

# Variational principle

$$E_T = \frac{\int \psi_T^*(R) \hat{H} \psi_T(R) dR}{\int \psi_T^*(R) \psi_T(R) dR} \geq E_0$$

# Variational principle

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- The energy  $E$  computed from any state  $\Psi$  which may or may not satisfy the electronic Schrodinger equation is an upper bound to the ground state energy  $E_0$ :

$$E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} ; \langle \psi | \hat{H} | \psi \rangle = \int_{\Omega} \psi^* \hat{H} \psi dx$$

$$E[\psi] \geq E_0$$

$$\hat{H}\psi_0 = E_0 \psi_0$$

$E_0$  = ground state energy


- Minimization of the energy with respect to all allowed N-electron wave functions gives the ground state  $\Psi_0$  and energy  $E[\Psi_0]=E_0$ :

$$E_0 = \min_{\psi} E[\psi]$$

# Variational principle

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$$E_{\text{ground}} \leq \langle \phi | H | \phi \rangle.$$

$$\phi = \sum_n c_n \psi_n.$$


Hamiltonian eigenfunctions:  
normalized and orthogonal

$$\langle \phi | H | \phi \rangle$$

$$= \left\langle \sum_n c_n \psi_n \left| H \right| \sum_m c_m \psi_m \right\rangle$$

$$= \sum_n \sum_m \langle c_n \psi_n | E_m | c_m \psi_m \rangle$$

$$= \sum_n \sum_m c_n^* c_m E_m \langle \psi_n | \psi_m \rangle$$

$$= \sum_n |c_n|^2 E_n. \quad E_n \geq E_g$$



$$\langle \phi | H | \phi \rangle \geq E_g \sum_n |c_n|^2 = E_g.$$

# Variational Principle

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- One may replace the Schroedinger Equation with the variational principle:

$$\delta E[\psi] = 0$$

When the Schroedinger equation is satisfied, the above principle is satisfied and viceversa.

**Method of Lagrange multipliers to restate variational principle for normalized  $\Psi$ :**  
extremization of  $\langle \Psi | \hat{H} | \Psi \rangle$  subject to the constraint  $\langle \Psi | \Psi \rangle = 1$  is equivalent to making stationary the quantity  $[\langle \Psi | \hat{H} | \Psi \rangle - E \langle \Psi | \Psi \rangle]$  without constraints, with  $E$  = Lagrange multiplier.

$$\delta [\langle \psi | \hat{H} | \psi \rangle - E \langle \psi | \psi \rangle] = 0$$

For a system of  $N_e$  electron and given nuclear potential  $v$ , this equation defines a procedure for going from  $N_e$  and  $v$  to the ground state wavefunction  $\Psi$  and hence, using the expectation value of the Hamiltonian, to the ground state energy  $E[v, N_e]$ .

**$E$  is a functional of the number of electrons  $N$  and the nuclear potential  $v$ .**

$\hat{V}_{eN}$

# Hartree-Fock approximation

- **Ansatz** for the many body electronic wavefunction
- Application of **the variational principle** → Hartree-Fock equations
- Equations are solved **self-consistently**

# The Hartree-Fock approximation

Approximation for the many-body electronic wavefunction which is expressed as an antisymmetrized product of N orthonormal single particle orbitals, each written as a product of a spatial orbital and a spin function:



Prof. D.R. Hartree,  
Cambridge, UK,  
1897- 1958



Prof. V.A. Fock,  
St. Petersburg, Russia  
1898-1974

$$\psi = \frac{1}{\sqrt{N!}} \cdot \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \dots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & & \psi_N(x_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(x_N) & \psi_2(x_N) & & \psi_N(x_N) \end{vmatrix}$$
$$= \frac{1}{\sqrt{N!}} \det[\psi_1 \psi_2 \dots \psi_N] \leftarrow \text{SLATER DETERMINANT}$$

single particle  
wave function

$$\psi_i = \phi_i(\vec{r}) \cdot \sigma_i$$

# The Hartree-Fock approximation

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If we approximate the many-body wavefunction by a Slater determinant, the energy expectation value  $E_{\text{HF}}$  is:

$$E_{\text{HF}} = \langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij})$$

The  $H_i$ ,  $J_{ij}$  and  $K_{ij}$  integrals are written in terms of single particle wavefunctions;  $J_{ij}$  are called Coulomb integrals and  $K_{ij}$  are called exchange integrals

$$H_i = \int \psi_i^*(\bar{x}) \left[ -\frac{1}{2} \nabla^2 + v(\bar{x}) \right] \psi_i(\bar{x}) d\bar{x}$$

$$J_{ij} = \iint \psi_i(\bar{x}_1) \psi_i^*(\bar{x}_1) \frac{1}{r_{12}} \psi_j^*(\bar{x}_2) \psi_j(\bar{x}_2) d\bar{x}_1 d\bar{x}_2$$

$$J_{ii} = K_{ii}$$

$$K_{ij} = \iint \psi_i(\bar{x}_1) \psi_j^*(\bar{x}_1) \frac{1}{r_{12}} \psi_j^*(\bar{x}_2) \psi_i(\bar{x}_2) d\bar{x}_1 d\bar{x}_2$$

# The Hartree-Fock differential equations

Minimization of  $E_{\text{HF}}$  subject to orthonormalization conditions for the single particle orbitals gives the Hartree-Fock differential equations:

$$\hat{F} \psi_i(\bar{x}) = \sum_{j=1}^N \epsilon_j \psi_j(\bar{x}) \quad \text{with} \quad \hat{F} = -\frac{1}{2} \nabla^2 + v + \hat{g}$$

$\epsilon$  : Hermitian matrix ( $\epsilon_{ji}^* = \epsilon_{ij}$ ) of Lagrange multipliers

$g = \hat{J} - \hat{K}$  ; for an arbitrary function  $f(\bar{x})$  :

$$\hat{J}(\bar{x}_1) f(\bar{x}_1) \equiv \sum_{k=1}^N \int \psi_k^*(\bar{x}_2) \psi_k(\bar{x}_2) \frac{1}{r_{12}} f(\bar{x}_1) d\mathbf{x}_2$$

$$\hat{K}(\bar{x}_1) f(\bar{x}_1) \equiv \sum_{k=1}^N \int \psi_k^*(\bar{x}_2) f(\bar{x}_2) \frac{1}{r_{12}} \psi_k(\bar{x}_1) d\mathbf{x}_2$$



# The Hartree-Fock differential equations

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Minimization of  $E_{\text{HF}}$  subject to orthonormalization conditions for the single particle orbitals gives the Hartree-Fock differential equations:

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$\epsilon$  : Hermitian matrix ( $\epsilon_{ji}^* = \epsilon_{ij}$ ) of Lagrange multipliers

Note that  $\hat{g}$  depends on the orbitals  $\psi_i$  and thus the Fock operator depends on the orbitals. Therefore solutions of the Hartree-Fock equations must proceed **iteratively**. The Fock operator is a **non linear** operator. Consequently the Hartree-Fock method is called a **non-linear** “**self-consistent**” field method.

# Orbital energies

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$$\epsilon_i \equiv \epsilon_{ii} = \langle \psi_i | \hat{F} | \psi_i \rangle = H_i + \sum_{j=1}^N (J_{ij} - K_{ij})$$

$$\Downarrow$$
$$E_{\text{HF}} = \sum_{i=1}^N \epsilon_i - V_{ee}$$

$V_{ee}$  is the total electron - electron repulsion energy

$$V_{ee} = \int \psi_{\text{HF}}^*(x^N) \left[ \sum_{i < j} \frac{1}{r_{ij}} \right] \psi_{\text{HF}}(x^N) dx^N$$

$$\Downarrow$$
$$V_{ee} = \frac{1}{2} \sum_{i,j}^N (J_{ij} - K_{ij})$$

Total molecular energy:

$$W_{\text{HF}} = \sum_{i=1}^N \epsilon_i - V_{ee} + V_{nn}$$

# Systems with an even number of electrons: Restricted Hartree-Fock approximation (RHF)

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- The single particle orbitals  $\psi_i$  are taken to comprise  $N/2$  orbitals of the form  $\phi_k\alpha(s)$  [spin up orbitals] and  $N/2$  orbitals of the form  $\phi_k\beta(s)$  [spin down orbitals]; the radial part  $\phi_k$  is the same for up and down spins.

$$E_{\text{HF}} = \langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle = 2 \sum_{i=1}^{N/2} H_i + \frac{1}{2} \sum_{i,j=1}^{N/2} (2J_{ij} - K_{ij})$$

Now the integrals  $H_i$ ,  $J_{ij}$  and  $K_{ij}$  are written in terms of the radial part of the single particle wavefunctions  $\phi_k$  and the Hartree-Fock equation reads

$$\hat{F} \phi_k(\vec{r}) = \sum_{l=1}^{N/2} \mathcal{E}_{kl} \phi_l(\vec{r})$$

Since a Slater determinant is invariant by unitary transformation within the subspace of occupied single particle orbitals (but for a phase factor) and so are the operators  $\hat{J}_l$  and the Fock operator  $\hat{F}$ , one may choose a unitary transformation which diagonalizes the Hermitian matrix  $\mathcal{E}$ .

# Solution of Hartree-Fock equations

How do we solve the Hartree-Fock equations, i.e. an eigenvalue problem where the operator depends on the solutions? **Using an self-consistent iterative procedure**

Guess an initial Slater determinant:  $\psi \approx \psi \equiv |\psi_1^{in} \dots \psi_N^{in}|$

Constructs the Coulomb and exchange potentials using the orbitals from the guessed Slater determinant  $J[\{\psi_i^{in}\}] ; K[\{\psi_i^{in}\}]$

Construct the Fock operator and **solve the eigenvalue problem** (e.g. my matrix diagonalization, after expanding the single particle orbitals in a suitable **basis set**, for example a Gaussian basis set):

$$\hat{F}[\{\psi_i^{in}\}; \vec{r}] \psi_m^{out} = \epsilon_m^{out} \psi_m^{out}$$

$$\psi^{in} \approx \psi^{out}$$

yes

NO

$$\psi \approx \alpha \psi^{in} + \beta \psi^{out}$$

Self-consistency attained; Compute total energies and orbital energies

# Basis sets for the expansion of single particle wavefunctions: atomic and Slater type orbitals

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Historically, calculations for molecules were performed expanding single particle orbitals of molecules (or molecular orbitals) as a **linear combination of atomic orbitals (AO)**:

$$\psi_i = \sum_{\mu=1}^n c_{\mu i} \phi_{\mu}$$

where  $\psi_i$  is the i-th molecular orbital,  $c_{\mu i}$  are the coefficients of the linear combination,  $\phi_{\mu}$  is the  $\mu$ -th atomic orbital, and  $n$  is the number of atomic orbitals.

Atomic Orbitals (AO) are solutions of the Hartree-Fock equations for the atom, i.e. wave functions for a single electron in the atom. [However in the literature the term AO has been used to designate also other types of atomic-like basis functions.]

**Slater Type Orbitals (STO's)** have also been used as basis functions due to their similarity to atomic orbitals of the hydrogen atom. They are expressed in spherical coordinates:

$$\phi_i(\zeta, n, l, m; r, \theta, \phi) = N r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi)$$

where  $N$  is a normalization constant,  $\zeta$  is called "exponent". The  $r, \theta$ , and  $\phi$  are spherical coordinates, and  $Y_{lm}$  is the angular momentum part (spherical harmonic). The  $n, l$ , and  $m$  are quantum numbers: principal, angular momentum, and magnetic; respectively.

Some reviews on basis sets (Ahlrich & Taylor, 1981), (Andzelm et al., 1984), (Dunning & Hay, 1977), (Feller & Davidson, 1986), (Feller & Davidson, 1990), (Poirier et al., 1985).

# Basis sets for the expansion of single particle wavefunctions: Gaussian orbitals

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- Atomic and Slater-type orbitals are not suitable for fast calculations of two-electron integrals appearing in the HF equations.
- **Gaussian Type Orbitals (GTOs) were introduced in Quantum Chemistry so as to efficiently carry out calculations of two center integrals; they still are the most popular basis set used in quantum chemistry methods.** STO functions can be approximated by summing up a number of GTOs with different exponents and coefficients. Even if one uses 4 or 5 GTO's to represent an STO, the calculations of J and K integrals is still much faster than using original STOs.
- An GTO (called also cartesian gaussian) is expressed as:

$$g(\alpha, l, m, n; x, y, z) = N e^{-\alpha r^2} x^l y^m z^n$$

where  $N$  is a normalization constant,  $\alpha$  is called "exponent". The  $x$ ,  $y$ , and  $z$  are cartesian coordinates. The  $l$ ,  $m$ , and  $n$  ARE NOT QUANTUM NUMBERS but simply integral exponents at cartesian coordinates.

# Basis sets for the expansion of single particle wavefunctions: Gaussian orbitals

## Possible Gaussian functions

$$\begin{aligned}1s &= Ne^{-\alpha r^2} \\ 2p_x &= Ne^{-\alpha r^2} x \\ 2p_y &= Ne^{-\alpha r^2} y \\ 2p_z &= Ne^{-\alpha r^2} z \\ 3d_{xx} &= Ne^{-\alpha r^2} x^2 \\ 3d_{xy} &= Ne^{-\alpha r^2} xy \\ 3d_{xz} &= Ne^{-\alpha r^2} xz \\ 3d_{yy} &= Ne^{-\alpha r^2} y^2 \\ 3d_{yz} &= Ne^{-\alpha r^2} yz \\ 3d_{zz} &= Ne^{-\alpha r^2} z^2 \\ 4f_{xxx} &= Ne^{-\alpha r^2} x^3 \\ 4f_{xxy} &= Ne^{-\alpha r^2} x^2 y \\ 4f_{xyz} &= Ne^{-\alpha r^2} xyz\end{aligned}$$

Sometimes, the so-called scale factor,  $f$  (not to be confused with an “ $f$ ” function) is used to scale all exponents in the related gaussians. In this case, a gaussian function is written as:

$$g(\alpha, l, m, n, f; x, y, z) = Ne^{-\alpha f^2 r^2} x^l y^m z^n$$

**A minimal basis set is the smallest possible set to describe a given system, i.e., it contains only one function per occupied atomic orbital in the ground state (see also supplemental material in “further reading” on myucdavis).**

# Basic concepts of quantum chemistry

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- Basis sets
- Electron correlation
- Beyond Hartree-Fock
  - Wavefunction expansion
  - Perturbation theory



# Basis sets

Numerical errors introduced by the use of basis sets: to be checked carefully!!!

# Basis set superposition errors

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Basis sets chosen to describe a given composite system (e.g. molecule AB) and those used to describe its isolated fragments (e.g. A and B) usually do not yield the same accuracy in the calculations of total energy and other observables. One way to correct for **numerical inaccuracies** introduced by basis set superposition errors (or **BSSE**) is to use so called counterpoise corrections.

## Counterpoise Correction

The uncorrected expressions for the intermolecular interaction energy is

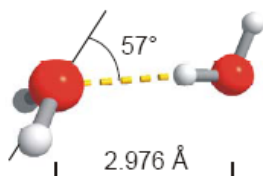
$$\Delta E_{UN} = E_{AB}(AB) - E_A(A) - E_B(B)$$

The counterpoise corrected expression for the intermolecular interaction energy is

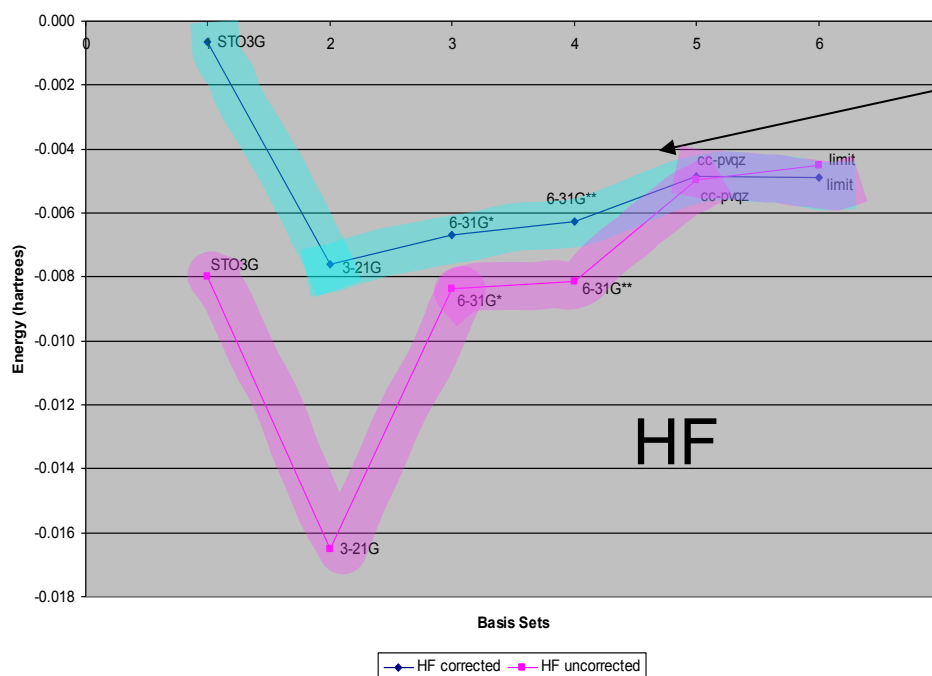
$$\Delta E_{CP} = E_{AB}(AB) - E_{AB}(A) - E_{AB}(B)$$

- $E_{AB}()$  total energy computed using the basis set of molecule AB.
- $E_A()$  total energy computed using the basis set of molecule A;  $E_B()$  total energy computed using the basis set of molecule B
- $E(AB)$  total energy of the molecule AB
- $E(A)$  total energy of the molecule A;  $E(B)$  total energy of the molecule B

# BSSE: the water dimer

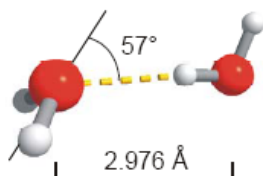


method	basis set	$R_{O...O}/\text{\AA}$	$R_{OH}/\text{\AA}$	$R_{OH}/\text{\AA}$	$R_{OH}/\text{\AA}$	$\angle HOH/^\circ$	$\angle HOH/^\circ$
RHF	3-21G	2.7966	0.9732	0.9657	0.9665	107.76	108.76
RHF	3-21G**	2.8277	0.9466	0.9406	0.9414	105.84	106.64
RHF	3-21+G**	2.8774	0.9466	0.9386	0.9405	109.04	109.37
RHF	6-31G*	2.9735	0.9518	0.9467	0.9483	105.38	105.84
RHF	6-31+G*	2.9632	0.9524	0.9424	0.085	106.55	106.60
RHF	6-31++G**	2.9878	0.9476	0.9425	0.9441	106.98	107.28
RHF	6-311++G**	3.0030	0.9454	0.9406	0.9421	106.07	106.64
B3LYP	6-311++G**	2.900	0.9700	0.9611	0.9629	105.21	105.60
MP2	6-311++G**	2.9156	0.9656	0.9588	0.9607	103.48	104.03
Exp.		2.976					

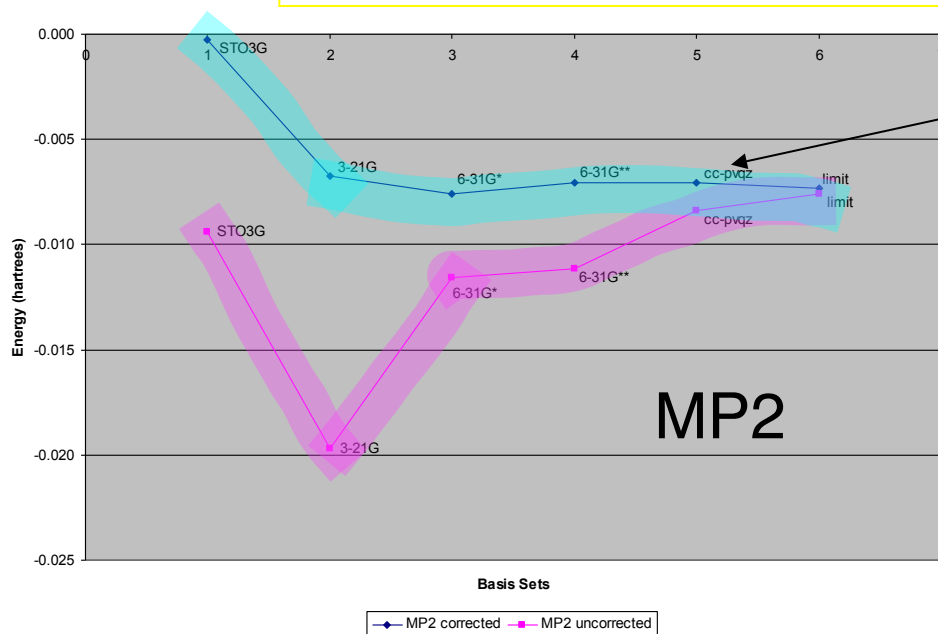


Counterpoise-corrected.

# BSSE: the water dimer



method	basis set	$R_{O...O}/\text{\AA}$	$R_{OH}/\text{\AA}$	$R_{OH}/\text{\AA}$	$R_{OH}/\text{\AA}$	$\angle\text{HOH}/^\circ$	$\angle\text{HOH}/^\circ$
RHF	3-21G	2.7966	0.9732	0.9657	0.9665	107.76	108.76
RHF	3-21G**	2.8277	0.9466	0.9406	0.9414	105.84	106.64
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Exp.		2.976					



Counterpoise-corrected.

# Electron correlation

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When we use one Slater Determinant to describe the many body wavefunction of electrons in the field of nuclei, we account for electron-electron repulsion by optimizing the one-electron single particle orbitals (or molecular orbitals-MO) in the presence of an average field of the other electrons. The result is that 'attraction' between electrons belonging to the same spatial MO is too strong. The HF approximation does not take into account that electronic motion is actually correlated (as one electron moves, the other respond). We define electronic correlation in the following way:

$$E_{\text{el.cor.}} = E_{\text{exact}} - E_{\text{HF}}$$

(B.O. approx; non-relativistic H)

# Discarding correlation has several consequences

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- **Equilibrium bond lengths are too short at the RHF level. (Potential well is too steep.) HF method ‘overbinds’ the molecule.**
- **Curvature of the PES near equilibrium is too great, vibrational frequencies are too high.**
- **The wavefunction contains too much ‘ionic’ character; dipole moments (and also atomic charges) at the RHF level are too large.**

Even for small molecules such as  $\text{H}_2$ , the correlation energy - is  $\sim 110$  kJ/mol, i.e. of the order of a chemical bond.

# Including electron correlation

- In quantum chemistry, there are many approaches to “recovering” the correlation energy which is missing in the HF approximation.
- These approaches fall into two classes:
  - Wavefunction expansion
  - Perturbation theory
- The most common wavefunction expansion approaches are Configuration Interaction “CI” and Coupled Cluster “CC” or “CCSD”.
- The most common perturbation approach is Moller-Plesset “MP2” or “MP4”.

# Configuration Interaction - Excited Slater Determinants

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Since the HF method yields the best single determinant wavefunction, it is commonly used as the reference on which subsequent improvements are based.

Consider a trial function which is a linear combination of Slater determinants:

$$\Psi = a_0 \Phi_{HF} + \sum_{i=1} a_i \Phi_i$$

← Multi-determinant wavefunction

$a_0$  is usually close to 1 ( $\sim 0.9$ ).

For  $N$  electrons,  $N/2$  orbitals are occupied in the RHF wavefunction.

**Questions: how do we choose the determinants  $\Phi_i$  and how do we determine the coefficients  $a_0$  and  $a_i$  ? In other words: how do we optimize a CI multi-body wavefunctions ?**



**Determinants  $\Phi_i$ :** generate excited Slater determinants by promoting up to N electrons from the N/2 occupied to M-N/2 virtual orbitals:

$a, b, c \dots =$ virtual MOs	9	—	—	$\downarrow$ $b$	—	$\downarrow$ $b$	$\downarrow$ $b$
	8	—	$\downarrow$ $a$	$\downarrow$ $a$	$\uparrow\downarrow$ $a, b$	$\downarrow$ $a$	$\downarrow$ $a$
	7	—	—	—	—	—	—
	6	—	—	—	—	$\downarrow$ $c$	$\uparrow\downarrow$ $c, d$
<hr/>							
$i, j, k \dots =$ occupied MOs	5	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $k$	— $k, l$
	4	$\uparrow\downarrow$	$\uparrow$ $i$	$\uparrow$ $i$	— $i, j$	$\uparrow$ $i$	$\uparrow$ $i$
	3	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
	2	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $j$	$\uparrow\downarrow$	$\uparrow$ $j$	$\uparrow$ $j$
	1	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
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		$\Psi_{HF}$	$\Psi_i^a$	$\Psi_{ij}^{ab}$	$\Psi_{ij}^{ab}$	$\Psi_{ijk}^{abc}$	$\Psi_{ijkl}^{abcd}$
Excitation level $\longrightarrow$		Ref.	Single	Double		Triple	Quadruple ...

# Represent the space containing all **N-fold excitations** by $\Psi(N)$

The complete CI wavefunction has the form

$$\Psi_{CI} = C_0 \Phi_{HF} + \Phi^{(1)} + \Phi^{(2)} + \Phi^{(3)} + \dots + \Phi^{(N)}$$

Where

$$\Phi_{HF} = \text{Hartree} - \text{Fock}$$

$$\Phi^{(1)} = \sum_i^{occ} \sum_a^{virt} C_i^a \Psi_i^a$$

Linear combination of Slater determinants with single excitations

$$\Phi^{(2)} = \sum_{i,j}^{occ} \sum_{a,b}^{virt} C_{ij}^{ab} \Psi_{ij}^{ab}$$

Double excitations

$$\Phi^{(3)} = \sum_{i,j,k}^{occ} \sum_{a,b,c}^{virt} C_{ijk}^{abc} \Psi_{ijk}^{abc}$$

Triples

$$\Phi^{(N)} = \sum_{i,j,k,\dots}^{occ} \sum_{a,b,c,\dots}^{virt} C_{ijk\dots}^{abc\dots} \Psi_{ijk\dots}^{abc\dots}$$

N-fold excitations

In principle, the complete  $\Psi_{CI}$  expanded in an infinite basis yields the exact solution to the Schrödinger eqn. (Non-relativistic, Born-Oppenheimer approx.). In any practical calculation such an expansion is truncated.

The various **coefficients**,  $C_{ijk\dots}^{abc\dots}$ , may be obtained, e.g. by **using the variational principle**

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$$E_{CI} = \frac{\langle \Psi_{CI} | H | \Psi_{CI} \rangle}{\langle \Psi_{CI} | \Psi_{CI} \rangle}$$

Expectation value of  $H_e$ .

$$\frac{\partial E_{CI}}{\partial C_{ijk\dots}^{abc\dots}} = 0$$

Energy is minimized with respect to coeff. C.

$$H\vec{C}_K = E_K\vec{C}_K$$

In a fashion analogous to the HF eqns, the CI Schrodinger equation can be formulated as a matrix eigenvalue problem.

The elements of the vector,  $\vec{C}_K$ , are the coefficients,  $C_{ijk\dots}^{abc\dots}$  and the eigenvalue,  $E_K$ , approximates the energy of the  $K^{\text{th}}$  state.

$E_1 = E_{CI}$  for the lowest state of a given symmetry and spin.

$E_2 = 1^{\text{st}}$  excited state of the same symmetry and spin, and so on.

# Some nomenclature and practical calculations

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**One-electron basis** (one-particle basis) refers to the basis set (e.g. gaussian functions or numerical functions on a grid) used to **expand the one-electron functions**, or Molecular Orbitals. This determines the accuracy obtained in describing single-particle or MO orbitals.

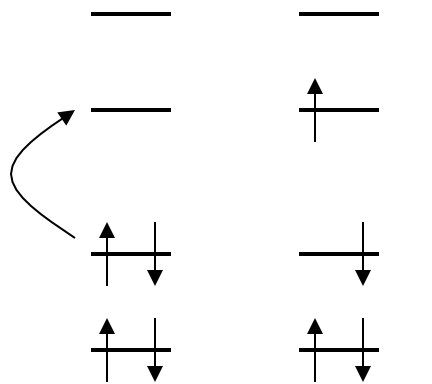
**Many-electron basis** (N-particle basis) refers to the **number of Slater determinants** used in the expansion of the CI wavefunction. The number of many-electron basis functions limits the accuracy obtained in the description of **electron correlation**.

*In practice,*

- **Complete CI** (Full CI) is rarely done even for small basis sets - too expensive. **Computational workload** scales with the number of many-electron basis functions as **M!**.
- Full CI within a given one-particle basis is the ‘benchmark’ for that basis since 100% of the correlation energy is recovered. Used to calibrate approximate correlation methods.
- CI expansion is usually **truncated** at a some excitation level, e.g. Singles and Doubles (**CISD**).

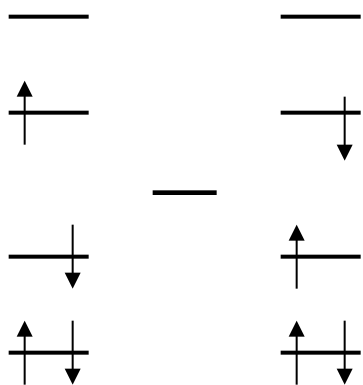
$$\Psi_{CI} = C_0 \Phi_{HF} + \Phi^{(1)} + \Phi^{(2)}$$

# Configuration State Functions



$\Phi_{\text{RHF}}$

$\Phi^{(1)}$



Singlet CSF

$$\Phi(1,2) = \phi_1\alpha(1)\phi_2\beta(2) - \phi_1\alpha(2)\phi_2\beta(1)$$

Consider a single excitation from the RHF reference.

Both  $\Phi_{\text{RHF}}$  and  $\Phi^{(1)}$  have  $S_z=0$ , but  $\Phi^{(1)}$  is not an eigenfunction of  $S^2$ .

Linear combination of singly excited determinants is an eigenfunction of  $S^2$ .

**Configuration State Function, CSF**  
(Spin Adapted Configuration, SAC)

Only CSFs that have the same multiplicity as the HF reference contribute to the correlation energy.

# Example of CI calculations for the water molecule

## Basis functions

Number of singlet CSFs as a function of excitation level for H<sub>2</sub>O with a 6-31G(d) basis ← (19 one particle basis functions)

Excitation level <i>n</i>	Number of <i>n</i> th excited CSFs	Total number of CSFs	Number of many- electron basis
1	71	71	
2	2 485	2 556	
3	40 040	42 596	← CISD
4	348 530	391 126	(~80-90% of
5	1 723 540	2 114 666	correlation energy)
6	5 033 210	7 147 876	
7	8 688 680	15 836 556	
8	8 653 645	24 490 201	
9	4 554 550	29 044 751	
10	1 002 001	30 046 752	← Full CI

# Example of CI calculations for the Neon atom

Weights of excited configurations for the Neon atom

Excitation level	Weight	Relative importance
0	0.9644945073	Ref.
1	0.0009804929	Singles 2
2	0.0336865893	Doubles 1
3	0.0003662339	Triples 4
4	0.0004517826	Quadruples 3
5	0.0000185090	$\text{Weight} = \sum_{ijk\dots}^{abc\dots} (C_{ijk\dots}^{abc\dots})^2$ for a given excitation level.
6	0.0000017447	
7	0.0000001393	
8	0.0000000011	

(Frozen core approx., 5s4p3d basis - 32 functions)

- CISD (singles and doubles) is the only method of general applicability. For modest sized molecules and basis sets, ~80-90% of the correlation energy is recovered.
- CISD recovers less and less correlation energy as the size of the molecule increases.

## Size Consistent and Size Extensive Methods

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**Size consistent** - the energy of two molecules (or fragments) computed at large separation equals twice the energy of the individual molecules (or fragments).

**Size extensive** - the energy scales properly with the number of particles.

1. Full CI is size consistent and extensive.
2. All forms of truncated CI are not. (Some forms of CI, e.g. Multi-Reference-CI are approximately size consistent and size extensive for a large enough reference space.)

Ex.  $(E_{\text{CISD}} \text{ of two } \text{H}_2 \text{ separated by } 100\text{\AA}) < 2(E_{\text{CISD}} \text{ of one } \text{H}_2)$



# Including electron correlation

- In quantum chemistry, there are many approaches to “recovering” the correlation energy which is missing in the HF approximation.
  - These approaches fall into two classes:
    - Wavefunction expansion
    - Perturbation theory
  - The most common wavefunction expansion approaches are Configuration Interaction “CI” and Coupled Cluster “CC” or “CCSD”.
- The most common perturbation approach is Moller-Plesset “MP2” or “MP4”.

# Møller-Plesset Perturbation Theory

We consider an Hamiltonian  $H_0$  and a “small” perturbation.

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \quad \longleftarrow \quad \lambda \text{ Determines the strength of the perturbation}$$

$$\hat{H}_0 \Phi_i = E_i \Phi_i, \quad i = 0, 1, 2, \dots, \infty \quad H_0 \text{ is the unperturbed Hamiltonian, e.g. HF:}$$

$$\hat{H}_0 = \sum_{i=1}^N \hat{F}_i = \sum_{i=1}^N \left( \hat{h}_i + \sum_{j=1}^N \left( \hat{J}_{ij} - \hat{K}_{ij} \right) \right)$$

$$\hat{H}' = \sum_{i=1}^N \sum_{j>1}^N g_{ij} - \sum_{i=1}^N \sum_{j=1}^N \langle g_{ij} \rangle \quad \longleftarrow$$

We choose the perturbation to be a two-electron operator, when  $H_0$  is the Hartree-Fock Hamiltonian.

$$\hat{H}\Psi = W\Psi \quad \longleftarrow$$

**Total Hamiltonian**

$$W = \lambda^0 W_0 + \lambda^1 W_1 + \lambda^2 W_2 + \dots \quad \longleftarrow$$

**Energy perturbation**

$$\Psi = \lambda^0 \Psi_0 + \lambda^1 \Psi_1 + \lambda^2 \Psi_2 + \dots \quad \longleftarrow$$

**Wave-function perturbation**

# Møller-Plesset Perturbation Theory

$W_0$  = sum over MO energies

$$W_1 = \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle = E(\text{HF})$$

$$W_2 = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} \frac{\langle \Phi_0 | \hat{H}' | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | \hat{H}' | \Phi_0 \rangle}{E_0 - E_{ij}^{ab}}$$

Use **second order perturbation theory** to evaluate corrections to the HF energy. The first contribution to the correlation energy comes from double excitations.

Explicit formula for 2<sup>nd</sup> order Møller-Plesset perturbation theory, MP2.

$$E(\text{MP2}) = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} \frac{[\langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle]^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

Møller C., Plesset M.S. , *Phys. Rev.* **46**: 618–622 (1934).

**4-center J and K integrals**

# Advantages and disadvantages of Møller-Plesset Perturbation Theory

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- MP2 computations on moderate sized systems ( $\sim 150$  basis functions) require an effort which is computationally affordable on moderate size machines.
- MP2 is **size-extensive** . Hence the error in evaluating energies remains relatively constant for different systems.
- **MP2 is not variational**
- **MP2 recovers  $\sim 80\text{-}90\%$  of the correlation energy of many molecules.**
- **MP2 can be extended to 4<sup>th</sup> order:** MP4(SDQ) and MP4(SDTQ).  
MP4(SDTQ) recovers  $\sim 95\text{-}98\%$  of the correlation energy; but scaling of MP2 becomes much worst ( $M^7$ ) than that of MP2 (in principle  $\sim M^5$ )

# Coupled Cluster Theory

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Perturbation methods add all types of corrections (excitations), e.g., S,D,T,Q,..to a given order (2nd,4th,... or MP@, MP4).

Coupled cluster (CC) methods include all corrections of a given type (e.g. S) to infinite order.

The CC wavefunction is

$$\Psi_{CC} = e^{\hat{T}} \Phi_0$$

$\Phi_0$  is the HF solution

$$e^{\hat{T}} = \hat{1} + \hat{T} + \frac{1}{2} \hat{T}^2 + \frac{1}{6} \hat{T}^3 + \dots = \sum_{k=0}^{\infty} \frac{1}{k!} \hat{T}^k$$

**Exponential operator** is used to generate excited Slater determinants

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_N$$

Cluster Operator

N is the number of electrons

# Coupled Cluster Theory

$$\hat{T}_1 \Phi_0 = \sum_i^{occ} \sum_a^{vir} t_i^a \Phi_i^a$$

$$\hat{T}_2 \Phi_0 = \sum_{i < j}^{occ} \sum_{a < b}^{vir} t_{ij}^{ab} \Phi_{ij}^{ab}$$

The T-operator acting on the HF reference generates **all  $i^{\text{th}}$  excited Slater Determinants**, e.g. doubles  $\Phi_{ij}^{ab}$ .

$$\left. \begin{array}{l} t_i^a \\ t_{ij}^{ab} \end{array} \right\}$$

Expansion coefficients are called **amplitudes**; they are equivalent to the  $a_i$ 's in the general multi-determinant wavefunction.

HF ref.  $\swarrow$

$$e^{\hat{T}} = \hat{1} + \hat{T}_1 + \left( \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right) + \left( \hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{1}{6} \hat{T}_1^3 \right) + \left( \hat{T}_4 + \hat{T}_3 \hat{T}_1 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{2} \hat{T}_2 \hat{T}_1^2 + \frac{1}{24} \hat{T}_1^4 \right) + \dots$$

$\nwarrow$  singles      doubles      triples      Quadruple excitations

We use the above written form of the exponential operator to generate Slater determinants

# Nomenclature of Coupled Cluster Theory

$$\hat{1}$$

HF reference

$$\hat{T}_1$$

Singly excited states

$$\left( \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right)$$

$$\hat{T}_2$$

*Connected* doubles

$$\hat{T}_1^2$$

*Dis-connected* doubles

$$\left( \hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{1}{6} \hat{T}_1^3 \right)$$

$$\hat{T}_3$$

*Connected* triples, ‘true’ triples

$$\hat{T}_2 \hat{T}_1$$

*‘Product’* Triples, disconnected triples

$$\hat{T}_1^3$$

$$\left( \hat{T}_4 + \hat{T}_3 \hat{T}_1 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{2} \hat{T}_2 \hat{T}_1^2 + \frac{1}{24} \hat{T}_1^4 \right)$$

$$\hat{T}_4$$

True quadruples - four electrons interacting

$$\hat{T}_2^2$$

Product quadruples - two non-interacting pairs

$$\hat{T}_3 \hat{T}_1, \hat{T}_2 \hat{T}_1^2, \hat{T}_1^4$$

Product quadruples, and so on.

# Coupled Cluster Theory

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If all cluster operators up to  $T_N$  are included, the method yields energies that are essentially equivalent to Full CI.

In practice, only the singles and doubles excitation operators are used → **Coupled Cluster Singles and Doubles model (CCSD)**.

$$e^{\hat{T}_1 + \hat{T}_2} = \hat{1} + \hat{T}_1 + \left( \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right) + \left( \hat{T}_2 \hat{T}_1 + \frac{1}{6} \hat{T}_1^3 \right) + \left( \frac{1}{2} \hat{T}_2^2 + \frac{1}{2} \hat{T}_2 \hat{T}_1^2 + \frac{1}{24} \hat{T}_1^4 \right)$$

However **triple** and **quadruple** excitations also enter into the energy expression (not shown) via products of **single and double amplitudes**.

It has been shown that in many cases the **connected triples term,  $T_3$** , is important. It can be included perturbatively at a modest cost to yield the **CCSD(T)** model. With the inclusion of connected triples, the CCSD(T) model yields energies close to the Full CI, for a the given basis.



# CC method: examples

Performance of the CC method: application to H<sub>2</sub>O

H <sub>2</sub> O	HF	CCSD	CCSD(T)	experiment
AE (kJ/mol)	652	960	976	975
$R_{\text{OH}}$ (pm)	94.0	95.4	95.7	95.8
$\Theta_{\text{HOH}}(^{\circ})$	106.3	104.5	104.2	104.4
$\mu_0$ (D)	1.96	1.87	1.85	1.85
$\omega_1$ (cm <sup>-1</sup> )	4231	3998	3958	3942
$\omega_2$ (cm <sup>-1</sup> )	4131	3893	3851	3832
$\omega_3$ (cm <sup>-1</sup> )	1748	1670	1658	1649
$\sigma_{\text{O}}$ (ppm)	337	337	338	344(17)
$\sigma_{\text{H}}$ (ppm)	31.1	30.9	30.9	30.1

Very large basis sets are required for errors smaller than 1 kJ/mol:

N <sub>2</sub> /CCSD	DZ	TZ	QZ	5Z	6Z	limit
corr. energy (mE <sub>h</sub> )	-309.3	-371.9	-393.1	-400.6	-403.7	-408(1)

# Comparison of different quantum chemistry methods

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	CI-SD	CI-SDTQ	MP2	MP4 (SDTQ)	CCSD	CCSD(T)
Scaling with $M$ (~ # of electrons)	$M^6$	$M^{10}$	$M^5$	$M^7$	$M^6$	$M^7$
Size extensive/ consistent	No	~ Yes	Yes	Yes	Yes	Yes
Variational	Yes	Yes	No	No	No	No
Requires good zero order trial wvfcts	Yes	~No	Yes	Yes	~No	No
General applicability	Yes	~No	Yes	Yes	~No	No