Advanced Physical Chemistry

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Quantum Chemistry

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Emphasis

Hartree-Fock method
Density-functional theory
Concepts
Hands-on experience

Text Book

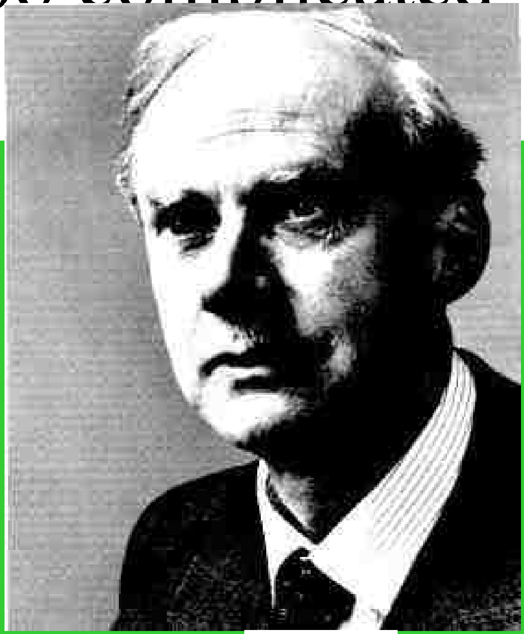
“Quantum Chemistry”, 4th Ed. Ira N. Levine

“Density-functional theory of atoms and molecules”, R.G. Parr and W. T. Yang

http://yangtze.hku.hk/teaching.php

Beginning of Computational Chemistry

In 1929, Dirac declared, “The underlying physical laws necessary for the mathematical theory of ...the whole of chemistry are thus completely know, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

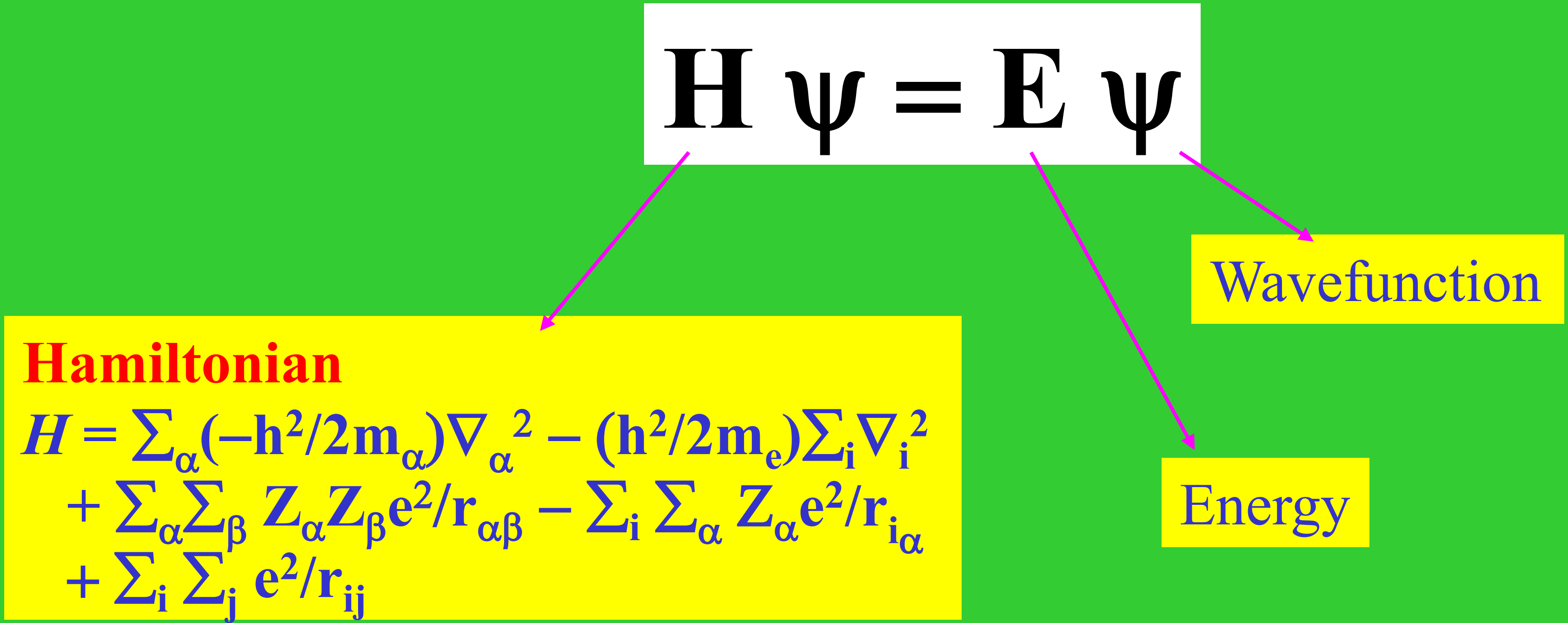


Dirac

Quantum Chemistry Methods

- Ab initio molecular orbital methods
- Semiempirical molecular orbital methods
- Density functional method

Schrödinger Equation



$$H\,\psi = E\,\psi$$

Wavefunction

Energy

Hamiltonian

$$H = \sum_\alpha(-h^2/2m_\alpha)\nabla_\alpha{}^2 - (h^2/2m_e)\sum_i\nabla_i{}^2 + \sum_\alpha\sum_\beta Z_\alpha Z_\beta e^2/r_{\alpha\beta} - \sum_i\sum_\alpha Z_\alpha e^2/r_{i_\alpha} + \sum_i\sum_j e^2/r_{ij}$$

Contents

1. Variation Method
2. Hartree-Fock Self-Consistent Field Method

The Variation Method

The variation theorem

Consider a system whose Hamiltonian operator H is time independent and whose lowest-energy eigenvalue is E_1. If ϕ is any normalized, well-behaved function that satisfies the boundary conditions of the problem, then

$$\int \phi^* H \phi \, d\tau \geq E_1$$

Proof:

Expand ϕ in the basis set $\{\psi_k\}$

$$\phi = \Sigma_k\, \alpha_k \psi_k$$

where

$\{\alpha_k\}$ are coefficients

$$H\psi_k = E_k \psi_k$$

then

$$\int \phi^* H\, \phi\, d\tau = \Sigma_k\, \Sigma_j\, \alpha_k^*\, \alpha_j\, E_j\, \delta_{kj}$$
$$= \Sigma_k\, |\alpha_k|^2\, E_k \geq E_1\, \Sigma_k\, |\alpha_k|^2 = E_1$$

Since is normalized, $\int \phi^* \phi\, d\tau = \Sigma_k\, |\alpha_k|^2 = 1$

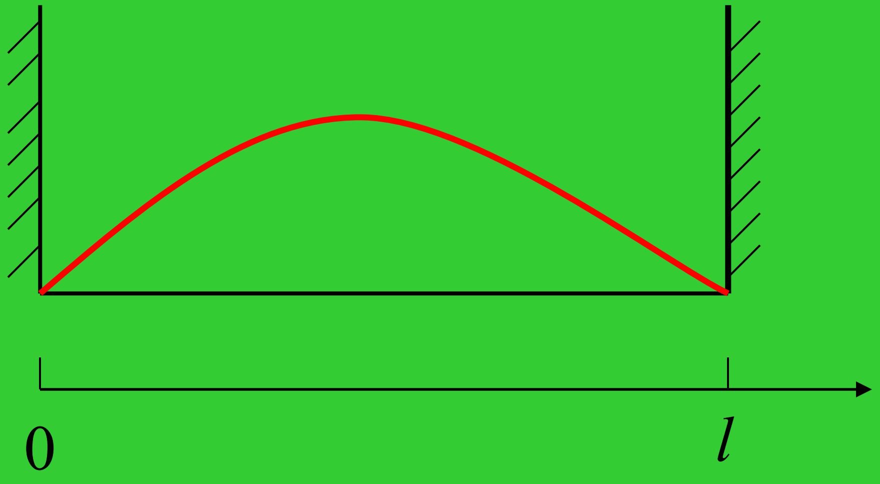
i. ϕ : trial function is used to evaluate the *upper limit* of ground state energy E_1

ii. ϕ = ground state wave function, $\int \phi^* H \phi \, d\tau = E_1$

iii. optimize paramemters in ϕ by minimizing

$$\int \phi^* H \phi \, d\tau \;/\; \int \phi^* \phi \, d\tau$$

Application to a particle in a box of infinite depth



Requirements for the trial wave function:

i. zero at boundary;

ii. smoothness ⇒ a maximum in the center.

Trial wave function: $\phi = x\,(l - x)$

$$\int \phi^* \, H \, \phi \, dx = -(h^2/8\pi^2 m) \int (lx - x^2) \, d^2(\mathrm{l}x - x^2)/dx^2 \, dx$$

$$= h^2/(4\pi^2 m) \int (x^2 - lx) \, dx$$

$$= h^2 l^3/(24\pi^2 m)$$

$$\int \phi^* \phi \, dx = \int x^2 \, (l - x)^2 \, dx = l^5/30$$

$$E_\phi = 5h^2/(4\pi^2 l^2 m) \geq h^2/(8ml^2) = E_1$$

Variational Method

(1) Construct a wave function $\phi(c_1,c_2,\bullet\bullet\bullet,c_m)$

(2) Calculate the energy of ϕ:

$$E_\phi \equiv E_\phi(c_1,c_2,\bullet\bullet\bullet,c_m)$$

(3) Choose $\{c_j^*\}$ $(i=1,2,\bullet\bullet\bullet,m)$ so that E_ϕ is minimum

Example: one-dimensional harmonic oscillator

Potential: $V(x) = (1/2)\, kx^2 = (1/2)\, m\omega^2x^2 = 2\pi^2 m\nu^2 x^2$

Trial wave function for the ground state:

$\phi(x) = \exp(-cx^2)$

$$\begin{aligned}\int \phi^*\, H\, \phi\, dx &= -(h^2/8\pi^2 m) \int \exp(-cx^2)\, d^2[\exp(-cx^2)]/dx^2\, dx \\ &\quad + 2\pi^2 m\nu^2 \int x^2 \exp(-2cx^2)\, dx \\ &= (h^2/4\pi^2 m)\, (\pi c/8)^{1/2} + \pi^2 m\nu^2\, (\pi/8c^3)^{1/2}\end{aligned}$$

$$\int \phi^*\phi\, dx = \int \exp(-2cx^2)\, dx = (\pi/2)^{1/2}\, c^{-1/2}$$

$$E_\phi = W = (h^2/8\pi^2 m)c + (\pi^2/2)m\nu^2/c$$

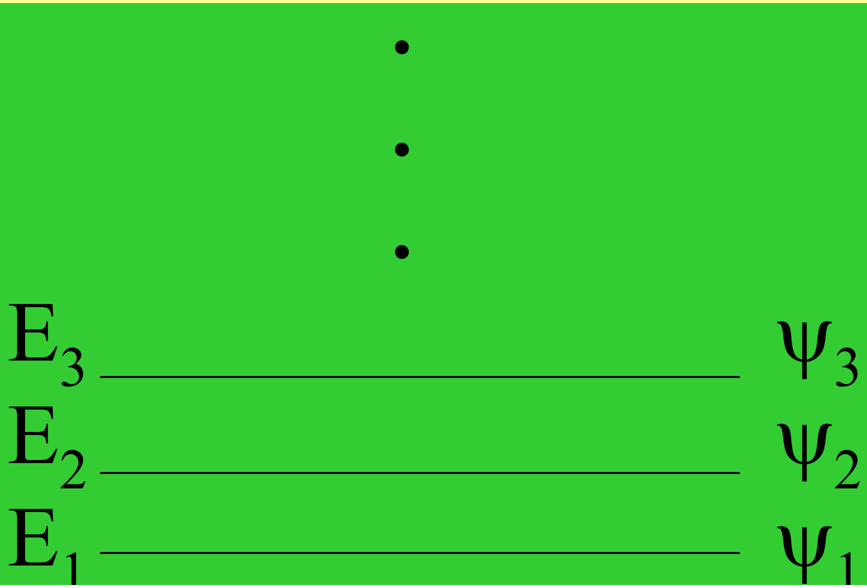
To minimize W,

$$0 = dW/dc = h^2/8\pi^2 m - (\pi^2/2)m\nu^2 c^{-2}$$

$$c = 2\pi^2 \nu m/h$$

$$\mathbf{W = (1/2)\, h\nu}$$

Extension of Variation Method



For a wave function ϕ which is orthogonal to the ground state wave function ψ_1, *i.e.*

$$\int d\tau\ \phi^* \psi_1 = 0$$

$$E_\phi = \int d\tau\ \phi^* H \phi \,/\, \int d\tau\ \phi^* \phi \ \geq\ E_2$$

the first excited state energy

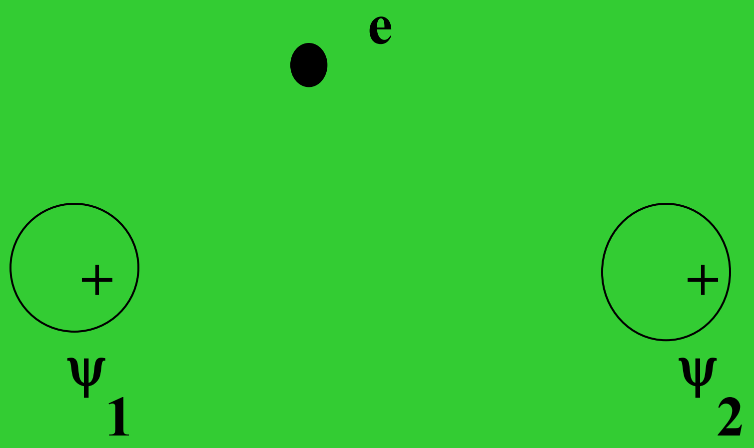
The trial wave function ϕ: $\int d\tau\ \phi^* \psi_1 = 0$

$\phi = \sum_{k=1} a_k\ \psi_k$

$\int d\tau\ \phi^* \psi_1 = |a_1|^2 = 0$

$E_\phi = \int d\tau\ \phi^* H\phi\ /\ \int d\tau\ \phi^* \phi = \sum_{k=2} |a_k|^2 E_k\ /\ \sum_{k=2} |a_k|^2$
$\geq \sum_{k=2} |a_k|^2 E_2\ /\ \sum_{k=2} |a_k|^2 =$
E_2

Application to H_2^+



$$\phi = c_1\psi_1 + c_2\psi_2$$

$$W = \int \phi^* H \phi \, d\tau \,/\, \int \phi^* \phi \, d\tau$$
$$= (c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22})$$
$$/\, (c_1^2 + 2c_1 c_2 S + c_2^2)$$

$$W\,(c_1^2 + 2c_1 c_2 S + c_2^2) = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}$$

Partial derivative with respect to c_1 $(\partial W/\partial c_1 = 0)$:

$$W\,(c_1 + S\,c_2) = c_1 H_{11} + c_2 H_{12}$$

Partial derivative with respect to c_2 $(\partial W/\partial c_2 = 0)$:

$$W\,(S\,c_1 + c_2) = c_1 H_{12} + c_2 H_{22}$$

$$(H_{11} - W)\,c_1 + (H_{12} - S\,W)\,c_2 = 0$$
$$(H_{12} - S\,W)\,c_1 + (H_{22} - W)\,c_2 = 0$$

To have nontrivial solution:

$$\begin{vmatrix} H_{11} - \mathrm{W} & H_{12} - S\,\mathrm{W} \\ H_{12} - S\,\mathrm{W} & H_{22} - \mathrm{W} \end{vmatrix} = 0$$

For H_2^+, $H_{11} = H_{22}$; $H_{12} < 0$.

Ground State: $E_g = \mathrm{W}_1 = (H_{11}+H_{12}) / (1+S)$

$$\phi_1 = (\psi_1+\psi_2) / \sqrt{2}(1+\mathrm{S})^{1/2}$$

bonding orbital

Excited State: $E_e = \mathrm{W}_2 = (H_{11}-H_{12}) / (1-S)$

$$\phi_2 = (\psi_1-\psi_2) / \sqrt{2}(1-\mathrm{S})^{1/2}$$

Anti-bonding orbital

Results: $D_\mathrm{e} = 1.76\ eV,\ \ R_\mathrm{e} = 1.32\ A$

Exact: $D_\mathrm{e} = 2.79\ eV,\ \ R_\mathrm{e} = 1.06\ A$

$1\ \mathrm{eV} = 23.0605\ \ \mathrm{kcal\ /\ mol}$

Further Improvements

Optimization of 1s orbitals

H $\pi^{-1/2}\, exp(-r)$

He$^+$ $2^{3/2}\, \pi^{-1/2}\, exp(-2r)$

Trial wave function: $k^{3/2}\, \pi^{-1/2}\, exp(-kr)$

$$E_g = W_1(k,R)$$

at each R, choose k so that $\partial W_1/\partial k = 0$

Results: $D_e = 2.36\ eV$, $R_e = 1.06\ A$

Inclusion of other atomic orbitals

Resutls: $D_e = 2.73\ eV$, $R_e = 1.06\ A$

Molecular Orbital (MO):

$$\phi = c_1\psi_1 + c_2\psi_2$$

$$(H_{11} - W) c_1 + (H_{12} - SW) c_2 = 0$$

$S_{11}=1$

$$(H_{21} - SW) c_1 + (H_{22} - W) c_2 = 0$$

$S_{22}=1$

Generally : $\{\psi_i\}$ a set of atomic orbitals, basis set

LCAO-MO $\boldsymbol{\phi = c_1\psi_1 + c_2\psi_2 + \ldots\ldots + c_n\phi_n}$

linear combination of atomic orbitals

$$\sum_{k=1}^{n} (H_{ik} - S_{ik}W) c_k = 0 \qquad i = 1, 2, \ldots\ldots, n$$

$$H_{ik} \equiv \int d\tau\ \psi_i^* H\ \psi_k \qquad S_{ik} \equiv \int d\tau\ \psi_i^* \psi_k \qquad S_{kk} = 1$$

The Born-Oppenheimer Approximation

Hamiltonian

$$
\begin{aligned}
H = {} & \sum_\alpha (-h^2/2m_\alpha)\nabla_\alpha{}^2 - (h^2/2m_e)\sum_i \nabla_i{}^2 \\
& + \sum_\alpha \sum_\beta Z_\alpha Z_\beta e^2/r_{\alpha\beta} - \sum_i \sum_\alpha Z_\alpha e^2/r_{i\alpha} \\
& + \sum_i \sum_j e^2/r_{ij}
\end{aligned}
$$

$$H\,\psi(r_i;r_\alpha) = E\ \psi(r_i;r_\alpha)$$

The Born-Oppenheimer Approximation:

(1) $\psi(\mathbf{r}_i;\mathbf{r}_\alpha) = \psi_{el}(\mathbf{r}_i;\mathbf{r}_\alpha)\,\psi_N(\mathbf{r}_\alpha)$

(2) $H_{el}(\mathbf{r}_\alpha) = -(\mathbf{h}^2/2\mathbf{m}_e)\sum_i \nabla_i^{\,2} - \sum_i\sum_\alpha \mathbf{Z}_\alpha \mathbf{e}^2/\mathbf{r}_{i\alpha}$
$+ \sum_i\sum_j \mathbf{e}^2/\mathbf{r}_{ij}$

$V_{NN} = \sum_\alpha\sum_\beta \mathbf{Z}_\alpha \mathbf{Z}_\beta \mathbf{e}^2/\mathbf{r}_{\alpha\beta}$

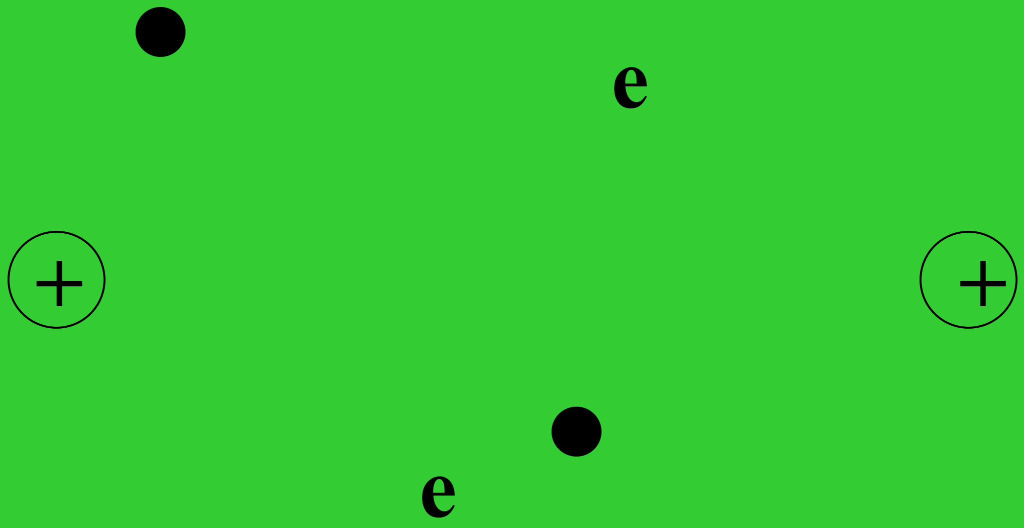
$H_{el}(\mathbf{r}_\alpha)\,\psi_{el}(\mathbf{r}_i;\mathbf{r}_\alpha) = E_{el}(\mathbf{r}_\alpha)\,\psi_{el}(\mathbf{r}_i;\mathbf{r}_\alpha)$

(3) $H_N = \sum_\alpha(-\mathbf{h}^2/2\mathbf{m}_\alpha)\nabla_\alpha^{\,2} + U(\mathbf{r}_\alpha)$

$U(\mathbf{r}_\alpha) = E_{el}(\mathbf{r}_\alpha) + V_{NN}$

$H_N(\mathbf{r}_\alpha)\,\psi_N(\mathbf{r}_\alpha) = E\,\psi_N(\mathbf{r}_\alpha)$

Hydrogen Molecule H_2



The Pauli principle

two electrons cannot be in the same state.

Wave function:

$$\phi(1,2) = \varphi_a(1)\varphi_b(2) + c_1\, \varphi_a(2)\varphi_b(1)$$

$$\phi(2,1) = \varphi_a(2)\varphi_b(1) + c_1\, \varphi_a(1)\varphi_b(2)$$

Since two wave functions that correspond to the same state can differ at most by a constant factor

$$\phi(1,2) = c_2\, \phi(2,1)$$

$$\varphi_a(1)\varphi_b(2) + c_1\varphi_a(2)\varphi_b(1) = c_2\varphi_a(2)\varphi_b(1) + c_2 c_1\varphi_a(1)\varphi_b(2)$$

$$c_1 = c_2 \qquad\qquad c_2 c_1 = 1$$

Therefore: $c_1 = c_2 = \pm 1$

According to the Pauli principle, $c_1 = c_2 = -1$

The Pauli principle (*different version*)

the wave function of a system of electrons must be antisymmetric with respect to interchanging of any two electrons.

Wave function ϕ of H_2 : ***Slater Determinant***

$$\psi(1,2) = 1/\sqrt{2!}\ [\phi(1)\alpha(1)\phi(2)\beta(2) - \phi(2)\alpha(2)\phi(1)\beta(1)]$$

$$= \quad 1/\sqrt{2!} \begin{vmatrix} \phi(1)\alpha(1) & \phi(2)\alpha(2) \\ \phi(1)\beta(1) & \phi(2)\beta(2) \end{vmatrix}$$

Energy: E_ψ

$$E_\psi = 2\int d\tau_1\, \phi^*(1)\,(T_e + V_{eN})\,\phi(1) \;+ V_{NN}$$
$$+ \int d\tau_1\, d\tau_2\, |\phi^2(1)|\; e^2/r_{12}\, |\phi^2(2)|$$
$$= \sum_{i=1,2} f_{ii} + J_{12} + V_{NN}$$

To minimize E_ψ under the *constraint* $\int d\tau\, |\phi^2| = 1$,

use **Lagrange's method**:

$$L = E\psi \;-\; 2\,\varepsilon\,[\int d\tau_1\, |\phi^2(1)| - 1]$$
$$\delta L = \delta E\psi \;-\; 4\,\varepsilon \int d\tau_1\, \phi^*(1)\delta\phi(1)$$
$$= 4\int d\tau_1\, \delta\phi^*(1)(T_e + V_{eN})\phi(1)$$
$$+4\int d\tau_1\, d\tau_2\, \phi^*(1)\phi^*(2)\, e^2/r_{12}\, \phi(2)\delta\phi(1)$$
$$- 4\,\varepsilon \int d\tau_1\, \phi^*(1)\delta\phi(1)$$
$$= 0$$

$$[\, T_e + V_{eN} + \int d\tau_2\, \phi^*(2)\, e^2/r_{12}\, \phi(2) \,]\, \phi(1) = \varepsilon\, \phi(1)$$

Average Hamiltonian

Hartree-Fock equation

$$(\, f + J \,)\, \phi = \varepsilon\, \phi$$

$f(1) = T_e(1) + V_{eN}(1)$ *one electron operator*

$J(1) = \int d\tau_2\, \phi^*(2)\, e^2/r_{12}\, \phi(2)$ *two electron Coulomb operator*

f*(1)** is the Hamiltonian of electron ***1 in the absence of electron ***2***;

J*(1)** is the mean Coulomb repulsion exerted on electron ***1 by ***2***;

ε is the energy of orbital **ϕ**.

LCAO-MO: $\phi = c_1\psi_1 + c_2\psi_2$

Multiple ψ_1 from the left and then integrate :

$c_1F_{11} + c_2F_{12} = \varepsilon\,(c_1 + S\,c_2)$

Multiple ψ_2 from the left and then integrate :

$$c_1 F_{12} + c_2 F_{22} = \varepsilon\,(S\,c_1 + c_2)$$

where,

$$F_{ij} = \int d\tau\ \psi_i^*\,(\boldsymbol{f} + \boldsymbol{J})\,\psi_j = H_{ij} + \int d\tau\ \psi_i^*\,\boldsymbol{J}\,\psi_j$$

$$S = \int d\tau\ \psi_1\ \psi_2$$

$$(F_{11} - \varepsilon)\,c_1 + (F_{12} - S\,\varepsilon)\,c_2 = 0$$

$$(F_{12} - S\,\varepsilon)\,c_1 + (F_{22} - \varepsilon)\,c_2 = 0$$

Secular Equation:

$$\begin{vmatrix} F_{11} - \varepsilon & F_{12} - S\varepsilon \\ F_{12} - S\varepsilon & F_{22} - \varepsilon \end{vmatrix} = 0$$

bonding orbital:

$$\varepsilon_1 = (F_{11}+F_{12}) / (1+S)$$

$$\phi_1 = (\psi_1+\psi_2) / \surd 2(1+S)^{1/2}$$

antibonding orbital:

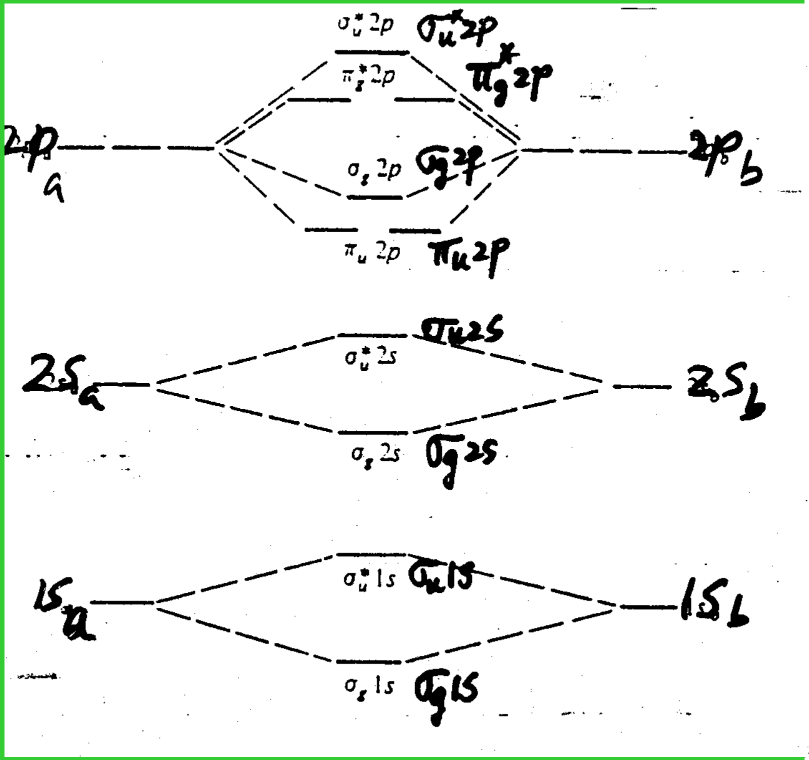
$$\varepsilon_2 = (F_{11}-F_{12}) / (1-S)$$

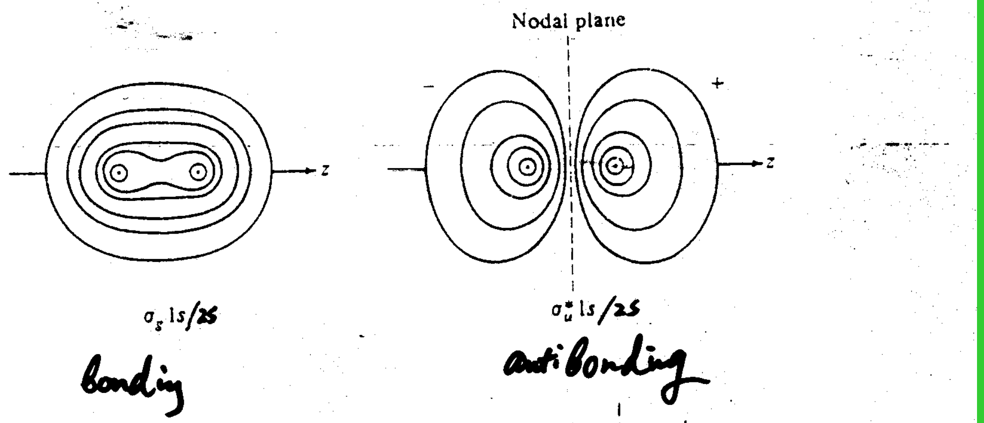
$$\phi_2 = (\psi_1-\psi_2) / \surd 2(1-S)^{1/2}$$

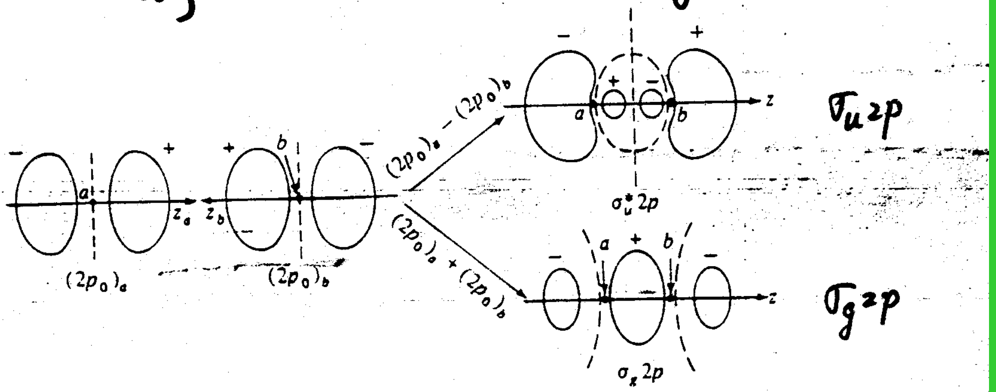
Molecular Orbital Configurations of Homo nuclear Diatomic Molecules H_2, Li_2, O, He_2, etc

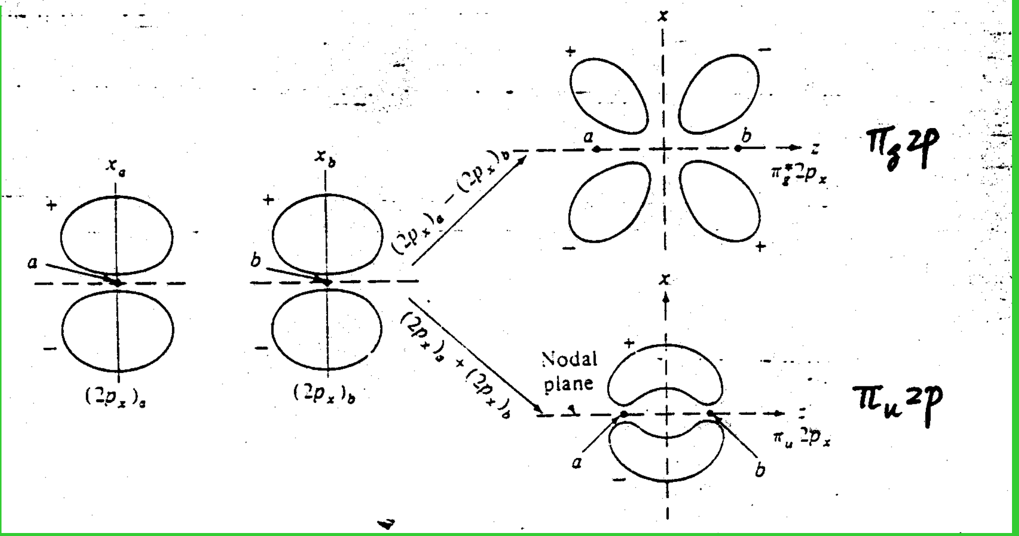
Moecule	Bond order	De/eV
H_2^+	⍰	2.79
H_2	1	4.75
He_2^+	⍰	1.08
He_2	0	0.0009
Li_2	1	1.07
Be_2	0	0.10
C_2	2	6.3
N_2^+	⍰	8.85
N_2	3	9.91
O_2^+	2⍰	6.78
O_2	2	5.21

The more the Bond Order is, the stronger the chemical bond is.

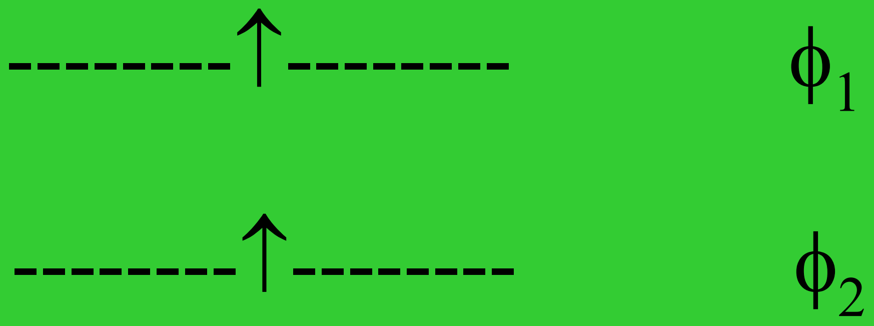








Bond Order:
one-half the difference between the number of bonding and antibonding electrons



ϕ_1

ϕ_2

$$\psi(1,2) = 1/\sqrt{2}\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\alpha(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\alpha(2) \end{vmatrix}$$

$$= \mathbf{1/\sqrt{2}}\ [\phi_1(1)\,\phi_2(2) - \phi_2(1)\,\phi_1(2)]\ \alpha(1)\,\alpha(2)$$

$$E_\psi = \int d\tau_1 d\tau_2\, \psi^* H\, \psi$$

$$= \int d\tau_1 d\tau_2\, \psi^* (T_1 + V_{1N} + T_2 + V_{2N} + V_{12} + V_{NN})\, \psi$$

$$\begin{aligned}
&= <\phi_1(1)|\; T_1 + V_{1N} |\phi_1(1)> \\
&\quad + <\phi_2(2)|\; T_2 + V_{2N} |\phi_2(2)> \\
&\quad + <\phi_1(1)\, \phi_2(2)|\; V_{12} \,|\, \phi_1(1)\, \phi_2(2)> \\
&\quad - <\phi_1(2)\, \phi_2(1)|\; V_{12} \,|\, \phi_1(1)\, \phi_2(2)> + V_{NN}
\end{aligned}$$

$$\begin{aligned}
&= \textstyle\sum_i <\phi_i(1)|\; T_1 + V_{1N}\, |\phi_i(1)> \\
&\quad + <\phi_1(1)\, \phi_2(2)|\; V_{12} \,|\, \phi_1(1)\, \phi_2(2)> \\
&\quad - <\phi_1(2)\, \phi_2(1)|\; V_{12} \,|\, \phi_1(1)\, \phi_2(2)> + V_{NN}
\end{aligned}$$

$$= \textstyle\sum_{i=1,2} f_{ii} + J_{12} - K_{12} + V_{NN}$$

Average Hamiltonian

Particle One: $f(1) + J_2(1) - K_2(1)$

Particle Two: $f(2) + J_1(2) - K_1(2)$

$$f(j) \equiv -(h^2/2m_e)\nabla_j^{\,2} - \sum_\alpha Z_\alpha/r_{j\alpha}$$

$$J_j(1)\,\theta(1) \equiv \theta(1) \int dr_2\, \phi_j^{*}(2)\, e^2/r_{12}\, \phi_j(2)$$

$$K_j(1)\,\theta(1) \equiv \phi_j(1) \int dr_2\, \phi_j^{*}(2)\, e^2/r_{12}\, \theta(2)$$

Hartree-Fock Equation:

$$[\,f(1) + J_2(1) - K_2(1)]\,\phi_1(1) = \varepsilon_1\,\phi_1(1)$$
$$[\,f(2) + J_1(2) - K_1(2)]\,\phi_2(2) = \varepsilon_2\,\phi_2(2)$$

Fock Operator:

$\mathbf{F(1)} \equiv f(1) + J_2(1) - K_2(1)$ Fock operator for *1*

$\mathbf{F(2)} \equiv f(2) + J_1(2) - K_1(2)$ Fock operator for *2*

Hartree-Fock Method

1. Many-Body Wave Function is approximated by Slater Determinant

2. Hartree-Fock Equation

$\boldsymbol{F}\,\phi_i = \varepsilon_i\,\phi_i$

$\boldsymbol{F}$ Fock operator

ϕ_i the *i*-th Hartree-Fock orbital

ε_i the energy of the *i*-th Hartree-Fock orbital

3. Roothaan Method (introduction of Basis functions)

$\phi_i = \sum_k c_{ki}\, \psi_k$ LCAO-MO

$\{ \psi_k \}$ is a set of atomic orbitals (or basis functions)

4. **Hartree-Fock-Roothaan equation**

$$\sum_j (F_{ij} - \varepsilon_i S_{ij})\, c_{ji} = 0$$

$$F_{ij} \equiv < \psi_i | \, F \, | \psi_j > \qquad S_{ij} \equiv < \psi_i | \psi_j >$$

5. Solve the **Hartree-Fock-Roothaan equation** self-consistently

Assignment one

8.40, 10.5, 10.6, 10.7, 10.8,
11.37, 13.37

The Condon-Slater Rules

$$<\phi_a(1)\phi_b(2)\phi_c(3)\ldots\phi_d(n) \mid f(1) \mid \phi_e(1)\phi_f(2)\phi_g(3)\ldots\phi_h(n)>$$

$$= <\phi_a(1) \mid f(1) \mid \phi_e(1)> < \phi_b(2)\phi_c(3)\ldots\phi_d(n) \mid \phi_f(2)\phi_g(3)\ldots\phi_h(n)>$$

$$= <\phi_a(1) \mid f(1) \mid \phi_e(1)>$$

if ***$b=f$, $c=g$, ..., $d=h$;*** **0, *otherwise***

$$<\phi_a(1)\phi_b(2)\phi_c(3)\ldots\phi_d(n) \mid V_{12} \mid \phi_e(1)\phi_f(2)\phi_g(3)\ldots\phi_h(n)>$$

$$= <\phi_a(1)\,\phi_b(2) \mid V_{12} \mid \phi_e(1)\,\phi_f(2)> < \phi_c(3)\ldots\phi_d(n) \mid \phi_g(3)\ldots\phi_h(n)>$$

$$= <\phi_a(1)\,\phi_b(2) \mid V_{12} \mid \phi_e(1)\,\phi_f(2)>$$

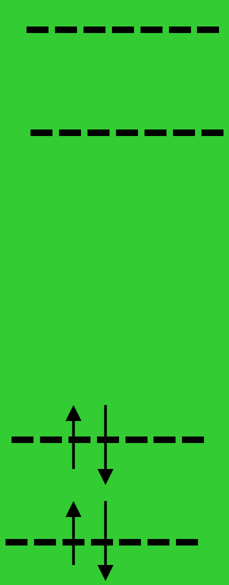
if ***$c=g$, ..., $d=h$;*** **0, *otherwise***

LUMO

the lowest unoccupied molecular orbital ⇒

HOMO

the highest occupied molecular orbital ⇒



Koopman’s Theorem

The energy required to remove an electron from a closed-shell atom or molecules is well approximated by minus the orbital energy ε of the AO or MO from which the electron is removed.

```
#  HF/6-31G(d)                                  Route section

water energy                                     Title

0    1                                          Molecule Specification
O   -0.464    0.177    0.0                      (in Cartesian coordinates
H   -0.464    1.137    0.0
H    0.441   -0.143    0.0
```

Basis Set $\phi_i = \sum_p c_{ip}$ $\boxed{?}_p$

Slater type orbitals (STO)

$$\boxed{?}_{nlm} = N\, r^{n-1} exp(-\xi r/a_0)\; Y_{lm}(\theta,\phi)$$

ξ the orbital exponent

*χ is used instead of ψ in the textbook

Gaussian type functions

$g_{ijk} = N\, x^i\, y^j\, z^k\, exp(-\alpha r^2)$

(primitive Gaussian function)

$\boxed{?}_p = \sum_u d_{up}\, g_u$

(contracted Gaussian-type function, CGTF)

u = {ijk} p = {nlm}

Basis set of GTFs

STO-3G, 3-21G, 4-31G, 6-31G, 6-31G*, 6-31G**

--→

complexity & accuracy

Minimal basis set: one STO for each atomic orbital (AO)

STO-3G: 3 GTFs for each atomic orbital
3-21G: 3 GTFs for each inner shell AO
2 CGTFs (w/ 2 & 1 GTFs) for each valence AO
6-31G: 6 GTFs for each inner shell AO
2 CGTFs (w/ 3 & 1 GTFs) for each valence AO
6-31G*: adds a set of d orbitals to atoms in 2nd & 3rd rows
6-31G**: adds a set of d orbitals to atoms in 2nd & 3rd rows
and a set of p functions to hydrogen

Polarization Function

Diffuse Basis Sets:

For excited states and in anions where electronic density is more spread out, additional basis functions are needed.

Diffuse functions to 6-31G basis set as follows:

6-31G* - adds a set of diffuse s & p orbitals to atoms
in 1st & 2nd rows (Li - Cl).

6-31G** - adds a set of diffuse s and p orbitals to atoms
in 1st & 2nd rows (Li- Cl) and a set of diffuse
s functions to H

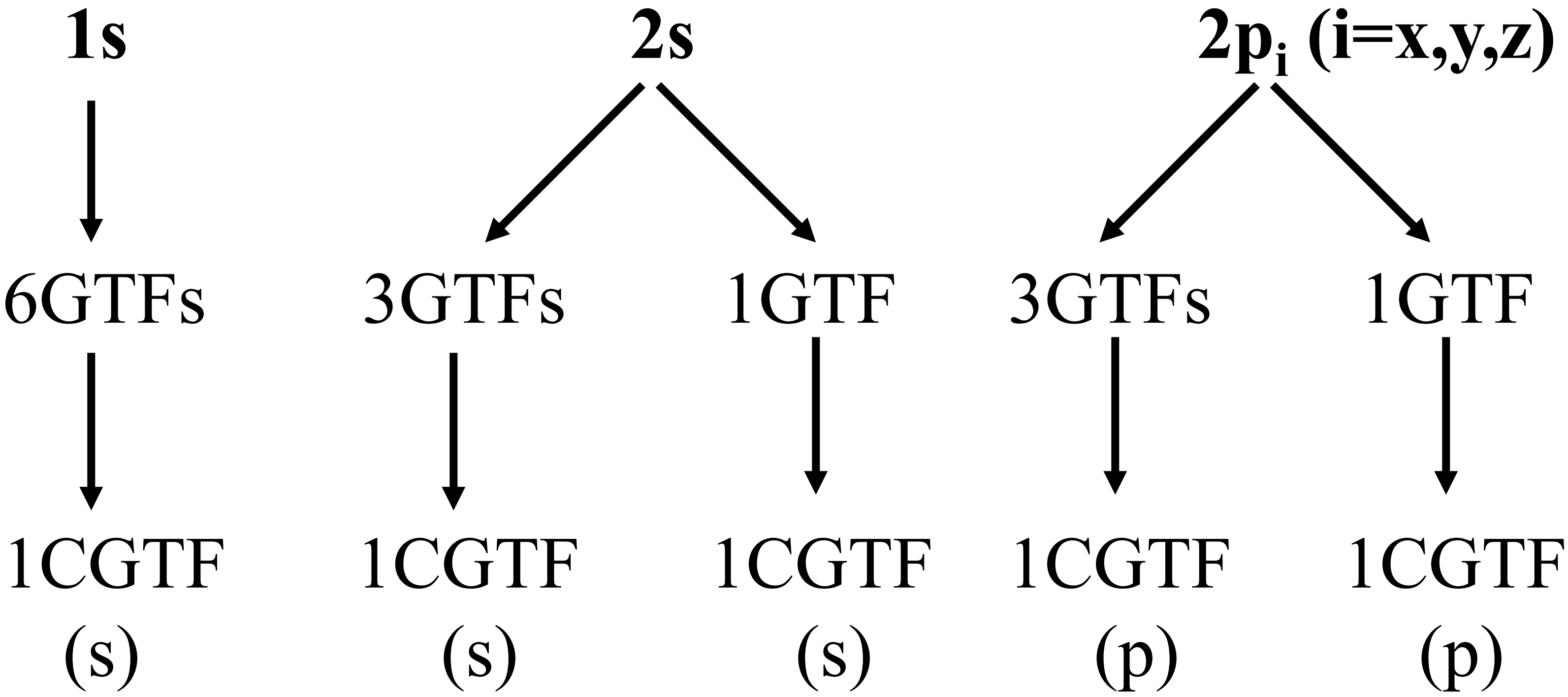
Diffuse functions + polarisation functions:

6-31+G*, 6-31++G*, 6-31+G** and 6-31++G** basis sets.

Double-zeta (DZ) basis set:

two STO for each AO

6-31G for a carbon atom: (10s4p) → [3s2p]



1s **2s** **2p$_i$ (i=x,y,z)**

6GTFs 3GTFs 1GTF 3GTFs 1GTF

1CGTF (s) 1CGTF (s) 1CGTF (s) 1CGTF (p) 1CGTF (p)

Minimal basis set:

One STO for each inner-shell and
valence-shell AO of each atom

example: C_2H_2 (2S1P/1S)
C: 1S, 2S, $2P_x$,$2P_y$,$2P_z$
H: 1S
total 12 STOs as Basis set

Double-Zeta (DZ) basis set:

two STOs for each and
valence-shell AO of each atom

example: C_2H_2 (4S2P/2S)
C: two 1S, two 2S,
two $2P_x$, two $2P_y$,two $2P_z$
H: two 1S (STOs)
total 24 STOs as Basis set

Split -Valence (SV) basis set

Two STOs for each inner-shell and valence-shell AO
One STO for each inner-shell AO

Double-zeta plus polarization set(DZ+P, or DZP)

Additional STO w/l quantum number larger
than the l_{max} of the valence - shell

☐ ($2P_x$, $2P_y$,$2P_z$) to H

☐ Five 3d Aos to Li - Ne , Na -Ar

☐ C_2H_5 O Si H_3 :

$$\underbrace{(6s4p1d}_{\text{Si}}/\underbrace{4s2p1d}_{\text{C,O}}/\underbrace{2s1p)}_{\text{H}}$$

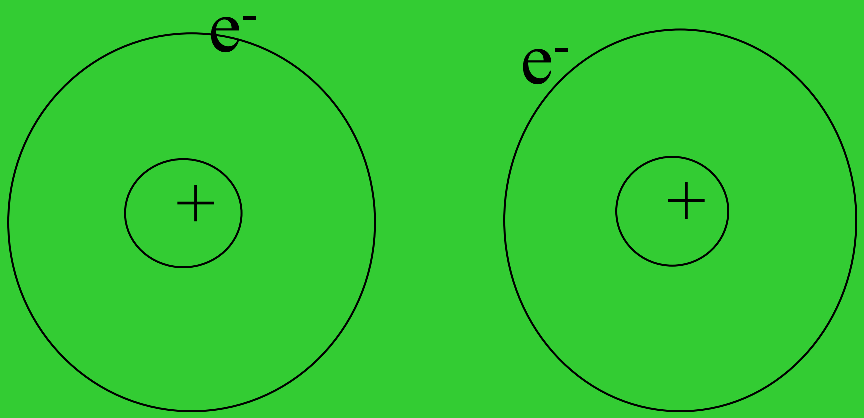
Assignment two: Calculate the structure, ground state energy, molecular orbital energies, and vibrational modes and frequencies of a water molecule using Hartree-Fock method with 3-21G basis set.

Ab Initio Molecular Orbital Calculation: H_2O (using HyperChem)

1. L-Click on (click on left button of Mouse) “Startup”, and select and L-Click on “Program/Hyperchem”.
2. Select “Build” and turn on “Explicit Hydrogens”.
3. Select “Display” and make sure that “Show Hydrogens” is on; L-Click on “Rendering” and double L-Click “Spheres”.
4. Double L-Click on “Draw” tool box and double L-Click on “O”.
5. Move the cursor to the workspace, and L-Click & release.
6. L-Click on “Magnify/Shrink” tool box, move the cursor to the workspace; L-press and move the cursor inward to reduce the size of oxygen atom.
7. Double L-Click on “Draw” tool box, and double L-Click on “H”; Move the cursor close to oxygen atom and L-Click & release. A hydrogen atom appears. Draw second hydrogen atom using the same procedure.

8. L-Click on “Setup” & select “Ab Initio”; double L-Click on 3-21G; then L-Click on “Option”, select “UHF”, and set “Charge” to 0 and “Multiplicity” to 1.
9. L-Click “Compute”, and select “Geometry Optimization”, and L-Click on “OK”; repeat the step till “Conv=YES” appears in the bottom bar. Record the energy.
10. L-Click “Compute” and L-Click “Orbitals”; select a energy level, record the energy of each molecular orbitals (MO), and L-Click “OK” to observe the contour plots of the orbitals.
11. L-Click “Compute” and select “Vibrations”.
12. Make sure that “Rendering/Sphere” is on; L-Click “Compute” and select “Vibrational Spectrum”. Note that frequencies of different vibrational modes.
13. Turn on “Animate vibrations”, select one of the three modes, and L-Click “OK”. Water molecule begins to vibrate. To suspend the animation, L-Click on “Cancel”.

The Hartree-Fock treatment of H_2



The Valence-Bond Treatment of H_2

$$f_1 = \psi_1(1)\,\psi_2(2)$$
$$f_2 = \psi_1(2)\,\psi_2(1)$$
$$\phi = c_1 f_1 + c_2 f_2$$

$$\begin{vmatrix} \underline{H}_{11} - W & \underline{H}_{12} - \underline{S}\,W \\ \underline{H}_{21} - \underline{S}\,W & \underline{H}_{22} - W \end{vmatrix} = 0$$

$$\underline{H}_{11} = \underline{H}_{22} = \langle\psi_1(1)\,\psi_2(2)|H|\psi_1(1)\,\psi_2(2)\rangle$$
$$\underline{H}_{12} = \underline{H}_{21} = \langle\psi_1(1)\,\psi_2(2)|H|\psi_1(2)\,\psi_2(1)\rangle$$
$$\underline{S} = \langle\psi_1(1)\,\psi_2(2)|\psi_1(2)\,\psi_2(1)\rangle\ [= S^2]$$

The Heitler-London ground-state wave function

$$\{[\psi_1(1)\,\psi_2(2) + \psi_1(2)\,\psi_2(1)]/\sqrt{2}(1+\underline{S})^{1/2}\}\ \ [\alpha(1)\beta(2)-\alpha(2)\beta(1)]/\sqrt{2}$$

Comparison of the HF and VB Treatments

HF LCAO-MO wave function for H_2

$$[\psi_1(1) + \psi_2(1)]\,[\psi_1(2) + \psi_2(2)]$$

$$= \psi_1(1)\,\psi_1(2) + \psi_1(1)\,\psi_2(2) + \psi_2(1)\,\psi_1(2) + \psi_2(1)\,\psi_2(2)$$

$$H^-\;\;H^+ \qquad\qquad H\;\;\;H \qquad\qquad H\;\;\;H \qquad\qquad H^+\;\;H^-$$

VB wave function for H_2

$$\psi_1(1)\,\psi_2(2) + \psi_2(1)\,\psi_1(2)$$

$$H\;\;\;H \qquad\qquad H\;\;\;H$$

At large distance, the system becomes

H .... H

MO: 50% H .... H

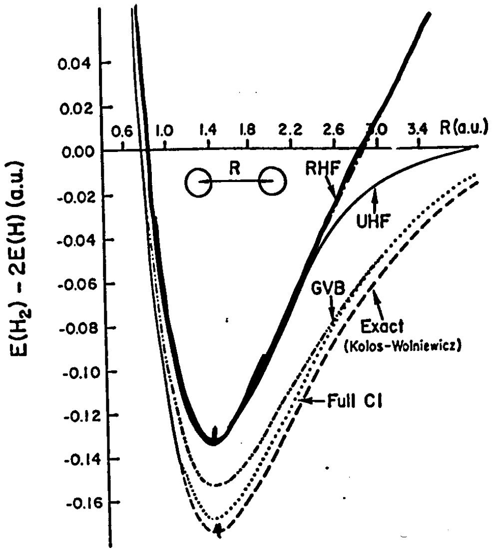
50% H^+............ H^-

VB: 100% H .... H

The VB is computationally expensive and requires chemical intuition in implementation.

The Generalized valence-bond (GVB) method is a variational method, and thus computationally feasible. (William A. Goddard III)

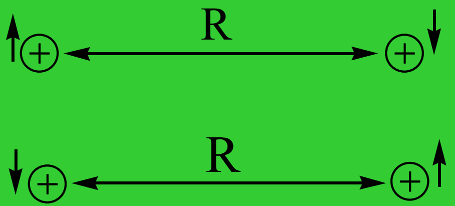
The Hartree-Fock treatment of H_2



The Valence-Bond Treatment of H_2

$$f_1 = \psi(1)\psi(2)$$
$$f_2 = \psi(2)\psi(1)$$

$$\Phi = c_1 f_1 + c_2 f_2$$



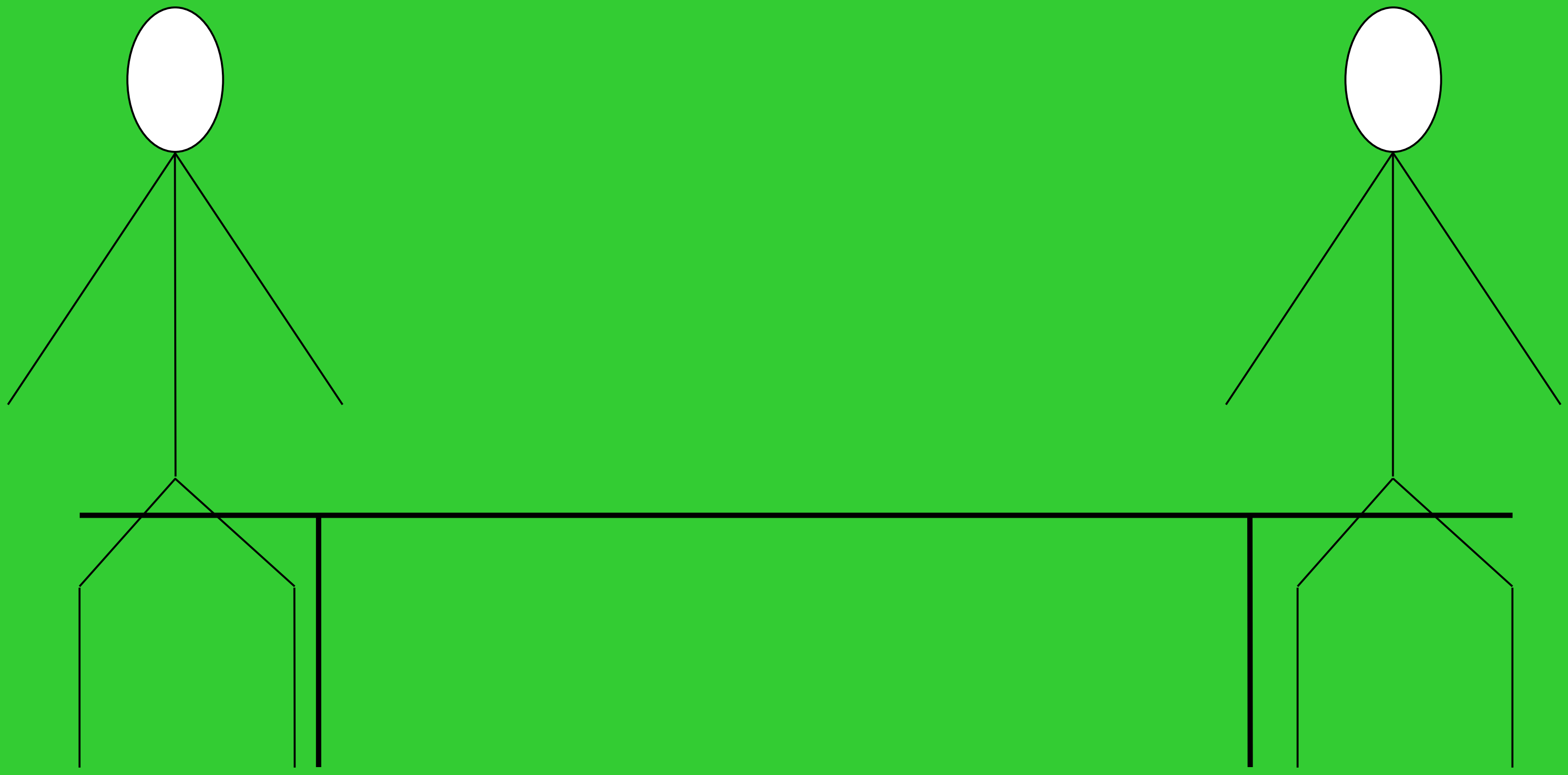
$$H_{11} = H_{22} = \langle \psi_1(1)\psi_2(2) | H | \psi_1(1)\psi_2(2) \rangle$$
$$H_{12} = H_{21} = \langle \psi_1(1)\psi_2(2) | H | \psi_1(2)\psi_2(1) \rangle$$
$$S = \langle \psi_1(1)\psi_2(2) | \psi_1(2)\psi_2(1) \rangle [= S^2]$$

$$\begin{vmatrix} H_{11} - W & H_{12} - SW \\ H_{21} - SW & H_{22} - W \end{vmatrix} = 0$$

The Heitler-London ground-state wave function

$$\{[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)] / \sqrt{2(1+S)}\}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] / \sqrt{2}$$

Electron Correlation



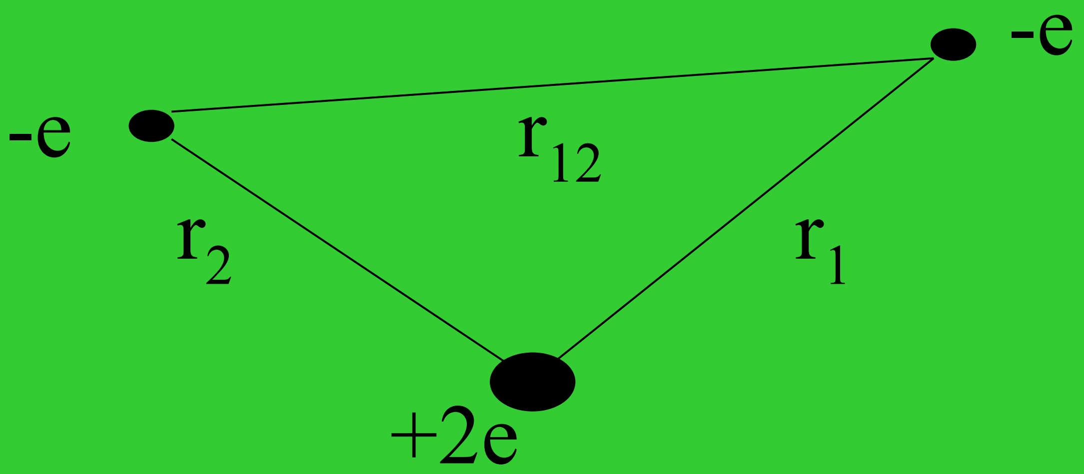
Human Repulsive Correlation

Electron Correlation: avoiding each other

Two reasons of the instantaneous correlation:
(1) Pauli Exclusion Principle (HF includes the effect)
(2) Coulomb repulsion (not included in the HF)

Beyond the Hartree-Fock

Configuration Interaction (CI)*
Perturbation theory*
Coupled Cluster Method
Density functional theory



$$H = -(h^2/2m_e)\,\nabla_1^{\,2} - 2e^2/r_1 - (h^2/2m_e)\,\nabla_2^{\,2} - 2e^2/r_2 + e^2/r_{12}$$

$H_1^{\,0}$ $H_2^{\,0}$ H'

$$H^0 = H_1{}^0 + H_2{}^0$$

$$\psi^{(0)}(1,2) = \mathrm{F}_1(1)\ \mathrm{F}_2(2)$$

$$H_1{}^0\ \mathrm{F}_1(1) = E_1\ \mathrm{F}_1(1)$$

$$H_2{}^0\ \mathrm{F}_2(1) = E_2\ \mathrm{F}_2(1)$$

$$E_1 = -2e^2/n_1{}^2a_0 \quad n_1 = 1, 2, 3, \ldots$$

$$E_2 = -2e^2/n_2{}^2a_0 \quad n_2 = 1, 2, 3, \ldots$$

Ground state wave function

$$\psi^{(0)}(1,2) = (1/\pi^{1/2})(2/a_0)^{3/2}exp(-2r_1/a_0) * (1/\pi^{1/2})(2/a_0)^{3/2}exp(-2r_1/a_0)$$

$$E^{(0)} = -4e^2/a_0$$

$$E^{(1)} = <\psi^{(0)}(1,2)|\ H'\ |\psi^{(0)}(1,2)> = 5e^2/4a_0$$

$$E \approx E^{(0)} + E^{(1)} = -108.8 + 34.0 = -74.8\ (\mathrm{eV})$$

[compared with exp. -79.0 eV]

Nondegenerate Perturbation Theory
(for Non-Degenerate Energy Levels)

$H = H^0 + H'$

$H^0\psi_n^{(0)} = E_n^{(0)}\,\psi_n^{(0)}$

$\psi_n^{(0)}$ is an eigenstate for unperturbed system

H' is small compared with H^0

Introducing a parameter λ

$$H(\lambda) = H^0 + \lambda H'$$
$$H(\lambda)\,\psi_n(\lambda) = E_n(\lambda)\,\psi_n(\lambda)$$
$$\psi_n(\lambda) = \psi_n^{(0)} + \lambda\,\psi_n^{(1)} + \lambda^2\,\psi_n^{(2)} + \ldots + \lambda^k\,\psi_n^{(k)} + \ldots$$
$$E_n(\lambda) = E_n^{(0)} + \lambda\,E_n^{(1)} + \lambda^2\,E_n^{(2)} + \ldots + \lambda^k\,E_n^{(k)} + \ldots$$

λ = 1, the original Hamiltonian

$$\boldsymbol{\psi_n = \psi_n^{(0)} + \psi_n^{(1)} + \psi_n^{(2)} + \ldots + \psi_n^{(k)} + \ldots}$$
$$\boldsymbol{E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \ldots + E_n^{(k)} + \ldots}$$

Where, $< \psi_n^{(0)} \mid \psi_n^{(j)} > = 0$, j=1,2,…,k,…

$$H^0\psi_n^{(0)} = E_n^{(0)}\,\psi_n^{(0)}$$

$\Rightarrow$solving for $E_n^{(0)}$, $\psi_n^{(0)}$

$$H^0\psi_n^{(1)} + H'\,\psi_n^{(0)} = E_n^{(0)}\,\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}$$

$\Rightarrow$solving for $E_n^{(1)}$, $\psi_n^{(1)}$

$$H^0\psi_n^{(2)} + H'\,\psi_n^{(1)} = E_n^{(0)}\,\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}$$

$\Rightarrow$ solving for $E_n^{(2)}$,$\psi_n^{(2)}$

The first order:

Multiplied $\psi_m^{(0)}$ from the left and integrate,

$$<\psi_m^{(0)} \mid H^0 \mid \psi_n^{(1)}> + <\psi_m^{(0)} \mid H' \mid \psi_n^{(0)}> = <\psi_m^{(0)}|\psi_n^{(1)}> E_n^{(0)} + E_n^{(1)} \delta_{mn}$$

$$<\psi_m^{(0)}|\psi_n^{(1)}> [E_m^{(0)} - E_n^{(0)}] + <\psi_m^{(0)} \mid H' \mid \psi_n^{(0)}> = E_n^{(1)} \delta_{mn}$$

For m = n, $\boldsymbol{E_n^{(1)} = <\psi_n^{(0)} \mid H' \mid \psi_n^{(0)}>}$ **Eq.(1)**

For m ≠ n, $<\psi_m^{(0)}|\psi_n^{(1)}> = <\psi_m^{(0)} \mid H' \mid \psi_n^{(0)}> / [E_n^{(0)} - E_m^{(0)}]$

If we expand $\psi_n^{(1)} = \sum c_{nm} \psi_m^{(0)}$,

$c_{nm} = <\psi_m^{(0)} \mid H' \mid \psi_n^{(0)}> / [E_n^{(0)} - E_m^{(0)}]$ for m ≠ n;

$$\boldsymbol{\psi_n^{(1)} = \sum_m <\psi_m^{(0)} \mid H' \mid \psi_n^{(0)}> / [E_n^{(0)} - E_m^{(0)}]\, \psi_m^{(0)}} \qquad \textbf{Eq.(2)}$$

The second order:

$$<\psi_m^{(0)}|H^0|\psi_n^{(2)}> + <\psi_m^{(0)}|H'|\psi_n^{(1)}> = <\psi_m^{(0)}|\psi_n^{(2)}>E_n^{(0)} + <\psi_m^{(0)}|\psi_n^{(1)}>E_n^{(1)} + E_n^{(1)}\,\delta_{mn}$$

Set m = n, we have

$$E_n^{(2)} = \sum_{m\neq n} |<\psi_m^{(0)}|H'|\psi_n^{(0)}>|^2 / [E_n^{(0)} - E_m^{(0)}] \qquad \text{Eq.(3)}$$

Discussion: (Text Book: page 522-527)

a. Eq.(2) shows that the effect of the perturbation on the wave function $\psi_n^{(0)}$ is to mix in contributions from the other zero-th order states $\psi_m^{(0)}$ $m \neq n$. Because of the factor $1/(E_n^{(0)}-E_m^{(0)})$, the most important contributions to the $\psi_n^{(1)}$ come from the states nearest in energy to state n.

b. To evaluate the first-order correction in energy, we need only to evaluate a single integral H'_{nn}; to evaluate the second-order energy correction, we must evalute the matrix elements ***H'*** between the n-th and all other states m.

c. The summation in Eq.(2), (3) is over all the states, not the energy levels.

Moller-Plesset (MP) Perturbation Theory

The MP unperturbed Hamiltonian H^0

$$H^0 = \Sigma_m F(m)$$

where $F(m)$ is the Fock operator for electron *m*. And thus, the perturbation H'

$$H' = H - H^0$$

Therefore, the unperturbed wave function is simply the Hartree-Fock wave function Φ.

Ab initio methods: MP2, MP4

Example One:

Consider the one-particle, one-dimensional system with potential-energy function

$V = b$ for $L/4 < x < 3L/4$,
$V = 0$ for $0 < x \leq L/4$ & $3L/4 \leq x < L$

and $V = \infty$ elsewhere. Assume that the magnitude of b is small, and can be treated as a perturbation. Find the first-order energy correction for the ground and first excited states. The unperturbed wave functions of the ground and first excited states are $\psi_1 = (2/L)^{1/2} \sin(\pi x/L)$ and $\psi_2 = (2/L)^{1/2} \sin(2\pi x/L)$, respectively.

Example Two:

As the first step of the Moller-Plesset perturbation theory, Hartree-Fock method gives the zeroth-order energy. Is the above statement correct?

Example Three:

Show that, for any perturbation *H'*, $E_1^{(0)} + E_1^{(1)} \geq E_1$ where $E_1^{(0)}$ and $E_1^{(1)}$ are the zero-th order energy and the first order energy correction, and E_1 is the ground state energy of the full Hamiltonian $H^0 + H'$.

Example Four:

Calculate the bond orders of Li_2 and Li_2^+.

Hohenberg-Kohn Theorems

1^{st} Hohenberg-Kohn Theorem: ***The external potential V(r) is determined, within a trivial additive constant, by the electron density ρ(r).***

Implication: electron density determines every thing.

$$
\begin{aligned}
E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle &= \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \\
&= E_0' + \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})] \, d\mathbf{r}
\end{aligned}
$$

$$
\begin{aligned}
E_0' < \langle \Psi | \hat{H}' | \Psi \rangle &= \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle \\
&= E_0 - \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})] \, d\mathbf{r}.
\end{aligned}
$$

$$E_0 + E_0' < E_0' + E_0$$

2nd Hohenberg-Kohn Theorem: *For a trial density $\rho'(r)$,*

$\tilde{\rho}(\mathbf{r})$

such that ρ' $\tilde{\rho}(\mathbf{r}) \geqslant 0$ d $\int \rho'$ $\int \tilde{\rho}(\mathbf{r})\, d\mathbf{r} = N$

$$E_0 \leqslant E_v[\tilde{\rho}]$$

Implication: Variati rmine ground state energy and density.

$$\begin{aligned} E_v[\rho] &= T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \\ &= \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + F_{\mathrm{HK}}[\rho] \end{aligned}$$

$$F_{\mathrm{HK}}[\rho] = T[\rho] + V_{ee}[\rho]$$

$$V_{ee}[\rho] = J[\rho] + \text{nonclassical term}$$

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + F_{\mathrm{HK}}[\tilde{\rho}] = E_v[\tilde{\rho}] \geqslant E_v[\rho]$$

the energy functional

$$E[\rho] = \int \rho(\mathbf{r})v(\mathbf{r})\,d\mathbf{r} + F[\rho]$$

$$F[\rho] = T[\rho] + V_{ee}[\rho]$$

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]$$

exchange-correlation energy

$$E_{xc}[\rho] \equiv T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

The energy functional

$$\begin{aligned} E[\rho] &= T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r} \\ &= \sum_{i}^{N/2}\sum_{s} \int \psi_i^*(\mathbf{r})\left(-\tfrac{1}{2}\nabla^2\right)\psi_i(\mathbf{r})\,d\mathbf{r} + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r} \end{aligned}$$

constrain the orbitals to be orthonormal, namely,

$$\int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})\,d\mathbf{x} = \delta_{ij}$$

Define the functional of the N orbitals

$$\Omega[\{\psi_i\}] = E[\rho] - \sum_i^N \sum_j^N \varepsilon_{ij} \int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})\,d\mathbf{x}$$

ε_{ij} are Lagrange multipliers for the constraints

$$\delta\Omega[\{\psi_i\}] = 0$$

which leads to the equations

$$\hat{h}_{\text{eff}}\psi_i = [-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}]\psi_i = \sum_j^N \varepsilon_{ij}\psi_j$$

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + v_{xc}(\mathbf{r})$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})}$$

	Ground State	Excited State	CPU Time (CH_3NH_2,6-31G*)	Correlation	Geometry	Size Consistent
HFSCF	√	×	1	0	OK	√
DFT	√	×	~1		√	√
CIS	×	√	<10		OK	×
CISD	√	√	17	80-90% (20 electrons)	√	×
CISDTQ	√	√	very large	98-99%	√	×
MP2	√	×	1.5	85-95% (DZ+P)	√	√
MP4	√	×	5.8	>90%	√	√
CCD	√	×	large	>90%	√	√
CCSDT	√	×	very large	~100%	√	√