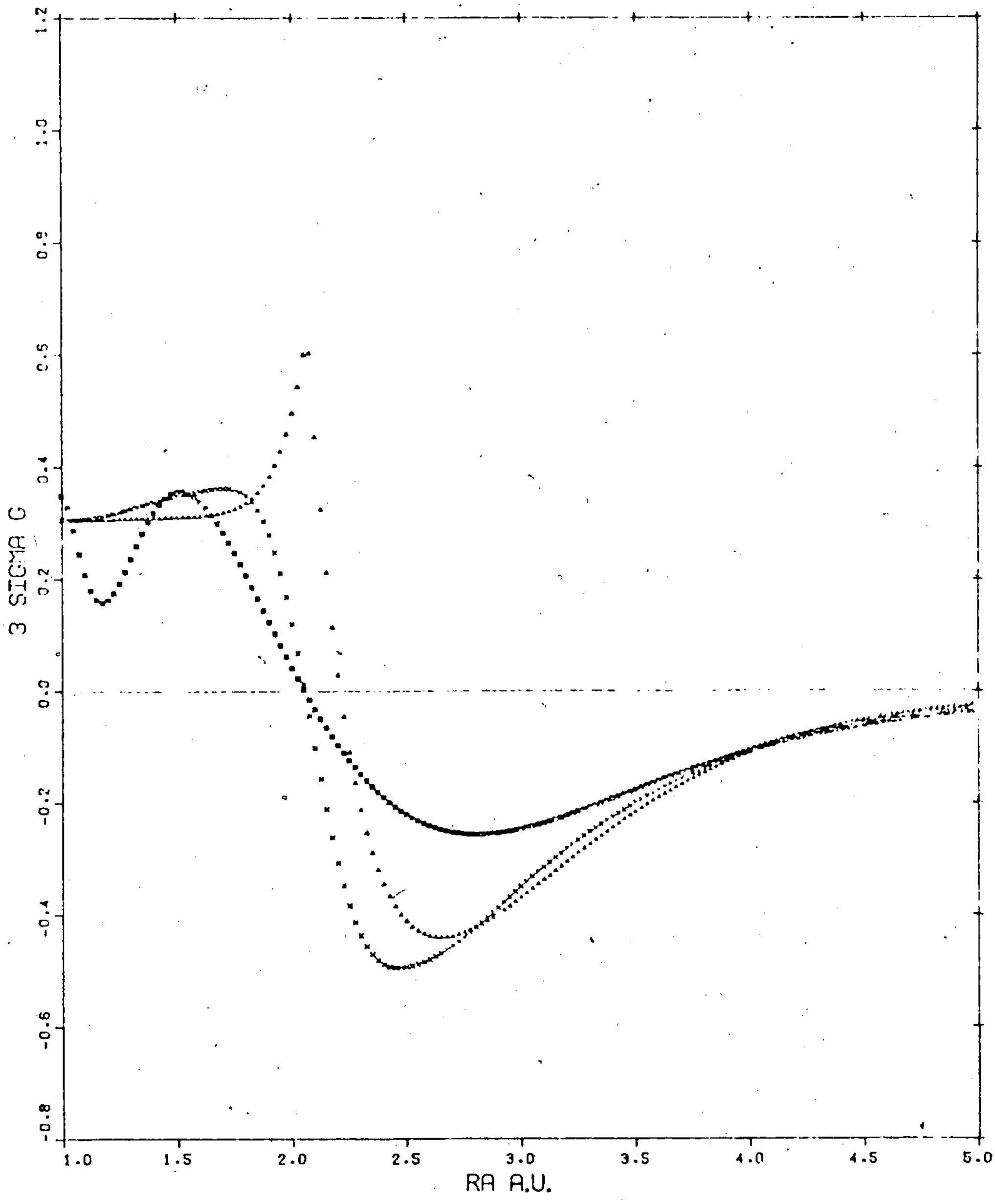


Fig. 6.5 N_2 MO PROFILES ALONG INTERNUCLEAR AXIS: $3\sigma_g$

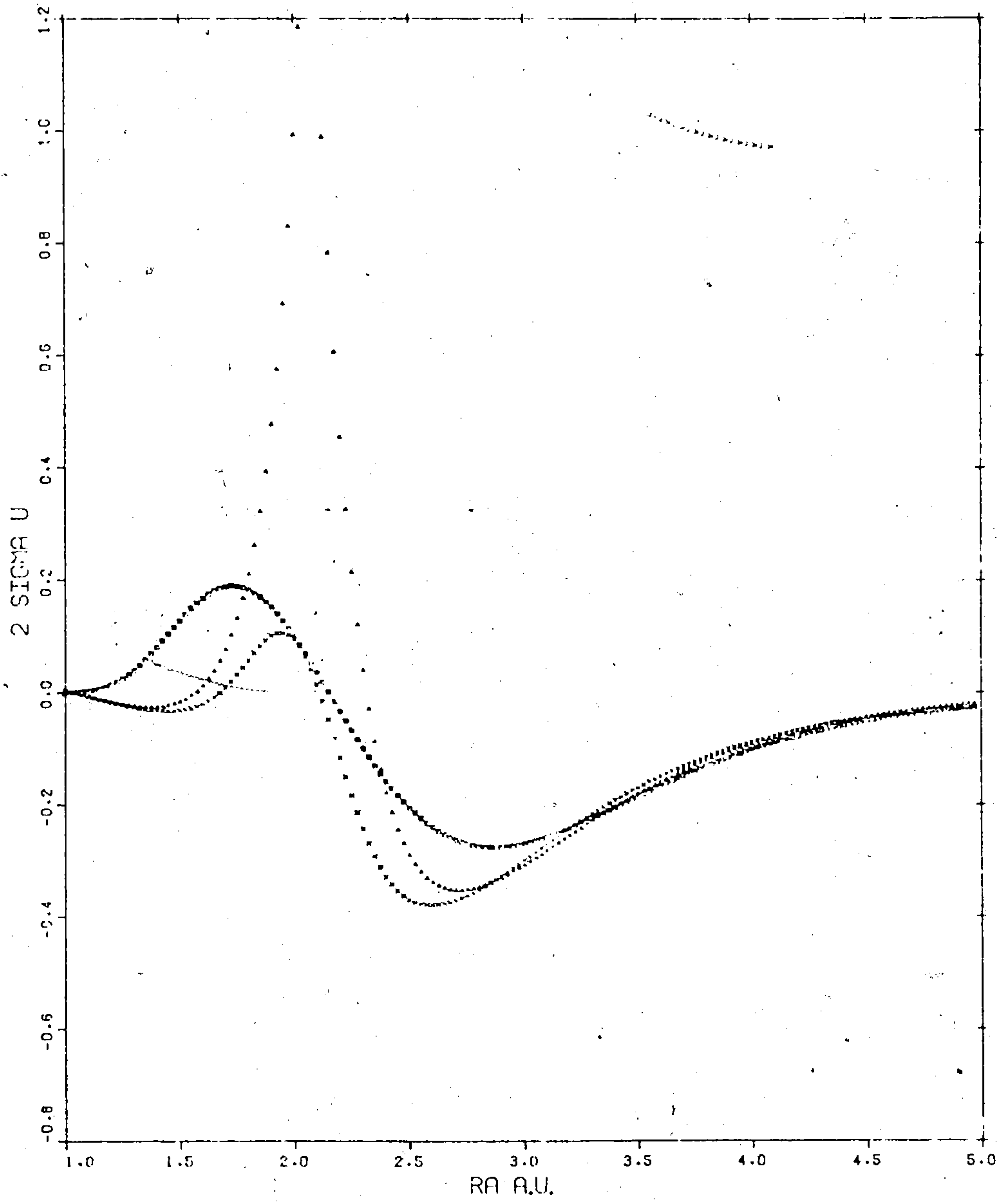


Fig. 6.6. N_2 MO PROFILES ALONG INTERNUCLEAR AXIS: $2\sigma_u$

min-STO MO closely in the outer region.

The profile of the $3\sigma_g$ orbital (Figure 6.5) is similar to that of $2\sigma_g$. Oscillations occur in the OCE-MP in the bonding region as it adjusts to maintain orthogonality to $2\sigma_g$. But all three MOs are otherwise quite close in this region. Again both OCE-MP and GTO-MP plunge to pass very close to the nuclear position, while min-STO goes to a maximum before plunging. The GTO-MP result then recovers to parallel the min-STO better than OCE-MP in the outer region.

Finally the $2\sigma_u$ (Figure 6.6) shows similar trends. The GTO-MP is able to closely mimic the min-STO in the inner region, then break off sharply to pass through the nuclear positions, meeting the min-STO again in the outer region. The OCE-MP does not seem capable of performing such intricate turns, but gets ready right from the start to cross at the nuclear positions and meet the others in the outer region.

One interesting feature stands out in the two model potential calculations, and that is the apparent desire of all σ orbitals to cross the axis close to the nuclear positions at all costs. We attempt to explain this feature. We believe it is dicated by the model potential seated at the nuclear position, and especially by the repulsive projection operator term $B\,|1s\rangle\langle 1s|$. This is a spherically symmetric term, which may be imagined as a tight circle at the nuclear position. Each σ orbital must minimise its overlap with this $|1s\rangle$ orbital, so as to minimise this repulsive term. The most favourable and simplest way is to cut across the circle, the negative overlap cancelling the positive out. More complicated crossings can be imagined which also minimise this overlap, but they all call for a flexibility which apparently neither OCE-MP nor GTO-MP basis sets are blessed with.

Related to this feature is the question of orbital energy. One may wonder how such apparently different functions as the min-STO and the model potential MOs can have comparable energies, seeing especially their behaviour at the nucleus, where the potential is strongest. The phenomenon is well-known in solid state physics and is based on cancellation of potential and kinetic energy terms. Here is an adaptation of its explanation, in the $2\sigma_g$ case [90]. The electron in the min-STO $2\sigma_g$, orbital may feel favourably the strong attractive nuclear field in the vicinity of the nucleus. But this negative potential energy is liable to be cancelled by the positive kinetic energy resulting from the rapid variations in the orbital ($\nabla^2\phi$ high here). On the other hand, the GTO-MP or OCE-MP $2\sigma_g$ orbital has a very small value in this region, and so has no significant gain in negative potential energy. At the same time, it does not experience a sizeable increase in kinetic energy either, since it does not execute any turns. The result of this cancellation, large against large in one case and small against small in the other, is that the orbital energies may be comparable.

Looking at the profiles only, however, the verdict is almost inescapable: the OCE-MP basis is not sufficiently complete to perform intricate turns, especially away from the origin. More terms would help in shaping the outer region, and even in smoothing out the oscillations in the bonding region. But this runs up against the redundancy problem. Nevertheless, the salient features are there, and these become more apparent when we analyse the two-dimensional behaviour of the MOs in the next section.

d. Two-Dimensional Structure

In Figures 6.7 - 6.10 are highly visual (and beautiful) illustrations of the shapes of our MOs, along with those from the other two works. They represent the values of the MOs (expressed in Cartesian coordinates) at grid points in the yz plane which contains the molecular axis. Thus the shape of the MOs appears as a surface f(x,y) (3-dimensional) over a rectangular region which is a cut through the molecular space. The dimensions are in atomic units, $-4.0 \leq y \leq 4.0$ a.u. and $-3.0 \leq z \leq 5.0$ a.u. The computer routine used plots a perspective view of this surface, complete with ripples, wiggles, hills, holes and horns. Positive values are plotted above the grid, negative ones below. Hidden lines are not shown, by our choice. The program even allows us to rotate and tilt the grid plane in order to get a better view. In all the figures, the values of the functions have been multiplied by 100, to enhance some of the parts where the gentle waves would otherwise barely disturb the grid surface.

Figure 6.7 shows the $2\sigma_g$ orbital. The min-STO is dominated by the sharp spikes warping the surface at the nuclear positions. The spikes come from the 1s components of this orbital. These, however, are chopped in the model potential calculations. The middle of the OCE-MP is thin and sharp. GTO-MP on the other hand mimics the min-STO except for the chopped horns, in which it resembles OCE-MP.

$3\sigma_g$ (Figure 6.8) shows attempts by OCE-MP to produce horns like the min-STO. The baskets underneath are shorter and fatter (more spread out). GTO-MP does a good job of tracing the min-STO except for horns at the nuclei.

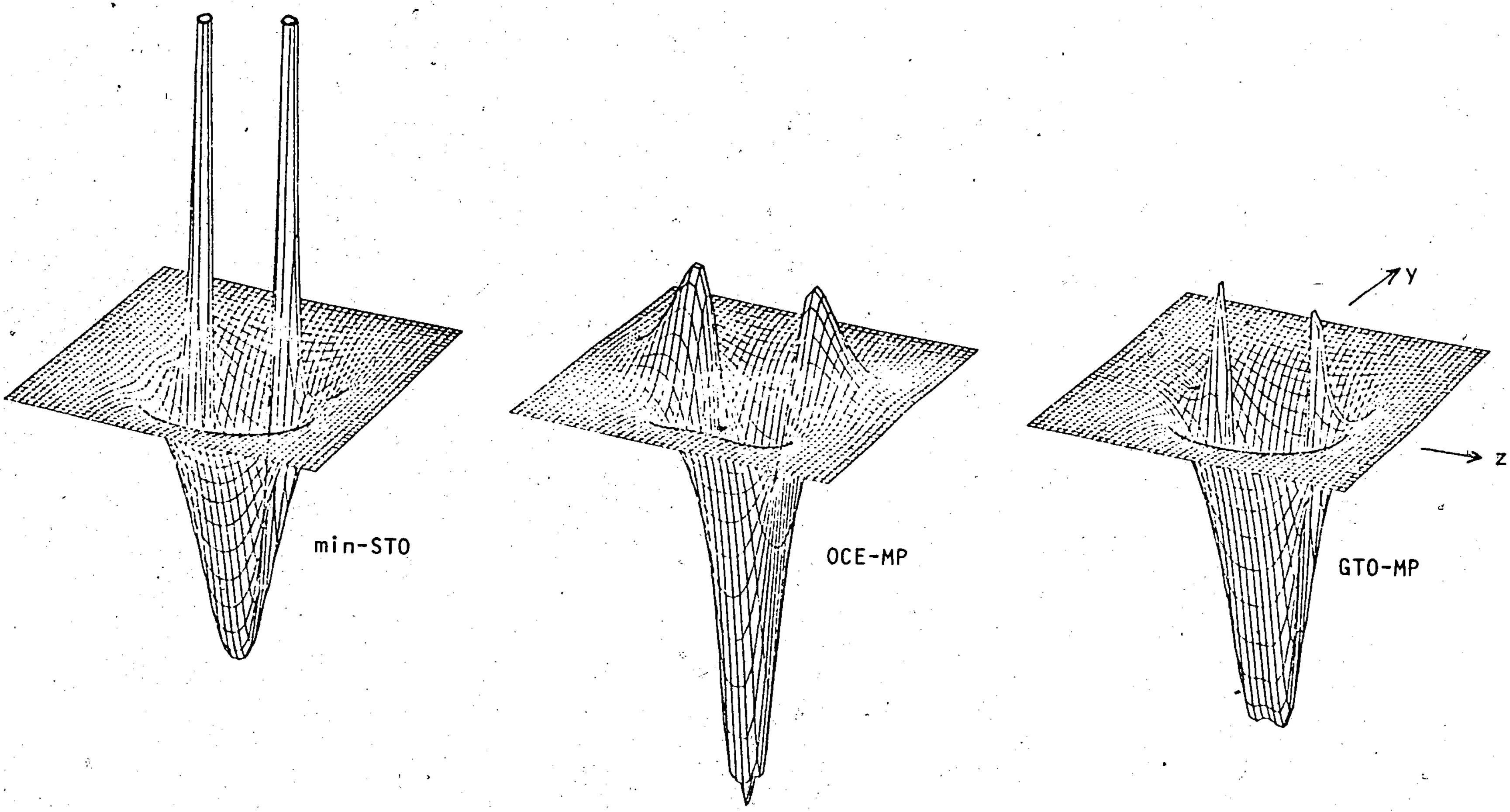


Fig. 6.7. N_2 $2\sigma_g$ MO surfaces in yz plane

[a] All surface figures plotted using the CPLT3D routine, written by P. Buttuls and a variable at the University of Alberta Computing Center.

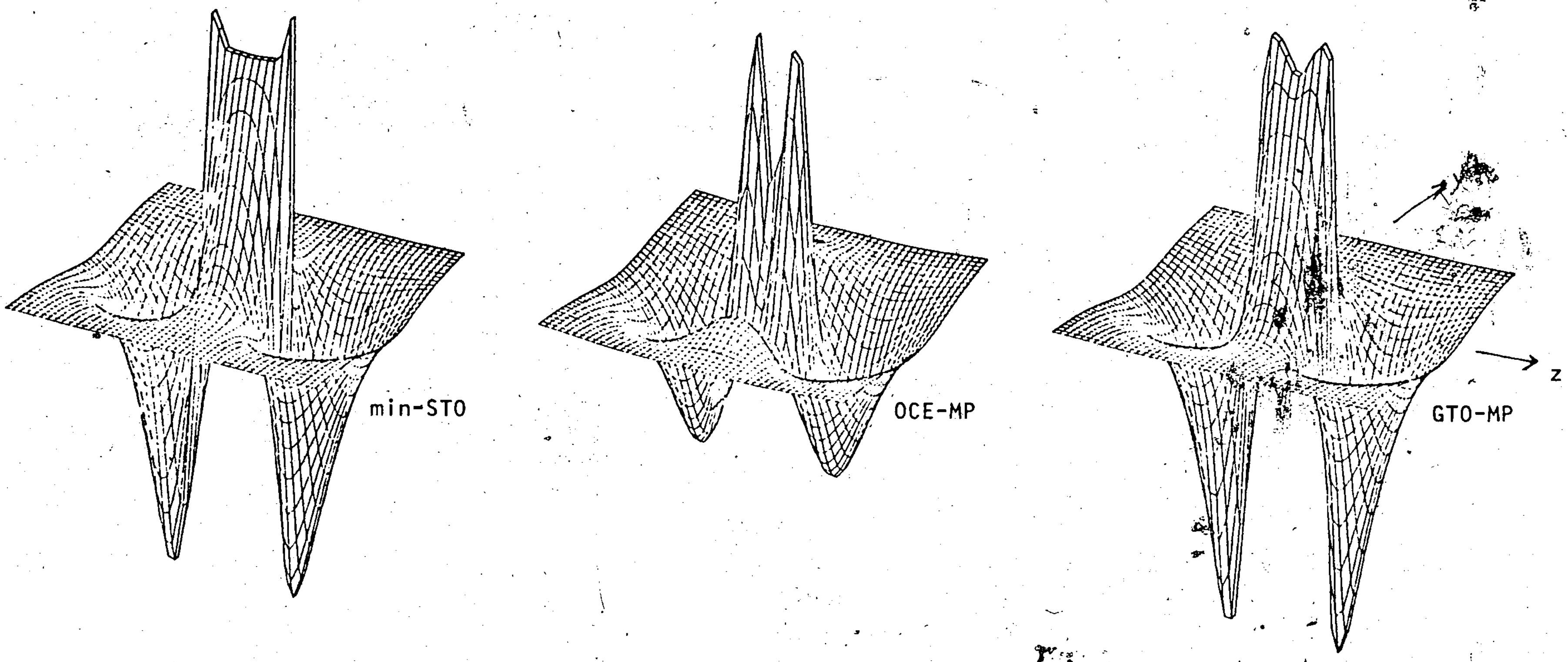


Fig. 6.8. N_2 $3\sigma_g$ MO surfaces in yz plane.

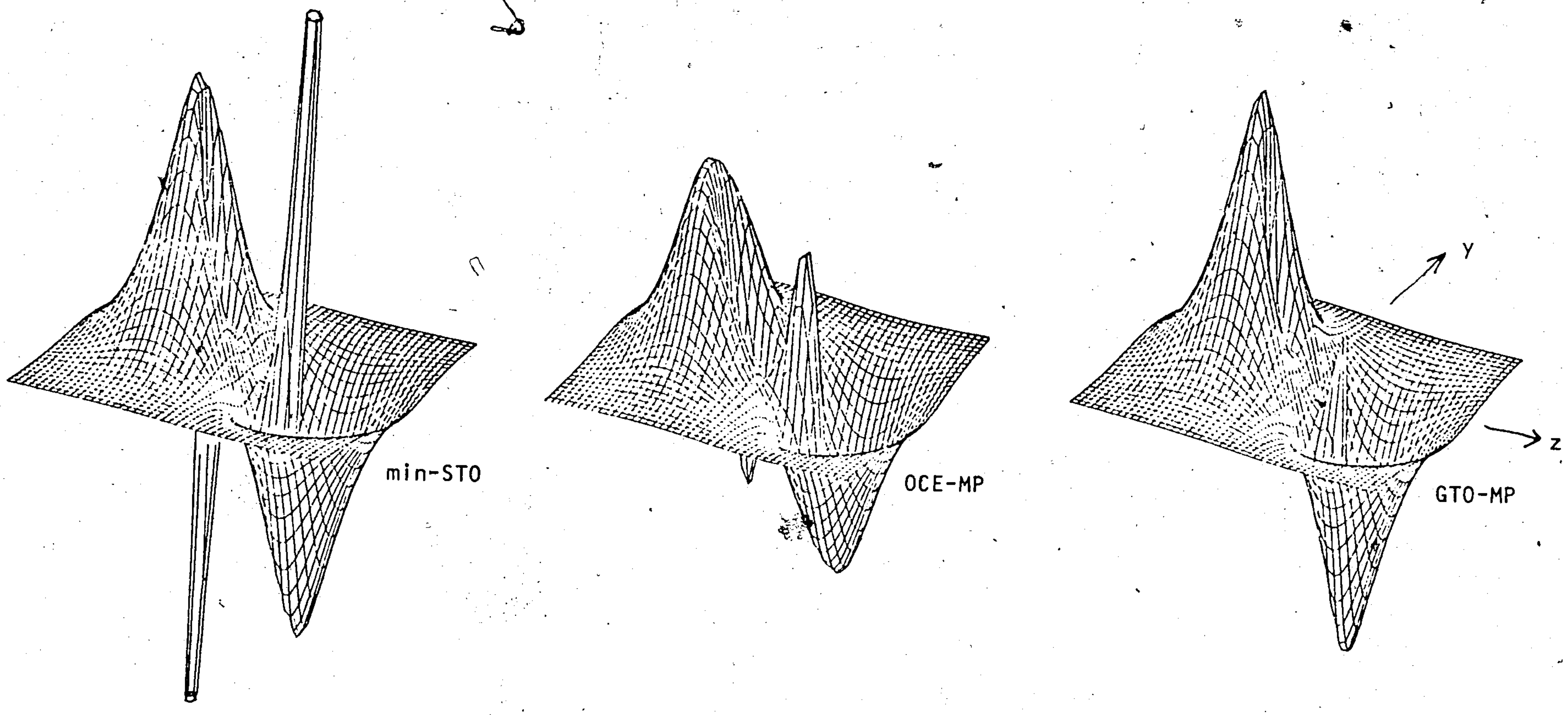


Fig. 6.9. N_2 $2\sigma_u$ MO surfaces in yz plane

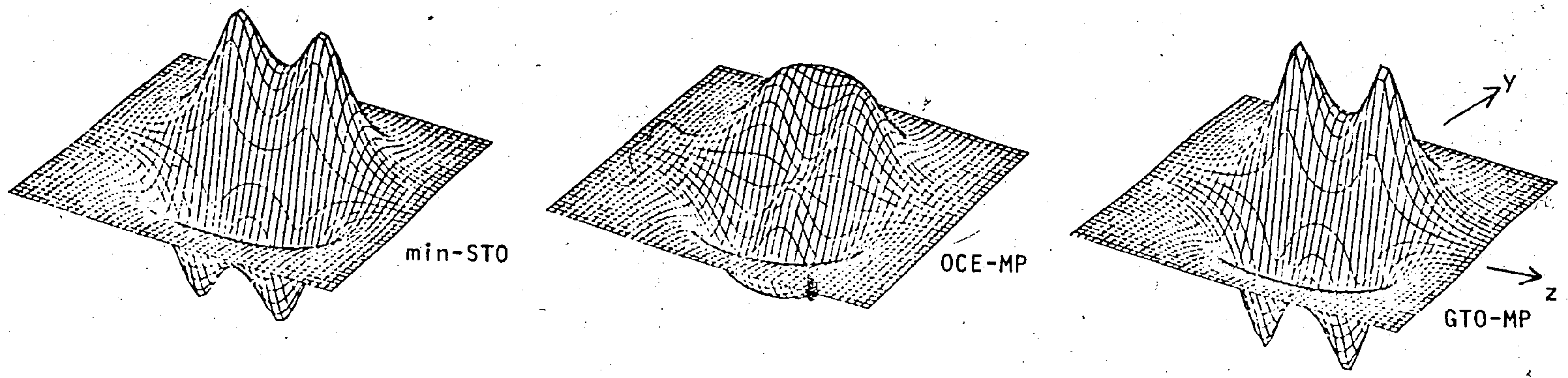


Fig. 6.10. N_2 $1\pi_u$ MO surfaces in yz plane.

$2\sigma_u$ (Figure 6.9) again shows min-STO with sharp spikes, and shorter ones for the model potential calculations. Again the outer baskets of OCE-MP are shorter and more spread out. GTO-MP is almost perfect except for the horns.

Finally, in $1\pi_u$ (Figure 6.10) OCE-MP has flattened, but has not quite produced the dip of the other two. This is not so serious, as the HF π orbital is in fact known to be flatter than the SZ result.

Figure 6.1 shows the total valence density plots for the three methods. For our purposes we have loosely defined this density as the sum of the squares of the contributing MOs

$$\sum_i |\phi_i|^2 = \sum_i \left(\sum_p C_{pi}\chi_p \right)^2 \qquad (6\text{-}6)$$

where $i = 2\sigma_g$, $3\sigma_g$, $2\sigma_u$ and $1\pi_{uy}$ only. This is because we are considering only the cross-section in the y-z plane to which $1\pi_{ux}$ does not contribute. Again we have multiplied the values by 100.

The min-STO cross-sectional valence density shows an undulating surface interrupted by sharp spikes sticking out of the valleys at the nuclear positions. These spikes are missing in the model potential calculations. The GTO-MP simulates rather closely the remaining wavefunction. The OCE-MP does not do badly either. More of the charge is piled in the bonding region, starving the outer. The oscillations around the middle remain. The OCE-MP density appears fatter and more spread out than the other two.

All in all, the salient features of the valence space are reproduced by OCE-MP method. The density plots bear close resemblance to the schematic ones in Chapter 4 (Figure 4.1), showing that the idea of the method was well-conceived.

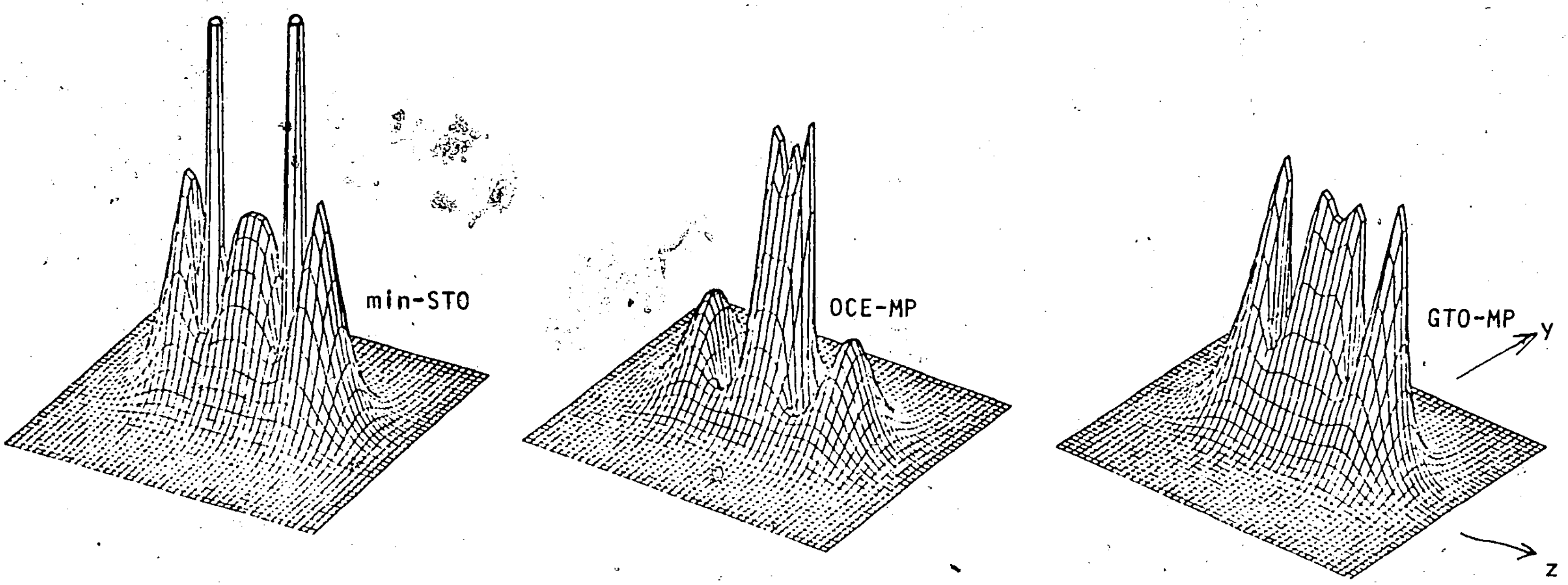


Fig. 6.11. N_2 Valence Density plots.

3. Redundancy Problem

In trying to add many basis functions to the expansion in order to properly describe the MOs, some pathological results were encountered. These cases were characterised by a blow-up of one or more of the orbital energies, sometimes dipping to -1000 a.u. and beyond. Accordingly, this would lower the total energy below the estimated value of -31.6 a.u., thus violating the variation principle. Another feature of such cases was the occurrence of pairs of large (> 2.0) but opposite - sign coefficients in the eigenvectors. In many such cases too, the computations failed to converge in 30 iterations, the limit imposed on our SCF program.

The disease was diagnosed as a redundancy problem, which has been mentioned by several workers in atomic, OCE [12] and even multicenter molecular calculations.[91a]. It stems from the fact that as more functions are added to a center, the overlap matrix elements between functions tend to increase. The overlap matrix becomes increasingly singular (determinant approaching zero), and thus difficult to diagonalise in the SCF procedure.

Several approaches were tried in order to eliminate or alleviate this redundancy problem. We replaced the diagonalisation routines in our program, which are based on the Cholesky decomposition method, [92] by the double Jacobi diagonalisation method of Huzinaga [93], but no improvement resulted. We tried to determine orbital exponents by least-squares fitting our radial functions to those of two-center MOs, but blow-ups occurred even in this scheme.

In the end, we could find no more convincing solution than the mere removal or change of the offending STO. Indeed, as far as we know, this is the only method reported in the literature, the only differences being in how to identify the offending functions. Moccia's criterion [12] was to avoid including functions which would result in eigenvalues of the overlap matrix with magnitudes lower than 10^{-4} - 10^{-5}. But this figure is dependent on the method of diagonalisation. We tried the method, using Jacobi diagonalisation, and found the threshold of safety to be 10^{-3}, but it was not precise in guaranteeing no redundancy in the SCF. Neither was the criterion of merely watching the overlap matrix elements. Redundancy seemed to set in if overlap between any two different STOs went over 0.95, but this could be complicated if overlap between some other pair was also large.

We decided to use the SCF program itself with few iterations (usually about 5) and watch the redundancy. Then we merely removed one or more of the STOs with large coefficients and continued. But the problem meant we could add no more than a few (about 5) functions of the same symmetry. One result is the difficulty in lowering the total energy to the value estimated from formula (4-6).

The problem was also triggered by machine optimisation of exponents starting from a normal basis. Since this procedure is based on lowering the energy, a small initial redundancy traps the procedure and becomes exacerbated. We fell back to manual optimisation, and that is why all orbital exponents are reported to no more than one decimal place. We believe this not to be such a mortal shortcoming, since the SCF procedure fine-tunes the coefficients to give the necessary flexibility.

It is the belief of this author that the redundancy problem in OCE is much more serious than commonly noted. It is intrinsic to any one-center technique, including atomic cases. It seems to go beyond the stability of the computer program used. Until it is overcome, it will continue to limit basis set size and flexibility.

4. Outlook into the Future

The redundancy problem hindered progress towards extended applications of OCE-MP envisaged at the beginning of the project. One of these was an investigation into the OCE-MP potential energy surface and orbital correlation diagram of N_2.

Mulliken [91a] and Briggs and Hayns [15a] have carried out computations on the ground-state correlation diagram, showing how each occupied MO changes with internuclear distance, from about $R = 2.0$ a.u. to the united atom limit $(R = 0)$. They have observed an interesting feature. Instead of MOs going smoothly from the molecular orbitals to the united atom Si orbitals, there is a region of disturbance around 0.6 a.u. Here the orbitals undergo dramatic change, and the orbital picture seems to correspond to the semi-united atom, Mg.

For this region of the N-N quasi-molecule, Briggs and Hayns found that the best basis set was a "triatomic" one, in which some basis functions, especially those involved in shaping the outer MOs, were put at the mid-point, with the core-like functions still seated at the nuclear centers. For shorter internuclear distances, the basis is purely one-center.

A similar procedure has been used by Sidis <u>et al</u> [15b] for the correlation diagram of Ar_2^+ quasi-molecule in atomic collisions.

The more diffuse outer MOs are expanded in terms of united atom (Kr) STOs at the mid-point.

It is therefore interesting to find out how far the OCE-MP method can go in describing the correlation diagram. McWilliams and Huzinaga [65] have made two-center GTO-MP calculations for short internuclear distances. Their orbital energies appear to be tracing the expected profiles. However, these workers hint at factors that might cause errors at short internuclear distances. One is the possible breakdown of the assumption that the interaction between the ionic cores is still correctly given by Equation (4-8), since at short distances there will be less-than-perfect shielding and quantum-mechanical repulsion between the 1s electron clouds. Secondly, orthogonality conditions of Equation (3-85) would be increasingly difficult to fulfil as overlapping between atomic basis functions centered at the two nuclei increases. For OCE-MP, only the first problem should be of concern.

We made a few attempts at doing OCE-MP calculations at shorter distances, using the basis developed at R = 2.068 a.u. but with scaled exponents. Redundancies developed, suggesting that the same painstaking optimisation procedure would have to be repeated. There are no short-cuts.

Also initiated were calculations on the SO_2 molecule, a more complicated case with model potentials at both the expansion center and the off-center nuclei. Although preliminary results look promising, experience tells us that, using our present methods, a lot of time will be required to polish them to acceptable values.

Finally the challenge of tackling the redundancy problem itself has been an exciting prospect, and we have tried to keep an eye open for any developments in this area. Help may soon be forthcoming from two different quarters. If the redundancy problem is considered as basically an SCF convergence problem, then one possible method to explore is Carbo's "level shift operator technique", which is claimed to produce unconditional convergence in SCF procedures [94a]. According to this method, the ordering of the orbital energies is locked and forced to remain constant throughout the SCF procedure. This should prevent any sudden dips which come from redundancy.

A more dramatic development may be the recently reported expansion multi-configurational scheme of Roothaan and Hopper [94b] in which the SCF equations, as we know them today, are dispensed with entirely, together with their attendant convergence problems. Apparently, in the new method, there is no eigenvalue problem to be solved, but instead a simple matrix inversion problem. This author dares to speculate that Roothaan has again built a framework which will take over molecular calculations in the near future. It should be rewarding to see how the OCE-MP method fares in the new framework.

D. Conclusion

The objective of this thesis was to develop a one-center expansion method coupled with model potentials (OCE-MP) in a way which would extend its use to molecules with heavy off-center nuclei, a prospect previously beyond reach. We have presented some of the theoretical background necessary for the study of problems in quantum chemistry, and have pin-pointed the position of the One-Center Expansion method in the hierarchy of approximations. We have detailed the reasoning behind the idea of the OCE-MP method, in a manner which appears convincing as to its suitability for application to molecules. We have constructed the mathematical framework of the method, the formal set of equations which must be solved. We have evolved a method to solve, to a high degree of accuracy, the new molecular integrals which arise in the formulation.

However, in the actual application of the method to real molecules, we have been hindered by what we consider to be a purely technical obstacle, the basis set redundancy problem. This has slowed progress towards more extensive testing of the procedure.

Nevertheless, the results obtained have shown that the method does yield valence electron distributions and orbital energies which are in good agreement with those obtained from more complete calculations. The method combines the saving qualities of both the OCE and MP procedures, resulting in a potentially useful package for further chemical applications. In summing up, the OCE-MP method seemed like a good idea at the time of conception and it still does at the end of this thesis.

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APPENDIX A

LEGENDRE FUNCTIONS AND THEIR CLEBSCH-GORDAN COEFFICIENTS

Legendre Functions

The Legendre functions we use are those defined by Harris and Michels, for the region $-1 \leq x \leq 1$, as follows:

$$P_\ell^m(x) = \frac{(-1)^m \, (1-x^2)^{|m|/2}}{2^\ell \, \ell!} \left(\frac{d}{dx}\right)^{\ell+|m|} (x^2-1)^\ell \quad . \tag{A-1}$$

For $m = |m| \geq 0$ they are precisely the same as the "usual" Associated Legendre function defined by Edmonds [76] For negative order, however, they differ slightly from those of Edmonds. We could say

$$^{HM}P_\ell^{|m|} = {}^{Ed}P_\ell^{|m|} \tag{A-2}$$

$$\begin{aligned} ^{HM}P_\ell^{-|m|} &= {}^{HM}P_\ell^{|m|} = {}^{Ed}P_\ell^{|m|} \\ &= (-1)^{|m|} \frac{(\ell+|m|)!}{(\ell-|m|)!} \, {}^{Ed}P_\ell^{-|m|} \quad . \end{aligned} \tag{A-3}$$

Below are some of the properties of these Legendre Functions which are used in this work: The HM Legendre functions of eqn (A-1) satisfy the orthogonality relation

$$\int_{-1}^{1} P_\ell^m(x) \, P_{\ell'}^m(x) \, dx = \delta_{\ell\ell'} \left(\frac{2}{2\ell+1}\right) \frac{(\ell + |m|)!}{(\ell - |m|)!} \tag{A-4}$$

and the recurrence relations

$$(\ell-|m|+1)\; P^{m}_{\ell+1}(x) \;-\; (2\ell+1)x\; P^{m}_{\ell}(x) \;+\; (\ell+|m|)P^{m}_{\ell-1}(x) = 0\;, \qquad \text{(A-5)}$$

$$(2\ell+1)(1-x^2)^{\frac{1}{2}}\; P^{m}_{\ell}(x) = P^{|m|+1}_{\ell-1}(x) \;-\; P^{|m|+1}_{\ell+1}(x)\quad, \qquad \text{(A-6)}$$

$$\begin{aligned}(2\ell+1)(1-x^2)^{\frac{1}{2}}\; P^{m}_{\ell}(x) &= (\ell-|m|+2)(\ell-|m|+1)\; P^{|m|-1}_{\ell+1}(x)\\ &\quad - (\ell+|m|)(\ell+|m|-1)\; P^{|m|-1}_{\ell-1}(x)\;, \qquad \text{(A-7)}\end{aligned}$$

These relations are easily derived from those of the usual ones, under the constraints of eqn (A-3). Thus, for example, for (A-6) we proceed as follows:

Start from Edmonds' eqns (2.5.1) and (2.5.22):

$$x\; P^{m}_{\ell}(x) \;-\; (\ell-m+1)(1-x^2)^{\frac{1}{2}}\; P^{m-1}_{\ell}(x) \;-\; P^{m}_{\ell-1}(x) = 0$$

$$P^{m}_{\ell+1}(x) \;-\; x\; P^{m}_{\ell}(x) \;-\; (\ell+m)(1-x^2)^{\frac{1}{2}}\; P^{m-1}_{\ell}(x) = 0\;.$$

Add them to get

$$\begin{aligned}P^{m}_{\ell+1}(x) \;-\; P^{m}_{\ell-1}(x) &= (1-x^2)^{\frac{1}{2}}\; P^{m-1}_{\ell}(x)\cdot \ell-m+1+\ell+m\\ &= (1-x^2)^{\frac{1}{2}}\; P^{m-1}_{\ell}(x)\,(2\ell+1)\;.\end{aligned}$$

Transform $m \to |m|$

$$P^{|m|}_{\ell+1}(x) \;-\; P^{|m|}_{\ell-1}(x) = (1-x^2)^{\frac{1}{2}}\; P^{|m|-1}_{\ell}(x)\cdot(2\ell+1)\;.$$

Putting $|m| \to |m| + 1$ gives

$$P_{\ell+1}^{|m|+1}(x) - P_{\ell-1}^{|m|+1}(x) = (2\ell+1)(1-x^2)^{\frac{1}{2}} P_\ell^{|m|}(x)$$

which by (A-3) applied to RHS gives

$$P_{\ell+1}^{|m|+1}(x) - P_{\ell-1}^{|m|+1}(x) = (2\ell+1)(1-x^2)^{\frac{1}{2}} P_\ell^{-|m|}(x) \quad . \tag{A-6}$$

Thus, for all m,

$$(2+1)\ P_\ell^m(x) \cdot (1-x^2)^{\frac{1}{2}} = P_{\ell+1}^{|m|+1} - P_{\ell-1}^{|m|+1}(x) \tag{A-7}$$

Also they satisfy the parity relation

$$P_\ell^m(-x) = (-1)^{\ell+m}\, P_\ell^m(x) \quad . \tag{A-8}$$

This is directly obtained from (A-1):

$$\begin{aligned} P_\ell^m(-x) &= \frac{(-1)^m(1-x^2)^{|m|/2}}{2^\ell\ \ell!} \left(\frac{d}{d(-x)}\right)^{\ell+|m|} (x^2-1)^\ell \\ &= \frac{(-1)^m(1-x^2)^{|m|/2}}{2^\ell\ \ell!} (-1)^{\ell+|m|} \left(\frac{d}{dx}\right)^{\ell+|m|} (x^2-1)^\ell \\ &= (-1)^{\ell+|m|}\ P_\ell^m(x) \quad . \end{aligned}$$

Clebsch-Gordan Coefficients

As is usual in all angular momentum vector coupling schemes, all the decomposition coefficients of eqn (4-116) can always be determined by integration and use of orthogonality relations:

$$C_{j\ell\ell'}^{mm'} = N \cdot \int_{-1}^{1} P_\ell^m(x)\ P_{\ell'}^{m'}(x)\ P_j^{m-m'}(x)\, dx \tag{A-9}$$

where N is some constant from orthonormality relations.

However, it will be shown that our rather unusual choice of Legendre functions defines Clebsch-Gordan coefficients of striking symmetry and beauty, properties which are taken advantage of in generating the coefficients by recursive methods.

When applied to the Legendre functions as defined in eqn (A-1), these coefficients satisfy

$$C^{\sigma\tau}_{\mu jk} = C^{\tau\sigma}_{\mu kj} = C^{-\sigma,-\tau}_{\mu jk} \quad . \qquad \text{(A-10)}$$

This identity rests solely on the first equality in eqn (A-3):

For

$$P^{\sigma}_{j} P^{\tau}_{k} = \sum_{\mu} C^{\sigma\tau}_{jk} P^{\sigma-\tau}_{\mu} = \sum_{\mu} C^{\sigma\tau}_{\mu jk} P^{\tau-\sigma}_{\mu} \quad . \qquad \text{(A-11)}$$

Multiplication is reflexive (commutative), so,

$$P^{\sigma}_{j} P^{\tau}_{k} = P^{\tau}_{k} P^{\sigma}_{j} = \sum_{\mu} C^{\tau\sigma}_{\mu kj} P^{\tau-\sigma}_{\mu} \qquad \text{(A-12)}$$

and because of (A-3),

$$P_{j} P^{\tau}_{k} = P^{-\sigma}_{j} P^{-\tau}_{k} = \sum_{\mu} C^{-\sigma,-\tau}_{\mu jk} P^{-(\sigma-\tau)}_{\mu} = \sum_{\mu} C^{-\sigma,-\tau}_{\mu jk} P^{\sigma-\tau}_{\mu} \quad . \qquad \text{(A-13)}$$

Here we have used (A-3) for

$$P^{\sigma-\tau}_{\mu} = P^{\tau-\sigma}_{\mu} = P^{-(\sigma-\tau)}_{\mu} \quad .$$

Relationships (A-10) cause all the distinct coefficients to fall into two classes:

$$\tau \geq \sigma \geq 0$$

or

$$\tau \geq -\sigma \geq 0 \quad .$$

These two classes are distinct and have to be generated according to two different recipes as follows:

a. $\tau \geq \sigma \geq 0$

For each pair (σ,τ), we perform the following steps

We define a new index ρ in (A-11) by

$$\rho = \tau - \sigma \quad .$$

Of course by (A-3), $P_\mu^{\sigma-\tau} = P_\mu^{-\rho} = P_\mu^{\rho}$. The starting formulas are then

$$C^{\sigma\tau}_{\mu\sigma\tau} = \left(\frac{2\rho+1}{2\tau+1}\right) \frac{\tau! \ (2\sigma)!}{\rho! \ \sigma!} \tag{A-14}$$

and

$$C^{\sigma\tau}_{\rho+1,\sigma,\tau+1} = \left(\frac{2\rho+3}{2\tau+3}\right) \frac{\tau! \ (2\sigma)!}{\tau! \ \sigma!} \quad . \tag{A-15}$$

These two formulas are obtained from explicit application of (A-9) and (4-116):

In (A-11) put $j = \sigma$, $k = \tau$, $\rho = \tau-\sigma$. Multiply both sides by P_ρ^ρ and integrate:

$$\int_{-1}^{1} P_\sigma^\sigma(x) \ P_\tau^\tau(x) \ P_\rho^\rho(x) \ dx = \int_{-1}^{1} \sum_\mu C^{\sigma\tau}_{\mu\sigma\tau} \ P_\rho^\rho(x) \ P_\rho^\rho(x) \ dx \quad .$$

The orthogonality relation (A-4) determines the right hand side to be

$$= C^{\sigma\tau}_{\mu\sigma\tau} \cdot \delta_{\mu\rho} \left(\frac{2}{2\rho+1}\right) \cdot \frac{(\rho+\rho)!}{0!}$$

$$= C^{\sigma\tau}_{\rho\sigma\tau} \cdot \frac{2\cdot(2\rho)!}{2\rho+1} \quad .$$

So

$$C^{\sigma\tau}_{\rho\sigma\tau} = \frac{2\rho+1}{2(2\rho)!} \int_{-1}^{1} P^{\sigma}_{\sigma}\, P^{\tau}_{\tau}\, P^{\rho}_{\rho}\, dx \quad . \tag{A-16}$$

To solve the integral in (A-16), we need explicit expressions for the Legendre functions, from (A-1)

$$P^{\sigma}_{\sigma} = \frac{(-1)^{\sigma}\ (1-x^2)^{\sigma/2}}{2^{\sigma}\ \sigma!} \left(\frac{d}{dx}\right)^{2\sigma} (x^2-1)^{\sigma}$$

$$= \frac{(-1)^{\sigma}\ (1-x^2)^{\sigma/2}\ (2\sigma)!}{2^{\sigma}\ \sigma!} \quad .$$

This is because in $\left(\frac{d}{dx}\right)^{2\sigma} (x^2-1)^{\sigma}$, all terms in the polynomial , $(x^2-1)^{\sigma}$ are annihilated by the differential operator $\left(\frac{d}{dx}\right)^{2\sigma}$, except the highest power $x^{2\sigma}$, which is reduced to $(2\sigma)!$.

Similar expressions for P^{τ}_{τ}; P^{ρ}_{ρ} result in

$$\int_{-1}^{1} P^{\sigma}_{\sigma}P^{\tau}_{\tau}P^{\rho}_{\rho}dx = \frac{(2\sigma)!(2\tau)!(2\rho)!}{2^{\sigma+\tau+\tau-\sigma}\ \sigma!\ \tau!\ \rho!} \int_{-1}^{1} (1-x^2)^{\frac{\sigma+\tau}{2} + \frac{\tau-\sigma}{2}} dx$$

$$= \frac{(2\sigma)!(2\tau)!(2\rho)!}{2^{2\tau}\cdot \sigma!\ \tau!\ \rho!} \int_{-1}^{1} (1-x^2)^{\tau}\, dx \quad . \tag{A-17}$$

We solve the integral by making the usual substitution

$$x = \sin\theta\ , \quad dx = \cos\theta\, d\theta \tag{A-17a}$$

to get

$$I = \int_{-1}^{1} (1-x^2)^{\tau}\, dx = \int_{-\pi/2}^{\pi/2} \cos^{2\tau}\theta \cdot \cos\theta\, d\theta \tag{A-17b}$$

$$= \int_{-\pi/2}^{\pi/2} \cos^{2\tau+1}\theta\, d\theta \quad . \tag{A-17c}$$

The standard integral

$$\cos n\ ax\ dx = \frac{1}{an} \cos^{n-1} ax \sin ax + \frac{n-1}{n} \cos^{n} ax\ dx \qquad \text{(A-18)}$$

gives

$$I = \frac{\cos^{2\tau} \theta \sin \theta}{2\tau} \Bigg|_{-\pi/2}^{\pi/2} + \frac{2\tau}{2\tau+1} \int_{-\pi/2}^{\pi/2} \cos^{2\tau-1} \theta\, d\theta$$

(A-18) can be applied repeatedly, to give

$$I = \frac{2\tau}{2\tau+1} \cdot \frac{2\tau-2}{2\tau-1} \cdot \frac{2\tau-4}{2\tau-3} \cdot \ldots \cdot \frac{2}{3} \int_{-\pi/2}^{\pi/2} \cos^{1} \theta\, d\theta$$

$$= \frac{2 \cdot 2^{\tau} \cdot ([illegible])([illegible]) \ldots 1}{(2\tau+1)!/[2\tau[illegible](2\tau-2)(2\tau-4)\ldots 2]}$$

$$I = \frac{2^{2\tau+1} (\tau!)^{2}}{(2\tau+1)!} \quad . \qquad \text{(A-19)}$$

Substituting (A-17) and (A-19) in (A-16) gives

$$C^{\sigma\tau}_{\rho\sigma\tau} = \frac{2\rho+1}{2(2\rho)!} \cdot \frac{(2\sigma)!(2\tau)!(2\rho)!}{2^{2\tau} \cdot \sigma!\ \tau!\ \rho!} \cdot \frac{2^{\tau+1} (\tau!)^{2}}{(2\tau+1)!}$$

$$= \left(\frac{2\rho+1}{2\tau+1}\right) \frac{\tau!\ (2\sigma)!}{\rho!\ \ \sigma!} \quad . \qquad \text{(A-14)}$$

Similarly for (A-15), where

$$\rho + 1 = \tau - \phi + 1$$

$$= \tau + 1 - \sigma$$

$$\int_{-1}^{1} P_{\sigma}^{\sigma} P_{\tau+1}^{\tau} P_{\rho+1}^{\rho}\, dx = C^{\rho}_{\rho+1,\sigma,\tau+1} \frac{2}{2\rho+3} (2\rho+1)! \quad . \qquad \text{(A-20)}$$

Using (A-5), with $|m| = \tau = \ell$ we get

$$P^{\tau}_{\tau+1} = (2\tau+1) \times P^{\tau}_{\tau} \quad ,$$

since $P^{\tau}_{\tau-1} = 0$ by definition (A-1). So explicitly,

$$P^{\tau}_{\tau+1} = \frac{(2\tau+1)(2\tau)!(1-x^2)^{\tau/2}}{\tau! \;\; 2^{\tau}} \times (-1)^{\rho} \qquad \text{(A-21)}$$

and similarly

$$P^{\rho}_{\rho+1} = \frac{(2\rho+1)(2\rho)!(1-x^2)^{\rho/2}}{\rho! \;\; 2^{\rho}} \times (-1)^{\rho} \quad . \qquad \text{(A-22)}$$

Eqn (A-20) then becomes

$$C^{\sigma\tau}_{\rho+1,\sigma,\tau+1} = \frac{(2\rho+3)(2\rho+1)!(2\sigma)!(2\tau+1)!(-1)^{\sigma+\tau+\rho}}{2(2\rho+1)! \; \tau! \; \rho! \; \sigma! \; 2^{\sigma+\tau+\rho}} \cdot \qquad \text{(A-23)}$$

$$\cdot \int_{-1}^{1} x^2(1-x^2)^{\tau} \; d\tau \quad . \qquad \text{(A-23)}$$

The integral here works out to be, after the trigonometrical substitution (A-17a), and use of (A-19)

$$\int_{-\pi/2}^{\pi/2} (\cos^{2\tau+1} - \cos^{2\tau+3}\theta) \; d\theta =$$

$$= \frac{2^{2\tau+1} \; \tau! \; \tau!}{(2\tau+1)!} - \frac{2^{2\tau+3} \; (\tau+1)!(\tau+1)!}{(2\tau+3)!}$$

$$= \frac{2^{2\tau+1}(2\tau+3)(2\tau+2)(\tau!)^2 - 2^{2\tau+3}[(\tau+1)!]^2}{(2\tau+3)!}$$

$$= \frac{2^{2\tau+2}(\tau+1)! \; \tau! \; \{(2\tau+3) - 2(\tau+1)\}}{(2\tau+3)!}$$

$$= \frac{2^{2\tau+2} \; (\tau+1)! \; \tau!}{(2\tau+3)!} \qquad \text{(A-24)}$$

which, when substituted into (A-23) furnishes

$$C^{\sigma\tau}_{\rho+1,\sigma,\tau+1} = \frac{(2\sigma)!(2\tau+1)!\;2^{2\tau+2}(\tau+1)!\tau!(2\rho+3)}{\tau!\;\rho!\;\sigma!\;2^{2\tau+1}\;(2\tau+3)!} \;.$$

But

$$\frac{(2\tau+1)!}{(2\tau+3)!} = \frac{1}{(2\tau+3)(2\tau+2)} = \frac{1}{2(2\tau+3)(\tau+1)} \;.$$

So

$$C^{\sigma\tau}_{\rho+1,\sigma,\tau+1} = \left(\frac{2\rho+3}{2\tau+3}\right)\frac{\tau!\;(2\sigma)!}{\rho!\;\sigma!} \;. \qquad \text{(A-15)}$$

Notice there is a typographical error in the Harris and Michels formula (151).

With these two inital expressions (A-14) and (A-15), all the rest of the $C^{\sigma\pi}_{\mu jk}$ in this class can be generated with the following recursive scheme.

First advance μ and k, keeping $j = \sigma$ fixed. The necessary relation for this is

$$\left(\frac{\mu+\rho}{2\mu+1}\right) C^{\sigma\tau}_{\mu jk} = \left(\frac{k+\tau}{2k+1}\right) C^{\sigma\tau}_{\mu-1,j,k-1} + \left(\frac{k-\tau+1}{2k+1}\right) C^{\sigma\tau}_{\mu-1,j,k-1}$$

$$- \left(\frac{\mu-\rho-1}{2\mu+3}\right) C^{\sigma\tau}_{\mu-2,j,k} \;. \qquad \text{(A-25)}$$

<u>Proof</u>: We apply (A-5) to P^{τ}_{k} in (A-12) to get

$$x\,P^{\tau}_{k} = \left(\frac{k-\tau+1}{2k+1}\right) P^{\tau}_{k+1} + \left(\frac{k+\tau}{2k+1}\right) P^{\tau}_{k-1} \qquad \text{(A-26)}$$

so that

$$x\,P_j^{\sigma}\,P_k^{\tau} = \left(\frac{k-\tau+1}{2k+1}\right) P_j^{\sigma}\,P_{k+1}^{\tau} + \left(\frac{k+\tau}{2k+1}\right) P_j^{\sigma}\,P_{k-1}^{\tau} \quad . \tag{A-27}$$

Eqn (A-12) can now be rewritten as

$$\sum_{\mu} C_{\mu jk}^{\sigma\tau} \cdot x\,P_{\mu}^{\rho} = \sum_{\mu} \left(\frac{k-\tau+1}{2k+1}\right) C_{\mu j,k+1}^{\sigma\tau}\,P_{\mu}^{\rho} + \left(\frac{k+\tau}{2k+1}\right) C_{\lambda jk-1}\,P_{\mu}^{\rho} \quad . \tag{A-28}$$

Again we apply (A-5) to xP_{μ}^{ρ} :

$$x\,P_{\mu}^{\rho} = \left(\frac{\mu-\rho+1}{2\mu+1}\right) P_{\mu+1}^{\rho} + \left(\frac{\mu+\rho}{2\mu+1}\right) P_{\mu-1}^{\rho} \quad . \tag{A-29}$$

Substituting (A-29) into (A-28) and examining the term associated with $P_{\mu-1}^{\rho}$, we find

$$\left(\frac{\mu-2-\rho+1}{2(\mu-2)+1}\right) C_{\mu-2,j,k}^{\sigma\tau} + \left(\frac{\mu+\rho}{2\mu+1}\right) C_{\mu jk}^{\sigma\tau}$$

$$= \left(\frac{k-\tau+1}{2k+1}\right) C_{\mu-1,j,k+1}^{\sigma\tau} + \left(\frac{k+\tau}{2k+1}\right) C_{\mu-1,j,k-1}^{\sigma\tau}$$

which is precisely (A-25).

In (A-25) and the other recurrence relations to follow, note that as befits a true angular momentum vector coupling coefficient, $C_{\mu jk}^{\sigma\tau}$ vanishes if <u>any</u> of the following happens:

i) $j < |\sigma|$

ii) $k < |\tau|$

iii) $\mu < \rho$

iv) $\mu + j + k$ not even

v) $|j-k| \leq \mu \leq j+k$ is not satisfied.

Incidentally, condition iv) ensures that μ jumps in steps of 2, and means that only Legendre functions of the same parity can be combined together meaningfully.

The restrictions cause eqn (A-25) to suffice for the generation of all the coefficients of the form $C^{\sigma\tau}_{\mu\sigma k}$.

Then the lower index j may be raised with the aid of

$$(\frac{j-\sigma}{2j-1})\, C^{\sigma\tau}_{\mu jk} = (\frac{k+\tau}{2k+1})\, C^{\sigma\tau}_{\mu,j-1,k-1} + (\frac{k-\tau+1}{2k+1})\, C^{\sigma\tau}_{\mu,j-1,k+1}$$

$$- (\frac{j+\sigma-1}{2j-1})\, C^{\sigma\tau}_{\mu,j-2,k} \quad . \qquad \text{(A-30)}$$

This equation is obtained in s atraightforward manner. Apply (A-5) to xP^{σ}_{j} in (A-26) to give

$$\sum_{\mu} (\frac{j-\sigma+1}{2j+1})\, C^{\sigma\tau}_{\mu,j+1,k}\, P^{\rho}_{\mu} + (\frac{j+\sigma}{2j+1})\, C^{\sigma\tau}_{\mu,j-1,k}\, P^{\rho}_{\mu} \}$$

$$= \sum_{\mu} \{ (\frac{k-\tau+1}{2k+1})\, C^{\sigma\tau}_{\mu,j,k+1}\, P^{\rho}_{\mu} + (\frac{k+\tau}{2k+1})\, C^{\sigma\tau}_{\mu,j,k-1}\, P^{\rho}_{\mu} \} .$$

Examine the term in P^{ρ}_{μ} and put $j \rightarrow j-1$ which gives (A-30) immediately.

This generates all the coefficients needed.

Case: $\tau \geq -\sigma \geq 0$

<u>Step 1</u>: set $-\sigma = \nu$ so that

$$\rho = \tau - \sigma$$

$$= \tau + \nu \quad . \qquad \text{(A-31)}$$

Step 2: Start from the explicit formulae

$$C^{-\nu\tau}_{\rho\nu\tau} = \frac{\rho!\ (2\nu)!}{(2\rho)!}\frac{(2\tau)!}{\nu!\ \tau!} \tag{A-32}$$

and

$$C^{-\nu\tau}_{\rho+1,\nu,\tau+1} = \frac{\rho!\ (2\nu)!(2\tau+1)!}{(2\rho+1)!\ \nu!\ \tau!} \quad . \tag{A-33}$$

These are obtained in a manner similar to that used for (A-14) and (A-15), and noting especially that $P^{-\nu}_{\nu} = P^{\nu}_{\nu}$.

Step 3: The formula for advancing μ and k is now

$$\left(\frac{k-\tau}{2k-1}\right) C^{-\nu\tau}_{\mu jk} = \left(\frac{\mu-\rho}{2\mu-1}\right) C^{-\nu,\tau}_{\mu-1,j,k-1} + \left(\frac{\mu+\rho+1}{2\mu+3}\right) C^{-\nu}_{\mu+1,j,k-1}$$

$$- \left(\frac{k+\tau-1}{2k-1}\right) C^{-\nu\tau}_{\mu+1,j,k-2} \tag{A-34}$$

obtained in the same way as (A-25).

Step 4: j is raised by use of the formula

$$\left(\frac{j-\nu}{2j-1}\right) C^{-\nu\tau}_{\mu jk} = \left(\frac{\mu-\rho}{2\mu-1}\right) C^{-\nu\tau}_{\mu-1,j-1,k} + \left(\frac{\mu+\rho+1}{2\mu+3}\right) C^{-\nu\tau}_{\mu+1,j-1,k}$$

$$- \left(\frac{j+\nu-1}{2j-1}\right) C^{-\nu\tau}_{\mu,j-2,k} \tag{A-35}$$

which is obtained along the same lines as (A-30).

Notice the symmetry $(j,\nu) \leftrightarrow (k,\tau)$ in (A-34) and (A-35), which was taken advantage of in programming.

A few further comments on the structure of the Clebsch-Gordan coefficients follow. In general, the members of the two classes are unrelated, being, as they are, defined with respect to linear combination of Legendre functions of different orders .

	Class		Order ρ	Effective Limits on μ	
				lower	upper
a.	$C^{\sigma\tau}_{\mu jk}$	$\tau \geq \sigma \geq 0$	$\tau-\sigma \leq \tau$	max $(\lvert j-k\rvert, \tau-\sigma)$	$j+k$
b.	$C^{-\nu\tau}_{\mu jk}$	$\tau \geq \nu \geq 0$ $(\nu = -\sigma)$	$\tau+\nu \geq \tau$	max $(\lvert j-k\rvert, \tau+\nu)$	$j+k$

Thus in general the number of terms in class b. is less than that in a. for the same $(|\sigma|, |\tau|)$ pair.

The two sets a. and b. intersect when either one or both of the upper indices σ, τ are zero. This identity was used in checking the programs for the two schemes.

The coefficients were also checked against those calcualted by hand, using the

$$P_j^{|m|}(x)\, P_j^{|m|}(x) = \sum_J C^{|m|,|m|}_{J\ell\ell'}\, P_J^0(x) \qquad \text{(A-36)}$$

for the special case of two equal and positive m values. Huzinaga [81] has carefully compiled a set of these coefficients for all combinations up to 4f orbitals, using explicit expressions for the Legendre polynomials and proceeding in a pedestrian manner.

APPENDIX B

BESSEL FUNCTIONS AND RELATED INTEGRALS

Definitions

In this work, we use two types of spherical Bessel functions, defined in terms of the corresponding ordinary Bessel functions by the formulae:

$$j_n(x) = \left(\frac{\pi}{2x}\right)^{\frac{1}{2}} J_{n+\frac{1}{2}}(x) \qquad \text{(B-1)}$$

$$k_n(x) = \left(\frac{2}{\pi x}\right)^{\frac{1}{2}} K_{n+\frac{1}{2}}(x) \qquad \text{(B-2)}$$

where n is a positive integer or zero. The ordinary Bessel functions J_ν and K_ν are as defined in Abramowitz and Stegun, [80] Chapters 9 and 10.

The conventions used are:

$\vec{z} = x + iy$; x, y real

n is a positive integer or zero

ν, μ are unrestricted complex numbers otherwise indicated.

J_ν are called Ordinary Bessel Functions of the first kind, of order ν. $J_{\pm\nu}(z)$ are some of the solutions to the differential equation

$$z^2 \frac{d^2w}{dz^2} + z \frac{dw}{dz} + (z^2 - \nu^2)\, w = 0 \quad , \qquad \text{(B-3)}$$

the other solutions being ordinary Bessel functions of the second kind

$Y_\nu(z)$ (also called Weber's Functions), and of the third kind $H_\nu^{(1)}(z)$, $H_\nu^{(2)}(x)$ (also called the Hankel Functions).

The functions $K_\nu(z)$ are called Modified Bessel functions of the Second Kind of order ν. They are solutions to the differential equation

$$z^2 \frac{d^2w}{dz^2} + z \frac{dw}{dz} - (z^2 + \nu^2)w = 0 \quad , \tag{B-4}$$

the other solutions being $I_{\pm\nu}(x)$, the Modified Bessel functions of the first kind.

The functions j_n defined by eqn (B-1) are called the Spherical Bessel Functions of the first kind, and they satisfy the differential equation

$$z^2w'' + 2zw' + [z^2-n(n+1)]w = 0 \quad , \tag{B-5}$$

where $n = 0, \pm 1, \pm 2, \ldots$ along with $y_n(z)$, second kind and $h_n^{(1)}(z)$, $h_n^{(2)}(z)$, third kind, which are defined similarly.

Finally k_n, called Modified Spherical Bessel functions of the third kind, satisfy, along with i_n defined similarly, the differential equation

$$z^2w'' + 2zw' - [z^2+n(n+1)]w = 0 \quad . \tag{B-6}$$

Some Recurrence Relations

The spherical Bessel functions j_n, k_n satisfy the following recurrence relations:

$$\left(\frac{2n+1}{x}\right) j_n(x) = j_{n+1}(x) + j_{n-1}(x) \tag{B-7}$$

$$\left(\frac{2n+1}{x}\right) k_n(x) = k_{n+1}(x) - k_{n-1}(x) \quad . \tag{B-8}$$

Starting points for the recurrence relations are the special values

$$j_0(x) = x^{-1} \sin x = \frac{\sin x}{x} \tag{B-9}$$

$$j_{-1} = \frac{\cos x}{x} \tag{B-10}$$

$$k_0(x) = e^{-x}/x \tag{B-11}$$

$$k_{-1}(x) = e^{-x}/x \quad . \tag{B-12}$$

The functions $k_n(x)$ are calculated by the direct use of the recurrence relation, eqn (B-8), starting from (B-11) and (B-12), and generating k_{n+1} from k_n and k_{n-1}. This recurrence scheme is satisfactory for k_n. There is of course no need to compute $j_n(x)$ in this work, since these functions appear only in integrals which are evaluated analytically.

Some Integrals

We record a few standard integrals involving Bessel Functions, which are needed in the main text.

1. $$\int_0^\infty t^\mu J_\nu(t)\, dt = \frac{2^\mu \Gamma\left(\frac{\nu+\mu+1}{2}\right)}{\Gamma\left(\frac{\nu-\mu+1}{2}\right)} \tag{B-13}$$

defined under the conditions

$$R(\mu+\nu) > -1, \quad R\mu < \frac{1}{2}$$

Abramowitz and Stegun. Formula (11.4.16). This formula is used to prove

$$2. \quad \int_0^\infty \frac{t^{\nu+1} J_\nu(at)}{(t^2+z^2)^{\mu+1}}\, dt = \frac{a^\mu z^{\nu-\mu}}{2^\mu \Gamma(\mu+1)} K_{\nu-\mu}(z) \qquad \text{(B-14)}$$

defined only under the conditions

$$a > 0, \quad R(z) > 0, \quad -1 < R\nu < 2R\mu + \frac{3}{2}$$

Abramowitz and Stegun. Formula (11.4.44).

This formula is used to derive the last equality in eqn (4-148) and (4-149). For example,

$$W^{L1}_{i_1 0} = \left(\frac{2}{\pi R}\right)^{\frac{1}{2}} \int_0^\infty \frac{k^{L+(3/2)} J_{L+(1/2)}(kR)}{(k^2+\delta_1^2)^{i_1}}\, dk$$

$$= \frac{\delta_1^{L+1}}{(i_1-1)!} \left(\frac{R}{2\delta_1}\right)^{i_1-1} \left(\frac{2}{\pi\delta_1 R}\right)^{\frac{1}{2}} K_{i_1-L-(3/2)}(\delta_1 R) \qquad (4\text{-}148)$$

We check that the conditions under which the integral is defined are satisfied. In our case, they apepar as

$\nu = L + \frac{1}{2} > -1$ since $L \geq 0$

$\mu = i_1 - 1$

$$\left.\begin{aligned} z &= \delta_1 > 0 \\ a &= R > 0 \end{aligned}\right\} \quad \text{These two are significant conditions}$$

$t = k$

and

$$2(i-1) + 3/2 > L + 1/2$$

implies

$$2i > L + 1 \quad .$$

Under these conditions the integral becomes

$$W^{L1}_{i_1 0} = \left(\frac{2}{\pi R}\right)^{\frac{1}{2}} \cdot \frac{R^{i_1-1} \cdot \delta_1^{L+\frac{1}{2}+1-i} \cdot K_{L+\frac{1}{2}+1-i_1}(\delta_1 R)}{2^{i_1-1} \quad (i_1-1)!} \quad .$$

We use the identity (Abramowitz and Stegun, eqn (10.2.16)

$$K_{(n+\frac{1}{2})} = K_{-(n+\frac{1}{2})} \qquad \text{(B-15)}$$

to give

$$W^{L1}_{i_1 0} = \frac{\delta_1^{L+1}}{(i_1-1)!} \left(\frac{R}{2\delta_1}\right)^{i_1-1} \left(\frac{2}{\pi\delta_1 R}\right)^{\frac{1}{2}} L_{i_1-L-\frac{3}{2}}(\delta_1 R) \qquad \text{(4-148)}$$

which, by (B-2), gives also

$$W^{L1}_{i_1 0} = \frac{\delta_1^{L+1}}{(i_1-1)!} \left(\frac{R}{2\delta_1}\right)^{i_1-1} k_{i_1-L-2}(\delta_1 R) \quad . \qquad \text{(B-16)}$$

Similarly

$$W^{L1}_{0 i_2} = \frac{\delta_1^{L+1}}{(i_2-1)!} \left(\frac{R}{2\delta_1}\right)^{i_1-1} k_{i_2-L-2}(\delta_2 R) \quad . \qquad \text{(B-16a)}$$

3. $$\int_0^\infty \frac{J_\nu(at)dt}{t^\nu(t^2+z^2)} = \frac{\pi}{2z^{\nu+1}} \quad I_\nu(az) - L_\nu(az) \quad , \qquad \text{(B-17)}$$

where the conditions $a > 0$, $Rz > 0$, $R\nu > -\frac{5}{2}$ must hold. This integral could be used to prove eqn (4-146) and eqn (4-147) directly, with

$$\nu = \frac{1}{2}, \quad z = R\delta_1, \quad a = 1, \quad t = kR,$$

if one indulges in the details of defining $I_\nu(az)$ an $L_\nu(az)$. The latter are called Modified Struve functions.

APPENDIX C

FOURIER TRANSFORMS OF SLATER TYPE ORBITALS

Radial Transform $(n\ell\delta)^T$

The quantity $(n\ell\delta)^T$ given in integral form in eqn (4-110) is proportional to the radial dependence of the Fourier transform of a STO of the form $N\cdot r^n e^{-\delta r} P_\ell(\cos\theta)$, i.e., $(\ell\sigma)$-orbital. It has the representation (Geller, [25], eqn 17)

$$(n\ell\delta)^T = \frac{2^\ell \, \ell! \, (n-\ell+1)! \, \delta^{n-\ell+1} \, k^\ell}{(k^2+\delta^2)^{n+2}} \times \sum_{s=0}^{[\frac{1}{2}(n-\ell+1)]} (-1)^s \binom{n+\ell+2}{2s+2\ell+1} \binom{s+\ell}{s} \left(\frac{k}{\delta}\right)^{2s} \qquad (4\text{-}124)$$

where [a] means the largest integer in a). Using this equation, a number of recurrence relations involving $(n\ell\delta)^T$ may be deduced. A more convenient method is to use eqn (4-110) directly plus the properties of spherical Bessel functions. We use the latter method to derive some of these relations:

1. $$k(n\ell\delta)^T + (n-\ell)(n-1,\ell+1,\delta)^T = \delta(\mu,\ell+1,\delta)^T \quad . \qquad (C\text{-}1)$$

<u>Proof:</u> Use of differentiation formula for spherical Bessel functions j_ℓ (Abramowitz and Stegun, eqn 10.1.23)

$$\left(\frac{1}{z}\frac{d}{dz}\right)^m [z^{\ell+1} j_\ell(z)] = z^{\ell+1-m} j_{\ell-1}(z) \qquad (C\text{-}2)$$

with m = 1 this gives

$$\frac{d}{dz}\left[z^{\ell+1} j_\ell(z)\right] = z^{\ell+1} j_{\ell-1}(z) \quad . \tag{C-3}$$

We examine

$$\frac{d}{dz}\left[z^{n+2} j_\ell(z)\right] = \frac{d}{dz}\left[z^{n-\ell+1} \cdot z^{\ell+1} j_\ell(z)\right] \quad .$$

By parts:

$$= \frac{d}{dz}\left(z^{n-\ell+1}\right) \cdot z^{\ell+1} j_\ell(z) + z^{n-\ell+1} \frac{d}{dz}\left(z^{\ell+1} j_\ell(z)\right)$$

using (C-3)

$$= (n-\ell+1)\, z^{n-\ell} \cdot z^{\ell+1} j_\ell(z) + z^{n-\ell+1} \cdot z^{\ell+1} j_{\ell-1}(z)$$

$$= (n-\ell+1)\, z^{n+1} j_\ell(z) + z^{n+2} j_{\ell-1}(z) \quad . \tag{C-4}$$

Now, in (4-110) we put

$$kr = z, \quad dr = \frac{dz}{k}$$

to get

$$(n\ell\delta)^T = \int_0^\infty \frac{z^{n+2}}{k^{n+2}}\, j_\ell(z)\, e^{-\frac{\delta}{k} z} \cdot \frac{dz}{k}$$

$$= \left(\frac{1}{k}\right)^{n+3} \int_0^\infty \underbrace{z^{n+2} j_\ell(z)}_{f}\; \underbrace{e^{-\frac{\delta}{k} z}}_{g'}\, dz \quad . \tag{C-5}$$

Integration by parts gives

$$(n\ell\delta)^T = \left(\frac{1}{k}\right)^{n+3} \left\{ z^{n+2} j_\ell(z)\, e^{-\frac{\delta}{k}} \left(\frac{-k}{\delta}\right) \right|_0^\infty$$

since $j_\ell(z) \to z^\ell$

$$= \int_0^\infty \frac{d}{dz}\left[z^{n+2}\, j_\ell(z)\right] e^{-\frac{\delta}{k}z} \left(\frac{-k}{\delta}\right) dz\} \quad .$$

Using (C-4):

$$(n\ell\delta)^T = \left(\frac{1}{k}\right)^{n+3} \cdot \frac{k}{\delta}\int_0^\infty \{(n-\ell+1)\, z^{n+1}\, j_\ell(z) + z^{n+2}\, j_{\ell-1}(z)\} \times$$

$$\times\; e^{-\frac{\delta}{k}z}\, dz$$

$$= \frac{n-\ell+1}{\delta} \cdot \left(\frac{1}{k}\right)^{n+2} \int_0^\infty z^{n+1}\, e^{-\frac{\delta}{k}z}\, j_\ell(z)\, dz$$

$$+ \frac{k}{\delta}\left(\frac{1}{k}\right)^{n+3} \int_0^\infty z^{n+2}\, e^{-\frac{\delta}{k}z}\, j_{\ell-1}(z)\, dz$$

or using (C-5),

$$(n\ell\delta)^T = \frac{n-\ell+1}{\delta}\,(n-1,\ell,\delta)^T + \frac{k}{\delta}\,(n,\ell-1,\delta)^T \quad . \qquad \text{(C-5a)}$$

Eqn (C-1) follows immediately from the transformation $\ell \to \ell+1$, $\ell-1 \to \ell$ and a little rearrangement.

2. $$\frac{2\ell+1}{k}\,(n-1,\ell,\delta)^T = (n,\ell+1,\delta)^T + (n,\ell-1,\delta)^T \quad . \qquad \text{(C-6)}$$

Proof: We use the recurrence relation for spherical Bessel functions (Abramowitz and Stegun, eqn 10.1.19):

$$j_\ell(kr) = \frac{kr}{2\ell+1}\,[j_{\ell-1}(kr) + j_{\ell+1}(kr)] \quad . \qquad \text{(B-7)}$$

In (4-110), this gives

$$(n\ell\delta)^T = \frac{k}{2\ell+1}\{\int_0^\infty r^{(n+1)+2}\, j_{\ell-1}(kr)\, e^{-\delta r}\, dr + \int_0^\infty r^{(n+1)+2}\, j_{\ell+1}\, e^{-\delta r}\, dr\}$$

$$= \frac{k}{2\Pi+1}\{(n+1,\ell-1,\delta)^T + (n+1,\ell+1,\delta)^T\} \quad .$$

Putting $n \to n-1$ gives (C-6).

3. $$(n+\ell+2)(n,\ell-1,\delta)^T + (n-\ell+1)(n,\ell+1,\delta)^T = \delta(\frac{2\ell+1}{k})\,(n,\ell,\delta)^T \quad . \qquad \text{(C-7)}$$

<u>Proof</u>: In (C-5a) multiply by $(2\ell+1)$ and rearrange:

$$\delta(\frac{2\ell+1}{k})(n\ell\delta)^T = (n-\ell+1)(n-1,\ell,\delta)^T\cdot(\frac{2\ell+1}{k}) + (2\ell+1)(n,\ell-1,\delta)^T \, . \qquad \text{(C-8)}$$

Use (C-6) to replace $(n-1,\ell,\delta)^T$ in this equation, giving

$$\delta(\frac{2\ell+1}{k})(n\ell\delta)^T = (n-\ell+1)\ \{(n,\ell-1,\delta)^T\} + (n,\ell+1,\delta)^T + (2\ell+1)(n,\ell-1,\delta)^T$$

$$= (n+\ell+2)(n,\ell-1,\delta)^T + (n-\ell+1)(n,\ell+1,\delta)^T \quad . \qquad \text{(C-7)}$$

4. $$\delta(n\ell\delta)^T + k(n,\ell+1,\delta)^T = (n+\ell+2)(n-1,\ell,\delta)^T \quad . \qquad \text{(C-9)}$$

<u>Proof</u>: In (C-1) put $\ell \to \ell-1$

$$\delta(n,\ell,\delta)^T = (n-\ell+1)(n-1,\ell,\delta)^T + k(n,\ell-1,\delta)^T \quad . \qquad \text{(C-10)}$$

Add (C-10) to (C-11) to get (C-9).

5. $$(k^2+\delta^2)(n,\ell,\delta)^T + (n-\ell)k(n-1,\ell+1,\delta)^T = (n+\ell+2)\delta(n-1,\ell,\delta)^T \quad . \qquad \text{(C-12)}$$

Proof: In (C-1) put $\ell \rightarrow \ell+1$, then multiply by k:

$$k^2(n,\ell,\delta)^T + k(n-\ell)(n-1,\ell+1,\delta)^T = k\delta(n,\ell+1,\delta)^T \quad . \qquad \text{(C-13)}$$

Multiply (C-9) by δ:

$$\delta^2(n\ell\delta)^T + k\delta(n,\ell+1,\delta)^T = \delta(n+\ell+2)(n-1,\ell,\delta)^T \quad . \qquad \text{(C-14)}$$

Add (C-13) to (C-14) to get (C-12).

6. $$(k^2+\delta^2)(n,\ell,\delta)^T + (n-\ell)(n+\ell+1)(n-2,\ell,\delta)^T = 2(n+1)\delta(n-1,\ell,\delta)^T \quad . \qquad \text{(C-15)}$$

Proof: In (C-9) put $n \rightarrow n-1$, then multiply by $(n-\ell)$:

$$(n-\ell)(n+\ell+1)(n-2,\ell,\delta)^T = k(n-\ell)(n-1,\ell+1,\delta)^T + (n-\ell)\delta(n-1,\ell,\delta)^T \quad . \qquad \text{(C-16)}$$

Add this to (C-12) to get

$$\begin{aligned}(k^2+\delta^2)(n,\ell,\delta)^T &+ (n-\ell)(n+\ell+1)(n-2,\ell,\delta)^T \\ &= \{\delta(n+\ell+2) + \delta(n-\ell)\}(n-1,\ell,\delta)^T \\ &= (2n+2)\delta(n-1,\ell,\delta)^T \quad . \qquad \text{(C-15)}\end{aligned}$$

Note the difference between this equation and eqn (203) of Harris and Michels, which is believed to be in error.

7. $$(n+\ell+2)k(n-1,\ell,\delta)^T + (n-\ell)\delta(n-1,\ell+1,\delta)^T = (k^2+\delta^2)(n,\ell+1,\delta)^T \qquad \text{(C-17)}$$

Proof: Multiply (C-9) by k:

$$k\delta(n,\ell,\delta)^T + k^2(n,\ell+1,\delta)^T = k(n+\ell+2)(n-1,\ell,\delta)^T \qquad \text{(C-18)}$$

and (C-1) by δ:

$$\text{(C-1)} \times \delta\text{:} \; -k\delta(n,\ell,\delta)^T + \delta^2(n,\ell+1,\delta)^T = \delta(n-\ell)(n-1,\ell+1,\delta)^T \qquad \text{(C-19)}$$

Add (C-18) to (C-19) to get (C-17).

8. $$(\ell-1,\ell,\delta)^T = \left(\frac{2\ell k}{k^2+\delta^2}\right)(\ell-2,\ell-1,\delta)^T \qquad \text{(C-20)}$$

Proof: In (C-17) put $n = \ell$

$$(\ell,\ell+1,\delta) = \frac{(2\ell+2)k}{k^2+\delta^2}\,(\ell-1,\ell,\delta)^T \qquad \text{(C-21)}$$

$\ell \rightarrow \ell-1$ gives (C-20) immediately.

9. $$(\ell,\ell,\delta)^T = \frac{(2\ell+2)\delta}{k^2+\delta^2}\,(\ell-1,\ell,\delta)^T \qquad \text{(C-22)}$$

Proof: In (C-15) put $n = \ell$.

The nine numbered recurrence relations above permit the stepwise generation of all $(n,\ell,\delta)^T$ for $n+1 \geq \ell \geq 0$, starting from $(-1,0,\delta)^T$, which has the form

10. $$(-1,0,\delta)^T = (k^2 + \delta^2)^{-1} \quad . \tag{C-23}$$

This initial value is obtained in the following manner: Explicitly, n = -1 in (4-110) gives

$$(-1,0,\delta)^T = \int_0^\infty r\, j_0(kr)\, e^{-\delta r}\, dr \quad . \tag{C-24}$$

Using (C-5) and (B-1) we get

$$\begin{aligned}(-1,0,\delta)^T &= \frac{1}{k^2} \int_0^\infty z\, j_0(z)\, e^{-\frac{\delta}{k} z}\, dz \\ &= \frac{1}{k^2} \underbrace{\int_0^\infty \sin z\, e^{-\frac{\delta}{k} z}\, dz}_{I} \quad .\end{aligned} \tag{C-25}$$

The integral I is solved by repeated integration by parts

$$\begin{aligned}I = \int_0^\infty \underbrace{\sin z}_{f}\, e^{-\frac{\delta}{k} z}\, dz &= \left(\frac{-k}{\delta}\right) e^{-\frac{\delta}{k} z} \sin z \Big|_0^\infty \\ &\quad + \frac{k}{\delta} \int_0^\infty \cos z \cdot e^{-\frac{\delta}{k} z}\, dz \\ &= \frac{k}{\delta} \left[-\frac{k}{\delta} \cos z\, e^{-\frac{\delta}{k} z} \Big|_0^\infty + \frac{k}{\delta} \underbrace{\int_0^\infty (-\sin z) e^{-\frac{\delta}{k} z}\, dz}_{-I} \right] \\ &= \frac{k^2}{\delta^2} (1 - I) \quad .\end{aligned}$$

So that

$$I\left(\frac{k^2}{\delta^2} + 1\right) = \frac{k^2}{\delta^2}$$

or

$$I = \frac{k^2}{k^2+\delta^2} \quad . \tag{C-26}$$

Substituting (C-26) into (C-25) gives (C-23).

It was formula (C-23) which first endeared us to the method of Harris and Michels: the capacity to solve attraction integrals with a Yukawa potential (eqn (4-73)).

We derive here an identity which is interesting in its own right, but which HM did not report.

Starti[illegible]om (C-20) we reduce $\ell \to \ell-1$ systematically:

$$(\ell-1,\ell,\delta)^T = \frac{2\ k}{k^2+\delta^2}\,(\ell-2,\ell-1,\delta)^T \quad . \qquad \text{(C-20)}$$

$$= \frac{2\ell k}{k^2+\delta^2}\cdot\frac{2(\ell-1)k}{(k^2+\delta^2)}\,(\ell-3,\ell-2,\ell-1)^T$$

$$\vdots$$

$$= \left(\frac{2k}{k^2+\delta^2}\right)^m \ell(\ell-1)(\ell-2)\ \ldots\ (\ell-m+1)(\ell-m-1,\ell-m,\delta)^T$$

$$\vdots$$

11. $$(\ell-1,\ell,\delta)^T = \left(\frac{2k}{k^2+\delta^2}\right)^{\ell}\ \ell!\ (-1,0,\delta)^T \quad . \qquad \text{(C-20a)}$$

However in this work, it is clear that our main interest is not in generating the $(n,\ell,\delta)^T$, but the auxiliary functions $B_{n\ell i}(\delta)$ of eqns (4-128) - (4-131). This we do in the next section.

Auxiliary Function $B_{n\ell i}(\delta)$

The recurrence relations for $B_{n\ell i}(\delta)$ are deduced from those of $(n,\ell,\delta)^T$. For this purpose, we depend heavily on eqn (4-125).

A few relations follow.

1. $$B_{-101} = 1 \quad . \tag{C-27}$$

This is obtained by inserting (C-23) into (4-125). There is only one term in the summation: $i = 1$.

2. $$B_{\ell-1,\ell,\ell+1} = 2\ell\, B_{\ell-2,\ell-1,\ell} \quad . \tag{C-28}$$

Proof: In (4-125), put $\ell = n-1$. This means $\frac{2\ell+2}{2} \leq i \leq \ell+1$, or $i = \ell+1$. Again there is only one term, giving

$$(\ell-1,\ell,\delta)^T = k^\ell\, B_{\ell-1,\ell,\ell+1} \cdot (k^2+\delta^2)^{-(\ell+1)} \quad . \tag{C-29}$$

Putting $\ell \to \ell-1$ in (c-29), we get

$$(\ell-2,\ell-1,\delta)^T = k^{\ell-1}\, B_{\ell-2,\ell-1,\ell}\, (k^2+\delta^2)^{-(\ell)} \quad , \tag{C-30}$$

which of course has only one term. Combine (C-29) and (C-30) using (C-22) to get

$$k^\ell\, B_{\ell-1,\ell,\ell+1} (k^2+\delta^2)^{-(\ell+1)} = \frac{2k\ell}{k^2+\delta^2} \cdot k^{\ell-1}\, B_{\ell-2,\ell-1} (k^2+\delta^2)^{-\ell}$$

which is precisely (C-28).

An explicit relation for $B_{\ell-1,\ell,\ell+1}$ can be obtained from (C-20a), when this is written as

$$\begin{aligned}(\ell-1,\ell,\delta)^T &= \left(\frac{2k}{k^2+\delta^2}\right)^\ell \ell!\, (k^2+\delta^2)^{-1} \\ &= k^\ell \cdot 2^\ell\, \ell!\, (k^2+\delta^2)^{-(\ell+1)}\end{aligned}$$

2a. $$B_{\ell-1,\ell,\ell+1} = 2^{\ell}\,\ell! \qquad \text{(C-28a)}$$

This can be used instead of (C-28) or (5-129).

3. $$B_{\ell,\ell,\ell+2} = (2\ell+2)\,\delta\,B_{\ell-1,\ell,\ell+1} \qquad \text{(C-31)}$$

Proof: In (5-125) put $n = \ell$. Then

$$\frac{1}{2}(\ell+\ell+3) \le i \le \ell+2$$

or $i = \ell+2$, again only one term. Thus

$$(\ell,\ell,\ell+2) = k^{\ell}\,B_{\ell,\ell,\ell+2}\,(k^2+\delta^2)^{-(\ell+2)} \qquad \text{(C-32)}$$

Using (C-22) and (C-29), (C-31) results.

Notice the slight difference from HM eqn 67, which we believe to contain a misprint.

Using (C-28a), we get an explicit expression

3a. $$\begin{aligned} B_{\ell,\ell,\ell+2} &= (2\ell+2)\delta \cdot 2^{\ell}\,\ell! \\ &= 2^{\ell+1} \cdot (\ell+1)!\,\delta \qquad \text{(C-31a)} \end{aligned}$$

which can be used instead of (C-31) or (5-130).

4. $$\begin{aligned} B_{n\ell i} = 2(n+1)\delta\,B_{n-1,\ell,i-1} - (n-\ell)(n+\ell+1) \\ \cdot\,B_{n-2,\ell,i-1} \qquad \text{(C-33)} \end{aligned}$$

Proof: We rewrite (C-15) in terms of (5-125):

$$(n\ell\delta)^T = \frac{2(n+1)(n-1,\ell,\delta)^T}{(k^2+\delta^2)} - \frac{(n-\ell)(n+\ell+1)(n-2,\ell,\delta)^T}{(k^2+\delta^2)}$$

becomes, by (5-125),

$$k^\ell \sum_i B_{n\ell i}(k^2+\delta^2)^{-i} = k^\ell \sum_i 2(n+1)\delta B_{n-1,\ell,i}(k^2+\delta^2)^{-(i+1)}$$

$$+ k^\ell \sum_i [-(n-\ell)(n+\ell+2)B_{n-2,\ell,i}(k^2+\delta^2)^{-(i+1)}] .$$

Equating terms associated with the same power (-i) of $(k^2+\delta^2)$, (C-33) results immediately.

Again we note the apparent misprint in HM formula (68).

Equation (C-33) does not, of course, mean all the terms in the right hand side necessarily exist at the same time, because their existence is governed by the limits on i (eqn (5-125). But a counter check on the formulas is that (C-33) reduces to (C-31) or (C-28) under the appropriate conditions.

Basically, we used (5-128) - (5-131) to generate all $B_{n\ell i}$ needed in (5-134), both with δ_1 and δ_2. In the case $\delta_1 = \delta_2$, of course, once is enough.