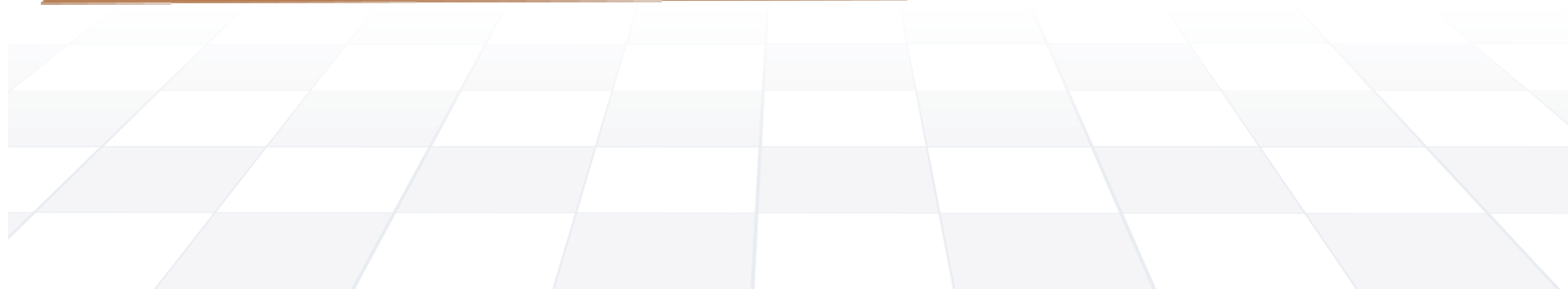


# Hartree-Fock: Review

And answers to basic questions on QM  
and Computational Chemistry

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# • Overview

- Computational chemistry:
  - **What** is the calculated quantity?  
**Which** equation is solved (“calculation level”)?
  - **How** is it solved? (i.e. what mathematical method is used to solve it)
- Chemical precision
- Calculation types
- Review of quantum mechanical wavefunctions
- BO approximation
- HF approximation
- Basis sets
- Spin-pairing
- Reference energies



# • Chemical precision

$$\Delta x / x \sim 1\%$$

- Energy:  $[E] \sim 1 \text{ kJ} / \text{mole} \Rightarrow \Delta E = 0.01 \text{ kJ} / \text{mole}$

$$\sim 0.001 \text{ hartree} \Rightarrow \Delta E = 10^{-5} \text{ hartree}$$

What is the chemical precision of energy? Length? Gradient? etc.

- Length:  $[\ell] \sim 1 \text{ \AA} \Rightarrow \Delta \ell = 0.01 \text{ \AA}$

- Angle:  $[\theta] \sim 1 - 10^\circ \Rightarrow \Delta \theta = 0.1^\circ$

- Energy Gradient:  $[E] / [\ell] \sim \frac{1 \text{ kJ} / \text{mole}}{1 \text{ \AA}} \Rightarrow \Delta F = 0.01 \frac{\text{kJ} / \text{mole}}{\text{ \AA}}$

- Population:  $[n] \sim 1 \Rightarrow \Delta n = 0.01$

- Charge:  $[q] \sim 1e \Rightarrow \Delta q = 0.01e$

- Dipole:  $[\mu] \sim [q][\ell] \sim 1e \text{ \AA} \sim 1D \Rightarrow \Delta \mu \sim 0.01D$



# • Calculation types

- **Single point:**  $E(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$

- Convergence criterion: 
$$\Delta E(\{\mathbf{R}_i\}) \leq \Delta E^{SP}$$

- **Geometric optimization (iterative calculation):**

$$E(\{\mathbf{R}_i^1\}) \rightarrow E(\{\mathbf{R}_i^2\}) \rightarrow \dots \rightarrow E(\{\mathbf{R}_i^{n-1}\}) \rightarrow E(\{\mathbf{R}_i^n\})$$

- Convergence criteria: 
$$\Delta E(\{\mathbf{R}_i^j\}) \leq \Delta E^{SP}$$

$$E(\{\mathbf{R}_i^{n-1}\}) - E(\{\mathbf{R}_i^n\}) \leq \Delta E^{GO}$$

$$-\frac{\partial E(\{\mathbf{R}_i^n\})}{\partial \mathbf{R}_i} \leq F_{\max}^{GO}, \frac{1}{N} \sum_i \left( -\frac{\partial E(\{\mathbf{R}_i^n\})}{\partial \mathbf{R}_i} \right) \leq F_{\text{avg}}^{GO}$$

$$|\mathbf{R}_i^n - \mathbf{R}_i^{n-1}| \leq \delta \mathbf{R}_{\max}^{GO}, \frac{1}{N} \sum_i |\mathbf{R}_i^n - \mathbf{R}_i^{n-1}| \leq \delta \mathbf{R}_{\text{avg}}^{GO}$$

$$n \leq n_{\text{cutoff}}^{GO}$$

# Quantum Mechanics

## Wave-functions and probabilities

- The state of the system is completely given by its wavefunction,  $\psi$ .
- The spatial part of a single-particle wavefunction is the orbital,  $\varphi(\mathbf{r})$ .
- For instance, the single particle (e.g. electron) probability density:

$$\varphi^* \varphi = |\varphi(x, y, z)|^2 = \rho(x, y, z)$$

The probability to find an electron somewhere in all space:

$$\langle \varphi(x, y, z) | \varphi(x, y, z) \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \varphi(x, y, z)^* \varphi(x, y, z) dx dy dz = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\varphi(x, y, z)|^2 dx dy dz = 1$$

Example:

The probability “p” to find the electron in a cubic volume:

$$p = \int_0^1 dx_1 \int_3^4 dy_1 \int_5^6 dz_1 |\varphi(x_1, y_1, z_1)|^2$$

$$x_1 \in [0, 1]$$

$$y_1 \in [3, 4]$$

$$z_1 \in [5, 6]$$



# • Quantum Mechanics

## Many-electron probabilities (e.g. molecules)

- Joint probability (single electron) density:

$$\rho(x, y, z) = n \sum_{m_{si}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \left| \psi(x, y, z, x_2, y_2, z_2, \dots, x_n, y_n, z_n, m_{s1}, m_{s2}, \dots, m_{sn}) \right|^2 dx_2 dy_2 dz_2 \dots dx_n dy_n dz_n$$

$$\int \rho(x, y, z) dV = n$$

- Probability to find charge at a given position:

Example: What is the probability “p” to find one electron between [2.5,3] Å

and the second electron between [-5,4] Å?

$$p = \sum_{m_{si}} \int_{-5.0}^{4.0} \int_{2.5}^3 \left| \psi(x_1, x_2, m_{s1}, m_{s2}) \right|^2 dx_1 dx_2$$

# • Quantum Mechanics

## Physical operators

- Each classical dynamical variable is associated with a QM operator. If the spectrum (i.e. the possible values) of this variable is strictly real, then the operator is a Hermitian one.
- The value of the variable is given by the expectation value of the operator in a given state,

$$X = \langle \hat{X} \rangle = \langle \psi | \hat{X} | \psi \rangle$$

- For example:

$$\langle \hat{H} \rangle = \langle \psi | \hat{H} | \psi \rangle = E$$

$$\langle \hat{\mu} \rangle = \langle \psi | e \sum_j^n \mathbf{r}_j | \psi \rangle$$

- The wavefunction cannot be measured directly, only operators can.



## • BO approximation

- The molecular wavefunction is decomposed as a product of a nuclear one and an electronic one:  $|\Psi(\{R_i\}, \{r_j\})\rangle = |\chi(\{R_i\})\psi(\{r_j\}; \{R_i\})\rangle$
- The electrons move much faster than the nuclei, so the electronic equation is solved for a static nuclear configuration:

$$\hat{H}_e |\psi(\{r_j\}; \{R_i\})\rangle = E_e(\{R_i\}) |\psi(\{r_j\}; \{R_i\})\rangle$$

- The nuclear equation is solved using a Potential Energy Surface (PES) which is given by the mutual repulsion of the nuclei and by the electronic energy as a function of nuclear configuration:

$$[\hat{H}_N + E_e(\{R_i\})] |\chi(\{R_i\})\rangle = E_N |\chi(\{R_i\})\rangle$$

- The approximation holds as long as nuclear motion is not sufficient to cause transitions between electronic states (i.e. the process is adiabatic):

$$\frac{\partial \mathbf{R}_i}{\partial t} < \frac{|\langle \psi_2 | \hat{H}_e | \psi_1 \rangle|^2}{\hbar \left( \frac{\partial E_{e,2}}{\partial \mathbf{R}_i} - \frac{\partial E_{e,1}}{\partial \mathbf{R}_i} \right)}$$



# • The Hartree-Fock wavefunction

- Under the BO approximation, solving the n-electron problem.
- Decomposition of many-particle wavefunction as a product of single particle wavefunctions:

$$\psi(\{\mathbf{r}_i\}, \{m_{s,i}\}) \sim \prod_{i=1}^N \phi_i(\mathbf{r}_i) \sigma_i = \prod_{i=1}^N \Phi_i(\xi_i)$$

- $\phi$  is the spatial part (orbital),  $\sigma$  is the spin part ( $\alpha=\uparrow$ ,  $\beta=\downarrow$ ), and the two together ( $\Phi$ ) are called a spin-orbital or “spinor”.
- For example, the ground state of the Helium atom

$$\psi_g^{He}(\mathbf{r}_1, \mathbf{r}_2, m_{s1}, m_{s2}) \sim 1s(\mathbf{r}_1) \alpha 1s(\mathbf{r}_2) \beta$$

- Antisymmetrization (electrons are fermions)

$$\psi_g^{He}(\mathbf{r}_1, \mathbf{r}_2, m_{s1}, m_{s2}) = 1s(\mathbf{r}_1) \alpha 1s(\mathbf{r}_2) \beta - 1s(\mathbf{r}_1) \beta 1s(\mathbf{r}_2) \alpha$$

- Slater determinant:

$$\psi(\{\mathbf{r}_i\}, \{m_{s,i}\}) = \frac{1}{\sqrt{n}} \begin{vmatrix} \Phi_1(\xi_1) & \Phi_2(\xi_1) & \cdots & \Phi_n(\xi_1) \\ \Phi_1(\xi_2) & \Phi_2(\xi_2) & \cdots & \Phi_n(\xi_2) \\ \vdots & \vdots & \ddots & \vdots \\ \Phi_1(\xi_n) & \Phi_2(\xi_n) & \cdots & \Phi_n(\xi_n) \end{vmatrix}$$

# • HF approximation

- Mean field approximation

- The Schrodinger equation under the Hartree-Fock approximation for the n-electron wavefunction becomes separable into n one-electron equations (the HF equations).\*
- HF equation for each electron solved separately, for a given state of all the other electrons. The solution is the orbital (or spinor) and orbital energy.

$$\hat{F}_i(\xi_i) |\Phi_i(\xi_i)\rangle = \varepsilon_i |\Phi_i(\xi_i)\rangle$$

- The electrostatic potential under which each electron moves is that created by the nuclei, and by the distribution of each of the other electrons. This is an “averaged” or mean field, in that the instantaneous position of each of the other electrons is averaged over.\*\*

- \*Static correlation

- The HF wavefunction is not always a reasonable representation of the n electron state. Using it entails neglect of static correlation.

- \*\*Dynamical correlation

- Since each electron is affected only by the average of the other electrons, the motion of the electrons is not correlated.

- Neglect of correlation is the main shortcoming of the HF method

$$E_{\text{Exact Schrodinger}} - E_{\text{HF-limit}} \equiv E_{\text{corr.}} \leq 0$$



# • The Self Consistent Field (SCF) Method

- Solving the n one-electron equations while taking into account that the solution to each affects all the others (i.e. the solution to each electron enters the equations for each of the other electrons via the electrostatic potential term).
- Starting from an initial guess, we solve for each electron.
- Once we've solved for all the electrons, we use the solutions to build updated electrostatic potential terms for each electron.
- Each time we solve for all the electrons is called a HF iteration.
- We continue iterating until convergence is achieved, in which case the solution is referred to as "self consistent".

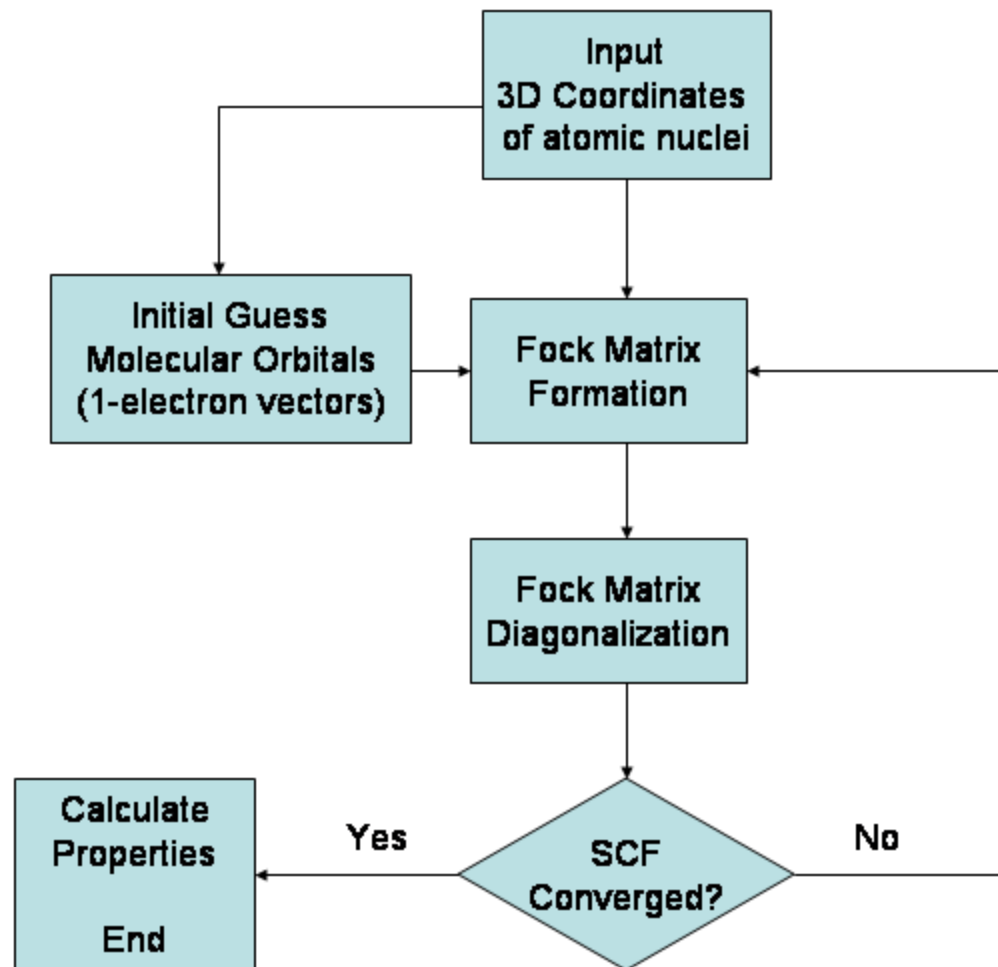
$$\left\langle \psi^n(\{\xi_i\}) \left| \hat{H} \right| \psi^n(\{\xi_i\}) \right\rangle - \left\langle \psi^{n-1}(\{\xi_i\}) \left| \hat{H} \right| \psi^{n-1}(\{\xi_i\}) \right\rangle \leq E_{\max}^{SP}$$

$$\left\langle \Phi_i^n(\xi_i) \left| \hat{F} \right| \Phi_i^n(\xi_i) \right\rangle - \left\langle \Phi_i^{n-1}(\xi_i) \left| \hat{F} \right| \Phi_i^{n-1}(\xi_i) \right\rangle \leq \varepsilon_{\max}^{SCF}$$

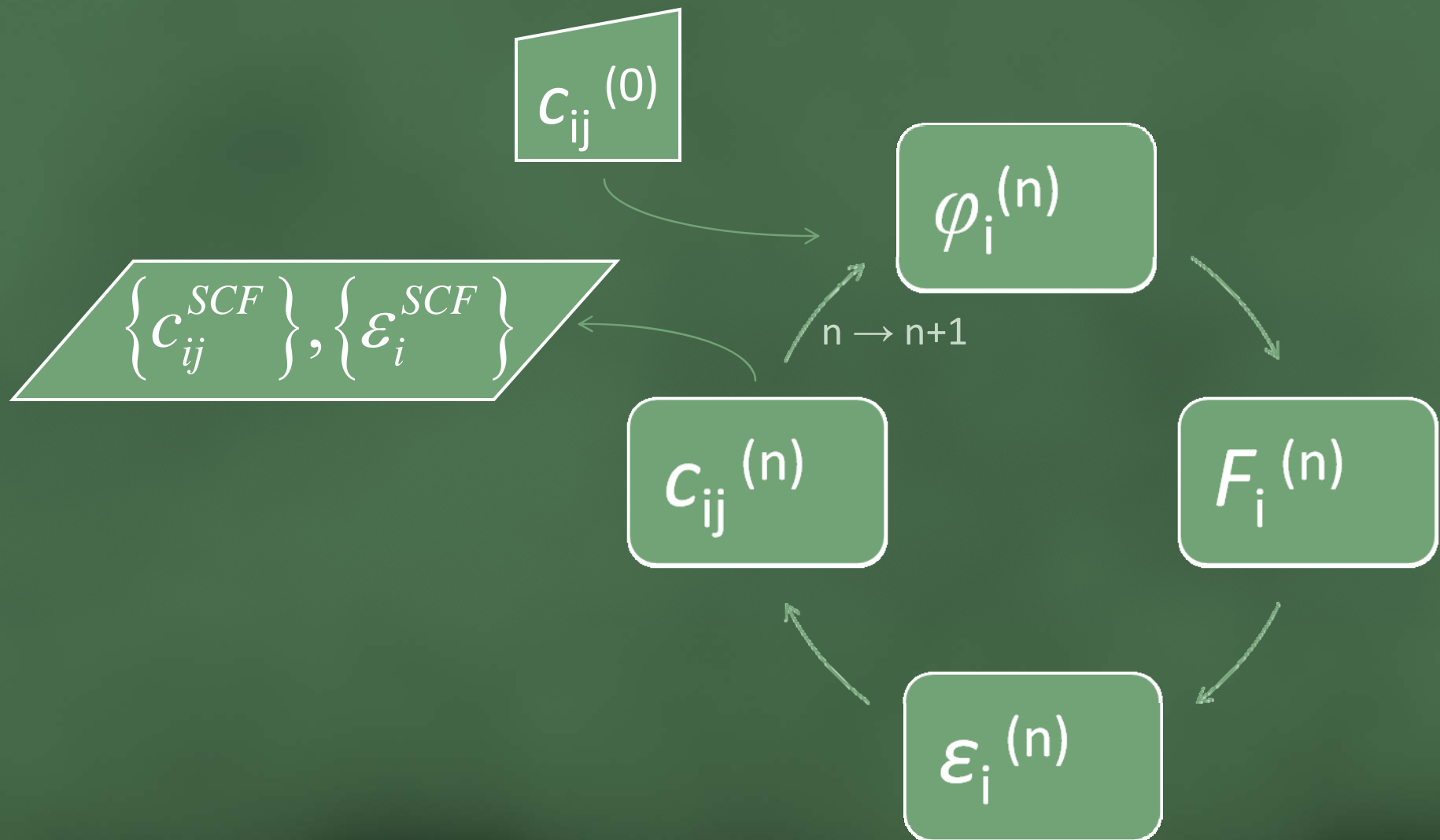
$$\left\langle \chi_j \left| \phi_i^n(\mathbf{r}_i) - \phi_i^{n-1}(\mathbf{r}_i) \right\rangle \leq c_{\max}^{SCF}$$



# • The Self Consistent Field (SCF) Method



# • The Self Consistent Field (SCF) Method



# • Basis sets

- The orbital of each electron may span all space, however realistically it is mostly distributed near the nuclei.
- From past experience in quantum chemistry we learn that some of the electrons in molecules (especially the inner ones, i.e. “core”) occupy orbitals which are little changed from the orbitals of the constituent atoms.
- We use the common language of atomic orbitals (AOs) as a basis in which to describe the molecular orbitals (MOs)
- Molecular Orbitals as a Linear Combination of Atomic Orbitals (MO-LCAO):  
$$\phi_i(\mathbf{r}) = \sum_{j=1}^m c_{ij} \chi_j(\mathbf{r}) \Rightarrow \langle \chi_j(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle = c_{ij}$$
- The MO-LCAO coefficients,  $c_{ij}$ , tell how much a given basis function (AO) comprises the MO in question.
- Each basis function is likewise expanded in primitives: STO, Gaussians, Hylleraas, elliptical...
- Spanning all space using a finite basis set is an approximation.

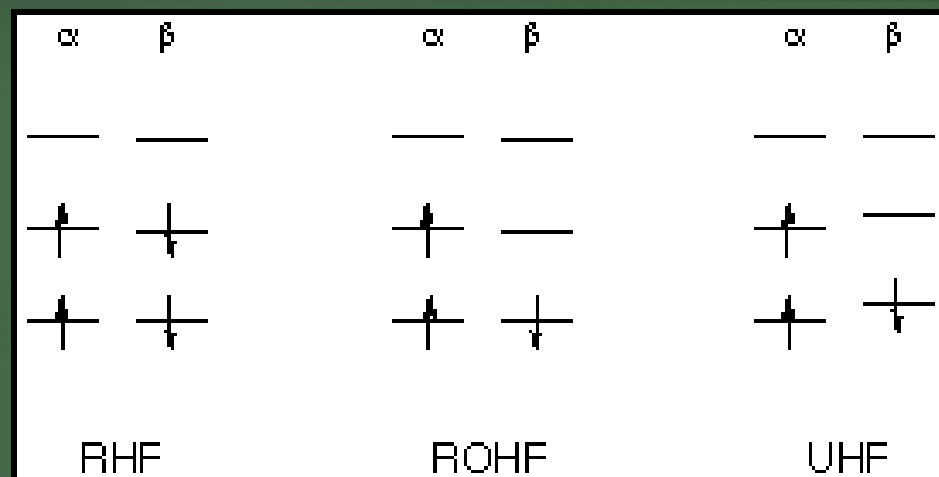


# • Spin pairing

- Spin multiplicity  $M = 2S + 1$ 
  - One of the necessary input parameters (other than nuclear configuration and total charge / number of electrons)
- Closed shell  $S = \langle \psi | \hat{S} | \psi \rangle = 0 \Rightarrow M = 1$ 
  - No unpaired electrons.
  - Most molecules are closed shell.
- Open shell  $S = \langle \psi | \hat{S} | \psi \rangle \neq 0 \Rightarrow M > 1$ 
  - Unpaired electron or electrons.
  - Opened shelled atoms or molecules (either neutrally charged or ions) are usually unstable and chemically reactive – radicals.

# • Spin pairing

- Restricted Hartree-Fock (RHF)
  - Closed shell only
- Restricted Open-shelled Hartree-Fock (ROHF)
- Unrestricted Hartree-Fock (UHF)
  - Orbitals equivalent to spinors.
- Due to the variational principle,  $E^{ROHF} \geq E^{UHF}$
- If  $n$  is the number of electrons, RHF requires  $m=n/2$  basis functions, ROHF requires  $m=n/2+1$ , and UHF requires  $m=n$ .





# • Reference energies

- **Steric energy** (MM): Zero when all nuclei are at rest, all springs are at equilibrium **and** all nuclei are separated by infinite distances

$$E = \frac{1}{2} m_i v_i^2 + V$$

$$V = \sum_{i \neq j}^N \frac{1}{2} k_{ij} (\mathbf{R}_i - \mathbf{R}_i^{eq})^2 + \sum_{i,j,k}^N \frac{1}{2} k_{ijk} (\theta_{ijk} - \theta_{ijk}^{eq})^2 + \sum_{i,j,k,\ell}^N \sum_{n=1}^5 \frac{1}{2} k_{ijk\ell} \left\{ 1 + \cos \left( n [\phi_{ijk\ell} - \phi_{ijk\ell}^{eq}] \right) \right\}$$

$$+ \sum_{i \neq j}^N \frac{q_i q_j}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_{i \neq j}^N \epsilon_{ij} \left[ \left( \frac{R_{ij}^m}{|\mathbf{R}_i - \mathbf{R}_j|} \right)^{12} - 2 \left( \frac{R_{ij}^m}{|\mathbf{R}_i - \mathbf{R}_j|} \right)^6 \right]$$

- **HF energy** (QM): Zero when all particles (nuclei and electrons) are at rest, and are separated by infinite distances

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \left\langle \Psi \left| \sum_{i=1}^N \left( -\frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i < j \leq N} \frac{q_i q_j}{r_{ij}} \right) \right| \Psi \right\rangle$$

- Can a molecule have negative energy?



# • Summary

- Computational chemistry: **What** is the calculated quantity? **Which** equation is solved (“calculation level”)? **How** is it solved? (i.e. what mathematical method is used to solve it)
- Chemical precision: Energy, length, angle, force, charge, population
- Calculation types: **Single point** vs. **geometric optimization**
- Review of quantum mechanical wavefunctions
- **BO** approximation
- **HF** approximation
  - HF wavefunction & **Slater determinant**
  - **SCF** algorithm: HF iterations
- Basis sets: **AOs** , **MOs** and **MO-LCAO**
- Spin-pairing: **RHF**, **ROHF**, **UHF**
- Reference energy: **Steric energy** (MM ) vs. **HF energy** (QM)