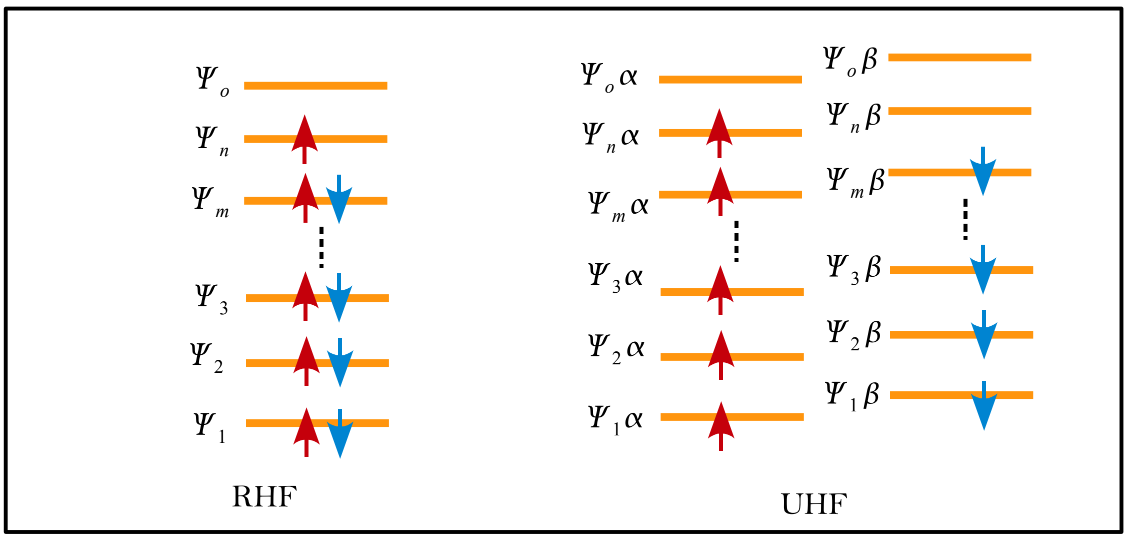
Ab initio **calculations and Density Functional Theory**

In this lecture, we shall consider some advanced quantum mechanics calculation beyond the Hartree-Fock method. We will consider the properties that can be calculated using the *ab initio* method. Finally the commonly used density functional theory will be introduced.

1. Open-shell Systems

In the context of atomic orbitals, open-shell is a valance shell is not completely filled by electrons through chemical bonding with other atoms or molecules. A closed-shell is a shell completely filled with electrons, corresponding to a state with all Molecular Orbitals doubly occupied or empty (singlet).

The Roothaan-Hall equations are not applicable to open-shell systems, which contain one or more unpaired electrons. Two approaches have devised to treat open-shell systems: Spin-restricted Hartree-Fock theory (RHF) and spin-unrestricted (UHF) theory.



1.1 The Spin-restricted Hartree Fock (RHF) Method

The RHF method uses doubly and singly occupied molecular orbitals, which have the same spatial wavefunctions for both alpha spin and beta spin.

The closed-shell Hartree-Fock method is a special case of RHF.

1.2 The Spin-unrestricted Hartree-Fock Method

The UHF method uses two distinct sets of molecular orbitals: one for alpha spin, and one for beta spin.

Two Fock matrices are used:

$$\hat{F}^{\alpha} C^{\alpha} = S C^{\alpha} E^{\alpha} \quad (1)$$

$$\hat{F}^{\beta} C^{\beta} = S C^{\beta} E^{\beta} \tag{2}$$

Fock matrix elements have the follow form

$$F^{\alpha}_{\mu\nu} = H^{core}_{\mu\nu} + \sum_{\sigma=1}^{K} \sum_{\lambda=1}^{K} \left[(P^{\alpha}_{\lambda\sigma} + P^{\beta}_{\lambda\sigma})(\mu\nu|\lambda\sigma) - P^{\alpha}_{\lambda_\sigma}(\mu\lambda|\nu\sigma) \right] \tag{3}$$

$$F^{\beta}_{\mu\nu} = H^{core}_{\mu\nu} + \sum_{\sigma=1}^{K} \sum_{\lambda=1}^{K} \left[(P^{\alpha}_{\lambda\sigma} + P^{\beta}_{\lambda\sigma})(\mu\nu|\lambda\sigma) - P^{\beta}_{\lambda_\sigma}(\mu\lambda|\nu\sigma) \right] \tag{4}$$

The UHF uses two density matrices, which are

$$P^{\alpha}_{\mu\nu} = \sum_{i}^{\alpha_{occ}} c^{\alpha}_{\mu i} c^{\alpha}_{\nu i} \quad \text{and} \quad P^{\beta}_{\mu\nu} = \sum_{i}^{\beta_{occ}} c^{\beta}_{\mu i} c^{\beta}_{\nu i} \tag{5}$$

where $\alpha_{occ} + \beta_{occ}$ equals the total number of electrons.

The total electron density is

$$\rho^{elec}(\boldsymbol{r}) = \rho^{\alpha}(\boldsymbol{r}) + \rho^{\beta}(\boldsymbol{r}) = \sum_{\mu=1}^{K} \sum_{\nu=1}^{K} [P^{\alpha}_{\mu\nu} + P^{\beta}_{\mu\nu}] \phi_{\mu}(\boldsymbol{r}) \phi_{\nu}(\boldsymbol{r}) \tag{6}$$

In open-shell systems, there is an extra spin density, which can be defined

$$\rho^{spin}(\boldsymbol{r}) = \rho^{\alpha}(\boldsymbol{r}) - \rho^{\beta}(\boldsymbol{r}) = \sum_{\mu=1}^{K} \sum_{\nu=1}^{K} [P^{\alpha}_{\mu\nu} - P^{\beta}_{\mu\nu}] \phi_{\mu}(\boldsymbol{r}) \phi_{\nu}(\boldsymbol{r}) \tag{7}$$

The UHF is more general, and more appropriate for a number of problems such as deassociation.

One *drawback* for the UHF method: A single Slater determinant of different orbitals for different spins is not a satisfactory wavefunction of total spin operator $\hat{S}^2$ (More determinants are necessary because the ground state is contaminated by "excited" states).

The unrestricted Hartree-Fock method uses more frequently and in preference to the RHF method. The answer is that UHF is simpler to code, it is easier to develop post-HF methods, and it is unique.

2. Configuration Interaction

In computational quantum mechanics, P**ost-Hartree-Fock** methods add electron correlation which is a more accurate way of including the repulsions between electrons than in the Hartee-Fock method where repulsions are only averaged.

Usually, post-Hartree-Fock methods give more accurate results than Hartree-Fock calculations, although the added accuracy comes with the price of added computational cost.

One way to provide consider the instantaneous electron correlation is "configuration interaction". The corrections to the wavefunction will mix in contributions from excited configurations producing **Configuration Interaction**.

Two meanings are connected to the term *configuration interaction* in this context:

- Mathematically, *configuration* simply describes the linear combination of Slater determinants used for the wavefunction Ψ .
- *Interaction* means the mixing (interaction) of different electronic configurations (states). Due to the long CPU time and immense hardware required for CI calculations, the method is limited to relatively small systems.

How to do a Configuration Interaction Calculation?

The definition of configuration state function (CSFs) Φ_i

We express the the true wavefunction to the Schroedinger equation as a linear combination of the CSFs

$$\Psi=\sum_i c_i \Phi_i$$

Variation of the coefficients c_i leads to the equation

$$det(H_{ij}-E\,S_{ij})=0$$

where $H_{ij}=\langle \Phi_i \hat{H} \Phi_j \rangle$ and $S_{ij}=\langle \Phi_i \hat{H} \Phi_j \rangle$.

If a Hartree-Fock calculation is performed with K basis functions, then 2K spin orbitals are obtained. If these 2K spin orbitals are filled with N electrons ($N<2\mathrm{K}$) then there will be $2\mathrm{K}-N$ unoccupied virtual orbitals.

Full CI calculation

A CI calculation that includes all possible configuration functions with proper symmetry is called a full CI calculation.

The total number of ways to permute N electrons and K orbitals is $\frac{(2\mathrm{K})!}{N!(2\mathrm{K}-N)!}$. This is a large number except values of K and N. That is why full CI calculations are only suitable for very small systems.

CIS, CISD, and CISD

Configuration interaction singles and doubles only consider wavefunctions that differ from HF wavefunctions by a single or double wavefunction.

Even at the CIS and CISD levels, the number of excited states are still enormous. It is desirable to restrict the spin orbitals that are involved in substitutions. For example only excitations involving HOMO and LUMO are considered. (Alternatively, some consider excitations involving valence orbitals).

MCSCF

In a traditional CI calculation the determinants in the expansion $\Psi = \sum_i c_i \Phi_i$ are those obtained from a Hartree-Fock calculation; only the coefficients $c_0, c_1, \ldots$ are permitted to vary.
A better (i.e., lower energy) wavefunciton should be obtained if the coefficients of the basis functions themselves can vary as well as the coefficient of the determinants. This approach is known as the multiconfiguration self-consistent field (MCSCF) method. One MCSCF technique has attracted a lot of attention, and this method is called complete active-space SCF method CASSCF. (Orbitals are classified into 3 sets: double occupied orbitals, orbitals unoccupied in all configurations, and all the remaining orbitals. The list of configurations is generated by considering all possible arrangements of the active electrons among the active orbitals).

3. Many-body Perturbation Theory

In 1934, Møller and Plesset proposed a perturbation treatment of atoms and molecules in which the unperturbed form is the HF wavefunction, and this form of many-body perturbation theory is called ***Møller-Plesset perturbation theory.***

Perturbation theory in a nutshell.

We can write the perturbed Hamiltonian as

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \tag{8}$$

The eigenfunctions ψ_i and eigenvalues can now be expanded in series of λ

$$\Psi_i = \Psi_i^{(0)} + \lambda \Psi_i^{(1)} + \lambda^2 \Psi_i^{(0)} + \cdots = \sum_{n=0} \lambda^n \Psi_i^{(n)} \tag{9}$$

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(0)} + \cdots = \sum_{n=0} \lambda^n E_i^{(n)} \tag{10}$$

These energies can be calculated from the wavefunctions

$$E_i^{(0)} = \int \Psi_i^{(0)} \hat{H}_0 \Psi_i^{(0)} d\tau \tag{11}$$

$$E_i^{(1)} = \int \Psi_i^{(0)} \hat{H}' \Psi_i^{(0)} d\tau \tag{12}$$

$$E_i^{(2)} = \int \Psi_i^{(0)} \hat{H}' \Psi_i^{(1)} d\tau \tag{13}$$

$$E_i^{(3)} = \int \Psi_i^{(0)} \hat{H}' \Psi_i^{(2)} d\tau \tag{14}$$

In MP perturbation theory, the unperturbed "Hamiltonian" is

$$\hat{H}_0 = \sum_{i=1}^{N} = \sum_{i=1}^{N} \left(\hat{H}^{core} + \sum_{j=1}^{N/2} (2\hat{J}_j - \hat{K}_j) \right) \tag{15}$$

The unperturbed energy equals the orbital energies for the occupied orbitals

$$E_0^0 = \sum_{i=1}^{occupied} \epsilon_i \tag{16}$$

The true Hamiltonian is

$$\hat{H} = \sum_{i=1}^{N} \hat{H}^{core} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{r_{ij}} \tag{17}$$

The perturbation term is given by

$$\hat{H}' = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{r_{ij}} - \sum_{j=1}^{N/2} (2\hat{J}_j + \hat{K}_j) \tag{18}$$

Two properties about Slater determinants D:

The Hamiltonian Operator can be written

$$\hat{H} = \sum_{i=1}^{n} \hat{f}_i + \sum_{i=1}^{n-1} \sum_{j>i} \hat{g}_{ij} \tag{19}$$

where the one-electron operator $\hat{f}_i$ involves only coordinates and momentum operator of electron i and the two electron operator involves coordinates and momentum operators of electron i and j. now we have

$$\langle D \left| \sum_{i=1}^{n} \hat{f}_i \right| D \rangle = \sum_{i=1}^{n} \langle \psi_i(\boldsymbol{r_i}) | \hat{f}_i | \psi_j(\boldsymbol{r_i}) \rangle \tag{20}$$

and

$$\langle D \left| \sum_{i=1}^{n-1} \sum_{j>i} \hat{g}_{ij} \right| D \rangle = \\ \sum_{i=1}^{n-1} \sum_{j>i} \left[\langle \psi_i(\boldsymbol{r_i}) \psi_j(\boldsymbol{r_j}) | \hat{g}_{ij} | \psi_i(\boldsymbol{r_i}) \psi_j(\boldsymbol{r_j}) \rangle - \delta_{m_{si}, m_{sj}} \langle \psi_i(\boldsymbol{r_i}) \psi_j(\boldsymbol{r_j}) | \hat{g}_{ij} | \psi_j(\boldsymbol{r_i}) \psi_i(\boldsymbol{r_j}) \rangle \right] \tag{21}$$

The first order perturbation energy is given by

$$E_0^{(1)} = \int \Psi_0^{(0)} \hat{H}' \Psi_0^{(0)} d\tau = -\sum_{i=1}^{N/2} \sum_{j=1}^{N/2} \frac{1}{r_{ij}} [2(ii|jj) - (ij|ji)] \tag{22}$$

The sum of the zeroth-order and first-order energies thus corresponds to the Hartree-Fock energy, which has the from

$$E_0^{(0)} + E_0^{(1)} = \sum_{i}^{N} \epsilon - \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (2\mathrm{J}_{ij} - K_{ij}) \tag{23}$$

The expression for the Hartree-Fock energy is given by HF calculations:

$$E_{HF}=\int D*\hat{H}_{el}D\,d\tau=2\sum_{i=1}^{N/2}H_{ii}^{core}+\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}(2J_{ij}-K_{ij}) \quad (24)$$

$$H_{ii}^{core}=\int\psi_i^*(\boldsymbol{r_i})\hat{H}^{core}\psi_i(\boldsymbol{r_i})d\boldsymbol{r_i} \quad (25)$$

The Hartree-Fock energy can also be expressed (not including the nuclei Coubomb energy V_{NN})

$$E_{HF}=\sum_{i}^{N/2}\epsilon_i+\sum_{i}^{N/2}H_{ii}^{core} \quad (26)$$

where $\hat{F}\psi_i=\epsilon_i\psi_i$. since

$$\sum_{i}^{N/2}\epsilon_i=\sum_{i=1}^{N/2}H_{ii}^{core}+\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}(2J_{ij}-K_{ij}) \quad (27)$$

$$E_{HF}=\sum_{i=1}^{N}\epsilon_i-\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}(2J_{ij}-K_{ij}) \quad (28)$$

T0 obtain an improvement on the HF energy it is necessary to use MP perturbation theory to at least second order (MP2).

The higher-order wavefunction $\Psi_0^{(1)}$ is expressed as linear combinations of solutions to the zeroth-order Hamiltonian

$$\Psi_0^{(1)}=\sum_j c_j^{(1)}\Psi_j^{(0)} \quad (29)$$

The $\Psi_j^{(0)}$ is equation will include single, double, etc excitations obtained by promoting electrons into virtual orbitals obtained from HF calculations.

The second order energy is given by

$$E_0^{(2)}=\sum_{i}^{occ}\sum_{j>i}^{occ}\sum_{a}^{vir}\sum_{b>a}^{vir}\frac{\int\int\chi_i(\boldsymbol{r_i})\chi_j(\boldsymbol{r_j})\frac{1}{r_{ij}}[\chi_a(\boldsymbol{r_i})\chi_b(\boldsymbol{r_j})-\chi_b(\boldsymbol{r_i})\chi_a(\boldsymbol{r_j})]\,d\boldsymbol{r_i}\,d\boldsymbol{r_j}}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j} \quad (30)$$

where χ represents spin-orbitals (including spins). Those integrals will be non-zero for double excitations, according to Brillouin theorem.

MP3 and MP4 are also available is standard ab initio packages like Gaussian03.

What is the difference between MP perturbation methods and CI methods?

- Size-independent
- computationally intensive (often restricted to single-point calculations)

- Not variational method. Sometimes provides energies lower than the true "energy".
- At the MP2 level, it is the most common method to consider electronic correlation.
- MP2/6-31G* indicates a second-order Moller-Plesset calculation with the 6-31G* basis set.

4. Density Functional Theory

A more recent development which has now overtaken "wavefunction methods" as the favorite technique of computational quantum mechanics is Density Functional Theory.

A functional means a function of functions.

The central idea underpinning DFT is not particularly new (as seen in the Thomas-Fermi model in 1920). The real break-through came with a paper by Hohenberg and Kohn (1964), who showed the ground state energy and other properties can be uniquely defined by the electron density. (Walter Kohn and John Pople shared the 1998 Nobel Prize).

The density function is always determined from the wavefunction using

$$\rho(\boldsymbol{r})=N\int\int\cdots\int\left|\Psi(\boldsymbol{r},\boldsymbol{r}_2,\cdots,\boldsymbol{r}_n)^2\right|dx_2\cdots dx_N \tag{31}$$

where r_1 has been singled out for replacement by unlabelled three-dimensional variable $\mathbf{r}$. (integration is over all spin and electron coordinates except $\boldsymbol{r}_1$)

The conceptual basis of DFT is a pair of theorems due to H-K. The first theorem:

If the density function $\rho(\boldsymbol{r})$ for the ground state of a quantum system is known, then the N-electron wavefunction $\Psi(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_n)$ is in principle determined.

(Proof here).

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

The second H-K theorem is a variational principle for the density functional, requiring that

$$E_0\leq E[\rho] \tag{33}$$

The energy functional is conveniently divided into four contributions

$$E[\rho]=E^K[\rho]+E^V[\rho]+E^J[\rho]+E^{XC}[\rho] \tag{34}$$

The potential energy of nuclear-electronic and internuclear interactions is given by

$$E^V[\rho]=-\sum_{\alpha}Z_\alpha\int\rho\frac{(\boldsymbol{r})}{\boldsymbol{r}-\boldsymbol{R}_A}d\tau+\sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta}{R_{AB}} \tag{35}$$

The electron-electron Coulomb energy is

$$E^J[\rho]=\frac{1}{2}\int\int\frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}}d\tau_1 d\tau_2 \tag{36}$$

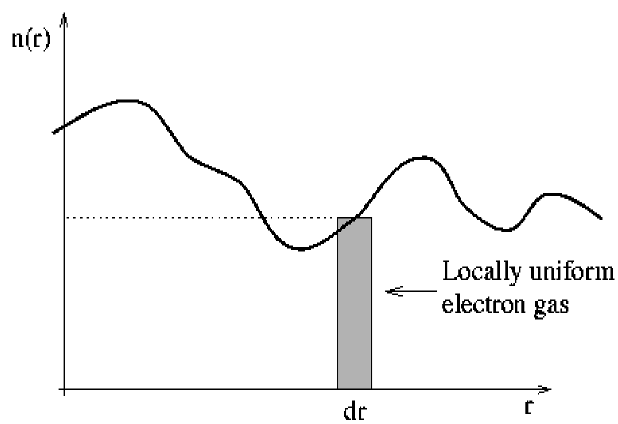
An exact form for the kinetic energy functional is not known, but as a first approximation

$$E^K[\rho]=\frac{3}{10}(3\pi^2)^{2/3}\int[\rho(\boldsymbol{r})]^{5/3}d\tau \tag{37}$$

which is suggested the Thomas-Fermi atomic model. A correction considering the gradient of electron density is added to this energy (*Weizsacker correction*)

$$\Delta E_W^K[\rho]=\frac{\lambda}{8}\int\frac{|\nabla\rho(\boldsymbol{r})|^2}{\rho(\boldsymbol{r})}d\tau \tag{38}$$

The exchange-correlation part is the most challenging. One treatment is called Local Density Approximation (LDA) : $E^{XC}=\int\rho(\boldsymbol{r})\epsilon^{XC}[\rho(\boldsymbol{r})]d\tau$, where ϵ^{XC} is the exchange-correlation energy per electron as a function of the density in the uniform electron gas. (Local Spin Density Approximation LSDA considers the electron density due to spin up or spin down).



$$E^{XC}=E^X+E^C \tag{39}$$

An early approximation to the exchange part of this contribution is known as the $X\alpha$ functional

$$E^X[\rho]=-\frac{9}{8}\alpha\frac{3}{\pi}^{1/3}\int[\rho(\boldsymbol{r})]^{4/3}d\tau \tag{40}$$

Now there have been several functional forms for E^{XC} , for example, B3LYP (becker 3-parameter, Lee, Yang, Par), PBE (Perdew-Burke-Ernzerhof 96) PW92 (Perdew-Wang 92).

An alternative computational scheme which as proven very successful is based on a hybrid between DFT and the HF method. The Kohn-Sham equations are a generalization of the HF equations

$$\left(-\frac{1}{2}\nabla^2-\sum_\alpha\frac{Z_\alpha}{|\boldsymbol{r}-\boldsymbol{R}_\alpha|}+V^J[\rho]+V^{XC}[\rho]\right)\psi_i(\boldsymbol{r})=\epsilon_i\psi_i(\boldsymbol{r}) \tag{41}$$

Where the last functional includes correlation (absent in HF) as well as exchange. At each stage of an iterative computation, the density is computed using the wavefunctions.

The exchange-correlation functional is formally related to the exchange-correlation energy in equation 34

$$V^{XC}[\rho]=\frac{\delta E^{XC}[\rho]}{\delta \rho} \qquad (42)$$

Computational Homework (due April 29)

Geometry and binding energy studies of water-water, benzene-benzene, water-benzene dimers.

1) Run geometrical optimization on the three dimers using DFT methods.
2) Calculate the binding energies for the three molecules.
3) Visualize the HOMOs and LUMOs of the optimized molecules.
4) Report the results.