



CHAPTER II

THEORY

2.1 Background

The basis for atoms and molecules is formed by the coulombic attraction between a set of positively charged nuclei surrounding by a number of electrons [47, 48]. The potential between two particles with charges q_i and q_j separated by a distance r_{ij} (in centimeter-gram-second (cgs) unit) is given by

$$V_{ij} = V(r_{ij}) = \frac{q_i q_j}{r_{ij}} \quad (2.1)$$

Due to electron displays both wave- and particle-like characteristics thus; it cannot be described by classical mechanics. However, it can be described by the quantum mechanical equation *i.e.* the time dependent Schrödinger equation.

$$\hat{H}\Psi = ih \frac{\partial \Psi}{\partial t} \quad (2.2)$$

\hat{H} is the Hamiltonian operator; h is Planks constant divided by 2π and i is the imaginary number. The simpler version of Equation (2.2) is the time-independent (or static) Schrödinger equation given by:

$$\hat{H}\Psi = E\Psi \quad (2.3)$$

For a general N particle system the Hamiltonian operator contains kinetic (T) and potential (V) operators for all particles.

$$\hat{H} = T + V$$
$$T = \sum_{i=1}^N T_i = -\sum_{i=1}^N \frac{h^2}{2m_i} \nabla_i^2$$

$$\nabla_i^2 = \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)$$

$$V = \sum_{i=1}^N \sum_{j>1}^N V_{ij} = \sum_{i=1}^N \sum_{j>1}^N \frac{q_i q_j}{r_{ij}} \quad (2.4)$$

Where ∇_i^2 is the Laplacian operator acting on particle i . The potential energy operator is the Coulomb potential Equation (2.4). Due to nuclei are 1836 times much heavier than electrons, their velocities are much smaller. The Schrödinger equation can be separated into two parts, where one-part describes the electronic wavefunction for a fixed nuclear geometry, and another part describes the nuclear wavefunction. The energy from the electronic wavefunction plays the role of a potential energy. This separation is called Born-Oppenheimer approximation. The Born-Oppenheimer approximation is usually a very good approximation. For the hydrogen molecule the error is of the order of 10^{-4} a.u., and for systems with heavier nuclei, the approximation becomes better [48].

The Potential Energy Surfaces (PES) is known when a large number of nuclear geometries (and possibly also for several electronic states) has been solved by the electronic Schrödinger equation. This can then be used for solving the nuclear part of the Schrödinger equation. If there are N nuclei, there are $3N$ coordinates that define the geometry. Of these coordinates, three coordinates describe translation and another three coordinates describe rotation of the molecule. For a linear molecule, only two coordinates are necessary to describe the rotation. Thus, the molecular vibrations could be defined by $3N - 6(5)$ coordinates. It should be noted that nuclei are heavy enough for quantum effect to be almost negligible, they behave to a good approximation as classical particles.

The typical molecular Hamiltonian operator [48] consists of the kinetic term for electrons (T_e) and nuclei (T_n), the attraction between electrons and nuclei (V_{ne}), inter-electronic (V_{ee}) and internuclear (V_{nn}) repulsions. Casting the Hamiltonian into mathematical notation, we have

$$\begin{aligned}
\hat{H} &= -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}} \\
&= T_e + T_n + V_{ne} + V_{ee} + V_{nn}
\end{aligned} \tag{2.5}$$

where i and j run over electrons, k and l run over nuclei, m_e is the mass of the electron, m_k is the mass of nucleus k , e is the charge on the electron, Z is an atomic number, and r_{ab} is the distance between particles a and b . All are in cgs unit.

Applying the Born-Oppenheimer approximation Equation (2.6) is separated to

$$\hat{H} = \hat{H}_{\text{nu}} + \hat{H}_{\text{elec}} \tag{2.6}$$

where \hat{H}_{nu} is nuclear Hamiltonian. Thus,

$$\begin{aligned}
\hat{H} &= -\sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 + \left\langle -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} \right\rangle + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}} \\
&= -\sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 + E_{\text{elec}}(\{r_k\}) + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}} \\
&= -\sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 + E_{\text{tot}}(\{r_k\})
\end{aligned} \tag{2.7}$$

and \hat{H}_{elec} is electronic Hamiltonian

$$\hat{H}_{\text{elec}} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} \tag{2.8}$$

If the electronic Schrödinger equation ($H_{\text{elec}} \Psi_{\text{elec}} = \epsilon \Psi$) is solved, the nuclear Schrödinger equation can also be solved. Even for the simplest molecular system, the electronic Schrödinger equation can still not be solved exactly.

Additional approximation is needed.

2.2 Spatial Orbitals and Spin Orbitals

We define an orbital as a wavefunction for a single particle, an electron. Because we are concerned with electronic structure of a molecular, molecular orbitals will be used for the wavefunctions of the electrons in a molecule. A spatial orbital $\psi_i(\mathbf{r})$, is a function of the position vector \mathbf{r} and describes the spatial distribution of an electron such that $|\psi_i(\mathbf{r})|^2 d\mathbf{r}$ is the probability of finding the electron in the small volume element $d\mathbf{r}$ surrounding \mathbf{r} . Spatial molecular orbitals will usually be assumed to form an orthonormal set

$$\int d\mathbf{r} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) = \delta_{ij} \quad (2.9)$$

If the set of spatial orbitals $\{\psi_i\}$ is complete, then any arbitrary function $f(\mathbf{r})$ could be exactly expanded as

$$f(\mathbf{r}) = \sum_{i=1}^K a_i \psi_i(\mathbf{r}) \quad (2.10)$$

where a_i is a coefficient. The finite set of orbitals $\{\psi_i / i = 1, 2, \dots, K\}$, span a certain region of the complete space.

An electron is necessary to specify its spin. The wavefunction for an electron that describes both its spatial distribution and its spin is a spin orbital, $\chi(\mathbf{x})$, where \mathbf{x} indicates both space (\mathbf{r}) and spin (ω) coordinates [49].

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases} \quad (2.11)$$

2.3 Slater Determinants

The wavefunction for an N -electron system, is a function of x_1, x_2, \dots, x_N . A many electron wavefunction must be antisymmetric with respect to the interchange of the coordinate x of any two electrons. This requirement is also called the Pauli Exclusion Principle.

$$\Psi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\Psi(x_1, \dots, x_j, \dots, x_i, \dots, x_N) \quad (2.12)$$

Slater determinant can be used to represent the antisymmetric wavefunction.

$$\Psi(x_1, x_2, \dots, x_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \quad (2.13)$$

The factor $(N!)^{-1/2}$ is a normalization factor. The Slater determinant has N electrons [Slater determinants formed from orthonormal spin orbitals are normalized.] It is convenient to introduce a short-hand notation for a normalized Slater determinant, which includes the normalization constant and only shows the diagonal elements of the determinant,

$$\Psi(x_1, x_2, \dots, x_N) = \left| \chi_i(x_1) \chi_j(x_2) \cdots \chi_k(x_N) \right\rangle \quad (2.14)$$

2.4 The Hartree-Fock Approximation

In the Hartree-Fock method, the electron-electron interaction is treated within the model of independent electrons, *i.e.* each electron moves in the average potential of other electrons. The advantage of the model of independent electrons is that it allows searching for a wavefunction in the form of the product of one-electron functions

(orbitals). The Hartree-Fock approximation constitutes the first step towards more accurate approximations [49]. The simplest antisymmetric wavefunction is a single Slater determinant [50]. [As a consequence, there is a non-zero probability that two electrons are located at the same point in the space.] It can be used to describe the ground state of an N -electron system. The variation principle could be applied to obtain the lowest possible energy E_0 of $\{\chi_i\}$ orbital space.

The $E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$, expressed in terms spin orbitals $\{\chi_i | i = 1, 2, \dots, N\}$, is given by Equation (2.16),

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \quad (2.15)$$

$$E_0 = \sum_i^N [i|h|i] + \frac{1}{2} \sum_i^N \sum_j^N [ii|jj] - [ij|ji] \quad (2.16)$$

For a closed-shell system, which contains $N/2$ orbitals with α spin and $N/2$ with β spin Equation (2.16) can be written as

$$E_0 = 2 \sum_i^{N/2} (i|h|i) + \sum_{ab}^{N/2} 2(ii|jj) - (ij|ji) \quad (2.17)$$

The first term is called the one-electron integral

$$(i|h|i) = h_{ii} = \int d\mathbf{r} \psi_i^*(\mathbf{r}_1) \left(-\frac{1}{2} \nabla_1^2 - \sum_{k=1}^M \frac{Z_k}{r_{1k}} \right) \psi_i(\mathbf{r}_1) \quad (2.18)$$

Thus h_{ii} is the average kinetic and nuclear attraction energy of an electron described by the wavefunction $\psi_i(\mathbf{r}_1)$. The -second term in Equation (2.18) is the two-electron integral

$$J_{ij} = (ii|jj) = \int d\mathbf{r}_1 d\mathbf{r}_2 |\psi_i(\mathbf{r}_1)|^2 \frac{1}{r_{12}} |\psi_j(\mathbf{r}_2)|^2 \quad (2.19)$$

which is the classical coulomb repulsion between the charge clouds $|\psi_i(\mathbf{r}_1)|^2$ and $|\psi_j(\mathbf{r}_2)|^2$. Thus, this integral is called a coulomb integral, J_{ij} .

The -third term is

$$K_{ij} = (ij|ji) = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{r}_2) \psi_i(\mathbf{r}_2) \quad (2.20)$$

and does not have any classical interpretation. It is called an exchange integral, K_{ij} .

Rewrite the Hartree-Fock energy for a closed-shell system using notations of coulomb and exchange integrals, we obtained

$$E_0 = 2 \sum_i h_{ii} + \sum_{ij} 2J_{ij} - K_{ij} \quad (2.21)$$

The variation flexibility in the wavefunction is in the choice of spin orbitals. By minimizing E_0 with respect to the choice of spin orbitals, one can derive an equation, called the Hartree-Fock equation, which determines the optimal spin orbitals. The Hartree-Fock equation is an equation of the form

$$f(i)\chi_a(\mathbf{x}_i) = \varepsilon_a \chi(\mathbf{x}_i) \quad (2.22)$$

where $f(i)$ is an effective one-electron operator, called the Fock operator. The Fock operator has the form

$$f(i) = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^M \frac{Z_k}{r_{ik}} + v^{\text{HF}}(i) \quad (2.23)$$

where $v^{\text{HF}}(i)$ is the average potential experienced by the i^{th} electron due to the presence of the other electrons. The essence of the Hartree-Fock approximation is to replace the complicated many electron problem by a one-electron problem in which

electron-electron repulsion is treated in an average way. The procedure for solving the Hartree-Fock equation is called the self-consistent field (SCF) method [49].

The basic idea of the SCF method is simple. By making an initial guess at the spin orbitals, one can calculate the average field (*i.e.*, v^{HF}) seen by each electron and then solve the eigenvalue equation in Equation (2.22) for a new set of spin orbitals. Using these new spin orbitals, one can obtain new fields and repeat the procedure until self-consistency is reached (*i.e.*, until the fields no longer change and the spin orbitals used to construct the Fock operator are the same as its eigenfunctions), as in Figure 2.1.

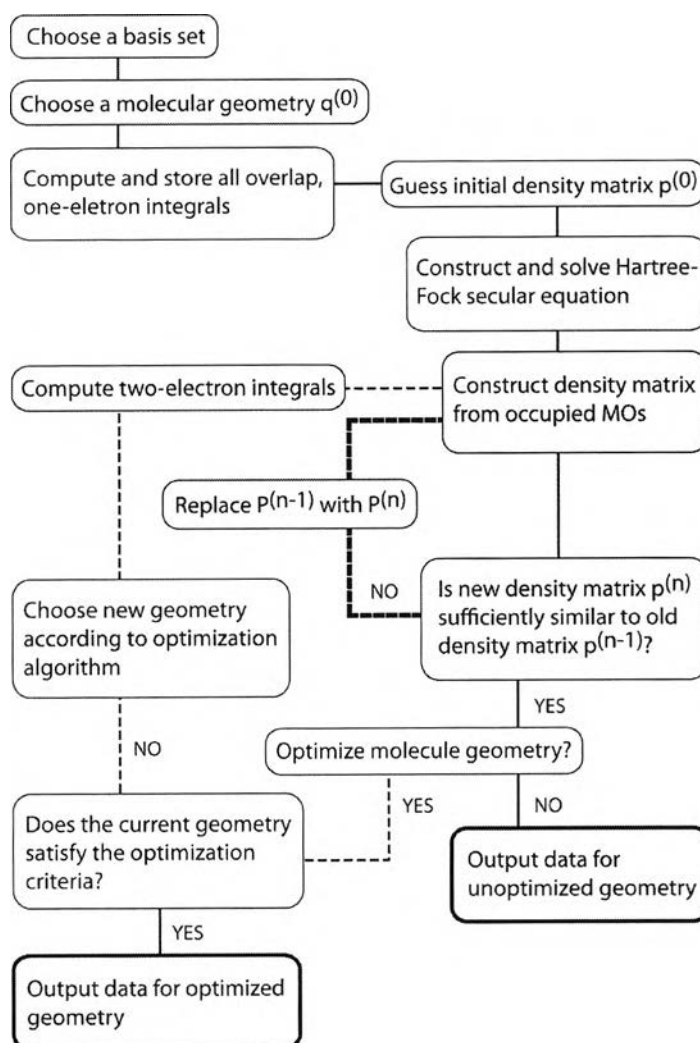


Figure 2.1 Flow chart of the HF SCF procedure [48]. Note data for an unoptimized geometry is referred to as deriving from a so-called single-point calculation.

The solution of the Hartree-Fock eigenvalue problem Equation (2.22) yields a set $\{\chi_k\}$ of orthonormal Hartree-Fock spin orbitals with orbital energies $\{\epsilon_k\}$. The N spin orbitals with the lowest energies are called the occupied or hole spin orbitals. The Slater determinant formed from these orbitals is the Hartree-Fock ground state wavefunction and is the best variation approximation to the ground state of the system, of the single determinant form.

The Hartree-Fock equation can also be solved by introducing a finite set of spatial basis functions $\{\phi_\mu(r) | \mu = 1, 2, \dots, K\}$. Using a basis set of K spatial functions $\{\phi_\mu\}$, leads to a set of $2K$ spin orbitals (K with α spin K and with β spin) can be obtained.

$$\psi_i = \sum_{\mu=1}^{2K} C_{\mu i} \phi_\mu \quad (2.24)$$

2.4.1 The Restricted and Unrestricted Hartree-Fock Models

The Hartree-Fock solution is usually characterized by having doubly occupied spatial orbitals, *i.e.*, two spin orbitals χ_p and χ_q share the same spatial orbital $\psi_i(r)$ connected with an α and a β spin function, respectively and have the same orbital energy. If we impose this double occupancy right from the start, we arrive at the restricted Hartree-Fock (RHF) approximation. Situations where the RHF picture is inadequate are provided by any system containing unpaired electron or open shell. There are two possibilities for how one can treat such species within the Hartree-Fock approximation. Either we stay as closely as possible to the RHF picture and doubly occupy all spatial orbitals with paired electrons and singly occupy all spatial orbitals with unpaired electron or allow each spin orbital to have its own spatial part. The former is the restricted open shell HF scheme (ROHF) while the latter is unrestricted Hartree-Fock variant (UHF). In UHF the α and β orbitals do not share the same effective potential but experience different potentials, v^{HF}_α and v^{HF}_β . As a consequence, the α

and β orbitals differ in their spatial characteristics and have different orbital energies, as in Figure 2.2.

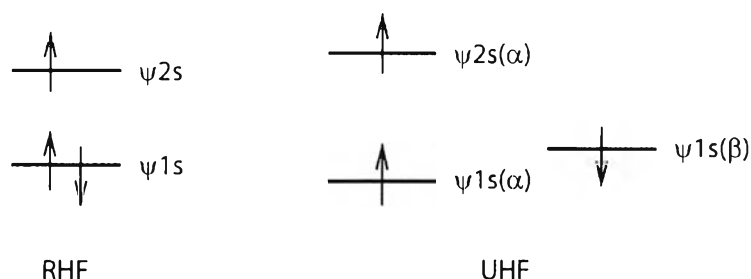


Figure 2.2 Relaxation of a restricted single determinant to an unrestricted single determinant [49].

The UHF scheme affords equations that are much simpler than their ROHF counterparts. Particularly, the ROHF wavefunction is usually composed not of a single Slater determinant, but corresponds to a limited linear combination of a few determinants where the expansion coefficients are determined by the symmetry of the state. On the other hand, in the UHF scheme we are always dealing with single-determinants wavefunctions. However, the major disadvantage of the UHF technique is the UHF wavefunctions is not an eigenfunction of the total spin operator, \hat{S}^2 .

2.4.2 Electron Correlation

The difference between Hartree-Fock energy (E_0) and the exact energy (E_{exact}), is called the correlation energy [51].

$$E^{\text{corr}} = E_{\text{exact}} - E_0 \quad (2.25)$$

Electron correlation (E^{corr}) is a negative or zero quantity because E_0 and $E_{\text{exact}} < 0$ and $|E_{\text{exact}}| \geq |E_0|$. The E^{corr} value indicates the error introduced through the HF scheme. First, E^{corr} is mainly caused by the instantaneous repulsion of the electrons, which is not covered by the effective HF potential. The electrons often get too close to each other in the Hartree-Fock scheme because the electrostatic interaction is

treated in only an average manner. Consequently, the electron-electron repulsion term is too large. As a result, E_0 is above E_{exact} . This term of the correlation energy is related to $1/r_{12}$ term, which controls the electron-electron repulsion in the Hamiltonian. When the distance r_{12} between electrons 1 and 2 (r_{12}) is the short, the correlation energy becomes larger. This correlation is known as dynamical electron correlation since it involves the actual movements of the individual electrons in a short range effect. The second main contribution to E^{corr} is the non-dynamical or static correlation. In fact, the ground state Slater determinant in a certain condition is not exactly correct for the true ground state. For example in a hydrogen molecule (H_2), the correlation energy is small only $0.04 E_h$ and almost negligible. In contrast, when the bond between H atoms stretches, the correlation energy gets larger to $0.25 E_h$. Figure 2.3 shows the limit of very large distance convergence computed (RHF and UHF), compared with the exact potential curves for the ground state of the hydrogen molecule [52].

At this point the dynamical correlation is so small because when the two H atoms become completely separated with infinite distance ($R_{\text{H-H}} \rightarrow \infty$), there is no electron-electron repulsion due to ($1/R_{\text{H-H}} \rightarrow 0$).

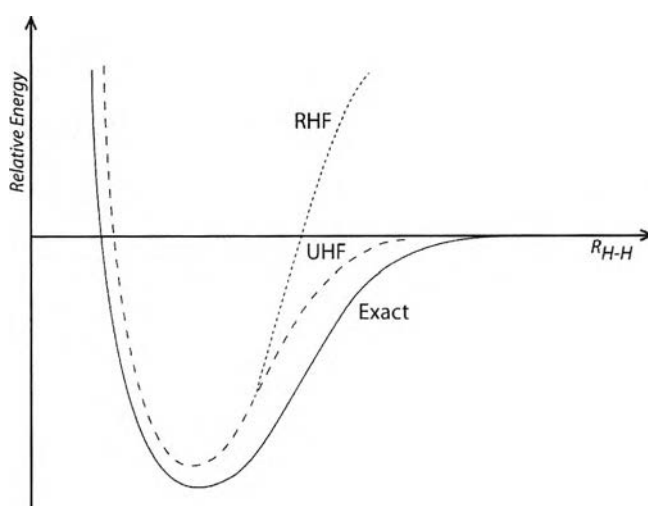


Figure 2.3 Potential curves for H_2 [52]

Unlike the dynamical correlation discussed before, these non-dynamical contributions are a long range effect and the more important it becomes the more the bond is stretched (Cook and Karplus, 1987) [53]. However, we also see from Figure 2.3 that using the unrestricted (UHF) scheme rather than RHF cures the problem. At H-H distance of some 1.24Å an unrestricted solution lower than the RHF one appears and develops into a reasonable potential curve. However, resulting UHF wavefunction no longer resembles the H₂ singlet ground state. At large internuclear distances it actually converges to a physically unreasonable 1:1 mixture between a singlet ($S=0$, hence $S(S+1) = 0$) and a triplet ($S = 1$, hence $S(S+1) = 2$) as indicate by the expectation value of the \hat{S}^2 operator, $\langle \hat{S}^2 \rangle = 1$. The correct energy emerges because the UHF wavefunction breaks the inversion symmetry inherent to a homonuclear diatomic such as H₂ and localizes one electron with spin down at one nucleus and the second one with opposite spin at the other nucleus [49].

Finally, we want to point out that E^{corr} is not restricted to the direct contributions connected to the electron-electron interaction. As this quantity measures the difference between the expectation value of \hat{H} with a Slater determinant $\langle \Psi | T + V_{ne} + V_{ee} | \Psi \rangle$ and the correct energy obtained from the exact wavefunction Ψ_0 , it should come as no surprise that there are also correlation contributions due to the kinetic energy or even the nuclear-electron term. For example, if the average distance between the electrons is too small at the Hartree-Fock level, this automatically will lead to a kinetic energy that is too large and nuclear-electron attraction which is too strong.

The error resulting from HF approximation is known as correlation energy. The reliability (and applicability) of HF is rather limited. While the method gives reasonable structures, calculated reaction energies show large errors. However, the electron correlation can be somehow estimated by methods such as perturbation theory.

2.5 Perturbation Theory

Perturbation theory leads to an expression for the desired solution in terms of a power series in some "small" parameters that quantify the deviation from the exactly solvable problem. Perturbation methods can be used in quantum mechanics for adding corrections to solutions that employ an independent-particle approximation, and the theoretical framework is then called Many-Body Perturbation Theory (MBPT). It is possible to determine the eigenfunctions and eigenvalues of the more complete operator from using exact eigenfunctions and eigenvalues of the basic operator. Rayleigh–Schrödinger perturbation theory is used for achieving this purpose. The Hamiltonian operator \hat{H} of this theory can be written as

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}' \quad (2.26)$$

Where $\hat{H}^{(0)}$ is an operator for which we can find eigenfunctions, \hat{H}' is a perturbing operator, and λ is a dimensionless parameter that, as it varies from 0 to 1, maps $\hat{H}^{(0)}$ into \hat{H} . The ground-state eigenfunctions and eigenvalues can be expanded as Taylor series in powers of the perturbation parameter λ .

$$\Psi_0 = \lambda^0 \Psi_0^{(0)} + \lambda^1 \frac{\partial \Psi_0^{(0)}}{\partial \lambda} \Big|_{\lambda=0} + \frac{1}{2!} \lambda^2 \frac{\partial^2 \Psi_0^{(0)}}{\partial \lambda^2} \Big|_{\lambda=0} + \frac{1}{3!} \lambda^3 \frac{\partial^3 \Psi_0^{(0)}}{\partial \lambda^3} \Big|_{\lambda=0} + \dots \quad (2.27)$$

$$a_0 = \lambda^0 a_0^{(0)} + \lambda^1 \frac{\partial a_0^{(0)}}{\partial \lambda} \Big|_{\lambda=0} + \frac{1}{2!} \lambda^2 \frac{\partial^2 a_0^{(0)}}{\partial \lambda^2} \Big|_{\lambda=0} + \frac{1}{3!} \lambda^3 \frac{\partial^3 a_0^{(0)}}{\partial \lambda^3} \Big|_{\lambda=0} + \dots \quad (2.28)$$

$a_0^{(0)}$ is the eigenvalue for $\Psi_0^{(0)}$, which is the appropriate normalized ground-state eigenfunction for $\hat{H}^{(0)}$. Equation (2.27) and (2.28) are usually written as

$$\Psi_0 = \lambda^0 \Psi_0^{(0)} + \lambda^1 \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \dots \quad (2.29)$$

and

$$a_0 = \lambda^0 a_0^{(0)} + \lambda^1 a_0^{(1)} + \lambda^2 a_0^{(2)} + \lambda^3 a_0^{(3)} + \dots \quad (2.30)$$

where the superscripts (n) term are referred to ' n th-order corrections' to the zeroth order term and are defined by comparison to Equation (2.27) and (2.28).

Thus, the equations can be written as

$$(\hat{H}^{(0)} + \lambda \hat{H}')|\Psi_0\rangle = a|\Psi_0\rangle \quad (2.31)$$

$$\begin{aligned} (\hat{H}^{(0)} + \lambda \hat{H}')|\lambda^0\Psi_0^{(0)} + \lambda^1\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \lambda^3\Psi_0^{(3)} + \dots\rangle = \\ (\lambda^0 a_0^{(0)} + \lambda^1 a_0^{(1)} + \lambda^2 a_0^{(2)} + \lambda^3 a_0^{(3)} + \dots)|\lambda^0\Psi_0^{(0)} + \lambda^1\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \lambda^3\Psi_0^{(3)} + \dots\rangle \end{aligned} \quad (2.32)$$

For Equation (2.32) using the terms with the same power λ , the left and right sides of this equation can be paired as followed

$$\lambda^0: \quad \hat{H}^{(0)}|\Psi_0^{(0)}\rangle = a_0^{(0)}|\Psi_0^{(0)}\rangle \quad (2.33)$$

$$\lambda^1: \quad \hat{H}^{(0)}|\Psi_0^{(1)}\rangle + \hat{H}'|\Psi_0^{(0)}\rangle = a_0^{(0)}|\Psi_0^{(1)}\rangle + a_0^{(1)}|\Psi_0^{(0)}\rangle \quad (2.34)$$

$$\lambda^2: \quad \hat{H}^{(0)}|\Psi_0^{(2)}\rangle + \hat{H}'|\Psi_0^{(1)}\rangle = a_0^{(0)}|\Psi_0^{(2)}\rangle + a_0^{(1)}|\Psi_0^{(1)}\rangle + a_0^{(2)}|\Psi_0^{(0)}\rangle \quad (2.35)$$

$$\lambda^3: \quad \hat{H}^{(0)}|\Psi_0^{(3)}\rangle + \hat{H}'|\Psi_0^{(2)}\rangle = a_0^{(0)}|\Psi_0^{(3)}\rangle + a_0^{(1)}|\Psi_0^{(2)}\rangle + a_0^{(2)}|\Psi_0^{(1)}\rangle + a_0^{(3)}|\Psi_0^{(0)}\rangle \quad (2.36)$$

The goal of this theory is to determine the various n th-order corrections. The zeroth-order in Equation (2.33) is an unperturbed solution (power of $\lambda = 0$ and $a_0 = E_0$), whereas there are two unknowns first-order corrections (the wavefunction and eigenvalue) in Equation (2.34).

To solve Equation (2.34) to (2.36) $\Psi_0^{(0)}$ is multiplied on the left followed by integrating to normalize Ψ . In case of Equation (2.34), the result is

$$\langle \Psi_0^{(0)} | \hat{H}' | \Psi_0^{(0)} \rangle = a_0^{(1)} \quad (2.37)$$

which is the first-order correction to the eigenvalue. It is the expectation value of the perturbation operator over the unperturbed wavefunction. The $\Psi_0^{(1)}$ term can be expressed as a linear combination of the complete set of eigenfunctions of $\hat{H}^{(0)}$, i.e.

$$\Psi_0^{(1)} = \sum_{i>0} c_i \Psi_i^{(0)} \quad (2.38)$$

To determine the coefficients c_i in Equation (2.38), Equation (2.34) is multiplied on the left by $\Psi_j^{(0)}$ and integrates to obtain

$$\langle \Psi_j^{(0)} | \hat{H}^{(0)} | \Psi_0^{(1)} \rangle + \langle \Psi_j^{(0)} | \hat{H}' | \Psi_0^{(0)} \rangle = a_0^{(0)} \langle \Psi_j^{(0)} | \Psi_0^{(1)} \rangle + a_0^{(1)} \langle \Psi_j^{(0)} | \Psi_0^{(0)} \rangle \quad (2.39)$$

Using Equation (2.38), the expansion of Equation (2.39) is Equation (2.40)

$$\langle \Psi_j^{(0)} | \hat{H}^{(0)} | \sum_{i>0} c_i \Psi_i^{(0)} \rangle + \langle \Psi_j^{(0)} | \hat{H}' | \Psi_0^{(0)} \rangle = a_0^{(0)} \langle \Psi_j^{(0)} | \sum_{i>0} c_i \Psi_i^{(0)} \rangle + a_0^{(1)} \langle \Psi_j^{(0)} | \Psi_0^{(0)} \rangle \quad (2.40)$$

Because Equation (2.40) is in the form of the orthonormality of the eigenfunctions, the equation can be simplified to

$$c_j a_j^{(0)} + \langle \Psi_j^{(0)} | \mathcal{V} | \Psi_0^{(0)} \rangle = c_j a_0^{(0)} \quad (2.41)$$

$$c_j = \frac{\langle \Psi_j^{(0)} | \mathcal{V} | \Psi_0^{(0)} \rangle}{a_0^{(0)} - a_j^{(0)}} \quad (2.42)$$

Using the first-order eigenvalue and wavefunction corrections, the second-order correction can be determined

The third-order can be obtained from the first- and second-order corrections. The results for the eigenvalue correction are

$$a_0^{(2)} = \sum_{j>0} \frac{|\langle \Psi_j^{(0)} | V | \Psi_0^{(0)} \rangle|^2}{a_0^{(0)} - a_j^{(0)}} \quad (2.43)$$

and

$$a_0^{(3)} = \sum_{j>0, k>0} \frac{\langle \Psi_0^{(0)} | V | \Psi_j^{(0)} \rangle \langle \Psi_j^{(0)} | V | \Psi_k^{(0)} \rangle - \delta_{j,k} \langle \Psi_0^{(0)} | V | \Psi_0^{(0)} \rangle \langle \Psi_k^{(0)} | V | \Psi_0^{(0)} \rangle}{(a_0^{(0)} - a_j^{(0)})(a_0^{(0)} - a_k^{(0)})} \quad (2.44)$$

The example of the application of perturbation theory is Møller-Plesset perturbation.

2.5.1 Møller–Plesset Perturbation Theory

The application proposed by Moller and Plesset [54] (1934) is now known as the acronym MP n where n is the order of corrections in the perturbation theory is truncated, e.g., MP2, MP3, etc. The MP approach used $\hat{H}^{(0)}$ to be the sum of the one-electron Fock operators, known as the non-interacting Hamiltonian

$$\hat{H}^{(0)} = \sum_{i=1}^n f_i \quad (2.45)$$

where n is the number of basis functions and f_i is defined in the usual way according to Equation (2.23). In addition, $\Psi^{(0)}$ is assigned to be the HF wavefunction, which is a Slater determinant formed from the occupied orbitals. The eigenvalue of $\hat{H}^{(0)}$ is the sum of the occupied orbital energies.

$$\hat{H}^{(0)}\Psi^{(0)} = \sum_i^{\text{occ}} \varepsilon_i \Psi^{(0)} = a^{(0)} \quad (2.46)$$

The 'error' in Equation (2.46) is caused from counting twice of electron–electron repulsion. So, the correction term \hat{H}' that is difference between counting electron repulsion once and twice is added to improve the HF wavefunction and eigenvalues.

$$V = \sum_i^{\text{occ}} \sum_{j>1}^{\text{occ}} \frac{1}{r_{ij}} - \sum_i^{\text{occ}} \sum_j^{\text{occ}} (J_{ij} - \frac{1}{2}K_{ij}) \quad (2.47)$$

Next, the first-order correction $a_0^{(1)}$ to the zeroth-order eigenvalue is defined by Equation (2.46) and Equation (2.37).

$$\begin{aligned} a^{(0)} + a^{(1)} &= \langle \Psi^{(0)} | \hat{H}^{(0)} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | V | \Psi^{(0)} \rangle \\ &= \langle \Psi^{(0)} | \hat{H}^{(0)} + V | \Psi^{(0)} \rangle \\ &= \langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle \\ &= \langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle \\ &= E_{\text{HF}} \end{aligned} \quad (2.48)$$

The Hartree-Fock energy (E_{HF}) is the energy corrected through first-order in MP theory. The $a^{(1)}$ must be negative to deduce the overcounted electron–electron repulsion in $a^{(0)}$ term.

The set of all possible excited-state eigenfunctions and eigenvalues of the operator $\hat{H}^{(0)}$ were used to estimate the second-order correction by treating a finite basis approximation in Equation (2.43).

$$\sum_{j>0} \langle \Psi_j^{(0)} | \hat{H}' | \Psi_0^{(0)} \rangle = \sum_{j>0} \langle \Psi_j^{(0)} | \hat{H} - \hat{H}^{(0)} | \Psi_0^{(0)} \rangle$$

$$\begin{aligned}
&= \sum_{j>0} \left[\langle \Psi_j^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle - \langle \Psi_j^{(0)} | \hat{H}^{(0)} | \Psi_0^{(0)} \rangle \right] \\
&= \sum_{j>0} \left[\langle \Psi_j^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle - \sum_i^{\text{occ}} \varepsilon_i \langle \Psi_j^{(0)} | \Psi_0^{(0)} \rangle \right] \\
&= \sum_{j>0} \langle \Psi_j^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle
\end{aligned} \tag{2.49}$$

$a^{(0)}$ for each doubly excited determinant includes in the sum of the energies of the virtual orbitals and excludes the energies of the two orbitals from which excitation has taken place. Therefore, the second-order energy correction can be expressed as

$$a^{(2)} = \sum_i^{\text{occ}} \sum_{j>i}^{\text{occ}} \sum_a^{\text{vir.}} \sum_{b>a}^{\text{vir.}} \frac{[[ij|ab] - [ia|jb]]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{2.50}$$

The sum of $a^{(0)}$, $a^{(1)}$, and $a^{(2)}$ determine the MP2 energy.

MP2 calculations can be carried out and are rapidly converged because the scaling behavior of the MP2 method in Equation (2.50) is roughly N^5 , where N is the number of basis functions. MP theory for all n orders is size-consistent. Due to basis set limitations, the MP2 calculations always underestimate the correlation energy. The increasing of n orders, leads to unsuccessfully converge, even though the basis set size is limited [55]. MP3 calculation is much more expensive than MP2, but obtained result gives only little improvement over MP2. In addition, the MP4 level is much more expensive than MP2 and MP4 since the MP4 scales is N^7 , so it is difficult to converge. Figure 2.4 shows ideal calculation using HF (MP1), MP2, MP3 and MP4. The MP n results are oscillatory. MP2 is perfectly suited to use, but cannot be applied with periodic boundary conditions and large unit cells. Possible solutions are MP2 cluster calculations, but MP2 calculations are computationally demanding and large clusters may be needed to reach convergence.

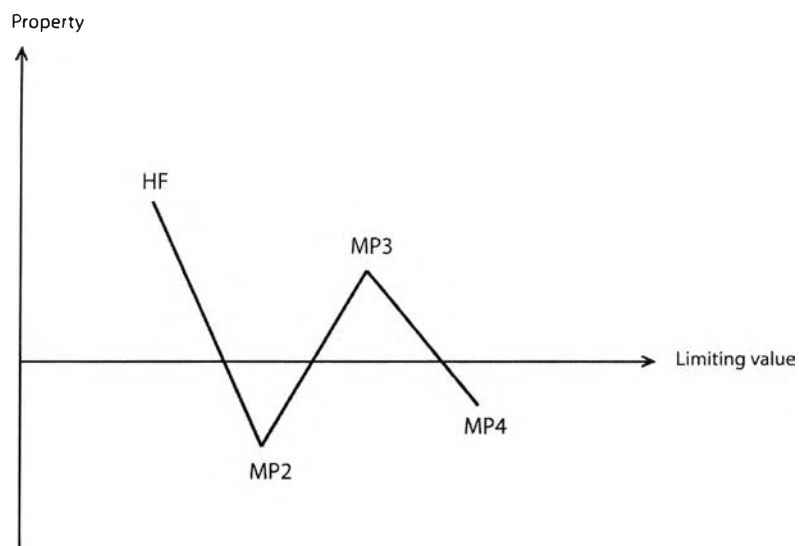


Figure 2.4 Typical oscillating behavior of results obtained with the MP method [55]

For reduce computational costs, a linear combination of atom-centered auxiliary basis functions P was used to approximate representation of products of virtual and occupied orbitals basis function v, μ or products of molecular orbitals.

$$\rho_{v\mu}(r) = v(r)\mu(r) \approx \tilde{\rho}_{v\mu}(r) = \sum c_{v\mu,P} P(r) \quad (2.51)$$

The advantage of Equation (2.51), data is reduced by minimizing the Coulomb self-interaction of the residual density $\rho - \tilde{\rho}$, the four-center integrals

$$(\mu\nu|\kappa\lambda) \approx \sum_{P,Q} (v\mu|P)(P|Q)^{-1}(Q|\kappa\lambda) \quad (2.52)$$

The right-hand side of Equation (2.52) consist only three center integrals $(\mu\nu|P)$. Equation (2.52) is called ri approximation [56] due to it similar an insertion of a resolution of identity.

For the system composed of more than hundred atoms, the resolution of identity (ri) approximation [56] together with corresponding auxiliary basis set is included in the MP2 calculation (ri-MP2). The ri-MP2 method uses four-center-two-

electron integrals with linear combinations of three-center integrals. This technique allows ri-MP2 calculate to use only about 10% of the time required by conventional MP2.

The ri-MP2 energy,

$$E_{\text{ri-MP2}} = \sum_{\sigma_1, \sigma_2} \sum_{i, a \in \sigma_1} \sum_{j, b \in \sigma_2} (t_{ij}^{ab})_{\text{ri}} [ia|jb]_{\text{ri}} \quad (2.53)$$

Using the ri approximation in the Coulomb metric

$$\begin{aligned} [ia|jb]_{\text{ri}} &= \sum_P^{\sigma_1} B_{ia}^P \sum_P^{\sigma_2} B_{jb}^P \\ i, a \in \sigma_1, j, b \in \sigma_2, \text{ and } B_{ia}^P &= \sum_Q [ia|Q][Q|P]^{-1/2} \end{aligned} \quad (2.54)$$

where σ_1 and σ_2 run over the spins and the t -amplitudes in the ri approximation are defined by inserting Equation (2.54) into Equation (2.55).

$$t_{ij}^{ab} = \begin{cases} \frac{[ia|jb] - [ib|ja]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} & \text{if } \sigma_1 = \sigma_2 \\ \frac{[ia|jb]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} & \text{if } \sigma_1 \neq \sigma_2 \end{cases} \quad (2.55)$$

Four-center-two-electron integral is $[ia|jb] - [ib|ja]$ by i, j refer to spin dependent in occupied and a, b in virtual molecular orbitals. ε denote the corresponding orbital energies.

Density functional theory method is the major approximations favorable over the perturbation theory methods, considering the fact that DFT does not require the use of such large flexible basis sets as is usually required for the perturbation theory calculations. MP2 and CCSD(T) methods are significantly more computer time consuming, scaling formally as N^5 and N^7 , respectively. Figure 2.5 summarized traditional *ab initio* methods, MP2, CCSD(T) methods, and DFT methods.

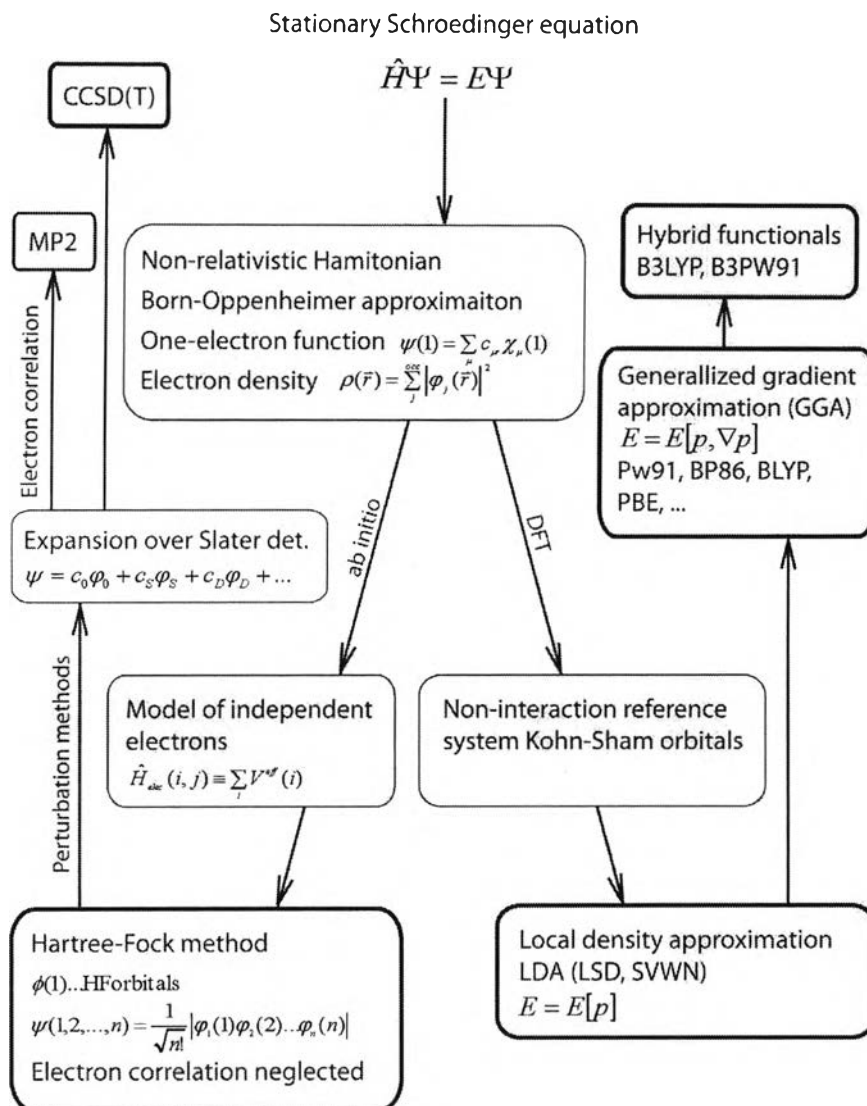


Figure 2.5 Traditional *ab initio* and DFT methods [57]

2.6 Density Functional Theory

Since the late 1980s and 1990s, density functional theory (DFT) has enjoyed an increase suddenly of interest that is an approach to the electronic structure of atoms and molecules. In 1964, Hohenberg and Kohn [58] who showed that the ground-state energy and other properties of a system are uniquely determined by the electron density based on one-electron orbitals [48, 52, 58-60]. In Hartree-Fock theory the many-electron wavefunction is expressed as a Slater determinant [50] which is constructed from a set

of N single-electron wavefunction (N being the number of electrons in the molecule). DFT also considers single-electron functions. However, whereas Hartree-Fock theory does indeed calculate the full N -electron wavefunction, density functional theory only attempts to calculate the total electronic energy and the overall electronic density distribution. The central idea underpinning DFT is that there is a relationship between the total electronic energy and the overall electronic density. This is not a particularly new idea; indeed an approximate model developed in the late 1920s (the Thomas-Fermi model) [61] contains some of the basic elements.

2.6.1 Density Functions

For one-electron wavefunction, $|\psi(r, \omega)|^2 d\tau d\omega$ gives the chance of finding the electron in the spatial volume element $d\tau$ with spin coordinate between ω and $\omega + d\omega$.

For a many-electron system with wavefunction $\Psi(r_1, \omega_1, r_2, \omega_2, \dots, r_n, \omega_n)$ then

$$|\Psi(r_1, \omega_1, r_2, \omega_2, \dots, r_n, \omega_n)|^2 d\tau_1 d\omega_1 d\tau_2 d\omega_2 \dots d\tau_n d\omega_n \quad (2.56)$$

gives the probability of finding simultaneously electron 1 in $d\tau_1 d\omega_1$, electron 2 in $d\tau_2 d\omega_2, \dots$, electron n in $d\tau_n d\omega_n$. The probability that electron 1 is in $d\tau_1 d\omega_1$ with other electrons anywhere is found by averaging over the remaining electrons.

$$\int (\dots \int |\Psi(r_1, \omega_1, r_2, \omega_2, \dots, r_n, \omega_n)|^2 d\tau_2 d\omega_2 \dots d\tau_n d\omega_n) d\tau_1 d\omega_1 \quad (2.57)$$

and, because electrons are indistinguishable, the probability must be the same for all electrons. We therefore define the one-electron density function as

$$\rho_1(r_1, \omega_1) = n \left(\int \dots \int |\Psi(r_1, \omega_1, r_2, \omega_2, \dots, r_n, \omega_n)|^2 d\tau_2 d\omega_2 \dots d\tau_n d\omega_n \right) \quad (2.58)$$

The two-electron density function is

$$\rho_2(\mathbf{r}_1, \omega_1, \mathbf{r}_2, \omega_2) = n(n-1) \left(\int \cdots \int |\Psi(\mathbf{r}_1, \omega_1, \mathbf{r}_2, \omega_2, \dots, \mathbf{r}_n, \omega_n)|^2 d\tau_3 d\omega_3 \cdots d\tau_n d\omega_n \right) \quad (2.59)$$

which is related to the probability that any two electrons will be found simultaneously at point \mathbf{r}_1, ω_1 and \mathbf{r}_2, ω_2 .

For every electron wavefunction that is an eigenfunction of the electron spin operator \hat{S}^2 , the one-electron density function always comprises an α^2 spin part and a β^2 spin part, with no cross-term involving $\alpha\beta$.

$$\rho_1(\mathbf{r}_1, \omega_1) = P^\alpha(\mathbf{r}_1)\alpha^2(\omega_1) + P^\beta(\mathbf{r}_1)\beta^2(\omega_1) \quad (2.60)$$

The electron densities for α and for β spin electrons are always equal in a singlet spin state, but in non-singlet spin states the densities may be different, giving a resultant spin density. If we evaluate the spin density function at the position of certain nuclei, it gives a value proportional to the isotropic hyperfine coupling constant that can be measured from electron spin resonance experiments.

2.6.2 The Hohenberg-Kohn Theorem

Hohenberg and Kohn's 1964 paper [58] was widely regarded by physicists, but its true importance in chemistry has only become apparent during the last decade or so. Density functional theory has become an increasingly important topic in chemistry. This culminated in the award of a half-part of the 1998 Chemistry Nobel Prize to Walter Kohn [62].

Theorem 1

The electron density $\rho(\mathbf{r})$ determines the external potential. Suppose there are two external potentials $v_1(\mathbf{r})$ and $v_2(\mathbf{r})$ arising from the same electron

density $\rho(\mathbf{r})$. There will be two Hamiltonians \hat{H}_1 and \hat{H}_2 with the same electron density with different wavefunctions Ψ_1 and Ψ_2 . If E_1 and E_2 are the ground-state energies for \hat{H}_1 and \hat{H}_2 respectively, then

$$E_1 < \int \Psi_2^* \hat{H}_1 \Psi_2 d\tau \quad (2.61)$$

that can rearrange the right-hand side as follows:

$$\int \Psi_2^* \hat{H}_1 \Psi_2 d\tau = \int \Psi_2^* \hat{H}_2 \Psi_2 d\tau + \int \Psi_2^* (\hat{H}_1 - \hat{H}_2) \Psi_2 d\tau \quad (2.62)$$

which gives
$$E_1 < E_2 + \int \rho(\mathbf{r}) [v_1(\mathbf{r}) - v_2(\mathbf{r})] d\tau \quad (2.63)$$

The above argument can be repeated with subscripts interchanged to give

$$E_2 < E_1 + \int \rho(\mathbf{r}) [v_2(\mathbf{r}) - v_1(\mathbf{r})] d\tau \quad (2.64)$$

Addition of these two in equalities, Equation (2.63) and Equation (2.64), gives

$$E_1 + E_2 < E_2 + E_1 \quad (2.65)$$

which is a contradiction.

Thus $v(\mathbf{r})$ is a unique function of the electron density; since $v(\mathbf{r})$ fixes the Hamiltonian we see that the full many-particle ground state is a unique functional of the electron density. Note that the theorem is restricted to electronic ground states.

Therefore, the energy functional is given by

$$\begin{aligned} E(\rho(\mathbf{r})) &= \int v(\mathbf{r})\rho(\mathbf{r})d\tau + F_{\text{HK}}[\rho(\mathbf{r})]d\tau \quad (2.66) \\ &= V_{\text{ne}}[\rho] + F_{\text{HK}}[\rho] \end{aligned}$$

where F_{HK} is Hohenberg-Kohn function.

Theorem 2

The second theorem proves by Hohenberg and Kohn in their 1964 contribution [58]. In plain words, this theorem states that $F_{\text{HK}}[\rho(r)]$, the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density, ρ . Thus,

$$\begin{aligned} E[\rho] < E[\tilde{\rho}] &= T[\tilde{\rho}] + V[\tilde{\rho}] + U[\tilde{\rho}] \\ &= T[\tilde{\rho}] + V_{\text{nc}}[\tilde{\rho}] + V_{\text{ec}}[\tilde{\rho}] \end{aligned} \quad (2.67)$$

$E(\tilde{\rho}(\mathbf{r}))$ assumes its minimum value for the correct $\rho(\mathbf{r})$, if the admissible functions $\rho(\mathbf{r})$ satisfies the condition

$$\int \rho(\mathbf{r}) d\tau = n \quad (2.68)$$

where n is the number of electrons. Any approximate density $\tilde{\rho}(\mathbf{r})$, by theorem 1, determines the Hamiltonian and wavefunction $\tilde{\Psi}$. Using this wavefunction in the variational expression we obtain

$$\begin{aligned} E[\tilde{\rho}(\mathbf{r})] &= \int \rho(\mathbf{r}) \tilde{\rho}(\mathbf{r}) d\tau + F_{\text{HK}}[\tilde{\rho}] \\ &= \int \tilde{\Psi}^* \hat{H} \tilde{\Psi} d\tau \geq E[\rho(\mathbf{r})] \end{aligned} \quad (2.69)$$

The main problem relating to practical applications of the Hohenberg and Kohn theorems are existence theorem and do not give us any clues as to calculation of the quantities involved.

2.6.3 The Kohn-Sham Equations

Kohn-Sham [60] provided a way to calculation Equation (2.69). For non-interacting system,

$$\begin{aligned}
 E[\rho] &= F_{HK}[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \\
 &= T_S[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}
 \end{aligned}
 \tag{2.70}$$

Applying non-interacting wavefunction $\psi_S = \prod_{i=1}^n \phi_i$

$$T_S[\rho] = \sum_i \left\langle \phi_i^{\text{KS}} \left| -\frac{1}{2} \nabla_i^2 \right| \phi_i^{\text{KS}} \right\rangle
 \tag{2.71}$$

For interacting system,

$$\begin{aligned}
 E[\rho] &= T_S[\rho] + V_{\text{ne}}[\rho] + J[\rho] + (T[\rho] + V_{\text{ee}}[\rho] - T_S[\rho] - J[\rho]) \\
 &= T_S[\rho] + V_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]
 \end{aligned}
 \tag{2.72}$$

$|\phi_i^{\text{KS}}\rangle$ is Kohn-Sham orbital which can be obtained from the Kohn-Sham equation.

$$f^{\text{KS}}(i)\chi(\mathbf{x}_i) = \epsilon\chi(\mathbf{x}_i)
 \tag{2.73}$$

which the one-electron Kohn and Sham operator f^{KS} defined as

$$\begin{aligned}
 f^{\text{KS}} &= -\frac{1}{2} \nabla^2 - \sum_{k=1}^M \frac{Z_k}{r_{ik}} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}} \\
 V_{\text{xc}} &= \frac{\delta E_{\text{xc}}}{\delta \rho}
 \end{aligned}
 \tag{2.74}$$

V_{xc} is a so-called functional derivative.

The Kohn-Sham equations very similar to standard HF equations both include terms for the kinetic energy of electrons, electron–nuclei interaction, and classical Coulomb interaction between electron densities [47, 48, 52, 62]. The Kohn-Sham equations differ from HF equations in that the exchange term is replaced with an exchange-correlation potential (E_{xc}) its form is not known. In most cases, exchange correlation functionals, is represented as a sum of exchange and correlation parts.

Notations for the majority of functional is derived from the initials of functional authors in some cases supplemented by the year of its publication. The combinations of exchange–correlation functional are divided into three groups.

2.6.4 The Local Density and Local Spin-Density Approximations

There is no systematic way in which the exchange correlation functional $V_{xc}[\rho]$ can be systematically improved. Starting from a model for which there is an exact solution, the uniform electron gas, E_{xc} can be written in the following form

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}))d\mathbf{r} \quad (2.75)$$

Here, $\varepsilon_{xc}(\rho(\mathbf{r}))$ is the exchange-correlation energy per particle of a uniform electron gas of density $\rho(\mathbf{r})$. This energy per particle is weighed with the probability that there is in fact an electron at this position in space. Writing E_{xc} in this way defines the local density approximation, LDA for short [52]. The quantity $\varepsilon_{xc}(\rho(\mathbf{r}))$ can be further split into exchange and correlation contributions,

$$\varepsilon_{xc}(\rho(\mathbf{r})) = \varepsilon_x(\rho(\mathbf{r})) + \varepsilon_c(\rho(\mathbf{r})) \quad (2.76)$$

The exchange part, ε_x , which represents the exchange energy of an electron in a uniform electron gas of a particular density is, apart from the pre-factor, equal to the form found by Slater in his approximation of the Hartree-Fock exchange and was originally derived by Bloch [63] and Dirac [64] in the late 1920's

$$\varepsilon_x = -\frac{3}{4}\sqrt{\frac{3\rho(\mathbf{r})}{\pi}} \quad (2.77)$$

On the basis of these results various authors have presented analytical expressions of ε_c based on sophisticated interpolation schemes. The most widely used representations of ε_c are the ones developed by Vosko, Wilk, and Nusair [65], 1980,

while the most recent and probably also most accurate one has been given by Perdew and Wang [66], 1992. The common short hand notation for the former implementations of the correlation functional is VWN. Hence, instead of the abbreviation LDA, which defines the model of the local density approximation, one frequently finds the acronym SVWN to identify the particular functional. For open-shell situations with an unequal number of α and β electrons, functionals of the two spin densities consistently lead to more accurate results. But also for certain situations with an even number of electrons, such as the H_2 molecule at larger separation, the unrestricted functionals perform significantly better because they allow symmetry breaking. Up to this point the local density approximation was introduced as a functional depending solely on $\rho(\mathbf{r})$. If we extend the LDA to the unrestricted case, we arrive at the local spin-density approximation, or LSDA.

$$E_{\text{XC}}^{\text{LSD}}[\rho_\alpha, \rho_\beta] = \int \rho(\mathbf{r}) \epsilon_{\text{XC}}(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r})) d\mathbf{r} \quad (2.78)$$

Just as for the simple, spin compensated situation where $\rho_\alpha(\mathbf{r}) = \rho_\beta(\mathbf{r}) = 1/2\rho(\mathbf{r})$, there are related expressions for the exchange and correlation energies per particle of the uniform electron gas characterized by $\rho_\alpha(\mathbf{r}) \neq \rho_\beta(\mathbf{r})$ the so-called spin polarized case. The degree of spin polarization is often measured through the spin-polarization parameter

$$\xi = \frac{\rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})}{\rho(\mathbf{r})} \quad (2.79)$$

ξ attains values from 0 (spin compensated) to 1 (fully spin polarized, *i.e.*, all electrons have only one kind of spin). In the following we do not differentiate between the local and the local spin-density approximation and use the abbreviation LDA for both, unless otherwise noted.

In general case of an open-shell atom or molecule. At a certain position \mathbf{r} in this system we have the corresponding spin densities $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$. In the

local spin-density approximation we now take these densities and insert them into Equation (2.79) obtaining $E_{xc}(\mathbf{r})$. Thus, we associate with the densities $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$ the exchange and correlation energies and potentials that a homogeneous electron gas of equal, but constant density and the same spin polarization ξ would have. This is now repeated for each point in space and the individual contributions are integrated as schematically indicated in Figure 2.6. Obviously, this approximation hinges on the assumption that the exchange-correlation potentials depend only on the local values of $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$.

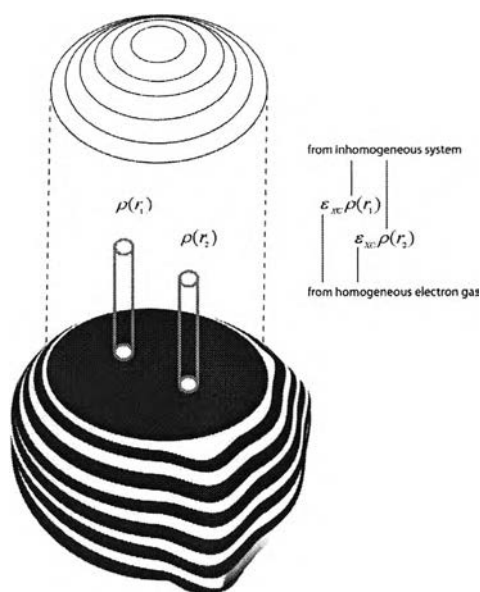


Figure 2.6 The local density approximation [52]

2.6.5 The Generalized Gradient Approximation

The situation changed significantly in the early eighties when the first successful extensions to the purely local approximation were developed. The logical first step in that direction was the suggestion of using not only the information about the density $\rho(\mathbf{r})$ at a particular point \mathbf{r} , but to supplement the density with information about the gradient of the charge density, $\nabla\rho(\mathbf{r})$ in order to account for the non-homogeneity of the true electron density. In other words, we interpret the local density

approximation as the first term of a Taylor expansion of the uniform density and expect to obtain better approximations of the exchange-correlation functional by extending the series with the next lowest term. Thus we arrive at (with σ and σ' indicating α or β spin)

$$E_{XC}^{GGA}[\rho_\alpha, \rho_\beta] = \int \rho \varepsilon_{XC}(\rho_\alpha, \rho_\beta) d\mathbf{r} + \sum_{\sigma, \sigma'} \int C_{XC}^{\sigma, \sigma'}(\rho_\alpha, \rho_\beta) \frac{\nabla \rho_\sigma}{\rho_\sigma^{2/3}} \frac{\nabla \rho_{\sigma'}}{\rho_{\sigma'}^{2/3}} d\mathbf{r} + \dots \quad (2.80)$$

This form of functional is termed the gradient expansion approximation (GEA) and it can be shown that it applies to a model system where the density is not uniform but very slowly varying. Functionals include the gradients of the charge density and where the hole constraints have been restored in the above manner are collectively known as generalized gradient approximations (GGA) [52]. These functionals are the workhorses of current density functional theory and can be generically written as

$$E_{XC}^{GGA}[\rho_\alpha, \rho_\beta] = \int f(\rho_\alpha, \rho_\beta, \nabla \rho_\alpha, \nabla \rho_\beta) d\mathbf{r} \quad (2.81)$$

In practice, E_{XC}^{GGA} is usually split into its exchange and correlation contributions

$$E_{XC}^{GGA} = E_X^{GGA} + E_C^{GGA} \quad (2.82)$$

and approximations for the two terms are sought individually. In fact, some of these functionals are not even based on any physical model. In other words, the actual form of E_X^{GGA} and E_C^{GGA} usually does not assist the understanding of the physics these functionals try to describe. This underlines the pragmatic character so typical for approximate density functional theory in general. We rewrite the exchange part of E_{XC}^{GGA} as

$$E_X^{GGA} = E_X^{LDA} - \sum_{\sigma} \int F(s_{\sigma}) \rho_{\sigma}^{4/3}(\mathbf{r}) d\mathbf{r} \quad (2.83)$$

The argument of the function F is the reduced density gradient for spin σ

$$s_{\sigma}(\mathbf{r}) = \frac{|\nabla\rho_{\sigma}(\mathbf{r})|}{\rho_{\sigma}^{4/3}(\mathbf{r})} \quad (2.84)$$

s_{σ} is to be understood as a local inhomogeneity parameter. It assumes large values not only for large gradients, but also in regions of small densities, such as the exponential tails far from the nuclei. Likewise, small values of s_{σ} occur for small gradients, typical for bonding regions, but also for regions of large density. For example, the combination of large density gradients and large densities close to the nuclei typically leads to values of s_{σ} in this region which are in between the reduced density gradients in the bonding and tail regions, respectively. Of course, the homogeneous electron gas is characterized by $s_{\sigma} = 0$ everywhere. Finally, a word on why we divide by the 4/3 power of ρ and not just by ρ itself. This is needed to make s_{σ} a dimensionless quantity: the dimension of the density is the inverse dimension of volume and hence $[\mathbf{r}]^{-3}$. Its gradient has therefore dimensions of $[\mathbf{r}]^{-4}$. But this is just the same dimension that $\rho^{4/3}$ has, because of $([\mathbf{r}]^{-3})^{4/3} = [\mathbf{r}]^{-4}$ and we arrive at the desired dimensionless reduced gradient.

For the function F two main classes of realizations, the first one is based on a GGA exchange functional developed by Becke [67], 1988b. As outlined above, this functional is abbreviated simply as B (sometimes one also finds B88)

$$F^{\text{B}} = \frac{\beta s_{\sigma}^2}{1 + 6\beta s_{\sigma} \sinh^{-1} s_{\sigma}} \quad (2.85)$$

β is an empirical parameter that was determined to 0.0042 by a least-squares fit to the exactly known exchange energies of the rare gas atoms He through Rn. In addition to the sum rules, this functional was designed to recover the exchange energy density asymptotically far from a finite system.

The second class of GGA exchange functionals use for F a rational function of the reduced density gradient. Prominent representatives are the early functionals by Becke [68], 1986 (B86) and Perdew [69], 1986 (P), the functional by Lacks and Gordon, 1993 (LG) or the recent implementation of Perdew, Burke, and

Ernzerhof, 1996 (PBE) [70]. As an example, we explicitly write down F of Perdew's 1986 exchange functional, which, just as for the more recent PBE functional, is free of semiempirical parameters:

$$F^{P86} = \left(1 + 1.296 \left(\frac{s_{\sigma}}{(24\pi^2)^{1/3}} \right)^2 + 14 \left(\frac{s_{\sigma}}{(24\pi^2)^{1/3}} \right)^4 + 0.2 \left(\frac{s_{\sigma}}{(24\pi^2)^{1/3}} \right)^6 \right)^{1/15} \quad (2.86)$$

Among the most widely used choices is the correlation counterpart of the 1986 Perdew exchange functional, usually termed P or $P86$. This functional employs an empirical parameter, which was fitted to the correlation energy of the neon atom. A few years later Perdew and Wang [69], 1991, refined their correlation functional, leading to the parameter free $PW91$. Another, nowadays even more popular correlation functional is due to Lee, Yang, and Parr [71], 1988 (LYP). Unlike all the other functionals mentioned so far, LYP is not based on the uniform electron gas but is derived from an expression for the correlation energy of the helium atom based on an accurate, correlated wavefunction presented in the context of wavefunction based theory by Colle and Salvetti [72], 1975. The LYP functional contains one empirical parameter. It differs from the other GGA functionals in that it contains some local components.

In principle, each exchange functional could be combined with any of the correlation functionals, but only a few combinations are currently in use. The exchange part is almost exclusively chosen to be Becke's functional which is either combined with Perdew's 1986 correlation functional or the Lee, Yang, Parr usually abbreviated as $BP86$ and $BLYP$, respectively. Sometimes also the $PW91$ correlation functional is employed, corresponding to $BPW91$. To be fair, all these flavors of gradient-corrected KS-density functional theory deliver results of similar quality as demonstrated by several studies which assess the performance of these functional.

2.7 Basis Set

A basis set is a set of functions used to describe the shape of the orbitals in an atom. Molecular orbitals and all wavefunctions are created by taking linear combinations of basis functions and angular functions [52]. The basis functions should have large amplitude in regions of space where the electron probability density is also large, and small amplitudes where the probability density is small. There are two guidelines for choosing the basis functions. One is that they should have a behavior which agrees with the physics of the problem; this ensures that convergence as more basis functions are added is reasonably rapid. The second guideline is practical: the chosen functions should make it easy to calculate all the required integrals.

The orbitals χ_i which are expressed through the $\{\eta_\mu\}$ are used to construct the approximate wavefunction. It has long been recognized that very large basis sets are needed if high quality wavefunctions that take also into account electron correlation are the target. In particular, basis functions with complex nodal structures (polarization functions) are necessary and in highly correlated calculations the basis set requirements soon lead to computationally very demanding procedures. On the other hand, in the Kohn-Sham scheme the orbitals play an indirect role and are introduced only as a tool to construct the charge density according to

$$\rho(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2 \quad (2.87)$$

One should therefore expect that the basis set requirements in Kohn-Sham calculations are less severe than in wavefunction based ones. In conventional wavefunction based approaches, such as the Hartree-Fock or configuration-interaction schemes, the set $\{\eta_\mu\}$ is almost universally chosen to consist of so-called cartesian Gaussian-type-orbitals, GTO of the general form

$$\eta^{\text{GTO}} = N x^l y^m z^n \exp[-\alpha r^2] \quad (2.88)$$

N is a normalization factor which ensures that $\langle \eta_\mu | \eta_\mu \rangle = 1$ (but note that the η_μ are not orthogonal, *i.e.*, $\langle \eta_\mu | \eta_\nu \rangle \neq 0$ for $\mu \neq \nu$). α represents the orbital exponent which determines how compact (large α) or diffuse (small α) the resulting function is. $L = l + m + n$ is used to classify the GTO as s-functions ($L = 0$), p-functions ($L = 1$), d-function ($L = 2$), *etc.* Note, however that for $L > 1$ the number of cartesian GTO functions exceeds the number of $(2l + 1)$ physical functions of angular momentum l . For example, among the six cartesian functions with $L = 2$, one is spherically symmetric and is therefore not a d-type but an s-type functions. Similarly the ten cartesian $L = 3$ functions include an unwanted set of three p-type functions.

The preference for GTO basis functions in HF and related methods is motivated by the computational advantages these functions offer, because very efficient algorithms exist for analytically calculating the huge number of four-center-two-electron integrals occurring in the Coulomb and HF- exchange terms. On the other hand, from a physical point of view, Slater-type-orbitals (STO) seem to be the natural choice for basis functions [49, 52]. They are simple exponentials that mimic the exact eigenfunctions of the hydrogen atom. Unlike the GTO functions, Slater-type-orbitals exhibit the correct cusp behavior at $r \rightarrow 0$ with a discontinuous derivative (while a GTO has a slope of zero at $r \rightarrow 0$) and the desired exponential decay in the tail regions as $r \rightarrow \infty$ (GTO fall off rapidly). A typical STO is expressed as

$$\eta^{\text{STO}} = N r^{n-1} \exp[-\zeta r] Y_{lm}(\Theta, \phi) \quad (2.89)$$

Here, n corresponds to the principal quantum number, the orbital exponent is termed ζ and Y_{lm} are the usual spherical harmonics that describe the angular part of the function. In fact as a rule of thumb one usually needs about three times more GTO than STO functions to achieve certain accuracy. Unfortunately, many-center integrals are notoriously difficult to compute with STO basis sets so we employ contracted GTO basis sets, in which several primitive Gaussian Functions (typically between three and six linear combination to give one contracted Gaussian function (CGF)

$$\eta_r^{\text{CGF}} = \sum_a^A d_{ar} \eta_a^{\text{GTO}} \quad (2.90)$$

The original motivation for contracting was that the contraction coefficients $d_{s,r}$ can be chosen in a way that the CGF resembles as much as possible a single STO function.

We should also mention that basis sets which do not actually comply with the LCAO scheme are employed under certain circumstances in density functional calculations, *i.e.*, plane waves. These are the solutions of the Schrödinger equation of a free particle and are simple exponential functions of the general form

$$\eta^{\text{PW}} = \exp[ik\tau] \quad (2.91)$$

where the vector k is related to the momentum p of the wave through $p = \hbar k$. Plane waves are not centered at the nuclei but extend throughout the complete space. They enjoy great popularity in solid state physics for which they are particularly adapted because they implicitly involve the concept of periodic boundary conditions. Unfortunately, the number of plane waves needed to arrive at an acceptable accuracy is usually daunting at best and for this and other reasons applications employing plane wave basis sets are very rare in molecular quantum chemistry. Irrespective of whether we use Gaussian functions, Slater type exponentials or numerical sets, certain categories of functions that can help to characterize the quality of a basis set have become customary in quantum chemistry. The simplest and least accurate expansion of the molecular orbitals utilizes only one basis function (or one contracted function in the case of CGF sets) for each atomic orbital up to and including the valence orbitals. These basis sets are for obvious reasons called minimal sets. A typical representative is the STO-3G basis set. For carbon, this basis set consists of five functions, one each describing the $1s$ and $2s$ atomic orbitals and three functions for the $2p$ shell (p_x , p_y , and p_z). One should expect no more than only qualitative results from minimal sets and nowadays they are hardly used anymore. The next level of sophistication is the double-

zeta basis sets. Here, the set of functions is doubled, *i.e.*, there are two functions for each orbital (the generic name 'double-zeta' for such basis set still points to the beginnings of computational quantum chemistry, when STO functions were in use, where the orbital exponent is called Zeta (ζ)). If we take into account that it is in the valence space where change in the electronic wavefunction occur during chemical processes, we can limit the double set of functions to the valence orbitals, while the chemically mostly inert core electrons are still treated in a minimum set. This defines the split-valence basis sets. Typical examples are the 3-21G or 6-31G Gaussian basis set developed by Pople and coworkers [73]. For example 6-31G has two sizes of basis function for each valence orbital. The core consists of 6 GTOs which are not split, while the valence orbitals are described by one orbital constructed from 3 primitive GTOs and one single GTO.

In most applications, such basis sets are augmented by polarization functions, *i.e.*, functions of higher angular momentum than those occupied in the atom, *e.g.*, p-functions for hydrogen or d-functions for the first row elements. Polarization functions have by definition more angular nodal planes than the occupied atomic orbitals and thus ensure that the orbitals can distort from their original atomic symmetry and better adapt to the molecular environment. Polarized double-zeta or split valence basis set are the mainstay of routine quantum chemical applications since usually they offer a balanced compromise between accuracy and efficiency. In terms of CGF type basis sets, typical examples are the standard 6-31G(d,p) sets of Hehre, Ditchfield, and Pople [74], 1972, and Hariharan and Pople, 1973, or the more recent SVP (split-valence polarization) sets of Schäfer, Horn, and Ahlrichs, 1992. Equivalents consisting of two STO functions per atomic orbital or two numerical functions are of comparable importance in their respective domains. In the latter case the doubling of the numerical functions can be achieved, for example, by adding numerically generated atomic orbitals from calculations only doubly or even higher positively charged ions.

It is obvious how these schemes can be extended by increasing the number of functions in the various categories. This results in triplet- or quadruple-zeta basis sets

which are augmented by several sets of polarization functions including functions of even higher angular momentum.

The exponents and contraction coefficient of most Gaussian basis sets have been optimized within the Hartree-Fock or correlated wavefunction based schemes. In the beginning it was not at all clear whether one could in fact use basis sets that were optimized for representing molecular orbitals in a HF or configuration interaction context to construct the density, as in the Kohn-Sham scheme. However, it fortunately turned out that the results are fairly insensitive with respect to the way the exponents and contraction coefficients have been determined, in particular for the calculation of properties such as energies or equilibrium geometries. Hence, in general it is probably not necessary to use basis sets explicitly optimized for a density functional approach, even though there are a number of special cases where this statement is an oversimplification. Nevertheless, most modern applications of Kohn-Sham density functional theory using Gaussian functions simply employ one of the many standard basis sets, irrespective of their origin in wavefunction based approaches. In most contemporary program packages the popular sets are provided in an internal basis set library. Should the desired set not be included in that internal library of the program chosen, it can usually be conveniently downloaded even in the appropriate input format from <http://www.emsl.pnl.gov:2080/forms/basisform.html> (Feller, Schuchardt, and Jones, 1998) [52].

2.8 Zero-Point Energy (ZPE)

The nuclei motion on the Born–Oppenheimer potential energy surface that is also accounted for in a quantum mechanical way, energy is 'tied up' in molecular vibrations. One consequence of the unpredictability principle is that polyatomic molecules, even at absolute zero, the molecules must always be moving, with a sum of potential and kinetic energy that exceeds the energy of the nearest minimum by some

non-zero amount. Within the harmonic oscillator approximation, the energy of the lowest vibrational level can be determined from

$$E = \left(n + \frac{1}{2} \right) h\nu \quad (2.92)$$

where n is the vibrational quantum number, h is Planck's constant (6.6261×10^{-34} J s) and ν is the vibrational frequency.

The sum of all of the harmonic-oscillator ground state energies over all molecular vibrations defines the Zero-point energy (ZPE). Thus the internal energy for a molecule at 0 K was defined by

$$U_0 = E_{\text{ele}} + \sum_i^{\text{modes}} \frac{1}{2} h\nu_i \quad (2.93)$$

where E_{ele} is the energy for the stationary point on the Born–Oppenheimer PES. U_0 is also often written as E_0 in thermochemical literature. Mode is a function of the atomic masses for the nuclei involved in the motion.

In order to predict the stretching frequency within the harmonic oscillator equation, all that is needed is the second derivative of the energy with respect to bond stretching computed at the equilibrium geometry. *i.e.*, k The importance of k has led to considerable effort to derive analytical expressions for second derivatives, and they are now available for HF, MP2, DFT, QCISD, CCSD, MCSCF and select other levels of theory, although they can be quite expensive at some of the more highly correlated levels of theory.

Scaling factor of ZPE in the range of 0.9–1.0 that depend on the calculation method and basis set used [75]. Due to overestimate frequencies of the most calculation methods were compared with the experimental values. This overestimation is due partially to the harmonic approximation and partially to electronic structure calculations. The scaling factors for the theoretical harmonic vibrational frequencies

were determined by a comparison with the corresponding experimental fundamentals utilizing a total of 1066 individual vibrations. Scaling factors suitable for low-frequency vibrations were obtained from least-squares fits of inverse frequencies. ZPE scaling factors were obtained from a comparison of the computed ZPVEs (derived from theoretically determined harmonic vibrational frequencies) with ZPVEs determined from experimental harmonic frequencies and anharmonicity corrections for a set of 39 molecules. Finally, scaling factors for theoretical frequencies that are applicable for the computation of thermal contributions to enthalpy and entropy have been derived. A complete set of recommended scale factors is presented. The most successful procedures overall are B3-PW91/6-31G(d), B3-LYP/6-31G(d), and HF/6-31G(d).