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

\[
H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum \frac{Z_A}{r_{iA}} + \sum \frac{1}{r_{ij}} + \sum \frac{Z_A Z_B}{R_{AB}} \quad \text{(in a.u.)}
\]

\( 1/r_{ij} \) 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

\[
E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \text{Vary orbitals to minimize } E, \quad \text{keeping orbitals orthogonal}
\]

\( h \phi_i = \epsilon_i \phi_i \rightarrow \text{orbitals and orbital energies} \)

\[
h_i = -\frac{1}{2} \nabla_i^2 - \sum \frac{Z_A}{r_{iA}} + (J_i - K_i)
\]

\[
J_i = \sum_{j \neq i} \int \frac{\phi_j(r_2)^2}{r_{12}} dr_2
\]

\[
K_i \phi_i(r_i) = \sum_{j \neq i} \int \frac{\phi_j(r_2)\phi_i(r_i)}{r_{12}} dr_2 \phi_j(r_i)
\]
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

\[ H = F + V \]

\[ F = \sum h_i \quad \rightarrow \quad F\phi_i = \varepsilon_i\phi_i \]

\[ V = \sum \left(\frac{1}{r_{ij}}\right) - \sum (J_i-K_i) \text{ (weaker than } \sum \frac{1}{rij}) \]

\[ E^{HF} = \langle \psi | H | \psi \rangle = \langle \psi | F | \psi \rangle + \langle \psi | V | \psi \rangle \]

\[ 0^{\text{th}} \text{ order} \quad 1^{\text{st}} \text{ order} \]

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
  \[
  \int \chi_a(r_1)\chi_b(r_2) \frac{1}{r_{12}} \chi_c(r_1)\chi_d(r_2) dr_1 dr_2
  \]
- 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)

\[ s \approx e^{-\alpha_r r^2} \]
\[ p \approx (x, y, z)e^{-\alpha_r r^2} \]

Usually these are contracted

\[ \text{e.g., } 1s = \sum_{j=1}^{3} c_j e^{-\alpha_r r^2} \]

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

<table>
<thead>
<tr>
<th>Basis set</th>
<th>H</th>
<th>Li-Ne</th>
<th>Na-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>1s</td>
<td>2s1p</td>
<td>3s2p</td>
</tr>
<tr>
<td>3-21G</td>
<td>2s</td>
<td>3s2p</td>
<td>4s3p</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>2s</td>
<td>3s2p1d</td>
<td>4s3p1d</td>
</tr>
<tr>
<td>6-31G(d,p)</td>
<td>2s1p</td>
<td>3s2p1d</td>
<td>4s3p1d</td>
</tr>
<tr>
<td>6-311G(d,p)</td>
<td>3s1p</td>
<td>4s3p1d</td>
<td>5s4p1d</td>
</tr>
<tr>
<td>6-311G(2df,2pd)</td>
<td>3s2p1d</td>
<td>4s3p2s1f</td>
<td>5s4p2d1f</td>
</tr>
<tr>
<td>6-311++G(d,p)</td>
<td>4s1p</td>
<td>5s4p1d</td>
<td>6s5p1d</td>
</tr>
<tr>
<td>cc-pVDZ</td>
<td>2s1p</td>
<td>3s2p1d</td>
<td>4s3p1d</td>
</tr>
<tr>
<td>cc-pVTZ</td>
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<td>4s3p2d1f</td>
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<tr>
<td>cc-pvQZ</td>
<td>4s3p2d1f</td>
<td>5s4p3d2f1g</td>
<td>6s5p3d2f1g</td>
</tr>
<tr>
<td>aug-cc-pVDZ</td>
<td>3s2p</td>
<td>4s3p2d</td>
<td>5s4p2d</td>
</tr>
</tbody>
</table>
• 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 \( r_{12} \to 0 \)
    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\(_2\) does not dissociate correctly: \(E(H_2, R = \text{inf.}) \neq 2*E(H)\)

\[
\sigma_g^2 = (L + R)^2 = (L^2 + R^2) + 2(LR + RL)
\]

\(\sigma_g, \sigma_u\) orbitals \(\rightarrow\) degenerate as \(R \rightarrow\) infinity

Solve by using \(\Psi = C_1 |\phi_g \phi_g| + C_2 |\sigma_u \sigma_u|\)
Closed-shell, $S = 0$

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

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

Diradical – HF also not valid