A Concise Introduction to *Ab Initio* and Hybrid Density Functional Theory

SABA M. MATTAR

PROFESSOR EMERITUS

AND

HONORARY RESEARCH PROFESSOR

UNIVERSITY OF NEW BRUNSWICK

I Historical Perspective of Quantum Mechanical Calculations.

Quantum mechanical calculations, that predict total energies, electronic structure and molecular properties, may be classified into three categories. The first are *ab initio* calculations. They are "first principles" computations that are independent of any empirical parameters. The second are density functional theory (DFT) computations that are very similar in their methodology to *ab initio* techniques. However, DFT methods require a density functional that describes how the exchange and correlation energies of a molecule depend on the electron density. Furthermore, this density functional has additional parameters tailored to give optimal molecular energies. Depending on the choice of the density functional and its parameters it may yield results that are even better than high level *ab initio* computations. *Ab initio* and DFT methods give accurate electronic structures and molecular properties. However, they are expensive and limited to relatively small molecules.

Semi-empirical methods constitute the third class of computations. They make use of different parameters in their energy Hamiltonian for every atom with a particular atomic number. For example carbon and nitrogen have different parameters but sp2 and sp3 hybridized carbons would have the same parameters.

Although the approximations used in semi-empirical methods are more drastic than those made in *ab initio* and DFT techniques, this is offset by the accuracy of the experimental semi-empirical parameters used. In some cases, semi-empirical methods may be more accurate than low level *ab initio* calculations. In general, semi-empirical methods are more appropriate in dealing with large molecules where trends are important and numerical accuracy of the calculations is not paramount.

The Restricted Form of the Hartree-Fock Equations

The starting point of all quantum mechanical computations is to find the eigenvalues, E, and eigenfunctions, Ψ , of the wave equation

$$H\left(x, y, z, ict\right)\Psi_{rel}\left(x, y, z, ict\right) = E\Psi_{rel}\left(x, y, z, ict\right) \qquad (A.1)$$

Here the (x,y,z,ict) notation means that the relativistic Hamiltonian, H , is a function of the four component space-time coordinates x, y, z, and ict for every particle of the system. When dealing with molecules containing light atoms, this relativistic Dirac

Supplementary Material for the ACERT workshop June 11-12, 2015, Cornell University

equation may be approximated by the conventional three component Schrodinger Equation

$$H(x, y, z)\Psi(x, y, z) = E\Psi(x, y, z) \tag{A.2}$$

For convenience the functionality (x,y,z) is omitted and (A.2) is rewritten as

$$H\Psi = E\Psi \tag{A.3}$$

In the above three equations, the H operator represents the different types of energy (kinetic, nuclear-nuclear, electron-nuclear, electron-electron.....etc) of all particles of the chemical system under consideration. The eigenfunctions, E_n, are the resulting total energy of the system in a particular quantum state, n. The eigenvectors, Ψ, are the multi-particle wave function of the system.

To define the H operator one needs to know the atomic numbers and spatial coordinates of all the nuclei and electrons. In addition, the total charge, total spin (S), spin multiplicity (2S+1), and spin state (M_S) must also be defined.

The nuclear and electronic components of the Schrodinger equation may be separated by invoking the Born-Oppenheimer approximation. The electronic component takes the form

$$H_{elec}\Psi_{elec} = E_{elec}\Psi_{elec} \tag{A.4}$$

In this case, H_{elec} is the Hamiltonian of all electron interactions and Ψ_{elec} is the corresponding electronic "many body" wave function. To solve this equation one assumes that the all the electrons are independent of one another and consequently their energies are additive. Thus the H_{elec} becomes the sum of "one electron" effective Hamiltonians, H_i^{eff}

$$H_{elec} = \sum_{i=1}^{N} H_i^{eff}, \tag{A.5}$$

where N is the number of electrons. Since electrons are identical Fermions then

$$H_{elec} = NH_i^{eff}, \tag{A.6}$$

and the Schrodinger equation in (A.4) is reduced to

$$H^{eff}\psi_{elec} = \varepsilon_{elec}\psi_{elec} \tag{A.7}$$

and can be solved numerically.   The lower case "one electron" eigenfunctions, ψ_{elec},
are known as "one-electron" molecular orbitals and the resulting eigenvalues, ε_n, are
called the orbital energies.   The total probability of finding an electron in space is related
to a specific quantized molecular orbital, ψ_i, via the relation

$$\iiint \psi_i^*\left(x,y,z\right)\psi_i\left(x,y,z\right)dxdydz = \int \left|\psi_i\left(x,y,z\right)\right|^2 d\tau = 1 \tag{A.8}$$

The electrons of the system in its ground state populate the molecular orbitals of
lowest energies first. A maximum of two electrons can occupy every orbital. When the
number of electrons is even, in most cases, each molecular orbital contains either two
electrons or is empty. This leads to a closed shell system. When the number of electrons
is odd then at least one orbital must be singly occupied. The total electronic spin is S=1/2
and the corresponding spin multiplicity is 2S+1 = 2 or a doublet state.   This is the
situation for the free radicals studied here.

The most convenient way to solve the eigenvalue problem of (A.7) is to represent
ψ_{elec} as an expansion of known functions centered around the nuclei. These functions are
known as atomic orbitals, φ , and thus

$$\psi_i = \sum_{v} C_{vi}\varphi_v \tag{A.9}$$

where the summation runs over the number of nuclei. Therefore (A.7) becomes

$$H^{eff} \sum_{v} C_{vi}\varphi_v = \varepsilon_{elec} \sum_{v} C_{vi}\varphi_v \tag{A.10}$$

and by multiplying from the left by φ_μ and rearranging one obtains

$$\sum_{v} C_{vi}\int \varphi_\mu H^{eff} \varphi_v d\tau = \varepsilon_{elec} \sum_{v} C_{vi}\int \varphi_\mu \varphi_v d\tau \tag{A.11}$$

This last equation takes the form

$$\sum_{v} C_{vi} H^{eff}_{\mu v} = \varepsilon_{elec} \sum_{v} C_{vi} S_{\mu v}. \tag{A.12}$$

or

$$H^{eff}C = \varepsilon_{elec}SC. \tag{A.13}$$

In (A.13) the overlap integral matrix elements, $S_{\mu v}$, are given by

$$S_{\mu v} = \int \varphi_\mu \varphi_v d\tau \tag{A.14}$$

and are the overlap between atomic orbitals situated on the μ and υ nuclei. If there is no overlap between these nuclei then $S_{\mu\nu} = 0$. On the other hand, if the overlap is complete then $S_{\mu\nu} = 1$. Hence the S matrix is positive and definite. Similarly $H_{\mu\nu}^{eff}$ is

$$H_{\mu\nu}^{eff} = \int \varphi_\mu H^{eff} \varphi_\nu d\tau. \tag{A.15}$$

The matrix Schrodinger equation of (A.13) is a compound eigenvalue problem because it contains two matrix operators $\mathbf{H}^{eff}$ and $\mathbf{S}$. Since $\mathbf{S}$ is a positive definite symmetric matrix, it can first be diagonalized by a similarity transformation to yield the diagonal matrix $\mathbf{s}$. The $\mathbf{s}^{-1/2}$ is then easily calculated taking the inverse square root of its diagonal elements s_{ii}. The non-diagonal form, $\mathbf{S}^{-1/2}$, is then obtained by the reverse similarity transformation and is used to diagonalize the Hamiltonian in Eq.(A.13). The end result, that yields the energy, is

$$\left(S^{\frac{1}{2}}C\right)^\dagger \left(S^{-\frac{1}{2}}HS^{-\frac{1}{2}}\right)\left(S^{\frac{1}{2}}C\right)=\varepsilon \tag{A.16}$$

Since electrons obey Fermi-Dirac statistics, their wave functions should be antisymmetric when a pair of electrons are exchanged in space. To fulfill this condition, Slater suggested that the multi-electron wave functions (spin orbitals), which written as a product of a spin part, $\sigma = \alpha, \beta$, and spatial component, ψ_i, must be expressed as determinants. For example the N electron wave function takes the normalized (spin restricted) form,

$$\chi\left(r_1, r_2, \cdots r_N\right) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1)\alpha & \psi_1(2)\alpha & \psi_1(3)\alpha & \cdots & \psi_1(N)\alpha \\ \psi_1(1)\beta & \psi_1(2)\beta & \psi_1(3)\beta & \cdots & \psi_1(N)\beta \\ \psi_2(1)\alpha & \psi_2(2)\alpha & \psi_2(3)\alpha & \cdots & \psi_2(N)\alpha \\ \psi_2(1)\beta & \psi_2(2)\beta & \psi_2(3)\beta & \cdots & \psi_2(N)\beta \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \psi_N(1)\beta & \psi_N(2)\beta & \psi_N(3)\beta & \cdots & \psi_N(N)\beta \end{vmatrix} \tag{A.17}$$

To properly apply the independent Hamiltonian approximation, all the Hamiltonian operators must be a function of a single electron or "one electron" operators. In general the electronic Hamiltonian operator for N electrons and M nuclei, in atomic units, is

$$H_{elec} = H_{kin} + H_{eN} + H_{ee}$$

$$= \frac{-1}{2}\sum_{i=1}^{N}\nabla^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} \tag{A.18}$$

The first term is the sum of the kinetic energies of the N electrons while the second term is the sum of the Coulomb attraction between all N electrons with M nuclei. They are the sum of a series of one electron operators. The last operator in Eq.(A.18) represents the electron-electron repulsions. Every one of its terms depends on the distance between the electrons i and j. It is a sum of "two electron" operators and causes the electrons to be dependent on one another. It impedes us from applying Eqs. (A.5)- (A.16) that solve the one-electron Schrodinger equation.

To overcome this problem, we make use of the Hartree-Fock approximation where H_{ee} is replaced by a sum of N operators. Each operator represents the energy of one-electron due to the average effects of the remaining N-1 electrons. This modified H_{elec} operator is now called the Fock operator, F. According to Roothan, we may now proceed to solve the Schrodinger equation starting from an equation equivalent to Eq. (A.13).

$$FC = \varepsilon_{elec}SC. \tag{A.19}$$

Where the Fock matrix elements, $F_{\mu v}$, are equivalent to those of Eq.(A.15) and take the form

$$F_{\mu v} = \frac{-1}{2}\int \varphi_\mu \nabla^2 \varphi_v \, d\tau - \sum_{A=1}^{M}\int \varphi_\mu \frac{Z_A}{r_A}\varphi_v d\tau + \sum_{\lambda,\sigma=1}^{N}\sum_{i=1}^{occup} C_{\mu i}C_{vi}$$
$$\times \left[\int \varphi_\mu(r)\varphi_v(r)\frac{1}{r_{rs}}\varphi_\lambda(s)\varphi_\sigma(s)\,d\tau_r d\tau_s - \int \varphi_\mu(r)\varphi_\lambda(r)\frac{1}{r_{rs}}\varphi_v(s)\varphi_\sigma(s)\,d\tau_r d\tau_s\right] \tag{A.20}$$

When the two electron integrals, involving the electrons r and s, are abbreviated using the "chemist's notation" we obtain

$$F_{\mu v} = \frac{-1}{2}\int \varphi_\mu \nabla^2 \varphi_v \, d\tau - \sum_{A=1}^{M}\int \varphi_\mu \frac{Z_A}{r_A}\varphi_v d\tau + \sum_{\lambda,\sigma=1}^{N}\sum_{i=1}^{occup} C_{\mu i}C_{vi}\left[(\mu v|\lambda\sigma) - \frac{1}{2}(\mu\lambda|v\sigma)\right] \tag{A.21}$$

The $(\mu\nu|\lambda\sigma)$ two electron integrals in Eq. (A.21) are the Coulomb repulsion between the electron clouds of the two electrons. The exchange integrals $(\mu\lambda|\nu\sigma)$ are a direct result of using the wave functions in the form of Slater determinants.

The $F_{\mu\nu}$ matrix elements depend on the $C_{\mu i}$ and $C_{\nu i}$ coefficients. Thus to generate the eigenvalue problem in Eq. (A.19) an initial guess of the $C_{\mu i}$ and $C_{\nu i}$ wave function coefficients is done. Eq. (A.19) is then solved in a fashion identical to that going from Eq. (A.13) to (A.16). This yields a set of eigenvalues or molecular orbital energies, ε_n, and the corresponding molecular orbitals with new $C_{\mu i}$ and $C_{\nu i}$ coefficients. These coefficients are used once more to determine a new Fock matrix, $F_{\mu\nu}$, which is used to construct a new eigenvalue equation similar to that of (A.20). The process is repeated until the difference between the new total energy of the molecule and the one from the previous iteration is less than a certain defined value. This iterative process is known as the Self-Consistent-Field (SCF) procedure. Another conversion criterion for stopping the SCF procedure is that the electronic density,

$$P_{\mu\nu} = \sum_{i=1}^{occup} C_{\mu i} C_{\nu i} \tag{A.22}$$

from one iteration to the next is less than a certain defined value.

The Unrestricted Form of the Hartree-Fock Equations

The previous description has assumed that the spatial components of the ith electron, ψ_i, of the $\psi_i\alpha$ and $\psi_i\beta$ spin orbitals are the same. This is known as the spin restricted Hartree-Fock (RHF) formalism. However, to obtain the correct spin density at a given point in space or compute the isotropic hyperfine coupling constants, a spin unrestricted formalism (UHF) must be used. In a spin unrestricted wave function, the spatial components of $\psi_i\alpha$ and $\psi_i\beta$ are not necessarily the same. Thus one may express them as $\psi_i^\alpha\alpha$ and $\psi_i^\beta\beta$.

Pople and Nesbet have derived the unrestricted Hartree-Fock equations. As a result, the wave functions come in pairs as:

$$\psi_i^{\alpha} = \sum_v C_{vi}^{\alpha} \varphi_v \tag{A.23}$$

for the α spin and

$$\psi_i^{\beta} = \sum_v C_{vi}^{\beta} \varphi_v \tag{A.24}$$

for the β spin. The corresponding Fock matrices take the form

$$F_{\mu v}^{\alpha} = H_{\mu v}^{\alpha} + \sum_{\lambda,\sigma=1}^{N} \left[P_{\lambda\sigma}^{T} \left(\mu v \middle| \lambda\sigma \right) - \frac{1}{2} P_{\lambda\sigma}^{\alpha} \left(\mu\lambda \middle| v\sigma \right) \right] \tag{A.25}$$

and

$$F_{\mu v}^{\beta} = H_{\mu v}^{\beta} + \sum_{\lambda,\sigma=1}^{N} \left[P_{\lambda\sigma}^{T} \left(\mu v \middle| \lambda\sigma \right) - \frac{1}{2} P_{\lambda\sigma}^{\beta} \left(\mu\lambda \middle| v\sigma \right) \right]. \tag{A.26}$$

Here $H_{\mu v}^{\alpha}$ and $H_{\mu v}^{\beta}$ are the one-electron operators for the α and β spins respectively. The densities in the previous two eqautions are defined as

$$P_{\mu v}^{T} = P_{\mu v}^{\alpha} + P_{\mu v}^{\beta} = \sum_{i=1}^{occup} C_{\mu i}^{\alpha} C_{vi}^{\alpha} + \sum_{i=1}^{occup} C_{\mu i}^{\beta} C_{vi}^{\beta} \tag{A.27}$$

At this stage it is worth noting that the **difference** between $P_{\mu v}^{\alpha}$ and $P_{\mu v}^{\beta}$ at a certain nucleus is proportional to the isotropic hyperfine coupling constant, a^{iso}, of that nucleus. It is very important to realize that $F_{\mu v}^{\alpha}$ and $F_{\mu v}^{\beta}$ are coupled to one another because they are functions of the total density, $P_{\mu v}^{T}$, in Eqs. (A.25) and (A.26).

This procedure ultimately leads to two coupled Hartree-Fock eigenvalue equations similar to Eq. (A.19). They are:

$$F^{\alpha}C^{\alpha} = \varepsilon_{elec}^{\alpha} SC^{\alpha} \tag{A.28}$$

and

$$F^{\beta}C^{\alpha} = \varepsilon_{elec}^{\beta} SC^{\beta}. \tag{A.29}$$

Finally these two equations are solved by the above mentioned SCF procedure to yield the molecular orbitals and their energies. Once this is accomplished, the total energy and any other molecular property may then be computed.

2. The Basic Principles of Hybrid Density Functional Techniques

Hybrid density functional (HDF) computations have become extremely popular in the last few years. They are now the preferred form of routine quantum mechanical calculations in most laboratories. The methods are popular and yield results that are very accurate.

As presented in the previous section, during the procedure of an electronic structure quantum mechanical computation one attempts to find the eigenvalues, E_{elec}, and eigenvectors, ψ_{elec}, of the non-relativistic Schrödinger equation

$$H_{elec} \Psi_{elec} = E_{elec} \Psi_{elec} \tag{A.30}$$

The electron density at a particular point in space, r_1, therefore takes the form

$$\rho(r_1) = \int \left| \Psi_{elec}(r_1, r_2, r_3.......r_N) \right|^2 dr_2 dr_3.......dr_N \tag{A.31}$$

The integration over the variables dr_2, dr_3...dr_N in Eq. (A.31) simplifies the expression for the electron density since it becomes only a function of r_1. As a result, molecular quantum mechanical computations may be greatly simplified if $\rho(r_1)$ can be used instead of $\Psi_{elec}(r_1, r_2, r_3.......r_N)$. Hohenberg and Kohn proposed that the energy, E_{elec}, depends only on $\rho(r_1)$ and E may be written as:

$$E = E[\rho]. \tag{A.32}$$

However this dependency is a complicated unknown function of the electron density (called a functional).

Later Kohn and Sham formulated a procedure for solving the Schrödinger equation using Eq.(A.32). The resulting equations are very similar to those used in the Hartree-Fock procedure. The very close similarity between these equations made it possible to use the Hartree-Fock computer codes, developed over the years, to perform density functional calculations without too many changes.

Just as in the case of Hartree-Fock theory, there exists a corresponding "restricted" version of the Roothan equations leading to restricted density functional methods. Similarly there are "unrestricted" density functional techniques that solve

equations equivalent to the those of Pople and Nesbet. A discussion of the more general unrestricted form of density functional theory will be given below.

In a fashion similar to Hartree-Fock theory, basis functions are introduced and the corresponding wavefunctions, known as the Kohn-Sham orbitals, are [2]

$$\psi_i^\alpha = \sum_v C_{vi}^\alpha \varphi_i \tag{A.33}$$

for the α spin and

$$\psi_i^\beta = \sum_v C_{vi}^\beta \varphi_i \tag{A.34}$$

for the β spin. From the coefficients of Eqs. (A.33) and (A.34) the corresponding spin density matrices may be obtained

$$P_{\mu v}^\alpha = \sum_{i=1}^{occup} C_{\mu i}^\alpha C_{vi}^\alpha \equiv \rho^\alpha \tag{A.35}$$

and

$$P_{\mu v}^\beta = \sum_{i=1}^{occup} C_{\mu i}^\beta C_{vi}^\beta \equiv \rho^\beta. \tag{A.36}$$

The total electron density is simply the sum of Eqs. (A.35) and (A.36)

$$P_{\mu v}^T = P_{\mu v}^\alpha + P_{\mu v}^\beta. \tag{A.37}$$

The main difference between the Kohn Sham orbitals in Eqs. (A.33) and (A.34) and the Hartree-Fock orbitals is that they are solutions to the Kohn-Sham equations, which in principle, have an exact electron density leading to exact total energies [2].

From the Pople-Nesbet equations, of the previous section where the μvth Fock matrix elements of the α and β spins are:

$$F_{\mu v}^\alpha = H_{\mu v}^\alpha + \sum_{\lambda\sigma} \left\{ P_{\lambda\sigma}^T \left(\mu v | \lambda\sigma \right) - P_{\lambda\sigma}^\alpha \left(\mu\lambda | v\sigma \right) \right\} \tag{A.38}$$

and

$$F_{\mu v}^\beta = H_{\mu v}^\beta + \sum_{\lambda\sigma} \left\{ P_{\lambda\sigma}^T \left(\mu v | \lambda\sigma \right) - P_{\lambda\sigma}^\beta \left(\mu\lambda | v\sigma \right) \right\} \tag{A.39}$$

The Kohn-Sham equations leave the Coulomb energy terms, $P_{\lambda\sigma}^T \left(\mu v | \lambda\sigma \right)$, unchanged but replace the exchange energy terms, $P_{\lambda\sigma}^{\alpha,\beta} \left(\mu\lambda | v\sigma \right)$, by the exchange correlations energy functionals, F^{XC}, to give [2]

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu}^{\alpha} + \sum_{\lambda\sigma} P_{\lambda\sigma}^{T} \left(\mu\nu|\lambda\sigma\right) + F_{\mu\nu}^{XC\alpha} \tag{A.40}$$

and

$$F_{\mu\nu}^{\beta} = H_{\mu\nu}^{\beta} + \sum_{\lambda\sigma} P_{\lambda\sigma}^{T} \left(\mu\nu|\lambda\sigma\right) + F_{\mu\nu}^{XC\beta} \tag{A.41}$$

These equations are solved, by the self-consistent-field (SCF) procedure in exactly the same way as the Pople-Nesbet equations. The resulting energy, where E_{XC} is the exchange-correlation energy becomes:

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu} \sum_{\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \left(\mu\nu|\lambda\sigma\right) + E_{XC} \tag{A.42}$$

The E_{XC} and F^{XC} are related to one another via the exchange-correlation energy density per unit volume, f. It is a function of both α and β spin electron densities. In fact

$$E_{XC} = \int f\left(\rho^{\alpha}, \rho^{\beta}\right) d\tau, \tag{A.43}$$

$$F_{\mu\nu}^{XC\alpha} = \int \left(\frac{\partial f\left(\rho^{\alpha}, \rho^{\beta}\right)}{\partial \rho^{\alpha}}\right) \varphi_{\mu}\varphi_{\nu} \, d\tau \tag{A.44}$$

and

$$F_{\mu\nu}^{XC\beta} = \int \left(\frac{\partial f\left(\rho^{\alpha}, \rho^{\beta}\right)}{\partial \rho^{\beta}}\right) \varphi_{\mu}\varphi_{\nu} \, d\tau \tag{A.45}$$

From the above treatment it is seen that the Kohn-Sham procedure avoids the complexity of post Hartree-Fock procedures such as configuration interaction. The correlation energy is obtained from an effective one-electron exchange-correlation term given in Eqs. (A.44) and (A.45).

Historically the first exchange energy functional was proposed by Slater at MIT and was based on the model of a uniform homogenous electron gas. It did not contain any electron-electron correlation energy terms [3]

$$f\left(\rho^{\alpha}, \rho^{\beta}\right) = -\frac{9}{4}\alpha\left(\frac{3}{4\pi}\right)^{\frac{1}{3}}\left[\left(\rho^{\alpha}\right)^{\frac{4}{3}} + \left(\rho^{\beta}\right)^{\frac{4}{3}}\right]. \tag{A.46}$$

leading to

$$F_{\mu\nu}^{XC\alpha} = -3\alpha\left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \int \left(\rho^{\alpha}\right)^{\frac{1}{3}} \varphi_{\mu}\varphi_{\nu} \, d\tau. \tag{A.47}$$

and

$$F_{\mu\nu}^{XC\beta} = -3\alpha \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \int \left(\rho^\beta\right)^{\frac{1}{3}} \varphi_\mu \varphi_\nu \, d\tau. \tag{A.48}$$

This is known as the local spin density (LSD) approximation.

While Eqs. (A.47) - (A.48) represent the exchange in a simple analytic form, there is no known simple form for the uniform electron gas correlation energy. LSD functionals that include electron-electron correlation terms are based on numerical Monte Carlo simulations of the homogeneous electron gas such as those obtained by Ceperly, Alder, Perdew and Zunger [4]. These numerical results are then fit to formulae which are, in turn, added as extra terms in Eqs.(A.47) - (A.48) as has been done by Vosko, Wilk and Nussair [5].

In reality molecular electron densities are higher near a nucleus and lower in the interatomic regions. They asymptotically go to zero at infinite distances. This density change implies that it has a gradient. Improved functionals that take this fact into account are called *generalized gradient functionals* [6].

$$F_{\mu\nu}^{XC\alpha} = \int \left\{ \frac{\partial f\left(\rho^\alpha, \rho^\beta\right)}{\partial \rho^\alpha} \varphi_\mu \varphi_\nu + \left[2\frac{\partial f\left(\rho^\alpha, \rho^\beta\right)}{\partial \gamma_{\alpha\alpha}} \nabla \rho^\alpha + \frac{\partial f\left(\rho^\alpha, \rho^\beta\right)}{\partial \gamma_{\alpha\beta}} \nabla \rho^\beta \right] \cdot \nabla\left(\varphi_\mu \varphi_\nu\right) \right\} d\tau. \tag{A.49}$$

In the last equation ∇ is the gradient operator and $\gamma_{ij} = \nabla \rho^i \cdot \nabla \rho^j$. As similar equation exists for the β spin.

Hybrid Density Functionals

If a percentage of the original Hartree-Fock exchange term is included in Eq. (A.49) better agreement between theory and experiment is obtained. This modified functional is known as a hybrid density functional (HDF). The most popular HDF is the B3LYP functional. This functional's exchange component consists of a 20% Hartree-Fock exchange term, an 8% Slater exchange term [3], given by Eqs. (A.47) - (A.48) and a 72% Becke-88 gradient exchange term [7] that takes the form

$$E_{XC} = -\frac{9}{4}\alpha \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \int \left[\left(\rho^\alpha\right)^{\frac{4}{3}} + \left(\rho^\beta\right)^{\frac{4}{3}} \right] g(x) d\tau. \tag{A.50}$$

with

$$g(x) = 1 + \frac{2}{3}\left(\frac{4\pi}{3}\right)^{\frac{1}{3}} \frac{bx^2}{\left[1 + 6bx\frac{3}{2}\left(\frac{3}{4\pi}\right)^{\frac{1}{3}}\sinh(x)\right]}, \tag{A.51}$$

and b =0.0042. The correlation component consists of 19% Vosko-Wilk-Nussair functional [61] and the rest is the Lee-Yang-Parr functional [8].

The percentages in the B3LYP functional were determined ***empirically*** by comparing the 42 ionization potentials, 56 atomization energies, 10 atomic energies and 8 proton affinities of a standard set of molecules known as the G1 set. HDF codes are now available commercially such as Gaussian and ORCA. In summary the B3LYP functional may be written in the condensed form as:

$$E_{XC}{}^{B3LYP} = 0.08E_X{}^{LSD} + 0.2E_X{}^{HF} + 0.72\ E_X{}^{Becke} + 0.19E_C{}^{VWN} + 0.81E_C{}^{LYP}.$$

Purdue, Ernzerhof and Burke [9], using Gorling-Levy perturbation theory [10] suggested that the empirical exchange coefficients be replaced by a ratio of 1/4. Adamo and Barone [11] have implemented this non-empirical functional which takes the form

$$E_{XC}{}^{B1LYP} = 0.75(E_X{}^{LSD} + E_X{}^{Becke}) + 0.25E_X{}^{HF} + E_C{}^{LYP}.$$

It is found to give superior results when compared to the B3LYP functional and has been used in our laboratories to compute the electronic structure, optimal geometries and hyperfine coupling constants of a variety of open shell free radicals.

References

[1]   P. Hohenberg and W. Kohn, Physical Review B, 136, (1964) B864.

[2]   W. Kohn and L. J. Sham, Physical Review , 140, (1965) A1133.

[3]   J. C. Slater, Quantum Theory of Molecules and Solids, Vol 4: The Self Consistent Field Theory for Moles and Solids (McGraw Hill, New York, 1974).

[4]   J. P. Perdew and A. Zunger, Phys. Rev. B, 23, (1981) 5048.

[5]   S. H. Vosko, L. Wilk and M. Nussair, Can. J. Phys. 58, (1980) 1200.

[6,7]   A. D. Becke, Phys. Rev. A, 38, (1988) 3098.

[8]   C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 37, (1988) 785.

[9]   J. P. Perdew, M. Ernzerhof and K. Burke, J. Chem. Phys., 105, (1996) 9982.

[10]   A. Gorling and M. Levy, Phys. Rev. B, 47, (1993) 13105.

[11]   C. Adamo, V. Barone, Chem. Phys. Lett. 274 (1997) 242.