INTERMOLECULAR POTENTIAL ENERGY OF TWO WATER MOLECULES IN THE DENSITY FUNCTIONAL FORMALISM

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Chapter I

A REVIEW OF THE WATER-WATER POTENTIAL ENERGY SURFACE

In this thesis we will study intermolecular forces using density functional methods. The concept of intermolecular forces is best translated into the notion of an electronic potential energy surface (1). If $U(\vec{R}_1,\ldots,\vec{R}_A)$ is the potential energy describing the interaction among the atoms in the molecules then,

$$\vec{F}_\beta = -\vec{\nabla}_\beta\, U(R_1,\ldots,\vec{R}_A), \qquad (I.1)$$

where $\vec{F}_\beta$ is the force acting on atom β. Here, the gradient operator is

$$\vec{\nabla}_\beta = \hat{i}\,\frac{\partial}{\partial x_\beta} + \hat{j}\,\frac{\partial}{\partial y_\beta} + \hat{k}\,\frac{\partial}{\partial z_\beta}. \qquad (I.2)$$

Our goal is to find the ground state electronic eigenvalue of the non-relativistic Born-Oppenheimer Hamiltonian (2) for N electrons. Written in the wave mechanics formulation, we must in principle solve

$$\hat{H}\,\Psi(x_1,\ldots,x_N;\vec{R}_1,\ldots,\vec{R}_A) = E(\vec{R}_1,\ldots,\vec{R}_A)\,\Psi(x_1,\ldots,x_N;\vec{R}_1,\ldots,\vec{R}_A) \qquad (I.3)$$

where $\hat{H}$ is,

$$\hat{H} = \sum_{i=1}^{N} \left(\frac{-\hbar^2}{2m}\right) \nabla_i^{\,2} + \sum_{i=1}^{N} \sum_{\alpha=1}^{A} \frac{(-Z_\alpha e^2)}{|\vec{r}_i - \vec{R}_\alpha|} + \sum_{1 \leq i < j \leq N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{1 \leq \alpha \leq \beta \leq A} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}. \qquad (I.4)$$

The electronic eigenvalue $E(\vec{R}_1,\ldots,\vec{R}_A)$ is the potential energy $U(\vec{R}_1,\ldots,\vec{R}_A)$ governing the motion of the nuclei. In the Born-Oppenheimer approximation the electrons redistribute themselves on a time scale much faster than the more massive nuclei. For this reason we solve the electronic problem with the nuclei fixed in place. Here $\{\vec{R}_\alpha, Z_\alpha\}$ are fixed positions and nuclear charges of A atomic nuclei composing the "supermolecule", that is all the atomic nuclei of the model system.

The problem of finding the lowest eigenvalue of $\hat{H}$, in which $\{\vec{R}_\alpha, Z_\alpha\}$ and N completely define the system, is posed in the N-electron Hilbert space; as the number of electrons N increases, the difficulty of carrying out the problem by traditional quantum chemistry techniques (3,4) increases also. By the "traditional quantum chemistry techniques" we mean molecular orbital calculations, augmented perhaps by configuration interaction studies. Therefore, the calculation of the potential energy surfaces using these kinds of traditional techniques - even semiempirical (3) as well as <u>ab initio</u> (4) calculations - are in fact computationally limited by the N dependence of the system. Therefore, if ever-larger sized systems are to be considered in ab initio calculations a radically new approach must be developed. In fact steps in this direction have already been taken by Gordon and Kim (5) in adopting what has been called the Modified Electron Gas [MEG] model for computing intermolecular potential energy surfaces. In this thesis, we shall discuss this electron gas model in the light of approximations to the rigorous ab initio approach of energy functionals of the electron density. We shall call all such approaches Density Functional Theories (DFT) (6).

Our interest centers on the calculation of the intermolecular potential energy suface for two interacting water molecules--the so-called water dimer. Our eventual aim is to use DFT for calculating energy surfaces in large biological molecules and other extended systems such as heavy metal pollutants interacting with water. Thus, choosing the water dimer is a natural first step in computing the interaction potential energies for systems of water and heavy metal pollutants. Such knowledge is now being sought by investigators locally in the Ground Water Resources Institute at O.S.U. Also, since we want to develop the DFT approach as a general method for all these problems knowing in advance that the water dimer has been done by traditional means gives us a "benchmark" against which to test the new ideas of DFT.

Before we explain the details of DFT for the water dimer calculation we shall briefly review some of the existing models of the water dimer interaction energy surface. An extensive review of the properties of water is given by Kauzmann and Eisenberg (7). To proceed with this review and compare the various models let us introduce the set of coordinates shown in Figure 1. There are 18 degrees of freedom in the water dimer system; for example, we may choose the follwing intramolecular and intermolecular coordinates.

$$[(x_{1A},x_{2A},\gamma_A),(x_{1B},x_{2B},\gamma_B)],$$
$$[\Theta_A,\alpha_A,\Theta_B,\alpha_B,\phi=(\phi_A-\phi_B),R_{oo}].$$

In addition, there are, of course, 6 coordinates referring to translation and rotation of the system as a whole. But we eliminate these rotational and translational coordinates since the electronic energy of the system will not be effected by the way we rotate and translate it in space. Thus, in principle the interaction energy depends upon 12 coordinates. However, we shall reduce the water dimer problem from 12 to 6 degrees of freedom by keeping the intramolecular coordinates (x_{1A},x_{2A},γ_A) and (x_{1B},x_{2B},γ_B) fixed. The problem will then depend only upon the intermolecular coordinates $[\alpha_A,\Theta_A,\alpha_B,\Theta_B,\phi\equiv(\phi_A-\phi_B),R_{oo}]$. That is, we focus upon intermolecular potential energy, not allowing the intramolecular coordinates to relax. Thus, our aim will be to find the potential energy function

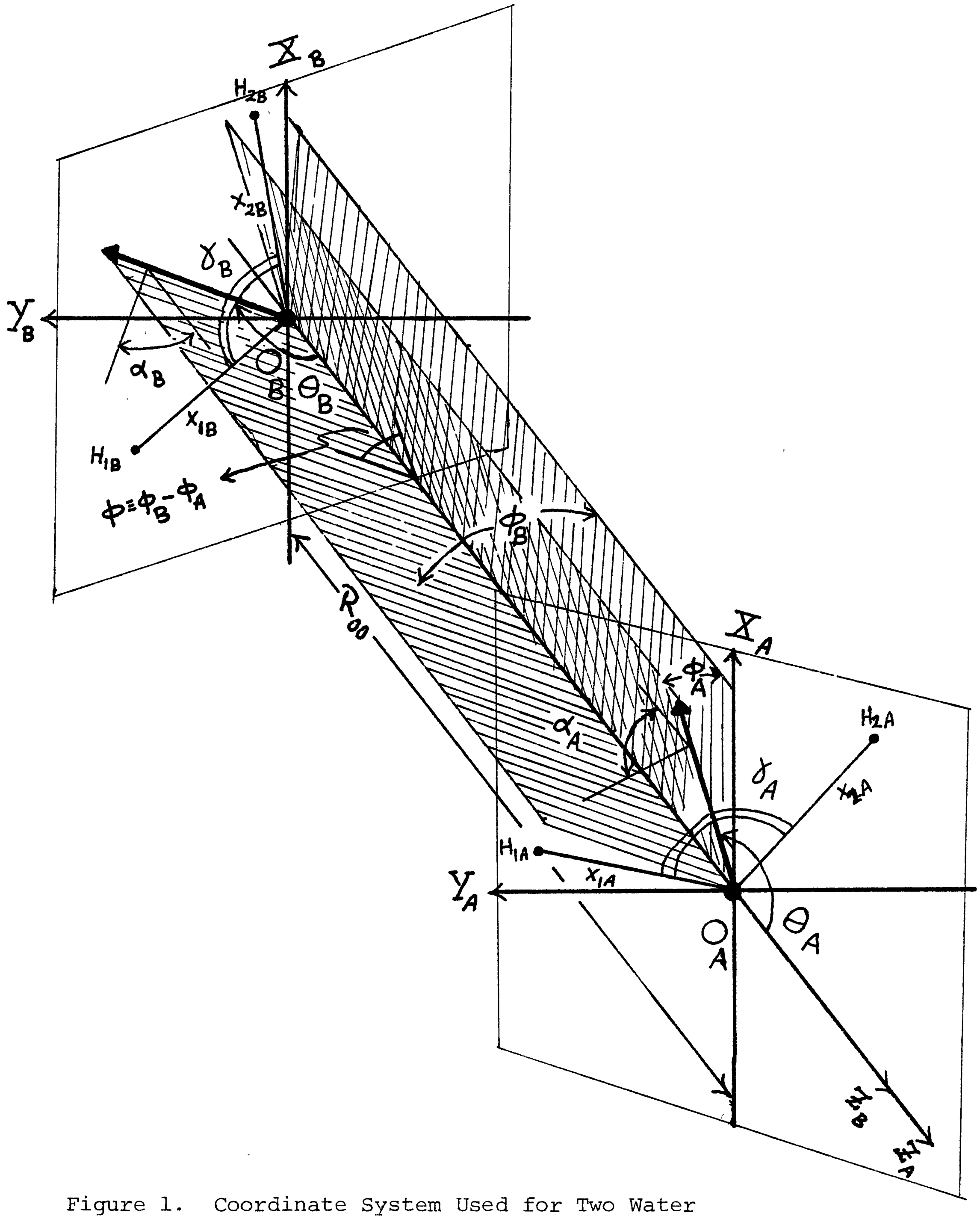

Figure 1. Coordinate System Used for Two Water Molecules

$U \equiv U(R_{oo}, \Theta_A, \Theta_B, \phi, \alpha_A, \alpha_B)$.

As shown in Figure 1, for molecule A: $x_{1A} \equiv H_{1A}-O_A, x_{2A} \equiv H_{2A}-O_A$ are the bond lengths, while $\sphericalangle\, H_{1A}O_AH_{2A} \equiv \gamma_A$ is the bond angle. Similarly, x_{1B}, x_{2B}, and γ_B are the bond lengths and the bond angle of water molecule B. For our considerations we choose the fixed bond lengths and the bond angles for both A and B water molecules to correspond to equilibrium geometry (8):

$$X_{1A} = X_{2A} = X_{1B} = X_{2B} = 0.96 \text{ A}, \qquad (I.5a)$$

$$\gamma_A = \gamma_B = 104.5^\circ. \qquad (I.5b)$$

The other 6 variables $\alpha_A, \Theta_A, \alpha_B, \Theta_B, \phi$, and R_{oo} (intermolecular coordinates) are defined as follows: as shown in the figure, two right handed coordinate systems have origins at the oxygen nuclei O_A and O_B, R_{oo} is the internuclear oxygen-oxygen distance. Each molecule labeled A or B defines a plane which containes the dipole moment $\vec{P}$ bisecting $\sphericalangle$ HOH. $\alpha_A(\alpha_B)$ is the dihedral angle between the plane of molecule A(B) and the reference plane formed by the $Z_A(Z_B)$ axis and the dipole $\vec{P}_A(\vec{P}_B)$. $\Theta_A(\Theta_B)$ is the polar angle locating a dipole $\vec{P}_A(\vec{P}_B)$. Finally, ϕ is the dihedral angle formed by the two reference planes containing the Z axis and the two dipole moments $\vec{P}_A$ and $\vec{P}_B$. In the "degenerate" case where a dipole moment $\vec{P}_A$ (or $\vec{P}_B$) lies along the Z axis ($\Theta=0$, or $\Theta=\pi$) we choose the XZ plane as the corresponding reference plane in measuring the angles α_A (or α_B) and ϕ.

It is impossible to present the entire six dimensional surface in a single figure. Therefore, we imagine holding five of the six variable fixed and plot U as a function of the remaining variable. For example, one can fix $\Theta_A, \Theta_B, \alpha_A, \alpha_B$, and ϕ, and then plot U as a function of R_{oo} .

We now turn to specific models of the water dimer potential energy surface. Classically each water molecule may be depicted by its multipole charge distribution. The interaction energy is then the pairwise sum of multipole products beginning with the dipole-dipole term since each molecule has no net charge.

<u>Dipole-Dipole Interaction</u>:

The potential energy function between any two molecular dipoles $\vec{P}_A$ and $\vec{P}_B$ depends on the intermolecular separation, R_{oo}, and on their mutual orientation. The relative orientation of $\vec{P}_A$ and $\vec{P}_B$ is often expressed in terms of the angles Θ_A, Θ_B, and $\phi \equiv (\phi_A - \phi_B)$ shown in Figure 2.
The dipole-dipole interaction energy in Gausssian units is

$$U_{AB}^{D-D}(\Theta_A, \Theta_B, R_{oo}, \phi \equiv (\phi_B - \phi_A)) = \frac{1}{R_{oo}^3} [\vec{P}_A \cdot \vec{P}_B - 3(\vec{P}_A \cdot \hat{R}_{oo})(\vec{P}_B \cdot \hat{R}_{oo})].$$

Letting the vectors

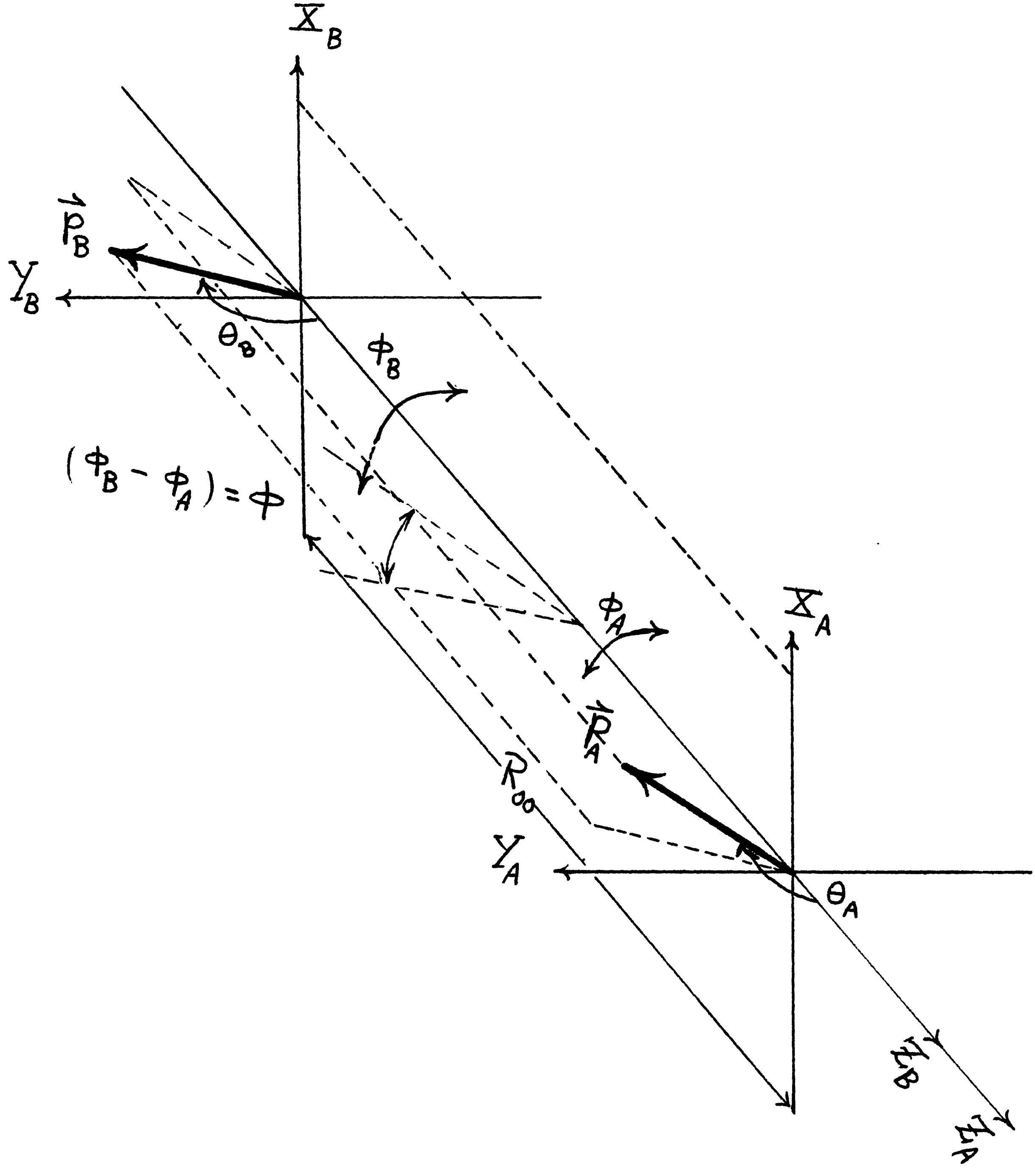

Figure 2. Coordinate System Used in Dipole-Dipole Calculations

$$\vec{P}_A = P\{\sin\Theta_A \cos\phi_A \hat{i} + \sin\Theta_A \sin\phi_A \hat{j} + \cos\Theta_A \hat{k}\}$$

$$\vec{P}_B = P\{\sin\Theta_B \cos\phi_B \hat{i} + \sin\Theta_B \sin\phi_B \hat{j} + \cos\Theta_B \hat{k}\}$$

and $R_{oo} = \hat{k}$, we find

$$U_{AB}^{D-D}(\Theta_A, \Theta_B, R_{oo}, \phi) = \frac{1}{R_{oo}^3}\{\sin\Theta_A \sin\Theta_B \cos\phi - 2 \cos\Theta_A \cos\Theta_B\}. \tag{I.6}$$

Clearly, in representing each water molecule by a dipole, U is not dependent on α_A and α_B since the hydrogen atoms are not really considered.

The value of U_{AB}^{D-D} is zero for infinite separation of $\vec{P}_A$ and $\vec{P}_B$. As the two dipole moments approach with fixed orientations to within several molecular diameters, U_{AB}^{D-D} is positive (repelling dipoles) or negative (attracting dipoles), depending on the dipolar orientations. These features of U_{AB}^{D-D} can be illustrated by the following simple cases:

I. Parallel Dipole Moments:

$\phi=0$, $\Theta_A=\Theta_B=0$,

$$U_{AB}^{D-D}(R_{oo}) = \frac{P^2}{R_{oo}^3} [0-2] = \frac{-2P^2}{R_{oo}^3}; \tag{I.6a}$$

II. Anti-Parallel Dipole Moments:

$\phi=0, \ \Theta_A=0, \ \Theta_B=\pi,$

$$U_{AB}^{D-D}(R_{oo}) = \frac{2P^2}{R_{oo}^3}.$$

The plots of the parallel and antiparallel dipole-dipole interaction energies are given in Figures 3a and 3b. Here we have used the experimental value of the molecules dipole (7) moment of water 1.83D.

There are higher order terms -- indeed an infinite series of multipoles products -- which should be added to the dipole-dipole contribution to give the total electrostatic potential energy of the interaction between any two molecules.

$$U_{AB_{TOT}} = U_{AB}^{D-D} + U_{AB}^{D-Q} + U_{AB}^{Q-Q} + \dots \quad . \qquad (I.7)$$

The first term is just the dipole-dipole interaction already considered . The next term describes the sum of the interactions of a dipole moment of one molecule with the quadrupole moment of the other molecule. The third term describes the interaction of the quadrupole moments of the molecules. The values of U_{AB}^{D-Q} and U_{AB}^{Q-Q} are generally much smaller than U_{AB}^{D-D}, and they fall off more rapidly with intermolecular separation, R_{oo}, being proportional to R_{oo}^{-4} and R_{oo}^{-5} respectively. Clearly, according to Equation (I.6) U_{AB}^{D-D} is proportional to R_{oo}^{-3}. Still other terms in the series of equation (I.7) describe dipole-octupole

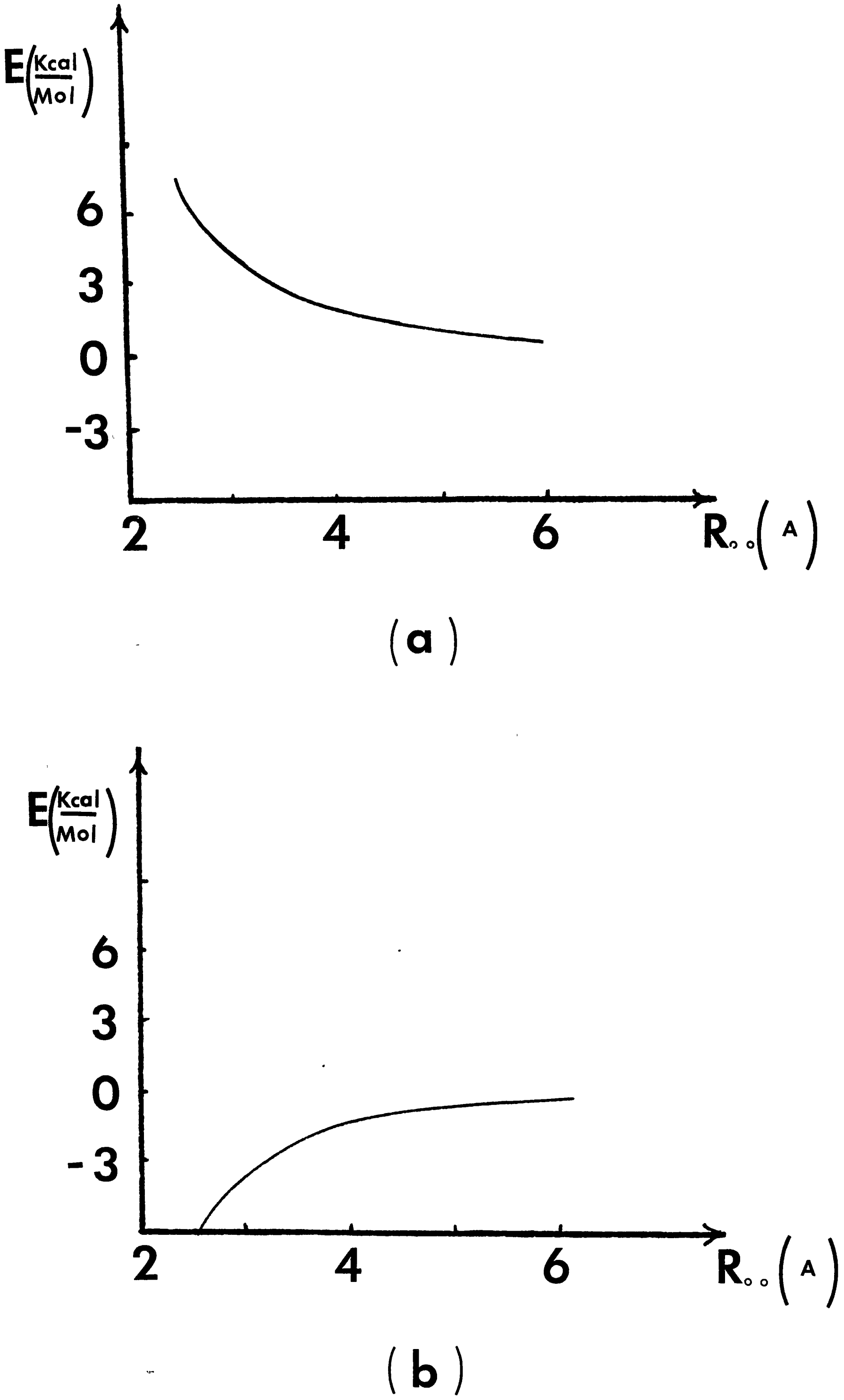

Figure 3. Dipole-Dipole Interaction Energies vs Separation for (top) anti-parallel Dipoles and (bottom) parallel

interactions, quadrupole-octupole interactions, etc. A detailed expansion of the multipole-multipole interaction energy between two classical, non-overlapping charge distributions is given by Hirschfelder, Curtiss, and Bird, Chapter 12, p. 835 (9).

Empirical Stillinger Potential:

To go a step beyond the dipole-dipole interaction, Stillinger (10), constructed a model to allow the water molecule to have a quadrupole moment as well as a dipole moment. Here we describe the electrostatic energy of the water molecule by a rigid four-point-charge model, the geometry for which appears in figure 4. The positive charges (+q), roughly the net charge on a hydrogen, have been located precisely 1A from the oxygen nucleus. The negative charges (-q), mimicing the oxygen lone-pair hybrids, have been symmetrically located above and below the molecular plane at distance 0.8A from the oxygen nucleus. Pairs of vectors connecting O to the point charges are all disposed at the precise tetrahedral angle $\Theta_t = 109^\circ\ 28'$. q a parameter used to fit experimental data is chosen as 1.13×10^{-10} esu. The point charges on the different molecules A and B are allowed to interact with on another pairwise and the interaction energy is computed directly according to Coulomb's law rather than the multipole expansion.

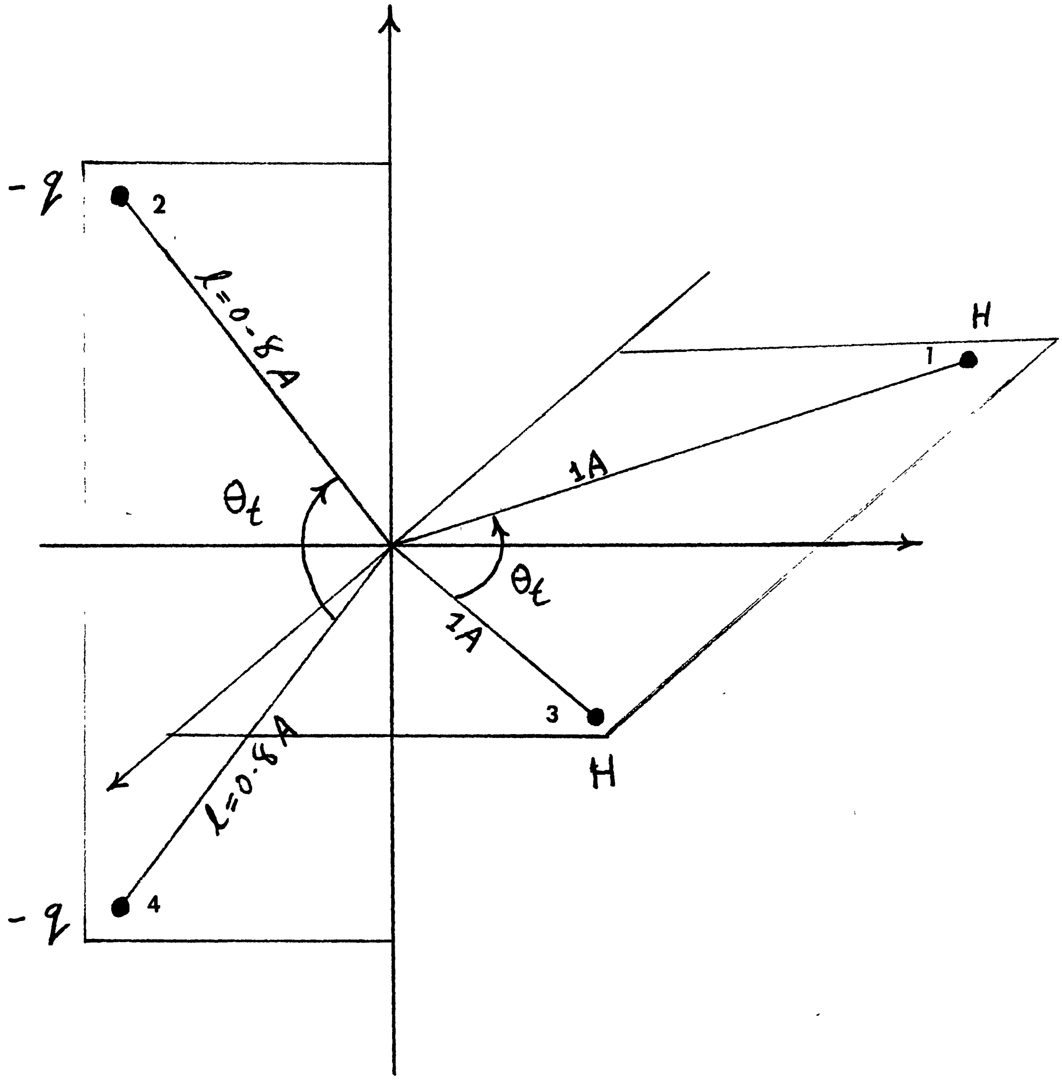

Figure 4. Stillinger's Four Point Charge Model of the water molecule. The positive charges lie in the molecular (H_2O) plane which is perpendicular to that formed by they oxygen nucleus and the negative charges. θ_t = 109.28°

$$V_{el}(A,B) = q^2 \sum_{\alpha=1}^{4} \sum_{\beta=1}^{4} \frac{(-1)^{\alpha+\beta}}{d_{\alpha\beta}(A,B)}. \qquad (I.8)$$

Here α and β enumerate the positive (α,B=1,3) and negative (α,B=2,4) charges on molecules A and B respectively and $d_{\alpha\beta}(A,B)$ is the distance between the two charges α and β on molecules A and B.

However this electrostatic interaction does not adequately represent the intermolecular potential energy. The quantum nature of the electronic charge distribution gives rise to a strong (Pauli exclusion principle) repulsion at short distances and a long range (Van der Waals dispersive) attraction at large distances. Both these effects are included in the Lennard-Jones potential

$$V_{LJ}(R_{oo}) = 4\varepsilon \left\{\left(\frac{\sigma}{R_{oo}}\right)^{12} - \left(\frac{\sigma}{R_{oo}}\right)^{6}\right\}, \qquad (I.9)$$

where ε = 5.2605 x 10^{-15} erg = 7.5750 kcal/mole and σ = 3.10A. ignoring the angular dependence of these interactions, we stipulate that V_{LJ} depends only on the oxygen-oxygen distance R_{oo} . The two parameters ε and σ have been chosen to fit various thermodynamic data. For small distances,$R_{oo} << \sigma$, the repulsive term $(\frac{\sigma}{R_{oo}})^{12}$ dominates the attractive term $-(\frac{\sigma}{R_{oo}})^{6}$. On the other hand, for $R_{oo} >> \sigma$ the attractive dispersion term $-(\frac{\sigma}{R_{oo}})^{6}$ is dominant. The Lennard-Jones potential energy function is shown in Figure 5. The minimum in V_{LJ} occurs at

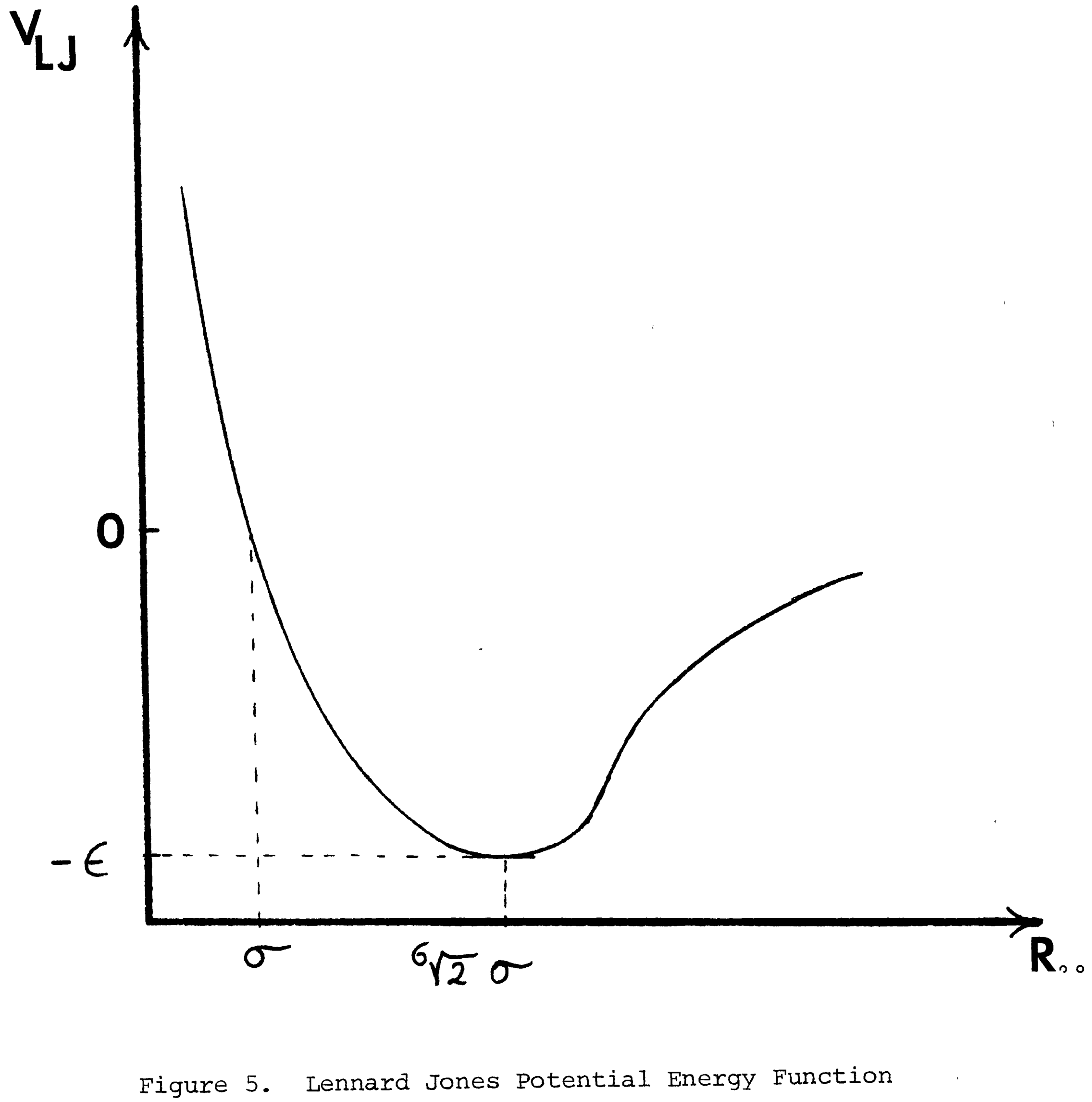

Figure 5. Lennard Jones Potential Energy Function

$$(R_{oo})_{min} = \sqrt[6]{2}\ \sigma = \sqrt[6]{2} \times 3.10A = 3.48A, \tag{I.10}$$

where V_{LJ} has the value $(-\varepsilon)$. That is, with Stillinger's choice of the parameters

$$V_{LJ}[(R_{oo})_{min}] = -\varepsilon = -7.5750 \text{ kcal/mole}. \tag{I.11}$$

By themselves, each of the two terms $V_{el}(A,B)$ and $V_{LJ}(R_{oo})$ gives an incomplete description of the water-water interaction. One might be tempted just to superimpose these two potential energy contributions in an attempt to describe the water-water interaction. But in doing so there are regions where the sum of the two terms does not accurately describe the total interaction. Stillinger (10) was led to introduce a "modulating" factor $S(R_{oo})$, to "turn on" and "turn off" the electrostatic potential. The final form for the Stillinger model water-water interation is

$$U(R_{oo},\alpha_A,\alpha_B,\theta_A,\theta_B,\phi) = V_{el}(A,B)\ S(R_{oo}) + V_{LJ}(R_{oo}). \tag{I.12}$$

The modulation function $S(R_{oo})$ shown in figure 6 smoothly varies between 0 at small distance and 1 at large distance:

$$S(R_{oo}) = \begin{cases} 0, & 0 \leqq R_{oo} \leqq R_L \\ \dfrac{(R_{oo}-R_L)^2(3R_U-R_L-2R_{oo})}{(R_U - R_L)^3}, & R_L \leqq R_{oo} \leqq R_U \\ 1, & R_U \leqq R_{oo} \end{cases}$$

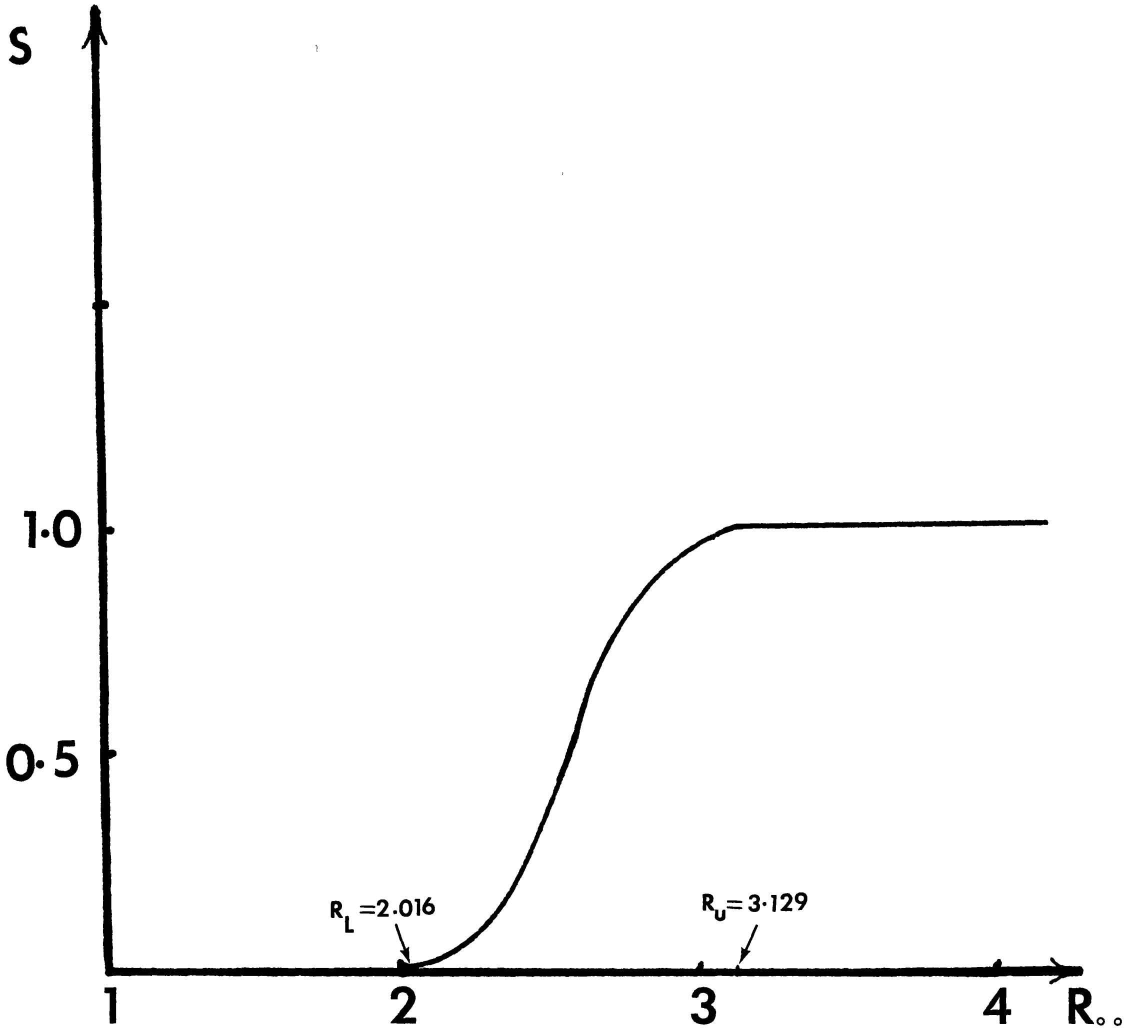

Figure 6. Plot of "Modulation Factor" $S(R_{oo})$ vs R_{oo} for the Stillinger Potential Energy Function

R_L and R_U provide two additional fitting parameters for the potential.

$R_L \equiv R_{Lower} = 2.0160$ A,
$R_U \equiv R_{Upper} = 3.1287$ A.

The details of the original choice of all the parameters in both the electrostatic term and Lennard-Jones term are given by Ben-Naim and F.H. Stillinger "Aspects of the Statistical-Mechanical Theory of Water" (11). The paramters used here in what is refered to as the ST2 potential are found in Stillinger's revision (10) of this original potential.

Ab Initio Calculations

The multipole-multipole expansion and Stillinger's empirical potential are simply an attempt to by-pass the basic problem of actually solving the Schroedinger eigenvalue problem. In recent years, however, quantum chemical methods have developed to the point where serious attempts are made to solve the problem without any empirical imput other than the charge and mass of the electron. These are the so-called ab-initio calculations. There are different levels of approximations with which we can approach these ab initio methods. Eventually we want to focus on the Density Functional Theory, the DFT method, but as a prelude we shall briefly review one of the standard ab initio series of calculations on the water-water system.

The atomic nuclei are fixed in place as the electronic "motion" is treated quantum mechanically by solving - at least at some level of approximation - the Schroedinger electronic eigenvalue equation. In the self-consistent field (SCF) approximations each electron is assigned its own orbital and the N-electron wave function approximated by the antisymmetrized product of these N orbitals. However the electronic distribution of charge in one orbital effects the electrons in the other orbitals by way of the "Coulomb" and "exchange" interactions. Thus the precise determination of the orbitals must be done iteratively, reaching self-consistentcy after a number of steps originating with a guess of the charge distribution in each orbital. In addition to the self-consistent field (SCF) ground state Φ_o, the procedure also generates a complete set of "model" states $\{\Phi_m\}$ which span the N electron Hilbert Space. However, it is recognized that the SCF wave function Φ_o is not in fact an eigenfunction of the true electronic Hamiltonian. There are effects which go beyond the orbital model inherent in the SCF scheme. These effects are generally known as "correlation effects". One method to account for these correlation effects is to recognize that the model states, since they are not eigenstates of the Hamiltonian, "mix" with Φ_o and with one another in expanding the exact ground state. This mixing is called "configuration interaction" (CI). A typical electronic structure calculation thus envisions generating a set of SCF orbitals, using the lowest N to construct Φ_o , with the remaining model configurations Φ_m obtained by replacing one or more of these "occupied" orbitals by virtual orbitals. Then the matrix representing the true Hamiltonian in this basis of N electron model functions is diagonalized to obtain the ground state energy. In practice the number of SCF orbitals generated and thus the number of model states considered is finite, resulting in an approximate value of the ground state energy.

We focus on one series of the ab initio calculations for the water dimer to illustrate the complexity of the problem. That series is the result of over ten years of research by Clementi and his coworkers (12,13,14). An initial self-consistent field (SCF) calcualtion (12) for the water dimer potential energy surface was subsequently improved by extensive configuration interaction (CI) (13) at sixty-six points corresponding to various locations and orientations of the two water molecules. Each of these sixty-six calculations involves generating a set of orbitals and "mixing" more than 5200 configurations constructed from these orbitals. The third paper by Clementi et. al. (14) gives us a more complete scan of the potential energy surface. Each extensive CI at 169 various locations and orientations of the two water molecules involves more than 10^4 configurations of the orbitals. Despite the elaborate inital (1976) CI calculation the newer (1983) CI calculation shows significant discrepancies with the former. Comparisons reveal appreciable deviations in the repulsive area of the potential energy surface.

Since it is impossible to represent the entire 6-dimensional energy surface $U(\alpha_A,\alpha_B,\Theta_A,\Theta_B,R_{oo},\phi)$, Clementi fixes five variable and lets the sixth vary. In most cases he fixes the angles, namely $\alpha_A,\alpha_B,\Theta_A,\Theta_B,\phi$, and allows R_{oo} to vary; thus, $U=U(R_{oo})$. Then he plots $U(R_{oo})$ vs R_{oo} (or whatever coordinate is allowed to vary) for the twenty different geometries (labled with capital letters) shown in Figure 7. The small arrows indicate how the variable is changed as each labeled molecule is moved relative to the central (fixed) molecule which is identified by the chemical symbols HOH. We reproduce three of Clementi's curves in Figure 8 (solid lines) U vs R_{oo} for geometrics D,F, and T. We give the values for the five fixed angles on each of these three graphs. In addition we plot (dotted lines) the dipole-dipole interaction energy for the corresponding choices of Θ_A,Θ_B, and ϕ. α_A and α_B in fact do not enter the dipole interaction energy expression.

If we compare the geometry D results with the corresponding dipole-dipole curve we see that the part of the curve with R_{oo} greater than 4A closely paralleis the attractive dipole-dipole curve. Similarly on comparing geometry F with the anti-parallel dipoles we see that for $R_{oo}>4A$ both curves represent a repulsion. These comparisons between the dipole curves and Clementi's D,F

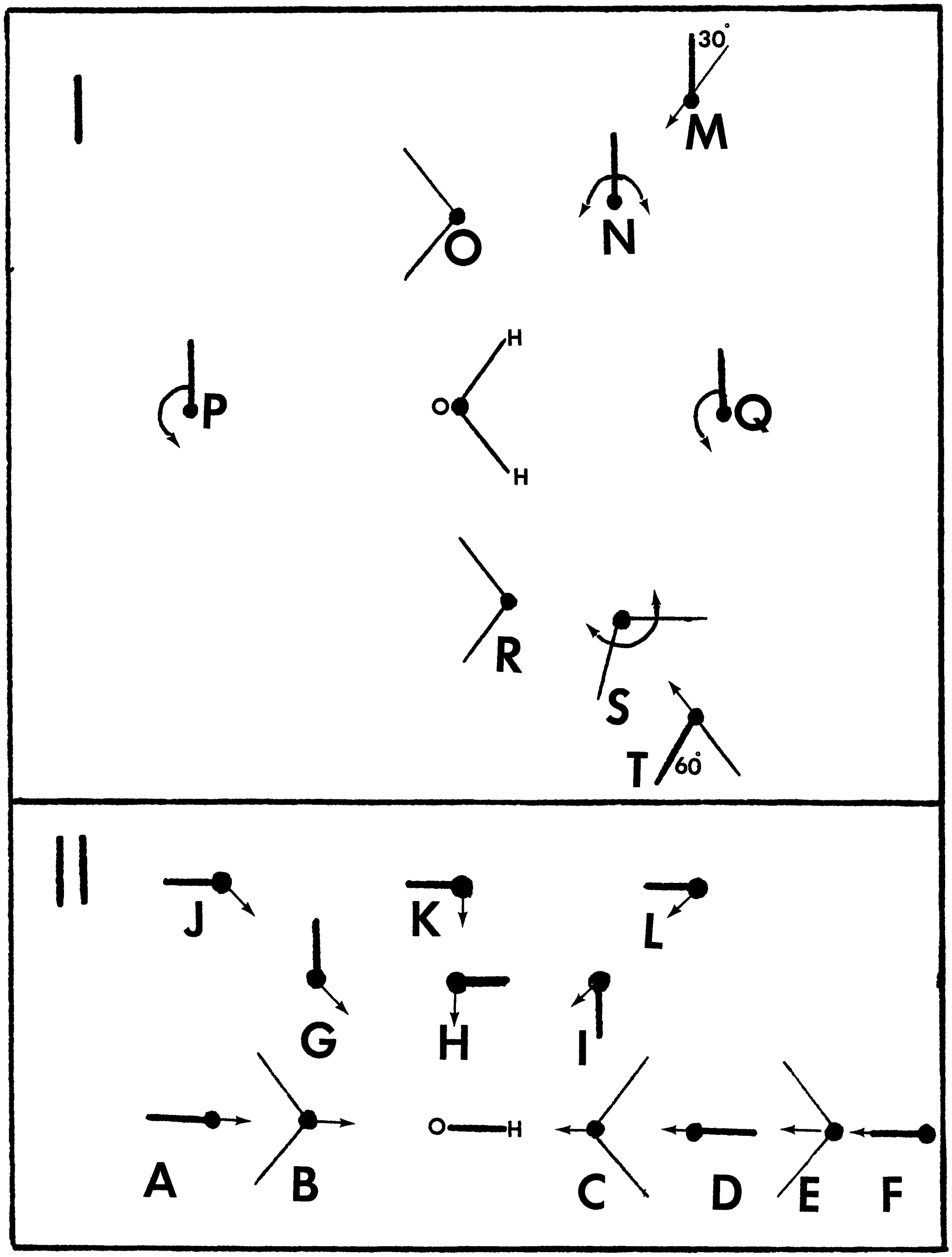

Figure 7. Different Geometries of Water-Dimer Used in Clementi's Calculations. In the view from the top of the molecular plane (z direction), II in the molecular plane (y direction), is identified by the chemical symbols for oxygen and hydrogen. The arrows mark the direction in which the potential surface is scanned

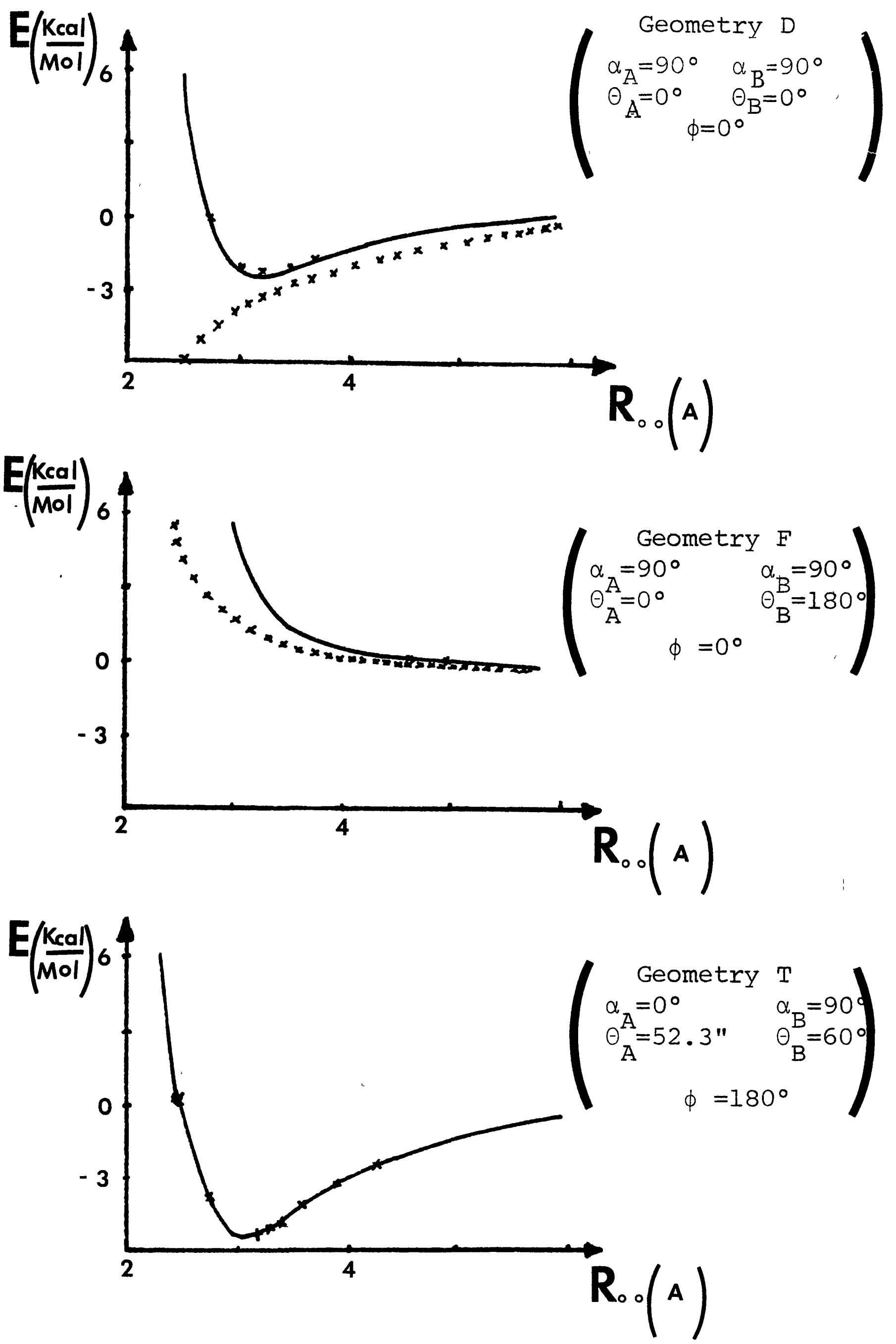

Figure 8. Interaction Energy vs. R_{oo} Separation for Three Geometries of the Water Dimer

geometries suggest to us that the dipole-dipole interaction has a dominate effect on the interaction energy of the water dimer, at least in the intermediate range of distances. At very near and far distances Clementi's curves deviate significantly from the dipole-dipole terms reflecting, for instance, the exclusion principle repulsion at small distances and the dispersion energy attraction at large distances. These quantum effects are obviously not in any strictly electrostatic model, much less a model restricted to the dipole-dipole terms.

Clementi found that for the fixed angles indicated the T geometry gives the lowest energy. The five fixed angles are $\alpha_A = 0°$, $\Theta_A = 52.3°$, $\alpha_B = 90°$, $\Theta_B = 60°$, and $\phi = 180°$. The lowest energy for these fixed angles occurs for $R_\infty = 2.97$ A. The second lowest energy is found with the M geometry for which $\alpha_A = 0°$, $\Theta_A = 52.3°$, $\alpha_B = 90°$, $\Theta_B = 30°$, $\phi = 180°$ at R_{oo} about 2.85A. That is, M differes from T in the change of Θ_B from 60° to 30°. By exploring the potential energy suface in the vicinity of these minima, Clementi chose an average oxygen-oxygen distance of 2.91A and fixing $\alpha_A = 0°$, $\Theta_A = 52.3°$, $\alpha_B = 90°$, $\phi = 180°$, let Θ_B vary. In figure 9 we plot $U(\Theta_B)$ vs Θ_B, corresponding to Clementi's case N. As Θ_B is varied, the minimum energy of -5.5 kcal/moles is obtained at $\Theta_B = 50°$.

The absolute minima for the Stillinger ST2 potential (1) and the Clementi potential (14) occur at almost the same geometry. Stillinger's and Clementi's values for the

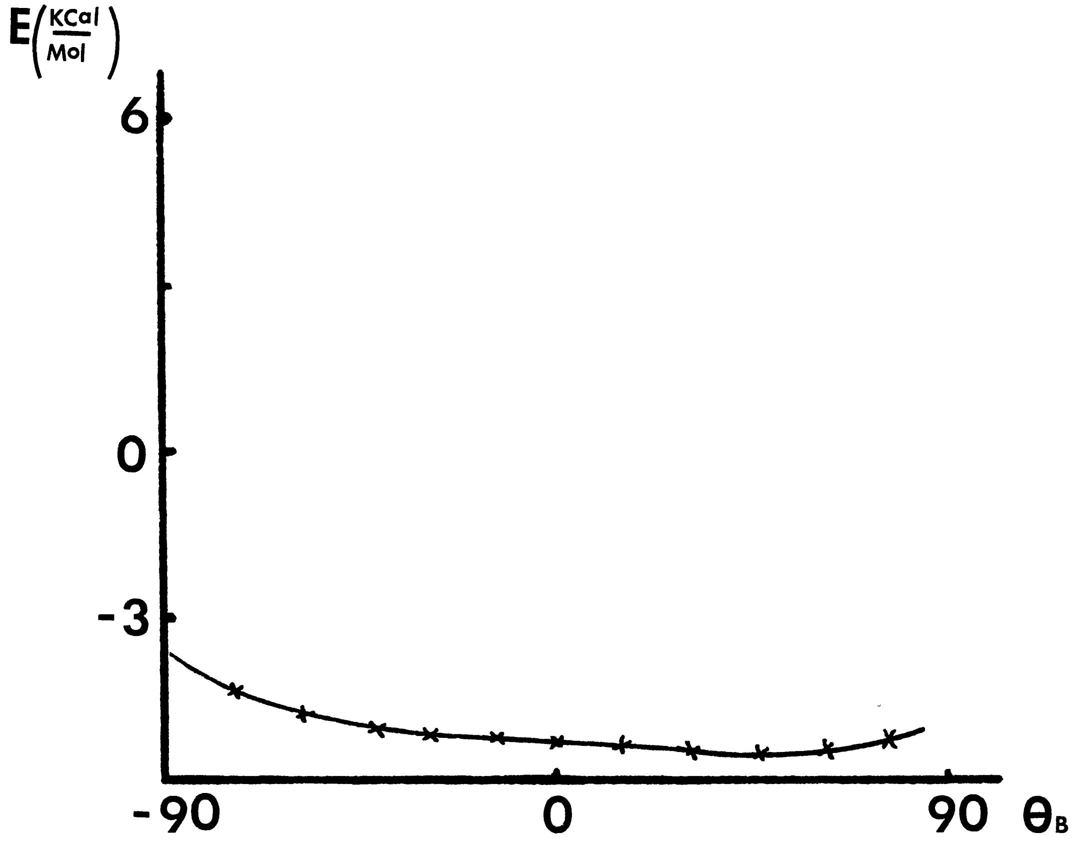

Figure 9. Interaction Energy vs Θ Orientation for Fixed R_{oo} Separation of the Water-Dimer for $-90^o<\theta<90^o$. Tick marks indicate calculated values at 15° intervals

geometrical parameters at which the minimum occurs are given in Table I. However, the values of the "absolute" minimum energies differ by about 20%, being -5.5 kcal/mole and -6.84 kcal/mole for Clementi and Stillinger respectively.

We close this chapter by noting that the geometry searches envsisioned by Clementi and Stillinger may be quite different in practice. Indeed, Clementi has to redo the entire electronic structure calculation point by point for each choice of the six variables; each calculation, involving an SCF and CI computation, is itself a gargantuan effort. On the other hand Stillinger need only add a number of coulomb interaction energies and evaluate the Lennard-Jones function. While each of Clementi's calculations provides a better value for the energy of interaction, Stillinger is able to sample the potential energy surface (using, or course, his empirical potential) at many more points. Thus there is a real question concerning Clementi's ability to search throughly all the required geometrical configurations. Clearly, we see the need for a fast yet accurate *ab initio* method for finding the potential energy surface.

TABLE I.
COMPARISON OF GEOMETRICAL PARAMETERS FOR THE MINIMUM ENERGY CONFIGURATION OF THE WATER DIMER FOUND BY STILLINGER AND BY CLEMENTI

Variable	Stillinger	Clementi
Θ_A	53.6°	52.3°
Θ_B	51.8°	50.0°
α_A	0.0°	0.0°
α_B	90.0°	90.0°
ϕ	180.0°	180.0°
R_{oo}	2.85A	2.91A

Chapter II

DENSITY FUNCTIONAL THEORY AS APPLIED TO TWO WATER MOLECULES

There is a rigorous alternative to the traditional quantum chemical approaches - one based on the Hohenberg-Kohn theorem (15). This remarkable theorem states that for a given placement of the nuclei there does exist a functional $\varepsilon(N,\rho_N)$ of the electron density $\rho_N(\vec{r})$ such that for all N representable densities $\rho_N(\vec{r})$, $\varepsilon(N,\rho_N)$ is an upper bound of the exact electronic ground state energy eigenvalue:

$$E(\vec{R}_1,\vec{R}_2,...,\vec{R}_A) \leqq \varepsilon(N,\rho_N(\vec{r});\vec{R}_1,\vec{R}_2,...,\vec{R}_A)$$

or in somewhat abbreviated notation

$$E(\underline{R}) \leqq \varepsilon(N,\rho_N(\vec{r});\underline{R}) \tag{II.1}$$

with the equality being attained for the true ground state density. Here, $\underline{R}$ stands for the collection of nuclear coordinates $\vec{R}_\alpha$ defining the supermolecular system. Of course, the functional also depends on the nuclear charges Z_α defining the system. For the water dimer,we have $A=6,\alpha=1,2,...,6$ and $N=20$.

The orginial paper of Hohenberg and Kohn proves the existence of such a functional. In fact, later developments (16,17,18) have shown that there is not just one functional but rather many such inequivalent functionals, all of which have the upper-bound property (II.1). In a sense, Hohenberg and Kohn discovered the existence of one such energy functional which according to these developments had the limitation of being defined over what have come to be called "V-representable" densities (19).

Now the water dimer ground state electronic eigenvalue is obtained as the solution of

$$\hat{H}(\hat{x}_i, \hat{p}_i; \vec{R}_1, \ldots, \vec{R}_A)\ \Psi(x_1, x_2, \ldots, x_N, \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_A)$$

$$= E(\vec{R}_1, \ldots, \vec{R}_A)\ \Psi(x_1, \ldots x_N; \vec{R}_1, \ldots, \vec{R}_A) \qquad \text{(II.2)}$$

where

$$\hat{H} = \sum_{i=1}^{N} \frac{-\hbar^2}{2m} \nabla_i^2 + \sum_{1 \leqq i \leqq j \leqq n} \frac{e^2}{|\vec{r}_e - \vec{r}_j|} + \sum_{i=1}^{N} \sum_{\alpha=1}^{A} \frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|}$$

$$+ \sum_{1 \leqq \alpha \leqq \beta \leqq A} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}.$$

Multiplying both sides of equation (II.2) from the left by the normalized eigenfunction Ψ and integrating overall space and spin coordinates we get

$$E(\vec{R}_1, \ldots \vec{R}_A) = \int dx_1 \ldots dx_n\ \Psi^* \hat{H}\ \Psi$$

$$= \int dx_1 \ldots dx_N \; \Psi^* \{ \sum_{i=1}^{N} \frac{-\hbar^2}{2m} \nabla_i^2 + \sum_{1 \leq i \leqq j \leq n} \frac{e^2}{r_{ij}} \} \; \Psi$$

$$+ \int dx_1 \ldots dx_N \; \Psi^* (\sum_{i=1}^{N} \sum_{\alpha=1} \frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|}) \; \Psi + \sum_{1 \leq \alpha < \beta \leq A} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

(II.3a)

Here in Eq. (II.3a) we have used the exact ground state electronic eigenfunction. More generally we can write, according to the Rayleigh-Ritz variational principle (20) that

$$E(\vec{R}_1 \ldots \vec{R}_A) \leq \int dx_1 \ldots dx_N \psi^* H \; \psi$$

$$= \int dx_1 \ldots dx_N \; \psi^* \{ \sum_{i=1}^{N} \frac{-\hbar^2}{2m} \nabla_i^2 + \sum_{1 \leq i \leqq j \leq n} \frac{e^2}{r_{ij}} \} \; \psi$$

$$+ \int dx_1 \ldots dx_N \; \psi^* (\sum_{i=1}^{N} \sum_{\alpha=1}^{A} \frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{r}_\alpha|}) \psi + \sum_{1 \leq \alpha < \beta \leq A} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} \qquad \text{(II.3b)}$$

where ψ is simply a normalized antisymmetric "trial" wave function. Since the electronic trial wave function must be antisymmetric under the exchange of particle labels, for example

$$\psi(x_1, x_2, \ldots x_N) = - \psi(x_2, x_1, x_3, \ldots x_N),$$

the probability density in configuration space is symmetric under the exchange of particle labels:

$$\psi^*\psi = \psi^*(x_1,x_2,\ldots,x_N)\psi(x_1,x_2,\ldots,x_N)$$

$$= \psi^*(x_2,x_1,x_3,\ldots,x_N)\ \psi\ (x_2,x_1,x_3,\ldots x_N).$$

For a particluar i the second term in Eq. (II.3b) will be

$$\int\psi^*(x_1,x_2,\ldots,x_N)\ (\sum_{\alpha=1}^{A}\frac{-Z_\alpha e^2}{|\vec{r}_i-\vec{R}_\alpha|})\ \psi(x_1,x_2,\ldots,x_N)\ dx_1\ldots dx_N$$

$$= \int dx_i[\sum_{\alpha=1}^{A}\frac{-Z_\alpha e^2}{|\vec{r}_i-\vec{R}_\alpha|}]\int\prod_{\substack{j=1\\j\neq i}}^{N} dx_j\psi^*(x_1,x_2,\ldots,x_N)\ \psi\ (x_1,x_2,\ldots,x_N)$$

$$= \int dx_i[\sum_{\alpha=1}^{A}\frac{-Z_\alpha e^2}{|\vec{r}_i-\vec{R}_\alpha|}]\ \int\prod_{\substack{j=1\\j\neq i}}^{N}dx_j|\psi\ (x_1,x_2,\ldots,x_N)|^2$$

where,

$$\int\prod_{\substack{j=1\\j\neq i}}^{N}\ dx_j|\psi(x_1,x_2,\ldots,x_N|^2=P(x_i)$$

is the probability density of finding any particle at x_i. The integration is over all space and spin coordinates except those of particle i. In general, as we let i range from 1 to N, then the second term will be

$$\sum_{i=1}^{N}\int dx_i[\sum_{\alpha=1}^{A}\frac{-Z_\alpha e^2}{|\vec{r}_i-\vec{R}_\alpha|}]P(x_i) = \sum_{i=1}^{N}\int d\vec{r}_i\ \sum_{\xi_i}[\sum_{\alpha=1}\frac{-Z_\alpha e^2}{|\vec{r}_i-\vec{R}_\alpha|}]\ P(\vec{r}_i,\xi_i)$$

$$= \int d\vec{r}[\sum_{\alpha=1}^{A}\frac{-Z_\alpha e^2}{|\vec{r}-\vec{R}_\alpha|}][N\sum_{\xi}\ P(\vec{r},\xi)]$$

$$= \int d\vec{r} \left[\sum_{\alpha=1}^{A} \frac{-Z_\alpha e^2}{|\vec{r} - \vec{R}_\alpha|} \right] \rho_N(\vec{r}).$$

Here the electronic density $\rho_N(\vec{r})$ is

$$\rho_N(\vec{r}) = N \sum_{\xi} P(\vec{r},\xi) = {}_{\rho_N}\langle \psi | \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i) | \psi \rangle_{\rho_N}. \qquad \text{(II.4)}$$

Thus,

$$\int \psi^*(x_1,x_2,\ldots,x_N) \left(\sum_{i=1}^{N} \sum_{\alpha=1}^{A} \frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} \right) \psi(x_1,x_2,\ldots,x_N)\, dx_1 \ldots dx_N$$

$$= \sum_{\alpha=1}^{A} \left[-Z_\alpha e^2 \int d\vec{r}\, \frac{\vec{\rho}_N(r)}{|\vec{r} - \vec{R}_\alpha|} \right] \qquad \text{(II.5)}$$

is explicily a functional of the density $\rho_N(\vec{r})$.

Now let us introduce the definition of the energy functional given by Levy (16).

$$\varepsilon(N,\rho_N(\vec{r});\underline{R}) \equiv \overset{\min}{\{|\psi\rangle_{\rho_N}\}} \left({}_{\rho_N}\langle \psi | \hat{H} | \psi \rangle_{\rho_N} \right). \qquad \text{(II.6)}$$

Here, what is envisioned is a search throughout the set of normalized N-electron states $\{|\psi\rangle_{\rho_N}\}$, each of which yielding the given electron density

$$\rho_N(\vec{r}) = {}_{\rho_N}\langle \psi | \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i) | \psi \rangle_{\rho_N} \qquad \text{(II.4)}$$

for one or more optimum states $|\tilde{\psi}\rangle_{\rho_N}$ for which the expectation value of $\hat{H}$ achieves a minimum. We refer to this formulation by Levy as the "constrained" variational definition of $\varepsilon(N,\rho_N;\underline{R})$, for clearly, the specified charge density $\rho_N(\vec{r})$ (a non-denumerable set of expectations values) limits our choice of N-electron state functions used in seeking the minimum expectation value of $\hat{H}$. It then follows from the Rayleigh Ritz variational principle in N electron Hilbert space that the inequality (II.1) (that is the Hohenberg-Kohn theorem) is satisfied using the definition (II.6). That is, the subsequent search of $\varepsilon(N,\rho_N,\underline{R})$ over all N-representable densities $\rho_N(\vec{r})$ for the minimum value of the functional $\varepsilon(N,\rho_N(\vec{r});\underline{R})$ will necessarily yield the exact eigenvlaue $E(\underline{R})$. Written in the following fashion

$$E(\underline{R}) = \{\overset{\min}{\rho_N}\}[\varepsilon(N,\rho_N;\underline{R})]=\{\overset{\min}{\rho_N}\}[\{|\Psi\overset{\min}{>}_{\rho_N}\}({}_{\rho_N}\langle\Psi|\hat{H}|\Psi\rangle_{\rho_N})] \quad \text{(II.7)}$$

we see that the computation of the ground-state eigenvalue $E(\underline{R})$ is cast into a two-tier variational search procedure: the innermost being a search over the set of N electron state vectors, all of which constrained to yield a specified density, and the outermost a search over all such N-electron densities. Clearly, the intuitive notion of relating chemical bonding and intermolecular forces to electronic charge density directly is most appealing. Indeed, many others (21), most notably Bader and his coworkers (22), have been at the forefront of seeking such understanding.

Our thesis is based on the following formal properties of energy functionals and the approximations thereto. We believe this original analysis of density functionals provides the proper context to organize a logical approach to calculating intermolecular forces. Levy's definition of energy functional can be cast into a more traditional form by explicity considering the terms in the electronic Hamiltonian. In particular we can use the result (II.5) to write the interaction with the fixed nuclei in terms of the density $\rho_N(\vec{r})$:

$$\varepsilon(N,\rho_N;\underline{R}) =$$

$$\min_{\{|\Psi>_{\rho_N}\}} \{\rho_N<\Psi|\sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_{i=1}^{N}\sum_{\alpha=1}^{A}\frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} + \sum_{i<j}^{N}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{\alpha<\beta}^{A}\frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}|\Psi>_{\rho_N}\}$$

$$= [\min_{\{|\Psi>_{\rho_N}\}} \{_{\rho_N}<\Psi|\sum_{i=1}^{N}\frac{-\hbar^2}{2m}\nabla_i^2 + \sum_{i<j}^{N}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}|\Psi>_{\rho_N}\} - \frac{e^2}{2}\int d\vec{r}\int d\vec{r}\,'\frac{\rho_N(\vec{r})\rho_N(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}]$$

$$+ \frac{e^2}{2}\int d\vec{r}\int d\vec{r}\,'\frac{\rho_N(\vec{r})\ \rho_N(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} + \sum_{\alpha=1}^{A}[-Z_\alpha e^2\int d\vec{r}\ \frac{\rho_N(\vec{r})}{|\vec{r} - \vec{R}_\alpha|}] + \sum_{\alpha<\beta}^{A}\frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} \qquad \text{(II.8)}$$

and note that the terms depending not upon the specific electronic wave function $|\Psi>_{\rho_N}$ but only upon the charge density ρ_N have been removed from the minimization prescription since the search is restricted to wave functions yielding the same charge denisty. The classical Coulombic self-interaction functional

$$J(\rho) \equiv \frac{e^2}{2}\int d\vec{r}\int d\vec{r}\,'\ \frac{\rho(\vec{r})\ \rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \tag{II.9}$$

has been added and appropriately subtracted to define the following functional which will occupy center stage:

$$\varepsilon_o\ (N,\rho_N) = [\{|\Psi>_{\rho_N}\}^{\min} \{\rho_N<\Psi|\sum_{i=1}^{N} - \frac{\hbar^2}{2m}\nabla_i^2 + \sum_{i<j}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}\ |\Psi>_{\rho_N}\} - J(\rho_N)]. \tag{II.10}$$

Again, the construction of the $\varepsilon_o(N,\rho_N)$ envisions a search over all N electron state functions $|\Psi>_{\rho_N}$ giving the specified electron density. It is clear from the invariance of the operators involved that the value of $\varepsilon_o(N,\rho_N)$ is unchanged by a rigid rotation and/or translation of $\rho_N(\vec{r})$ in space. The exact electronic ground state eigenvalue for a fixed $\underline{R}$ is then to be found in the search over all such N electron densities $\rho_N(\vec{r})$ for the minimum value of the functional

$$\varepsilon\ (N,\rho_N;\underline{R}) = \varepsilon_o(N,\rho_N) + J(\rho_N) + \sum_{\alpha=1}^{A}[-Z_\alpha e^2\int d\vec{r}\ \frac{\rho_N(\vec{r})}{|\vec{r} - \vec{R}_\alpha|}] + \sum_{\alpha<\beta}^{A} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}. \tag{II.11}$$

It must be kept in mind that the energy resulting from minimizing $\varepsilon(N,\rho_N;\underline{R})$ always corresponds to the electronic ground state for the given nuclear configuration, although in case of degeneracy such a minimum energy may be attained for more than one density.

Two points worth noting are the N dependence of each of the terms in Equation (II.11) and the dependence of the optimum density on the nuclear configuration. Clearly, in the second and third terms the N dependence enters exclusively through the density; in the first term, as the notation in Equation (II.10) suggests, an explicit dependence on N other than through $\rho_N(\vec{r})$ should be anticipated. To emphasize the fact that a different N electron density results in carrying out the minimization of (II.11) for each $(\underline{R})$ we write the optimum density $\tilde{\rho}(\vec{r};\underline{R})$ and the ground state energy

$$E(\underline{R}) = \{\overset{\min}{\rho_N}\}[\varepsilon(N,\rho_N;\underline{R})] =$$

$$\varepsilon_o(N,\tilde{\rho}_N(\underline{R})) + J(\tilde{\rho}_N(\underline{R})) + \sum_{\alpha=1}^{A} [-Z_\alpha e^2 \int d\vec{r}\, \frac{\tilde{\rho}_N(\vec{r},\underline{R})}{|\vec{r} - \vec{R}_\alpha|}] + \sum_{\alpha<\beta}^{A} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}. \quad \text{(II.12)}$$

Although there is no explicit dependence in the functional $\varepsilon_o(N,\rho_N)$ on the nuclear coordinates $\underline{R} = \{\vec{R}_\alpha\}$, there is an implicit dependence on these atomic positions in the correspoinding term in $E(\underline{R})$ through their appearance in the optimum density $\tilde{\rho}_N(\vec{r};\underline{R})$. In principle, the search envisioned in Equation (II.12) is over the same (total) set on N electron densities for each point on the potential energy surface. However, for neighboring points $\underline{R}$ and $\underline{R}'$ on this surface the two optimum densities $\tilde{\rho}_N(\vec{r};\underline{R})$ and $\tilde{\rho}_N(\vec{r},\underline{R}')$ must presumably be close in some geometrical sense (23). Thus, the search for the optimum density at the neighboring point $\underline{R}'$ may be restricted to the neighborhood of $\tilde{\rho}_N(\vec{r},\underline{R})$.

Most often the potential energy surface is computed relative to the electronic ground state of a fixed, asymptotic configuration of the nuclei, i.e. the "elemental molecular constituents" of the system.

Moreover, the internal coordinates of these molecules are frequently held fixed as they are rigidly translated and rotated relative to one another. In this spirit then the potential energy surface of the system can be expressed as

$$V(\vec{R}_1\vec{\Omega}_1 \ldots \vec{R}_M\, \vec{\Omega}_M; g_1, \ldots g_M) =$$

$$= \min_{\{\rho_N\}} \{\varepsilon_o(N,\rho_N) + J(\rho_N) + \sum_{m=1}^{M} \sum_{a=1}^{A_m} [-Z_{ma} e^2 \int d\vec{r} \frac{\rho_N(\vec{r})}{|\vec{r} - \vec{R}_{ma}|}]\}$$

$$+ \sum_{m=1}^{M} \sum_{1 \leq a < b \leq A_m} (\frac{Z_{ma} Z_{mb} e^2}{|\vec{R}_{ma} - \vec{R}_{mb}|}) + \sum_{1 \leq m < n \leq M} \sum_{a=1}^{A_m} \sum_{b=1}^{A_n} \frac{Z_{ma} Z_{nb} e^2}{|\vec{R}_{ma} - \vec{R}_{nb}|}$$

$$- \sum_{m=1}^{M} [\min_{\{\rho_{N_m}\}} \{\varepsilon_o(N_m, \rho_{N_m}) + J(\rho_{N_m}) + \sum_{a=1}^{A_m} [-Z_{ma} e^2 \int d\vec{r} \frac{\rho_{N_m}(\vec{r})}{|\vec{r} - \vec{R}^{\circ}_{ma}|}]\}$$

$$+ \sum_{1 \leq a < b \leq A_m} \frac{Z_{ma} Z_{mb} e^2}{|\vec{R}_{ma} - \vec{R}_{mb}|}] .$$

$$= \{\varepsilon_o(N, \tilde{\rho}_N(\underline{R})) + J(\tilde{\rho}_N(\underline{R})) + \sum_{m=1}^{M} \sum_{a=1}^{A_m} [-Z_{ma} e^2 \int d\vec{r} \frac{\tilde{\rho}_N(\vec{r};\underline{R})}{|\vec{r} - \vec{R}_{ma}|}]\}$$

$$- \sum_{m=1}^{M} \{\varepsilon_o(N_m, \tilde{\rho}_{N_m}(\underline{R}^{O}_m) + J(\tilde{\rho}_{N_m}(\underline{R}^{O}_m) + \sum_{a=1}^{A_m} [-Z_{ma} e^2 \int d\vec{r} \frac{\tilde{\rho}_{N_m}(\vec{r};\underline{R}^{\circ}_m)}{|\vec{r} - \vec{R}^{\circ}_{ma}|}]\}$$

$$+ \sum_{1 \leq m < n \leq M} \sum_{a=1}^{A_m} \sum_{b=1}^{A_n} \frac{Z_{ma} Z_{nb} e^2}{|\vec{R}_{ma} - \vec{R}_{nb}|} . \tag{II.13}$$

A word about the notation is in order here. We envision M molecules (elemental consitutuents) labeled m =1,2,...M, and in molecule m, N_m electrons and A_m atomic nuclei with charges Z_{ma} located at $\vec{R}_{ma}$, a = 1,2,...A_m. Thus, each α introduced above is now a particular molecule-atom index pair ma. Alternatively, the coordinates of the nuclei of molecule m may generally be specified in terms of the center of mass vector $\vec{R}_m$, three Euler angles $\vec{\Omega}_m$, and $3A_m - 6$ internal coordinates g_m of the molecule. We envision the internal coordinates g_m fixed as the location $\vec{R}_m$ and the orientation $\vec{\Omega}_m$ of each of the M molecules is changed. Thus, according to Equation (II.13) the potential energy of interaction V is considered a function of the 6M coordinates $\vec{R}_1\vec{\Omega}_1,\ldots\vec{R}_M,\vec{\Omega}_M$, parameterized by the M sets of $(3A_m-6)$ internal coordinates of the molecules. In general 6 of these 6M coordinates may be used to locate and orientate the center of mass coordinates of the M molecules, leaving V to depend nontrivially on 6M-6 coordinates.

In the second expression of Equation (II.13) the tilde again denotes the appropriate optimized densities obtained in carrying out the minimization procedures indicated in the first expression. As mentioned above the M independent minimizations carried out for the isolated molecules -- the asymptotic positions being indicated by $\vec{R}^o_{ma}$ -- necessarily yield the ground electronic state for each molecular species. Each species is in fact specified by the nuclear configuration and charges $\vec{R}_{ma}, Z_{ma}$, a=1, ...A_m, and the number of electrons N_m. Of course, there is the obvious restriction that $\sum_{m=1}^{M} N_m = N$, but in addition we must also presume that the partition of the N electrons among the M isolated molecules is the one yielding the lowest total sum of their electronic energies. Finally, our notation reminds us that the optimum charge densities do depend on the configuration of the atomic nuclei, although for each isolated molecule the minimized energy itself certainly can depend only upon its internal coordinates.

For the water dimer (M=2) there are three fixed internal coordinates for each of the two water molecules. Thus, with the molecules designated A and B as in chapter I:

$$g_1 \equiv g_A = \{x_{1A}, x_{2A}, \gamma_A\}$$

$$g_2 \equiv g_B = \{x_{1B}, x_{2B}, \gamma_B\}$$

$$\vec{R}_1 = \vec{R}_A = \frac{1}{2} R_{oo}\ \hat{k} + d\ \hat{p}_A(\theta_A, \phi_A)$$

$$\vec{R}_2 = \vec{R}_B = -\frac{1}{2} R_{oo}\ \hat{k} + d\ \hat{p}_B(\theta_B, \phi_B)$$

$$\vec{\Omega}_1 = \vec{\Omega}_A = \{\theta_A, \phi_A, \alpha_A\}$$

$$\vec{\Omega}_2 = \vec{\Omega}_B = \{\theta_B, \phi_B, \alpha_B\}.$$

Here we have chosen the origin of the coordinate system midway between the two oxygen nuclei and orientated their internuclear axis along the Z axis as in Figure 1. Here d=0.07A is the distance of the center of mass from the oxygen nucleus and the unit vectors are

$$\hat{p}_A = \sin\theta_A \cos\phi_A \hat{i} + \sin\theta_A \sin\phi_A \hat{j} + \cos\theta_A \hat{k}$$

and

$$\hat{p}_B = \sin\theta_B\cos\phi_B\hat{i} + \sin\theta_B\sin\phi_B\hat{j} + \cos\theta_B\hat{k}.$$

As pointed out in chapter I, the energy of interaction will depend only on $R_{oo}, \alpha_A, \theta_A, \alpha_B, \theta_B$, and $\phi = \phi_A - \phi_B$ for fixed value of $x_{1A}, x_{2A}, \gamma_A, x_{1B}, x_{2B}$, and γ_B. Finally, labeling the hydrogen atoms 1 and 2 and the oxygen atom 3 in molecule A and B we have for the nuclear charges $Z_{A\underset{=}{a}} \{Z_{A1}=1, Z_{A2}=1, Z_{A3}=8\}$ and $Z_{B\underset{=}{a}} \{Z_{B1}=1, Z_{B2}=1, Z_{B3}= 8\}$.

Although our language has suggested the "elemental constituents" were identifiable as "molecules", in fact it is clear that the mathematics is employed simply as a way of dividing the coordinates into two sets, those in one set - the so-called "internal coordinates" - being fixed throughout the entire consideration. Thus, we can in fact consider the motion of one fixed part of a molecule relative to another. Such considerations arise in conformational energy problems. Clearly, however, as different questions arise, the coordinates may be shifted from one set to the other.

Any N representable charge density may be written in terms of superimposing the optimum densities of the molecular constituents and then allowing that charge distribution to relax. We have

$$\rho_N(\vec{r}) = \sum_{m=1}^{M} \tilde{\rho}_{N_m}(\vec{r}; \vec{R}_m \vec{\Omega}_m g_m) + \Delta\rho \qquad \text{(II.14)}$$

where the translated optimum density for molecule m is

$$\tilde{\rho}_{N_m}(\vec{r};\vec{R}_m\vec{\Omega}_m g_m) = \tilde{\rho}_{N_m}(\vec{r};\vec{R}^o_m\vec{\Omega}^o_m g^o_m)\Bigg|_{\substack{\vec{R}^o_m \to \vec{R}_m \\ \vec{\Omega}^o{}_m \to \Omega_m \\ g_m \equiv g^o_m}} \qquad \text{(II.15)}$$

Equation (II.14) defines $\Delta\rho$ in terms of the variational charge density $\rho_N(\vec{r})$ and the exact molecular charge densities $\tilde{\rho}_{N_m}(\vec{r})$ assumed found in the asymptotic optimizations. In practice we could use those charge densities for the "elemental constituents" found by traditional quantum chemistry calculations. We must of course require that because of charge conservation

$$\int d\vec{r}\ \Delta\rho(\vec{r}) = 0.$$

Equation (II.13) can then be written in terms of $\Delta\rho$ and the intermolecular potential energy V expressed as a search over the N representable $\Delta\rho$'s:

$$V(\vec{R}_1\vec{\Omega}_1\ldots\vec{R}_M\vec{\Omega}_M;g_1..g_M) = \{\overset{\min}{\Delta\rho}\}\{[\varepsilon_o(N,[(\sum_{m=1}^{M}\tilde{\rho}_{N_m}) + \Delta\rho]) - \sum_{m=1}^{M}\varepsilon_o(N_m, \tilde{\rho}_{N_m})]$$

$$+ e^2\int d\vec{r}\Delta\rho(\vec{r})\int d\vec{r}'[\frac{\sum_{m=1}^{M}\tilde{\rho}_{N_m}(\vec{r}') + \sum_{m=1}^{M}\sum_{a=1}^{A_m} -Z_{ma}\delta(\vec{r}'-\vec{R}_{ma}) + \frac{\Delta\rho}{2}(\vec{r}')}{|\vec{r}-\vec{r}'|}]\}$$

$$+ \sum_{1\leqq m<n\leqq M}\{e^2[\int d\vec{r}\int d\vec{r}'\ \frac{\tilde{\rho}_{N_m}(\vec{r})\ \tilde{\rho}_{N_n}(\vec{r}')}{|\vec{r}-\vec{r}'|} + \sum_{a=1}^{A_m}\sum_{b=1}^{A_n}\frac{Z_{ma}\ Z_{nb}}{|\vec{R}_{ma}-\vec{R}_{nb}|}$$

$$+ \sum_{a=1}^{A_m} -Z_{ma}\int\frac{d\vec{r}\ \tilde{\rho}_{N_n}(\vec{r})}{|\vec{r}-\vec{R}_{ma}|} + \sum_{b=1}^{A_n} -Z_{nb}\int\frac{d\vec{r}\tilde{\rho}_{N_m}(\vec{r})}{|\vec{r}-\vec{R}_{nb}|}]\} \qquad \text{(II.16)}$$

Since we assume that the charge densities of the isolated molecules (or molecular fragments) are known, the variational search in (II.16) concerns only the first curley bracket (lines one and two) resulting in an optimum $\Delta\rho$ and a minimum value of this bracket. Terms in the second curley bracket (lines three and four) may be explicitly evaluated at once using the assumed $\tilde{\rho}_{N_m}$'s. These terms alone constitute the "classical rigid charge model" for intermolecular forces . The molecular charge densities for the molecular fragments could, for example, be used to define the various multipole moments, thus expressing this "classical Coulombic" interaction in the traditional multipole expansion. Finally, we may use the reciprocity theorem (24) to identify the second line itself as the <u>change</u> in the classical electrostatic energy obtained by changing the superimposed charge densities by $\Delta\rho$. The first line is entirely the quantum contribution to the intermolecular potential energy. We find this exact expression (II.16) to be a very convenient benchmark for analyzing various approximations on density functionals.

The prescriptions of the density functional formalism are thus clear. However, an explicit expression for $\varepsilon_o(N,\rho_N)$ as defined in Equation (II.10) has not yet been found in terms of ρ_N and N, although, we must quickly add, that efforts by many have taken us beyond the formal definition of Levy [16,17,18]. We shall now discuss some of the approximate forms for $\varepsilon_o(N,\rho_N)$.

The centerpiece of the Gordon-Kim model (5) is the choice of an explicit functional to approximate the exact prescription (II.10) of Levy. Thus, we begin by noting that $\varepsilon_o(N,\rho_N)$ may be analyzed in terms of traditional components (21):

$$\varepsilon_o(N,\rho_N) = \min_{\{|\Psi\rangle_{\rho_N}\}} [\,{}_{\rho_N}\langle\Psi| \sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_{i<j}^{N} \frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|\Psi\rangle_{\rho_N}\,] - J(\rho_N)$$

$$= {}_{\rho_N}\langle\tilde{\Psi}| \sum_{i=1}^{N} -\frac{\hbar}{2m}\nabla_i^2 + \sum_{i<j}^{N} \frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|\tilde{\Psi}\rangle_{\rho_N} - J(\rho_N)$$

$$= \varepsilon_{o,k}(N,\rho_N) + \varepsilon_{o,xc}(N,\rho_N). \qquad \text{(II.17)}$$

That is, although it is the expectation value of the operator sum $\hat{T} + \hat{V}_{ee}$ which is subject to the constrained variational procedure, nevertheless, once the optimum N-electron wave function $|\tilde{\Psi}\rangle\rho_N$ is found, it is possible to define separately the kinetic energy functional

$$\varepsilon_{o,k}(N,\rho_N) \equiv {}_{\rho_N}\langle\tilde{\Psi}| \sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2|\tilde{\Psi}\rangle_{\rho_N} \qquad \text{(II.18)}$$

and the exchange-correlation energy functional

$$\varepsilon_{o,xc}(N,\rho_N) = {}_{\rho_N}\langle\tilde{\Psi}| \sum_{i<j}^{N} \frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|\tilde{\Psi}\rangle_{\rho_N} - J(\rho_N). \qquad \text{(II.19)}$$

Although it is in fact only $\varepsilon_{o,xc}(N,\rho_N)$ that can be defined at this point with the introduction of a model (Hartree-Fock) reference state $|\Phi\rangle$ we may define as individual terms the "exchange energy" functional

$$\varepsilon_{o,x}(N,\rho_N) = \langle\Phi| \sum_{i<j} \frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|\,\Phi\rangle - J(\rho_N) \qquad \text{(II.20)}$$

and the "correlation energy" functional

$$\varepsilon_{o,c}(N,\rho_N) = {}_{\rho_N}\langle\tilde{\Psi}| \sum_{i<j}^{N} \frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|\tilde{\Psi}\rangle_{\rho_N} - \langle\Phi| \sum_{i<j}^{N} \frac{e^2}{|\vec{r}_i-\vec{r}_j|}|\Phi\rangle. \qquad \text{(II.21)}$$

The point remains, however, that with no one having yet carried out the variational search indicated in (II.17) none of these functionals is known explicitly in terms of N and ρ . In practice, the calculations based on the Gordon-Kim model replace the corresponding term with its asymptotic ($N\rightarrow\infty$) energy functional expression obtained from the extended ($N\rightarrow\infty$, $V\rightarrow\infty, \frac{N}{V} \rightarrow \rho$) electron gas (25).

$$\varepsilon_{o,k}(N,\rho) \rightarrow \lim_{N\rightarrow\infty} \varepsilon_{o,k}(N,\rho) = \varepsilon^{EG}_{o,k}(\rho) = (\frac{3h^2}{10m}) (3\pi^2)^{2/3} \int d\vec{r}\ \rho^{5/3},$$

$$\varepsilon_{o,x}(N,\rho) \rightarrow \lim_{N\rightarrow\infty} \varepsilon_{o,x}(N,\rho) = \varepsilon^{EG}_{o,x}(\rho) = - \frac{3e^2}{4}(\frac{3}{\pi})^{2/3} \int d\vec{r}\ \rho^{4/3},$$

$$\varepsilon_{o,c}(N,\rho) \rightarrow \mathrm{lin}_{N\rightarrow\infty}\ \varepsilon_{o,c}(N,\rho) = \varepsilon^{EG}_{o,c}(\rho) = \int d\vec{r}\ \rho\ E_{cor}(\rho). \qquad \text{(II.22)}$$

Here, the extended electron gas Hartree-Fock state is the usual Slater determinant of plane waves filling the Fermi sea. Explicit expression of the the integrand $E_{cor}(\rho)$ for various ranges of the density ρ are given by Parker, Snow and Pack (26). With $r_s = (4\pi\ a_o{}^3\rho/3)^{-1/3}$, where a_o is the Bohr radius, we have in atomic Rydberg units

$$E_{cor}(\rho) = \begin{cases} -0.0311\ \ln r_s - 0.048 + 0.009 r_s \ln r_s - 0.01 r_s,\ r_s \leqq 0.7, \\ -0.06156 + 0.01898\ \ln r_s,\ 0.7 < r_s < 10, \\ -0.438 r_s^{-1} + 1.325 r_s^{3/2} - 1.47 r_s^{-2} - 0.4\ r_s^{-5/2},\ 10 \leqq r_s,. \end{cases} \qquad \text{(II.23)}$$

Although in the extended electron gas the density is uniform, ρ is considered a function of position and normalized to N in applying the above expressions to finite many-electron systems. The two obvious facts - the inhomogeneity of ρ and the finite value of N - must be taken into account to introduce corrections to Equation (II.22). Additional corrections (27) involving the gradient of the density are known and may be included to account for the inhomogenous nature of the density in these finite many-electron systems. Rae (28) was the first to introduce a finite N correction to the functional part of the Gordon-Kim model in his consideration of the self-energy exchange correction. Later Waldman and Gordon (29) considered the possibility of correcting all three functionals for finite N by simply comparing the extended electron gas results with the self-consistent-field results for atoms and ions. However, they conclude that with the explicit inclusion of the induction and dispersion energies via the Drude model (vide infra) the correlation energy functional should simply be neglected. As a result Waldman and Gordon obtain finite N corrections for the kinetic and the exhange functionals in the form of N-dependent multiplicative factors of $\varepsilon^{EG}_{o,k}(\rho)$ and $\varepsilon^{EG}_{o,x}(\rho)$. Other modifications of these functionals, notably by Parr and his co-workers, have also been proposed. A bibliography of these functional modifications is included in Appendix A.

But even were the functional of Equation (II.10), or those of (II.18), (II.20), and (II.21) known precisely, the variational search indicated by $\overset{\min}{\Delta\rho}$ in Equation (II.16) in practice would be virtually impossible. Consequently, in the standard application of the Gordon-Kim model, in addition to using approximate functionals for $\varepsilon_o(N,\rho_N)$, the variational search over $\Delta\rho$ is never actually carried out to obtain the optimum charge density. Rather, with the charge densities for the isolated molecules obtained from traditional quantum chemical calculations, the charge density for the interacting system is approximated simply as the superposition of those molecular charge densities, rigidly translated and rotated with each molecule; that is, $\Delta\rho(\vec{r}) \equiv 0$.

Some of the consequences of the rigid superposition of charge densities are worth further comment. With $\Delta\rho \equiv 0$ (at all points $\vec{r}$) the term depicting the change in the classical electrostatic energy [the second line of Equation (II.16) (henceforth the "classical induction" term)] clearly vanishes. In fact, it must be noted that, consistent with the rigid superposition of charge densities, if the wave function for the interacting M molecules were approximated as the product of the rigidly translated normalized molecular wave functions for the isolated species (ignoring the exhange of electrons among the different factors), then also the difference of the energy functional terms would also vanish. That is, with $\{X_m\}$ an exclusive set of electronic coordinates associated with molecule m, we approximate

$$\tilde{\Psi}_{\rho_N}(x_1,x_2,\ldots x_N) \simeq \prod_{m=1}^{M} \tilde{\Psi}_{\tilde{\rho}_{N_m}}(\{X_m\};\underline{R}_m) \ . \qquad \text{(II.24)}$$

Then noting first that the superposition of charge densities holds,

$$\rho_N(\vec{r}) = {}_{\rho_N}\langle \tilde{\Psi} \,|\sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)\, |\tilde{\Psi}\rangle_{\rho_N} = \sum_{m=1}^{M} \tilde{\rho}_{N_m}(\vec{r} \ ; \vec{R}_m,\vec{\Omega}_m,g_m), \qquad \text{(II.25)}$$

we also now find that

$${}_{\rho_N}\langle\tilde{\Psi}|\sum_{m=1}^{M}[(T\{X_m\}) + V(\{X_m\})]+\sum_{m<n} V(\{X_m\},\{X_n\})|\tilde{\Psi}\rangle_{\rho_N} - J(\rho_N)$$

$$- [\sum_{m=1}^{M} \{_{\tilde{\rho}_{N_m}} \langle\tilde{\Psi}|T(\{X_m\}) + V(\{X_m\})\ |\tilde{\Psi}\rangle_{\tilde{\rho}_{N_m}} - J(\tilde{\rho}_{N_m})\}] = 0, \qquad \text{(II.26)}$$

where

$$T(\{X_m\}) = \sum_{i\in\{x_m\}} -\frac{\hbar^2}{2m}\nabla_i^2 \qquad \text{(II.27)}$$

$$V(\{X_m\}) = \sum_{i<j\in\{X_m\}} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \qquad \text{(II.28)}$$

$$V(\{X_m\},\{X_n\}) = \sum_{i\in\{X_m\}} \sum_{j\in\{X_n\}} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \qquad \text{(II.29)}$$

The removal of the sum Σ_m from the expectation value and the cancellation of the "cross terms" in $J(\rho_N)$ with the corresponding term arising from the sum $\Sigma_{m<n}\ V(\{X_m\},\{X_n\})$ happens precisely because antisymmetrization is ignored. The details of these cancellations are given in Appendix B. Therefore, with this superposition approximation for the charge density <u>and</u> the approximation Equation (II.24) for optimum wave function for the interacting system, all the terms in the first curley bracket of Equation (II.16) [the first and second lines] vanish leaving only the intermolecular Coulomb interaction terms of the rigid charge model. Of course, this wavefunction could not be optimum as required by Levy's prescription of the energy functional since it does not even possess the proper antisymmetry requirements. On the other hand simply antisymmetrizing and renormalizing the wavefunction (II.24) destroys the cancellation demonstrated in Equation (II.26) as it also fails to reproduce the superimposed charge density. Although the optimum wavefunction prescribed by Levy's constraint to satisfy the superposition of isolated molecular charge densities must be different than (II.24), it is reasonable to view this wave function as a zeroth order approximation. Thus, while there is nothing inconsistent with the superposition of charge density approximation and the non-vanishing of the quantum effects term in Eq. (II.16), it should be realized that these effects first enter at the level of exchange corrections to the zeroth order wave function which already contains intramolecular correlations. Considerations such as these will be important in our search for better approximate energy functionals, as well as a critical examination of the rigid superposition of charge densities ansatz.

In the "standard" Gordon-Kim model calculation, even though $\Delta\rho=0$, the approximate expressions currently used for $\varepsilon_o(N,\rho_N)$ lead to a non-vanishing difference $[\varepsilon_o(N,\rho_N) - \sum_{m=1}^{M} \varepsilon_o(N_m,\rho_{N_m})]$. It is generally concluded from the numercial results obtained (30-35) that these approximate calculations alone account for the short range, repulsive exchange forces. These, together with the rigid charge model contributions, seem to reflect sufficiently accurately the near region of the potential energy surface. That is, presumably the classical induction effects as given by the second line in Equation (II.16) are relatively unimportant at small separations. However, with the assumption $\Delta\rho=0$ it has been found that the modified electron gas functionals fail to reproduce accurately the long range dispersion forces. Moreover, all the calculations to date even at large distances neglect the explicit classical induction term. Consequently, some _ad hoc_ corrections must be introduced. But with $\Delta\rho$ entering both the expressions for the classical induction terms and the dispersion effects in ε_o, it is not at all clear how to correct -- but not to "overcorrect"

-- for the errors of using both approximate functionals and the rigid superposition of charge densities.

The usual "fix-ups" then incorporate long range forces either by the Drude model, as originally proposed by Kim and Gordon (5) and later modified by Waldman and Gordon (34), or by the Van der Waals expansions first considered by Rae (28) and developed by Pack and coworkers (30). In the Gordon Kim calculations the correlation energy functional term is simply neglected at all separations in favor of the Drude corrections. On the other hand, the Van der Waals corrections for longer intermolecular distances must be joined smoothly to the correlation energy functional results obtained for shorter distances.

In the Drude model corrected calculations of atom-diatomic potential energy surfaces (34) systematic discrepancies arise in the detailed angular dependence. These discrepancies have been attributed to the global manner in which the model polarizes the entire molecular valence shell without allowing for local variations when the atom is closer to one end of the diatomic than the other. On the other hand the angular dependent Van der Waal's coefficients, C_6 through C_8, are obtained from experimental data supplemented by quantum mechanical calculations. Consequently, the resulting angular dependence of these potential energy surfaces appears more realistic than those obtained with the Drude model; however most statements about their quantitative accuracy are equivocal. It is our hope that a deeper understanding of the density functionals will lead to expressions which have no need of these standard "fix-ups".

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APPENDIX A

CANCELATION OF QUANTUM EFFECTS IN THE PRODUCT WAVE FUNCTION APPROXIMATION

I GORDON-KIM MODEL AND REFINEMENTS

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APPENDIX B

APPROXIMATE DENSITY FUNCTIONAL USED IN THE GORDON KIM MODEL

Let us go through the details of the proof of those cancellations found in Eq. (II.26):

If we approximate

$$\tilde{\psi}_{\rho_N}(x_1,x_2,\ldots,x_N) = \prod_{m=1}^{M} \tilde{\psi}_{\tilde{\rho}_{N_m}}(\{X_m\};\underline{R}_m) \qquad \text{(B.1)}$$

where for the water dimer M=2, N=20, then we find

$$\rho_N(\vec{r}) = {}_{\rho_N}\langle\tilde{\psi}|\sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)|\tilde{\psi}\rangle_{\rho_N}$$

$$=\int dx_1\ldots dx_{20}\Big(\prod_{m=1}^{2}\tilde{\psi}_{\tilde{\rho}_{N_m}}(\{X_m\};\underline{R}_m)\Big)^{*}[\delta(\vec{r}-\vec{r}_1)+\ldots+\delta(\vec{r}-\vec{r}_{20})]$$

$$\times\ \Big(\prod_{m=1}^{2}\tilde{\psi}_{\tilde{\rho}_{N_m}}(\{X_m\};\underline{R}_m)\Big)$$

$$=\int dx_1\ldots dx_{20}(\tilde{\psi}^{*}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\tilde{\psi}^{*}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2))[\delta(\vec{r}-\vec{r}_1)+\ldots+\delta(\vec{r}-\vec{r}_{20})]$$

$$\times\ (\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\ \tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2))$$

where in this problem the exclusive sets of coordinates are

$$\{X_1\} \equiv \{x_1, x_2, \ldots, x_{10}\} \equiv \{\vec{r}_1, \xi_1, \vec{r}_2, \xi_2, \ldots, \vec{r}_{10}, \xi_{10}\},$$

and

$$\{X_2\} \equiv \{x_{11}, x_{12}, \ldots, x_{20}\} \equiv \{\vec{r}_{11}, \xi_{11}, \vec{r}_{12}, \xi_{12}, \ldots, \vec{r}_{20}, \xi_{20}\}.$$

Now let us calculate the first of these twenty terms. Performing the integration over $\vec{r}_1$ and using the delta function and the fact that each factor is normalized, we get

$$\sum_{\xi_1} \int d\vec{r}_2 \sum_{\xi_2} \ldots d\vec{r}_{10} \sum_{\xi_{10}} |\tilde{\psi}_{\tilde{\rho}_{N_m}} (\vec{r}, \xi_1, \vec{r}_2, \xi_2, \ldots, \vec{r}_{10}, \xi_{10})|^2$$

$$\times \int d\vec{r}_{11} \sum_{\xi_{11}} \ldots d\vec{r}_{20} \sum_{\xi_{20}} |\psi_{\rho_{Nm}} (\vec{r}_{11}, \xi_{11}, \ldots, \vec{r}_{20}, \xi_{20})|^2$$

$$= \sum_{\xi_1} \int d\vec{r}_2 \sum_{\xi_2} \ldots d\vec{r}_{10} \sum_{\xi_{10}} |\tilde{\psi}_{\tilde{\rho}_{Nm}} (\vec{r}, \xi_1, \vec{r}_2, \xi_2, \ldots, \vec{r}_{10}, \xi_{10})|^2$$

$$= \frac{\rho_{N_1}(\vec{r})}{N_1}$$

The integrals over the first ten delta function give us this same result while the second set (coordinates 11 thru 20) gives for each delta function $\tilde{\rho}_{N_2}(\vec{r})/N_2$. Thus, we get

$$\rho_N(\vec{r}) = \int dx_1 \ldots dx_{20} \tilde{\psi}^*_{\rho_N} \left(\sum_{i=1}^{20} \delta(\vec{r} - \vec{r}_i)\right) \psi_{\rho_N}$$

$$= \frac{\tilde{\rho}_{N_1}(\vec{r})}{N_1} (1+1+\ldots+1) + \frac{\tilde{\rho}_{N_1}(\vec{r})}{N_2} (1+1+\ldots+1)$$

$$= \frac{\tilde{\rho}_{N_1}(\vec{r})}{N_1} N_1 + \frac{\tilde{\rho}_{N_2}(\vec{r})}{N_2} N_2$$

$$=\sum_{m=1}^{2} \tilde{\rho}_{N_m}(\vec{r}). \qquad \text{(B.2)}$$

Now we consider the expression for the energy functional using the product form of the wave function. We have, using (II.27) as the definition of $T\{x_m\}|$,

$$_{\rho_N}\langle\psi|\sum_{m=1}^{M}(T\{x_m\})|\tilde{\psi}\rangle_{\rho_N} = {}_{\rho_N}\langle\tilde{\psi}|\sum_{m=1}^{M}\sum_{i\varepsilon\{X_m\}}-\frac{\hbar^2}{2m}\nabla_i^2|\tilde{\psi}\rangle_{\rho_N}.$$

For the water dimer M=2,N=20

$$_{\rho_N}\langle\tilde{\psi}|\sum_{m=1}^{2}\sum_{i\varepsilon\{X_m\}}-\frac{\hbar^2}{2m}\nabla_i^2|\tilde{\psi}\rangle=$$

$$\int dx_1\ldots dx_{20}\Big(\prod_{m=1}^{2}\tilde{\psi}_{\tilde{\rho}_{N_m}}(\{X_m\};\underline{R}_m)\Big)^{*}\Big[\sum_{m=1}^{2}\sum_{i\varepsilon\{X_m\}}-\frac{\hbar^2}{2m}\nabla_i^2\Big]\Big(\prod_{m=1}^{2}\tilde{\psi}_{\tilde{\rho}_{N_m}}(\{X_m\};\underline{R}_m)\Big)$$

$$=\int dx_1\ldots dx_{20}\tilde{\psi}^{*}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\tilde{\psi}^{*}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$\Big[\sum_{i=1}^{10}-\frac{\hbar^2}{2m}\nabla_i^2+\sum_{i=11}^{20}-\frac{\hbar^2}{2m}\nabla_i^2\Big]\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$=\int dx_1\ldots dx_{10}\tilde{\psi}^{*}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\Big(\sum_{i=1}^{10}-\frac{\hbar^2}{2m}\nabla_i^2\Big)\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)$$

$$\times\int dx_{11}\ldots dx_{20}\tilde{\psi}^{*}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$+\int dx_{11}\ldots dx_{20}\tilde{\psi}^{*}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)\Big(\sum_{i=11}^{20}-\frac{\hbar^2}{2m}\nabla_i^2\Big)\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$\times\int dx_1\ldots dx_{10}\tilde{\psi}^{*}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)$$

$$=\int dx_1\ldots dx_{10}\tilde{\psi}^{*}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\Big(\sum_{i=1}^{10}-\frac{\hbar^2}{2m}\nabla_i^2\Big)\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)$$

$$+\int dx_{11}\ldots dx_{20}\tilde{\psi}^{*}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)\left(\sum_{i=11}^{20}-\frac{\hbar^2}{2m}\nabla_i^2\right)\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};R_2)$$

$$={}_{\tilde{\rho}_{N_1}}\langle\tilde{\psi}|T\{X_1\}|\tilde{\psi}\rangle_{\tilde{\rho}_{N_1}}+{}_{\tilde{\rho}_{N_2}}\langle\tilde{\psi}|T\{X_2\}|\tilde{\psi}\rangle_{\tilde{\rho}_{N_2}}$$

$$=\sum_{m=1}^{2}{}_{\tilde{\rho}_{N_m}}\langle\tilde{\psi}|T\{X_m\}|\tilde{\psi}\rangle_{\tilde{\rho}_{N_m}}\ . \qquad (B.3)$$

This result cancels the identical term subtracted in (II.26). Similarly with $V\{x_m\}$ given by (II.28)

$${}_{\rho_N}\langle\tilde{\psi}|\sum_{m=1}^{M}V(\{X_m\})|\tilde{\psi}\rangle_{\rho_N}=$$

$$\int dx_1\ldots dx_{20}\left(\prod_{m=1}^{2}\tilde{\psi}_{\rho_{N_m}}(\{X_m\};\underline{R}_m)\right)^{*}\left[\sum_{m=1}^{2}V(\{X_m\})\right]\left(\prod_{m=1}^{2}\tilde{\psi}_{\tilde{\rho}_{N_m}}(\{X_m\};\underline{R}_m)\right)$$

$$=\int dx_1\ldots dx_{20}\tilde{\psi}^{*}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\tilde{\psi}^{*}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$\times[V(\{X_1\})+V(\{X_2\})]\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$=\int dx_1\ldots dx_{10}\tilde{\psi}^{*}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)V(\{X_1\})\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)$$

$$\times\int dx_{11}\ldots dx_{20}\tilde{\psi}^{*}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$+\int dx_{11}\ldots dx_{20}\tilde{\psi}^{*}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)V(\{X_2\})\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$\times\int dx_1\ldots dx_{10}\tilde{\psi}^{*}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)$$

$$=\int dx_1\ldots dx_{10}\tilde{\psi}^{*}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)V(\{X_1\})\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)$$

$$+\int dx_{11}\ldots dx_{20}\tilde{\psi}^{*}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)V(\{X_2\})\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$={}_{\tilde{\rho}_{N_1}}\langle\tilde{\psi}|V(\{X_1\})|\tilde{\psi}\rangle_{\tilde{\rho}_{N_1}} + {}_{\tilde{\rho}_{N_2}}\langle\tilde{\psi}|V(\{X_2\})|\tilde{\psi}\rangle_{\tilde{\rho}_{N_2}}$$

$$=\sum_{m=1}^{2} {}_{\tilde{\rho}_{N_m}}\langle\tilde{\psi}|V(\{X_m\})|\tilde{\psi}\rangle_{\tilde{\rho}_{N_m}} . \qquad (B.4)$$

Again this term cancels the substract identical term inequation (II.26). Now all the remains is

$${}_{\rho_N}\langle\tilde{\psi}|V(\{X_1\},\{X_2\})|\tilde{\psi}\rangle_{\rho_N} - J(\rho_N) + J(\tilde{\rho}_{N_1}) + J(\tilde{\rho}_{N_2}). \qquad (B.5)$$

We consider the classical self-energy term using (B.2).

$$J(\rho_N)= \frac{e^2}{2}\int d\vec{r}\int d\vec{r}\,'\frac{\rho_N(\vec{r})\ \rho_N(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}$$

$$= \frac{e^2}{2}\int d\vec{r}\int d\vec{r}\,'\frac{(\tilde{\rho}_{N_1}(\vec{r}) + \tilde{\rho}_{N_2}(\vec{r}))(\tilde{\rho}_{N_1}(\vec{r}\,') + \tilde{\rho}_{N_2}(\vec{r}\,'))}{|\vec{r}-\vec{r}\,'|}$$

$$= \frac{e^2}{2}\int d\vec{r}\int d\vec{r}\,'\frac{(\tilde{\rho}_{N_1}(\vec{r})\ \tilde{\rho}_{N_1}(\vec{r}\,') + \tilde{\rho}_{N_2}(\vec{r})\ \tilde{\rho}_{N_2}(\vec{r}\,') + 2\tilde{\rho}_{N_1}(\vec{r})\ \tilde{\rho}_{N_2}(\vec{r}\,'))}{|\vec{r}-\vec{r}\,'|}$$

$$=J(\tilde{\rho}_{N_1}) + J(\tilde{\rho}_{N_2}) + e^2\int d\vec{r}\int d\vec{r}\,'\frac{\tilde{\rho}_{N_1}(\vec{r})\ \tilde{\rho}_{N_2}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}. \qquad (B.6)$$

But clearly the first two terms above cancel the final two terms in the previous expression (B.5) leaving just

$$_{\rho_N}\langle\tilde{\psi}|V(\{X_1\},\{X_2\})|\tilde{\psi}\rangle_{\rho_N} - e^2\int d\vec{r}\int d\vec{r}\,'\frac{\tilde{\rho}_{N_1}(\vec{r})\,\tilde{\rho}_{N_2}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}. \qquad (B.7)$$

Now we shall show that these terms cancel. Using the definition (II.29), we obtain

$$_{\rho_N}\langle\tilde{\psi}|V(\{X_1\},\{X_2\})|\tilde{\psi}\rangle_{\rho_N} = {}_{\rho_N}\langle\tilde{\psi}|\sum_{i=1}^{10}\sum_{j=11}^{20}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}|\tilde{\psi}\rangle_{\rho_N}.$$

Let us evaluate one of the terms above, say for i=2,j=12

$$_{\rho_N}\langle\tilde{\psi}|\frac{e^2}{|\vec{r}_2-\vec{r}_{12}|}|\tilde{\psi}\rangle_{\rho_N} =$$

$$\int dx_1\ldots dx_{20}\,\tilde{\psi}^*_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\,\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$\text{X}\;\left(\frac{e^2}{|\vec{r}_2-\vec{r}_{12}|}\right)\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\,\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)$$

$$=\int d\vec{r}_2\int d\vec{r}_{12}\left(\frac{e^2}{|\vec{r}_2-\vec{r}_{12}|}\right)$$

$$\text{X}\;\Big[\sum_{\xi_2}\int\prod_{\substack{i=1\\ i\neq 2}}^{10}dx_i\;\tilde{\psi}^*_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\,\tilde{\psi}_{\tilde{\rho}_{N_1}}(\{X_1\};\underline{R}_1)\Big]$$

$$\text{X}\;\Big[\sum_{\xi_{12}}\int\prod_{\substack{j=11\\ j\neq 12}}^{20}dx_j\;\tilde{\psi}^*_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)\,\tilde{\psi}_{\tilde{\rho}_{N_2}}(\{X_2\};\underline{R}_2)\Big]$$

$$=\int dr\int dr\;\frac{e^2}{|\vec{r}_2-\vec{r}_{12}|}\;\left(\frac{\tilde{\rho}_{N_1}(\vec{r}_2)}{N_1}\right)\left(\frac{\tilde{\rho}_{N_2}(\vec{r}_{12})}{N_2}\right)$$

$$=\frac{e^2}{N_1N_2}\int d\vec{r}_2\int d\vec{r}_{12}\frac{\tilde{\rho}_{N_1}(\vec{r}_2)\,\tilde{\rho}_{N_2}(\vec{r}_{12})}{|\vec{r}_2-\vec{r}_{12}|}.$$

Then, performing the sums indicated above, we have

$$\rho_N\langle\tilde{\psi}|\sum_{i=1}^{1Q}\sum_{j=11}^{2Q}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}|\tilde{\psi}\rangle_{\rho_N}=\frac{e^2}{N_1N_2}\sum_{i=1}^{N_1}\sum_{j=11}^{N_2}\int d\vec{r}_i\int d\vec{r}_j\frac{\tilde{\rho}_{N_1}(\vec{r}_i)\,\tilde{\rho}_{N_2}(\vec{r}_j)}{|\vec{r}_i-\vec{r}_j|}$$

$$=e^2\int d\vec{r}_i\int d\vec{r}_j\,\frac{\tilde{\rho}_{N_1}(\vec{r}_i)\,\tilde{\rho}_{N_2}(\vec{r}_j)}{|\vec{r}_i-\vec{r}_j|}$$

$$=e^2\int d\vec{r}\int d\vec{r}\,'\frac{\tilde{\rho}_{N_1}(\vec{r})\,\tilde{\rho}_{N_2}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}. \qquad (B.8)$$

Thus, our proof is complete with the cancellation of these terms in (B.7).

VITA 2

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