NON-MUFFIN-TIN CORRECTIONS TO THE TOTAL MOLECULAR ENERGY IN THE MULTIPLE-SCATTERING Xα METHOD OF MOLECULAR CALCULATION

By

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NON-MUFFIN-TIN CORRECTIONS TO THE TOTAL MOLECULAR ENERGY IN THE MULTIPLE-SCATTERING Xα METHOD OF MOLECULAR CALCULATION

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An investigation of the muffin-tin (MT) approximation to the total electron density in the multiple-scattering Xα method of molecular calculations is carried out. A method is developed to improve upon the shortcomings of the MT approximation in the calculation of the Xα total energy by including the non-muffin-tin (NMT) correction to the density in the Xα total energy calculation. This results in a small NMT correction term to the total MT Xα energy which takes the form of numerical three- and six-dimensional integrals. It is shown that the method of including the NMT correction terms is analogous to the first order perturbation calculation and it is inferred from this and the smallness of the correction that the resulting total energy is quite close to the exact Xα energy. An extensive numerical sampling and integration scheme is developed with which to integrate the NMT correction term whose integrands are rather complex functions.

Calculations are performed on two molecules--C_2 and Ne_2-which it is argued should provide definitive tests for the method of improving the MT Xα total energy with the NMT correction. The multiple-scattering Xα method in the MT approximation predicts that the potential curves for both molecules in their ground states are repulsive. In reality both molecules in their ground state bind with C_2 binding with 0.468 Rydbergs and Ne_2 with 0.00023 Rydbergs. (The extremely small binding of Ne_2 is attributed to van der Waals attraction.)

It is found that in the case of both molecules with the NMT correction included a significant qualitative and quantatative improvement is made in the total energy. For C_2 three points on the potential curve near the equilibrium internuclear separation are calculated with the NMT correction and a thorough analysis of the correction and its component parts is made. For C_2 a binding potential curve is predicted which compares quite favorably with a CI calculation on C_2 and which predicts spectroscopic constants in substantial agreement with experiments. For Ne_2 only one point on the potential curve is calculated very near the experimental equilibrium internuclear separation. With the NMT correction binding is definitely predicted for Ne_2 but due to the difficulty of this particular calculation the error in the binding is such that the precise amount of binding cannot be specified.

In light of these results for these two dissimilar and difficult test case molecules we argue finally that not only does the NMT correction give results very close to the exact Xα results but also that these results provide additional evidence for the accuracy of the Xα approximation itself.

CHAPTER I

INTRODUCTION

1.1 Molecular Methods

The understanding of the chemical properties of materials from first principles has been the quest of quantum theory since its inception in the 1920's. In this quest quantum theory has provided the crucial frame of understanding and the calculational tools for many other fields of endeavor in physics, chemistry, and more recently biology. Within the field of quantum theory the main direction taken has been toward the calculation, prediction, and understanding of the properties of molecules (and of solids) of ever-increasing size, weight, and complexity.

There are several categories or methods of molecular calculation which can be broadly classified as ab initio, semi-empirical, and multiple-scattering $X\alpha$(MSXα). This dissertation is concerned with a particular aspect of the MSXα method. Specifically, the purpose of this dissertation is to investigate the effect of the so called "muffin-tin" (MT) approximation to the density in the total energy calculation in the MSXα method and to provide remedies for the shortcomings of this approximation.

The MSXα method is a relatively new method first

suggested by Slater (1965) and its implementation begun by Johnson (1966). The ab initio methods such as the LCAO-MO-SCF (linear combination of atomic orbitals-molecular orbital-self-consistent field) Hartree-Fock method are capable of usefully accurate calculations on smaller molecules such as water (H_2O) or ammonia (NH_3) (see Slater (1963a)) but due to the computational times involved cannot be realistically applied to larger molecules such as benzene (C_6H_6). The semi-empirical methods (see Pople and Beveridge (1970)) have been applied to systems such as benzene and even somewhat larger systems but their results are usually semi-quantitative. Further, they are parameter dependent (sometimes involving many parameters) and the selection of these parameters is something more of an art than a science. The MSXα method is a promising method since it is capable of an accuracy in ionization, transition, and total energies quite comparable to that of the ab initio LCAO-MO-SCF Hartree-Fock method but is about two orders of magnitude faster (see Slater and Johnson (1972)). This of course enhances the usefulness of the method making possible accurate calculations on larger systems such as sulfur hexaflouride (SF_6) (see Connolly and Johnson (1971)).

There are three distinguishing features of the MSXα method. It makes use of the Xα local density exchange approximation, the "muffin-tin" (MT) approximation to the total electron density and potential, and the multiple-scattering expansion of the molecular orbitals. The APW

(augmented-plane-wave) method and the KKR (Kohn-Korringa-Rostoker) methodsof solid state (see Slater (1963b)) employ an exactly analogous muffin-tin approximation. Hence similar conclusions may be drawn for these methods from the study of the muffin-tin approximation in the MSXα method. The MSXα method is a single particle molecular orbital self-consistent field method. The details of the method as well as the relevant references will be given in Chapter II of this dissertation. Two particularly comprehensive recent reviews on the subjects respectively of the Xα method and the MSXα theory are those of Slater (1972a) and Johnson (1973). The Xα approximation and the multiple-scattering formalism have been the subject of much study and even though reasonably well understood are still under development. However, the state of knowledge of the effects of the muffin-tin approximation in the MSXα theory and the developemnt of schemes for overcoming this approximation are neither as advanced nor as well developed as the former two.

1.2 The Muffin-Tin (MT) Approximation

In the MT approximation the coordinate space of a molecule is schematically divided into contiguous spherical regions surrounding the nuclei and a large outer sphere surrounding the whole molecule. Within the atomic spheres and outside the outer sphere the one-electron Xα potential and the total electron density are spherically averaged.

Between the atomic spheres and within the outer sphere in the so-called intersphere or interatomic region the potential and density are volume averaged to a constant.

The motivation behind the MT approximation of the density and potential is simple. Using the MT form of the total electron density ρ in the $X\alpha$ total energy formula--a functional of ρ which we will designate $\langle E_{X\alpha} \rangle$ --produces the MT $X\alpha$ total energy formula--a functional of the MT density $\overline{\rho}$ which we will call $\langle \overline{E_{X\alpha}} \rangle$. All of the integrals in $\langle \overline{E_{X\alpha}} \rangle$ may be reduced to one-dimensional numerical integrals whereas those of $\langle E_{X\alpha} \rangle$ involving ρ are three and six dimensional numerical integrals. From the MT $X\alpha$ energy functional $\langle \overline{E_{X\alpha}} \rangle$ we variationally derive (see Chapter III) the MT $X\alpha$ one-electron equations. The MT potential in this equation is related variationally to the MT approximation to the density which defines the functional $\langle E_{X\alpha} \rangle$. Hence the MT approximation of the $X\alpha$ potential follows from that of the density and there is really only one MT approximation--that of the density. The self-consistent solutions of the MT $X\alpha$ one-electron equations are the set of orbitals then which minimize the MT $X\alpha$ energy functional. In making the MT approximation to the X^{α} total energy we leave out the effect of the non-muffin-tin (NMT) components of the density upon the total $X\alpha$ energy. We call the difference between the $X\alpha$ total energy and MT total energy the NMT correction to the MT total energy.

Although it has been found that the ionization and

transition energies calculated by the MSXα method do not seem to be particularly sensitive to the MT approximation (see Connolly et al. (1971)) it has not been found that the MT Xα total energy calculations have been uniformly good. For example, fairly good symmetric mode potential curves for the ground states of Li_2 (see Johnson et al.(1972)) and CH_4 (see Danese (1972)) have been calculated in the MT approximation. Two solid state APW calculations employing the MT approximation by Averill (1971b)and Hattox (1972) on the compressibilities as well as other volume dependent properties of cesium and vanadium produced semi-quantitative results. However a conformational study of the water molecule by Connolly and Sabin (1972) using the MT approximation predicted the result that the water molecule was linear. These and other evidence have led to the conclusion that the MT approximation to the total energy is not always particularly good.

This dissertation has two purposes. One purpose is to investigate the effect of the MT approximation to the density upon the Xα total energy through an analysis of the non-muffin-tin corrections to the MT Xα total energy. The second purpose is to develop a general and practical method of evaluating the NMT correction to the MT Xα energy and thereby to improve upon the MT Xα energy calculation.

1.3 The Non-Muffin-Tin (NMT) Correction to the Muffin-Tin (MT) Xα Total Energy

In Chapter III we show how for a given set of assumed orbitals the Xα total energy $\langle E_{X\alpha} \rangle$ may be separated into two parts--the MT Xα total energy part $\langle \overline{E_{X\alpha}} \rangle$ and a second part which is the NMT part of $\langle E_{X\alpha} \rangle$ and which we designate as $\Delta\langle E_{X\alpha} \rangle$. In Chapter IV we examine the relationship between $\langle E_{X\alpha} \rangle$ and $\langle \overline{E_{X\alpha}} \rangle$ via $\Delta\langle E_{X\alpha} \rangle$. We show that using the set of orbitals which minimizes $\langle \overline{E_{X\alpha}} \rangle$ to calculate $\langle E_{X\alpha} \rangle$ is analogous to a first order perturbation calculation--$\Delta\langle E_{X\alpha} \rangle$ being the perturbation to $\langle \overline{E_{X\alpha}} \rangle$. Hence the energy calculated in this manner has only a second order dependence upon the difference between the exact Xα orbitals and the MT Xα orbitals. Because of this and because the NMT correction (estimated) in most cases appears to be quite small we argue that our approximation to the exact Xα energy should be fairly good. However, even though the correction may be small it can be quite important if one is interested in a small effect such as the binding of a molecule. Hence to be able to calculate binding energies accurately with this correction in cases in which the binding predicted by the MT approximation is either very bad or non-existent (unbound) would be a good test of this method.

The NMT correction $\Delta\langle E_{X\alpha} \rangle$ takes the form of three- and six-dimensional integrals which must be evaluated numerically. In Chapter V we develop an importance sampling

scheme which combined with the Monte-Carlo method of numerical integration results in an admittedly complex but nevertheless workable integration scheme whereby the numerical integrals of $\Delta\langle E_{X\alpha}\rangle$ may be performed in very reasonable calculational times.

In Chapter VI we give the results and conclusions. We chose as our test cases two relatively dissimilar but simple molecules--C_2 and Ne_2. However, they are difficult cases. Both are actually bound in their ground state but neither is bound in the MT Xα approximation. In fact for the ground state of C_2 the MT Xα approximation predicts a distinctly repulsive potential curve whereas in reality in its ground state C_2 is bound by 0.468 Rydbergs. This represents a rather drastic failure of the MT Xα method. The Ne_2 molecule is bound by the extremely small amount of 0.00023 Rydbergs. This binding is usually described as van der Waals binding. It might appear questionable as to whether the exact Xα method let alone the approximate Xα method with NMT correction would produce binding for this molecule. Our findings are however that the NMT correction results in binding for both cases. For C_2 it predicts a potential curve and spectroscopic constants for the ground state which compare quite favorable with a CI calculation by Fougere and Nesbet (1966) and with experiment. For Ne_2 definite binding is predicted, although due to statistical as well as other errors the amount of binding can only be determined approximately. From these

results and further analysis in Chapter VI we conclude that the NMT correction $\Delta\langle E_{XC}\rangle$ provides a significant qualitative and quantitative improvement to the MT Xα total energy. Further, due to the significant correlation of the results with experiment we feel these results represent additional evidence for the accuracy of the exact Xα approximation itself.

CHAPTER II

THE MOLECULAR Xα TOTAL ENERGY AND ONE-ELECTRON EQUATIONS

2.1 Introduction

The discussion in this chapter will be concerned with the basic Xα theory. This chapter is given as background for and an introduction to the next two chapters in which will be discussed first the muffin-tin approximation of the Xα total energy and then the relation between this energy and the exact Xα total energy. In this chapter we wish to emphasize that in exact Xα theory no restrictions are placed on the spatial form of the electron density ρ which is used in the evaluation of the Xα total energy $\langle E_{X\alpha} \rangle$. In the evaluation of the muffin-tin Xα total energy, $\overline{\langle E_{X\alpha} \rangle}$, a particular averaged form of the density, $\overline{\rho}$, is used. Since the form for the energy in the two cases is different it will be shown that the differential equations which the one-electron self-consistent orbitals must satisfy will also be different. Besides giving some of the general characteristics of the Xα theory in this chapter we will derive by the calculus of variations the one-electron differential equations which a set of orbitals must satisfy in order to make $\langle E_{X\alpha} \rangle$ a minimum.

2.2 Xα Theory

The Xα method as applied to atoms, molecules and solids is covered in detail in a forthcoming book by Slater (1973). Two review articles covering the subject have been recently published, one by Slater (1972a) and the other by Slater and Johnson (1972). The former contains a comprehensive bibliography of the Xα theory and its applications since 1965.

The Xα method is a one-electron self-consistent field (SCF) method and as such it is an approximate method and cannot give an exact treatment of many body problems. For example, in general it cannot give a complete description of multiplets, although spin-polarized Xα calculations can give partial information about multiplet separations (see Slater (1968)).

The Xα total energy for a molecule is expressed as a functional of the one-electron orbitals U_i. We may define the spin up and spin down charge densities ($\rho\uparrow$ and $\rho\downarrow$) as

$$\rho\uparrow = \sum_{i\uparrow} n_i U_i^* U_i; \quad \rho\downarrow = \sum_{i\downarrow} n_i U_i^* U_i; \quad \rho = \rho\uparrow + \rho\downarrow. \qquad (2.1)$$

The summation for each spin is carried out over the occupied spin orbitals for that particular spin. The occupation numbers n_i may have any value between zero and one (a feature different from Hartree-Fock in which the n_i must be either zero or one). The formula for total energy of a molecular system in the Xα method is (in Rydberg units)

$$\langle E_{X\alpha} \rangle = \sum_i n_i \int U_i^*(\vec{r}_1) [-\nabla_1^2 U_i(\vec{r}_1)] d\vec{r}_1 + \int \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}_1 - \vec{R}_\alpha|} \rho(\vec{r}_1) d\vec{r}_1$$

$$+ \frac{1}{2} \iint \frac{2\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \int \rho\uparrow(\vec{r}_1) U_{X\alpha\uparrow}(\vec{r}_1) d\vec{r}_1$$

$$+ \frac{1}{2} \int \rho\downarrow(\vec{r}_i) U_{X\alpha\downarrow}(\vec{r}_1) d\vec{r}_1 + \frac{1}{2} \sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}}^{N} \frac{2Z_\alpha Z_\beta}{R_{\alpha\beta}} . \quad (2.2)$$

In this formula the first term is the kinetic energy term and the summation in this term is over all states regardless of spin. The second term is the nuclear-electron Coulomb interaction term and the summation in this term is over all the nuclei α. The third term is the classical Coulomb interaction term and the fourth and fifth terms are the "exchange-correlation" terms (see Slater (1972a)). The last term is the classical nuclear interaction term. The exchange-correlation potential $U_{X\alpha\uparrow}$ is defined explicitly as

$$U_{X\alpha\uparrow}(\vec{r}_1) = -9\alpha[(3/4\pi)\rho\uparrow(\vec{r}_1)]^{1/3}, \quad (2.3)$$

and similarly for $U_{X\alpha\downarrow}$.

For simplicity in the present treatment we will assume that the orbitals for spin up and spin down electrons are identical. This results in a so called non-spin polarized version of the formalism. For a system like the ground state of the C_2 molecule, the main system of interest in the present work, in which the number of spin up and spin down electrons is equal and which near the molecular

equilibrium position in the ground state exists in a closed shell configuration, the results of spin-polarized and non-spin-polarized calculations are identical (i.e., they produce the same orbitals). Everything discussed here and in the following sections may be generalized for the spin-polarized case. The non-spin-polarized assumption does not preclude the possibility of fractional occupation numbers or non-closed shells. We may still think of the occupation numbers as varying from zero to one for a given orbital but are equal for both spins. If one does assume that the orbitals for spin up and spin down electrons are the same for every state and the number (fractional or not) of spin up and spin down electrons is the same, then

$$\rho\downarrow = \rho\uparrow = \rho/2,$$

and

$$U_{X\alpha\uparrow} = U_{X\alpha\downarrow} = U_{X\alpha} \tag{2.4}$$

where

$$U_{X\alpha}(\vec{r}_1) = -9\alpha[(3/8\pi)\rho(\vec{r}_1)]^{1/3}. \tag{2.5}$$

The Xα total energy will then be given by

$$\begin{aligned}\langle E_{X\alpha}\rangle = {} & \sum_i n_i \int U_i^*(\vec{r}_1)[-\nabla_1^2 U_i(\vec{r}_1)]d\vec{r}_1 + \int \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}_1-\vec{R}_\alpha|}\rho(\vec{r}_1)d\vec{r}_1 \\ & + \frac{1}{2}\iint \frac{2\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}d\vec{r}_1 d\vec{r}_2 + \frac{1}{2}\int \rho(\vec{r}_1)U_{X\alpha}(\vec{r}_1)d\vec{r}_1 \\ & + \frac{1}{2}\sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}}^{N} \frac{2Z_\alpha Z_\beta}{R_{\alpha\beta}}.\end{aligned} \tag{2.6}$$

The non-spin-polarized assumption and the resulting slightly simplier above form for $\langle E_{X\alpha} \rangle$ will be used in the rest of this study.

The exchange-correlation potential is linearly dependent on a parameter - the "α" parameter. At the present point of development of the Xα theory this parameter is chosen to be different for each atom varying from slightly less than one (0.98) for hydrogen to slightly greater than two-thirds for the heavier elements (see Schwarz (1972)). The means of determining α for free atoms has been discussed in the literature and is still under development (see Lindgren and Schwarz (1972)). It consists presently of adjusting the value of α until the Xα energy of the free atom equals the Hartree-Fock energy for the atom.

A further point must be discussed. As indicated the method of determining the α parameter is well defined for free atoms. However, when atoms are bound together into a molecule a prescription must be used to fix the value of α used in different parts of the molecule. A very simple and sensible way of doing this is to divide the molecule into regions and use the value of α for the free atom in a spherical region surrounding the atom or nucleus in the molecule. In the region left over between the spherical atomic regions use a weighted value of α between the atomic α values used. If the molecule is homonuclear, as for the cases C_2 and Ne_2 which are treated in this study, this is not

a problem since the same value of α is used throughout the molecule.

Although there are similarities the Xα method is different from Hartree-Fock in at least two important ways. First, the Xα theory as applied to molecules in the MSXα method treats the separation of molecules into their atomic constituents in a manner which leads to more physically meaningful separation limits (see Slater and Johnson (1972)). Thus for the H_2 molecule (to take the simplest possible case) the MSXα method "dissociates" the molecule into two neutral hydrogen atoms whereas Hartree-Fock theory predicts a separation limit which is a mixture of ionized and neutral states. (This point will be further discussed in Chapter VI where the NMT calculations for the potential curve of C_2 are discussed.) Second, the eigenvalues in the Xα method have a different relation to the total energy in that the eigenvalue ε_i for a state i is related to the Xα total energy as a partial derivative with respect to the occupation number n_i for the state i (see Slater et al. (1969))

$$\varepsilon_{iX\alpha} = \frac{\partial \langle E_{X\alpha} \rangle}{\partial n_i} . \qquad (2.7)$$

This relation leads to a different way of calculating transition and ionization energies, a subject to be briefly discussed later in this chapter. It also ensures that the method satisfies Fermi statistics. That is, the system has its lowest total energy when the levels of the lowest

eigenvalues are filled with n_i=1 up to the Fermi energy ϵ_F and all the levels above the Fermi energy are empty. Relation (2.7) also allows for the possibility of non-integral occupation numbers at the Fermi energy (see Slater et al. (1969) and Slater (1972a)). The point emphasized here is that the Xα theory is not just an approximation to Hartree-Fock theory but stands as a separate and in some ways superior theory (see also Slater and Johnson (1972)).

2.3 Derivation of the Xα One-Electron Equations

The Xα total energy as expressed in Eq. (2.6) is a functional of the orbital functions U_i. To find the ground state energy of the system represented by $\langle E_{X\alpha} \rangle$ we must find the set of orbitals $\{U_i\}$ such that $\langle E_{X\alpha} \rangle$ is stationary with respect to arbitrary variations of the U_i. The variation of $\langle E_{X\alpha} \rangle$ must take place subject to the restraints imposed by the orthonormality conditions of the orbitals. We can handle the restraint conditions by introducing a Lagrange multiplier, λ_{ij}, for each condition between two orbitals i and j. Note that we are working under the non-spin-polarized assumption and under this assumption the spin up and spin down orbitals are identical. I am also assuming for now that the number of spin up and spin down electrons for each orbital is identical, although perhaps fractional. Since the occupation number n_i for an orbital i may be fractional it is convenient to introduce a factor $n_i^{1/2} n_j^{1/2}$ with each Lagrange multiplier λ_{ij}. (It is clear that the

factor $n_i^{1/2} n_j^{1/2}$ may be absorbed into the Lagrange multiplier λ_{ij} but this leads to awkward expressions later.)

In order to find the minimum of $\langle E_{X\alpha} \rangle$ with respect to arbitrary variation of the $\{U_i\}$ we demand

$$\delta\{\langle E_{X\alpha} \rangle + \sum_{i,j} n_i^{1/2} n_j^{1/2} \lambda_{ij} \int U_i^*(\vec{r}_1) U_j(\vec{r}_1) d\vec{r}_1 = 0. \quad (2.8)$$

Since the U_i's are required to be orthonormal we take the λ_{ij}'s to be hermitean. (The summations over i and j are over all states, spin up and spin down.) If $\langle E_{X\alpha} \rangle$ is a minimum, it is a minimum for the variation of any orbital U_i, hence we vary Eq. (2.8) with respect to an orbital U_i. We first consider the variation of Eq. (2.6) using the functional derivative notation*

$$\delta\langle E_{X\alpha} \rangle = \int \frac{\delta}{\delta U_i^*(\vec{r})} \langle E_{X\alpha} \rangle \delta U_i^*(\vec{r}) d\vec{r} + (\text{Complex Conjugate}). \quad (2.9)$$

Here $\delta U_i^*(\vec{r})$ is an arbitrary variation of the function $U_i^*(\vec{r})$ over its whole range of definition. Consider the kinetic-energy part of $\langle E_{X\alpha} \rangle$ in Eq. (2.6) first

$$\int \frac{\delta}{\delta U_i^*(\vec{r})} \sum_i n_i \int U_i^*(\vec{r}_1) [-\nabla_1^2 U_i(\vec{r}_1)] \delta U_i^*(\vec{r}) d\vec{r}_1 d\vec{r} + (\text{Complex Conjugate})$$

$$= \iint n_i \delta U_i^*(\vec{r}) \delta(\vec{r}-\vec{r}_1) [-\nabla_1^2 \cdot U_i(\vec{r}_1)] d\vec{r}_1 d\vec{r}$$

$$+ \iint n_i U_i^*(\vec{r}_1) [-\nabla_1^2 \delta(\vec{r}-\vec{r}_1) \cdot \delta U_i(\vec{r})] d\vec{r}_1 d\vec{r}. \quad (2.10)$$

---

*See Appendix A.

Integrating over $\vec{r}_1$ and using the Hermitean property of the kinetic energy operator

$$\int \frac{\delta}{\delta U_i^*(\vec{r})} \sum_i n_i \int U_i^*(\vec{r}_1)[-\nabla_1^2 U_i(\vec{r}_1)]\delta U_i^*(\vec{r})d\vec{r}_1 d\vec{r} + (\text{Complex Conjugate})$$

$$= n_i \int \delta U_i^*(\vec{r})[-\nabla^2 U_i(\vec{r})]dr + (\text{Complex Conjugate}). \qquad (2.11)$$

Taking the variation of the Lagrange multiplier part in Eq. (2.8) gives

$$\delta\Big(\sum_{i,j} n_i^{1/2} n_j^{1/2} \lambda_{ij} \int U_i^*(\vec{r}_1) U_j(\vec{r}_1) d\vec{r}_1\Big)$$

$$= n_1^{1/2} \sum_j n_j^{1/2} \int \delta U_i(\vec{r}) U_j(\vec{r}) d\vec{r}$$

$$+ (\text{Complex Conjugate}). \qquad (2.12)$$

Now we must take the variation of the remaining part of $\langle E_{X\alpha} \rangle$ in Eq. (2.8) which we denote as V_T:

$$\delta V_T = \delta\Big\{\int \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}_1 - R_\alpha|} \rho(\vec{r}_1) d\vec{r}_1 + \frac{1}{2}\iint \frac{2\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

$$+ C\alpha \int \rho(\vec{r}_1)^{4/3} d\vec{r}_1\Big\} \qquad (2.13)$$

where $C\alpha = -(9/2)\alpha(3/8\pi)^{1/3}$. Each of the terms in V_T is a functional of the electron density ρ, hence we may write

$$\delta V_T = \frac{\delta}{\delta U_i^*(\vec{r})} V_T(\rho(r_1))\delta U_i^*(\vec{r})d\vec{r} + (\text{Complex Conjugate}),$$

$$= \iint \frac{\delta}{\delta\rho(r')} V_T(\rho(\vec{r}_1)) \frac{\delta\rho(r')}{\delta U_i^*(\vec{r})} \delta U_i^*(\vec{r}) d\vec{r}' d\vec{r} + (\text{Complex Conjugate}) \qquad (2.14)$$

Using expression (2.13) above

$$\frac{\delta V_T(\rho(\vec{r}_1))}{\delta\rho(\vec{r}')} = \int \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}_1-\vec{R}|} \cdot \frac{\delta\rho(\vec{r}_1)}{\delta\rho(\vec{r}')}\, d\vec{r}_1$$

$$+ \iint \frac{2\rho(\vec{r}_2)\,\delta\rho(\vec{r}_1)}{r_{12}\,\delta\rho(\vec{r}')}\, d\vec{r}_1 d\vec{r}_2 + C\alpha \int (4/3)\,\rho(\vec{r}_1)^{1/3}$$

$$\cdot \frac{\delta\rho(\vec{r}_1)}{\delta\rho(\vec{r}')}\, d\vec{r}_1. \qquad (2.15)$$

It should be noted that the second term occurs without the factor of 1/2 which it had in expression (2.13) above. This is so since the variables of the integral are dummy variables and the variation actually gives two terms which are identical. Replacing $\delta\rho(\vec{r}_1)/\delta\rho(\vec{r}')$ by $\delta(\vec{r}_1-\vec{r}')$ and integrating over $\vec{r}_1$ we have that

$$\frac{\delta V_T(\rho(\vec{r}_1))}{\delta\rho(\vec{r}')} = \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}'-\vec{R}_\alpha|} + \int \frac{2\rho(\vec{r}_2)}{|\vec{r}'-\vec{r}_2|}\, d\vec{r}_2$$

$$+ \frac{4}{3} C\alpha\rho(\vec{r}')^{1/3}. \qquad (2.16)$$

Still working on expression (2.14) consider the term $\delta\rho(\vec{r}')/\delta U_i^*(\vec{r})$:

$$\frac{\delta\rho(\vec{r}')}{\delta U_i^*(\vec{r})} = \frac{\delta}{\delta U_i^*(\vec{r})} \sum_i n_i U_i^*(\vec{r}')U_i(\vec{r}'),$$

$$= n_i \delta(\vec{r}'-\vec{r})U_i(\vec{r}'),$$

and

$$\frac{\delta\rho(\vec{r}')}{\delta U_i(\vec{r})} = n_i U_i^*(\vec{r}')\delta(\vec{r}'-\vec{r}). \qquad (2.17)$$

Substituting expressions (2.16) and (2.17) into expression (2.13) we have that

$$\delta V_T = \int\int n_i \delta U_i^*(\vec{r}) \{ \sum_{=1}^{N} \frac{-2Z_\alpha}{|\vec{r}'-R_\alpha|} + \int \frac{2\rho(\vec{r}_2)}{|\vec{r}'-\vec{r}_2|} d\vec{r}_2 + \frac{4}{3} C\alpha\rho(\vec{r}')^{1/3} \} U_i(\vec{r}') \delta(\vec{r}'-\vec{r}) d\vec{r}' d\vec{r}$$

$$+ \text{(Complex Conjugate)}. \qquad (2.18)$$

Performing the integration over $\vec{r}'$ we are left with

$$\delta V_T = \int n_i \delta U_i^*(\vec{r}) \{ \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}-\vec{R}_\alpha|} + \int \frac{2\rho(\vec{r}_2)}{|\vec{r}-\vec{r}_2|} d\vec{r}_2 + \frac{4}{3} C\alpha\rho(\vec{r})^{1/3} \} U_i(\vec{r}) d\vec{r} + \text{(Complex Conjugate)}. \qquad (2.19)$$

If the first terms in expressions (2.11), (2.12) and (2.19) are zero then so are their complex conjugates. Hence we drop the complex conjugate terms and Eq. (2.8) becomes

$$0 = \delta\{\langle E_{X\alpha} \rangle + \sum_{i,j} n_i^{1/2} n_j^{1/2} \lambda_{ij} \int U_i^*(\vec{r}_1) U_j(\vec{r}_1) d\vec{r}_1\},$$

$$= n_i^{1/2} \int \delta U_i^*(\vec{r}) \{ [-\nabla^2 + \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}-\vec{R}_\alpha|} + \int \frac{2\rho(\vec{r}_2)}{|\vec{r}-\vec{r}_2|} d\vec{r}_2 + \frac{4}{3} C\alpha\rho(\vec{r})^{1/3}] n_i^{1/2} U_i(\vec{r}) + \sum_j n_j^{1/2} \lambda_{ij} U_j(\vec{r}) \} d\vec{r}. \qquad (2.20)$$

Since this expression must be zero for arbitrary variation of the orbital $U_i(\vec{r})$ we may take the entire expression inside the curly bracket to be zero, hence:

$$\left[-\nabla^2 + \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}-\vec{R}_\alpha|} + \int \frac{2\rho(\vec{r}_2)}{|\vec{r}-\vec{r}_2|}\, d\vec{r}_2 + \frac{4}{3} C\alpha\rho(\vec{r})^{1/3}\right] n_i^{1/2} U_i(\vec{r})$$

$$= -\sum_j n_j^{1/2} \lambda_{ij} U_j(\vec{r}). \qquad (2.21)$$

We obtain the same type equation for each U_i.

In its present form Eq. (2.21) is a set of coupled equations due to the mixing by the Lagrange multipliers on the right hand side of the equation. The λ_{ij} matrix is Hermitean and hence may be diagonalized uniquely by some unitrary transformation. This transformation results in a transformation of the orbitals which may be defined such that the density remains invariant. If the density remains invariant then so does the operator on the left hand side of Eq. (2.21). This is easily shown. Note that the orbitals U_i in Eq. (2.24) occur with a coefficient $n_i^{1/2}$; we must take this into account. We postulate a transformation on the orbitals U_i involving a unitary transformation $\tilde{C}$ such that (using matrix notation)

$$\tilde{n}^{1/2}\tilde{U}' = \tilde{C}\tilde{n}^{1/2}\tilde{U}. \qquad (2.22)$$

In this expression, $\tilde{C}$ is an nxn unitary matrix, $\tilde{n}^{1/2}$ is an nxn diagonal matrix whose (i,i) element is $n_i^{1/2}$, and $\tilde{U}'$ and $\tilde{U}$ are the orbital vectors. Note that the same matrix $\tilde{n}^{1/2}$ occurs on both sides of Eq. (2.22), and Eq. (2.22) serves as the defining relation for the new orbitals U_i'. Another way of writing Eq. (2.22) is

$$n_i^{1/2}U_i' = \sum_j C_{ij} n_j^{1/2} U_j \qquad \text{for all } i. \tag{2.23}$$

Since $\tilde{C}$ is unitary

$$\tilde{C}^+\tilde{C} = \tilde{C}\tilde{C}^+ = \tilde{I}. \tag{2.24}$$

We defined ρ (the diagonal part of the first order density matrix) earlier as

$$\rho = \sum_i n_i U_i^* U_i = \sum_i (n_i^{1/2} U_i^*)(n_i^{1/2} U_i), \tag{2.25}$$

which we may write as

$$\rho = (\tilde{n}^{1/2}\tilde{U})^+ (\tilde{n}^{1/2}\tilde{U}). \tag{2.26}$$

Now consider $\tilde{\rho}$ where

$$\begin{aligned}
\tilde{\rho} &= (\tilde{n}^{1/2}\tilde{U}')^+ (\tilde{n}^{1/2}\tilde{U}') \\
&= (\tilde{C}\tilde{n}^{1/2}\tilde{U})^+ (\tilde{C}\tilde{n}^{1/2}\tilde{U}) \\
&= (\tilde{n}^{1/2}\tilde{U})\tilde{C}^+\tilde{C}(\tilde{n}^{1/2}\tilde{U}) \\
&= (\tilde{n}^{1/2}\tilde{U})^+ (\tilde{n}^{1/2}\tilde{U})
\end{aligned}$$

$$\tilde{\rho} = \rho. \tag{2.27}$$

This means that the unitary transformation postulated does not alter the form of the operator on the left hand side of Eq. (2.21).

Hence, taking each of the equations for the U_k, multiplying by C_{ik}, and summing over k on both sides of the

equation leads us to

$$[-\nabla^2 + \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}-\vec{R}_\alpha|} + \int \frac{2\rho(\vec{r}_2)}{|\vec{r}-\vec{r}_2|}\, d\vec{r}_2 + \frac{4}{3} C\alpha\rho(\vec{r})^{1/3}]n_i^{1/2} U_i(\vec{r})$$

$$= \sum_k \sum_j C_{ik}\lambda_{kj} n_j^{1/2} U_j(\vec{r}). \qquad (2.28)$$

We may write the right hand side of therms of a matrix element

$$\sum_k \sum_j C_{ik}\lambda_{kj} n_j^{1/2} U_j = (\tilde{C}\tilde{\lambda}\tilde{n}^{1/2}\tilde{U}); \qquad (2.29)$$

where $\tilde{\lambda}$ is the matrix of the λ_{ij}'s. But inserting unity,

$$(\tilde{C}\tilde{\lambda}\tilde{n}^{1/2}\tilde{U})_i = (\tilde{C}\tilde{\lambda}\tilde{C}^+\tilde{C}\tilde{n}^{1/2}\tilde{U})_i. \qquad (2.30)$$

We define a new matrix $\tilde{\lambda}'$ by

$$\tilde{\lambda}' = \tilde{C}\tilde{\lambda}\tilde{C}^+; \qquad (2.31)$$

and remembering that

$$\tilde{n}^{1/2}\tilde{U}' = \tilde{C}\tilde{n}^{1/2}\tilde{U},$$

we get

$$(\tilde{C}\tilde{\lambda}\tilde{n}^{1/2}\tilde{U})_i = (\tilde{\lambda}'\tilde{n}^{1/2}\tilde{U}')_i. \qquad (2.32)$$

However, since $\tilde{C}$ is an arbitrary unitary transformation, we may pick $\tilde{C}$ so as to diagonalize the $\tilde{\lambda}$ matrix

$$(\tilde{C}\tilde{\lambda}\tilde{n}^{1/2}\tilde{U})_i = \sum_j \lambda'_{ij}\delta_{ij} n_j^{1/2} U_j' = \lambda'_{ii} n_i^{1/2} U_i'. \qquad (2.33)$$

Inserting this in Eq. (2.28) and cancelling $n_i^{1/2}$ terms

$$[-\nabla^2 + \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}-\vec{R}_\alpha|} + \int \frac{2\rho(\vec{r}_2)}{|\vec{r}-\vec{r}_2|} d\vec{r}_2 + \frac{4}{3} C\alpha\rho(\vec{r})^{1/3}]U_i'(\vec{r})$$

$$= -\lambda_{ii}' U_i'(\vec{r}), \qquad (2.34)$$

and it is customary to denote $-\lambda_{ii}$ as ε_i.

For simplicity we may define a new potential $V_{X\alpha}(\rho,\vec{r})$ (where the ρ indicates the dependence of $V_{X\alpha}$ upon ρ)

$$V_{X\alpha}(\rho,\vec{r}) = \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}-\vec{R}_\alpha|} + \int \frac{2\rho(\vec{r}_2)}{|\vec{r}-\vec{r}_2|} d\vec{r}_2 + \frac{4}{3} C\alpha\rho(\vec{r})^{1/3}. \qquad (2.35)$$

Then Eq. (2.34) may be written

$$[-\nabla^2 + V_{X\alpha}(\rho,\vec{r})]U_i(\vec{r}) = \varepsilon_i U_i(\vec{r}). \qquad (2.36)$$

The potential $V_{X\alpha}(\rho,\vec{r})$ is usually referred to as the "Xα potential" and the Eqs. (2.36) are the one-electron self-consistent-field (SCF) equations for the set of orbitals $\{U_i\}$ which make $\langle E_{X\alpha}\rangle$ a minimum. Several things should be noted about these equations.

First, the quantity ε_i in Eqs.(2.36) is at this point only a Lagrange multiplier. The same is true of the Hartree-Fock equations except that in Hartree-Fock theory the ε_i are identified with ionization energies in an approximate way through the Koopman Theorem. In Xα theory the eigenvalues ε_i are related to the total energy $\langle E_{X\alpha}\rangle$ as a

partial derivative (see Slater (1972a) and Slater and Johnson (1972)),

$$\varepsilon_{iX\alpha} = \frac{\partial \langle E_{X\alpha} \rangle}{\partial n_i} \quad . \tag{2.37}$$

This relation causes the $X\alpha$ method to obey Fermi statistics and also leads to a different method of calculating ionization energies. In $X\alpha$ theory the correspondence is made between the ionization energy and the orbital "energy" ε_i calculated for a so-called "transistion state" in which the orbital occupation number is reduced by one-half. (See Slater (1972a) for the derivation of this concept. Further discussion here leads far afield from the main purpose of this dissertation.) This is a convenient method and yields comparatively good results where it has been tested against rigorous methods which take the difference of total energies of an atom or molecule and its positive ion as the ionization energy (see Slater and Wood (1971) and Connolly et al. (1972)).

Second, the solutions to the Eqs.(2.36) are self-consistent solutions since the potential $V_{X\alpha}$ depends upon the orbitals U_i through the density ρ. The SCF cycle as it is applied will be discussed in greater detail in the last section of the next chapter.

Third, the solutions to Eqs.(2.36) are three-dimensional functions which are not necessarily separable in a spherical or any other coordinate system. The only

restrictions put on the U_i so far is that they be the same for spin up and spin down electrons (a restriction we may relax) and that they satisfy Eqs.(2.36) above. The Xα potential $V_{X\alpha}(\vec{r})$ in Eqs.(2.36) may be a very structured function in three-dimensions for a molecule or solid. It may approach a muffin-tin form but in reality of course it does not have this simple form.

CHAPTER III

THE MT APPROXIMATION TO THE Xα TOTAL ENERGY AND ONE-ELECTRON EQUATIONS

3.1 Introduction

In this chapter we will discuss the muffin-tin (MT) approximation to the Xα total energy for a molecule and the MT one-electron equations which may be derived variationally from MT Xα energy functional. In this approximation one assumes a MT form for the electron density in the evaluation of the energy. First in the chapter we define the MT form in terms of a spatial averaging process and derive some of its properties. Then we will show how the exact Xα total energy $\langle E_{X\alpha} \rangle$ may be separated into a MT, $\overline{\langle E_{X\alpha} \rangle}$, and a non-muffin-tin (NMT), $\Delta\langle E_{X\alpha} \rangle$, part. From the energy functional $\overline{\langle E_{X\alpha} \rangle}$ we will derive the one-electron SCF equations which must be satisfied by a set of orbitals $\{U_i\}$ in order to make $\overline{\langle E_{X\alpha} \rangle}$ a minimum.

3.2 The MT Approximation

In the MT approximation, the space of a molecule is schematically divided into three types of regions. Spherical regions surround the atomic nuclei (region I),

the whole molecule is surrounded by a large outer sphere (region III), and the region left over within the outer sphere and between the atomic spheres (region II) is called the interatomic or intersphere region (Johnson (1966) and Johnson (1967)). Thus a molecule like C_2 may be represented as in Figure 3.1 where the points labeled "C" locate the carbon nuclei and the point labeled "0" the center of the outer sphere.

It is argued on intuitive physical ground that the potential $V_{X\alpha}$ and density ρ for a molecule must be very close to spherical in regions I and III and close to a constant in region II. This is what is assumed in the MT approximation. It will be shown that under this assumption the X_α total energy evaluation reduces to a simple form and the one-electron equations for the orbitals reduce to a separable central field form in regions I and III and to the form of an electron in a constant potential in region II. Actually it will be shown that both of these results follow simply from the assumption of a MT density $\bar{\rho}$ in the evaluation of the total energy.

The spherical average $\bar{f}(\vec{r})$ of any three-dimensional function $f(\vec{r})$ is defined in regions I or III as

$$\bar{f}(\vec{r}) = \frac{1}{4\pi} \int f(\vec{r}) \sin\theta d\theta d\phi. \qquad (3.1)$$

Thus $\bar{f}(\vec{r})$ is only a function of the radial coordinate r. The non-muffin-tin (NMT) part of $f(\vec{r})$, $\Delta f(\vec{r})$, is defined

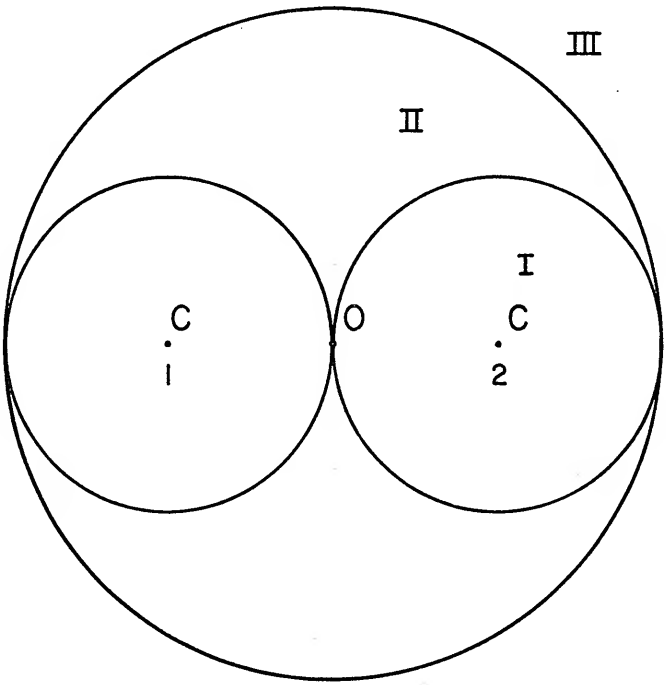


Figure 3.1. Schematic Representation of the C_2 Molecule in the MT Approximation.

$$\Delta f(\vec{r}) = f(\vec{r}) - \overline{f}(\vec{r}) \ . \tag{3.2}$$

In the intersphere region the MT part of a function $\overline{f}(\vec{r})$ is defined as

$$\overline{f}(\vec{r}) = \frac{1}{V_{IN}} \int_{IN} f(\vec{r}) d\vec{r} \ , \tag{3.3}$$

where the integral is only over the intersphere region and V_{IN} is the volume of the intersphere region. It should be noted that $\overline{f}(\vec{r})$ for the intersphere region is a constant (although for notational convenience a dependence on $\vec{r}$ is included). The NMT part $\Delta f(\vec{r})$ is defined in the intersphere region as

$$\Delta f(\vec{r}) = f(\vec{r}) - \overline{f}(\vec{r}) \tag{3.4}$$

just as above for the atomic-like regions.

From its definition the NMT part of the function $\Delta f(\vec{r})$ in an atomic or the intersphere region integrates to zero. Consider the integral of $\Delta f(\vec{r})$ in an atomic region:

$$\int \Delta f(\vec{r}) d\vec{r} = \int \left(f(\vec{r}) - \overline{f}(\vec{r}) \right) d\vec{r}$$

$$= \int \frac{1}{4\pi} \int f(\vec{r}') \sin\theta' d\theta' d\phi' \sin\theta d\theta d\phi r^2 dr. \tag{3.5}$$

The integral over the angles θ and ϕ contributes a factor of 4π and we have

$$\int \Delta f(\vec{r})d\vec{r} = \int f(\vec{r})r^2\sin\theta d\theta d\phi dr - \int f(\vec{r})r^2\sin\theta d\theta d\phi dr$$

$$\int \Delta f(\vec{r})d\vec{r} = 0 \quad . \tag{3.6}$$

Since this is true for the atomic-like as well as the intersphere region, the integral of $\Delta f(\vec{r})$ over the whole molecule is zero. Similarly, the integral of the product of a MT and NMT function is also zero. Let $\overline{g}(\vec{r})$ be the MT part of a function $g(\vec{r})$ and $\Delta f(\vec{r})$ the NMT part of a function $f(r)$. Then

$$\int \Delta f(\vec{r})\overline{g}(\vec{r})d\vec{r} = 0 \tag{3.7}$$

and vice versa. By these relations the total energy evaluation may, in the MT approximation,be reduced to a much simpler form.

To clarify the meaning of the averages we will take an example. (See Figure 3.1) Consider a function $1/r_1$ where r_1 is the radial distance from center 1 at position R_1 measured from some arbitrary origin. Inside the sphere surrounding center 1 the MT average of this function is trivially $1/r_1$. Inside the sphere surrounding center 2 at position R_2 the MT average is performed as an

angular average about center 2. In this case, the average of $1/r_1$ about center 2 is $1/|\vec{R}_1 - \vec{R}_2|$; that is, a constant throughout the region about Center 2.

3.3 The Separation of the Xα Total Energy into MT and NMT Parts

The Xα total energy $\langle E_{X\alpha} \rangle$ was given in the previous chapter (Eq. (2.6) as (in the non-spin polarized case)

$$\langle E_{X\alpha} \rangle = \sum_i n_i \int U_i^*(\vec{r}_1) - \nabla_i^2 U_i(\vec{r}_1) d\vec{r}_1 + \int \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}_1 - \vec{R}_\alpha|} \rho(\vec{r}_1) \cdot d\vec{r}_1 + \frac{1}{2} \iint \frac{2\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \int \rho(\vec{r}_1) U_{X\alpha}(\vec{r}_1) d\vec{r}_1 + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{2Z_\alpha Z_\beta}{R_{\alpha\beta}} . \qquad (2.6)$$

This is $\langle E_{X\alpha} \rangle$ obtained using some set of orbitals $\{U_i\}$ (not necessarily the set which minimize $\langle E_{X\alpha} \rangle$)and density ρ formed from these orbitals. For convenience we divide this expression into parts

$$\langle E_{X\alpha} \rangle = E_K + E_{Ne} + E_c + E_x + E_{NN} \qquad (3.8)$$

where parts are identified:

Kinetic, E_K

$$E_K = \sum_i n_i \int U_i^*(\vec{r}_1)[-\nabla_1^2 U_i(\vec{r}_1)]d\vec{r}_1 \; ; \qquad (3.9a)$$

Nuclear-electron, E_{Ne}

$$E_{Ne} = \int \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}_1 - \vec{R}_\alpha|} \rho(\vec{r}_1) d\vec{r}_1 \; ; \qquad (3.9b)$$

Coulomb, E_c

$$E_c = \frac{1}{2} \int\int \frac{2\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \; ; \qquad (3.9c)$$

Exchange, E_x

$$E_x = \frac{1}{2} \int \rho(\vec{r}_1) U_{X\alpha}(\vec{r}_1) d\vec{r}_1 \; ; \qquad (3.9d)$$

Nuclear-Nuclear, E_{NN}

$$E_{NN} = \frac{1}{2} \sum_{\alpha \neq \beta} \frac{2Z_\alpha Z_\beta}{R_{\alpha\beta}} \; . \qquad (3.9e)$$

We will now treat these terms one by one in the MT approximation to the density.

In the MT approximation to the density, ρ in Eq. (2.6) is replaced by $\bar{\rho}$. Here we will instead break ρ into its MT and NMT parts and consider the separation of Eq. (2.6) into its MT and NMT parts:

$$\rho(\vec{r}) = \overline{\rho}(\vec{r}) + \Delta\rho(\vec{r}) \ , \tag{3.10}$$

and similarly

$$\langle E_{X\alpha} \rangle = \langle \overline{E_{X\alpha}} \rangle + \Delta \langle E_{X\alpha} \rangle \ , \tag{3.11}$$

where $\langle \overline{E_{X\alpha}} \rangle$ is the result obtained from Eq. (2.6) where ρ is replaced by $\overline{\rho}$ and $\Delta\langle E_{X\alpha} \rangle$ is the difference between $\langle E_{X\alpha} \rangle$ and $\langle \overline{E_{X\alpha}} \rangle$. The kinetic E_K and nuclear-nuclear E_{NN} terms will not be affected at all. Thus we must consider the nuclear-electron E_{Ne}, Coulomb E_c, and exchange E_x terms.

Considering E_{Ne} first we may write Eq. (3.9b) as

$$E_{Ne} = \int \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}_1 - R_\alpha|} \left(\overline{\rho}(\vec{r}_1) + \Delta\rho(\vec{r}_1)\right) d\vec{r}_1 . \tag{3.12}$$

We may define a nuclear-electron potential V_{Ne} as

$$V_{Ne}(\vec{r}_1) = \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}_1 - \vec{R}_\alpha|} . \tag{3.13}$$

Just as for ρ, we may divide this potential in any region of the molecule and over the whole molecule into MT, $\overline{V}_{Ne}$, and NMT, ΔV_{Ne} parts

$$V_{Ne}(\vec{r}_1) = \overline{V_{Ne}}(\vec{r}_1) + \Delta V_{Ne}(\vec{r}_1) \ . \tag{3.14}$$

As shown in Section (3.2) the integral over the whole molecule of a MT with a NMT function is zero. Hence Eq. (3.12) reduces to

$$E_{Ne} = \int \bar{V}_{Ne}(\vec{r}_1)\bar{\rho}(\vec{r}_1)d\vec{r}_1 + \int \Delta V_{Ne}(\vec{r}_1)\Delta\rho(\vec{r}_1)d\vec{r}_1 \ . \quad (3.15)$$

This expression is exact. (The explicit forms for $\Delta\rho$, ΔV_{Ne}, and any other such quantities will be given in the next chapter and Appendices C and D.) In the MT approximation to $\langle E_{X\alpha}\rangle$ only the first term in Eq. (3.15) is retained.

Next we consider the Coulomb term E_c. Substituting for ρ we get

$$E_c = \frac{1}{2}\int\int \frac{2(\bar{\rho}(\vec{r}_1) + \Delta\rho(\vec{r}_1))(\bar{\rho}(\vec{r}_2) + \Delta\rho(\vec{r}_2))}{r_{12}} d\vec{r}_2 d\vec{r}_1$$

$$= \frac{1}{2}\int\int \frac{2\bar{\rho}(\vec{r}_1)\bar{\rho}(\vec{r}_2)}{r_{12}} d\vec{r}_2 d\vec{r}_1 + \int\int \frac{2\Delta\rho(\vec{r}_1)\bar{\rho}(\vec{r}_2)}{r_{12}} d\vec{r}_2 d\vec{r}_1$$

$$+ \frac{1}{2}\int\int \frac{2\Delta\rho(\vec{r}_1)\Delta\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 d\vec{r}_1 \ . \quad (3.16)$$

There are two cross terms from the multiplication; but, since they are identical by interchange of dummy variables, the second integral has a factor of one instead of one-half as originally. We may rearrange the first and second terms into a similar form

$$E_c = \frac{1}{2}\int \bar{\rho}(\vec{r}_1)\int \frac{2\bar{\rho}(r_2)}{r_{12}}\, d\vec{r}_2 d\vec{r}_1 + \int \Delta\rho(\vec{r}_1)\int \frac{2\bar{\rho}(\vec{r}_2)}{r_{12}}\, d\vec{r}_2 d\vec{r}_1$$

$$+ \frac{1}{2}\int\int \frac{2\Delta\rho(\vec{r}_1)\Delta\rho(\vec{r}_2)}{r_{12}}\, d\vec{r}_2 d\vec{r}_1 \ . \qquad (3.17)$$

We define a new potential $V_c(\bar{\rho}, \vec{r}_1)$ (the $\bar{\rho}$ is included to indicate that V_c is calculated using the MT density)

$$V_c(\bar{\rho},\vec{r}_1) = \int \frac{2\bar{\rho}(\vec{r}_2)}{r_{12}}\, d\vec{r}_2 \ . \qquad (3.18)$$

This potential itself may be separated into MT and NMT parts, $\bar{V}_c(\bar{\rho},\vec{r}_1)$ and $\Delta V_c(\bar{\rho},\vec{r}_1)$ respectively

$$V_c(\bar{\rho},\vec{r}_1) = \bar{V}_c(\bar{\rho},\vec{r}_1) + \Delta V_c(\bar{\rho},\vec{r}_1) \ . \qquad (3.19)$$

Inserting these into expression (3.17) and taking integrals of MT with NMT functions to be zero we are left with

$$E_c = \frac{1}{2}\int \bar{\rho}(\vec{r}_1)\bar{V}_c(\bar{\rho},\vec{r}_1)\, d\vec{r}_1 + \int \Delta\rho(\vec{r}_1)\Delta V_c(\bar{\rho}, \vec{r}_1)\, d\vec{r}_1$$

$$+ \frac{1}{2}\int\int \frac{2\Delta\rho(\vec{r}_1)\Delta\rho(\vec{r}_2)}{r_{12}}\, d\vec{r}_2 d\vec{r}_1 \ . \qquad (3.20)$$

Again, this expression for E_c is exact but only the first term is retained in the MT approximation to $\langle E_{X\alpha} \rangle$. Note that $\bar{V}_c(\bar{\rho}, \vec{r}_1)$ is a radial function in an atomic-like region and a constant in the intersphere region. Further $\bar{V}_c(\bar{\rho},\vec{r}_1)$ may be evaluated at any point in the molecule in terms of one-dimensional integrals. Thus the first term in Eq. (3.20) is in effect a two-dimensional integral, the second term in effect a four-dimensional integral, and the last term is a six-dimensional integral.

Continuing, we have the exchange term of the total energy E_x which we handle in a different manner. We write Eq. (3.9d) as

$$E_x = C_\alpha \int \rho(\vec{r}_1)^{4/3} d\vec{r}_1 \tag{3.21}$$

where

$$C_\alpha = -(9/2)\alpha(3/8\pi)^{1/3} \ . \tag{3.22}$$

Adding and subtracting $C_\alpha \bar{\rho}(\vec{r}_1)^{4/3}$ to the integrand of Eq. (3.21) we have

$$E_x = C_\alpha \int \bar{\rho}(\vec{r}_1)^{4/3} d\vec{r}_1 + C_\alpha \int \left(\rho(\vec{r}_1)^{4/3} - \bar{\rho}(\vec{r}_1)^{4/3}\right) d\vec{r}_1 \tag{3.22}$$

where the first term is that retained in the MT approximation to $\langle E_{X\alpha} \rangle$.

Now we have completed the separation, for a given set of orbitals $\{U_i\}$ and density ρ, of $\langle E_{X\alpha} \rangle$ into its parts $\langle \overline{E_{X\alpha}} \rangle$ and $\Delta \langle E_{X\alpha} \rangle$:

$$\langle E_{X\alpha} \rangle = \langle \overline{E_{X\alpha}} \rangle + \Delta \langle E_{X\alpha} \rangle \quad . \tag{3.11}$$

where

$$\langle \overline{E_{X\alpha}} \rangle = \sum_i n_i \int U_i^*(\vec{r}_1) [- \nabla_1^2 U_i(\vec{r}_1)] d\vec{r}_1 + \int \bar{\rho}(\vec{r}_1) \bar{V}_{Ne}(\vec{r}_1) d\vec{r}_1$$

$$+ \frac{1}{2} \int \bar{\rho}(\vec{r}_1) \bar{V}_c(\bar{\rho}, \vec{r}_1) d\vec{r}_1 + C_\alpha \int \bar{\rho}(\vec{r}_1)^{4/3} d\vec{r}_1$$

$$+ \frac{1}{2} \sum_{\alpha \neq \beta} \frac{2 Z_\alpha Z_\beta}{R_{\alpha\beta}} \; ; \tag{3.23}$$

and

$$\Delta \langle E_{X\alpha} \rangle = \int \Delta\rho(\vec{r}_1) \Delta V_{Ne}(\vec{r}_1) d\vec{r}_1 + \int \Delta\rho(\vec{r}_1) \Delta V_c(\bar{\rho}, \vec{r}_1) d\vec{r}_1$$

$$+ \frac{1}{2} \int \int \frac{2 \Delta\rho(\vec{r}_1) \Delta\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 d\vec{r}_1 + C_\alpha \int (\rho(\vec{r}_1)^{4/3} - \bar{\rho}(\vec{r}_1)^{4/3}) d\vec{r}_1 \; .$$

(3.24)

Again, we emphasize that no approximations have been made in Eq. (3.11)--only a separation.

3.4 The Derivation of the MT Xα One-Electron Equations

In the MT approximation for the Xα method the orbitals $\tilde{U}_i$ from which $\bar{\rho}$ is formed are determined as those orbitals which make expression $\overline{\langle E_{X\alpha} \rangle}$ of Eq. (3.23) a minimum. We designate these orbitals as "$\tilde{U}_i$" to distinguish them from the "U_i" which in Chapter II were the orbitals which made $\langle E_{X\alpha} \rangle$ a minimum. The two sets of orbitals although perhaps nearly identical are not the same. We will derive the one-electron equations for the set $\{\tilde{U}_i\}$ in the manner of Sec. (2.2); that is using functional derivatives. For simplicity in the following derivation we will leave out the Lagrange multipliers and the complex conjugate terms since they are handled in an exactly analogous manner as they were in Section (2.2). We wish to concentrate here on the difference between $\bar{\rho}$ and ρ as well as on the form that the potential will take in the one-electron differential equations.

In forming the variation of $\overline{\langle E_{X\alpha} \rangle}$, the form of the kinetic energy term will be the same as for the exact Xα method and the nuclear-nuclear term does not contribute anything. Hence

$$\delta \langle E_{X\alpha} \rangle = \int n_i \, \tilde{U}_i^*(\vec{r}) [- \nabla^2 \tilde{U}_i(\vec{r})] d\vec{r} + \delta \bar{V}_T \qquad (3.25)$$

where

$$\bar{V}_T = \int \bar{\rho}(\vec{r}_1) \bar{V}_{Ne}(\vec{r}_1) d\vec{r}_1 + \frac{1}{2} \int \bar{\rho}(\vec{r}_1) \bar{V}_c(\bar{\rho}, \vec{r}_1) d\vec{r}_1$$

$$+ C_\alpha \int \bar{\rho}(\vec{r}_1)^{4/3} d\vec{r}_1 . \qquad (3.26)$$

As indicated previously the functions $\bar{\rho}$, $\bar{V}_{Ne}$, $\bar{V}_c$, and $\bar{\rho}^{4/3}$ are radial functions in the atomic-like regions (regions I and III) and constants in the intersphere region. Hence we may divide $\bar{V}_T$ into a sum over the various regions performing the angular integrations in the atomic-like regions and the volume integration in the intersphere region:

$$\bar{V}_T = \sum_{\alpha=0}^{N} 4\pi \int [\bar{\rho}(r_1)\bar{V}_{Ne}(r_1) + \tfrac{1}{2}\bar{\rho}(r_1)\bar{V}_c(\bar{\rho}, r_1) + C_\alpha \bar{\rho}(\vec{r}_1)^{4/3}] r_1^2 dr_1$$

$$+ V_{IN}[\bar{\rho}_{IN}\bar{V}_{Ne,IN} + \tfrac{1}{2}\bar{\rho}_{IN}\bar{V}_{c,IN}(\bar{\rho}) + C_\alpha \bar{\rho}_{IN}^{4/3}] \qquad (3.27)$$

where $\alpha=0$ corresponds to the outer sphere region, V_{IN} is the volume of the intersphere region, and the subscript "IN" indicate volume averages over the intersphere region.

The variation of $\bar{V}_T$ may be written as

$$\delta\bar{V}_T = \int \frac{\delta}{\delta\tilde{U}_i^*(\vec{r})} \bar{V}_T \delta\tilde{U}_i^*(\vec{r}) d\vec{r} . \qquad (3.28)$$

Since $\bar{V}_T$ depends on $\tilde{U}_i^*$ only through $\bar{\rho}$ we may apply the chain rule of differentiation generalized to functional derivatives to find $\delta\bar{V}_T$. Hence

$$\delta\bar{V}_T = \sum_{\alpha=0}^{N} \int \int \delta\tilde{U}_i^*(\vec{r}) \frac{\delta}{\delta\bar{\rho}(r')} 4\pi \int [\bar{\rho}(r_1)\bar{V}_{Ne}(r_1) + \tfrac{1}{2}\bar{\rho}(r_1)\bar{V}_c(\bar{\rho}, r_1)$$

$$+ C_\alpha \bar{\rho}(r_1)^{4/3}]r_1^2 dr_1 \frac{\delta\bar{\rho}(r')}{\delta\tilde{U}_i^*(\vec{r})} r'^2 dr' d\vec{r}$$

$$+ \int \delta\tilde{U}_i^*(\vec{r}) \frac{\delta}{\delta\bar{\rho}} V_{IN} [\bar{\rho}_{IN}\bar{V}_{Ne,IN} + \frac{1}{2}\bar{\rho}_{IN}\bar{V}_{c,IN} + C_\alpha \bar{\rho}_{IN}^{4/3}]$$

$$x \frac{\delta\bar{\rho}}{\delta\tilde{U}_i^*(\vec{r})} d\vec{r} \ . \qquad (3.29)$$

Taking the terms one by one we have first the nuclear-electron term in an atomic region

$$\frac{\delta}{\delta\bar{\rho}(r')} \int \bar{\rho}(r_1)\bar{V}_{Ne}(r_1) r_1^2 dr_1 = \int \frac{\delta\bar{\rho}(r_1)}{\delta\bar{\rho}(r')} \bar{V}_{Ne}(r_1) r_1^2 dr_1$$

$$= \int \delta\ (r_1 - r')\bar{V}_{Ne}(r_1) r_1^2 dr_1$$

$$= \bar{V}_{Ne}(r') . \qquad (3.30)$$

The functional derivative in the intersphere region is

$$\frac{\delta}{\delta\bar{\rho}}(\bar{\rho}_{IN}\bar{V}_{Ne,IN}) = \bar{V}_{Ne,IN} \ . \qquad (3.31)$$

In taking the functional derivative of the Coulomb part of V_T it is easier to return to the earlier form of this term which is given

$$4\pi\frac{1}{2}\int\bar{\rho}(r_1)\bar{V}_c(\bar{\rho},r_1)r_1^2dr_1$$

$$= \frac{1}{2}\iint\frac{2\bar{\rho}(r_1)\bar{\rho}(r_2)}{r_{12}}\,d\vec{r}_2d\vec{r}_1 \qquad (3.32)$$

Then the functional derivative is

$$\frac{\delta}{\delta\bar{\rho}(r')}\frac{1}{2}\iint\frac{2\bar{\rho}(r_1)\bar{\rho}(r_2)}{r_{12}}\,d\vec{r}_2d\vec{r}_1$$

$$= \frac{1}{2}\int\delta(r_1 - r')\int\frac{2\bar{\rho}(r_2)}{r_{12}}\,d\vec{r}_2d\vec{r}_1$$

$$+ \frac{1}{2}\int\delta(r_2 - r')\int\frac{2\bar{\rho}(r_1)}{r_{12}}\,d\vec{r}_1d\vec{r}_2$$

$$= \int\delta(r_1 - r')\int\frac{2\bar{\rho}(r_2)}{r_{12}}\,d\vec{r}_2d\vec{r}_1 \qquad (3.33)$$

since r_1 and r_2 are dummy variables. By the definition of $V_c(\bar{\rho},\vec{r}_1)$ we have

$$\frac{\delta}{\delta\bar{\rho}(r')}\frac{1}{2}\iint\frac{2\bar{\rho}(r_1)\bar{\rho}(r_2)}{r_{12}}\,d\vec{r}_2d\vec{r}_1$$

$$= \int\delta(r_1 - r')V_c(\bar{\rho},\vec{r}_1)d\vec{r}_1. \qquad (3.34)$$

Doing the angular integration if in an atomic region and multiplying and dividing by 4π, and doing the volume integration and multiplying and dividing by V_{IN} if in the intersphere region we get

$$\frac{\delta}{\delta\bar{\rho}(r')}\,\frac{1}{2}\int\int\frac{2\bar{\rho}(r_1)\bar{\rho}(r_2)}{r_{12}}\,d\vec{r}_2 d\vec{r}_1 = \begin{cases} 4\pi\bar{V}_c(\bar{\rho},r') & \text{for atomic regions} \\ V_{IN}\bar{V}_{c,IN} & \text{for the intersphere region} \end{cases} \tag{3.35}$$

The last term of $\bar{V}_T$ to consider is the exchange term. For an atomic region it is

$$4\pi\,\frac{\delta}{\delta\bar{\rho}(r')}\,C_\alpha\int\bar{\rho}(r_1)^{4/3}r_1^2dr_1 = 4\pi\tfrac{4}{3}\,C_\alpha\int\bar{\rho}(r_1)^{1/3}\delta(r_1-r')r_1^2dr_1$$

$$= 4\pi\tfrac{4}{3}\,C_\alpha\bar{\rho}(r')^{1/3}\ ; \tag{3.36}$$

and for the intersphere region it is

$$\frac{\delta}{\delta\bar{\rho}}\,C_\alpha V_{IN}\bar{\rho}_{IN}^{4/3} = V_{IN}\,\tfrac{4}{3}\,C_\alpha\bar{\rho}_{IN}^{1/3}\ .$$

Finally, collecting terms for the functional derivative of $\bar{V}_T$ in Eq. (3.29) we have

$$\delta\bar{V}_T = \sum_{\alpha=0}^{N} \int\int \delta\tilde{U}_i^*(\vec{r})\, 4\pi [\bar{V}_{Ne}(r') + \bar{V}_c(\bar{\rho}, r') + \frac{4}{3} C_\alpha \bar{\rho}(r')^{1/3}]$$

$$\times \frac{\delta\bar{\rho}(r')}{\delta\tilde{U}_i^*(\vec{r})}\, r'^2 dr' d\vec{r}$$

$$+ \int \delta\tilde{U}_i^*(\vec{r})\, V_{IN} [\bar{V}_{Ne,IN} + \bar{V}_{c,IN}(\bar{\rho}) + \frac{4}{3} C_\alpha \bar{\rho}_{IN}^{1/3}]$$

$$\times \frac{\delta\bar{\rho}}{\delta\tilde{U}_i^*(\vec{r})}\, d\vec{r} \quad . \tag{3.37}$$

Now, we must consider the term $\delta\bar{\rho}/\delta\tilde{U}_i^*(\vec{r})$ in the atomic-like and in the intersphere regions. In an atomic-like region

$$\frac{\delta\bar{\rho}(r')}{\delta\tilde{U}_i^*(\vec{r})} = \frac{\delta}{\tilde{U}_i^*(\vec{r})} \frac{1}{4\pi} \int \sum_i n_i \tilde{U}_i^*(\vec{r}') \tilde{U}_i(\vec{r}') \sin\theta' d\theta' d\phi'$$

$$= \frac{1}{4\pi} \int n_i \delta(\vec{r}' - \vec{r}) \tilde{U}_i(\vec{r}') \sin\theta' d\theta' d\phi' \quad . \tag{3.38}$$

Note that we may combine the angular integration over the primed coordinates with the radial integration over the primied coordinate in Eq. (3.37). Now consider the functional derivative of $\bar{\rho}$ in the inter-atomic region:

$$\frac{\delta\bar{\rho}_{IN}}{\delta\tilde{U}_i^*(\vec{r})} = \frac{\delta}{\delta\tilde{U}_i^*(\vec{r})} \frac{1}{V_{IN}} \int_{IN} \sum_i n_i \tilde{U}_i^*(\vec{r}') \tilde{U}_i(\vec{r}') d\vec{r}'$$

$$= \frac{1}{V_{IN}} \int n_i \delta(\vec{r}' - \vec{r}) \tilde{U}_i(\vec{r}') d\vec{r}'$$

$$= \frac{1}{V_{IN}} n_i \tilde{U}_i(\vec{r}) \quad . \tag{3.39}$$

Substituting the expressions of Eqs. (3.38) and (3.39) in Eq. (3.37) we have

$$\delta\bar{V}_T = \sum_{\alpha=0}^{N} \int\int \delta\tilde{U}_i^*(\vec{r}) [\bar{V}_{Ne}(r') + \bar{V}_c(\bar{\rho}, r') + \frac{4}{3} C_\alpha \bar{\rho}(r')^{1/3}]$$

$$\times n_i \delta(\vec{r}' - \vec{r}) \tilde{U}_i(\vec{r}') d\vec{r}' d\vec{r}$$

$$+ \int \delta\tilde{U}_i^*(\vec{r}) [\bar{V}_{Ne,IN} + \bar{V}_c(\bar{\rho})_{IN} + \frac{4}{3} C_\alpha \bar{\rho}_{IN}^{1/3}]$$

$$\times n_i \tilde{U}_i(\vec{r}) d\vec{r} \quad . \tag{3.40}$$

We may now recombine the integrations over all the regions

and perform the primed integration in Eq. (3.40) to get

$$\delta\overline{V}_T = \int n_i \delta\tilde{U}_i^*(\vec{r}) [\overline{V}_{Ne}(\vec{r}) + \overline{V}_c(\overline{\rho}, \vec{r}) + \frac{4}{3} C_\alpha \overline{\rho}(\vec{r})^{1/3}] \tilde{U}_i(\vec{r}) d\vec{r} \ . \tag{3.41}$$

In this expression it is understood that $\overline{\rho}$, $\overline{V}_{Ne}$, $\overline{V}_c$, and $\overline{\rho}^{1/3}$ are radial functions in the atomic-like regions and constants in the intersphere region. We may conbine the potentials above into one potential $\overline{V}_{X\alpha}$:

$$\overline{V}_{X\alpha}(\overline{\rho}, \vec{r}) = \overline{V}_{Ne}(\vec{r}) + \overline{V}_c(\overline{\rho}, \vec{r}) + \frac{4}{3} C_\alpha \overline{\rho}(\vec{r})^{1/3} \tag{3.42}$$

Finally we combine Eq. (3.41) and with Eq. (3.25). In doing so we include the diagonalized Lagrange multiplier $\overline{\varepsilon}_i$ which was left out of Eq. (3.25) but understood. (Note that we use $\overline{\varepsilon}_i$ here in contrast to the ε_i of Eq. (2.36)):

$$0 = \int \delta\tilde{U}_i^*(\vec{r}) [-\nabla^2 + \overline{V}_{X\alpha}(\overline{\rho}, \vec{r}) - \overline{\varepsilon}_i] \tilde{U}_i(\vec{r}) d\vec{r} \ . \tag{3.43}$$

Since $\delta\tilde{U}_i^*$ is arbitrary it implies that the rest of the integrand in Eq. (3.43) is zero:

$$[-\nabla^2 + \overline{V}_{X\alpha}(\overline{\rho}, \vec{r})]\tilde{U}_i(\vec{r}) = \overline{\varepsilon}_i \tilde{U}_i(\vec{r}). \tag{3.44}$$

The solutions to this equation, $\tilde{U}_i(\vec{r})$, occupied from that of

the lowest energy up to the Fermi level so as to be consistent with the total number of electrons in the molecule are the set of orbitals $\{\tilde{U}_i\}$ which make $\overline{\langle E_{X\alpha} \rangle}$ as given in Eq. (3.23) a minimum. It should be noted that the potential of Eq. (3.44) is of muffin-tin form and hence the solutions to Eq. (3.44) are separable in spherical coordinates. Both of these facts follow from the assumption of a muffin-tin form for the density. The $\bar{\varepsilon}_i$ eigenvalues have the same property as the ε_i for the exact Xα method; namely (see Eq. (2.37)),

$$\bar{\varepsilon}_i = \frac{\partial \overline{\langle E_{X\alpha} \rangle}}{\partial n_i} \quad . \tag{3.45}$$

The orbitals $\tilde{U}_i$ are SCF orbitals as is implicit in Eq. (3.44). The details of the SCF cycle will be discussed at the end of the next chapter (Section 4.4).

3.5 The MT Xα One-Electron Orbitals and the Multiple-Scattering (MS) Formalism

The MT form of the Xα theory is that used for computation since the equations for the $\tilde{U}_i$ are separable in spherical coordinates and hence readily solvable as one-dimensional second order differential equations. Historically this fact was noted first; that is, that if the potential were of MT form the equations were separable and could be solved using well-known techniques. As shown above in Section

(3.4) this result follows simply from the assumption of a MT density which transforms the energy function from $\langle E_{X\alpha} \rangle$ to $\langle \overline{E_{X\alpha}} \rangle$. In the following paragraphs of this section a brief discussion of the multiple-scattering formalism will be given. For a more complete exposition consult Appendix B, Johnson (1966), and Johnson (1967).

With the separable form of the differential equations for the $\tilde{U}_i$ (Eq. (3.44)) we may use the partial wave expansions of multiple-scattering theory in the three regions of the molecule. Within an atomic sphere α or the outer sphere ($\alpha = 0$) we may expand the orbital function $\tilde{U}_i$ for state i for eigenvalue $\bar{\varepsilon}_i$.

$$\tilde{U}_i^{\alpha} = \sum_{\ell,m} C_{\ell m}^{i\alpha} R_\ell(r_\alpha, \bar{\varepsilon}_i) Y_{\ell m}(\hat{r}_\alpha) \ , \tag{3.46}$$

where the $C_{\ell m}^{i\alpha}$ are expansion coefficients to be determined, the $Y_{\ell m}$ are real spherical harmonics, and the atomic-like R_ℓ satisfy the central field differential equation

$$\left[-\frac{1}{r_\alpha^2} \frac{d}{dr_\alpha} \left(r_\alpha^2 \frac{d}{dr_\alpha} \right) + \frac{\ell(\ell+1)}{r_\alpha^2} + \bar{V}_{X\alpha}(\bar{\rho}, r_\alpha) - \bar{\varepsilon}_i \right] R_\ell(r_\alpha, \bar{\varepsilon}_i) = 0 \ . \tag{3.47}$$

In the intersphere region the potential $V_{X\alpha}(\bar{\rho}, \vec{r})$ is averaged to a constant $\bar{V}_{IN}$ in the MT approximation and the differential equation to be solved is

$$[\nabla^2 + \bar{\varepsilon}_i - \bar{V}_{IN}]\tilde{U}_i(\vec{r}) = 0 \ . \qquad (3.48)$$

The solution to this equation may be expressed as a multicenter partial wave expansion which for $\bar{\varepsilon}_i < \bar{V}_{IN}$ is given by

$$\tilde{U}_i(\vec{r}) = \sum_{\alpha=1}^{N} \sum_{\ell,m} A_{\ell m}^{i\alpha} k_\ell^{(1)}(\kappa_i r_\alpha) Y_{\ell m}(\hat{r}_\alpha) + \sum_{\ell,m} A_{\ell m}^{io} i_\ell(\kappa_i r_o) Y_{\ell m}(\hat{r}_o) \ , \qquad (3.49)$$

where the $A_{\ell m}^{i\alpha}$ are expansion coefficeints to be determined, the $Y_{\ell m}$ are real spherical harmonics, $r_\alpha = |\vec{r} - \vec{R}_\alpha|$ (where $\vec{R}_\alpha$ is the location of the αth nucleus), and $\kappa_i = (\bar{\varepsilon}_i - \bar{V}_{IN})^{1/2}$. The $k_\ell^{(1)}$ and i_ℓ are respectively the modified spherical Hankel function of the first kind and the modified spherical Bessel function. For $\bar{\varepsilon}_i > \bar{V}_{IN}$ the expansion for the orbital in the intersphere region is done respectively in terms of the ordinary Neumann and ordinary Bessel functions.

To find the eigenvalues and the A and C expansion coefficients one requires the orbitals $\tilde{U}_i$ and their first derivatives to be continuous across the sphere boundaries. This leads to a secular equation from which the eigenvalues $\bar{\varepsilon}_i$ and the A and C coefficients can be determined. For the details refer to Appendix B.

The $X\alpha$ approximation, the muffin-tin approximation to the density, and the multiple scattering formalism as

outlined above together constitute the multiple-scattering Xα (MSXα) method of molecular calculation as it is currently implemented.

3.6 Explicit Expressions for the Components of the NMT Correction $\Delta\langle E_{X\alpha}\rangle$

The expression for the NMT correction $\Delta\langle E_{X\alpha}\rangle$ is given by

$$\Delta\langle E_{X\alpha}\rangle = \int \Delta\rho(\vec{r}_1)\Delta V_{Ne}(\vec{r}_1)d\vec{r}_1 + \int \Delta\rho(\vec{r}_1)\Delta V_c(\bar{\rho},\vec{r}_1)d\vec{r}_1 + \frac{1}{2}\iint \frac{2\Delta\rho(\vec{r}_1)\Delta\rho(\vec{r}_2)}{r_{12}}\, d\vec{r}_2 d\vec{r}_1 + C_\alpha \int (\rho(\vec{r}_1)^{4/3} - \bar{\rho}(\vec{r}_1)^{4/3})d\vec{r}_1. \qquad (3.24)$$

Of the terms contained in the integrands, the meaning of $\Delta\rho(\vec{r}_1)$ is clear and its explicit expression in terms of the partial wave expansions of the multiple-scattering theory is given in Appendix C. The third term whose integrand contains the second order product $\Delta\rho(\vec{r}_1)\Delta\rho(\vec{r}_2)$ may be argued on intuitive grounds to be small compared to the other terms. However, we have actually performed a calculation of this term and found it to be quite small. The result of this check calculation will be given in Chapter VI and this term will not be considered further here. (The manner of performing the six - dimensional integration for this

term, particularly the method used to handle the $1/r_{12}$ singularity, is given in Appendix F). The meaning of the integrand of the exchange term is transparent presenting no conceptual or calculational difficulties. The remaining two terms--$\Delta V_{Ne}(\vec{r})$ and $\Delta V_c(\bar{\rho}, \vec{r})$--are more complicated and will be derived in detail.

Deriving the expressions for these two terms in the three types of regions of a molecule--atomic, outer, and intersphere--is a tedious but straight-forward exercise in electrostatics. Of the two, $\Delta V_{Ne}(\vec{r})$ is the simpler and we will give the derivation for its explicit regional expressions in this section. The Coulomb term $\Delta V_c(\bar{\rho}, \vec{r})$ is more involved and we will give in this section the explicit expressions for this term in each part of the molecule. It will be shown that some of these terms are exactly analogous to the nuclear-electron terms and these need no derivation. The other terms of $\Delta V_c(\bar{\rho}, \vec{r})$ have no counterpart in the nuclear-electron terms and the derivation of these terms is relegated to Appendix D.

The NMT Nuclear-electron Terms--$\Delta V_{Ne}(\vec{r})$

The explicit definition of $V_{Ne}(\vec{r})$ is given, once again as

$$V_{Ne}(\vec{r}) = \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r} - \vec{R}_\alpha|} . \qquad (3.13)$$

The function $\Delta V_{Ne}(\vec{r})$ is defined by

$$\Delta V_{Ne}(\vec{r}) = V_{Ne}(\vec{r}) - \bar{V}_{Ne}(\vec{r}) \ . \qquad (3.14)$$

Hence our task is to derive expressions for $\bar{V}_{Ne}(\vec{r})$ in the three regions of the molecule. Repeating, the muffin-tin average in an atomic or the outer sphere region is an angular average--an average performed in the region of interest. The muffin-tin average in the intersphere region is a volume average over the intersphere region.

We may divide $V_{Ne}(\vec{r})$ into four types of potentials depending upon where the point $\vec{r}$ is located and where the nuclei are located: $V_{Ne}^{\alpha,\alpha}$, $V_{Ne}^{\alpha,\beta}$, $V_{Ne}^{o,\alpha}$, and $V_{Ne}^{IN,\alpha}$. These are defined:

$V_{Ne}^{\alpha,\alpha}$: The potential of interaction between an electron in the αth atomic region and the αth nucleus located in that atomic region.

$V_{Ne}^{\alpha,\beta}$: The potential of interaction between an electron in the αth atomic region and the βth nucleus located in the βth atomic region.

$V_{Ne}^{o,\alpha}$: The potential of interaction between an electron in the outer sphere region and the αth nucleus.

$V_{Ne}^{IN,\alpha}$: The potential of interaction between an electron in the intersphere region and the αth nucleus.

We need to find the muffin-tin average for each one of these potentials.

In the following the nuclei are located by vectors

$\vec{R}_\alpha$(α=1,..., N) measured from an arbitrary origin "0". The point $\vec{r}$ in the potential $V_{Ne}(\vec{r})$ may be located in any of the three regions: 1) In an atomic region "α" it is designated $\vec{r}_\alpha$ where $\vec{r}_\alpha$ is the vector from the nucleus α to the point $\vec{r}$. 2) In the outer sphere region "o" it is designated $\vec{r}_o$ where $\vec{r}_o$ is the vector from the center of the outer sphere to the point $\vec{r}$. 3) In the intersphere region "IN" it is designated $\vec{r}_{IN}$ (sometimes $\vec{r}_o$ for convenience) where $\vec{r}_{IN}$ is measured from the center of the outer sphere.

Beginning with $V_{Ne}^{\alpha\ \alpha}$ we have

$$V_{Ne}^{\alpha,\alpha}(\vec{r}) = \frac{-2Z_\alpha}{|\vec{r} - \vec{R}_\alpha|}$$

$$= \frac{-2Z_\alpha}{r_\alpha} \quad . \tag{3.50}$$

Since this is already a spherical function in the αth region the angular average makes no difference and

$$\overline{V}_{Ne}^{\alpha,\alpha}(\vec{r}) = V_{Ne}^{\alpha,\alpha}(\vec{r}) \quad , \tag{3.51}$$

and hence

$$\Delta V_{Ne}^{\alpha,\alpha}(\vec{r}) = 0 \quad . \tag{3.52}$$

For $V_{Ne}^{\alpha,\beta}$ we have

$$V_{Ne}^{\alpha,\beta}(\vec{r}) = \frac{-2Z_\beta}{|\vec{r} - \vec{R}_\beta|}, \tag{3.53}$$

where $\vec{r}$ is in the αth region. We may use another set of vectors which are illustrated in Figure 3.2(a):

$$\vec{r} - \vec{R}_\beta = \vec{r}_\alpha + \vec{R}_\alpha - \vec{R}_\beta$$

$$= \vec{r}_\alpha - \vec{R}_{\alpha\beta} \ . \tag{3.54}$$

The expansion for $1/|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|$ where $|\vec{r}_\alpha| < |\vec{R}_{\alpha\beta}|$ is given by

$$\frac{1}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{m=+\ell} \frac{4\pi}{2\ell + 1} \frac{r_\alpha^\ell}{R_{\alpha\beta}^{\ell+1}} Y_{\ell m}(\hat{r}_\alpha) Y_{\ell m}^*(\hat{R}_{\alpha\beta}) \ . \tag{3.55}$$

In this expression $\vec{R}_{\alpha\beta}$ is of course fixed and $\vec{r}_\alpha$ is variable. The angular average is performed in the αth region and in performing this average we note that

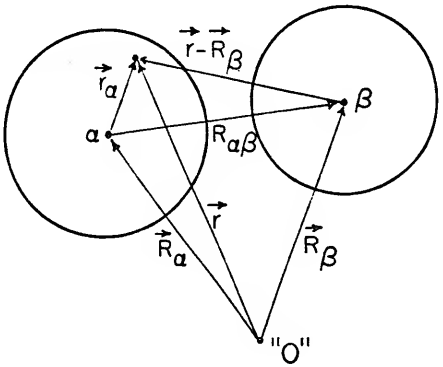
$$\int Y_{\ell m}(\hat{r}) d\Omega = 4\pi \delta(\ell)\delta(m) Y_{oo} \ . \tag{3.56}$$

Hence

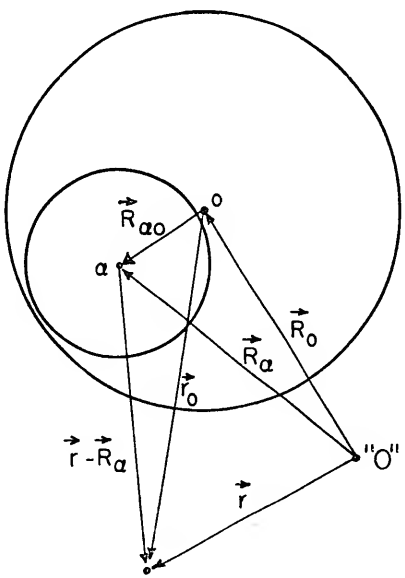
$$\bar{V}_{Ne}^{\alpha,\beta}(\vec{r}) = \frac{-2Z_\beta}{4\pi} \int \frac{1}{|\vec{r} - \vec{R}_{\alpha\beta}|} d\Omega_\alpha , \tag{3.57}$$

and from Eq. (3.55) and Eq. (3.56)

$$\bar{V}_{Ne}^{\alpha,\beta}(\vec{r}) = \frac{-2Z_\beta}{R_{\alpha\beta}} \ . \tag{3.58}$$



(a)



(b)

Figure 3.2. Vector Relationships Used for the Derivation of (a) $V^{\alpha,\beta}_{Ne}$ and (b) $V^{o,\alpha}_{Ne}$

Hence

$$\Delta V_{Ne}^{\alpha,\beta}(\vec{r}) = \frac{-2Z_\beta}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|} - \frac{-2Z_\beta}{R_{\alpha\beta}} , \qquad (3.59)$$

Then, within an atomic sphere α the total potential $\Delta V_{Ne}^{\alpha}(\vec{r})$ is given by

$$\Delta V_{Ne}^{\alpha}(\vec{r}) = \sum_{\substack{\beta=1 \\ \beta\neq\alpha}}^{N} -2Z_\beta \left(\frac{1}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|} - \frac{1}{R_{\alpha\beta}} \right) . \qquad (3.60)$$

For $V_{Ne}^{o,\alpha}(\vec{r})$ the point $\vec{r}$ is in the outer sphere region

$$V_{Ne}^{o,\alpha}(\vec{r}) = \frac{-2Z_\alpha}{|\vec{r}_o - \vec{R}_{\alpha o}|} , \qquad (3.61)$$

where the vectors $\vec{r}_o$ and $\vec{R}_{\alpha o}$ are defined in Figure 3.2(b)

$$\vec{r}_o = \vec{r} - \vec{R}_o \quad \text{and} \quad \vec{R}_{\alpha o} = \vec{R}_o - \vec{R}_{\alpha o} . \qquad (3.62)$$

Again we expand $1/|\vec{r}_o - \vec{R}_{\alpha o}|$ where $|\vec{r}_o| > |\vec{R}_{\alpha o}|$

$$\frac{1}{|\vec{r}_o - \vec{R}_{\alpha o}|} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{m=+\ell} \frac{4\pi}{2\ell+1} \frac{R_{\alpha o}^{\ell}}{r_o^{\ell+1}} Y_{\ell m}(\hat{R}_{\alpha o}) Y_{\ell m}^{*}(\hat{r}_o) . \qquad (3.63)$$

Taking the spherical average in the outer sphere region we get

$$\bar{V}_{Ne}^{o,\alpha}(\vec{r}) = \frac{-2Z_\alpha}{4\pi} \int \frac{1}{|\vec{r}_o - \vec{R}_{\alpha o}|} d\Omega_o \ , \tag{3.64}$$

or

$$\bar{V}_{Ne}^{o,\alpha}(\vec{r}) = -\frac{2Z_\alpha}{r_o} \ . \tag{3.65}$$

Hence in the outer sphere region $\Delta V_{Ne}^{o}(\vec{r})$ is given by

$$\Delta V_{Ne}^{o}(\vec{r}) = \sum_{\alpha=1}^{N} -2Z_\alpha \left(\frac{1}{|\vec{r}_o - \vec{R}_{\alpha o}|} - \frac{1}{r_o} \right) . \tag{3.66}$$

The derivation of $\bar{V}_{Ne}(\vec{r})$ in the intersphere region is a bit more involved due to the odd shape of the intersphere region. We must perform a complete three-dimensional integration over this region and this is accomplished by first integrating the potential over the whole region inside the outer sphere and then subtracting the integral of the potential over each atomic region. The potential $V_{Ne}^{IN,\alpha}(\vec{r})$ is defined

$$V_{Ne}^{IN,\alpha}(\vec{r}) = \frac{-2Z_\alpha}{|\vec{r} - \vec{R}_\alpha|} \ , \tag{3.67}$$

where $\vec{r}$ is in the intersphere region. First we will integrate

this function over the volume inside the outer sphere. To do this we use the same set of coordinates as for the case $V_{Ne}^{o,\alpha}$ above only now $|\vec{r}_o|$ may be less or greater than $|\vec{R}_{\alpha o}|$. We get (skipping the by now familiar expansion step):

$$\int \frac{1}{|\vec{r}_o - \vec{R}_{\alpha o}|} \, d\Omega_o = \frac{4\pi}{r_o} \quad \text{for } |\vec{r}_o| > |\vec{R}_{\alpha o}|; \quad (3.68)$$

and

$$\int \frac{1}{|\vec{r}_o - \vec{R}_{\alpha o}|} \, d\Omega_o = \frac{4\pi}{R_{\alpha o}} \quad \text{for } |\vec{r}_o| < |\vec{R}_{\alpha o}|. \quad (3.69)$$

Hence, the volume integration of $V_{Ne}^{IN,\alpha}$ inside the outer sphere is

$$-2Z_\alpha \int \frac{1}{|\vec{r}_o - \vec{R}_{\alpha o}|} \, d\vec{r}_o = -2Z_\alpha \{ \frac{4\pi}{R_{\alpha o}} \int_0^{R_{\alpha o}} r_o^2 dr_o + 4\pi \int_{R_{\alpha o}}^{b_o} r_o dr_o \}, \quad (3.70)$$

where b_o is the radius of the outer sphere. Continuing

$$-2Z_\alpha \int \frac{1}{|\vec{r}_o - \vec{R}_{\alpha o}|} \, d\vec{r}_o = -2Z_\alpha \left(\frac{b_o^2}{2} - \frac{R_{\alpha o}^2}{6} \right). \quad (3.71)$$

In integrating $1/|\vec{r}_o - \vec{R}_{\alpha o}|$ over the atomic regions there are two cases to consider: one in which we integrate

over the αth sphere where the αth nucleus is located and the other type case where we integrate over the other (N-1) atomic spheres β. Within the αth sphere $\vec{r} - \vec{R}_\alpha = \vec{r}_\alpha$ and

$$-2Z_\alpha \int \frac{1}{|\vec{r}_\alpha|} d\vec{r}_\alpha = -2Z_\alpha \frac{4\pi b_\alpha^2}{2} \quad . \tag{3.72}$$

Within the βth sphere we decompose the vector $\vec{r} - \vec{R}_\alpha$ as before in Eq. (3.54) (See Figure 3.2(a))

$$\vec{r} - \vec{R}_\alpha = \vec{r}_\beta + \vec{R}_\beta - \vec{R}_\alpha$$

$$= \vec{r}_\alpha - \vec{R}_{\alpha\beta}. \tag{3.72}$$

Then

$$-2Z_\alpha \int \frac{1}{|\vec{r}_\beta - \vec{R}_{\alpha\beta}|} d\vec{r}_\beta = -2Z_\alpha \frac{4\pi}{R_{\alpha\beta}} \int_0^b r_\beta^2 dr_\beta$$

$$= -2Z_\alpha \frac{4\pi b_\beta^3}{3R_{\alpha\beta}} \quad , \tag{3.73}$$

where b_β is the radius of the βth sphere. Hence with the result of this last equation, Eq. (3.71), and Eq. (3.72) we have that $\bar{V}_{Ne}^{IN}(\vec{r})$ in the intersphere region is given by

$$\bar{V}_{Ne}^{IN}(\vec{r}_{IN}) = \frac{4\pi}{V_{IN}} \sum_{\alpha=1}^{N} -2Z_\alpha \left(\frac{b_o^2}{2} - \frac{R_{\alpha o}^2}{6} - \frac{b_\alpha^2}{2} - \frac{1}{3} \sum_{\substack{\beta=1 \\ \beta\neq\alpha}}^{N} \frac{b_\beta^3}{R_{\alpha\beta}} \right) \quad (3.74)$$

where V_{IN} is the volume of the intersphere region and is given by

$$V_{IN} = \frac{4\pi}{3} \left(b_o^3 - \sum_{\alpha=1}^{N} b_\alpha^3 \right). \quad (3.75)$$

Then $\Delta V_{Ne}^{IN}(\vec{r}_{IN})$ at any point $\vec{r}_{IN}$ in the intersphere region is given by

$$\Delta V_{Ne}^{IN}(\vec{r}_{IN}) = \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r}_{IN} - \vec{R}_\alpha|} - \bar{V}_{Ne}^{IN}(\vec{r}_{IN}) \quad . \quad (3.76)$$

The NMT Coulomb Terms--$\Delta V_c(\bar{\rho}, \vec{r})$

The expressions for the function $\Delta V_c(\bar{\rho}, \vec{r})$ in different regions of the molecule are somewhat more complicated than those for $\Delta V_{Ne}(\vec{r})$. The basic integral for $V_c(\bar{\rho}, \vec{r})$ is given by

$$V_c(\bar{\rho}, \vec{r}) = 2\int \frac{\bar{\rho}(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}. \quad (3.77)$$

The point $\vec{r}$ may be in any of the three types of regions of

the molecule--atomic, outer, or intersphere. In each case of course the integration over $\vec{r}'$ is over all space. For a given point $\vec{r}$ we may divide the total potential at $\vec{r}$ into a contribution from the region in which $\vec{r}$ is located and contributions from the other individual regions of the molecule. To find $\Delta V_c(\bar{\rho}, \vec{r})$ at each point $\vec{r}$ we must first derive $\overline{V_c}(\bar{\rho}, \vec{r})$ in the region in which $\vec{r}$ is located for the contribution of the integral from each region of the molecule. The derivation proceeds in the same manner as above for $\Delta V_{Ne}(\vec{r})$ with the basic difference that instead of a potential produced by nuclear point charges we now deal with a potential produced by spherical radial charge distributions in the atomic and outer sphere regions and by a constant charge throughout the intersphere region. Just as we divided the nuclear-electron term into four types we divide the Coulomb term into ten types of contributions. (For a reference covering many aspects of this section see J. W. D. Connolly & J. R. Sabin (1972)).

In the αth atomic sphere the potential V_c^α may be divided into parts as follows

$$V_c^\alpha = V_c^{\alpha,\alpha} + \sum_{\substack{\beta=1 \\ \beta\neq\alpha}}^{N} V_c^{\alpha,\beta} + V_c^{\alpha,o} + V_c^{\alpha,IN} \qquad (3.78)$$

where the terms on the right hand side correspond to contributions to the potential at a point in the αth sphere arising from MT chage distributions

-- in the αth sphere itself - $V_c^{\alpha,\alpha}$

-- in the other (N-1) β atomic spheres - $V_c^{\alpha,\beta}$

-- in the outer sphere - $V_c^{\alpha,o}$

-- in the intersphere region - $V_c^{\alpha,IN}$.

Using the same kind of notation and definitions we may divide the potential V_c^{IN} in the intersphere region into parts

$$V_c^{IN} = \sum_{\alpha=1}^{N} V_c^{IN,\alpha} + V_c^{IN,o} + V_c^{IN,IN}. \qquad (3.79)$$

Similarly for V_c^o the potential in the outer sphere region

$$V_c^o = \sum_{\alpha=1}^{N} V_c^{o,\alpha} + V_c^{o,o} + V_c^{o,IN} \quad . \qquad (3.80)$$

In the following we will give the explicit expression for each of these ten types of potentials and also the MT form for each, ΔV_c of course being the difference of the two. At the end of the list we will indicate the parallel nature of some of these MT averages to those of the nuclear-electron case which were derived above. For the rest, the derivation of the MT averages will be given in Appendix D. Before giving the list of expressions we give here the definitions (some repeated) of the important symbols which are used:

b_α -- radius of atomic sphere (α=0 for outer sphere)

Q_α -- total charge contained in sphere α

$R_{\alpha\beta}$ -- distance between two atomic sphere centers α and β

$R_{\alpha o}$ -- distance of atomic center α from outer sphere center

$\bar{\rho}_{IN}$ -- average charge density in intersphere region

V_{IN} -- volume of intersphere region

$\bar{\sigma}_\alpha(r) = 4\pi r^2 \bar{\rho}_\alpha(r)$ -- radial charge density in αth sphere. (3.81)

Since there are ten types of potentials they will begiven in the order of potential, MT potential, and NMT part of potential without comments or other divisions:

$$V_c^{\alpha,\alpha}(\vec{r}_\alpha) = \frac{2}{r_\alpha}\int_0^{r_\alpha} \bar{\sigma}_\alpha(r')dr' + 2\int_{r_\alpha}^{b_\alpha} \frac{\bar{\sigma}_\alpha(r')}{r'}dr'$$

$$\bar{V}_c^{\alpha,\alpha}(\vec{r}_\alpha) = V_c^{\alpha,\alpha}(\vec{r}_\alpha)$$

$$\Delta V_c^{\alpha,\alpha}(\vec{r}) = 0 \qquad (3.82a)$$

$$\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} V_c^{\alpha\beta}(\vec{r}_\alpha) = \sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} \frac{2Q_\beta}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|}$$

$$\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} \overline{V_c^{\alpha\beta}(\vec{r}_\alpha)} = \sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} \frac{2Q_\beta}{R_{\alpha\beta}}$$

$$\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} \Delta V_c^{\alpha\beta}(\vec{r}_\alpha) = \sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} 2Q_\beta \left(\frac{1}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|} - \frac{1}{R_{\alpha\beta}} \right) \qquad (3.82b)$$

$$V_c^{\alpha,o}(\vec{r}_\alpha) = 2 \int_{b_o}^{\infty} \frac{\bar{\sigma}_{ouT}(r')}{r'} dr'$$

$$\bar{V}_c^{\alpha,o}(\vec{r}_\alpha) = V_c^{\alpha,o}(\vec{r})$$

$$\Delta V_c^{\alpha,o}(\vec{r}_\alpha) = 0 \qquad (3.82c)$$

$$V_c^{\alpha,IN}(\vec{r}_\alpha) = 4\pi\bar{\rho}_{IN}\left(b_o^2 - b_\alpha^2 - \frac{1}{3}|\vec{r} - \vec{R}_{\alpha o}|^2 + \frac{1}{3}r_\alpha^2 - \frac{2}{3}\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} \frac{b_\beta^3}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|}\right.$$

$$\overline{V_c^{\alpha,IN}}(\vec{r}_\alpha) = 4\pi\bar{\rho}_{IN}\left(b_o^2 - b_\alpha^2 - \frac{1}{3}R_{\alpha o}^2 - \frac{2}{3}\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} \frac{b_\beta^3}{R_{\alpha\beta}}\right)$$

$$\Delta V_c^{\alpha,IN}(\vec{r}_\alpha) = 4\pi\bar{\rho}_{IN}\Big(-\frac{1}{3}\left(|\vec{r}_\alpha + \vec{R}_{\alpha o}|^2 - R_{\alpha o}^2\right) + \frac{1}{3}r_\alpha^2$$

$$-\frac{2}{3}\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} b_\beta^3\left(\frac{1}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|} - \frac{1}{R_{\alpha\beta}}\right) \qquad (3.82d)$$

$$\sum_{\alpha=1}^{N} V_c^{IN,\alpha}(\vec{r}_{IN}) = \sum_{\alpha=1}^{N} \frac{2Q_\alpha}{|\vec{r}_{IN} - \vec{R}_{o\alpha}|}$$

$$\sum_{\alpha=1}^{N} \overline{V_c^{IN,\alpha}}(\vec{r}_{IN}) = \frac{8\pi}{V_{IN}} \sum_{\alpha=1}^{N} Q_\alpha\Big(\Big(\frac{b_o^2}{2} - \frac{R_{o\alpha}^2}{6}\Big) - \frac{b_\alpha^2}{2} - \frac{1}{3}\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} \frac{b_\beta^3}{R_{\alpha\beta}}\Big)$$

$$\sum_{\alpha=1}^{N} \Delta V_c^{IN,\alpha}(\vec{r}_{IN}) = \sum_{\alpha=1}^{N} 2Q_\alpha\Big\{\frac{1}{|\vec{r}_{IN} - \vec{R}_{o\alpha}|} - \frac{4\pi}{V_{IN}}\Big[\Big(\frac{b_o^2}{2} - \frac{R_{o\alpha}^2}{6}\Big) - \frac{b_\alpha^2}{2}$$

$$-\frac{1}{3}\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} \frac{b_\beta^3}{R_{\alpha\beta}}\Big]\Big\} \qquad (3.82e)$$

$$V_c^{IN,o}(\vec{r}_{IN}) = 2\int_{b_o}^{\infty} \frac{\bar{\sigma}_{ouT}(r')}{r'}\,dr'$$

$$\overline{V_c^{IN,o}}(\vec{r}_{IN}) = V_c^{IN,o}(\vec{r})$$

$$\Delta V_c^{IN,o}(\vec{r}_{IN}) = 0 \qquad (3.82f)$$

$$V_c^{IN,IN}(\vec{r}_{IN}) = 4\pi\bar{\rho}_{IN}\left(b_o^2 - \frac{1}{3}r_{IN}^2 - \frac{2}{3}\sum_{\alpha=1}^{N}\frac{b_\alpha^3}{|\vec{r}_{IN} - \vec{R}_{o\alpha}|}\right)$$

$$\overline{V_c^{IN,IN}}(\vec{r}_{IN}) = 4\pi\bar{\rho}_{IN}\left(b_o^2 - \frac{4\pi}{3V_{IN}}\left[\frac{b_o^5}{5} - \sum_{\alpha=1}^{N} b_\alpha^3\left(\frac{b_\alpha^2}{5} + \frac{R_{o\alpha}^2}{3}\right)\right]\right.$$

$$\left. - \frac{8\pi}{3V_{IN}}\sum_{\alpha=1}^{N} b_\alpha^3\left[\frac{b_o^2}{2} - \frac{b_\alpha^2}{2} - \frac{R_{o\alpha}^2}{6} - \frac{1}{3}\sum_{\substack{\beta=1 \\ \beta\neq\alpha}}^{N}\frac{b_\beta^3}{R_{\alpha\beta}}\right]\right)$$

$$\Delta V_c^{IN,IN}(\vec{r}_{IN}) = V_c^{IN,IN}(\vec{r}_{IN}) - \overline{V_c^{IN,IN}}(\vec{r}_{IN}) \qquad (3.82g)$$

$$\sum_{\alpha=1}^{N} V_c^{o,\alpha}(\vec{r}_o) = \sum_{\alpha=1}^{N}\frac{2Q_\alpha}{|\vec{r}_o - \vec{R}_{o\alpha}|}$$

$$\sum_{\alpha=1}^{N} \overline{V_c^{o,\alpha}}(\vec{r}_o) = \sum_{\alpha=1}^{N}\frac{2Q_\alpha}{r_o}$$

$$\sum_{\alpha=1}^{N} \Delta V_c^{o,\alpha}(\vec{r}_o) = \sum_{\alpha=1}^{N} 2Q_\alpha \left(\frac{1}{|\vec{r}_o - \vec{R}_{o\alpha}|} - \frac{1}{r_o} \right) \qquad (3.82h)$$

$$V_c^{o,o}(\vec{r}_o) = \frac{2}{r_o} \int_{b_o}^{r_o} \sigma_{ouT}(r')dr' + 2 \int_{r_o}^{\infty} \frac{\sigma_{ouT}(r')}{r'} dr'$$

$$\overline{V_c^{o,o}}(\vec{r}_o) = V_c^{o,o}(\vec{r}_o)$$

$$\Delta V_c^{o,o}(\vec{r}_o) = 0 \qquad (3.82i)$$

$$V_c^{o,IN}(\vec{r}_\alpha) = 2\bar{\rho}_{IN} \left(\frac{4\pi b_o^3}{3r_o} - \sum_{\alpha=1}^{N} \frac{4\pi b_\alpha^3}{3|\vec{r}_o - \vec{R}_{o\alpha}|} \right)$$

$$\overline{V_c^{o,IN}}(\vec{r}_o) = 2\bar{\rho}_{IN} \left(\frac{4\pi b_o^3}{3r_o} - \sum_{\alpha=1}^{N} \frac{4\pi b_\alpha^3}{3r_o} \right) = \frac{2\rho_{IN} V_{IN}}{r_o}$$

$$\Delta V_c^{o,IN}(\vec{r}_o) = -2\bar{\rho}_{IN} \sum_{\alpha=1}^{N} \frac{4\pi b_\alpha^3}{3} \left(\frac{1}{|\vec{r}_o - \vec{R}_{o\alpha}|} - \frac{1}{r_o} \right) \qquad (3.82j)$$

In examining these terms it will be noted that the expressions for $\bar{V}_c^{\alpha,\alpha}$ (and $\bar{V}_c^{o,o}$), $\bar{V}_c^{\alpha,\beta}$, $\bar{V}_c^{IN,\alpha}$, and $\bar{V}_c^{o,\alpha}$

exactly parallel the expressions for $\overline{V}_{Ne}^{\alpha,\alpha}$, $\overline{V}_{Ne}^{\alpha,\beta}$, $\overline{V}_{Ne}^{IN,\alpha}$, and $\overline{V}_{Ne}^{o,\alpha}$. The difference is that $-Z_\alpha$ is replaced in the latter case by Q_α in the former. Of the remaining terms $\Delta V_c^{IN,o}$ and $\Delta V_c^{\alpha,o}$ are zero and are relatively simple expressions to derive. This leaves three NMT potentials whose MT average is relatively complicated and which have no counterpart in the nuclear-electron potentials derived above: $\Delta V_c^{\alpha,IN}$, $\Delta V_c^{IN,IN}$ and $\Delta V_c^{o,IN}$. These three potentials, their MT average, and their NMT parts are derived in detail in Appendix D.

This completes the survey of the component terms which form the NMT correction $\Delta\langle E_{X\alpha}\rangle$ to the MT energy $\overline{\langle E_{X\alpha}\rangle}$. In actual calculations they are not necessarily used in their present form and many are combined together for convenience (especially the counterparts of the nuclear-electron and Coulomb terms).

CHAPTER IV

THE RELATIONSHIP BETWEEN THE MT Xα TOTAL ENERGY $\overline{\langle E_{X\alpha} \rangle}$ AND THE Xα TOTAL ENERGY $\langle E_{X\alpha} \rangle$

4.1 Introduction

In Chapter II we derived the differential equation which must be satisfied by a set $\{U_i\}$ in order to minimize the Xα total energy $\langle E_{X\alpha} \rangle$. In Chapter III we showed how, for a given set of orbitals $\{U_i\}$, $\langle E_{X\alpha} \rangle$ could be separated exactly into a MT part $\overline{\langle E_{X\alpha} \rangle}$ and a NMT part $\Delta\langle E_{X\alpha} \rangle$; we also derived the muffin-tin differential equation which must be satisfied by a set $\{\tilde{U}_i\}$ in order to make $\overline{\langle E_{X\alpha} \rangle}$ a minimum. In this chapter we shall examine the relationship between $\overline{\langle E_{X\alpha} \rangle}$ and $\langle E_{X\alpha} \rangle$ more closely in order to elucidate (which is our main purpose) more fully the effect of the muffin-tin approximation to the total density in the total energy evaluation. This is accomplished by using the set $\{\tilde{U}_i\}$ to evaluate the non-muffin-tin correction $\Delta\langle E_{X\alpha} \rangle$ to the muffin-tin total energy $\overline{\langle E_{X\alpha} \rangle}$. We shall show that this approximation to $\langle E_{X\alpha} \rangle$ is analagous to performing Rayleigh-Schroedinger first order perturbation theory in ordinary quantum mechanics and hence our result for $\langle E_{X\alpha} \rangle$ is correct to second order in the differences between the set $\{\tilde{U}_i\}$ and the true Xα orbitals $\{U_i\}$. We will discuss the extension of this method to excited states and will also show the analogous second and

higher order corrections to $\overline{\langle E_{X\alpha} \rangle}$ do not exist in our present method. We shall indicate how a first order approximation similar to that implemented in the calculation of the approximate total energy may also be used to calculate corrections to the muffin-tin eigenvalues, although no calculations of these corrections have been performed in the present study.

At the end of the chapter we discuss the SCF cycle, at which points in the hypothetically exact SCF cycle muffin-tin approximations are performed, and how the approximate method for calculating $\overline{\langle E_{X\alpha} \rangle}$ fits into the present muffin-tin scheme for calculating $\langle E_{X\alpha} \rangle$.

Only the development of an efficient multi-dimensional multi-center numerical sampling and integration scheme has made possible the practical evaluation of the non-muffin-tin correction $\Delta\langle E_{X\alpha} \rangle$ since it involves up to six-dimensional numerical integrations. This sampling and integration scheme is discussed in detail in Chapter V.

4.2 The Explicit Relationship Between $\overline{\langle E_{X\alpha} \rangle}$ and $\langle E_{X\alpha} \rangle$

In Chapter III we showed that $\langle E_{X\alpha} \rangle$ could, for a given set of orbitals $\{U_i\}$ and density ρ formed from the set $\{U_i\}$, be broken into muffin-tin and non-muffin-tin parts

$$\langle E_{X\alpha} \rangle = \overline{\langle E_{X\alpha} \rangle} + \Delta\langle E_{X\alpha} \rangle \ , \qquad (3.11)$$

where

$$\langle \overline{E_{X\alpha}} \rangle = \sum_i \eta_i \int U_i^*(\vec{r}_1)[-\nabla_1^2 U_i(\vec{r}_1)]d\vec{r}_1 + \int \bar{\rho}(\vec{r}_1)\bar{V}_{NE}(\vec{r}_1)d\vec{r}_1$$

$$+ \frac{1}{2}\int \bar{\rho}(\vec{r}_1)\bar{V}_c(\bar{\rho}, \vec{r}_1)d\vec{r}_1 + C_\alpha \int \bar{\rho}(\vec{r}_1)^{4/3}d\vec{r}_1$$

$$+ \frac{1}{2}\sum_{\alpha\neq\beta} \frac{2Z_\alpha Z_\beta}{R_{\alpha\beta}} , \qquad (3.23)$$

and

$$\Delta\langle E_{X\alpha}\rangle = \int \Delta\rho(\vec{r}_1)\ \Delta V_{NE}(\vec{r}_1)d\vec{r}_1 + \int \Delta\rho(\vec{r}_1)\ \Delta V_c(\bar{\rho}, \vec{r}_1)d\vec{r}_1$$

$$+ \frac{1}{2}\int\int \frac{2\Delta\rho(\vec{r}_1)\ \Delta\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 d\vec{r}_1 + C_\alpha \int [\rho(\vec{r}_1)^{4/3}$$

$$- \bar{\rho}(\vec{r}_1)^{4/3}]d\vec{r}_1 . \qquad (3.24)$$

The definition of $\Delta\rho$ has given as the difference between the density formed from the orbitals $\{U_i\}$ and the muffin-tin density (see Eqs. (3.1) and (3.3)) formed from the same orbitals:

$$\Delta\rho = \rho - \bar{\rho} . \qquad (3.10)$$

The terms ΔV_{NE} and $\Delta V_c(\bar{\rho})$ are defined respectively in Eqs. (3.14) and (3.19).

In Chapter II we showed that the set of orbitals $\{U_i\}$ which make $\langle E_{x\alpha} \rangle$ a minimum are solutions to:

$$[-\nabla^2 + V_{x\alpha}(\rho, \vec{r})] U_i(\vec{r}) = \varepsilon_i U_i(\vec{r}), \tag{2.36}$$

where

$$V_{x\alpha}(\rho, \vec{r}) = \sum_{\alpha=1}^{N} \frac{-2Z_\alpha}{|\vec{r} - \vec{R}_\alpha|} + \int \frac{2\rho(\vec{r}_2)}{|\vec{r} - \vec{r}_2|} d\vec{r}_2 + \frac{4}{3} C_\alpha \rho(\vec{r})^{1/3} . \tag{2.35}$$

In Chapter III we showed that the set of orbitals $\{\tilde{U}_i\}$ which make $\langle \overline{E_{x\alpha}} \rangle$ a minimum are solutions to

$$[-\nabla^2 + \overline{V}_{x\alpha}(\overline{\rho}, \vec{r})]\tilde{U}_i(\vec{r}) = \overline{\varepsilon}_i \tilde{U}_i(\vec{r}), \tag{3.44}$$

where

$$\overline{V}_{x\alpha}(\overline{\rho}, \vec{r}) = \overline{V}_{Ne}(\vec{r}) + \overline{V}_c(\overline{\rho}, \vec{r}) + \frac{4}{3} C_\alpha \overline{\rho}(\vec{r})^{1/3} \tag{3.40}$$

with the definitions of $\overline{V}_{Ne}$ and $\overline{V}_c(\overline{\rho})$ given in Section 3.3.

Ideally we would like to solve Eq. (2.36) for the set $\{U_i\}$ and use these orbitals to form $\langle E_{x\alpha} \rangle$. However, in practice this has not been done up to the present for two reasons: 1) we have not had a practical means for solving Eq. (2.36) for the $\{U_i\}$ and 2) the integrations in Eq. (2.2) where $\langle E_{x\alpha} \rangle$ is defined involve up to six-dimensional numerical integrals. Concerning the first reason as pointed

out in Section 2.3 we have at present no practical means available for determining the solutions to Eq. (2.36). This is of course not to say that the solutions can not be obtained. Concerning the second reason, we will show in the next chapter how a practical scheme may be devised to perform the numerical integrations involved in a direct evaluation of $\langle E_{x\alpha} \rangle$ or $\Delta\langle E_{x\alpha} \rangle$.

In the present implementation of the X_α muffin-tin multiple-scattering method (MSXα for short) we solve for the set $\{\tilde{U}_i\}$ and the quantity $\langle \overline{E_{x\alpha}} \rangle$. Hence, although we can not obtain the $\{U_i\}$ to minimize $\langle E_{x\alpha} \rangle$ exactly, we can easily obtain the $\{\tilde{U}_i\}$ which minimize $\langle \overline{E_{x\alpha}} \rangle$; and, use them to calculate $\Delta\langle E_{x\alpha} \rangle$ and therefore $\langle E_{x\alpha} \rangle$ in a first order approximation. As indicated before, for some molecules--CH_4 and Li_2 for example (Johnson, et al. (1972))--the total energies calculated from $\langle \overline{E_{x\alpha}} \rangle$ with the $\{\tilde{U}_i\}$ are quite good and it has been found that in even the worst cases--C_2 being an example--the relative error (estimated) in the total energy is always small. This being the case, we might expect that using the set $\{\tilde{U}_i\}$ to calculate the non-muffin-tin correction $\Delta\langle E_{x\alpha} \rangle$ to the muffin-tin energy $\langle \overline{E_{x\alpha}} \rangle$ should give improved results; that is, results somewhat closer to the true X_α energy. At any rate this should give a good estimate of the size of the non-muffin-tin correction $\Delta\langle E_{x\alpha} \rangle$ and therefore indicate whether the exclusion of this term is a major source of error in current MSX_α calculations.

This approximation--using the $\{\tilde{U}_i\}$to calculate

$\langle E_{x\alpha} \rangle$ --is quite analogous to first order Rayleigh-Schroedinger perturbation theory. In the usual quantum mechanical treatment (see, for example, Merzbacher (1965)) one has a Hamiltonian H which may be conveniently separated into a zero order Hamiltonian H_o and a perturbation V:

$$H = H_o + V \ . \tag{4.1}$$

Further one has a solution for the ground state Ψ_o which minimizes the expectation valve of H_o

$$\varepsilon_o = \langle \Psi_o | H_o | \Psi_o \rangle \ , \tag{4.2}$$

and

$$\delta \langle \Psi_o | H_o | \Psi_o \rangle = 0 \ . \tag{4.3}$$

The first order correction ε_1 to the zero order energy ε_o is the diagonal matrix element of the perturbation V

$$\varepsilon_1 = \langle \Psi_o | V | \Psi_o \rangle \ . \tag{4.4}$$

Hence the total energy ε in the first order approximation is given

$$\varepsilon = \varepsilon_o + \varepsilon_1 \ , \tag{4.5}$$

and

$$\varepsilon = \langle \Psi_o | H_o + V | \Psi_o \rangle \ . \tag{4.6}$$

In analogy, in the present case we have instead of an expectation value a functional $\langle E_{x\alpha} \rangle$ which we may separate into a zero order part $\langle \overline{E_{x\alpha}} \rangle$ and a perturbation $\Delta \langle E_{x\alpha} \rangle$:

$$\langle E_{x\alpha} \rangle = \langle \overline{E_{x\alpha}} \rangle + \Delta \langle E_{x\alpha} \rangle \ . \tag{4.7}$$

We have a set of orbitals $\{\tilde{U}_i\}$ which minimizes the functional $\langle \overline{E_{x\alpha}} \rangle$:

$$\delta \langle \overline{E_{x\alpha}} \rangle = 0 \ . \tag{4.8}$$

Using the set $\{\tilde{U}_i\}$ we may calculate $\Delta \langle E_{x\alpha} \rangle$ which we see to be analogous to the first order correction in Rayleigh-Schroedinger perturbation theory. Hence we may calculate $\langle E_{x\alpha} \rangle$ with the set $\{\tilde{U}_i\}$

$$\langle E_{x\alpha}(\{\tilde{U}_i\}) \rangle = \langle \overline{E_{x\alpha}(\{\tilde{U}_i\})} \rangle + \Delta \langle E_{x\alpha}(\{\tilde{U}_i\}) \rangle \tag{4.9}$$

which is seen to be analogous to Eq. (4.6). If we take the difference between each hypothetical exact X_α orbital U_i and the corresponding muffin-tin X_α orbital $\tilde{U}_i$ to be δU_i then the energy of Eq. (4.9) is correct up to $(\delta U_i)^2$ effects for all the orbitals. This is just to say that the total energy is not very sensitive to details of the orbitals--a well-known fact. This of course does not imply that the individual parts of the total energy in this first order approximation will be accurate to the same order as the total

energy. In fact, since we are using the $\{\tilde{U}_i\}$ to calculate the kinetic energy we may expect that the first order approximation will not satisfy the Virial Theorem although an exact Xα calculation for a molecule with the same value of α throughout does satisfy this theorem. (See Slater (1972b) for the proof of this result and further discussion.) We will return to this point again in the discussion of the results for C_2 in Chapter VI. A more accurate way of testing the quality of the orbitals would be to calculate the forces on the nuclei using the Hellman-Feynman Theorem since the forces depend on integrals in which the density occurs linearly. However, our main concern in this study is the total energy.

The total Xα energy for a single-excitation excited state is calculated, self consistently (see Section 4.4), with an electron removed from one of the occupied orbitals of the ground state to one of the unoccupied higher energy orbitals of the molecule (see Slater et al. (1969), Slater and Wood (1971), and Slater (1972a)). The total energy of the excited state is a functional, just as for the ground state, of the one-electron density matrix; for an excited state it is defined with one electron removed from a ground state orbital to one of the higher energy orbitals. The orbitals self-consistently obtained minimize the energy functional defined by this one-electron density matrix. Double excitations are treated similarly. (Considering for a moment the orbitals obtained, as an example, for a

singly excited state, it should be noted that these orbitals will be orthogonal to each other but not necessarily orthogonal to the orbitals obtained for the ground state Xα energy functional.)

If one were to draw an analogy with a configuration interaction (CI) calculation it would be seen that within the Xα (that is, $\rho^{1/3}$) approximation the Xα total energy for the ground or an excited state corresponds to a diagonal energy matrix element obtained in the CI expansion. In contrasting the diagonal energy elements of a CI expansion to the Xα energy for an excited state or the ground state a particular qualitative difference exists in that in the Xα method the energy is calculated self-consistently whereas in a CI calculation the energy matrix elements are basis set dependent since a limited basis is always used. (This self-consistency allows the Xα theory to satisfy the Hellman-Feynman and Virial Theorems. See Chapter VI for further comment on this subject.)

In the present method described in this chapter we calculate $\langle E_{X\alpha} \rangle$ (both MT and NMT parts) with the set of orbitals $\{\tilde{U}_i\}$ which minimize $\langle \overline{E_{X\alpha}} \rangle$. Since the NMT correction $\Delta\langle E_{X\alpha} \rangle$ is a functional of the one-electron density, the NMT correction for an excited state is calculated in exactly the same way as for the ground state. There is no difference.

Since we have shown our present method to be equivalent to a first order perturbation calculation the question naturally arises as to whether the method may be extended to higher orders. The answer is no. No, because to extend the

method to higher orders would require the calculation of off-diagonal matrix elements of the "Hamiltonian" which, as we have indicated above, do not exist in nor are consistent with the basic Xα theory. From this we conclude that any fundamental improvements to be made in the calculation of exact Xα energies beyond our present approximate method must come from improvement in the methods of orbital calculation (see Chapter VI Section 6.5 for some further discussion).

For our main test calculations we picked the C_2 molecule since for this molecule the muffin-tin approximation gives a rather bad result for the binding energy. Muffin-tin calculations give the result that C_2 at its experimental equilibrium separation is unbound by 0.90 Rydbergs whereas in reality it is bound by 0.47 Rydbergs (the total muffin-tin energy of C_2 to three figures is 150 Rydbergs). We estimate then that the muffin-tin result is inaccurate by about 1.2 Rydbergs. We may expect the C_2 molecule to be a bad case for two reasons. First, it is a homonuclear diatomic molecule which means that 75% of the volume inside the outer sphere is included in the constant potential intersphere region (see Figure 3.1). The muffin-tin approximation is more severe in the intersphere region since at the equilibrium separation $\approx$ 3 of the 12 electrons of the C_2 molecule are in that region where the density and potential are both averaged to a constant. Secondly, the C_2 molecule has σ_g, σ_u and π_u valence states. The π_u state is a highly structured state

with 42 percent of its density the intersphere region. However, the muffin-tin approximation averages away this fine structure and its effect on the total energy. Hence we feel that C_2 is a good test case which should stretch the first order approximation to the limit of its validity. To anticipate the results given later, the calculation of the non-muffin-tin correction $\Delta\langle E_{X\alpha}\rangle$ for C_2 has resulted in a significant qualitative and quantitative improvement in the potential curve for C_2. In addition a point calculation at the approximate experimental equilibrium separation for Ne_2--a molecule qualitatively different from C_2--has corroborated this trend for the non-muffin-tin correction. Hence on the basis of the relative insensitivity of the functional $\langle E_{X\alpha}\rangle$ to changes in the orbitals and on the basis of the significant improvement of the results we feel that the non-muffin-tin correction $\Delta\langle E_{X\alpha}\rangle$ to the muffin-tin Xα total energy $\langle\overline{E_{X\alpha}}\rangle$ represents a significant and practical improvement to current MSXα calculational methods. Further discussion with complete results will be given in Chapter VI.

4.3 First Order Corrections to the Eigenvalues

We may also calculate a first order perturbation correction to the eigenvalues of the muffin-tin single-electron Xα equations. (This of course may be done for transistion state eigenvalues as well as any other configuration with integral or non-integral occupation numbers.)

If we compare the exact Xα single-electron equations of Eq. (2.36) with the muffin-tin single-electron Xα equations of Eq. (3.44) we see that the two differ in the potential. We may take the difference between the two potentials $V_{X\alpha}(\rho)$ and $\overline{V}_{X\alpha}(\overline{\rho})$ to be $\Delta V_{X\alpha}(\rho)$:

$$\Delta V_{X\alpha}(\rho,\vec{r}) = \Delta V_{Ne}(\vec{r}) + \Delta V_{C}(\rho,\vec{r}) + \frac{4}{3} C_{\alpha}(\rho(\vec{r})^{1/3} - \overline{\rho}(\vec{r})^{1/3}). \quad (4.10)$$

The first term $\Delta V_{Ne}(\vec{r})$ is defined in Eq. (3.14) and the last term is self-evident. However the second term needs further elucidation. Beginning with the potential $V_{C}(\rho,\vec{r})$ we may split it into a muffin-tin and a non-muffin-tin part--

$$V_{C}(\rho,\vec{r}) = \overline{V_{C}}(\rho,\vec{r}) + \Delta V_{C}(\rho,\vec{r}). \quad (4.11)$$

Separating the density into $\overline{\rho}$ and $\Delta\rho$ in each part--

$$V_{C}(\rho,\vec{r}) = \overline{V}_{C}(\overline{\rho},\vec{r}) + \overline{V}_{C}(\Delta\rho,\vec{r}) + \Delta V_{C}(\overline{\rho},\vec{r}) + \Delta V_{C}(\Delta\rho,\vec{r}). \quad (4.12)$$

Substracting $\overline{V}_{C}(\overline{\rho},\vec{r})$ we get--

$$V_{C}(\rho,\vec{r}) - \overline{V}_{C}(\overline{\rho},\vec{r}) = \overline{V}_{C}(\Delta\rho,\vec{r}) + \Delta V_{C}(\overline{\rho},\vec{r}) + \Delta V_{C}(\Delta\rho,\vec{r}). \quad (4.13)$$

Hence, we rewrite Eq. (4.10) as--

$$\Delta V_{X\alpha}(\rho,\vec{r}) = \Delta V_{Ne}(\vec{r}) + \overline{V}_{C}(\Delta\rho,\vec{r}) + \Delta V_{C}(\overline{\rho},\vec{r}) + \Delta V(\Delta\rho,\vec{r}) + \frac{4}{3} C_{\alpha}(\rho(\vec{r})^{1/3} - \overline{\rho}(\vec{r})^{1/3}). \quad (4.14)$$

We may consider $\Delta V_{X\alpha}(\rho,\vec{r})$ to be the perturbation to $\bar{V}_{X\alpha}(\bar{\rho},\vec{r})$ in Eq. (3.44). Then the first order perturbation correction $\Delta\varepsilon_i$ to the eigenvalue of Eq. (3.44) which we call $\bar{\varepsilon}_i$ is--

$$\Delta\varepsilon_i = \int U_i^*(\vec{r})\Delta V_{X\alpha}(\rho,\vec{r})U_i(\vec{r})d\vec{r} \tag{4.15}$$

or since no derivatives are involved

$$\Delta\varepsilon_i = \int \rho_i(\vec{r})\Delta V_{X\alpha}(\rho,\vec{r})d\vec{r}.$$

Substituting Eq. (4.14) we have--

$$\begin{aligned}\Delta\varepsilon_i = &\int \Delta\rho_i(\vec{r})\Delta V_{Ne}(\vec{r})d\vec{r} + \int \bar{\rho}_i(\vec{r})\bar{V}_C(\Delta\rho,\vec{r})d\vec{r} \\ &+ \int \Delta\rho_i(\vec{r})\Delta V_C(\bar{\rho},\vec{r})d\vec{r} + \int \Delta\rho_i(\vec{r})\Delta V(\Delta\rho,\vec{r})d\vec{r} \\ &+ \int \rho_i(\vec{r})\ \tfrac{4}{3}C_\alpha(\rho(\vec{r})^{1/3} - \bar{\rho}(\vec{r})^{1/3})d\vec{r}\ .\end{aligned} \tag{4.16}$$

We have made use of the properties of muffin-tin and non-muffin-tin functions in reducing Eq. (4.14) to Eq. (4.16). The last term and first term may not be simplified further.

The integrand of the second term involves the function $\bar{V}_C(\Delta\rho,\vec{r})$ and since this is an inconvenient function to evaluate we rearrange this term as follows:

$$\int \bar{\rho}_i(\vec{r})\bar{V}_C(\Delta\rho,\vec{r})d\vec{r} = \int \bar{\rho}_i(\vec{r})V_C(\Delta\rho,\vec{r})d\vec{r} \qquad (4.17)$$

$$= \iint \frac{2\bar{\rho}_i(\vec{r})\Delta\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\, d\vec{r}'d\vec{r}$$

$$= \int \Delta\rho(\vec{r}') \int \frac{2\bar{\rho}_i(\vec{r})}{|\vec{r}-\vec{r}'|}\, d\vec{r}d\vec{r}'$$

$$= \int \Delta\rho(\vec{r})V_C(\bar{\rho}_i,\vec{r})d\vec{r}$$

$$\int \bar{\rho}_i(\vec{r})\bar{V}_C(\Delta\rho,\vec{r})d\vec{r} = \int \Delta\rho(\vec{r})\Delta V_C(\bar{\rho}_i,\vec{r})d\vec{r}.$$

The last function $\Delta V_C(\bar{\rho}_i,\vec{r})$ is easier to calculate than the original function $\bar{V}_C(\Delta\rho,\vec{r})$. Hence we rewrite Eq. (4.16) as--

$$\Delta\varepsilon_i = \int \Delta\rho_i(\vec{r})\Delta V_{Ne}(\vec{r})d\vec{r} + \int \Delta\rho(\vec{r})\Delta V_C(\bar{\rho}_i,\vec{r})d\vec{r} \qquad (4.18)$$

$$+ \int \Delta\rho_i(\vec{r})\ \Delta V_C(\bar{\rho},\vec{r})d\vec{r} + \int \Delta\rho_i(\vec{r})\Delta V_C(\Delta\rho,\vec{r})d\vec{r}$$

$$+ \frac{4}{3} C_\alpha \int \rho_i(\vec{r})\ (\rho(\vec{r})^{1/3} - \bar{\rho}(\vec{r})^{1/3}).$$

It should be observed that this correction $\Delta\varepsilon_i$ to the eigenvalue $\bar{\varepsilon}_i$ has a very similar form to the correction $\Delta\langle E_{X\alpha}\rangle$ to the muffin-tin energy $\langle\overline{E_{X\alpha}}\rangle$ and it can be easily calculated in the same way. The effect of such first order corrections to the eigenvalues is expected to be significant for molecules such as benzene (C_6H_6) which have relatively large intersphere regions. Since the present work is concerned

with the effect of the non-muffin-tin correction to the muffin-tin energy no calculations to date have been performed for these eigenvalue corrections.

4.4 The SCF Cycle

Self-consistency is implied in the muffin-tin Xα equations Eqs.(3.44) and in the exact Xα equations Eqs.(2.36) since in both the Xα potential--$\bar{V}_{X\alpha}(\bar{\rho})$ or $V_{X\alpha}(\rho)$--depends on the orbitals through respectively the muffin-tin or exact Xα electron density. In Figure 4.1 we give a conceptual flow chart for the principal steps in the SCF cycle for both the exact and the muffin-tin Xα calculation. The dashed lines in the diagram represent the steps taken in an exact Xα calculation and the solid lines correspond to the conceptual steps taken in a muffin-tin Xα calculation.

To begin the iteration cycle to reach self-consistency it is the usual practice to assume for the molecular Xα potential a superposition of calculated Xα atomic potentials. It is not necessary to use such potentials but they prove to be a good starting point. From these superposed potentials a muffin-tin potential is formed and from this potential via the multiple-scattering (MS) equations the eigenvalues and A and C expansion coefficients (see Sec. (3.5) and Appendix B) are determined. From the A and C coefficients we form orbitals $\{U_i\}$ or $\{\tilde{U}_i\}$ which it should be emphasized are continuous and have continuous first derivatives throughout all space--they are not themselves muffin-tin functions and hence

Figure 4.1. The dotted lines in this figure represent the flow path for an exact Xα calculation and the solid lines represent the conceptual steps taken in a MT Xα calculation.

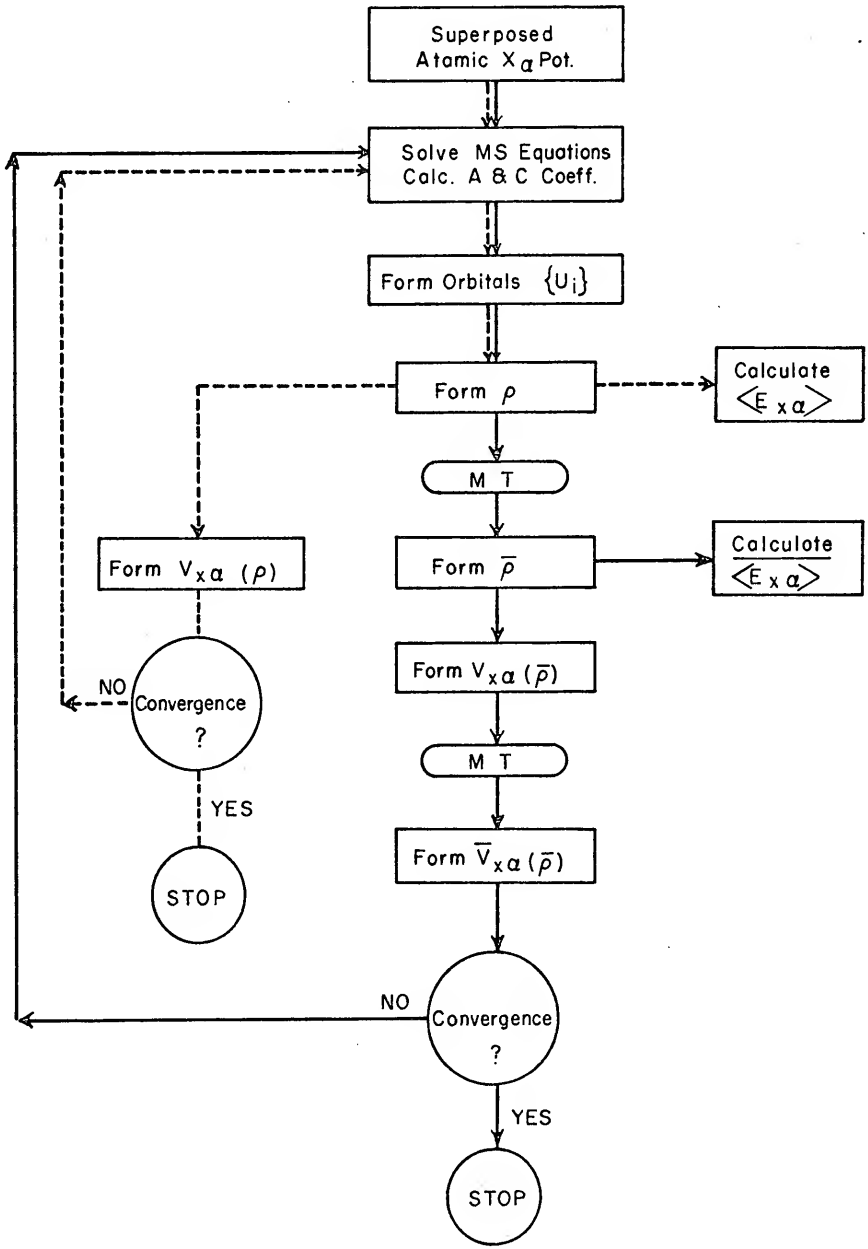


Figure 4.1. Flow Diagram for Conceptual Exact Xα Calculation and a Conceptual MT Xα Calculation.

neither is the density formed from these orbitals. For the exact Xα case having formed the density we then form the new potential $V_{X\alpha}(\rho)$ and the energy $\langle E_{X\alpha}\rangle$. After this we test the convergence criterion which is usually related to the new potential or density and if the convergence criterion is met we are finished. If not then we return to solve the MS equations again and continue iterating in this manner until the convergence criterion is met. The muffin-tin case is similar except that as indicated we have two additional steps--of applying the muffin-tin average to the density and to the potential. As indicated in Figure 4.1 we form the energy $\langle\overline{E_{X\alpha}}\rangle$ from the muffin-tin density $\overline{\rho}$.

In actual MSXα calculations orbitals, density and the "un-muffin-tinned" potential are never formed. Instead the muffin-tin density is formed directly from the A and C coefficients and the muffin-tin potential $\overline{V}_{X\alpha}(\overline{\rho})$ is formed directly from $\overline{\rho}$ (See Appendices C and D). This calculational cycle is shown in Figure 4.2 by the solid lines. In the same figure the dashed lines indicate the steps performed in the calculation of $\Delta\langle E_{X\alpha}\rangle$, the non-muffin-tin first order correction to the functional $\langle\overline{E_{X\alpha}}\rangle$. In this branch of the diagram we form ρ and Δρ from the A anc C coefficients and from these we calculate $\Delta\langle E_{X\alpha}\rangle$. We then combine $\langle\overline{E_{X\alpha}}\rangle$ and $\Delta\langle E_{X\alpha}\rangle$ to form $\langle E_{X\alpha}\rangle$.

Figure 4.2. The dotted lines in this figure represent the flow path for the calculation of $\Delta\langle E_{X\alpha}\rangle$ and the solid lines represent the flow path for an actual MT Xα calculation.

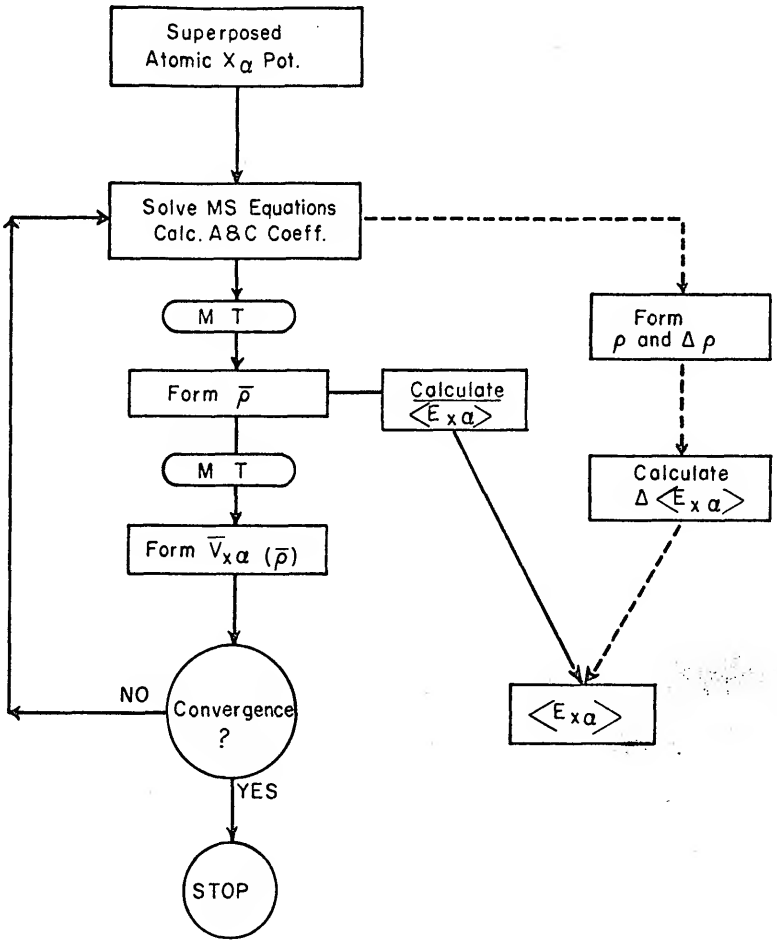


Figure 4.2. Flow Diagram for an Actual MT Xα Calculation and the Major Steps in the NMT Calculation.

CHAPTER V

NUMERICAL INTEGRATION AND IMPORTANCE SAMPLING

5.1 Introduction

The NMT correction $\Delta\langle E_{x\alpha}\rangle$ to the MT $X\alpha$ energy $\langle\overline{E_{x\alpha}}\rangle$ as derived in Chapter III (Eq. (3.24)) and discussed in Chapter IV is in the form of three-and six-dimensional integrals. These integrals must be evaluated numerically and there are two basic types of methods which might be used: the Monte Carlo method or the Haselgrove and Conroy methods. Although the Haselgrove and Conroy methods of numerical integration have enjoyed some degree of success in applications to quantum theoretical problems (see Haselgrove (1961), Conroy (1967), and Ellis and Painter (1970)) they are not adapted to integrating discontinuous functions as are the integrals of $\Delta\langle E_{x\alpha}\rangle$. Hence we have used the Monte Carlo method in these calculations. For a discussion of the theoretical basis for the Monte Carlo evaluation of definite integrals and statistical error analysis see Appendix E and references contained therein.

For a definite integral F of a one-dimensional function f(x)

$$F = \int_a^b f(x)\,dx, \tag{5.1}$$

the Monte Carlo estimate $\hat{F}$ in direct random sampling of the points on the interval (a, b) is given by (see particularly Conroy (1964) and Kahn (1964))

$$\hat{F} = \frac{(b - a)}{N} \sum_{i=1}^{N} f(x_i), \tag{5.2}$$

The absolute statistical error in $\hat{F}$ is proportional to σ_x which is approximated by $\sigma_x = s/N^{1/2}$ where

$$s^2 = \frac{1}{N} \sum_{i=1}^{N} (\hat{F} - (b - a) f(x_i))^2. \tag{5.3}$$

The error ε is interpreted such that the approximate $\hat{F}$ is within $\pm 1\sigma_x$ of F with $\approx$ 64% certainty and within $\pm 2\sigma_x$ with $\approx$ 95% certainty. The quantity s^2 of Eq. (5.3) is an approximation to the quantity σ^2, the variance for the integrand $f(x)$, and in the limit of $N \to \infty$ S^2 is equal to σ^2. The quantity σ has a fixed value for a given function $f(x)$ and hence it is seen that the error ε is proportional to $N^{-1/2}$ where N is the number of random points selected.

This is rather slow convergence as a function of the number of points used. In practical calculations if the cost in time of evaluating the integrand points is high or σ for the function being integrated large then it often will mean that the cost in time of a Monte Carlo evaluation of the integral of sufficient accuracy for the purpose at hand

will be prohibitively high. Hence means must usually be found to reduce the variance σ^2. There are a number of ways of accomplishing this, Kahn (1956) in particular presents a lucid and complete exposition on the subject.* One of the most useful methods of variance reduction and one particularly suited to our present integrations is importance sampling. Importance sampling may be described as a transformation of the integrand and integration variable such that the new integrand is a "smoother" function with smaller σ. Or importance sampling may be described as a means of sampling or picking points in the more "important"--"important" in the sense of making a larger contribution to the Monte Carlo average-regions of the integrand more often. The two descriptions are equivalent but qualitative rather than precise.

In outline, in the body of this chapter we will describe importance sampling first in one dimension and then generalize the discussion to n dimensions. We will discuss the requirements of the present integrands (those of $\Delta\langle E_{x\alpha}\rangle$) which dictate using a rather involved but effective three-dimensional, multicentered, and overlapping sampling scheme. Later in the chapter we will discuss some of the specific forms of the sampling functions used in the present calculations and will end the chapter with a brief note on the Haselgrove and Conroy integration methods.

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*Kahn (1956) lists and discusses six categories of variance reduction: importance sampling, Russian Roulette and splitting, use of expected valves, correlation and regression, systematic sampling, and stratified sampling.

In evaluating the integrals of the NMT correction $\Delta\langle E_{x\alpha}\rangle$ direct Monte Carlo sampling is prohibitively time consuming even as a test case. We have found importance sampling to be essential and it appears at this point that it provides the key to making the calculation of $\Delta\langle E_{x\alpha}\rangle$ a routine part of the MSXα computer codes.

5.2 Importance Sampling in One-Dimension

As explained in Appendix E the statistical mean value $\bar{F}$ of a function f(x) of a random variable x is the integral of f(x) with P(x) the probability distribution function (PDF) for the random variable x:

$$\bar{F} = \int f(x)P(x)dx \ , \tag{5.4}$$

where P(x) satisfies two criteria:

$$\begin{aligned} &1) \quad P(x) > 0 \text{ for all } x \\ &2) \quad \int P(x)dx = 1 \ . \end{aligned} \tag{5.5}$$

In the integral of Eq. (5.1) and its Monte Carlo approximate in Eq. (5.3) we took P(x) to be a constant; that is, we picked points at random with uniform probability on the interval (a, b). Eq. (5.4) is the general form for a mean value and any definite integral may be put into this form with an arbitrary PDF P(x) by a simple transformation:

$$F = \int_a^b f(x)dx$$

$$= \int_a^b I_p(x) P(x) dx, \tag{5.6}$$

where

$$I_p(x) = f(x)/P(x). \tag{5.7}$$

In evaluating this integral by Monte Carlo the approximate $\hat{F}_p$ to F is given by

$$\hat{F}_p = \frac{1}{N} \sum_{i=1}^{N} I_p(x_i). \tag{5.8}$$

The variance σ_p^2 for $\hat{F}_p$ will be different for every PDF P(x) used although for $N \to \infty$ all of the $\hat{F}_p$ will have the same value F. Nevertheless the error which is proportional to σ_p will be different for different P(x)'s. Naturally the question is asked whether or not there exists an optimum PDF for a given integrand f(x) and the answer is yes.

The optimum PDF is that P(x) such that $I_p(x)$ equals a constant C_p for all values of x. For such a PDF, Eq. (5.6) becomes

$$F = \int_a^b I_p(x)\ P(x) dx = \int_a^b C_p\ P(x) dx, \tag{5.9}$$

and the Monte Carlo average is

$$\hat{F}_p = \frac{1}{N} \sum_{i=1}^{N} C_p = C_p\ . \tag{5.10}$$

Then

$$\sigma_p = \left\{ \frac{1}{N} \sum_{i=1}^{N} (\hat{F}_p - C_p)^2 \right\}^{1/2} = 0 \qquad (5.11)$$

and hence

$$\sigma_{xp} = \sigma_p / N^{1/2} = 0 \quad \text{for all N.} \qquad (5.12)$$

The value of mean is $C_p = F$ with a statistical error which is identically zero. (See Conroy (1964) and Kahn (1956).) However, since

$$P(x) = f(x)/C_p, \qquad (5.13)$$

the indicated integral in Eq. (5.9) over P(x) is equivalent to the original integral over f(x). Thus using such a PDF to obtain zero error in the average or mean $\hat{F}_p$ is tantamount to knowing the value of the integral in question in advance.

In practice what one does is pick a PDF P(x) which approximates the integrand f(x) as closely as possible but which still may be readily integrated--analytically or numerically. That is we pick a P(x) such that

$$I_p(x) = f(x)/P(x)$$

$$= C_p(1 + \delta(x)) \qquad (5.14)$$

where C_p is a constant and $\delta(x) << 1$ for all x. The more closely

we approximate f(x) (within a multiplicative constant) the smaller the error σ_{xp} a given number of points.

If the integrand f(x) has zeros (or nodes in higher dimensional cases) then we must divide the range of integration at these zeros and integrate separately the parts of the integral so divided. We must do this if we wish to avoid having a P(x) with zeros (or nodes). We may, instead, let P(x) have some finite value at the zeros of f(x) but then of course we can not do as good a job fitting P(x) (to a multiplicative constant) to f(x).

In practice if we have f(x) evaluated at a number of points we may fit a function g(x) to these points. Then if g(x)>0 for all x we may normalize g(x) and thus produce a bona fide PDF from g(x). This is a desirable feature from a practical viewpoint. If we have g(x) fitted to f(x) at a number of points we may define a normalized G(x) such that

$$G(x) = \frac{1}{\int_a^b g(t)\,dt}\, g(x) \quad . \tag{5.15}$$

Then Eq. (5.6) may be written

$$F = \int_a^b f(x)\,dx$$

$$= \int_a^b [f(x)/G(x)]\, G(x)\,dx$$

$$= \int_a^b \left(\int_a^b g(t)\,dt\right) \left(f(x)/g(x)\right) \left(\frac{g(x)}{\int_a^b g(t)\,dt}\right) dx. \tag{5.16}$$

We may define $I_G(x)$ as

$$I_G(x) = \left(\int_a^b g(t)\,dt\right) \left(f(x)/g(x)\right) \tag{5.17}$$

then Eq. (5.16) may be expressed

$$F = \int_a^b I_G(x)\; G(x)\,dx\ . \tag{5.18}$$

If $g(x)$ is fitted well to $f(x)$ over its entire range of integration, then the function $I_G(x)$ will very closely approach a constant over the entire range and the variance σ_G^2 of $I_G(x)$ should be small. We may change the variable of integration by defining $H(x)$ by

$$dH = G(x)\ dx\ . \tag{5.19}$$

With the $G(x)$ defined in Eq. (5.15)

$$dH = \frac{g(x)}{\int_a^b g(t)\,dt}\ dx\ . \tag{5.20}$$

We may set the limits of the integration such that H varies from H(a) = 0 to H(b) = 1 by defining H(x)

$$H(x) = \frac{1}{\int_a^b g(t)\,dt} \int_a^x g(t)dt \,. \tag{5.21}$$

If we let

$$y = H(x), \tag{5.22}$$

then

$$x = H^{-1}(y) \tag{5.23}$$

and we may rewrite Eq. (5.18) as

$$F = \int_0^1 I_G(H^{-1}(y))dy \,. \tag{5.24}$$

To evaluate this integral by Monte Carlo we pick values randomly between 0 and 1 for the function y and invert these values to find the corresponding values of the variable x through relation Eq. (5.23). In this manner we select random values with the probability distribution G(x) (see Appendix E). With these values of x we evaluate the integrand $I_G(x)$ and form the Monte Carlo average as in Eq. (5.8) for $\hat{F}_p$. Eq. (5.24) above and this procedure is the essense of importance sampling. Note that in the procedure described here one may begin with a function g(x) which is fitted to the function f(x) and through Eqs.

(5.17) and (5.21) produce a normalized PDF G(x) and arrive at the final form Eq. (5.24). This method has obvious advantages in practical applications.

5.3 Importance Sampling in n-Dimensions

The generalization of importance sampling from one-dimension to n-dimensions is direct. Instead of a PDF and integrand of one variable we now have n independent variables, a multidimensional integrand $f(x_1,\ldots, x_n)$, and PDF $P(x_1,\ldots, x_n)$ so that

$$F = \int_{a_1}^{b_1} \cdots \int_{a_n}^{b_n} f(x_1,\ldots, x_n)\, dx_1 \ldots dx_n \,, \qquad (5.25)$$

$$F = \int_{a_1}^{b_1} \cdots \int_{a_n}^{b_n} [f(x_1,\ldots, x_n)/P(x_1,\ldots, x_n)]\, P(x_1,\ldots, x_n) dx_1 \ldots dx_n$$

Since $P(x_1,\ldots, x_n)$ is a PDF then $P(x_1,\ldots, x_n)>0$ for all values of the coordinates x_i in the domain of definition of $P(x_1,\ldots, x_n)$ and the integral of $P(x_1,\ldots, x_n)$ is equal to one (1). In order to evaluate the integral F in Eq. (5.25) by Monte Carlo we must be able to pick points at random from the PDF $P(x_1,\ldots, x_n)$ of n independent variables. We can do this if we transform to n new independent variables $\{h_i\}$ which vary between zero (0) and one (1) and are related to the set of coordinates $\{x_i\}$ by

$$\prod_{i=1}^{n} dh_i = P(x_1, \ldots, x_n) \prod_{k=1}^{n} dx_k \, . \tag{5.26}$$

In this change of coordinates $P(x_1, \ldots, x_n)$ is the Jacobian for the transformation, hence

$$P(x_1, \ldots, x_n) = \begin{vmatrix} \frac{\partial h_1}{\partial x_1} & \frac{\partial h_1}{\partial x_2} & \cdots & \\ \frac{\partial h_2}{\partial x_1} & \frac{\partial h_2}{\partial x_2} & \cdots & \\ \vdots & \vdots & & \frac{\partial h_n}{\partial x_n} \end{vmatrix} \tag{5.27}$$

Such a transformation depending on the form of $P(x_1, \ldots, x_n)$ may be difficult. What we have done in practice is to assume a product form for $P(x_1, \ldots, x_n)$. This of course may limit the capability of $P(x_1, \ldots, x_n)$ to approximate a particularly intricate integrand and hence to produce a good sampling scheme. However, it does product a very workable method of importance sampling. Hence we assume

$$P(x_1, \ldots, x_n) = \prod_{i=1}^{n} P_i(x_i), \tag{5.28}$$

then Eq. (5.26) becomes

$$\prod_{i=1}^{n} dh_i = \prod_{k=1}^{n} P_k(x_k)\,dx_k \,. \tag{5.29}$$

With this form, sampling is done independently for each dimension and the form taken by the sampling functions is like that in one-dimension except that we have a product of n such functions.

The NMT correction $\Delta\langle E_{x\alpha}\rangle$ consists of three-and six-dimensional integrals. From Chapter III we have (Eq. (3.24))

$$\Delta\langle E_{x\alpha}\rangle = \int \Delta\rho(\vec{r}) \cdot \Delta V_{Ne}(\vec{r})\,d\vec{r} + \int \Delta\rho(\vec{r}) \cdot \Delta V_{c}(\bar{\rho},\vec{r})\,d\vec{r}$$

$$+ C_\alpha \int \left(\rho(\vec{r})^{4/3} - \bar{\rho}(\vec{r})^{4/3}\right) d\vec{r}$$

$$+ \frac{1}{2} \int\int \frac{2\Delta\rho(\vec{r}_1)\ \Delta\rho(\vec{r}_2)}{r_{12}}\, d\vec{r}_1 d\vec{r}_2 \,. \tag{3.24}$$

The last term is a six-dimensional term and may be evaluated directly as a six-dimensional integral or as a three-dimensional integral within a three-dimensional integral. Since this integral is second order in $\Delta\rho$ it might be argued on intuitive grounds that this integral is small relative to the other integrals in $\Delta\langle E_{x\alpha}\rangle$. Actual direct six-dimensional integration of this integral has revealed that it is quite small

compared to the other integrals and so it will not be discussed further here. The method of handling the r_{12}^{-1} singularity in the integrand of this term is a method due to Boys and Rajagopal (1966) and is discussed in Appendix F. We devote our attention in the rest of the chapter to the remaining three-dimensional terms.

The integrands of the three-dimensional integrals may be combined into one term which we will call $\Delta I(\vec{r})$

$$\Delta I(\vec{r}) = \Delta\rho(r) \cdot \Delta V_{Ne}(\vec{r}) + \Delta\rho(\vec{r}) \cdot \Delta V_{c}(\bar{\rho}, \vec{r}) + C_{\alpha}(\rho(\vec{r})^{4/3} - \bar{\rho}(\vec{r})^{4/3}) \quad . \tag{5.30}$$

In Figure 5.1 we give a contour plot of $\Delta I(\vec{r})$ over part of the C_2 molecule. The contours of the plot give the values of $\Delta I(\vec{r})$ in a plane which coincides with the X-Z plane of the molecule and cuts through the Z axis upon which the two carbons are symmetrically located with respect to the origin. In the plot we give only the positive X and the positive Z quadrant of the plane. In the figure the heavy lines indicate the boundaries of the carbon atom and outer sphere. The thin solid lines indicate positive and the dotted lines indicate negative values of $\Delta I(\vec{r})$. The value of each contour is labelled on the contour. In examining the figure one can see that $\Delta I(\vec{r})$ is a fairly complicated function which is distinguished by a number of nodes and discontinuities. In

Figure 5.1. The function $\Delta I(\vec{r})$ which is contour plotted in this figure is the integrand of the NMT correction $\Delta\langle E_{X\alpha}\rangle$ and is defined in Eq. (5.30).

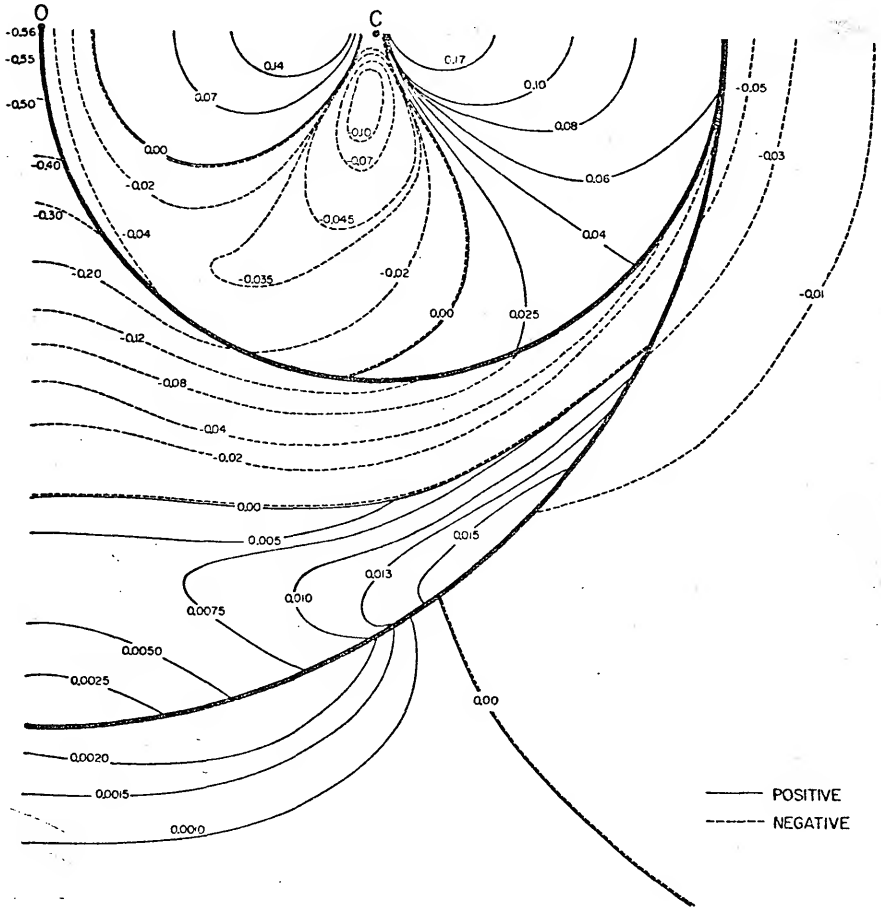


Figure 5.1. Contour Plot of $\Delta I(\vec{r})$ in the X-Z Quadrant of the C_2 Molecule.

searching for appropriate sampling functions we must have functions which have discontinuities in the same places and approximately the same magnitude as those of $\Delta I(\vec{r})$. We must also have functions which divide the integration region at least approximately along node lines. Of course not all of these features can be built into simple sampling functions, but we have been able to reproduce most of these features. In particular it may be observed that the discontinuities occur along sphere boundaries and so should not be particularly hard to position in a sampling function. Also it may be observed that a kind of shell surrounds the carbon sphere boundary which overlaps into the outer sphere region and in the center region or bond region of the molecule.

It seems evident then that it will be easiest to fabricate a sampling function which is a sum of sampling functions on different centers, some of which overlap. As in one-dimension we will begin with sampling functions $g_\alpha(\vec{r})$ such that $g_\alpha(\vec{r}) > 0$ for all values of $\vec{r}$ for which $g_\alpha(\vec{r})$ is defined and we will attempt to fit these $g_\alpha(\vec{r})$'s in combination to the complicated features of $\Delta I(\vec{r})$. Later in the chapter we will consider specific forms for the $g_\alpha(\vec{r})$'s.

At a given point then $g(\vec{r})$ will be represented as a sum of functions g_α from different centers α with weights ω_α

$$g(\vec{r}) = \sum_\alpha \omega_\alpha \, g_\alpha(\vec{r} - \vec{r}_\alpha) \tag{5.31}$$

(The weights are necessary only when g_α overlap). Although

it is not necessary we will assume for now that each g_α has a product form in spherical coordinates

$$g_\alpha(\vec{r} - \vec{r}_\alpha) = g_r^\alpha(|\vec{r} - \vec{r}_\alpha|)g_\theta^\alpha(\theta_\alpha)g_\phi^\alpha(\phi_\alpha) \qquad (5.32)$$

where θ_α and ϕ_α are measured about the αth center. Some of the g_α's actually used are of a different form but it has proven to be convenient in our work to mainly use the spherical coordinate form. The g_α's are all of limited range and zero outside that range. They are such however that their sum which is $g(\vec{r})$ is not zero anywhere over the region of integration except along the boundaries of disjoint sampling regions. Note that the range of these functions may be limited in r, θ, or ϕ.

Assuming the form for $g(\vec{r})$ given in Eq. (5.31) we transform the Eq. (3.24) (where we ignore the six-dimensional term)

$$\Delta\langle E_{x\alpha}\rangle = \int \Delta I(\vec{r})\, d\vec{r}$$

$$= \int \Delta I(\vec{r}) \frac{\sum_\alpha \omega_\alpha g_\alpha(\vec{r} - \vec{r}_\alpha)}{\sum_\beta \omega_\beta g_\beta(\vec{r} - \vec{r}_\beta)}\, d\vec{r} \,. \qquad (5.33)$$

This form separates the integral into a sum of integrals over the range of definition of the individual g_α's

$$\Delta\langle E_{x\alpha}\rangle = \sum_{\alpha} \omega_{\alpha} \int [\Delta I(\vec{r})/\sum_{\beta} \omega_{\beta} g_{\beta}(\vec{r} - \vec{r}_{\beta})]\, g_{\alpha}(\vec{r} - \vec{r}_{\alpha}) d\vec{r}. \quad (5.34)$$

We define $\Delta I_c(\vec{r})$

$$\Delta I_c(\vec{r}) = \Delta I(\vec{r})/\sum_{\beta} \omega_{\beta} g_{\beta}(\vec{r} - \vec{r}_{\beta}) \ . \quad (5.35)$$

If we do a good job of fitting the g_{α}'s to $\Delta I(\vec{r})$ then $\Delta I_c(\vec{r})$ should close to a constant in each integral in the sum in Eq. (5.34) and the convergence of each integral should be good.

With $\Delta I_c(\vec{r})$ substituted in Eq. (5.35) we have

$$\Delta\langle E_{x\alpha}\rangle = \sum_{\alpha} \omega_{\alpha} \int \Delta I_c^{\alpha}(\vec{r}) g_{\alpha}(\vec{r} - \vec{r}_{\alpha}) dr \ . \quad (5.36)$$

(We designate ΔI_c as ΔI_c^{α} for convenience in the region α). We will define a new variable h_{α} by

$$d\vec{h}_{\alpha} = g_{\alpha}(\vec{r} - \vec{r}_{\alpha}) d\vec{r} \quad (5.37)$$

where

$$d\vec{h}_{\alpha} = dh_r^{\alpha} dh_{\theta}^{\alpha} dh_{\phi}^{\alpha} \ . \quad (5.38)$$

We defined $g_{\alpha}(\vec{r} - \vec{r}_{\alpha})$ as a simple product form in

Eq. (5.32) and substituting it in Eq. (5.37) we have

$$dh_r^\alpha dh_\theta^\alpha dh_\phi^\alpha = g_r^\alpha(|\vec{r} - \vec{r}_\alpha|)g_\theta^\alpha(\theta_\alpha)g_\phi^\alpha(\phi_\alpha)|\vec{r} - \vec{r}_\alpha|^2 \sin\theta_\alpha d|\vec{r} - \vec{r}_\alpha| d\theta_\alpha d\phi_\alpha. \tag{5.39}$$

Hence the variable transformations are independent and we may do each separately. Letting $\vec{t}_\alpha = \vec{r} - \vec{r}_\alpha$ we have

$$\begin{aligned} dh_r^\alpha &= t_\alpha^2 g_r^\alpha(t_\alpha)dt_\alpha \\ dh_\theta^\alpha &= \sin\theta_\alpha g_\theta^\alpha(\theta_\alpha)d\theta_\alpha \\ dh_\phi^\alpha &= g_\phi^\alpha(\phi_\alpha)d\phi_\alpha. \end{aligned} \tag{5.40}$$

Each of the relations of Eq. (5.40) may be integrated as in Eq. (5.21) for one-dimension to produce an H_α which varies from zero (0) to one (1) and also a normalized g_α which we will call G_α.

To illustrate this we will carry through the variable transformation for dh_r^α. We will assume the function $g_r^\alpha(t_\alpha)$ of Eq. (5.32) and Eq. (5.40) to be defined only between the values of t_α of t_I^α and t_F^α. Then to normalize $g_r^\alpha(t_\alpha)$ over the range to get G_r^α we have

$$G_r^\alpha(t_\alpha) = \frac{g_r(t_\alpha)}{\int_{t_I^\alpha}^{t_F^\alpha} g_r^\alpha(t_\alpha)t_\alpha^2 dt_\alpha} \tag{5.41}$$

as in Eq. (5.15) for one-dimension. Then as before (see Eq. (5.21)) we may define $H_r^\alpha(t_\alpha)$ as

$$H_r^\alpha(t_\alpha) = \frac{1}{\int_{t_I^\alpha}^{t_F^\alpha} g_r^\alpha(t_\alpha) t_\alpha^2 dt_\alpha} \int_{t_I^\alpha}^{t_\alpha} g_r^\alpha(t_\alpha) t_\alpha^2 dt_\alpha \ . \qquad (5.42)$$

We may define similar functions for θ_α and ϕ_α. For convenience we define a constant $C_{\alpha r}$

$$C_{\alpha r} = \int_{t_I^\alpha}^{t_F^\alpha} g_r^\alpha(t_\alpha) t_\alpha^2 dt_\alpha \qquad (5.43)$$

and similarly for $C_{\alpha\theta}$ and $C_{\alpha\phi}$.

If we define $Y_{\alpha r}$, $Y_{\alpha\theta}$, $Y_{\alpha\phi}$, as follows

$$Y_{\alpha r} = H_r^\alpha(t_\alpha), \qquad Y_{\alpha\theta} = H_\theta^\alpha(\theta_\alpha), \qquad Y_{\alpha\phi} = H_\phi^\alpha(\phi_\alpha) \qquad (5.44)$$

then

$$\begin{aligned} |\vec{r} - \vec{r}_\alpha| = t_\alpha &= H_r^\alpha \ (Y_{\alpha r})^{-1} \\ \theta_\alpha &= H_\theta^\alpha \ (Y_{\alpha\theta})^{-1} \\ \phi_\alpha &= H_\phi^\alpha \ (Y_{\alpha\phi})^{-1} . \end{aligned} \qquad (5.45)$$

Then Eq. (5.36) may be written

$$\Delta\langle E_{x\alpha}\rangle = \sum_{\alpha} \omega_\alpha C_{\alpha r} C_{\alpha\theta} C_{\alpha\phi} \int_0^1 \int_0^1 \int_0^1 \Delta I_c^\alpha (H_r^\alpha \quad (Y_{\alpha r})^{-1}, H_\theta^\alpha \quad (Y_{\alpha\theta})^{-1},$$

$$H_\phi^\alpha \quad (Y_{\alpha\phi})^{-1}) \quad dY_{\alpha r} dY_{\alpha\theta} dY_{\alpha\phi} \,. \tag{5.46}$$

There is no approximation in Eq. (5.46), the variables of integration of Eq. (5.33) have only been transformed and the original single integral split into a sum of integrals over regions α --some of which overlap. With this form we perform the Monte Carlo average for each of the integrals in the sum of Eq. (5.46). To do this we select points randomly between zero and one for each of the three H's (H_r^α, H_θ^α, H_ϕ^α) invert to find the appropriate coordinate and combine the coordinates to locate one point $\vec{r}_i$ at which the integrand $\Delta I_c(\vec{r})$ is evaluated. From these values of $\Delta I_c(\vec{r}_i)$ we form the Monte Carlo average. For a particular region α we define $\Delta\hat{\varepsilon}_\alpha$ where

$$\Delta\hat{\varepsilon}_\alpha = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \omega_\alpha C_{\alpha r} C_{\alpha\theta} C_{\alpha\phi} \Delta I_c^\alpha (t_{\alpha i}, \theta_{\alpha i}, \phi_{\alpha i}) \tag{5.47}$$

and then $\Delta\langle\hat{E}_{x\alpha}\rangle$ is given by

$$\Delta\langle\hat{E}_{x\alpha}\rangle = \sum_{\alpha} \Delta\hat{\varepsilon}_\alpha \tag{5.48}$$

which is equivalent to Eq. (5.46).

For a region α we calculate s_α^2

$$s_\alpha^2 = \frac{1}{N_\alpha} \sum_{i=1}^{N} [\Delta\hat{\varepsilon}_\alpha - (\omega_\alpha C_{\alpha r} C_{\alpha\theta} C_{\alpha\phi} \Delta I_c^\alpha(t_{\alpha i}, \theta_{\alpha i}, \phi_{\alpha i}))]^2, \quad (5.49)$$

and $\sigma_{x\alpha}$ by

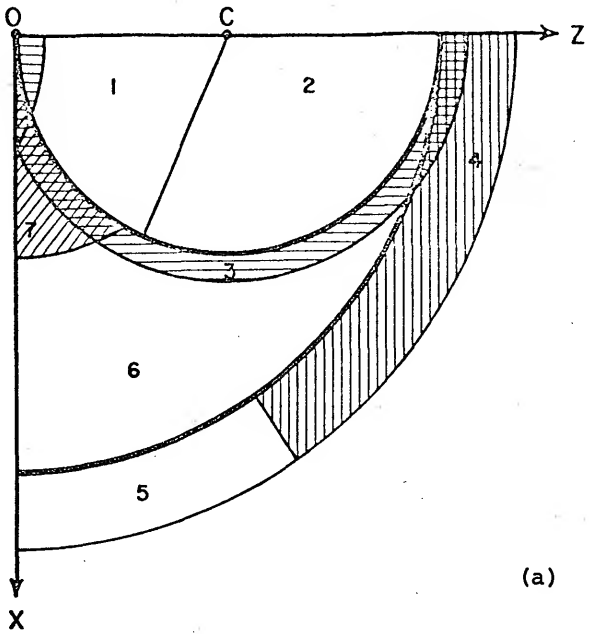
$$\sigma_{x\alpha} = s_\alpha / N_\alpha^{1/2} . \quad (5.50)$$

The statistical error for $\Delta\hat{\varepsilon}_\alpha$ is then proportional to $\sigma_{x\alpha}$ as explained in Appendix E. To find the total σ_x for $\Delta\langle\hat{E}_{x\alpha}\rangle$ we have (see Mosteller et al. (1961))

$$\sigma_x = [\sum_\alpha \sigma_{x\alpha}^2]^{1/2}. \quad (5.51)$$

5.4 Some Specific Sampling Functions

Returning to Figure 5.1 one can see that the contour plot of $\Delta I(\vec{r})$ defined in Eq. (5.30) may be divided into regions delineated by the carbon and outer sphere boundaries, approximately by node lines, and/or by large changes in magnitude in $\Delta I(\vec{r})$. In Figures 5.2(a) and 5.2(b) below we have reproduced Figure 5.1 along with a schematic delineating some possible sampling regions numbered 1-7. Those regions which overlap have been "hatched" in Figure 5.2(a) to



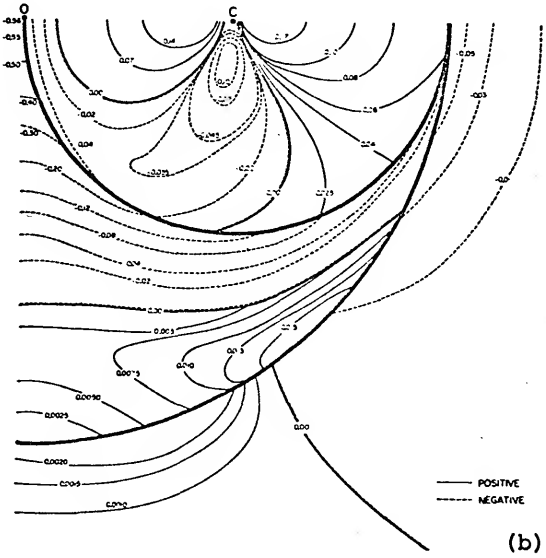


Figure 5.2. Schematic Plot (a) and Contour Plot (b) of $\Delta I(\vec{r})$.

indicate the overlapping. (As explained earlier the C-C axis is coincident with the Z axis of the coordinate system used with the center of the C-C bond at the origin labelled "0". The contour plot as well as the schematic are taken from the X-Z quadrant of the X-Z plane of the molecule. One would have to rotate the figures about the Z-axis to get a true three-dimensional impression of the actual functions involved).

The carbon region is divided in the angle θ (measured from Z axis) into two sampling regions numbered 1 and 2. The sampling within each region was taken to be uniform in r, θ, and ϕ except for the $r^2\sin\theta$ included in the spherical volume element. (If sampling is being done in spherical coordinates this factor is assumed. In fitting a sampling function to the contours this factor is not considered). Fitting an exponential or gaussian sampling function for the radial dependence within either region did not significanlty improve the convergence for the Monte Carlo average for that region.

In the outer sphere region as in the carbon region the sampling was divided into two regions in the angle θ at θ_o-regions #4 and #5. Number 4 we call a polar region and it is duplicated at the opposite end of the molecule. Number 5 we call an equator region and it is located between θ_o and $\pi-\theta_o$. Notice that a region #3 from around the carbon region overlaps the polar region. In the polar region we have to subtract off the #3 overlapping sampling function (whatever

it is) from $\Delta I(\vec{r})$ before fitting to the remainder. We have found that for C_2 a good fit could be obtained to the remainder with an exponential $\exp(-a(r_o - b_o))$ (where r_o is measured from "0" and b_o is the outer sphere radius and a is to be determined by fitting) in radius and a $\cos^4\theta$ function in θ. The sampling in ϕ due to cylindrical symmetry is taken to be uniform. In the outer equator region--#5-- a good fit was $\sin^4\theta$ in θ and a gaussian $\exp(-a(r_o - b_o)^2)$ in radius.

In examining the contours of $\Delta I(\vec{r})$ in Figure 5.2(b) one may observe that the carbon is surrounded by a kind of negative shell and thus in the sampling we have surrounded the carbon with a shell region--#3. Notice that this shell region overlaps with the outer sphere polar region, the other carbon region, the shell region from the other carbon (indicated in the schematic near "0"), and also another region--#7-- indicated by diagonal hatching. In this shell region uniform smapling is used in θ and ϕ (measured from carbon nucleus) and a gaussian is used to fit the radial behavior--$\exp(-a(r_c - b_c)^2)$ where a must be determined by the fit, r_c is measured from the carbon nucleus and b_c is the carbon sphere radius.

The large region #6 does not possess many notable features, particularly it does not possess large changes in magnitude of $\Delta I(\vec{r})$. This consideration and the fact that it is a very peculiar shape led us in actual calculations to use a simple uniform sampling in X, Y, Z in this region.

The last remaining region is #7 in the bond region

of the molecule and we call it the bond sampling region or function. For this region we developed a more specialized function the derivation of which is given in Appendix G. Basically the bond function is a gaussian but it is only integrated over the bond region indicated by diagonal hatching in Figure 5.2(a). This region is a sphere centered on "0" with the intersection of this sphere with the carbon spheres excluded. This bond function provided the radial dependence and the angular sampling was uniform in θ and ϕ.

This completes the survey of sampling functions indicated by the regions in the schematic of Figure 5.2(a). Other sampling functions are possible but the above were used for calculations and with careful fitting were sufficient to reduce the number of integration points needed to an acceptable level for our actual calculations. Typically for C_2 we found it necessary to use approximately 1000 integration points in the carbon sphere an outer sphere and about 3000 integration points in the intersphere region. Let there be no doubt that sampling is of <u>crucial</u> importance in reducing the number of sampling points to this level and it is hoped that the sampling may be improved further. The current process of fitting is a bit laborious but semi-automated in the codes developed thus far. It is our belief that the process can eventually be completely automated.

With regard to the kind of sampling functions used it should be emphasized that they must be such as to be easily integrated (analytically or numerically) and also inverted.

To understand this please refer to the discussion in Section 5.3 particularly to Eqs. (5.42), and (5.45), and (5.46) and the discussion following Eq. (5.46). Thus in setting up sampling regions one should avoid creating odd shaped regions such as #6 in Figure 5.2(a) unless one intends to use simple uniform sampling in such regions (which really is not importance sampling at all). The overlapping of sampling functions indicated in the schematic of Figure 5.2(a) is automatically provided for by the basic scheme of decomposing the integral to be integrated into regional integrals with appropriate weights where the regions overlap. This is not a limitation on the kind of sampling functions used; rather in some instances, such as the intersection of regions #'s 1, 3, and 7, it appears to be a necessity which can not be avoided. In the case of region #6 above uniform sampling due to the nature of $\Delta I(\vec{r})$ in that region proved to be sufficient to obtain good convergence with a reasonable number of points (we actually used 800 points in region #6). The limit to the usefulness of importance sampling in a complicated case such as we have for C_2 is basically the limit to the practitioneer's ingenuity.

5.5 A Note on the Haselgrove and Conroy Methods of Numerical Integration

We stated in the introduction that the Haselgrove and Conroy methods were not adapted to integrating discontinuous

functions (see Haselgrove (1961) and Conroy (1967)). This assessment may be borneout by careful examination of these authors' respective papers. In both cases the analysis of the error in the estimates of integrals evaluated with these methods is proportional to the largest Fourier component of the integrand to be integrated. In the case of $\Delta I(\vec{r})$ (see Figure 5.1) we have no way of calculating or even estimating the largest Fourier components. In both methods discontinuous functions are either marginal to or completely excluded from the class of functions to which the methods may be profitably applied. For details the reader may refer to the above mentioned papers. As an actual matter of fact in our study we applied the open Haselgrove method to several of the regions and obtained for the same number of points virtually identical results as with Monte Carlo.

CHAPTER VI

RESULTS AND CONCLUSIONS

6.1 Introduction

The two major approximations in the application of the MSXα method (as well as APW and KKR methods) are the Xα ($\rho^{1/3}$) local exchange approximation and the MT approximation. The two approximations, although not fundamentally connected nor dependent, are nevertheless in practice interwoven; and, hence, it has been difficult in practice to separate and assess in a definitive way the impact of the two approximations upon calculated results. The research of this dissertation represents an attack on this problem; particularly, this research has been an investigation of the effect of the MT approximation to the density upon the Xα total energy $-\langle E_{X\alpha} \rangle$. There have been two goals. First, to understand the MT approximation to the Xα total energy through an analysis of the NMT correction to the MT Xα total energy and the improvement obtained by the inclusion of the NMT correction in the total energy. Second, to develop a general and practical method of evaluating the NMT correction to the MT Xα total energy. We believe these two goals have been in large measure achieved. In achieving these two goals, we have, because of the improvement

provided by the inclusion of the NMT correction, achieved a significant extension of the MSXα method opening new areas for useful calculations on larger and heavier molecules. The achievement of a better understanding of the MT approximation has led to a better understanding of the Xα approximation; and, it appears from the results obtained thus far (which are reported later in this chapter), that of the two approximations the MT approximation is by far the most severe.

In the main body of this chapter we will discuss the detailed results of calculations of the NMT correction $\Delta\langle E_{X\alpha}\rangle$ to the MT energy $\overline{\langle E_{X\alpha}\rangle}$ for two test case molecules- C_2 and Ne_2. We will present results and detailed analysis for three points on the C_2 potential curve for the $^1\Sigma_g^+$ ground state of C_2 (four points counting the dissociated atomic limit). The molecule C_2 in particular was picked as a test case because of the rather drastic failure of the MT MSXα calculations to predict a binding curve as they should have for the $^1\Sigma_g^+$ ground state of C_2- in fact the MT calculations predicted a distinctly repulsive curve for this state. One point near the experimental equilibrium position for Ne_2 was calculated as an additional test case, for its intrinsic interest, and for possible correlation with some solid state calculations. The Ne_2 molecule, although a homonuclear, covalently bound molecule just as C_2 and like C_2 also unbound in the MT approximation, has a somewhat qualitatively

different charge structure than C_2. There is particular interest in Ne_2 because of a number of recent APW calculations performed on rare gas crystals which have all predicted cohesion of these solids-even by about the correct amounts (See Trickey and Averill (1972); Trickey, Averill, and Green (1972); and Trickey, Green, and Averill (submitted for publication (1973)). These results have been disputed by some physicists on the ad hoc assumption that the Xα method per se is not capable in principle of producing such results; that is, binding of a rare gas crystal or molecule by van der Waals attraction.

To anticipate the principal findings, the addition of the NMT correction to the MT Xα total energy for C_2 and Ne_2 results not just in a qualitative improvement but in a significant quantatative improvement in the Xα total energy for these two molecules. With the inclusion of the NMT correction not only binding but binding of approximately the correct amount is predicted for both molecules. For C_2 very good spectroscopic constants (see Table 6.3) are predicted which compare very favorably with a CI calculation performed by Fougere and Nesbet (1966). In the case of Ne_2 the binding predicted (which agrees favorably with experiment) at approximately the experimental equilibrium position is six orders of magnitude smaller than the total energy of the molecule (the binding for C_2 is about four orders of magnitude smaller than the total energy of

the molecule). From this result it may be rightly concluded that the MSXα method with the inclusion of the NMT correction in the Xα total energy is capable of reproducing fine effects--even those as relatively small as the binding of Ne_2.

Parenthetically we should like to point out that the calculation of the NMT correction $\Delta\langle E_{X\alpha}\rangle$ has not from a programming and calculational point of view been an easy task. However, it has proven tractable and has been made possible through the development of the admittedly complex but nevertheless workable sampling and integration scheme described in Chapter V. This scheme has at present reached the point of very reasonable computational times even though it involves the integration of very complicated three- and six-dimensional integrals. At present we have only worked with small molecules but there is no difficulty in extending the sampling and integration scheme to larger and more structured molecules. One molecule of particular interest for future work for example is the water (H_2O) molecule; i.e., whether or not MSXα calculations with the NMT correction can predict the correct bond angle between the hydrogens in the water molecule.

Summarizing the text up to the present point, in Chapters II and III we emphasized the difference between $\overline{\langle E_{X\alpha}\rangle}$ and $\langle E_{X\alpha}\rangle$ and the two sets of orbitals, $\{\tilde{u}_i\}$ and $\{u_i\}$ respectively, which minimize these two different energy

functionals. In Chapter III we emphasized that there is only one MT approximation--that of the density. The so-called MT approximation to the potential follows from the variation of the MT total energy functional $\overline{\langle E_{X\alpha} \rangle}$ which leads to the one-electron equations for the set of orbitals $\{\tilde{u}_i\}$ which minimize $\overline{\langle E_{X\alpha} \rangle}$. Also in Chapter III we discussed the explicit form for the NMT correction $\Delta\langle E_{X\alpha} \rangle$ to the MT Xα energy $\overline{\langle E_{X\alpha} \rangle}$. In Chapter IV, the key chapter of this dissertation, we discussed the explicit connection between $\overline{\langle E_{X\alpha} \rangle}$ and $\langle E_{X\alpha} \rangle$ through the NMT correction $\Delta\langle E_{X\alpha} \rangle$. In particular we showed that in our present method in which we use the set of orbitals $\{\tilde{u}_i\}$ which minimize $\overline{\langle E_{X\alpha} \rangle}$ to calculate $\Delta\langle E_{X\alpha} \rangle$ our procedure is analagous to a first order perturbation calculation in Rayleigh-Schroedinger perturbation theory. We showed further that the same method could be applied to the calculation of the total Xα energy for excited states. We also showed that the method could not be extended in any consistent way to the second or higher orders of a perturbation series. These topics will be discussed again later in this chapter in the light of our results (see Section 6.4). Also in Chapter IV we showed that the one-electron Xα eigenvalues could be corrected by a first order perturbation correction very analagous to that of the total energy. This topic also will be discussed further below (see Section 6.5). In Chapter V we discussed in detail the sampling and integration

scheme which we have used and which has made the calculation of $\Delta\langle E_{X\alpha}\rangle$ with the set $\{\tilde{u}_i\}$ both possible and realistic.

In the body of this chapter we will discuss briefly the qualitative features of the C_2 and Ne_2 molecules and the relevant so-called MSXα "parameters" used in these calculations--the sphere radii and the choice of the α exchange parameter. We will analyze the results for one of the three calculated points on the C_2 potential curve--that at 2.48 Bohr--in great detail through a series of contour and line plots of the numerous quantities involved in the calculation of $\Delta\langle E_{X\alpha}\rangle$. Following this we give a breakdown of the regional contributions to $\Delta\langle E_{X\alpha}\rangle$ from various sampling regions as described in Section 5.3. Next we give the potential curve for C_2 obtained in these calculations as well as the predicted spectroscopic constants--dissociation energy, equilibrium separation, and force constant. Following this we give the Ne_2 results for the Ne_2 point calculation. In the light of the results for the two molecules we review the arguments of Chapter IV concerning the improvement obtained by the calculation of the NMT correction term and make our main inferences from the results and conclusions about the method. In further discussion we consider the ramifications of the Virial Theorem and the correlation of the Ne_2 result with APW solid state calculations on the rare gas crystals. Finally (see Section 6.5), we consider in the light of our present

results further tests of the method, future work in new directions, and some crucial questions raised by this research. One crucial question which is raised by this research but not resolved is the question of the quality of the MT Xα orbitals themselves.

6.2 The C_2 and Ne_2 Molecules

Basic Descriptions

The C_2 molecule in the ground state consists of two carbon atoms covalently bound together in a $^1\Sigma_g^+$ state. That is, its wave function has zero component of angular momentum about the molecular axis, has even inversion symmetry through the center of the molecule, and has positive parity. Its molecular orbital configuration is $(1\sigma_g)^2$ $(1\sigma_u)^2$ $(2\sigma_g)^2$ $(2\sigma_u)^2$ $(1\pi_u)^4$.

Similarly the Ne_2 molecule in its ground state also exists in a $^1\Sigma_g^+$ state. Its molecular orbital configuration is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_g)^4(1\pi_u)^4(3\sigma_g)^2(3\sigma_u)^2$.

Thus both molecules in the ground state exist in closed shell configurations. Both may be adequately treated in the non-spin-polarized approximation as far as their multiplet structure is concerned.

MSXα "Parameters" - Sphere Radii and α Exchange Parameter

In the MT approximation (see Section 3.2 and Figure 3.1) for C_2 and Ne_2 we surround each of the carbon or neon

nuclei with spheres of equal radii such that the spheres are tangent to each other at the center of the axis joining the nuclei. Hence these radii are always one-half the separation between the nuclei. The outer sphere is such that it is centered on the center of the bond axis and its radius is such that it just touches the carbon spheres at the "ends" of the MT molecule. Thus the outer sphere's radius is equal to the separation distance between the carbon nuclei or neon nuclei.

A given molecule may dissociate into many different final atomic and molecular products depending upon the energy of the dissociation. In our present calculations we chose the lowest energy dissociation limit for both C_2 and Ne_2. For Ne_2 this is simple, the dissociation limit consists of two neutral Ne atoms in their ground state. Hence for the Ne_2 calculation we have used the α exchange parameter for the neutral closed shell Ne atom--an α of 0.72997 as originally determined by Schwarz (1972). With such an α the Ne_2 molecule in the Xα method will separate into two neutral Ne atoms at infinite separation with the energy of two neutral Ne atoms (see Slater (1972a)).

For C_2 the situation is slightly more complicated. The free carbon atom is an open shell atom in its ground state which in the central field model has a configuration of $(1s)^2\ (2s)^2\ (2p)^2$. From the configuration of two identical p electrons one may form three multiplets: ^1S, ^3P, and ^1D. Of these, the ^3P is lowest in energy for carbon and

in our case of C_2 in the $^1\Sigma_g^+$ ground state we wish to dissociate it into two carbon atoms in their lowest energy state - both carbons in the ^3P state. Of all the possible dissociation curves for the C_2 molecule this gives us the one of lowest energy at equilibrium and lowest energy at infinite separation. A spin-polarized calculation may be performed for the carbon atom and it will give the energy of the ^3P state. Hence for the $X\alpha$ carbon atom we pick α so as to give us the energy of the carbon atom in the ^3P state. This gives us an α of 0.75331 (J.H. Wood, private communication) and this is the α we have used for the C_2 calculations.

6.3 Features of the C_2 Molecule and $\Delta\langle E_{X\alpha}\rangle$ at an Internuclear Separation of 2.48 Bohr

In this section in order to show clearly some of the more important functions involved in the calculation of $\Delta\langle E_{X\alpha}\rangle$ and the meaning and relationship of these functions we will give a discussion of a series of contour and line plots of these functions. The discussion, detailed as it is, will reveal some of the qualitative characteristics of the NMT correction and its components as well as the MT approximation itself, some of which characteristics we argue will be universally present although in modified form from molecule to molecule. In the discussion we will examine only some of the salient features of these detailed plots in the interests of space, brevity, and perspective. The reader may examine these

plots in greater detail if he so desires - the researcher has done so at great length. In the contour and line plots we will examine two valence orbitals, the total density (formed from the MT Xα orbitals), the NMT density $\Delta\rho$, and the integrand of $\Delta\langle E_{X\alpha}\rangle$ and its component parts.

All of the contours as well as line plots of this section are for C_2 at a separation of 2.48 Bohr (which it will be seen in the next section is virtually at the minimum of the potential curve for C_2 with the NMT correction included). The line plots* are taken over the molecule including both nuclei and taken out to a distance of 3.1 Bohr from the center of the molecule (essentially to the "edge" of the molecule end-on). The vertical scale of the line plots (see Figure 6.1 for example) is the value of the function plotted taken in the X-Z plane of the molecule where the origin of the corrdinate system is centered on the center of the bond axis with the Z axis taken along the bond axis. The lines are uniformly spaced across the molecule in the X-Z plane. When plotted each line of the line plot is displaced slightly vertically and horizontally (to the left) from the preceding line below it. This gives a quasi-perspective to the plot. The zero value of the function plotted may be determined usually by taking the

*The line plotter program which has been of great use was made available to the researcher by Dr. N.H.F. Beebe of the QTP of the University of Florida. The program was originally written by Dr. Harold McIntosh of the University of Mexico.

point of the line plot farthest from the center of the plot since all values, positive and negative, are plotted from zero and the whole plot positioned on the page depending on the maximum and minimum values of the functions plotted. The contour plots consist only of the positive X-Z quadrant of a coordinate system similarly situated as above for the line plots. The values of the contours (of equal values) are labelled on the figures. The values on the contours are absolute and are not scaled as are most of the line plots which were scaled to fit the page (unless otherwise specified).

In Figures 6.1 and 6.2 we give line plots respectively of the valence $2\sigma_g$ and valence $2\sigma_u$ states of the C_2 molecule. These two orbitals are part of the set of orbitals $\{\tilde{u}_i\}$ which are solutions to the Xα one-electron equations with the MT potential $\overline{V}_{X\alpha}(\overline{\rho},\vec{r})$ - we refer to these as the MT Xα orbitals (see Eq. (3.44)). These two orbitals have respectively eigenvalues of -1.348 Ryd and -0.688 Ryd. The σ_g orbital has a partial wave expansion (see Section 3.5 and Appendix B) including terms of $\ell=0$ and $\ell=2$ in the outer sphere and $\ell=0$, 1, and 2 in the carbon sphere. The σ_u orbital has a partial wave expansion including $\ell=1$ and $\ell=3$ in the outer sphere and $\ell=0$, 1 and 2 in the carbon sphere. The expansions in the outer sphere and carbon spheres are matched in the multiple-scattering formalism to solutions for the intersphere region (solutions for a

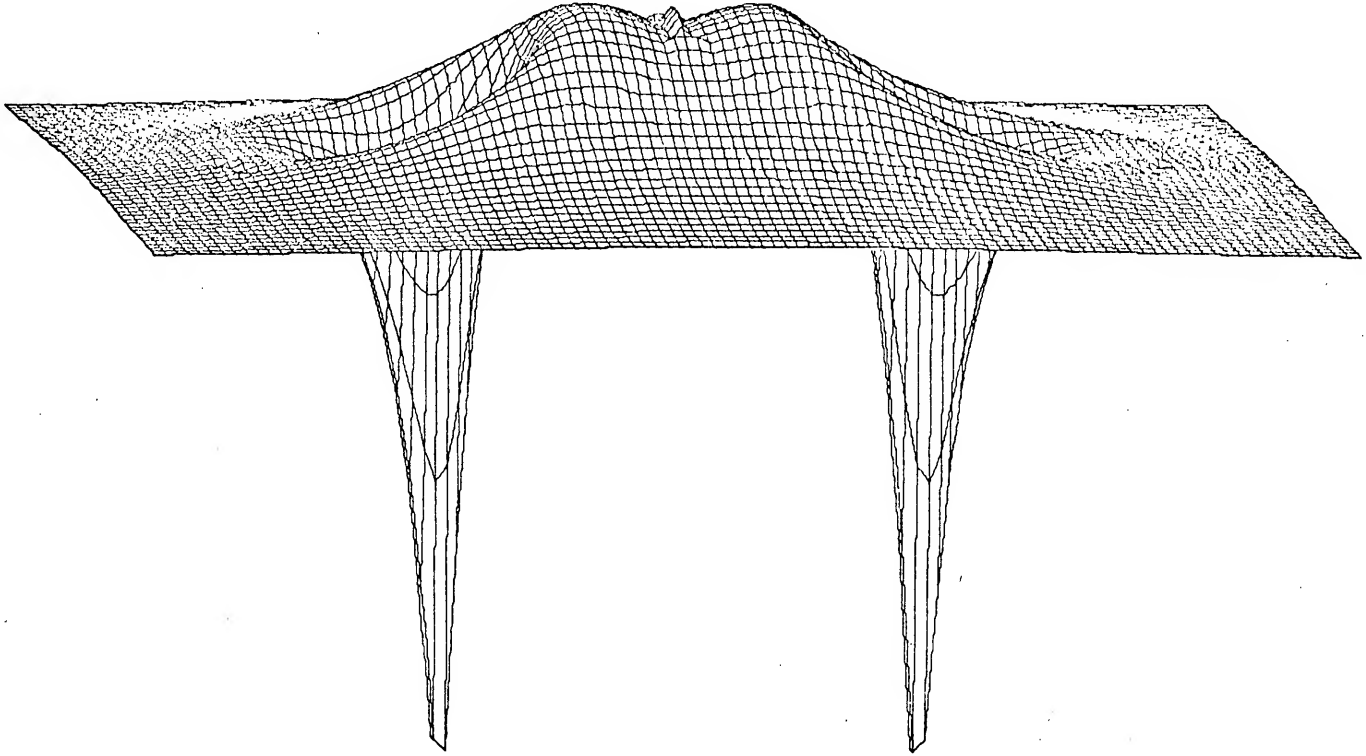


Figure 6.1. Line Plot of the σ_g Valence Orbital of the C_2 Molecule.

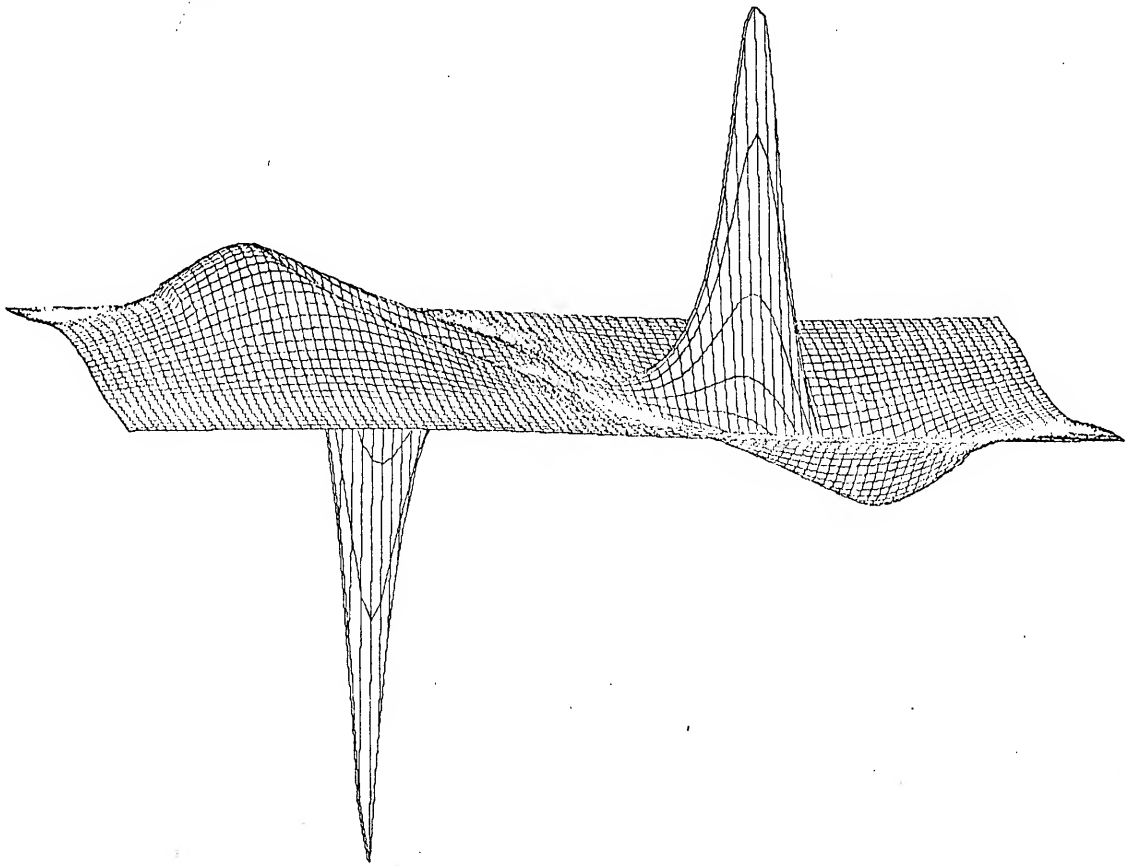


Figure 6.2. Line Plot of the σ_u Valence Orbital of the C_2 Molecule.

constant potential) of the same ℓ (and m) values at the sphere boundaries. The multiple-scattering formalism ensures that these orbitals and their first derivatives match as closely as possible at the sphere boundaries for a given truncated partial wave expansion (see Eyges (1958) and Johnson (1972)). Examining the plots it can be seen that these two orbitals are approximately continuous at all points except perhaps for the σ_g orbital at the center of the bond region. (It is difficult to make a judgement about this discontinuity since the small "blip" in the wave function is approximately the size of the horizontal step length of the plot - that is, 0.08 inches.) Slight discontinuities in the first derivatives of the two orbitals may be observed towards the ends of the molecule where the outer sphere and carbon spheres touch and also at the center of the σ_g orbital where the two carbon spheres are tangent. The points in the molecule where spheres are tangent are the points at which it is most difficult to obtain an orbital which is continuous and has continuous first derivative. At such points it is possible for three potentials of differing values to exist depending upon from which direction (region) the point of tangency is approached. Hence, at such points it will be necessary to employ partial wave expansions including higher ℓ values.

In Figure 6.3 we give a line plot of the total charge density for the C_2 molecule. The value of the charge

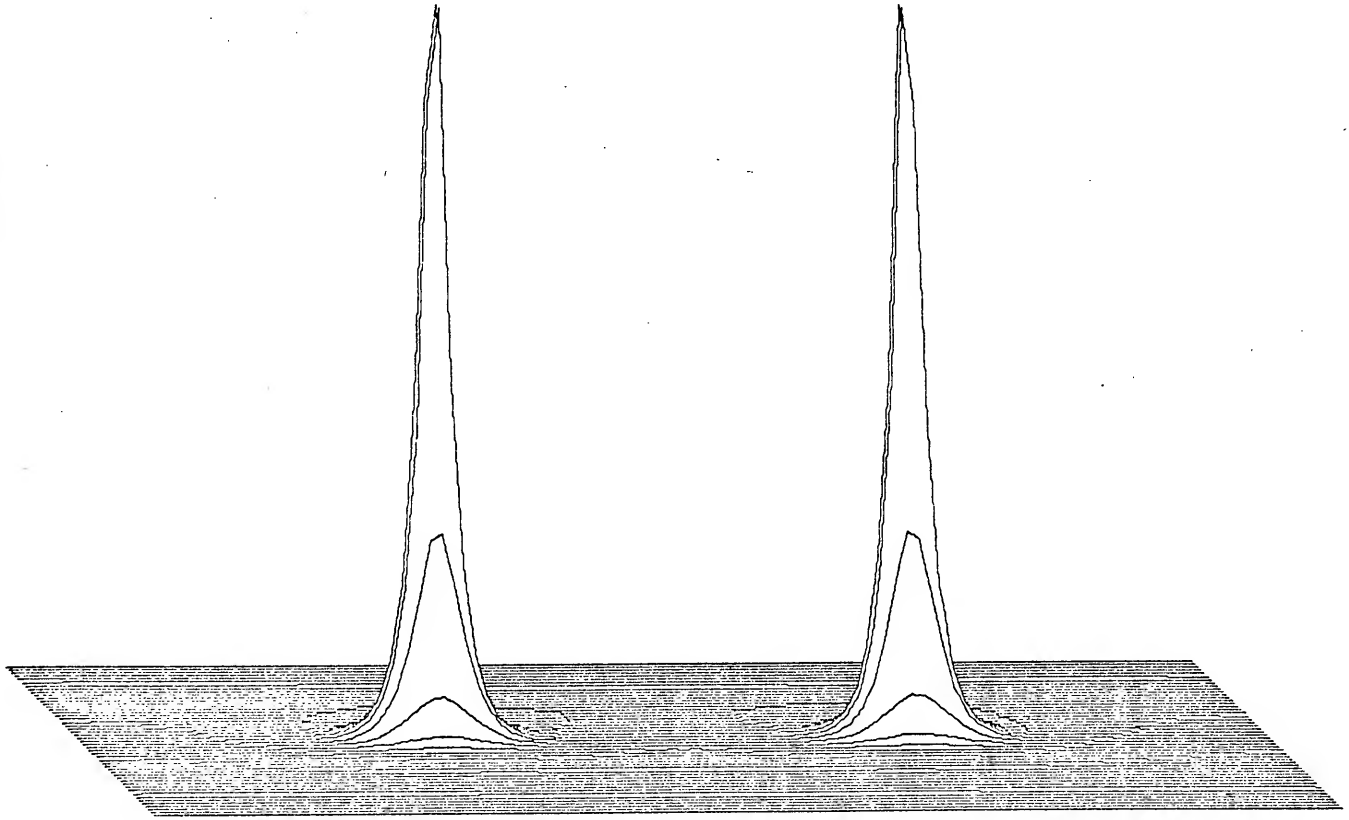


Figure 6.3. Line Plot of the Total Electron Density of the C_2 Molecule.

density at the carbon nucleus is 127.6 electrons/(Bohr)^3 and the value at the midpoint between the nuclei is 0.20 electrons/(Bohr)^3. The total density plotted here is formed from the set of orbitals $\{\tilde{u}_i\}$ which are solutions to the MT Xα one-electron equations. It may be surmised, observing the plot of Figure 6.3, that the MT approximation to the density, at least in its grosser effects, must be a fairly good approximation, since it can be seen that in the region of the nuclei the density is quite spherical and very near constant (on the scale of this plot) in a large portion of the region between and around the main part of the peaks at the carbon nuclei.

In Figure 6.4 we give a line plot of $\Delta\rho(\vec{r})$ - the difference between the density $\rho(\vec{r})$ of Figure 6.3 and the MT average of the same density - and in Figure 6.5 we give a contour plot of $\Delta\rho(\vec{r})$ in the X-Z quadrant of the molecule. The line plot of $\Delta\rho(\vec{r})$ is scaled to fit the page. The largest absolute value of $\Delta\rho(\vec{r})$ is 0.14 electrons/(Bohr)^3 which occurs at the center of the C_2 bond axis. Hence there is a difference of scale of x 911 between Figure 6.4 for $\Delta\rho(\vec{r})$ and Figure 6.3 for $\rho(\vec{r})$. It may be appreciated from this that $\Delta\rho(\vec{r})$ might be considered a small perturbation to $\overline{\rho}(\vec{r})$ or $\rho(\vec{r})$ throughout most of the molecule. However, in parts of the intersphere region this is not true. The value of $\overline{\rho}$ in the intersphere region for C_2 at a=2.48 Bohr is 0.063 electrons/(Bohr)^3 and it may be seen

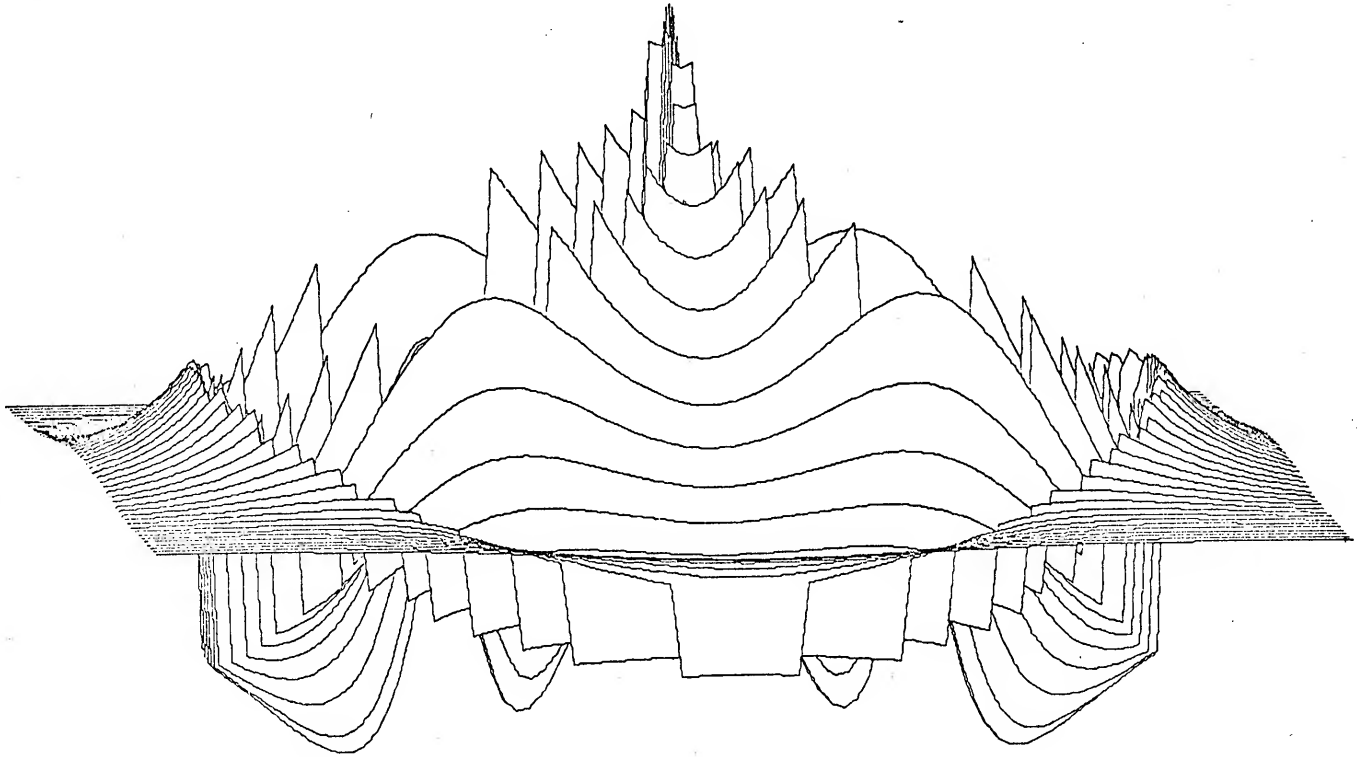


Figure 6.4. Line Plot of $\Delta\rho(\vec{r})$ for the C_2 Molecule.

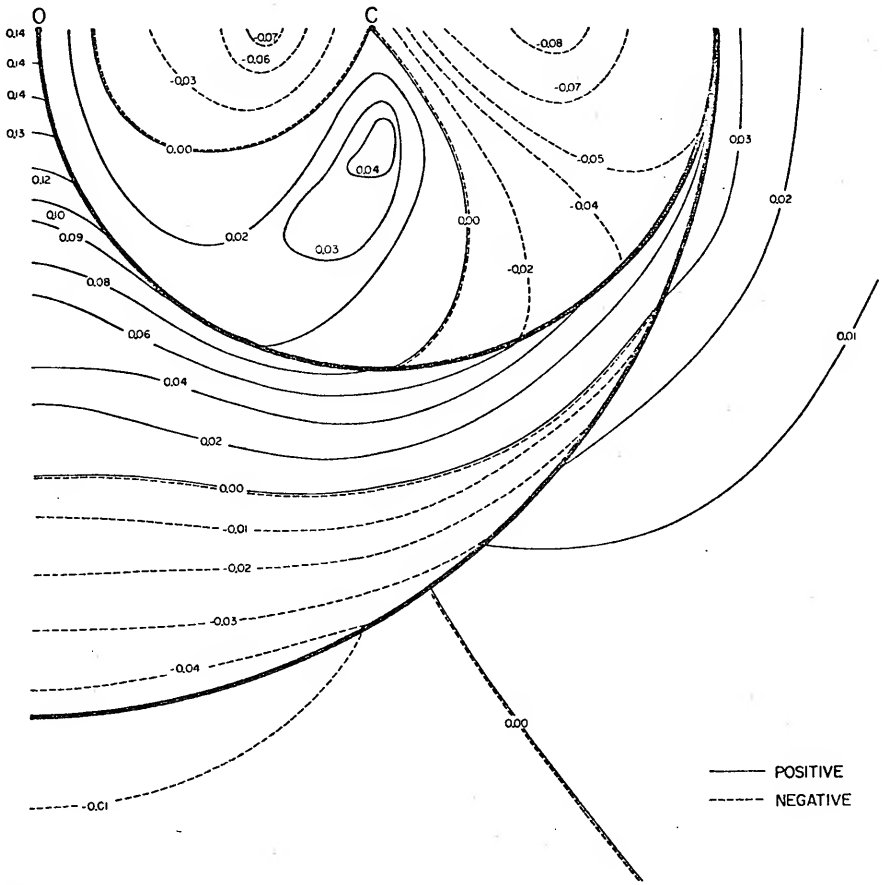


Figure 6.5. Contour Plot of $\Delta\rho(\vec{r})$ in the X-Z Quadrant of the C_2 Molecule.

from Figure 6.5 that $\Delta\rho(\vec{r})$ is, in absolute value, larger than $\overline{\rho}$ in many parts of the interphere region. Hence it may be understood that finer effects such as molecular binding or point properties of the molecule - effects which depend principally on the charge structure in the bonding or valence parts of the molecule - may be inadequately treated by the MT approximation. Considering Figure 6.5 we observe that the MT approximation has two kinds of effects. First, there is a gross effect since the MT averaging of the charge density to a constant in the intersphereregion has the effect of pulling charge out of the bonding region between the nuclei and spreading it over the whole intersphere region. This of course will tend to weaken any binding of the molecule. Second, the MT average has the effect both in the atomic and the intersphere region of averaging away the finer details of the charge density - which details give each molecule its distinctiveness. A priori, the impact of this second kind of effect is harder to predict and it can be well appreciated that its effect will vary greatly from molecule to molecule. However, we can conclude that this averaging away of the finer details of the charge density will have greater impact in molecules with more structured bonding such as π-bonded systems like C_2 or benzene (C_6H_6). (Most of the arguments advanced here concerning the NMT correction to the total energy are valid also for the NMT correction to the eigenvalues due to the

great similarity of the form of the corrections in both cases. (See Section 4.3.))

The actual integrand of $\Delta\langle E_{X\alpha}\rangle$ as indicated already in Section 5.3 is a very complex function. This function which we called $\Delta I(\vec{r})$ in Chapter V is defined as (ignoring terms in $\Delta\rho(r_1)\Delta\rho(r_2)/r_{12}$ whose integral is negligibly small)

$$\Delta I(\vec{r}) = \Delta\rho(\vec{r})\Delta V_{Ne}(\vec{r}) + \Delta\rho(\vec{r})\Delta V_c(\bar{\rho},\vec{r}) + C_\alpha(\rho(\vec{r})^{4/3} - \bar{\rho}(\vec{r})^{4/3}), \tag{6.1}$$

where

$$C_\alpha = -(9/2)\alpha(3/8\pi)^{1/3}, \tag{6.2}$$

and

$$\Delta\langle E_{X\alpha}\rangle = \int \Delta I(\vec{r})d\vec{r}. \tag{6.3}$$

(See Eq. (5.33) and Eq. (3.24)). For our present discussion we will define two functions $\Delta I_{CL}(\vec{r})$ and $\Delta I_X(\vec{r})$ such that

$$\Delta I_{CL}(\vec{r}) = \Delta\rho(\vec{r})\Delta V_{Ne}(\vec{r}) + \Delta\rho(\vec{r})\Delta V_c(\bar{\rho},\vec{r}), \tag{6.4}$$

$$\Delta I_X(\vec{r}) = C_\alpha(\rho(\vec{r})^{4/3} - \bar{\rho}(\vec{r})^{4/3}), \tag{6.5}$$

and

$$\Delta I(\vec{r}) = \Delta I_{CL}(\vec{r}) + \Delta I_X(\vec{r}). \tag{6.6}$$

In Figures 6.6 and 6.7 we give respectively the contour and the line plot of $\Delta I_{CL}(\vec{r})$ and we will briefly analyze this function here. To aid this discussion, and that of $\Delta I_X(\vec{r})$ to follow, in Figure 6.8 we give a schematic break down of the X-Z quadrant of the molecule into numbered regions. (This same schematic was given and discussed in Chapter V, Section 5.3.) These numbered regions are those used in the numerical sampling and integration and roughly divide the molecule into qualitatively different regions. Most of the features of Figures 6.6 and 6.7 may be understood on the basis of simple considerations. Consider the bond region and shell region of Figure 6.6 (respectively regions #7 and #3 in Figure 6.8). In the intersphere region $\bar{V}_{Ne}$ is the volume average of V_{Ne} over the intersphere region. It is obvious for a homonuclear case that $\bar{V}_{Ne}$ must be more positive than V_{Ne} itself near the atomic sphere boundaries and therefore ΔV_{Ne} must be negative in the vicinity of the atomic sphere boundaries - and hence also in the bond region and outer-polar region (#4 in Figure 6.8). The same argument may be made for ΔV_c only the sign of ΔV_c near the atomic sphere boundaries will be positive. One may further expect that for a homonuclear case that the sum of the two terms will for the most part in regions #3, 4 and 7 be dominated by the nuclear term since the nuclear charge cannot be completely shielded if any charge at all is present in the intersphere and outer sphere regions. Since $\Delta\rho$ is

Figure 6.6. The function $\Delta I_{CL}(\vec{r})$ plotted in this figure is defined in Eq. (6.4).

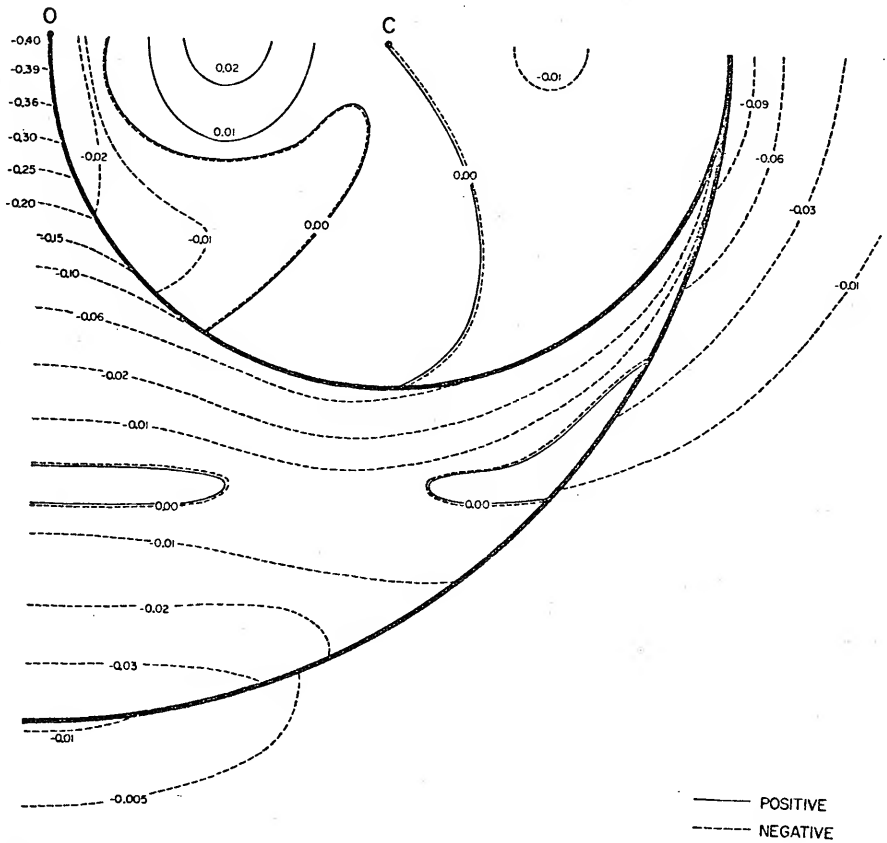


Figure 6.6. Contour Plot of $\Delta I_{CL}(\vec{r})$ in the X-Z Quadrant of the C_2 Molecule.

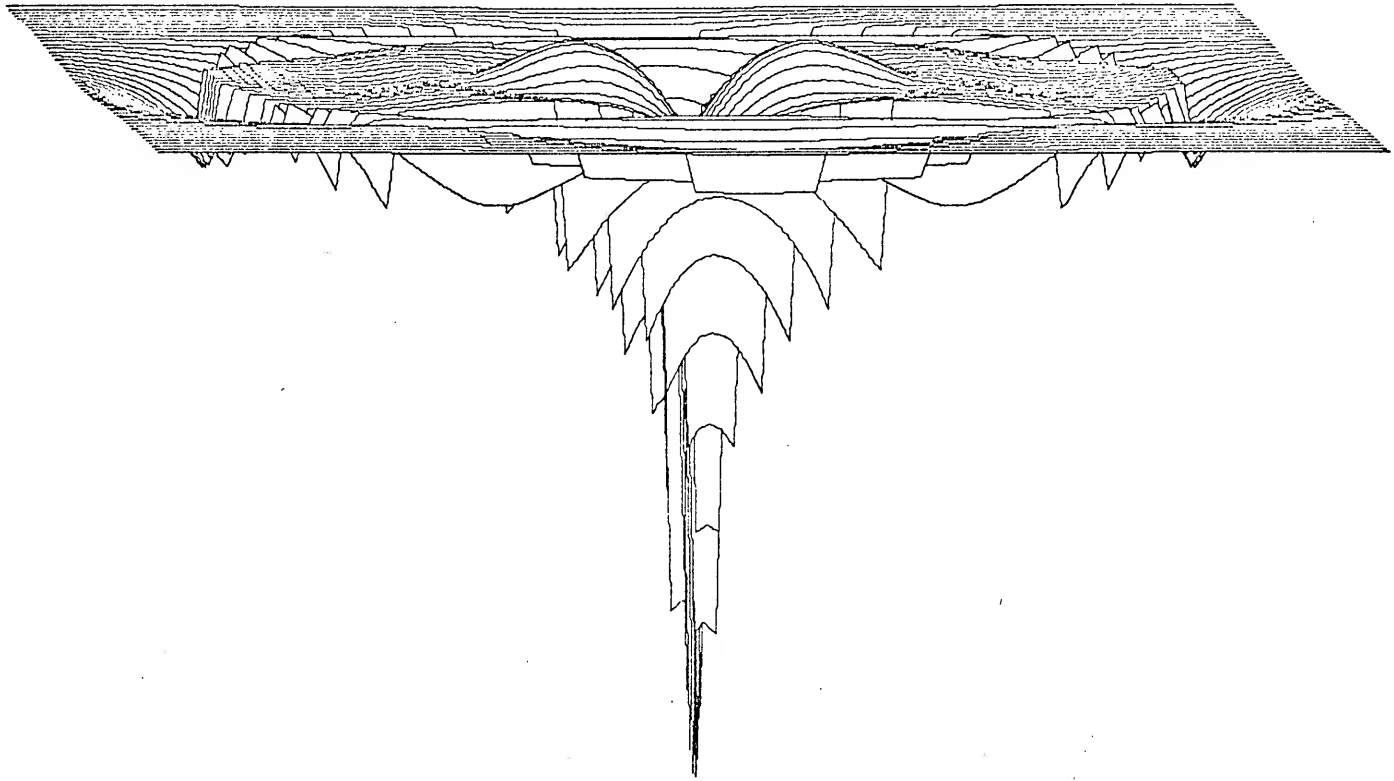


Figure 6.7. Line Plot of $\Delta I_{CL}(\vec{r})$ for the C_2 Molecule.

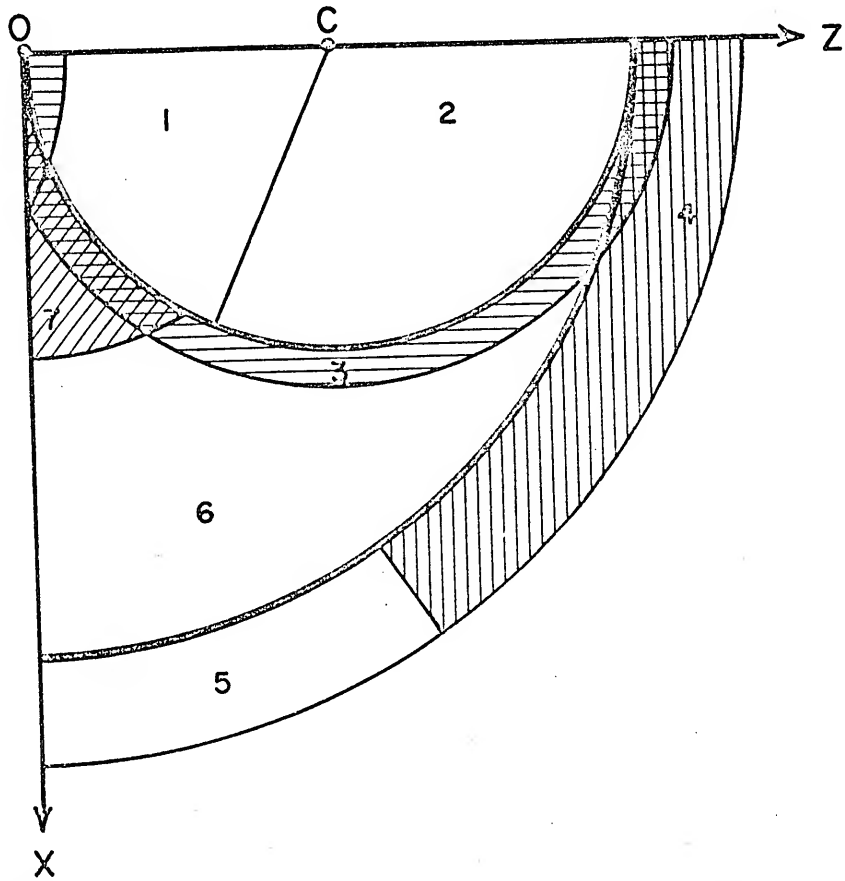


Figure 6.8. Schematic Division of the X-Z Quadrant of the C_2 Molecule into Sampling Regions.

positive in the shell, bond, and outer-polar regions (see Figure 6.5) we find that the function $\Delta I_{CL}(\vec{r})$ is negative in these same regions. It may be noted that in the inter-sphere region near the "equator" of the molecule (region #6 in Figure 6.8) that the function $\Delta I_{CL}(\vec{r})$ is small but negative. Similar arguments to those above may be made for the sign of $\Delta I_{CL}(\vec{r})$ in this region and in a relative sense its magnitude. However, even though its relative magnitude is small, the contribution of the integral of $\Delta I_{CL}(\vec{r})$ over region #6 is not negligible due to the large volume of this region. We have found in calculations that such volume effects can be quite important and must always be kept in mind when trying to assess the relative importance of various regions of the molecule.

In Figures 6.9 and 6.10 we give respectively the contour and the line plots of $\Delta I_X(\vec{r})$. Some of the simpler or qualitative features of $\Delta I_X(\vec{r})$ (see Eq. (6.5)) may be understood in terms of the features of $\Delta\rho(\vec{r})$. If $\Delta\rho(\vec{r})$ is negative at any point it means that $\overline{\rho}(\vec{r})^{4/3}$ is greater than $\rho(\vec{r})^{4/3}$ at that point and hence this difference will also be negative. To complete the function $\Delta I_X(\vec{r})$ we must multiply the difference by $C\alpha$, a negative factor. Hence $\Delta I_X(\vec{r})$ will be negative generally whenever $\Delta\rho(\vec{r})$ is positive and vice versa. Thus $\Delta I_X(\vec{r})$ is negative in the bond region (see Figure 6.9) where $\Delta\rho(\vec{r})$ is positive (see Figure 6.5). A noticeable feature of $\Delta I_X(\vec{r})$ is that it has its largest magnitude in

Figure 6.9. The function $\Delta I_{\chi}(\vec{r})$ plotted in this figure is defined in Eq. (6.5).

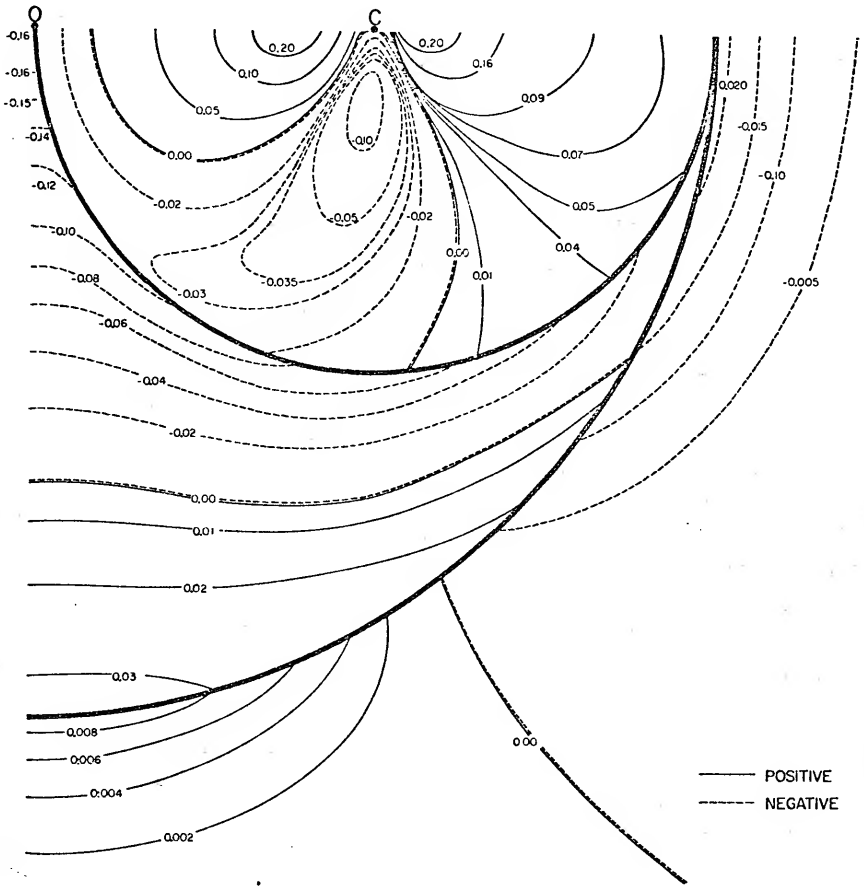


Figure 6.9. Contour Plot of $\Delta I_X(\vec{r})$ in the X-Z Quadrant of the C_2 Molecule.

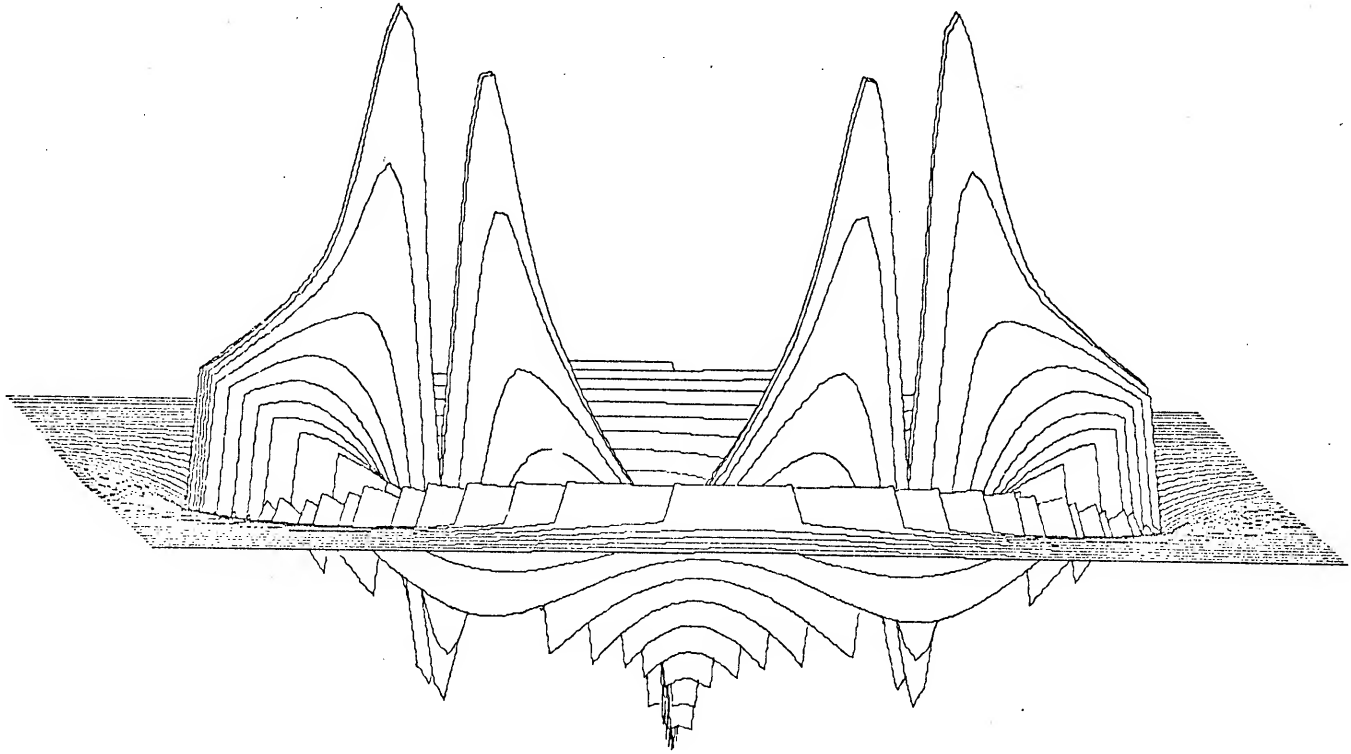


Figure 6.10. Line Plot of $\Delta I_X(\vec{r})$ for the C_2 Molecule.

the regions just around the carbon nuclei - see Figure 6.9. Note that although $\Delta\rho(\vec{r})$ may be of comparable value to $\bar{\rho}(\vec{r})$ is the intersphere region, the value of $\Delta I_X(\vec{r})$ is still small (relatively) since the magnitudes of $\rho(\vec{r})$ and $\bar{\rho}(\vec{r})$ are small. In the atomic region, particularly near the nucleus, the ratio of the magnitude of $\Delta\rho(\vec{r})$ to $\bar{\rho}(\vec{r})$ is quite small, going to zero at the nucleus itself. However, the magnitude of $\rho(\vec{r})$ is much greater than in the intersphere region and a small relative difference between $\bar{\rho}(\vec{r})$ and $\rho(\vec{r})$ may, in absolute terms, be large. Hence $\Delta I_X(\vec{r})$ in the atomic regions as a result can assume relatively (compared to the intersphere region) large values as may be observed particularly well in Figure 6.10. It should be pointed out, as may be seen in Figure 6.9 that $\Delta I_X(\vec{r})$ has large positive and large negative parts inside the carbon sphere which when integrated nearly cancel. Other than the large values assumed by $\Delta I_X(\vec{r})$ in the atomic region we note that it is negative in the bond, shell, and outer-polar regions just as $\Delta I_{CL}(\vec{r})$.

Finally, in Figures 6.11 and 6.12 we give respectively the contour and the line plots of $\Delta I(r)$ which is the sum of $\Delta I_{CL}(\vec{r})$ and $\Delta I_X(\vec{r})$ (see Eq. (6.6) above) and the function to be integrated to obtain $\Delta\langle E_{X\alpha}\rangle$. A number of interesting features may be noted in the function $\Delta I(\vec{r})$. The two functions $\Delta I_{CL}(\vec{r})$ and $\Delta I_X(\vec{r})$ have the same sign and reinforce each other in the bond, shell and outer-polar regions; and

Figure 6.11. The function $\Delta I(\vec{r})$ plotted in this figure is defined in Eq. (6.1).

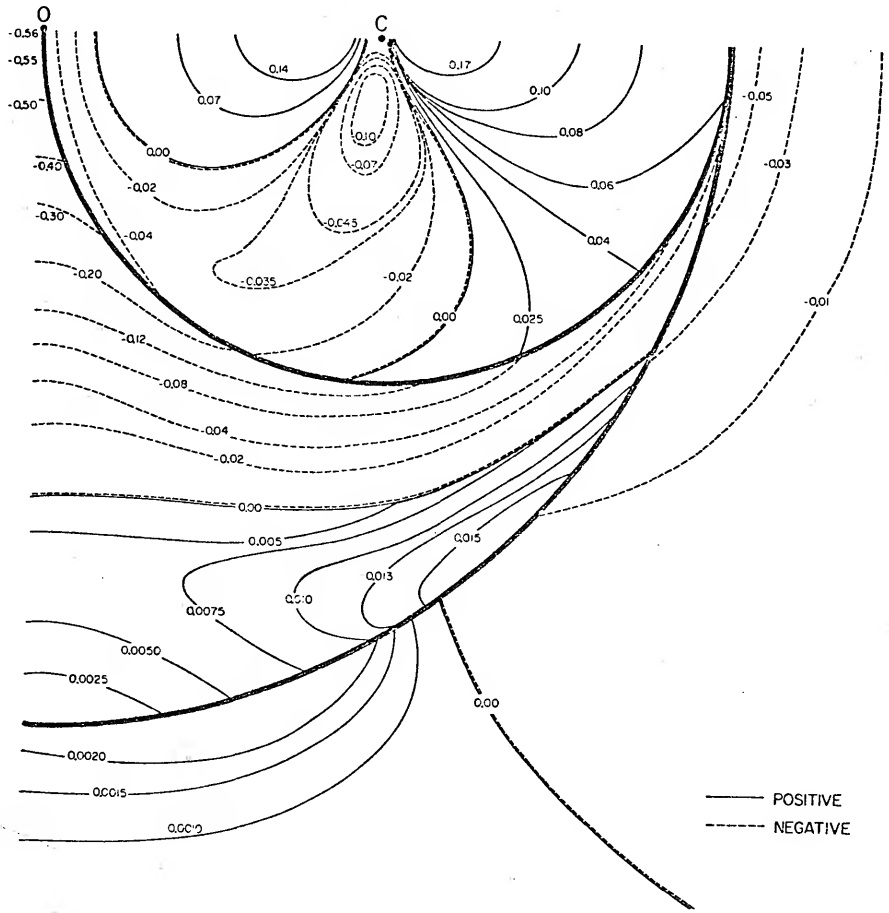


Figure 6.11. Contour Plot of $\Delta I(\vec{r})$ in the X-Z Quadrant of the C_2 Molecule.

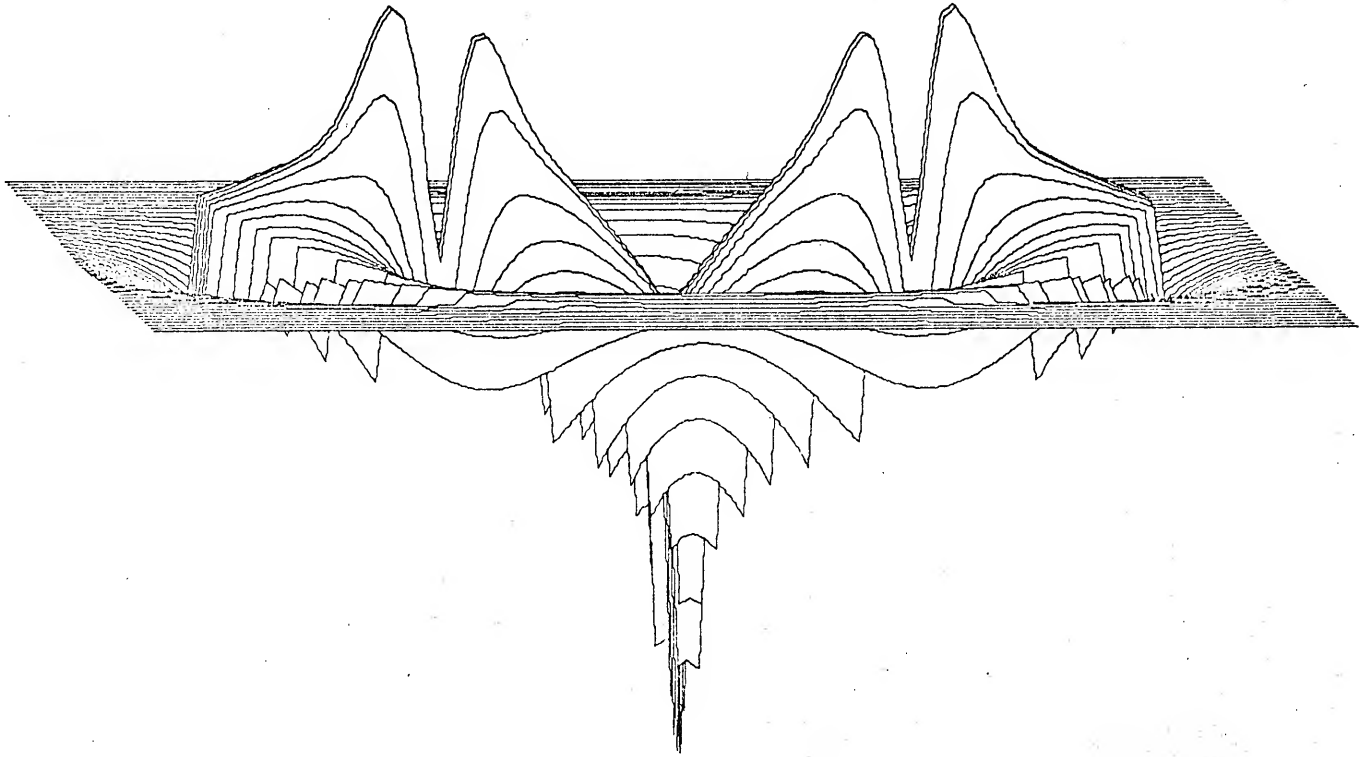


Figure 6.12. Line Plot of $\Delta I(\vec{r})$ for the C_2 Molecule.

this is a feature which, on the basis of our arguments above, we may always expect for a homonuclear system (be it diatomic or not). However, the two functions $\Delta I_{CL}(\vec{r})$ and $\Delta I_X(\vec{r})$ almost cancel in the equator region of the intersphere region (region #6 in the schematic of Figure 6.8). This feature we believe is not necessarily a general feature and is peculiar to C_2. It is seen in Figure 6.12 that the function $\Delta I_X(\vec{r})$ seems to dominate in the carbon atomic sphere but this is deceptive since it has large positive and negative parts which upon integration over the carbon sphere almost cancel. For the case of Ne_2 (to be discussed briefly below) it was found that the function $\Delta I_X(\vec{r})$ dominated in almost all regions of the molecule. In general it appears we may make qualitative arguments about the separate structures of $\Delta I_{CL}(\vec{r})$ and $\Delta I_X(\vec{r})$ but it seems quite difficult if not impossible to make quantatative statements about the relative magnitude of $\Delta I_{CL}(\vec{r})$ and $\Delta I_X(\vec{r})$ in any detailed way. In fact it is for this reason that the contour and line plots reproduced in this section have proven invaluable for the analysis of the NMT correction $\Delta\langle E_{X\alpha}\rangle$ and its parts and at this point of the development of the NMT theory cannot be dispensed with. As discussed in Chapter V it necessary to be able to fit sampling functions to the function $\Delta I(\vec{r})$ in order to be able to integrate it with a realistic number of integration points (the cost of calculation being roughly proportional to the number of

integration points) to an acceptable degree of accuracy. The results for the integrals of $\Delta I(\vec{r})$ for the various sampling regions depicted schematically in Figure 6.8 for C_2 and Ne_2 are given in the next section of this chapter.

In the Ne_2 calculation it was found that the exchange function $\Delta I_X(\vec{r})$ dominated the Coulombic function $\Delta I_{CL}(\vec{r})$ in almost all parts of the molecule. The reason why $\Delta I_{CL}(\vec{r})$ should be small for Ne_2 and large for C_2 may be understood in terms of the features of the two molecules and their separated atoms. The carbon atom in its ground state is an open shell atom and hence has a somewhat structured charge density in the outer part of the atom. It may be expected then that in binding to another carbon atom the charge in the valence or bonding parts of the molecule will also be fairly structured. In fact in the MT approximation the C_2 molecule has approximately 3.0 electronic units of charge in the intersphere region, which region roughly encompasses the bonding parts of the molecule. As explained above this leads to large components of the NMT Coulombic function in the bond, shell, and outer polar regions. The Ne atom on the other hand is a closed shell atom which means that its total charge density is spherically symmetric. When binding with another Ne atom we would not expect a large amount of structure in the molecule or large displacement of charge from the original atomic structure. For the Ne_2 molecule in the MT approximation

there are only 0.08 units of electronic charge in the inter-sphere region. Hence we may expect the function $\Delta I_{CL}(\vec{r})$ to be quite small in the bond, shell, and outer polar regions compared to C_2. The exchange function $\Delta I_X(\vec{r})$ as explained has roughly the negative of the behavior of $\Delta\rho(\vec{r})$ which in the case of Ne_2 is rather small in magnitude compared to C_2. It turned out in the Ne_2 calculation whose results are reported below that the exchange contribution to $\Delta\langle E_{X\alpha}\rangle$ was approximately one order of magnitude larger than the Coulombic contribution.

6.4 The Results for C_2 and Ne_2 and Principle Conclusions

Results and Interpretation

In this section we give the main numerical results for the calculations of the NMT corrections for C_2 and Ne_2. For C_2, our principle test molecule, we have calculated the NMT correction for three inter-nuclear separations; for Ne_2 we have calculated the NMT correction at one separation near the experimental equilibrium separation. The basic calculational results for C_2 and Ne_2 are given respectively in Tables 6.1 and 6.4. In these tables for each inter-nuclear separation we list the contribution to the total NMT correction from each of the sampling regions which are indicated schematically in Figure 6.8. The total NMT correction is simply the sum of the individual regional contributions. As discussed in Chapter V, Section 5.3, each

regional contribution is calculated as a mean value and with each regional contribution in the tables we list the standard deviation of the mean - σ_x - for that regional contribution. (The error in the calculated mean is such that it lies within $\pm 1\sigma_x$ of the true mean with 64% certainty and within $\pm 2\sigma_x$ of the true mean with 95% certainty.) From the individual σ_x's for each region we form a composite σ_x for the total NMT correction (see Eq. (5.51)).

In Table 6.1 we give the basic results for C_2. In accord with simple intuition we see that the NMT correction increases with decreasing internuclear separation. The #'s of the regions correspond to those of Figure 6.8. For the three internuclear separations it may be observed that the bond and shell regions (respectively regions #7 and #3) make the largest negative contribution to the NMT correction followed by the outer-polar region (region #4). The total contribution for the carbon region (#1 and #2 combined) is small but negative at all three points. As mentioned in the previous section the function $\Delta I(\vec{r})$ inside the carbon region is dominated by the exchange function $\Delta I_X(\vec{r})$ but a large amount of cancellation takes place in the integration of $\Delta I_X(\vec{r})$ over the entire carbon spherical volume. Other than region #2 in the carbon sphere, the largest single positive contribution comes from the intersphere equator region (region #6).

In Table 6.2 we give the MT energy for the three points,

TABLE 6.1

THE NMT CORRECTION FOR C_2 AND ITS REGIONAL PARTS AS A FUNCTION OF INTERNUCLEAR SEPARATION

		a = 2.26 (Bohr)		a = 2.48 (Bohr)		a = 2.70 (Bohr)	
Region*		Energy (Ryd)	σ_X (Ryd)	Energy (Ryd)	σ_X (Ryd)	Energy (Ryd)	σ_X (Ryd)
Carbon-In	(#1)	-0.2281	0.0034	-0.2372	0.0045	-0.1620	0.0062
Carbon-Out	(#2)	+0.1702	0.0043	+0.2061	0.0054	+0.1514	0.0070
Shell	(#3)	-0.6395	0.0088	-0.7393	0.0082	-0.7661	0.0079
Outer-Polar	(#4)	-0.2683	0.0032	-0.2234	0.0028	-0.1605	0.0047
Outer-Equator	(#5)	+0.0580	0.0004	+0.0500	0.0007	+0.0443	0.0007
Intersphere	(#6)	+0.1335	0.0040	+0.1729	0.0034	+0.1892	0.0037
Bond	(#7)	-0.6543	0.0072	-0.5371	0.0063	-0.3498	0.0016
Total		-1.4285	0.0138	-1.3080	0.0132	-1.0535	0.0137

*See Figure 6.8 for indentification of regions by number

TABLE 6.2

THE NMT BINDING ENERGY FOR C_2 AS A FUNCTION OF INTERNUCLEAR SEPARATION

Energy (Ryd)	Separation (Bohr)		
	2.26	2.48	2.70
Kinetic Energy	+152.0572	+151.8904	+151.6726
MT Energy	-149.6517	-149.8561	-150.0119
NMT COrrection	- 1.4285	- 1.3080	- 1.0535
NMT Energy	-151.0802	-151.1641	-151.0654
Binding Energy	- 0.3258	- 0.4097	- 0.3110
σ_X	0.0138	0.0132	0.0137

Energy of Separated Atom Limit = -150.7544 (Ryd)

the NMT corrections, and the total NMT energy for C_2. Comparing the total NMT energy with dissociated atomic limit of -150.7544 Ryd we arrive at the tabulated binding energies. A simple examination will already reveal that the NMT correction has resulted in a definite improvement in the total energy of C_2. With the NMT correction a binding curve with a minimum is predicted whereas previously in the MT approximation a distinctly repulsive curve was predicted. In Figure 6.13 we graph the three NMT C_2 points along with the original MT values for the C_2 potential curve. In the same graph we also give a potential curve obtained from a configuration interaction (CI) calculation by Fougere and Nesbet (1966) and also one point for a good Hartree-Fock calculation by Buenker et al. (1967). With these comparisons the significance of the NMT corrections becomes clear. The inclusion of the NMT correction in the MSXα total energy calculation has resulted in a dramatic qualitative and quantitative improvement in the total Xα energy.

In Table 6.2 we give the binding energy at each point and σ_x for the binding energy at that point. For example at 2.48 Bohr we have a binding energy of -0.4097 Ryd with error of ±0.026 Ryd for 95% certainty or ±0.013 Ryd for 64% certainty. Taking this last figure our binding energy at 2.48 Bohr is -0.41 ± 0.01 Ryd. On the graph of Figure 6.13 this error bar barely shows. Assuming the binding energies at the three points are accurate to four figures we have calculated the spectroscopic constants for C_2

Figure 6.13. The MT and NMT points plotted in this figure are taken from Table 6.2. The CI points are taken from Fougere and Nesbet (1966) and the one HF point is from Buenker et al. (1967).

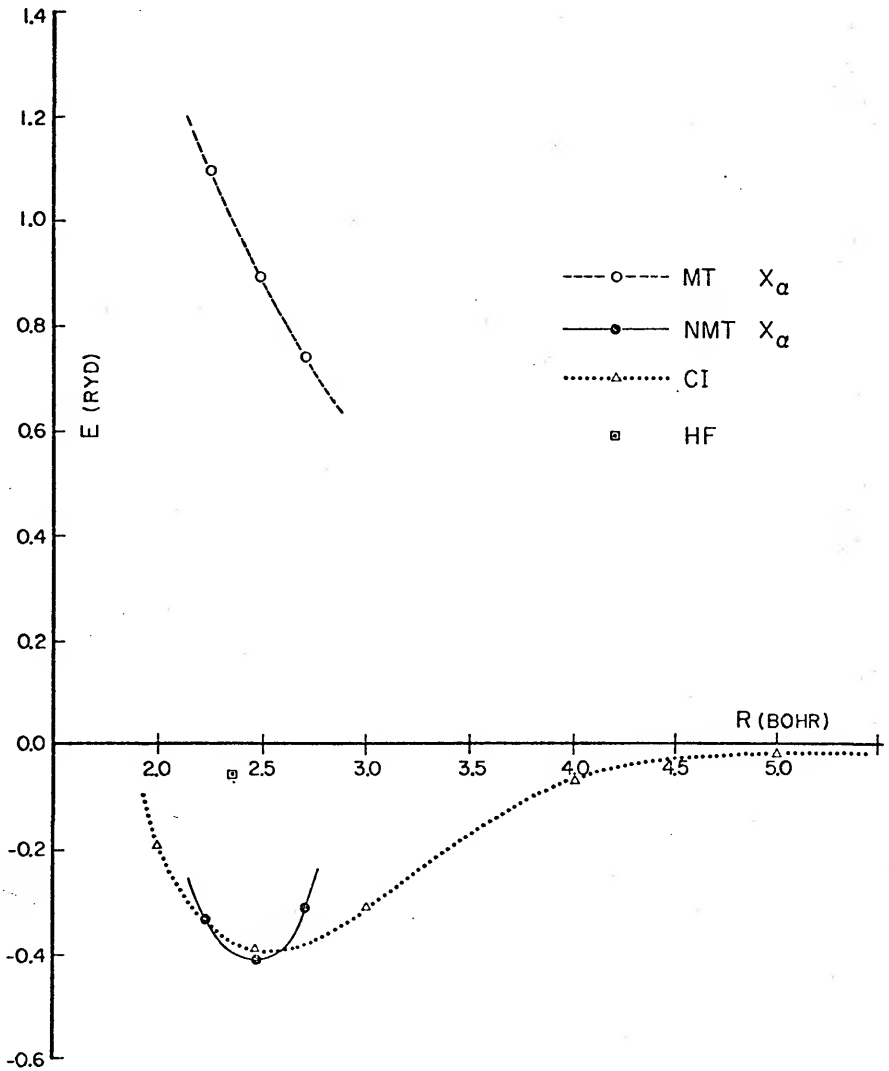


Figure 6.13. MT, NMT, and CI Potential Curves for the $^1\Sigma_g^+$ Ground State of C_2.

which are given in Table 6.3. We see that even if these constants are assumed accurate to only two figures of accuracy they still compare more favorably with experiment than the CI calculation reported.

With regard to the question of accuracy and comparison we should like to point out that Fougere and Nesbet (1966) actually performed three CI calculations using different but steadily improving basis functions. Their results which we have reported in Table 6.3 are those for their best basis set. In their calculations they were calculating the energies of a number of excited states as well as the ground state and their basis set was not tailored to give good results for the ground state. However, with their three basis sets they obtained dissociation energies for the ground state respectively of 2.94, 6.76, and 5.39 (ev) for their steadily improving basis sets. Needless to say this is a wide variation in dissociation energy and does indicate an unwanted dependence on the basis set assumed which is apparently not easy to avoid.

The calculation on Ne_2 was performed for several reasons. It was performed in some degree to corroborate our findings for C_2 (although this may have been accomplished with an easier test case than Ne_2), but also because of its intrinsic interest and implications vis-a-vis the exact $X\alpha$ approximation. It was further performed to explore the correlation between any binding predicted for molecular

TABLE 6.3

SPECTROSCOPIC CONSTANTS FOR C_2

Source	Dissociation Energy (ev)	Eq. Separation (Å)	Frequency (Cm^{-1})
NMT Calculation[a]	5.58	1.3077	1922
Configuration-Interaction[b]	5.39	1.3559	1503
Experiment[c]	6.36	1.2422	1856

[a]Results predicted from NMT calculations (See Table 6.1)

[b]Fougere, P. F. and Nesbet, R. K., J. Chem. Phys. 44, 285 (1966).

[c]Ballik, E. A. and Ramsay, D. A., Astrophys. J. 137, 84 (1963).

Ne_2 and the cohesion predicted for the rare gas crystals of argon, krypton, and xenon by APW Xα solid state calculations (see Trickey, Averill, and Green (1972) and private communication from S.B. Trickey).

In Table 6.4 we give the basic results for Ne_2 at an internuclear separation of 6.0 Bohr. (At 6.0 Bohr we are slightly outside the experimental equilibrium position - see de Graaf and Mozer (1971)). Somewhat in contrast to C_2, there are only two dominant contributions - a large negative contribution from the shell region (#3 in Figure 6.8) and a large positive contribution from the intersphere equator region (#6 in Figure 6.8) which together account for the main part of the NMT correction. Although the results are not given here, the contribution to the total NMT correction from the exchange part (the integral of $\Delta I_X(\vec{r})$) was approximately an order of magnitude larger than the contribution from the Coulombic part (the integral of $\Delta I_{CL}(\vec{r})$). In this respect the NMT correction for Ne_2 has a qualitatively different nature than that for C_2. This difference may be understood as argued earlier in Section 6.3 in terms of the differing character of the constituent atoms in C_2 and Ne_2 although both molecules may still be considered covalently bound (see Slater (1972b)). In Table 6.5 we give the binding energy predicted for Ne_2 at 6.0 Bohr with the NMT correction included in the total energy. The error quoted for the NMT correction in Table 6.4 and

TABLE 6.4

THE NMT CORRECTION FOR Ne_2 AND ITS REGIONAL PARTS AT THE NUCLEAR SEPARATION 6.0 (BOHR)

Region *		Energy (Ryd)	σ_X (Ryd)
Neon - In	(#1)	-0.000305	0.0000442
Neon - Out	(#2)	+0.000535	0.0000742
Shell	(#3)	-0.006669	0.0000444
Outer-Polar	(#4)	-0.000219	0.0000382
Outer-Equator	(#5)	+0.000163	0.0000235
Intersphere	(#6)	+0.004033	0.0000353
Bond	(#7)	-0.000680	0.0000066
Total		-0.003142	0.000113

* See Figure 6.8 for identification of regions by number.

TABLE 6.5

THE NMT BINDING ENERGY OF Ne_2 AT THE INTERNUCLEAR SEPARATION 6.0 (BOHR)

Energy Component	Energy (Ryd)
Kinetic Energy	+514.1587
MT Energy	-514.12985
NMT Correction	- 0.00314
NMT Energy	-514.13299
X_α Atoms	-514.13266
Binding Energy	- 0.00033 $\pm$ 0.00011

the binding energy in Table 6.5 is $\pm 1\sigma_x$ for the mean values of these quantities. Finally in Table 6.6 we compare the NMT predicted binding energy with a Hartree-Fock calculation for Ne_2 and the experimental binding or well depth inferred from liquid scattering measurements. It appears that our result is overbound.

It should be noted that we are dealing with extremely small numbers and there are a number of problems connected with this. The MSXα main computer code is written in single precision which for the IBM computer used in these calculations gives eight significant figures of accuracy (seven figures in reality). In order to obtain sufficient accuracy in the NMT total energy and dissociated Xα atom energy to be able to calculate the very small binding energy it was necessary to use double precision in the computer code which gives sixteen figures of accuracy. It was found that the total MT energy was somewhat sensitive in the seventh and eighth figures of accuracy to the number of ℓ values used in the partial wave expansion. With these problems and the size of the σ_x for the Ne_2 binding we do not think the precise amount of binding indicated should be taken literally but rather as indicative. We do have binding of approximately the right amount - more than this we cannot say. Further with regard to comparing with experiment some caution is also needed. The experimental well depth given in Table 6.6 for Ne_2 is inferred from a Lennard-Jones (6-12)

TABLE 6.6

COMPARISONS OF THE NMT BINDING ENERGY AT THE INTERNUCLEAR SEPARATION 6.0 (BOHR) WITH OTHER SOURCES

Source	Energy (ev) [c]
NMT Calculation	0.0045 ± 0.0015
Hartree Fock[a]	-0.003
Experiment[b]	0.0031

[a] Gilbert and Wahl (1967)

[b] Graaf and Mozer (1971)

[c] A positive value indicates binding and a negative value indicates no binding.

potential fitted to experimental data obtained from scattering experiments. The scattering experiments are performed on a fluid of Ne at finite density and temperature. See de Graaf and Mozer (1971) for more details. As such there is experimental error in the well depth reported as well as model dependence in the assumption of the Lennard-Jones potential form. It has been suggested by some researchers that the well depth is actually greater than predicted (see Verlet (1967)).

It should be noted that the binding is an order of magnitude smaller than the total NMT correction. The principle error in the total NMT correction is mainly the statistical error which is about 5% of the total correction. Hence we can consider the total NMT correction for Ne_2 as not only indicative but quantitatively accurate to ±5%.

It should be noted that the NMT correction result does predict binding whereas the only other calculation performed for Ne_2 (other than Thomas-Fermi calculations - see Abrahamson (1963)) is a Hartree-Fock of good quality performed by Gilbert and Wahl (1967) which does not predict binding at 6.0 Bohr (or at any other internuclear separation). It predicts the molecule is unbound by approximately the amount it is actually bound at 6.0 Bohr. Here, just as in the case of C_2, it is seen that the Xα result with the principle part of the MT approximation removed gives a result

qualitatively different from and superior to the Hartree-Fock result.

The potential curve for Ne_2 over a wide range of internuclear separation has been calculated by the MSXα method in the MT approximation by Konowalow et al. (1972). The basic conclusion from this work was that the MSXα potential curve in the MT approximation was not of very good quality. This potential curve predicted no binding of course and was above the experimental curve for all separations. It deviated further from the experimental curve as the internuclear separation was decreased. (In assessing the results of Konowalow et al. it should be noted that these authors failed to use double precision machine codes or to extensively explore the dependence on ℓ value in the partial wave expansion.) However, based on the size and accuracy of the total NMT correction at 6.0 Bohr and the fact that the NMT correction should (as argued earlier) become larger for decreasing internuclear separation we believe we can safely predict that with the NMT correction the potential curve for Ne_2 will be substantially changed and improved.

Main Conclusions

The NMT calculations reported here eliminate the dependence upon the NMT approximation except through the MT dependence of the orbitals $\{\tilde{u}_i\}$ which are solutions to the

one-electron Xα equations with the MT potential $\bar{V}_{X\alpha}(\bar{\rho},\vec{r})$. This dependence occurs in the total energy $\langle E_{X\alpha}\rangle$ only as a second order dependence upon the difference between the MT Xα orbitals $\{\tilde{u}_i\}$ and the exact Xα orbitals $\{u_i\}$. This result follows from the fact that our present calculations are analagous to a first order perturbation calculation. That is, we calculate the true Xα energy functional $\langle E_{X\alpha}\rangle$ using the orbitals which minimize the MT Xα energy functional $\overline{\langle E_{X\alpha}\rangle}$. We accomplish this by calculating $\overline{\langle E_{X\alpha}\rangle}$ and $\Delta\langle E_{X\alpha}\rangle$, the perturbation to the functional $\overline{\langle E_{X\alpha}\rangle}$, with the set of orbitals $\{\tilde{u}_i\}$. The NMT correction may be calculated for an excited in exactly the same way as for the ground state since the correction is a functional of the total density. As shown in Chapter IV the method of correcting the MT total energy for NMT corrections to the MT density may not be extended in any consistent way to second or higher orders in a perturbation series of which our present NMT correction is the first order term.

We argued in Chapter IV that we had hope of obtaining good results with the present method for two reasons. First, it would appear (although this is, strictly speaking, conjecture) that on the basis of the present successes of the MSXα method (and the KKR and APW methods of solid state) with the MT approximation in calculating both good total energies and ionization energies (see Connolly, et al. (1972), Danese (1972), Connolly and Johnson (1971), Johnson

et al. (1972), Averill (1972), Hattox (1972), Trickey et al. (1972), and Slater (1972b)) that the present MT Xα orbitals (the set $\{\tilde{u}_i\}$) are apparently not too far from and certainly not drastically different than the exact Xα orbitals (the set $\{u_i\}$). If this is true then second order orbital effects in the total energy must be quite negligible. Second, it appears that the NMT correction is, even in the cases where the MT approximation to the total energy seems to fail in an important way (the binding of C_2 and Ne_2 for example), a relatively small correction to the total energy. If this is true then any other corrections to the total energy. If this is true then any other corrections to the total energy due to NMT effects must be smaller still.

It now may be argued in light of the analysis and results given in this chapter that our arguments of Chapter IV, repeated here, are valid. Namely, that due to the significant qualitative and quantative improvement of the total energies of our two dissimilar and difficult test case molecules-C_2 and Ne_2-we conclude that the NMT correction $\Delta\langle E_{X\alpha}\rangle$ represents the principle NMT correction to the MT total energy $\overline{\langle E_{X\alpha}\rangle}$ and hence gives a total energy very close to the exact Xα total energy. Moreover, this leads us to a further conclusion; namely, that in view of the good correlation with experiment obtained in our present NMT calculations on two difficult systems the exact Xα

approximation for the total energy must itself be a quite good approximation. This final conclusion corroborates with additional arguments advanced by Slater (1972b) that the exact X_α method does represent a good approximation to physical systems since it among other things leads rigorously to both the (electrostatic) Hellman-Feynman theorem and the virial theorem. (Some ramifications of the virial theorem as related to our present work are discussed below in some additional notes.)

From the above discussion it is seen that an important question raised by research but not completely resolved concerns the quality of the MT X_α orbitals themselves. The Hellman-Feynman theorem (Feynman (1939)) can be used to calculate the forces on nuclei in a molecular system but it is necessary to use the exact wave function in order to satisfy this theorem. It is well known that the theorem gives rather unreliable results for approximate wave functions (see Hirschfelder and Eliason (1967), Salem and Wilson (1962), and Coulson and Deb (1971)). At any rate the Hellman-Feynman theorem provides a powerful tool for analysis (Slater (1963a)) even for approximate wave functions (see Bader, Hennekker, and Cade (1967) and Coulson and Deb (1971)). It appears then that a good test of the quality of the MT X_α orbitals would be provided by employing them in a calculation of the forces exerted on the nuclei of a molecule by means of the Hellman-Feynman theorem. Such a

future test seems especially important in view of our present discussion and of the recent proof by Slater that the exact Xα method rigorously leads to the Hellman-Feynman theorem.

It is also our conclusion from the research of this dissertation that any further improvements upon the MT approximation beyond the present NMT correction $\Delta\langle E_{X\alpha}\rangle$ to the MT energy (or NMT corrections to the eigenvalues which were described in Chapter IV) must come through the calculation of exact or more exact solutions to the exact Xα one-electron equations (see Eq. (2.36) and the end of Section 2.3). In this regard it has recently come to our attention that progress has been made in this direction by Williams (1970) and Evans and Keller (1971) in solid state applications and more recently by Rösch and Johnson (1973) in applications of the MSXα method. This development of the MSXα method is presently in a rather rudimentary state. If exact Xα orbitals were available our method of calculating $\Delta\langle E_{X\alpha}\rangle$, as indicated in Chapter IV, would give the exact Xα energy $\langle E_{X\alpha}\rangle$ instead of the present first order perturbation approximation to $\langle E_{X\alpha}\rangle$. This is definitely a development to look forward to.

As stated, our goals have not only been to analyze, understand, and improve upon the MT approximation with the NMT correction $\Delta\langle E_{X\alpha}\rangle$ but also at the same time to provide a practical and general means of evaluating the NMT

corrections. The system of sampling and numerical integration to accomplish this feat has been discussed in Chapter V. We can state that for the simple type of system for which we have performed calculation - namely homonuclear diatomic molecules - the method of integration is not unduly difficult to apply and quite realistic in terms of computation times (that is, in terms of computer funds). Typically, at the scheme's present state of program development, one point on a potential curve takes approximately the time of several iterations of the SCF cycle of the MSXα program for the molecule under consideration. (Usually it takes about ten iterations of the SCF cycle to convergence a molecular calculation.) Without any doubt, in the researcher's opinion, these times can be improved upon significantly. It is only a matter of further development of a computer code which is not as yet completely optimized. Further, there are no conceptual or practical difficulties in applying the integration method for $\Delta\langle E_{X\alpha}\rangle$ to larger molecules of more complex structure.

With this our main conclusions from and discussion to the results is completed. In the next and final section of the dissertation we will discuss some further implications of our research which are perhaps not germane to our main discussion but are, nevertheless, we feel important. We will also discuss some other further applications and tests of the method.

6.5 Further Discussion and Future Work

In this section we will discuss the following topics in order: the connection of our work with the virial theorem, the correlation of the Ne_2 result with solid state calculations on the rare gas crystals, NMT corrections to the MT Xα eigenvalues, and further test molecules to consider.

The Connection with the Virial Theorem

For simplicity in this short note we will restrict our discussion to diatomic molecules. If we have the exact wave function as a function of internuclear separation R we may calculate the kinetic energy T(R), total energy E(R), and the derivative dE(R)/dR. Then the virial theorem takes the following simple form (see Slater (1963a))

$$T(R) = -E(R) - R\,dE(R)/dR. \qquad (6.7)$$

It has recently been shown by Slater (1972b) that the exact Xα method in the case in which the same exchange parameter α is used throughout the system of interest satisfies the virial theorem. Hence the above relation would be true but with T(R), E(R), and dE(R)/dR calculated by the Xα method. (It should be noted that Slater's proof did not involve the usual scaling arguments but was completely general.) Our present method of calculating the approximate Xα total energy via the inclusion of our NMT correction

does not at all satisfy the virial theorem. From relation (6.7) it may easily be seen that at the equilibrium position of a potential curve where $dE(R)/dR = 0$,

$$T(R) = -E(R). \qquad (6.8)$$

A quick examination of Table 6.1 for our results for C_2 will reveal that Eq. (6.8) is not satisfied. The explanation is simple. The virial theorem for the Xα method is satisfied only if the orbitals used in the calculation are variationally derived from the Xα energy functional; that is, they must be SCF orbitals satisfying the Xα one-electron equations (see Rudge (1968), Ross (1968), Averill (1971) and Slater (1972b)). In our method this is not the case since we use the set of orbitals $\{\tilde{U}_i\}$ which are variationally derived from $\overline{\langle E_{X\alpha} \rangle}$ the MT Xα energy functional to calculate the Xα energy functional $\langle E_{X\alpha} \rangle$. Hence relation (6.7) will not be satisfied.

Ne_2 and Rare Gas Crystals

As already mentioned we performed the Ne_2 calculation in order, among other things, to correlate the results with solid state calculations performed on some of the rare gas crystals. The basic thrust behind these calculations was to test some of the limits of the Xα approximation itself. The binding of Ne_2 is extremely small as molecular binding goes - 0.0031 to be exact - and is usually explained

in terms of van der Waals forces. The same is true of the rare gas crystals. It is generally thought that in order to be able to explain van der Waals binding one needs a fairly sophisticated wave function, in fact that van der Waals binding is a phenomena which can be explained only in terms of direct electron-electron correlation.

What are the results? As already shown we have found binding for the Ne_2 molecule with the inclusion of our NMT correction to the total energy. As explained we believe our results to be quite close to the exact Xα total energy. Similarly, for the rare gas crystals argon, krypton, and xenon Trickey et al. (1972) and Trickey et al. (1973) have calculated the cohesion of these crystals using the APW Xα method with the MT approximation. It has also been reported (private communication from S.B. Trickey) that preliminary calculations on the Ne crystal also indicate cohesion. The error for our Ne_2 calculation was rather large and although we cannot predict the precise amount of binding we can say with definiteness that the Ne_2 molecule is bound (see Table 6.6). The workers in solid state have somewhat higher accuracy and have found that the argon crystal binds with almost precisely the experimental cohesion (almost two place agreement) while krypton and xenon are slightly underbound. The preliminary calculations on the Ne crystal indicated that it may be slightly overbound. The important point is that the molecular and solid state calculations correlate and correlate rather well.

Although the APW Xα calculations were performed in the MT approximation it may be argued that the MT effects in the solid are definitively less than those in a homonuclear diatomic molecule. First, it may be observed for both C_2 and Ne_2 that the principle NMT contribution in both of these somewhat dissimilar cases came from the intersphere region. In a fcc or bcc solid the amount of intersphere volume per atom is over a factor of two smaller than in the diatomic molecule. Further, in the solid each atom is surrounded by neighbors which means that the charge in the outer finges of the atoms is more spherically symmetric or evenly distributed. This is in contrast to the homonuclear diatomic in which each atom has one neighbor which necessarily leads to a somewhat greater distortion of the electron density.

The results hence indicate that the Xα method itself possesses a degree of sophistication not suspected by many in being able to produce semi-quantatively binding for van der Waals bound systems. Slater (1972b) has argued that these results may be explained simply in terms of covalent binding and that the difference between a system such as C_2 and one such as Ne_2 is one of degree rather than kind.

NMT Corrections to the MT Eigenvalues

As shown in Section 4.3 the NMT correction to the MT eigenvalue takes almost the same form as the NMT correction

to the MT total energy (compare Eq. (4.19) to Eq. (3.24)). The principle difference is that instead of the total NMT desnity we now have the NMT part for the density of the particular state for which we are calculating the correction. This means that the existing sampling and integration method used for the total energy correction may also be used for the eigenvalue correction. Although the MSXα method with the MT approximation has been generally more successful calculating transition and ionization energies than total energies some anomalies have been observed which, just as the anomalies for the MT total energy calculations, seem to be directly related to attributes of the MT approximation. For example, it is generally observed that the very highest valence state ionization energies do not have the same relative accuracy as deeper states. The higher valence states are more diffuse and spread over the molecule more as a whole and hence these orbitals in a real sense sample the vagaries of the MT approximation more than lower and more localized states. Some effects in the case of ring type molecules seem to be directly related to the size of the relatively large intersphere region of this type of molecule. For example, for benzene it has been found that the separations between a number of the higher valence states are fairly accurate in the MT approximation but the levels are uniformly shifted too low in energy. By arbitrarily adjusting the MT averaged potential in the intersphere

region it has been found that these levels can be uniformly shifted higher in energy thus preserving the original separations and at the same time bringing the levels into better agreement with experiment (J.W.D. Connolly, private communication). This definitely is an effect of the MT approximation. Thus the NMT corrections to the eigenvalues are an area to which the methods developed in this research can be almost immediately and beneficially applied.

Further Test Molecules

It must be realized that even though the results of this research seem conclusive, further tests must be made to completely "calibrate" the method. Two molecules which seem particularly attractive are methane (CH_4) and water (H_2O). It has been found in previous research by the author (unpublished) that the MT total energy for CH_4 is fairly sensitive to the sphere radii picked for carbon and hydrogen. With the NMT correction, this effect should be diminished if not extinguished. If so, then this would eliminate the arbitrariness in the present MSXα method as regards picking sphere radii. As the C_2 and Ne_2 calculations, it seems a NMT calculation on the water molecule would be an acid test of the method. Can the MSXα method with the NMT correction correctly predict the bond angle between the hydrogens in the water molecule? Previous MT calculations on the water molecule by Connolly and Sabin

(1972) predicted that the water molecule was linear in its ground state. In addition, many other MO LCAO calculations have been done on water and its excited states and this would provide good comparisons with the NMT corrected Xα method. The water molecule would also provide a good test case for calculating the equilibrium configuration of the ground state via Hellman-Feynman force calculations using MT Xα orbitals. Again just as for the total energy MO LCAO results exist with which to compare (see Coulson and Deb (1971)).

APPENDIX A

FUNCTIONAL DERIVATIVES

The discussion of functional derivatives given in this appendix is of the nature of an outline rather than a complete treatment. For a more rigorous mathematical discussion of functional derivatives one may consult Volterra (1930) and Courant and Hilbert (1937). The major part of the discussion given here is taken from Volterra.

The kind of functionals discussed in Chapters II and III of the text are common in mathematical physics and consists simply of the integral of a function. Taking a simple example in one-dimension, let F be a functional of a function y where F is the integral of y(t) over a definite interval (a, b):

$$F = \int_a^b y(t)dt \ . \qquad (A.1)$$

For changes or variations in the function y(t) over its range of definition in the interval (a, b) the functional F will of course change or vary. In particular, the total variation δF of F for a variation $\delta y(t)$ of y(t) over the interval (a, b) is expressed as a functional

$$\delta F = \int_a^b \frac{\delta F(y(t))}{\delta y(\xi)} \, \delta y(\xi) d\xi \, . \tag{A.2}$$

The expression $\delta F(y(t))/\delta y(\xi)$ is called the first functional derivative of the functional F with respect to the function $y(t)$ at the point ξ. It is a functional of $y(t)$ and a function of the parameter ξ. This functional first derivative may be analogously defined as the ordinary first derivative of a function.

For a function of n variables $f(y_1, \ldots, y_n)$ the total differential df is defined as

$$df = \sum_{i=1}^{n} \frac{\partial f}{\partial y_i} \, dy_i \, . \tag{A.3}$$

The functions $\partial f/\partial y_i$ are defined as a limit

$$\frac{\partial f}{\partial y_i} = \lim_{h \to o} \frac{\Delta_i f}{h} \tag{A.4}$$

where

$$\Delta_i f = f(y_1, \ldots, y_i + h, \ldots, y_n) - f(y_1, \ldots, y_i, \ldots, y_n) \tag{A.5}$$

and where h is an incremental change of the variable y_i alone. For functionals the analogous construct to the ordinary partial derivatives of Eq. (A.3) is the functional

derivative expression $\delta F(y(t))/\delta y(\xi)$ of Eq. (A.2). Instead of n individual variables y_i we now have a continuous range of variables y(t) and concommitantly instead of the discontinuous index i we now have a continuous variable ξ. We can make the definition of $\delta F/\delta y$ precise.

Using the functional F of Eq. (A.1) as our example we give y(t) an increment $\delta y(t)$ such that over an interval (m, n) of (a, b): $|\delta y(t)| < \varepsilon$, $\delta y(t)$ does not change sign, and the interval (m, n) always contains ξ in its interior. We define ΔF as

$$\Delta F = \int_n^m (y(t) + \delta y(t))dt - \int_n^m y(t)dt \qquad (A.6)$$

and we define Δy as

$$\Delta y = \int_n^m \delta y(t)dt \qquad (A.7)$$

and let $h = (m - n)$. If

1) the ratio $\Delta F/\Delta y$ is always less than a finite number M;
2) there exists a determinate and finite limit to $\Delta F/\Delta y$ as ε and h simultaneously tend to zero subject to the condition that the point ξ is always in the interior of the interval (m, n);
3) the ratio $\Delta F/\Delta y$ tends to its limit uniformly with respect to all possible functions y(t) and all points ξ interior to (a, b)

then this limit is called the first derivative of the functional F with respect to the function y(t) at the point ξ:

$$\frac{\delta F(y(t))}{\delta y(\xi)} = \lim_{\substack{h \\ \varepsilon}\to 0} \frac{\Delta F}{\Delta y} . \tag{A.8}$$

The functional derivative of Eq. (A.8) is seen to be a functional of y(t) and a function of ξ.

In case of a function of n variables the total differential df was given in Eq. (A.3). Analogously, in the case of a functional derivative we have an infinite number of derivatives depending on y(t) and the continuous variable ξ over the interval (a, b). Hence the total variation of the functional F for arbitrary variation δy(t) of the function y(t) over the interval (a, b) is the integral (in contrast to the sum of Eq. (A.3))

$$\delta F = \int_a^b \frac{\delta F(y(t))}{\delta y(\xi)} \, \delta y(\xi) d\xi . \tag{A.9}$$

We may define functional derivatives of second and higher order. This being the case it is possible to perform functional Taylor series expansions of functionals in terms of functions and such expansions are quite useful in some branches of physics particularly statistical mechanics (Percus 1967)). We may define a chain rule for functional derivatives

$$\frac{\delta F(\phi(y(t)))}{\delta y(\xi)} = \int_a^b \frac{\delta F(\phi(y(t)))}{\delta \phi(\eta)} \frac{\delta \phi(\eta)}{\delta y(\xi)} \, d\eta. \tag{A.10}$$

Basically all of the operations possible with ordinary derivatives have their analogs in functional derivatives.

There is an alternative form for δF used by Courant and Hilbert (1937) which we mention here for pedagogical purposes. In this form one lets $\delta y(t) = \varepsilon\phi(t)$ in Eq. (A.2), then

$$\delta F = \lim_{\varepsilon \to o} \frac{\Delta F}{\varepsilon} \tag{A.11}$$

and

$$\lim_{\varepsilon \to o} \frac{\Delta F}{\varepsilon} = \left\{ \frac{d}{d\varepsilon} F(y(t) + \varepsilon\phi(t)) \right\}_{\varepsilon=o} \tag{A.12}$$

and this last expression leads to

$$\delta F = \int_a^b \frac{\delta F(y(t))}{\delta \phi(\xi)} \phi(\xi) d\xi \, . \tag{A.13}$$

One particular functional derivative is worth noting:

$$\frac{\delta y(s)}{\delta y(\xi)} = \delta(s - \xi). \tag{A.14}$$

The meaning of this result may be illustrated in a simple way.

Let

$$F = \int y(t)\delta(t - s)dt \tag{A.15}$$

or

$$F = y(s). \tag{A.16}$$

Then

$$\delta F = \delta y(s) \tag{A.17}$$

and

$$\delta F = \int \frac{\delta F(y(t))}{\delta y(\xi)} \delta y(\xi)d\xi \tag{A.18}$$

or

$$\delta F = \int \frac{\delta y(s)}{\delta y(\xi)} \delta y(\xi)d\xi . \tag{A.19}$$

This implies

$$\delta y(s) = \int \frac{\delta y(s)}{\delta y(\xi)} \delta y(\xi)d\xi \tag{A.20}$$

or

$$\frac{\delta y(s)}{\delta y(\xi)} = \delta(s - \xi) \tag{A.21}$$

Since this is true for arbitrary functions $y(t)$.

APPENDIX B

THE MULTIPLE-SCATTERING FORMALISM*

With the MT form for the Xα potential, $\bar{V}_{X\alpha}(\bar{\rho},\vec{r})$, the one-electron orbitals as discussed in Section (3.5) of the text in the atomic sphere and outer sphere regions may be conveniently expanded in a partial wave expansion. Thus orbital $\tilde{U}_i^\alpha$ for state i within an atomic sphere α of radius b_α with eigenvalue $\bar{\varepsilon}_i$ may be expanded

$$\tilde{U}_i^\alpha(\vec{r}) = \sum_{\ell,m} C_{\ell m}^{i\alpha} R_\ell(r_\alpha,\bar{\varepsilon}_i) Y_{\ell m}(\hat{r}_\alpha) \qquad r_\alpha < b_\alpha \quad (B.1)$$

where the $C_{\ell m}^{i\alpha}$ are expansion coefficients to be determined, the $Y_{\ell m}$ are (for convenience of calculation) real spherical harmonics, and the atomic-like R_ℓ's satisfy the central field differential equation

$$\left[-\frac{1}{r_\alpha^2}\frac{d}{dr_\alpha}\left(r_\alpha^2\frac{d}{dr_\alpha}\right) + \frac{\ell(\ell+1)}{r_\alpha^2} + \bar{V}_{X\alpha}(\bar{\rho},\vec{r}_\alpha) - \bar{\varepsilon}_i\right] R_\ell(r_\alpha,\bar{\varepsilon}_i) = 0, \quad (B.2)$$

where $\bar{V}_{X\alpha}(\bar{\rho}_1\vec{r}_\alpha)$ is the spherically averaged MT potential given in Eq. (3.42) of the text. The expansion in the outer sphere region is similarly (for $|\vec{r}-\vec{r}_o| > b_o$, where b_o is

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*The main references for this appendix are K.H. Johnson (1966) and K.H. Johnson (1972).

the radius of outer sphere)

$$\tilde{U}_i^o(\vec{r}) = \sum_{\ell,m} C_{\ell m}^{io} R_\ell(r_o,\bar{\varepsilon}_i) Y_{\ell m}(\hat{r}_o) \qquad b_o \leq r_o < \infty \tag{B.3}$$

For the intersphere region the potential $\bar{V}_{X\alpha}(\bar{\rho},\vec{r})$ is averaged to a constant $\bar{V}_{IN}$ hence the differential equation to be solved is

$$[\nabla^2 + \bar{\varepsilon}_i - \bar{V}_{IN}]\tilde{U}_i(\vec{r}) = 0. \tag{B.4}$$

The solution to this equation may be expressed as a multicenter partial wave expansion which for $\bar{\varepsilon}_i < \bar{V}_{IN}$ is

$$\tilde{U}_i(\vec{r}) = \sum_{\alpha=1}^{N} \sum_{\ell,m} A_{\ell m}^{i\alpha} k_\ell(\kappa_i r_\alpha) Y_{\ell m}(\hat{r}_\alpha)$$

$$+ \sum_{\ell,m} A_{\ell m}^{io} i_\ell(k_i r_o) Y_{\ell m}(\hat{r}_o), \tag{B.5}$$

where the $A_{\ell m}^{i\alpha}$ and $A_{\ell m}^{io}$ are expansion coefficients to be determined, the $Y_{\ell m}$ are real spherical harmonics, and $r_\alpha = |\vec{r}-R_\alpha|$. The variable κ_i is defined

$$\kappa_i = (\bar{\varepsilon}_i - \bar{V}_{IN})^{1/2} \tag{B.6}$$

and for $\bar{\varepsilon}_i < \bar{V}_{IN}$ is imaginary. The summation α is over all the nuclear centers. The modified spherical Hankel functions $k_\ell^{(1)}(\kappa r)$ and modified spherical Bessel functions $i_\ell(\kappa r)$ are related respectively to the ordinary spherical Hankel functions $h_\ell^{(1)}(\kappa r)$ and ordinary spherical Bessel functions $j_\ell(\kappa r)$ of imaginary argument:

$$k_\ell^{(1)}(x) = -(i)^{-\ell} h_\ell^{(1)}(ix)$$
$$i_\ell(x) = (i)^{-\ell} j_\ell(ix) \tag{B.7}$$

For energy $\bar{\varepsilon}_i > \bar{V}_{IN}$ we expand the orbital for state i in the intersphere region

$$\tilde{U}_i(\vec{r}) = \sum_{\alpha=1}^{N} \sum_{\ell,m} A_{\ell m}^{i\alpha}\, \eta_\ell(\kappa_i r_\alpha) Y_{\ell m}(\hat{r}_\alpha)$$

$$+ \sum_{\ell,m} A_{\ell m}^{io}\, j_\ell(\kappa_i r_o) Y_{\ell m}(\hat{r}_o) \qquad \text{(B.8)}$$

where κ_i is now real and $\eta_\ell(\kappa r)$ and $j_\ell(\kappa r)$ are respectively the ordinary spherical Neumann and Bessel functions.

The number of ℓ values used in the expansions of Eqs. (B.1), (B.3), (B.8) may be unlimited. However, in practice, the orbitals are rapidly convergent in ℓ, hence the summations are usually over a modest number of ℓ values thus significantly limiting the number of coefficients to be calculated. This is one of the chief virtues of the MSXα method.

It may be shown that the C and A coefficients in the above expansion are related as follows

$$A_{\ell m}^{i\alpha} = (-1)^{\ell+1} \kappa_i b_\alpha^2 [i_\ell(\kappa_i b_\alpha), R_\ell(b_\alpha, \bar{\varepsilon}_i)] C_{\ell m}^{i\alpha} \quad \bar{\varepsilon}_i < \bar{V}_{IN}$$

$$A_{\ell m}^{io} = (-1)^{\ell+1} \kappa_i b_o^2 [R_\ell(b_o, \bar{\varepsilon}_i), k_\ell^{(1)}(\kappa_i b_o)] C_{\ell m}^{io} \quad \bar{\varepsilon}_i < \bar{V}_{IN}$$

$$A_{\ell m}^{i\alpha} = \kappa_i b_\alpha^2 [j_\ell(\kappa_i b_\alpha), R_\ell(b_\alpha, \bar{\varepsilon}_i)] C_{\ell m}^{i\alpha} \quad \bar{\varepsilon}_i > \bar{V}_{IN}$$

$$A_{\ell m}^{io} = \kappa_i b_o^2 [R_\ell(b_o, \bar{\varepsilon}_i), \eta_\ell(\kappa_i b_o)] C_{\ell m}^{io} \quad \bar{\varepsilon}_i > \bar{V}_{IN} \qquad \text{(B.9)}$$

Here the bracket relation [ ] is the Wronskian such that $[u,v] = u \frac{dV}{dX} - V \frac{du}{dX}$.

The A coefficients as well as the eigenvalue $\bar{\varepsilon}_i$ may be found for a state i by demanding that the orbital $\tilde{U}_i$ as well as its first derivative be continuous at each sphere boundary of the MT potential. This condition leads to a set of equations for the $A_{\ell m}^{i\alpha}$ coefficients

$$(t_\ell^\alpha(\bar{\varepsilon}))^{-1} A_{\ell m}^{i\alpha} = \sum_{\substack{\beta=0 \\ \beta\neq\alpha}}^{N} \sum_{\ell' m'} G_{\ell m,\ell' m'}^{\alpha\beta}(R_{\alpha\beta},\bar{\varepsilon}) A_{\ell' m'}^{i\beta} \qquad (B.10)$$

for α,ℓ, and m varying over their respective ranges. The t and G quantities introduced here are defined as follows:

$$\begin{aligned}
t_\ell^\alpha(\bar{\varepsilon}) &= -\frac{[\dot{i}(\kappa b_\alpha), R_\ell(b_\alpha,\bar{\varepsilon})]}{[k_\ell^{(1)}(\kappa b_\alpha), R_\ell(b_\alpha,\bar{\varepsilon})]} \quad ; \quad \bar{\varepsilon} < \bar{V}_{IN} \\
t_\ell^o(\bar{\varepsilon}) &= -\frac{[k_\ell^{(1)}(\kappa b_o), R_\ell(b_o,\bar{\varepsilon})]}{[\dot{i}_\ell(\kappa b_o), R_\ell(b_o,\bar{\varepsilon})]} \quad ; \quad \bar{\varepsilon} < \bar{V}_{IN} \\
t_\ell^\alpha(\bar{\varepsilon}) &= -\frac{[j_\ell(\kappa b_\alpha), R_\ell(b_\alpha,\bar{\varepsilon})]}{[\eta_\ell(\kappa b_\alpha), R_\ell(b_\alpha,\bar{\varepsilon})]} \quad ; \quad \bar{\varepsilon} > \bar{V}_{IN} \\
t_\ell^o(\bar{\varepsilon}) &= -\frac{[\eta_\ell(\kappa b_o), R_\ell(b_o,\bar{\varepsilon})]}{[j_\ell(\kappa b_o), R_\ell(b_o,\bar{\varepsilon})]} \quad ; \quad \bar{\varepsilon} > \bar{V}_{IN}
\end{aligned} \qquad (B.11)$$

and

$$G_{\ell m,\ell' m'}^{\alpha\beta}(R_{\alpha\beta},\bar{\varepsilon}) = (1-\delta_{\alpha\beta}) 4\pi (-1)^{\ell+\ell'} \sum_{L,M} I_{LM} \cdot (\ell m,\ell' m') k_L^{(1)}(\kappa R_{\alpha\beta}) Y_{LM}(\hat{R}_{\alpha\beta}) \quad \bar{\varepsilon} < \bar{V}_{IN} ;$$

$$G_{\ell m,\ell' m'}^{\alpha o}(R_{\alpha o},\bar{\varepsilon}) = 4\pi (-1)^{\ell+\ell'} \sum_{L,M} I_{LM}(\ell m,\ell' m') \cdot \dot{i}_L(\kappa R_{\alpha o}) Y_{LM}(\hat{R}_{\alpha o}) \quad \bar{\varepsilon} < \bar{V}_{DV};$$

$$G^{\alpha\beta}_{\ell m,\ell' m'}(R_{\alpha\beta},\bar{\varepsilon}) = (1-\delta_{\alpha\beta})4\pi(i)^{\ell-\ell'}\sum_{L,M}(i)^{-L}I_{LM}(\ell m,\ell' m')$$

$$\cdot\ \eta_L(\kappa R_{\alpha\beta})Y_{LM}(\hat{R}_{\alpha\beta}) \qquad \bar{\varepsilon} > \bar{V}_{IN}$$

$$G^{\alpha o}_{\ell m,\ell' m'}(R_{\alpha o},\bar{\varepsilon}) = 4\pi(i)^{\ell-\ell'}\sum_{L,M}(i)^{-L}I_{LM}(\ell m,\ell' m')$$

$$\cdot\ j_L(\kappa R_{\alpha o})Y_{LM}(\hat{R}_{\alpha o}) \qquad \bar{\varepsilon} > \bar{V}_{IN}. \tag{B.12}$$

Here the I_{LM} quantities are Gaunt coefficients

$$I_{LM}(\ell m,\ell' m') = \iint Y_{\ell m}(\hat{r})Y_{LM}(\hat{r})Y_{\ell' m'}(\hat{r})\cdot \sin\theta d\theta d\phi \tag{B.13}$$

with the conditions that they are non-zero for $|\ell-\ell'| \leq L \leq \ell+\ell'$ and $\ell+\ell'+L$ even.

The zeroes of the secular equation of the coefficients of the $A^{i\alpha}_{\ell m}$ given in expression (B.10) correspond to the eigenvalues $\bar{\varepsilon}_i$. The secular equation is given by

$$\mathrm{Det}\left|\left[t^{\alpha}_{\ell}(\bar{\varepsilon}_i)^{-1}\delta_{\ell\ell'}\delta_{mm'}\delta_{\alpha\beta} + G^{\alpha\beta}_{\ell m,\ell' m'}(R_{\alpha\beta},\bar{\varepsilon}_i)\right]\right| = 0. \tag{B.14}$$

The functions $t^{\alpha}_{\ell}(\varepsilon)$ depend on the value of the radial wave function R_{ℓ} and its derivative at the sphere boundary α, and therefore implicity on the potential $\bar{V}_{X\alpha}(\bar{\rho},\vec{r})$. The functions $G^{\alpha\beta}_{\ell m,\ell' m'}(\varepsilon)$ are independent of the potential <u>per se</u> but depend implicity upon the energy $\bar{\varepsilon}$ through their dependence on κ. Since the determinant is a non-linear function of $\bar{\varepsilon}$ it is computed over a range of energies

bracketing each eigenvalue $\bar{\varepsilon}_i$ (where the determinant goes through zero and changes sign) and inverse interpolated to find its zero and therefore $\bar{\varepsilon}_i$. Once the eigenvalue $\bar{\varepsilon}_i$ is found the coefficients $A_{\ell m}^{i\alpha}$ may be found as components of the eigenvector for this eigenvalue.

The size of this equation for a given eigenvalue depends upon the number of atoms and the number of ℓ and m values used for the expansion on each atomic site. The size of the secular equation to be solved may be considerably reduced by using the symmetry properties of the molecule under consideration.

It should be pointed out, since it is important in forming the density for actual calculation, that all elements of the matrix of the secular equation (B.14) are real but not all of them are symmetric in the form given. In particular for $\bar{\varepsilon}_i < \bar{V}_{IN}$ the $G_{\ell m,\ell' m'}^{\alpha\beta}$ are not symmetric under interchange of $(\alpha,\beta),(\ell,\ell')$, and (m,m') (see expressions (B.12)). We may make the matrix symmetric by defining new primed quantities as follows for $\bar{\varepsilon}_i < \bar{V}_{IN}$:

$$G_{\ell m,\ell' m'}^{\alpha\beta'}(\bar{\varepsilon}) = (-1)^{\ell'} G_{\ell m,\ell' m'}^{\alpha\beta}(\bar{\varepsilon})$$
$$t_{\ell}^{\alpha'}(\bar{\varepsilon}) = (-1)^{\ell} t_{\ell}^{\alpha}(\bar{\varepsilon}) \qquad \text{(B.15a)}$$

and we also redifine the A coefficients (this is true for $\alpha=0$ as well)

$$A_{\ell' m'}^{i\alpha'} = (-1)^{\ell'} A_{\ell' m'}^{i\alpha} \; . \qquad \text{(B.15b)}$$

For $G^{\alpha\beta}_{\ell m,\ell' m'}(\bar{\varepsilon})$, $t^{\alpha}_{\ell}(\bar{\varepsilon})$ and $A^{i\alpha'}_{\ell' m'}$, for $\bar{\varepsilon} > \bar{V}_{IN}$ no modification is necessary since the $G^{\alpha\beta}_{\ell m,\ell' m'}(\bar{\varepsilon})$ are already symmetric. Equation (B.10) may now be written in exactly the same form with primed quantities (for $\bar{\varepsilon} > \bar{V}_{IN}$ the primed elements are the same as the original unprimed elements):

$$[t^{\alpha'}_{\ell}(\bar{\varepsilon})]^{-1} = \sum_{\substack{\beta=0 \\ \beta\neq\alpha}}^{N} \sum_{\ell' m'} G^{\alpha\beta,}_{\ell m,\ell' m'}(R_{\alpha\beta},\bar{\varepsilon}) A^{i\alpha'}_{\ell' m'}, \qquad (B.16)$$

Further, the relation between the A and C coefficients is modified for $\bar{\varepsilon} < \bar{V}_{IN}$:

$$A^{i\alpha'}_{\ell m} = (-1)^{\ell} A^{i\alpha}_{\ell m} = -\kappa b_{\alpha}^{2}[\dot{i}_{\ell}(\kappa b_{\alpha}), R_{\ell}(b_{\alpha},\bar{\varepsilon})] C^{i\alpha}_{\ell m}. \qquad (B.17)$$

We may redefine new primed C coefficients so that the original relationships of equation (B.9) are maintained:

$$C^{i\alpha'}_{\ell m} = (-1)^{\ell} C^{i\alpha}_{\ell m} \qquad (B.18)$$

Then for $\bar{\varepsilon} < \bar{V}_{IN}$

$$A^{i\alpha'}_{\ell m} = (-1)^{\ell+1} \kappa b_{\alpha}^{2}[\dot{i}_{\ell}(\kappa b_{\alpha}), R_{\ell}(b_{\alpha},\bar{\varepsilon})] C^{i\alpha'}_{\ell m},$$

$$A^{io'}_{\ell m} = (-1)^{\ell+1} \kappa b_{o}^{2}[R_{\ell}(b_{o}\bar{\varepsilon}), k^{(1)}_{\ell}(\kappa b_{o})] C^{io'}_{\ell m}. \qquad (B.19)$$

These phase relationships are discussed here since they are important in forming the density from the molecular orbitals as generated in existing MSXα computer codes. The present codes are written in terms of the primed quantities for calculational convenience. Specific details of the formation of the density and non-muffin (NMT) part of the density are discussed in Appendix G.

APPENDIX C

THE NMT TOTAL DENSITY

The total one-electron charge density is defined (See Section 2.2)

$$\rho(\vec{r}) = \sum_i n_i U_i^*(\vec{r}) U_i(\vec{r}) \quad , \tag{C.1}$$

where the summation is over all states including spin, the n_i are occupation numbers which vary from zero to one, and the U_i are one-electron orbitals (See Slater (1972). (The density may be broken into spin up and spin down parts.) The total density may be written as a sum of the densities for each state

$$\rho(\vec{r}) = \sum_i n_i \rho_i(\vec{r}) \quad , \tag{C.2}$$

where

$$\rho_i(\vec{r}) = U_i^*(\vec{r}) U_i(\vec{r}) \quad . \tag{C.3}$$

In the present case we are assuming the orbitals to be solutions to the MT one-electron equations and we denote these as $\tilde{U}_i$ (See Section 3.4). The multiple-scattering partial wave

expansions for the orbitals were discussed in the preceding appendix, Appendix B. In this appendix the explicit expressions for $\Delta\rho(\vec{r})$ (defined in Section 3.2) are derived. The definition of $\Delta\rho(\vec{r})$ is the difference at the point $\vec{r}$ between the density $\rho(\vec{r})$ as defined in Eq. (C.1) above and the MT density $\overline{\rho}(\vec{r})$ at $\vec{r}$ (both $\rho(\vec{r})$ and $\overline{\rho}(\vec{r})$ are evaluated with the $\{\tilde{U}_i\}$):

$$\Delta\rho(\vec{r}) = \rho(\vec{r}) - \overline{\rho}(\vec{r}) \ . \qquad (C.4)$$

The MT density in the atomic and outer sphere regions is defined as the angular average of $\rho(\vec{r})$ itself:

$$\overline{\rho}(\vec{r}) = \frac{1}{4\pi} \int \rho(\vec{r})\, d\Omega \qquad (C.5)$$

where $d\Omega$ is the angular element. In the intersphere region $\overline{\rho}(\vec{r})$ is defined as the volume average of $\rho(\vec{r})$ over the intersphere region, it is a constant, and we shall call it $\overline{\rho}_{IN}$:

$$\overline{\rho}_{IN} = \frac{1}{V_{IN}} \int_{IN} \rho(\vec{r})\, d\vec{r} \ , \qquad (C.6)$$

where V_{IN} is the volume of the intersphere region (Remember that $\overline{V}_{IN}$ is the average x_α MT potential in the intersphere region).

$\Delta\rho(\vec{r})$ in the Atomic and Outer Sphere Regions

In Appendix B the partial wave expansion for an orbital $\tilde{U}_i$ for state i in an atomic region α (or outer region where $\alpha = 0$) with eigenvalue $\bar{\varepsilon}_i$ was given as

$$\tilde{U}_i^{\alpha}(\vec{r}) = \sum_{\ell,m} C_{\ell m}^{i\alpha} R_\ell(r_\alpha, \bar{\varepsilon}_i) Y_{\ell m}(\hat{r}_\alpha) . \qquad r < b_\alpha \qquad (C.7)$$

The expansion in the outer sphere region is quite similar. With this definition of U_i^{α} and its components we may write $\rho_i^{\alpha}(\vec{r})$, the density for state i in the αth atomic region, as

$$\rho_i^{\alpha}(\vec{r}) = \sum_{\ell,m} \sum_{\ell'm'} C_{\ell'm'}^{i\alpha\,*} C_{\ell m}^{i\alpha} R_{\ell'}^{*}(r_\alpha, \bar{\varepsilon}_i) R_\ell(r_\alpha, \bar{\varepsilon}_i)$$

$$\times Y_{\ell'm'}^{*}(\hat{r}_\alpha) Y_{\ell m}(\hat{r}_\alpha) . \qquad (C.8)$$

To obtain $\bar{\rho}_i^{\alpha}(\vec{r})$ we take the angular average of this last expression. The only angular functions are the $Y_{\ell m}$'s. The angular average of a pair of $Y_{\ell m}$'s takes the form

$$\frac{1}{4\pi} \int Y_{\ell'm'}^{*}(\hat{r}) Y_{\ell m}(\hat{r}) d\Omega = \frac{1}{4\pi} \delta(\ell, \ell') \delta(m, m') \qquad (C.9)$$

due to the orthonormality of these functions. Substituting

this in Eq. (C.8) we get

$$\bar{\rho}_i^{\alpha}(\vec{r}) = \sum_{\ell,m} \sum_{\ell',m'} \frac{1}{4\pi} C_{\ell'm'}^{i\alpha *} C_{\ell m}^{i\alpha} R_{\ell'}^{*}(r_\alpha, \bar{\varepsilon}_i) R_\ell(r_\alpha, \bar{\varepsilon}_i) \delta(\ell,\ell') \delta(m,m') \ . \tag{C.10}$$

Note that all quantities in the expansion of $\tilde{U}_i^{\alpha}$ are real. Hence employing this fact and summing over ℓ' and m' we are left with

$$\bar{\rho}_i^{\alpha}(\vec{r}) = \sum_{\ell,m} \frac{(C_{\ell m}^{i\alpha})^2}{4\pi} R_\ell^2(r_\alpha, \bar{\varepsilon}_i) \ . \tag{C.11}$$

(In present codes of the MSX_α programs the $C_{\ell m}^{i\alpha}$ are normalized such that if the charge in sphere α for the ith state is Q_i^{α} then

$$Q_i^{\alpha} = \int \bar{\rho}_i^{\alpha}(r_\alpha) d\vec{r}_\alpha \tag{C.12}$$

$$= \int \sum_{\ell,m} \frac{(C_{\ell m}^{i\alpha})^2}{4\pi} R_\ell^2(r_\alpha, \bar{\varepsilon}_i) d\vec{r}_\alpha \tag{C.13}$$

$$= \int_0^{b_\alpha} \sum_{\ell,m} C_{\ell m}^{i\alpha 2} R_\ell^2(r_\alpha, \bar{\varepsilon}_i) r_\alpha^2 dr_\alpha \ . \tag{C.14}$$

Note that there exists a relative ambiguity between $C_{\ell m}^{i\alpha}$ and $R_\ell(r_\alpha)$ for a given ℓ value. There is no ambiguity as regards

the product $C^{i\alpha}_{\ell m} R_\ell(r_\alpha)$ and the $C^{i\alpha}_{\ell m}$ are determined such that this is the case. (Note that for the outer sphere region the integral in Eq. (C.14) extends from b_o to ∞).)

For a state i in the αth spherical region $\Delta\rho_i^\alpha(\vec{r})$ is defined

$$\Delta\rho_i^\alpha(\vec{r}) = \rho_i^\alpha(\vec{r}) - \bar{\rho}_i^\alpha(\vec{r}) \tag{C.15}$$

Since the $\tilde{U}_i^\alpha$ are real we may express $\Delta\rho_i^\alpha(\vec{r})$ in terms of Eq. (C.8) and Eq. (C.11) as

$$\Delta\rho_i^\alpha(\vec{r}) = \Big(\sum_{\ell,m} C^{i\alpha}_{\ell m} R_\ell(r_\alpha, \bar{\varepsilon}_i)\, Y_{\ell m}(\hat{r}_\alpha) \Big)^2$$

$$- \sum_{\ell,m} \frac{(C^{i\alpha}_{\ell m})^2}{4\pi} R_\ell^2(r_\alpha, \bar{\varepsilon}_i) \,. \tag{C.16}$$

The total $\Delta\rho^\alpha(\vec{r})$ in region α is simply the sum over the $\Delta\rho_i^\alpha(\vec{r})$ for all states

$$\Delta\rho^\alpha(\vec{r}) = \sum_i n_i \, \Delta\rho_i^\alpha(\vec{r}) \,. \tag{C.17}$$

$\Delta\rho(\vec{r})$ in the Intersphere Region

In Appendix B the partial wave expansion for an orbital $\tilde{U}_i$ for state i in the intersphere region with $\bar{\varepsilon}_i < \bar{V}_{IN}$ was given

$$\tilde{U}_i(\vec{r}) = \sum_{\alpha=1}^{N} \sum_{\ell,m} A_{\ell m}^{i\alpha} k_\ell^{(1)}(K_i r_\alpha) Y_{\ell m}(\hat{r}_\alpha) + \sum_{\ell,m} A_{\ell m}^{io} i_\ell(K_i r_o) Y_{\ell m}(\hat{r}_o). \tag{C.18}$$

For $\bar{\varepsilon}_i > V_{IN}$ the expansion was given

$$\tilde{U}_i(\vec{r}) = \sum_{\alpha=1}^{N} \sum_{\ell,m} A_{\ell m}^{i\alpha} \eta_\ell(K_i r_\alpha) Y_{\ell m}(\hat{r}_\alpha) + \sum_{\ell,m} A_{\ell m}^{io} j_\ell(K_i r_o) Y_{\ell m}(\hat{r}_o). \tag{C.19}$$

In Eq. (C.6) we defined the MT density in the intersphere region $\bar{\rho}_{IN}$ as

$$\bar{\rho}_{IN} = \frac{1}{V_{IN}} \int_{IN} \rho(\vec{r}) d\vec{r} \tag{C.6}$$

which may be simply expressed as

$$\bar{\rho}_{IN} = Q_{IN}/V_{IN} \tag{C.20}$$

where Q_{IN} is the total charge in the intersphere region. Taking the expressions for $\tilde{U}_i$ in Eq. (C.18) or Eq. (C.19) respectively for states with $\bar{\varepsilon}_i < \bar{V}_{IN}$ or $\bar{\varepsilon}_i > \bar{V}_{IN}$, squaring, and summing over all the states gives the total density in the intersphere region. Taking the difference between this expression and $\bar{\rho}_{IN}$ given in Eq. (C.20) gives $\Delta\rho(\vec{r})$ for the intersphere region:

$$\Delta\rho(\vec{r}) = \sum_i \Big(\sum_{\alpha=1}^{N} \sum_{\ell,m} A_{\ell m}^{i\alpha} \left\{ \frac{k_\ell^{(1)}(K_i r_\alpha)}{\eta_\ell(K_i r_\alpha)} \right\} Y_{\ell m}(\hat{r}_\alpha)$$

$$+ \sum_{\ell,m} A_{\ell m}^{io} \left\{ \frac{i_\ell(K_i r_o)}{j_\ell(K_i r_o)} \right\} Y_{\ell m}(\hat{r}_o) \Big)^2$$

$$-Q_{IN}/V_{IN} \qquad \text{for} \quad \left\{ \begin{array}{l} \bar{\varepsilon}_i < \bar{V}_{IN} \\ \bar{\varepsilon}_i > \bar{V}_{IN} \end{array} \right\} . \qquad \text{(C.21)}$$

APPENDIX D

EXPLICIT EXPRESSIONS FOR $\Delta V_c^{\alpha,IN}$, $\Delta V_c^{IN,IN}$ AND $\Delta V_c^{o,IN}$*

In this appendix we will derive the explicit expressions for $\Delta V_c^{\alpha,IN}$, $\Delta V_c^{IN,IN}$, and $\Delta V_c^{o,IN}$. To derive the three NMT potentials above we must derive expressions for $V_c^{\alpha,IN}$, $V_c^{IN,IN}$, and $V_c^{o,IN}$ and having these apply the MT averages to obtain the functions $\bar{V}_c^{\alpha,IN}$, $\bar{V}_c^{IN,IN}$, and $\bar{V}_c^{o,IN}$. The NMT potentials are simply the difference between the two. To reiterate, the basic type of integral we must solve to obtain the potentials $V_c^{\alpha,IN}$, $V_c^{IN,IN}$, and $V_c^{o,IN}$ has the following form

$$V_c(\bar{\rho}, \vec{r}) = 2 \int \frac{\bar{\rho}(\vec{r}')}{|\vec{r} - \vec{r}'|} \qquad (D.1)$$

$\underline{\Delta V_c^{\alpha,IN}(\bar{\rho}, \vec{r}_\alpha)}$

The potential $V_c^{\alpha,IN}$ corresponds to the potential inside the αth sphere arising from the constant intersphere charge

$$V_c^{\alpha,IN}(\bar{\rho}, \vec{r}) = 2 \int \frac{\bar{\rho}_{IN}}{|\vec{r} - \vec{r}_{IN}|} d\vec{r}_{IN} . \qquad (D.2)$$

*The definitions of the symbols used in this appendix are those given in section (3.6) of the main text.

To integrate over the intersphere region due to its odd shape we must first integrate over the volume inside the outer sphere and then subtract the integrals over the atomic regions. This can be readily done since $\bar{\rho}_{IN}$ is a constant. For a convenient set of vectors to be used see Figure D.1:

$$\vec{r} - \vec{r}_{IN} = \vec{r}_\alpha + \vec{R}_\alpha - \vec{r}_o - \vec{R}_o ,$$

$$= (\vec{r}_\alpha + \vec{R}_{\alpha o}) - \vec{r}_o . \qquad (D.3)$$

In the integration over the volume inside the outer sphere $(\vec{r}_\alpha + \vec{R}_{\alpha o})$ is fixed and $\vec{r}_o$ the variable of integration. We employ the expansion for $1/|\vec{r} - \vec{r}'|$

$$\frac{1}{|\vec{r} - \vec{r}'|} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{m=+\ell} \frac{4\pi}{2\ell + 1} \frac{r_<^\ell}{r_>^{\ell+1}} Y_{\ell m}(\hat{r}) Y^*_{\ell m}(\hat{r}') . \qquad (D.4)$$

We distinguish two cases: $|\vec{r}_o| < |\vec{r}_\alpha + \vec{R}_{\alpha o}|$ and $|\vec{r}_o| > |\vec{r}_\alpha + \vec{R}_{\alpha o}|$. The angular integration in the first case gives

$$\int \frac{1}{|(\vec{r}_\alpha + \vec{R}_{\alpha o}) - \vec{r}_o|} \, d\Omega_o = \frac{4\pi}{|\vec{r}_\alpha + \vec{R}_{\alpha o}|} ; \qquad (D.5)$$

and in the second case gives

$$\int \frac{1}{|(\vec{r}_\alpha + \vec{R}_{\alpha o}) - \vec{r}_o|} \, d\Omega_o = \frac{4\pi}{r_o} . \qquad (D.6)$$

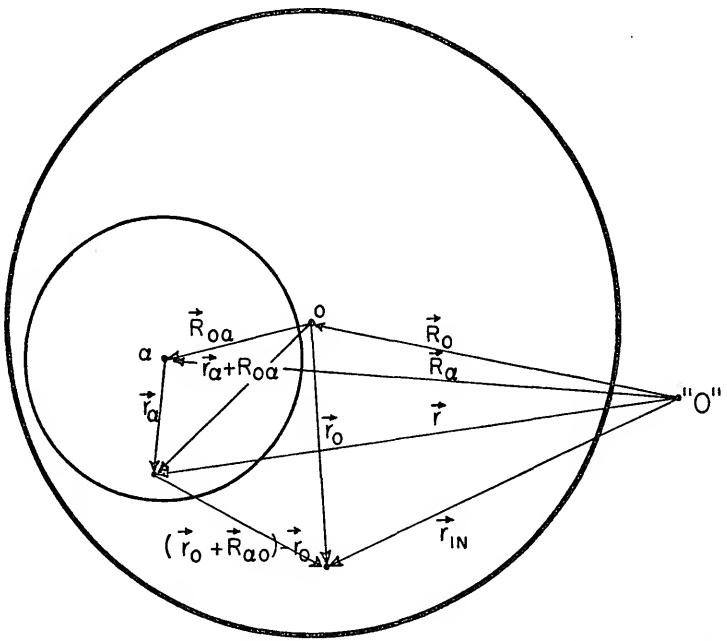

Figure D.1. Atomic-Inner Vector Relationships Used in the Derivation of $\Delta V_c^{\alpha,IN}$ and $\Delta V_c^{IN,IN}$.

Completing the radial integrations we get

$$2\int_{r_o<b_o} \frac{\bar{\rho}_{IN}}{|(\vec{r}_\alpha + \vec{R}_{\alpha o}) - \vec{r}_o|}\, d\vec{r}_o = 8\pi\bar{\rho}_{IN} \left\{ \frac{1}{|\vec{r}_\alpha + \vec{R}_{\alpha o}|} \int_0^{|\vec{r}_\alpha+\vec{R}_{\alpha o}|} r_o^2 dr_o \right.$$

$$\left. + \int_{|\vec{r}_\alpha+\vec{R}_{\alpha o}|}^{b_o} r_o dr_o \right\} ,$$

$$= 8\pi\bar{\rho}_{IN} \left(\frac{|\vec{r}_\alpha + \vec{R}_{\alpha o}|^2}{3} + \frac{b_o^2}{2} - \frac{|\vec{r}_\alpha + \vec{R}_{\alpha o}|^2}{2} \right) ,$$

$$= 4\pi\bar{\rho}_{IN} \left(b_o^2 - \frac{1}{3} |\vec{r}_\alpha + \vec{R}_{\alpha o}|^2\right) . \qquad \text{(D.7)}$$

We now must integrate over the atomic regions and there are two cases--that in which the integration point is inside the αth sphere and that in which it isn't. Considering the first case we use vectors $\vec{r}$ and $\vec{r}_\alpha$ with the αth nucleus as origin. For $|\vec{r}| < |\vec{r}_\alpha|$ we have for the angular integration

$$\int \frac{1}{|\vec{r} - \vec{r}_\alpha|}\, d\Omega_\alpha = \frac{4\pi}{r_\alpha} , \qquad \text{(D.8)}$$

and for $|\vec{r}| > |\vec{r}_\alpha|$ we have

$$\int \frac{1}{|\vec{r} - \vec{r}_\alpha|} \, d\Omega_\alpha = \frac{4\pi}{r} \, . \tag{D.9}$$

Doing the radial integrations we get

$$2\int_{r<b_\alpha} \frac{\bar{\rho}_{IN}}{|\vec{r} - \vec{r}_\alpha|} = 8\pi\bar{\rho}_{IN} \left\{ \frac{1}{r_\alpha} \int_0^{r_\alpha} r^2 dr + \int_{r_\alpha}^{b_\alpha} r dr \right\} ,$$

$$= 8\pi\bar{\rho}_{IN} \left(\frac{r_\alpha^2}{3} + \frac{b_\alpha^2}{2} - \frac{r_\alpha^2}{2} \right) ,$$

$$= 4\pi\bar{\rho}_{IN} \left(b_\alpha^2 - \frac{1}{3} r_\alpha^2 \right) . \tag{D.10}$$

The other part of the integrations over the atomic regions is the integrations over the (N-1) $\beta \neq \alpha$ spheres. For these we use coordinates (See Figure D.2)

$$\vec{r}_\alpha + \vec{R}_\alpha - \vec{r}_\beta - \vec{R}_\beta = (\vec{r}_\alpha - \vec{R}_{\alpha\beta}) - \vec{r}_\beta \tag{D.11}$$

The only case here is $|\vec{r}_\alpha - \vec{R}_{\alpha\beta}| > |\vec{r}_\beta|$. Hence for the βth sphere

$$2 \int \frac{\bar{\rho}_{IN}}{|(\vec{r}_\alpha + \vec{R}_{\alpha\beta}) - \vec{r}_\beta|} \, d\vec{r}_\beta = 8\pi\bar{\rho}_{IN} \frac{1}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|} \int_0^{b_\beta} r_\beta^2 dr_\beta$$

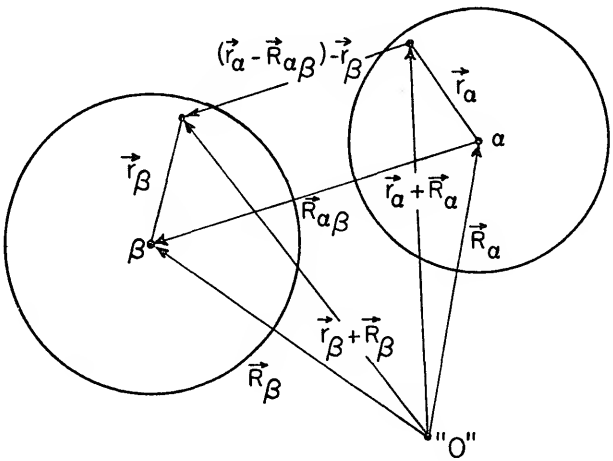

Figure D.2. Atomic-Atomic Vector Relationships Used in the Derivation of $\Delta V_c^{\alpha,IN}$ and $\Delta V_c^{IN,IN}$.

$$= 4\pi\bar{\rho}_{IN} \frac{2}{3} \frac{b_\beta^3}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|} . \qquad (D.12)$$

Combining the results of Eqs. (D.7) and (D.10), and (D.12) we have

$$V_c^{\alpha,IN}(\bar{\rho}, \vec{r}_\alpha) = 4\pi\bar{\rho}_{IN}\Big(b_o^2 - b_\alpha^2 - \frac{1}{3}|\vec{r}_\alpha + \vec{R}_{\alpha o}|^2 + \frac{1}{3} r_\alpha^2$$

$$- \frac{2}{3} \sum_{\substack{\beta=1 \\ \beta=\alpha}}^{N} \frac{b_\beta^3}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|}\Big) . \qquad (D.13)$$

To obtain $\bar{V}_c^{\alpha,IN}$ we must perform the angular average of $V_c^{\alpha,IN}$ in the αth sphere. The constant and radial terms will not be affected, hence

$$\bar{V}_c^{\alpha,IN}(\bar{\rho}, \vec{r}_\alpha) = 4\pi\bar{\rho}_{IN}\Big\{\Big(b_o^2 - b_\alpha^2 + \frac{1}{3} r_\alpha^2\Big) - \frac{1}{3}\frac{1}{4\pi}\int|\vec{r}_\alpha + \vec{R}_{\alpha o}|^2 d\Omega_\alpha$$

$$- \frac{2}{3} \sum_{\substack{\beta=1 \\ \beta\neq\alpha}}^{N} b_\beta^3 \frac{1}{4\pi} \int \frac{1}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|} d\Omega_\alpha . \qquad (D.14)$$

$$\frac{1}{4\pi}\int|\vec{r}_\alpha + \vec{R}_{\alpha o}|^2 d\Omega_\alpha = \frac{1}{2}\int_{-1}^{+1} (r_\alpha^2 + R_{\alpha o}^2 - 2r_\alpha R_{\alpha o}\xi)\, d\xi ,$$

$$= (r_\alpha^2 + R_{\alpha o}^2) . \qquad (D.15)$$

$$\frac{1}{4\pi}\int \frac{1}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|}\, d\Omega_\alpha = \frac{1}{R_{\alpha\beta}} . \qquad (D.16)$$

Substituting Eq. (D.15) and Eq. (D.16) in Eq. (D.14) and cancelling the r_α^2 terms we get

$$\bar{V}_c^{\alpha,IN}(\bar{\rho}, \vec{r}_\alpha) = 4\pi\rho_{IN}\left(b_o^2 - b_\alpha^2 - \frac{1}{3}R_{\alpha o}^2 - \frac{2}{3}\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N}\frac{b_\beta^3}{R_{\alpha\beta}}\right). \qquad (D.17)$$

Finally, $\Delta V_c^{\alpha,IN}(\bar{\rho}, \vec{r}_\alpha)$ is given by

$$\Delta V_c^{\alpha,IN}(\bar{\rho}, \vec{r}_\alpha) = 4\pi\bar{\rho}_{IN}\left(\frac{1}{3}r_\alpha^2 - \frac{1}{3}\left(|\vec{r}_\alpha + \vec{R}_{\alpha o}|^2 - R_{\alpha o}^2\right)\right.$$

$$\left. - \frac{2}{3}\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} b_\beta^3\left(\frac{1}{|\vec{r}_\alpha - \vec{R}_{\alpha\beta}|} - \frac{1}{R_{\alpha\beta}}\right)\right). \qquad (D.18)$$

This result is given in Eq. (3.82d) of the text.

$\underline{\Delta V_c^{IN,IN}(\bar{\rho}, \vec{r}_{IN})}$

The potential $V_c^{IN,IN}(\bar{\rho}, \vec{r}_{IN})$ is the potential at a point in the intersphere region due to the constant charge contained throughout the intersphere region. To calculate this potential we proceed as above for $V_c^{\alpha,IN}$ except that the point at which the potential is evaluated is now in the

intersphere region. Hence we integrate first over the volume inside the outer sphere. The point at which the potential is evaluated will be designated $\vec{r}_{IN}$ and the integration variable simply $\vec{r}$. Distinguishing the two cases $|\vec{r}| < |\vec{r}_{IN}|$ and $|\vec{r}| > |\vec{r}_{IN}|$, performing the expansion of $1/|\vec{r} - \vec{r}_{IN}|$, and performing the angular integrations we arrive at

$$2\int_{r<b_o} \frac{\bar{\rho}_{IN}}{|\vec{r} - \vec{r}_{IN}|}\, d\vec{r} = 8\pi\bar{\rho}_{IN} \left\{ \frac{1}{r_{IN}} \int_0^{r_{IN}} r^2 dr + \int_{r_{IN}}^{b_o} r dr \right\},$$

$$= 8\pi\rho_{IN} \left(\frac{r_{IN}^2}{3} + \frac{b_o^2}{2} - \frac{r_{IN}^2}{2} \right),$$

$$= 4\pi\bar{\rho}_{IN} \left(b_o^2 - \frac{1}{3} r_{IN}^2 \right) . \qquad \text{(D.19)}$$

Now we must perform the integrations over the N atomic sphere regions. To do this we use a simple result from electrostatics. The point $\vec{r}_{IN}$ is located outside the atomic spheres. The charge density $\bar{\rho}_{IN}$ is uniform inside each of the atomic spheres α and acts as though a point charge Q_α located at the point $\vec{R}_{o\alpha}$ where

$$Q_\alpha = \frac{4\pi}{3} b_\beta^3 \bar{\rho}_{IN} . \qquad \text{(D.20)}$$

Hence the potential from this charge at the point $\vec{r}_{IN}$ is

given by $2Q_\alpha/|\vec{r}_{IN} - \vec{R}_{o\alpha}|$. Hence the expression for $V_o^{IN,IN}(\bar{\rho}, \vec{r}_{IN})$ is given by

$$V_c^{IN,IN}(\bar{\rho}, \vec{r}_{IN}) = 4\pi\bar{\rho}_{IN} \left(b_o^2 - \frac{1}{3}r^2 - \frac{2}{3}\sum_{\alpha=1}^{N} \frac{b_\alpha^3}{|\vec{r}_{IN} - \vec{R}_{o\alpha}|} \right) . \tag{D.21}$$

The MT average of $V_c^{IN,IN}(\bar{\rho}, \vec{r}_{IN})$ over the intersphere region is the volume average over the intersphere region and once again we must find the integral by first integrating $V_c^{IN,IN}(\bar{\rho}, \vec{r}_{IN})$ over the volume inside the outer sphere and then substracting off the integrals of the same over all the atomic regions. (In the following we use $\vec{r}$ for the argument of $V_c^{IN,IN}$ instead of $\vec{r}_{IN}$ to avoid confusion.) Hence (we use the subscript on the integral symbol to indicate over which spherical region the integral is taken)

$$\bar{V}_c^{IN,IN}(\bar{\rho}, \vec{r}) = \frac{1}{V_{IN}} \int_{S_o} V_c^{IN,IN}(\bar{\rho}, \vec{r}) d\vec{r}$$

$$- \frac{1}{V_{IN}} \sum_{\alpha=1}^{N} \int_{S_\alpha} V_c^{IN,IN}(\bar{\rho}, \vec{r}) d\vec{r} . \tag{D.22}$$

The constant term in $V_c^{IN,IN}(\bar{\rho}, \vec{r})$ will remain unchanged so we write using Eq. (D.21)

$$\overline{V}_c^{IN,IN}(\bar{\rho}, \vec{r}) = 4\pi\bar{\rho}_{IN} b_o^2 - \frac{4\pi\bar{\rho}_{IN}}{V_{IN}} \frac{1}{3} \{ \int_{S_o} r^2 dr - \sum_{\alpha=1}^{N} \int_{S_\alpha} r^2 dr \}$$

$$- \frac{4\pi\bar{\rho}_{IN}}{V_{IN}} \frac{2}{3} \sum_{\alpha=1}^{N} b_\alpha^3 \{ \int_{S_o} \frac{1}{|\vec{r} - \vec{R}_o|} d\vec{r}$$

$$- \sum_{\beta=1}^{N} \int_{S_\beta} \frac{1}{|\vec{r} - \vec{R}_{o\alpha}|} d\vec{r} \}. \qquad (D.23)$$

In the integrals involving r^2, r is measured from an arbitrary origin and it is convenient here to pick this origin coincident with the origin of the outer sphere. Then for the integral in S_o, $\vec{r}$ is simply $\vec{r}_o$. For the integrals in the S_α, $\vec{r}$ is separated into $\vec{r}_\alpha + \vec{R}_{o\alpha}$:

$$\int_{S_o} r_o^2 d\vec{r}_o = \frac{4\pi}{5} b_o^5 . \qquad (D.24)$$

$$\int_{S_\alpha} r^2 d\vec{r} = \int_{S_\alpha} |\vec{r}_\alpha + \vec{R}_{o\alpha}|^2 d\vec{r}_\alpha ,$$

$$= 2\pi \int_0^{b_\alpha} \int_{-1}^{+1} (r_\alpha^2 + R_{o\alpha}^2 - 2r_\alpha R_{o\alpha}\xi) d\xi r_\alpha^2 dr_\alpha ,$$

$$= 4\pi \int_0^{b_\alpha} (r_\alpha^2 + R_{o\alpha}^2) r_\alpha^2 dr_\alpha ,$$

$$\int_{S_\alpha} r^2 d\vec{r} = \frac{4\pi b_\alpha^5}{5} + \frac{4\pi b_\alpha^3}{3} R_{o\alpha}^2 . \qquad (D.25)$$

The other integrals involving $1/|\vec{r} - \vec{R}_{o\alpha}|$ may also be simply done

$$\int_{S_o} \frac{1}{|\vec{r} - \vec{R}_{o\alpha}|} d\vec{r} = \int_0^{R_{o\alpha}} \left(\frac{4\pi}{R_{o\alpha}} \right) r_o^2 dr_o + \int_{R_o}^{b_o} \left(\frac{4\pi}{r_o} \right) r_o^2 dr_o ,$$

$$= \frac{4\pi R_{o\alpha}^2}{3} + \frac{4\pi b_o^2}{2} - \frac{4\pi R_{o\alpha}^2}{2} ,$$

$$= 2\pi (b_o^2 - \frac{1}{3} R_{o\alpha}^2) . \qquad (D.26)$$

We may divide the sum of integrals in Eq. (D.23) into two cases

$$\sum_{\beta=1}^{N} \int_{S_\alpha} \frac{1}{|\vec{r} - \vec{R}_{o\alpha}|} d\vec{r} = \int_{S_\alpha} \frac{1}{|\vec{r} - \vec{R}_{o\alpha}|} d\vec{r} + \sum_{\substack{\beta=1 \\ \beta=\alpha}}^{N} \int_{S_\beta} \frac{1}{|\vec{r} - \vec{R}_{o\alpha}|} d\vec{r} .$$

(D.27)

The first of the two cases

$$\int_{S_\alpha} \frac{1}{|\vec{r} - \vec{R}_{o\alpha}|} d\vec{r} = \int \frac{1}{r_\alpha} d\vec{r}_\alpha ,$$

$$= 2\pi b_\alpha^2 . \qquad (D.28)$$

In the second type case $\beta \neq \alpha$ we use the set of vectors given above in Figure D.2

$$\vec{r} - \vec{R}_{o\alpha} = \vec{r}_\beta - \vec{R}_{\alpha\beta} . \qquad (D.29)$$

As above in Eq. (D.16) the angular integration gives $4\pi/R_{\alpha\beta}$ hence,

$$\int_{S_\beta} \frac{1}{|\vec{r}_\beta - \vec{R}_{\alpha\beta}|} d\vec{r} = \frac{4\pi}{3} \frac{b_\beta^3}{R_{\alpha\beta}} . \qquad (D.30)$$

Substituting the results of Eqs. (D.24), (D.25), (D.26), (D.28), and (D.30) into Eq. (D.23) we get

$$\bar{V}_c^{IN,IN}(\bar{\rho}, \vec{r}) = 4\pi\bar{\rho}_{IN} b_o^2 - \frac{4\pi\bar{\rho}_{IN}}{V_{IN}} \frac{1}{3} \left\{ \frac{4\pi}{5} b_o^5 \right.$$

$$\left. - \sum_{\alpha=1}^{N} \left(\frac{4\pi b_\alpha^5}{5} + \frac{4\pi b_\alpha^3}{3} R_{o\alpha}^2 \right) \right\}$$

$$- \frac{8\pi\bar{\rho}_{IN}}{3V_{IN}} \sum_{\alpha=1}^{N} b_\alpha^3 \{2\pi b_o^2 - \frac{2\pi}{3} R_{o\alpha}^2 - 2\pi b_\alpha^2 - \sum_{\substack{\beta=1 \\ \beta\neq\alpha}}^{N} \frac{4\pi}{3} \frac{b_\beta^3}{R_{\alpha\beta}} \} .$$

(D.31)

We rearrange this to read

$$\bar{V}_c^{IN,IN}(\bar{\rho}, \vec{r}) = 4\pi\bar{\rho}_{IN} \{ b_o^2 - \frac{4\pi}{3V_{IN}} [\frac{b_o^5}{5} - \sum_{\alpha=1}^{N} b_\alpha^3 (\frac{b_\alpha^2}{5} + \frac{R_{o\alpha}^2}{3})]$$

$$- \frac{4\pi}{3V_{IN}} \sum_{\alpha=1}^{N} b_\alpha^3 [b_o^2 - b_\alpha^2 - \frac{1}{3} R_{o\alpha}^2 - \frac{2}{3} \sum_{\substack{\beta=1 \\ \beta\neq\alpha}}^{N} \frac{b_\beta^3}{R_{\alpha\beta}}] \}. \quad (D.32)$$

The NMT potential $\Delta V_c^{IN,IN}(\bar{\rho}, \vec{r}_{IN})$ is obtained by taking the difference of Eq. (D.23) and Eq. (D.32)

$$\Delta V_c^{IN,IN}(\bar{\rho}, \vec{r}_{IN}) = V_c^{IN,IN}(\bar{\rho}, \vec{r}_{IN}) - \bar{V}_c^{IN,IN}(\bar{\rho}, \vec{r}_{IN}).$$

(D.33)

This result is given in Eq. (3.82g) of the text.

$\underline{\Delta V_c^{o,IN}(\bar{\rho}, \vec{r}_o)}$

The potential $V_c^{o,IN}(\bar{\rho}, \vec{r}_o)$ is the potential at a point $\vec{r}_o$ in the outer sphere region arising from the constant charge $\bar{\rho}_{IN}$ in the intersphere region. This

potential is that produced by the outer sphere of radius b_o of constant charge density $\bar{\rho}_{IN}$ minus the potentials produced by the atomic spheres α of radii b_α at positions $\vec{R}_{o\alpha}$ of the same constant charge density $\bar{\rho}_{IN}$. We may write down the result from simple electrostatic theory:

$$V_c^{o,IN}(\bar{\rho}, \vec{r}_o) = \left(\frac{4\pi}{3} b_o^3 \right) \bar{\rho}_{IN} \frac{2}{r_o} - \sum_{\alpha=1}^{N} \left(\frac{4\pi}{3} b_\alpha^3 \right) \bar{\rho}_{IN} \frac{2}{|\vec{r}_o - \vec{R}_{o\alpha}|} . \quad (D.34)$$

Figure D.3 identifies the relevant vectors. Simplifying this expression

$$V_c^{o,IN}(\bar{\rho}, \vec{r}_o) = 2\bar{\rho}_{IN} \left(\frac{4\pi b_o^3}{3r_o} - \sum_{\alpha=1}^{N} \frac{4\pi b^3}{3|\vec{r}_o - \vec{R}_{o\alpha}|} \right). \quad (D.35)$$

To derive $\bar{V}_c^{o,IN}$ we perform the angular average of $V_c^{o,IN}$ in the outer sphere region. The first term in Eq. (D.35) is a function of the radius only and hence remains unchanged. The angular average of the other terms is of the form

$$\frac{1}{4\pi} \int \frac{1}{|\vec{r}_o - \vec{R}_{o\alpha}|} d\Omega_o = \frac{1}{r_o} . \quad (D.36)$$

Hence

$$\bar{V}_c^{o,IN}(\bar{\rho}, \vec{r}_o) = 2\bar{\rho}_{IN} \left(\frac{4\pi b_o^3}{3r_o} - \sum_{\alpha=1}^{N} \frac{4\pi b_\alpha^3}{3r_o} \right), \quad (D.37)$$

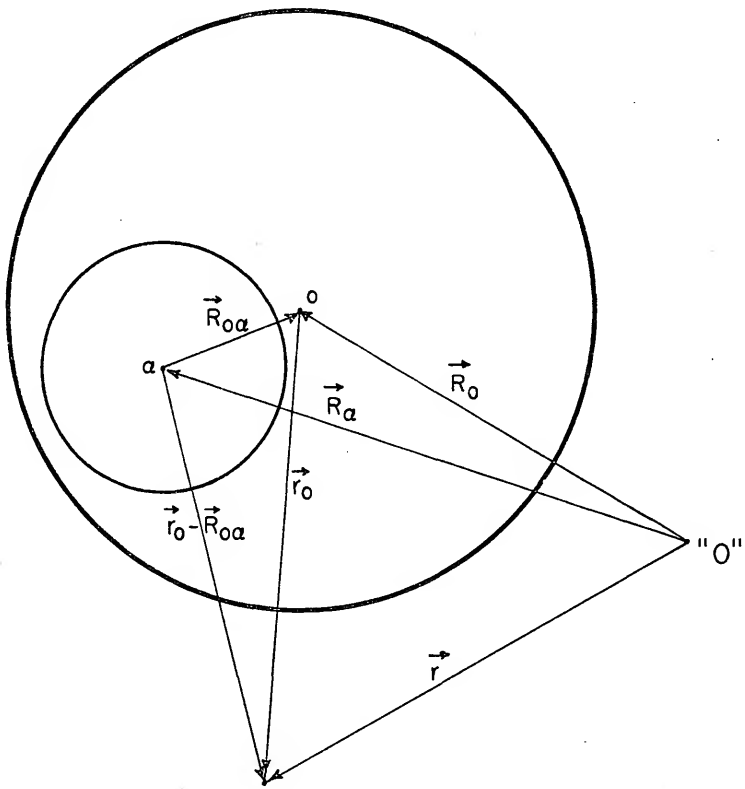

Figure D.3. Atomic-Outer Vector Relationships Used in the Derivation of $\Delta V_c^{o,IN}$.

or simply,

$$\overline{V}_c^{o,IN}(\bar{\rho}, \vec{r}_o) = \frac{2\bar{\rho}_{IN} V_{IN}}{r_o} ,$$

$$= \frac{2Q_{IN}}{r_o} , \qquad \text{(D.38)}$$

a result which actually may be arrived at by simpler considerations. Finally $\Delta V_c^{o,IN}(\bar{\rho}, \vec{r}_o)$ is given by

$$\Delta V_c^{o,IN}(\bar{\rho}, \vec{r}_o) = -2\bar{\rho}_{IN} \sum_{\alpha=1}^{N} \frac{4\pi b_\alpha^3}{3} \left(\frac{1}{|\vec{r}_o - \vec{R}_{o\alpha}|} - \frac{1}{r_o} \right). \qquad \text{(D.39)}$$

This result is given in Eq. (3.82j) of the text.

APPENDIX E

THE STATISTICAL EVALUATION OF DEFINITE INTEGRALS*

The statistical mean value $\bar{F}$ of a function $f(x)$ of a random variable x is the integral of $f(x)$ with $P(x)$ the probability distribution function (PDF) for the random variable x (See Cramer (1955), Feller (1957), and Mosteller et al. (1961)):

$$\bar{F} = \int_a^b f(x)P(x)dx \ . \tag{E.1}$$

For $P(x)$ to be a PDF it must satisfy two criteria:

1) $P(x) > 0$ for all x.

2) $$\int_a^b P(x)dx = 1 \ . \tag{E.2}$$

Any definite integral F may be put in the form of Eq. (E.1)

$$F = \int_a^b f(x)dx$$

$$= \int [f(x)/g(x)]g(x)dx, \tag{E.3}$$

*A good reference for most of the material in this appendix is Feller (1957).

where we restrict g(x) to have the properties of a DPF as given in Eq. (E.2). Once in the form of Eq. (E.3) the value of the integral will correspond to the mean value of the new function [f(x)/g(x)].

Such a mean may be formed to an approximation as an average over a finite set of points and this procedure is justified by a well known theorem (For a discussion of this theorem see Doob (1953), Mosteller et al. (1961), Feller (1957), and Kahn (1964)):

THEOREM: The Strong Law of Large Numbers

Let $X_1, \ldots X_N$ be a sequence of mutually independent random numbers with probability distribution P(x) and let F(x) be a function of the random variable x with mean $\bar{F}$. If $S_N = f(X_1) + \ldots + F(X_N)$ then for any $\varepsilon > 0$ as N goes to infinity the inequality

$$|S_N - N\bar{F}| < \varepsilon \qquad \text{(E.4)}$$

will be satisfied with probability one.

Hence we may find the approximate mean value $\hat{F}$ of f(x) as

$$\hat{F} = \frac{1}{N} \sum_{i=1}^{N} f(x_i)$$

$$\lim_{N \to \infty} \hat{F} = \bar{F} , \qquad \text{(E.5)}$$

where the x_i are picked with probability P(x).

As indicated in Eq. (E. 3) any definite integral may be put in the form of Eq. (E. 1) and hence may be evaluated as a mean value. This result is the basis for the Monte Carlo evaluation of definite integrals in which $\overline{F}$ is identified with F.

Finding the $\{x_i\}$ with P(x) involves picking random values of the function P(x) over its range and inverting to find the values of x. This suggests that we change variables in Eq. (E.3) by defining a new independent variable h. Let

$$dh = g(x)dx \tag{E.6}$$

Then

$$F = \int_a^b [f(x)/g(x)]g(x)dx \tag{E.7}$$

$$= \int_{h(a)}^{h(b)} [f(x)/g(x)]dh$$

(where x implicitly depends upon h). In our present discussion g(x)dx is the probability of the event represented by g(x) occuring within dx of the point x. From Eq. (E.6) we see that the larger g(x) at x the larger is dh for a given dx. Thus if we pick points randomly on the values of h between h(a) and h(b) and invert to find the corresponding values of x, we will be picking points with probability g(x). For general references on this subject see Kahn (1956), Harris (1966), and Conroy (1964).

For a simple definite integral as in Eq. (E.3) the first possibility one might consider as a PDF is simple uniform selection or sampling of points on the interval (a, b). That is; P(x) = C (where C is a constant). Since P(x) must satisfy the properties listed in Eq. (E.2)

$$\int_a^b C\,dx = 1$$

$$= C(b - a) \qquad \text{(E.8)}$$

or, C = 1/(b - a). To use this PDF with Eq. (E.3) we write

$$F = \int_a^b f(x)\,dx$$

$$= \int_a^b [f(x)/C]C\,dx \; . \qquad \text{(E.9)}$$

With this PDF for large N we may approximate F with

$$F = \frac{(b - a)}{N} \sum_{i=1}^{N} f(x_i) \; , \qquad \text{(E.10)}$$

a simple intuitive result made rigorous.

It is obvious in this discussion that the integral of Eq. (E.3) must exist for the result in Eq. (E.10) to have any meaning. If f(x) has singularities or an infinite number of discontinuities, for example, the results of Eq. (E.10) will be meaningless. Hence in applying the Law of Large

Numbers to the evaluation of definite integrals one must exercise caution.

The Law of Large Numbers does not at all indicate how accurate an average is for a given number of points. The means of setting error bars on the averages of Eq. (E. 10) (or any transformed version of the integral and integrand) is provided by a second well known theorem from statistics (For discussion of this theorem see Cramer (1946) and Feller (1957):

THEOREM: The Central Limit Theorem

Let $x_1, \ldots, x_N$ be a sequence of mutually independent ramdom numbers with probability distribution $P(x)$ and let $f(x)$ be a function of the ramdom variable x with mean $\bar{F}$ and variance σ^2. If $S_N = f(x_1) + \ldots + f(x_N)$ then for any $\varepsilon > 0$ as N increases the probability that the following inequality holds approaches the normal probability distribution $\phi(\varepsilon)$:

$$\text{Prob.} \left\{ \left| \frac{S_N - N\bar{F}}{\sigma N^{1/2}} \right| < \varepsilon \right\} = \phi(\varepsilon)$$

where the variance is defined as

$$\sigma^2 = \int (\bar{F} - f(x))^2 \, P(x) dx$$

and the normalized normal distribution is given by

$$\phi(\varepsilon) = \frac{1}{(2\pi)^{1/2}\sigma} \, e^{-\frac{\varepsilon^2}{2\sigma^2}}. \qquad \text{(E.11)}$$

The Central Limit Theorem is one of the most important

theorems in applied statistics and the theorem and its remifications are discussed in almost every book on statistics. The proof of this theorem is intricate requiring the use of measure theory and is discussed in Feller (1957) and Loève (1963).

For a definite integral such as in Eq. (E.3) with value $\bar{F}$ and approximate value $\hat{F}$ as calculated in Eq. (E.5) the theorem says that the probability that $\hat{F}$ is within $\delta\sigma/N^{1/2}$ of F is given by

$$\text{Prob.}\ \{|F - \hat{F}| < \delta\} = \frac{1}{(2\pi)^{1/2}} \int_{-\frac{\delta N^{1/2}}{\sigma}}^{+\frac{\delta N^{1/2}}{\sigma}} e^{-x^2/2}\, dx\ . \qquad \text{(E.12)}$$

The quantity $\sigma_x = \sigma/N^{1/2}$ gives one a measure of the error of an average $\hat{F}$ as calculated in Eq. (E.5). For example, the probability that $\hat{F}$ is within $\pm 1\sigma_x$ of F is $\approx$ 64% and the probability that it is within $\pm 2\sigma_x$ of F is $\approx$ 95%. There are two problems connected with the Central Limit Theorem in practice:

1) The Theorem is in terms of an infinite limit which we of course never have in practice.

2) The σ in the Theorem is the exact σ for the function f(x). In practice we usually must content ourselves with an approximation to σ calculated as follows and usually

referred to as s

$$s = \sqrt{\sum_{i=1}^{N} \frac{(F - f(x_i))^2}{N}} \quad . \tag{E.13}$$

A way of estimating the severity of these problems for a given definite integral is to examine the stability of the approximate mean $\hat{F}$ as a function of N. When the relative fluctuations of $\hat{F}$ are "small" one may safely apply the Theorem. The term "small" will depend on the problem at hand and judgement must be exercised by the practitioner. According to Kahn (1964), an expert in the field of Monte Carlo theory and application, the problem of using finite N in applying the Central Limit Theorem is usually not as difficult as approximating σ by s.

All of the above results may be generalized to multidimensional integrals (See Kahn (1964), Conroy (1964), and Metropolis et al. (1953)). Consider the following multidimensional generalization of Eq. (E.3)

$$F = \int_{a_1}^{b_1} \cdots \int_{a_n}^{b_n} f(x_1, \ldots, x_N)\, P(x_1, \ldots, x_N)\, dx_1, \ldots dx_N . \tag{E.14}$$

In the Monte Carlo evaluation of this integral N points in $\vec{x}$ space (where $x_i = \{x_1, \ldots, x_N\}$) are picked with the PDF $P(x_1, \ldots, x_N)$ and the average over the points performed

$$\hat{F} = \frac{1}{N} \sum_{i=1}^{N} f(x_{1i}, \ldots, x_{Ni}) \ . \qquad \text{(E. 15)}$$

The advantage of using Monte Carlo evaluation for higher dimensional integrals is that the work involved in the calculation depends on σ and although σ usually increases with the dimensionality there is no reason why it should do so. Using standard techniques for the evaluation of definite integrals (Simpson's method for example), the work required increases exponentially. The drawback for Monte Carlo is that the error in the computed average is proportional to $N^{-1/2}$. Usually in practice means must be found for reducing the variance σ^2 and therefore the error in the computed average in order to avoid having to use a prohibitively large number of points to obtain an average with an acceptable error bound.

APPENDIX F

THE $1/r_{12}$ SINGULARITY

In Chapters V and VI we indicated that the following integral, second order in $\Delta\rho(\vec{r})$, was a negligible term

$$\int\int \frac{\Delta\rho(\vec{r}_1)\ \Delta\rho(\vec{r}_2)}{r_{12}}\ d\vec{r}_1 d\vec{r}_2. \tag{F.1}$$

This integral was calculated as a numerical six-dimensional integral and this would be a straight-forward operation except for the $1/r_{12}$ singularity. This integral is evaluated numerically as a double sum

$$\int\int \frac{\Delta\rho(\vec{r}_1)\ \Delta\rho(\vec{r}_2)}{r_{12}}\ d\vec{r}_1\ d\vec{r}_2 = \sum_s \sum_t \frac{\Delta\rho(\vec{r}_s)\ \Delta\rho(\vec{r}_t)\ U_s U_t}{|\vec{r}_s - \vec{r}_t|} \tag{F.2}$$

where U_s and U_t are weight factors analogous or proportional to the regional sampling factors of Chapter V (See Eqs. (5.31) and (5.33)). If we use the same grid for both three-dimensional spaces we will of course get a divergence every time $\vec{r}_s$ is the same as $\vec{r}_t$. If we use different grids, we still have a problem if a point $\vec{r}_s$ should be quite close to

another point $\vec{r}_t$. There is a method to circumvent this problem which we will describe in this appendix. The method is due to Boys and Rajagopal (1966) and for the sake of completeness we wish to reproduce their arguments here.

We must recognize that to use a finite number of points for an integration over a finite or infinite space it is necessary to assume some knowledge about the behavior of the integrand over that space. One usually assumes that the integrand can be approximated by a finite linear combination of some specific expansion functions. In particular, we may take a number of expansion functions $g_k(\vec{r})$ (this g_k should not be confused with the g_α regional sampling functions of Chapter V), the same number as the number of integration points, and we may assume these expansion functions to be localized about individual integration points. Then

$$\Delta\rho(\vec{r}) = \sum_k C_k g_k(\vec{r}) \tag{E.3}$$

and

$$g_k(\vec{r}_\ell) = \delta_{k\ell}. \tag{E.4}$$

This last relation means that $g_k(\vec{r})$ has the value unity at $\vec{r}$ equal to $\vec{r}_k$ and is either zero or very much less than unity at any other integration point.

Since the weight functions U_s are chosen to give

the correct integral for $\Delta\rho(\vec{r})$ there is a relation between the $g_k(\vec{r})$ and the weights U_s; namely

$$\int g_k(\vec{r})\,d\vec{r} = \sum_k U_s g_k(\vec{r}_s) = U_k \quad . \tag{E.5}$$

We may make the assumption that the expansion functions $g_k(\vec{r})$ are gaussian

$$g_k(\vec{r}) = \exp(-a_k(\vec{r} - \vec{r}_k)^2). \tag{E.6}$$

According to Boys and Rajagopal other forms are possible but this form for $g_k(\vec{r})$ is particularly convenient. Then from Eq. (E.5)

$$\int g_k(\vec{r})\,d\vec{r} = U_k = (\pi/a_k)^{3/2} \tag{E.7}$$

and this last result is used to determine a_k.

Then we may rewrite Eq. (E.2) above as

$$\int\int \frac{\Delta\rho(\vec{r}_1)\ \Delta\rho(\vec{r}_2)}{r_{12}}\,d\vec{r}_1 d\vec{r}_2 = \sum_s \sum_t \Delta\rho(\vec{r}_s)\ \nabla\rho(\vec{r}_t) \int\int \frac{g_s(\vec{r}_1)\ g_t(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

$$= \sum_s \sum_t \Delta\rho(\vec{r}_s)\ \Delta\rho(\vec{r}_t)\ U_s U_t Q_{st} \tag{E.8}$$

where

$$Q_{st} = \frac{\int\int g_s(\vec{r}_1) g_t(\vec{r}_2) \vec{r}_{12}^{-1} \, d\vec{r}_1 d\vec{r}_2}{\int g_s(\vec{r}_1) d\vec{r}_1 \int g_t(\vec{r}_2) d\vec{r}_2} . \qquad \text{(E.9)}$$

This last six-dimensional integral where g_s and g_t are gaussians is finite and may be performed even when s = t

$$Q_{ss} = \left(\frac{2a_s}{\pi} \right)^{1/2} = \frac{2^{1/2}}{U_s^{1/3}} . \qquad \text{(E.10)}$$

For $|\vec{r}_s - \vec{r}_t|$ larger than the approximate radii of g_s and g_t the function Q_{st} will be equal to $|\vec{r}_s - \vec{r}_t|^{-1}$. After some investigation Boys and Rajagopal settle on the form

$$Q_{st} = [U_s^{1/2} U_t^{1/2} / 2^{3/2} + |\vec{r}_s - \vec{r}_t|^3]^{-1/3} . \qquad \text{(E.11)}$$

As mentioned earlier Boys and Rajagopal found that the results were not particularly sensitive to the precise form assumed for $g_k(\vec{r})$ and inaccuracies decreased with increasing number of integration points. The form of the integral (E.1) given in Eq. (E.8) is easily programmable and eliminates the problem with the r_{12}^{-1} singularity in the numerical integration of integrals like (E.1).

Using this method as reported in the concluding chapter, Chapter VI, we found a value of 0.00011 Ryd. for

the integral (E.1) for the C_2 molecule at a separation of 2.48 Bohr. Hence this term is quite negligible compared to the total NMT correction of -1.31 Ryd. and predicted binding energy of the C_2 molecule. Since this term is so small its precise value is not important, only its order of magnitude is relevant.

APPENDIX G

THE BOND SAMPLING FUNCTION

As described in Chapter V the bond sampling function consists of a gaussian defined over the volume of a master sphere with the volume of two other spheres which are of equal radii and tangent at the origin of the master sphere excluded. This volume for a certain radius R_o of the master sphere and radii R_o, for the two other spheres is indicated by the hatching of Figure G.1(a). In order to be able to pick points at random from such a sampling function we must be able to integrate the gaussian over the hatched volume indicated in Figure G.1(a), we must have this integral as a function of the radius of the master sphere R_o. The distance between the origin of the master sphere and either of the other two identical spheres is D.

The easiest way to perform this integral is to integrate the gaussian over the volume of the entire master sphere and subtract twice the integral of the gaussian over the intersected volume of one of the other spheres. The integral over the intersected volume may be divided into two kinds of integrals as shown by the horizontal and vertical hatching in Figure G.1(b). In Figures G.1(c) and G.1(d) we show these two integrals separated. In these Figures

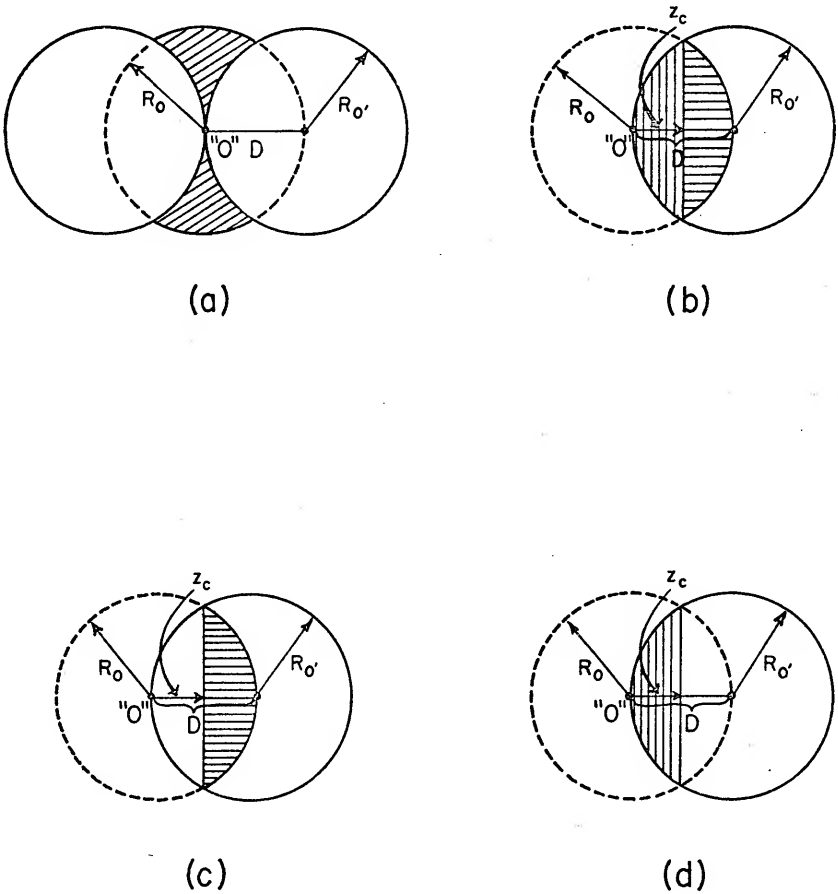

Figure G.1. Volume Integral Relationships Used in the Derivations of the Bond Sampling Function.

we indicate the distance of the plane of intersection from the origin "0" by z_C. If we take the integral over the master sphere to be I_M, that indicated in Figure G.1(c) as I_{oC}, and that indicated in Figure G.1(d) as I_{IC}, then I_B, the integral of the hatched region in Figure G.1(a), is given by

$$I_B = I_M - 2(I_{oC} + I_{IC}) \tag{G.1}$$

In both the integrals I_{oC} and I_{IC} the integrand has cylindrical symmetry about the axis joining the two sphere centers (see Figures G.1(e) and G.1(d)). To do these integrals we use cylindrical coordinates with the origin placed at the origin of the master sphere ("0") and the z-axis along the axis joining the sphere centers. We take the volume element dV to be

$$dV = \rho d\rho dz d\phi \tag{G.2}$$

In these coordinates a gaussian $e^{-\alpha r^2}$ may be written

$$e^{-\alpha r^2} = e^{-\alpha(\rho^2+z^2)} \tag{G.3}$$

The integral I_{oC} (see Figure G.1(c)) is given by

$$I_{oC} = 2\pi \int_{z_o}^{R_o} \int_{o}^{(R_o^2-z^2)^{1/2}} e^{-\alpha(\rho^2+z^2)} \rho d\rho dz, \tag{G.4}$$

$$= -\frac{\Pi}{\alpha} \int_{z_C}^{R_o} e^{-\alpha z^2} e^{-\alpha\rho^2} \Big|_{o}^{(R_o^2-z^2)^{1/2}} dz,$$

$$= \frac{\pi}{\alpha} \int_{z_c}^{R_o} e^{-\alpha z^2} [1 - e^{-\alpha(R_o^2 - z^2)}] dz,$$

$$= \frac{\pi}{\alpha} \int_{z_c}^{R_o} e^{-\alpha z^2} - \frac{\pi}{\alpha} e^{-\alpha R_o^2} \int_{z_c}^{R_o} dz,$$

$$= \frac{\pi}{\alpha} \cdot \frac{\pi^{1/2}}{2\alpha^{1/2}} \cdot \frac{2}{\pi^{1/2}} \int_{z_c}^{R_o} e^{-\alpha z^2} \alpha^{1/2} dz - \frac{\pi}{\alpha} e^{-\alpha R_o^2} (R_o - z_c).$$

then

$$I_{oC} = \frac{1}{2} \left(\frac{\pi}{\alpha}\right)^{3/2} [\mathrm{erf}(\alpha^{1/2} R_o) - \mathrm{erf}(\alpha^{1/2} z_c)]$$

$$- \frac{\pi}{\alpha} e^{-\alpha R_o^2} (R_o - z_c). \qquad \text{(G.5)}$$

Here erf is the standard error function defined by

$$\mathrm{erf}(x) = \frac{2}{\pi^{1/2}} \int_o^x e^{-z^2} dz \qquad \text{(G.6)}$$

The integral I_{IC} (see Figure G.1(d)) is given by

$$I_{IC} = 2\pi \int_o^{z_c} \int_o^{(2R_o' z - z^2)^{1/2}} e^{-\alpha(\rho^2 + z^2)} \rho d\rho dz,$$

$$= - \frac{\pi}{\alpha} \int_o^{z_c} e^{-\alpha z^2} e^{-\alpha \rho^2} \Big|_o^{(2R_o' z - z^2)^{1/2}} dz,$$

$$= \frac{\pi}{\alpha} \int_o^{z_c} e^{-\alpha z^2} [1 - e^{-\alpha(2R_o' z - z^2)}] dz,$$

$$= \frac{\pi}{\alpha} \int_o^{z_c} e^{-\alpha z^2} dz - \frac{\pi}{\alpha} \int_o^{z_c} e^{-\alpha R_o' z} dz, \qquad \text{(G.7)}$$

then

$$I_{IC} = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{3/2} \operatorname{erf}(\alpha^{1/2} z_c) + \frac{\pi}{2\alpha^2 R_o'} \cdot [e^{-2\alpha R_o' z_c} - 1]. \quad \text{(G.8)}$$

The integral I_M is given by

$$I_M = 4\pi \int_o^{R_o} r^2 e^{-\alpha r^2}\, dr,$$

$$= 4\pi \left[-\frac{1}{2\alpha} r e^{-\alpha r^2} \Big|_o^{R_o} + \frac{1}{2\alpha} \int_o^{R_o} e^{-\alpha r^2}\, dr\right],$$

$$= 4\pi \left[-\frac{R_o}{2\alpha} e^{-\alpha R_o^2} + \frac{1}{2\alpha} \frac{\pi^{1/2}}{2\alpha^{1/2}} \operatorname{erf}(\alpha^{1/2} R_o)\right], \quad \text{(G.9)}$$

then,

$$I_M = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{3/2} 2\operatorname{erf}(\alpha^{1/2} R_o) - \frac{2\pi R_o}{\alpha} e^{-\alpha R_o^2}. \quad \text{(G.10)}$$

Then from Eq. (G.1)

$$I_B = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{3/2} 2\operatorname{erf}(\alpha^{1/2} R_o) - \frac{2\pi R_o}{\alpha} e^{-\alpha R_o^2}$$

$$- \left(\frac{\pi}{\alpha}\right)^{3/2} [\operatorname{erf}(\alpha^{1/2} R_o) - \operatorname{erf}(\alpha^{1/2} z_c)]$$

$$+ \frac{2\pi}{\alpha} (R_o - z_c) e^{-\alpha R_o^2} - \left(\frac{\pi}{\alpha}\right)^{3/2} \operatorname{erf}(\alpha^{1/2} z_c)$$

$$- \frac{\pi}{\alpha^2 R_o'} [e^{-2\alpha R_o' z_c} - 1]. \quad \text{(G.11)}$$

Cancelling terms this becomes

$$I_B = \frac{\pi}{\alpha^2 R_o'} - \frac{\pi}{\alpha^2 R_o'} [2\alpha z_c R_o' e^{-\alpha R_o^2} + e^{-2\alpha z_c R_o'}]. \quad \text{(G.12)}$$

It may be shown that for the case of the two spheres intersecting the master sphere having the same radii R_o, and being separated from the master sphere by distance D that

$$z_c = \frac{R_o^2 + D^2 - R_o^2}{2D}, \tag{G.13}$$

and this may be substituted for z_c in Eq. (G.11). If R_o, = D, then

$$z_c = \frac{R_o^2}{2D}, \tag{G.14}$$

and

$$2\alpha z_c R_o = \alpha R_o^2. \tag{G.15}$$

Substituting this last result in Eq. (G.11) we have

$$I_B = \frac{\pi}{\alpha^2 R_o} [1 - (1+\alpha R_o^2)e^{-\alpha R_o^2}] \tag{G.16}$$

for the special case. Eq. (G.11) with Eq. (G.12), or Eq. (G.15), gives us the integral of the gaussian $\exp(-\alpha r^2)$ over the hatched volume in Figure G.1(a) as a function of the master sphere radius R_o.

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BIOGRAPHICAL SKETCH

John Bryan Danese was born February 11, 1944, in Jacksonville, Florida. He attended school in Jacksonville through high school graduating from Bishop Kenny High School in June, 1962. In September, 1962, he entered the University of Florida as an undergraduate and received a Bachelor of Science in Physics in April, 1966. As an undergraduate he co-oped during the summers with Southern Bell Telephone and Telegraph Company in the Equipment Engineering Department of that company.

In September, 1966, he entered the Graduate School of the University of Florida as a student in the Department of Physics. He joined the Quantum Theory Project, a joint research group between the Departments of Physics and Chemistry at the University of Florida, on June 16, 1971. It is within the Quantum Theory Project that the research of this dissertation has been carried out.

John Bryan Danese is married to the former Donna Paige Olson and has one child, aged seven, Andrea Jill. He is a student member of the American Institute of Physics and a member of the University of Florida chapter of Sigma Pi Sigma.

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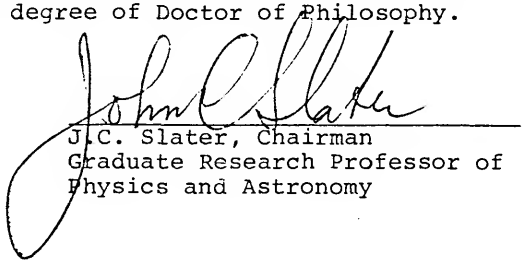

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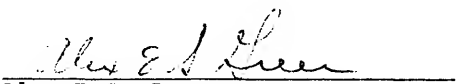

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