

# Electronic Structure Methods

- One-electron models – e.g., Huckel theory
- Semiempirical methods – e.g., AM1, PM3, MNDO
- Single-reference based *ab initio* methods
- Hartree-Fock
  - Perturbation theory – MP2, MP3, MP4
  - Coupled cluster theory – e.g., CCSD(T)
- Multi-configurational based *ab initio* methods
  - MCSCF and CASSCF (also GVB)
  - MR-MP2 and CASPT2
  - MR-CI
- *Ab Initio* Methods for IPs, EAs, excitation energies
  - CI singles (CIS)
  - TDHF
  - EOM and Greens function methods
  - CC2

- Density functional theory (DFT)- Combine functionals for exchange and for correlation
  - Local density approximation (LDA)
  - Perdew-Wang 91 (PW91)
  - Becke-Perdew (BP)
  - BeckeLYP (BLYP)
  - Becke3LYP (B3LYP)
  - Time dependent DFT (TDDFT) (for excited states)
- Hybrid methods
  - QM/MM
  - Solvation models

Why so many methods to solve  $H\psi = E\psi$ ?

Electronic Hamiltonian, BO approximation

$$H = -\frac{1}{2} \sum \nabla_i^2 - \sum \frac{Z_A}{r_{iA}} + \sum_{i < j} \frac{1}{r_{ij}} + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} \quad (\text{in a.u.})$$

$1/r_{ij}$  is what makes it tough (nonseparable)!!

Hartree-Fock method:

- Wavefunction antisymmetrized product of orbitals

$$\Psi = |\phi_1(\tau_1) \cdots \phi_N(\tau_N)| \leftarrow \text{Slater determinant}$$

accounts for indistinguishability of electrons

In general,  $\tau$  refers to both spatial and spin coordinates

For the 2-electron case

$$\Psi = |\phi_1(\tau_1)\phi_2(\tau_2)| = \frac{1}{\sqrt{2}} [\phi_1(\tau_1)\phi_2(\tau_2) - \phi_2(\tau_1)\phi_1(\tau_2)]$$

Energy minimized – variational principle

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \begin{array}{l} \text{Vary orbitals to minimize } E, \\ \text{keeping orbitals orthogonal} \end{array}$$

$h_i \phi_i = \varepsilon_i \phi_i \rightarrow$  orbitals and orbital energies

$$h_i = -\frac{1}{2} \nabla_i^2 - \sum \frac{Z_A}{r_{iA}} + (J_i - K_i) \quad J_i = \sum_{j \neq i} \int \frac{\phi_j(r_2)^2}{r_{12}} dr_2$$

$$K_i \phi_i(r_1) = \sum_{j \neq i} \int \frac{\phi_j(r_2)\phi_i(r_2)}{r_{12}} dr_2 \phi_j(r_1)$$

## Characteristics

- Each  $e^-$  “sees” average charge distribution due to other  $e^-$ . (It is a mean field method.)

- Electron correlation missing

In-out

Left-right

- $h$  depends on the orbitals one is trying to solve. Requires an iterative (self-consistent) solution.

### Partitioning of Hamiltonian

$$H = F + V$$

$$F = \sum h_i \longrightarrow F\phi_i = \varepsilon_i\phi_i$$

$$V = \sum(1/r_{ij}) - \sum(J_i - K_i) \text{ (weaker than } \sum 1/r_{ij}\text{)}$$

$$E^{\text{HF}} = \langle \psi | H | \psi \rangle = \langle \psi | F | \psi \rangle + \langle \psi | V | \psi \rangle$$

0<sup>th</sup> order      1<sup>st</sup> order

Note:  $E$  not just a sum of orbital energies  
(would double count Coulomb interactions)

## Solution of the HF problem

- Introduce a basis set (usually atomic orbitals)
- Evaluate 1- and 2-electron integrals
- Generate an initial guess for the MO's
- Construct Fock matrix
- Diagonalize → new orbitals and orbital energies
- Rebuild Fock matrix + iterate (SCF)

Stop when specified convergence criterion met

## Observations

- Brute force  $(1/8)N^4$  2-el. integrals

$$\int \chi_a(r_1)\chi_b(r_2)\frac{1}{r_{12}}\chi_c(r_1)\chi_d(r_2)dr_1dr_2$$

- Clever codes - scale as  $N^3$  or weaker
- Can be multiple solutions!!

These are nonlinear equations, and the solution can depend on the initial guess or the iterative procedure might not converge.

Most QC codes using GTOs (Gaussians)

$$s \approx e^{-\alpha_i r^2}$$

$$p \approx (x, y, z)e^{-\alpha_i r^2}$$

Usually these are **contracted**

$$\text{e.g., } 1s = \sum_{j=1}^3 c_j e^{-\alpha_j r^2}$$

The contraction coeffs.  $c_j$  and exponents  $\alpha_j$  are fixed and are different for each element.

The above function counts as “3” for the integral evaluation, but only “1” for the size of the SCF.

**Example: 3-21G** - 1s (3 primitives), tight 2s2p (2 primitives), extended 2s'2p' (1 primitive)

**Conventional vs. direct SCF**

**Conventional** – store integrals

**Direct** – compute integrals “on the fly”

Essential for big systems

## Some common Gaussian basis sets

Basis set	H	Li-Ne	Na-Ar
STO-3G	1s	2s1p	3s2p
3-21G	2s	3s2p	4s3p
6-31G(d)	2s	3s2p1d	4s3p1d
6-31G(d,p)	2s1p	3s2p1d	4s3p1d
6-311G(d,p)	3s1p	4s3p1d	5s4p1d
6-311G(2df,2pd)	3s2p1d	4s3p2s1f	5s4p2d1f
6-311++G(d,p)	4s1p	5s4p1d	6s5p1d
cc-pVDZ	2s1p	3s2p1d	4s3p1d
cc-pVTZ	3s2p1d	4s3p2d1f	5s4p2d1f
cc-pvQZ	4s3p2d1f	5s4p3d2f1g	6s5p3d2f1g
aug-cc-pVDZ	3s2p	4s3p2d	5s4p2d

- General remarks about atom-centered basis sets

- Pople basis sets

- (...) – polarization functions

- “+” diffuse functions – anions, polarizability

- Dunning correlation-consistent basis sets

- Valence double-zeta, triple-zeta, etc.

- Aug  $\Rightarrow$  adds one diffuse function of each angular momentum type already in the basis.

- Cusp conditions

- $\Psi'$  discontinuous as  $r_{12} \rightarrow 0$

- Never achieved in a single configurational wavefunction

- Requires very high angular momentum basis functions

- Also makes it hard to satisfy the virial theorem

$$\langle V \rangle / \langle T \rangle = -2$$

- Basis set superposition error (BSSE)

- Consider AB – A uses functions on B and B uses functions on A to lower their energies – artificial energy lowering at short distances.

- Counterpoise correction

- Linear dependency problems

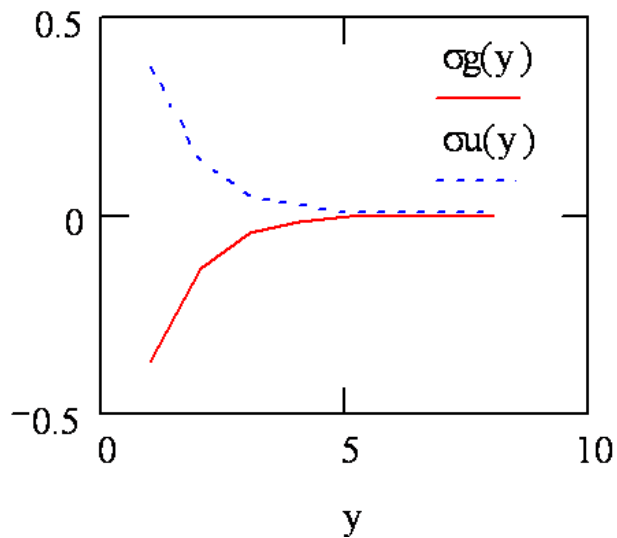
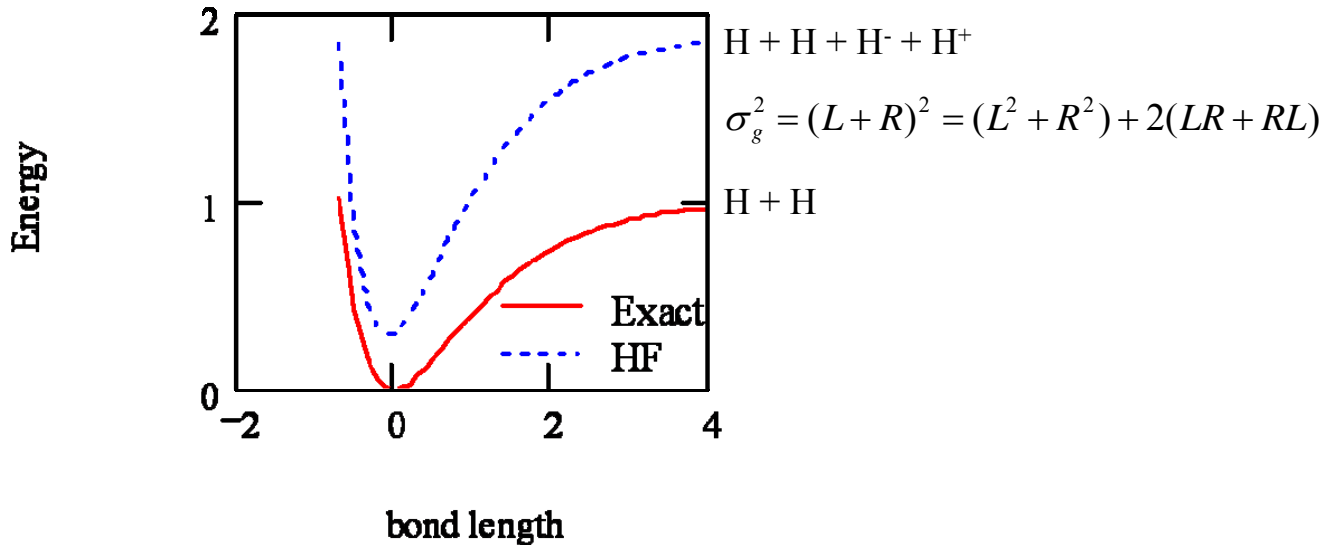
- Plane-wave basis sets

- Commonly employed by physics/materials science community

- At present only used with DFT methods

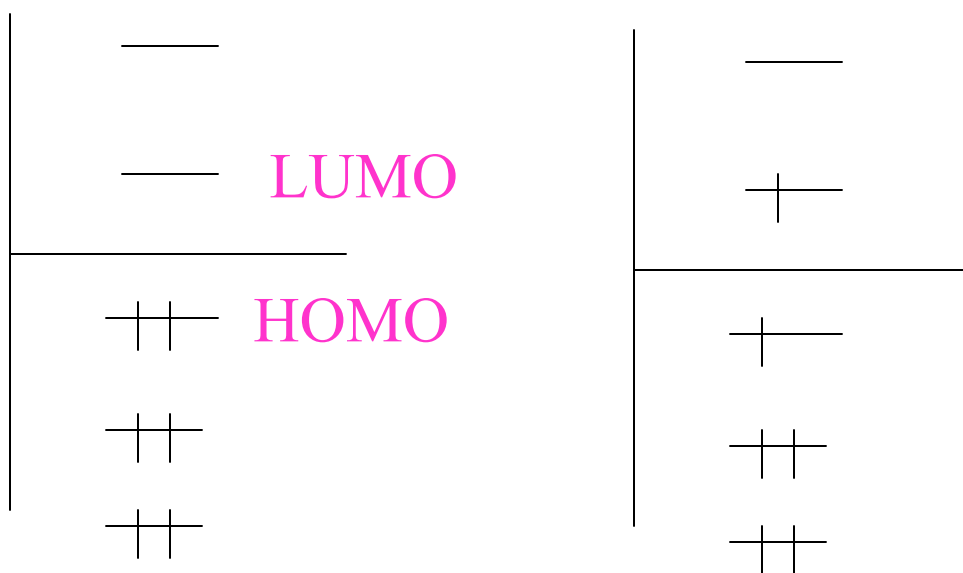
# Hartree-Fock calculations

The HF potential for H<sub>2</sub> does not dissociate correctly: E(H<sub>2</sub>, R = inf.) ≠ 2\*E(H)



$\sigma_g, \sigma_u$  orbitals  
 → degenerate  
 as  $R \rightarrow \text{infinity}$

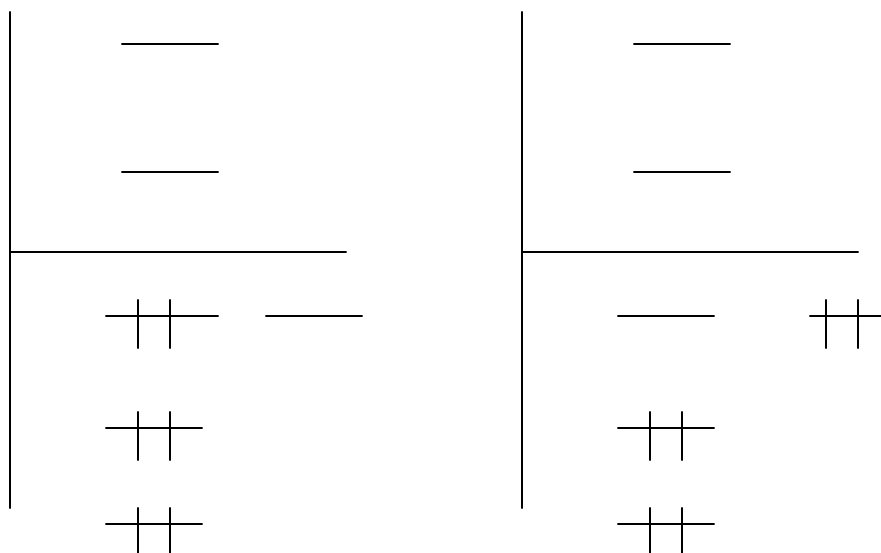
Solve by using  $\Psi = C_1 |\varphi_g \overline{\varphi_g}| + C_2 |\sigma_u \overline{\sigma_u}|$



Closed-shell,  $S = 0$

Open-shell, singlet ( $S = 0$ ) or triplet ( $S = 1$ )

Open-shell singlet cannot be described by HF method!!!!



Diradical – HF also not valid