

E 2.1

$$\langle \Psi_i^\alpha | \Psi_j^\beta \rangle = \delta_{ij}$$

$$\chi_{2i-1}(\bar{x}) = \Psi_i^\alpha(\bar{r}) \alpha(\omega)$$

$$\chi_{2i}(\bar{x}) = \Psi_i^\beta(\bar{r}) \beta(\omega)$$

$$\begin{aligned}\langle \chi_{2i-1} | \chi_{2i} \rangle &= \langle \Psi_i^\alpha | \Psi_i^\beta \rangle \langle \alpha | \beta \rangle = \\ &= \delta_{ij} \langle \alpha | \beta \rangle = 0\end{aligned}$$

$$\langle \chi_{2i} | \chi_{2i} \rangle = \langle \Psi_i^\beta | \Psi_i^\beta \rangle \langle \beta | \beta \rangle = 1$$

E 2.2

$$\Psi^{HP}(\vec{x}_1, \dots, \vec{x}_N) = \chi_i(\vec{x}_1) \chi_j(\vec{x}_2) \dots \chi_k(\vec{x}_N)$$

$$\sum_{i=1}^N h(i) \Psi^{HP} = \chi_j(\vec{x}_2) \dots \chi_k(\vec{x}_N) h(1) \chi_i(\vec{x}_1) + \\ + \chi_i(\vec{x}_1) \dots \chi_k(\vec{x}_N) h(2) \chi_j(\vec{x}_2) + \dots = \varepsilon_i + \varepsilon_j + \dots + \varepsilon_k$$

E 2.3

$$\Psi(\bar{x}_1, \bar{x}_2) = \frac{1}{\sqrt{2}} [\chi_i(\bar{x}_1) \chi_j(\bar{x}_2) - \chi_j(\bar{x}_1) \chi_i(\bar{x}_2)]$$

$$\begin{aligned}\langle \Psi | \Psi \rangle &= \frac{1}{2} \left[\underbrace{\langle \chi_i(x_1) \chi_j(x_2) | \chi_i(x_1) \chi_j(x_2) \rangle}_{+} + \underbrace{\langle \chi_j(x_1) \chi_i(x_2) | \chi_j(x_1) \chi_i(x_2) \rangle}_{-} \right. \\ &\quad \left. - \langle \chi_i(x_1) \chi_j(x_2) | \chi_j(x_1) \chi_i(x_2) \rangle - \langle \chi_j(x_1) \chi_i(x_2) | \chi_i(x_1) \chi_j(x_2) \rangle \right]\end{aligned}$$

$$= \frac{1}{2} [1 + 1 - 0 - 0] = 1$$

E 2.6

$$\Psi_1 = \frac{1}{\sqrt{2(1+s_{12})}} (\Phi_1 + \Phi_2)$$

$$\Psi_2 = \frac{1}{\sqrt{2(1-s_{12})}} (\Phi_1 - \Phi_2)$$

$$\langle \Psi_1 | \Psi_1 \rangle = \frac{1}{2(s_{12}+1)} \underbrace{\langle \Phi_1 + \Phi_2 | \Phi_1 + \Phi_2 \rangle}_{1+1+2s_{12}} = 1$$

$$\langle \Psi_1 | \Psi_2 \rangle = \frac{1}{2\sqrt{1-s_{12}^2}} \underbrace{\langle \Phi_1 - \Phi_2 | \Phi_1 + \Phi_2 \rangle}_{1-1-s_{12}+s_{12}} = 0$$

E 2.11

$$|K\rangle = |\chi_1 \chi_2 \chi_3\rangle$$

...

$$\begin{aligned} \langle K | H | K \rangle &= \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 3 | h | 3 \rangle \\ &+ \frac{1}{2} [\langle 111 | 11 \rangle + \langle 121 | 12 \rangle + \langle 131 | 13 \rangle + \\ &+ \langle 211 | 21 \rangle + \langle 221 | 22 \rangle + \langle 231 | 23 \rangle + \\ &+ \langle 311 | 31 \rangle + \langle 321 | 32 \rangle + \langle 331 | 33 \rangle] = \\ \langle \text{uuu} | \text{uuu} \rangle &= 0 \quad \langle 121 | 12 \rangle = \langle 211 | 21 \rangle \end{aligned}$$

$$= \sum_{i=1}^3 \langle i | h | i \rangle + \langle 121 | 12 \rangle + \langle 131 | 13 \rangle + \langle 231 | 23 \rangle$$

E2.18

$$E_0^{(2)} = \frac{1}{4} \sum_{abrs} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

$$|\langle ab || rs \rangle|^2 = (\langle ab | rs \rangle - \langle ab | sr \rangle)(\langle rs | ab \rangle - \langle rs | ba \rangle)$$

$$= \langle ab | rs \rangle \langle rs | ab \rangle - \langle ab | sr \rangle \langle rs | ab \rangle - \langle ab | sr \rangle \langle rs | ba \rangle$$

$$+ \langle ab | sr \rangle \langle rs | ba \rangle =$$

$$a \leftrightarrow b, r \leftrightarrow s$$

$$= 2 \langle ab | rs \rangle \langle rs | ab \rangle - \langle ab | rs \rangle \langle sr | ab \rangle - \langle ab | rs \rangle \langle rs | ba \rangle$$

$$\sum_{\substack{ab \\ rs}} \langle ab | rs \rangle \langle sr | ba \rangle = \left(\sum_a \sum_b + \sum_a \sum_{\bar{b}} + \sum_{\bar{a}} \sum_b + \sum_{\bar{a}} \sum_{\bar{b}} \right) \times$$

$$\times \left(\sum_{rs} + \sum_{\bar{r}s} + \sum_{r\bar{s}} + \sum_{\bar{r}\bar{s}} \right) =$$

$$= \sum_{abrs}^{N/2} \langle ab | rs \rangle \langle sr | ba \rangle + \sum_{\substack{ab \\ rs}} \langle ab | r\bar{s} \rangle \langle \bar{s}r | \bar{b}a \rangle +$$

$$+ \sum_{\substack{ab \\ rs}} \langle \bar{a}b | \bar{r}s \rangle \langle \bar{s}\bar{r} | \bar{b}\bar{a} \rangle + \sum_{\substack{ab \\ rs}} \langle \bar{a}\bar{b} | \dots \rangle =$$

$$= 4 \sum_{abrs}^{N/2} \langle ab | rs \rangle \langle sr | ba \rangle$$

$$\sum_{ab} \langle ab | rs \rangle \langle sr | ab \rangle = \left(\sum_a \sum_b + \sum_{\bar{a}} \sum_{\bar{b}} + \sum_{\bar{a}} \sum_b + \sum_{\bar{a}} \sum_{\bar{b}} \right) \left(\sum_{sr} \sum_{\bar{s}\bar{r}} + \sum_{\bar{s}r} \sum_{\bar{s}\bar{r}} + \sum_{s\bar{r}} \sum_{\bar{s}\bar{r}} + \sum_{\bar{s}\bar{r}} \sum_{\bar{s}\bar{r}} \right)$$

$$= \sum_{ab} \sum_{sr} + \sum_{\bar{a}\bar{b}} \sum_{\bar{s}\bar{r}} = 2 \sum_{abrs}^{N/2}$$

Since $\langle rs | ba \rangle = \langle sr | ab \rangle$, we get

$$\frac{1}{4} \sum_{absr} |\langle ab || rs \rangle|^2 = \sum_{ab}^{N/2} \sum_{rs=N/2+1}^K \left(2 \langle ab | rs \rangle \langle rs | ab \rangle - \langle ab | rs \rangle \langle rs | ba \rangle \right)$$

E 2.22

$$\Psi_{\uparrow\downarrow}^{\text{HP}} = \Psi_1(\mathbf{r}_1) \alpha(1) \Psi_2(\mathbf{r}_2) \beta(2)$$

$$\Psi_{\downarrow\uparrow}^{\text{HP}} = \Psi_1(\mathbf{r}_1) \beta(1) \Psi_2(\mathbf{r}_2) \alpha(2)$$

$$\begin{aligned} \langle \Psi_{\uparrow\downarrow}^{\text{HP}} | H | \Psi_{\downarrow\uparrow}^{\text{HP}} \rangle &= \langle \Psi_1 \alpha \Psi_2 \beta | h(1) + h(2) | \Psi_1 \beta \Psi_2 \alpha \rangle \\ &+ \langle \Psi_1 \alpha \Psi_2 \beta | \frac{1}{r_{12}} | \Psi_1 \alpha \Psi_2 \beta \rangle = \\ &= (\Psi_1 | h | \Psi_1) + (\Psi_2 | h | \Psi_2) + (\Psi_1 | \Psi_2 | \Psi_2 | \Psi_1) = \\ &= h_{11} + h_{22} + J_{12} \end{aligned}$$

$$\begin{aligned} \langle \Psi_{\downarrow\uparrow}^{\text{HP}} | H | \Psi_{\downarrow\uparrow}^{\text{HP}} \rangle &= \langle \Psi_1 \beta \Psi_2 \beta | h(1) + h(2) | \Psi_1 \beta \Psi_2 \beta \rangle \\ &+ \langle \Psi_1 \beta \Psi_2 \beta | \frac{1}{r_{12}} | \Psi_1 \beta \Psi_2 \beta \rangle = h_{11} + h_{22} + J_{12} \end{aligned}$$

$$\langle \Psi_{\uparrow\downarrow}^{\text{HP}} | H | \Psi_{\uparrow\downarrow}^{\text{HP}} \rangle = \langle \Psi_{\downarrow\uparrow}^{\text{HP}} | H | \Psi_{\downarrow\uparrow}^{\text{HP}} \rangle$$

E 2.32 (b)

$$\boxed{s^2 = s_+ s_- - s_z + s_z^2}$$

$$s^2 = s_- s_+ + s_z + s_z^2$$

$$s_+ s_- = (s_x + i s_y)(s_x - i s_y) = s_x^2 + s_y^2 + i \underbrace{(s_y s_x - s_x s_y)}_{-i s_z}$$

$$= s_x^2 + s_y^2 + s_z^2$$

$$s^2 = s_x^2 + s_y^2 + s_z^2 = s_+ s_- - s_z + s_z^2$$

E 2.33

$$s^2 |\alpha\rangle = \frac{3}{4} |\alpha\rangle \quad \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$s^2 |\beta\rangle = \frac{3}{4} |\beta\rangle \quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\boxed{s^2 = \frac{3}{4} I}$$

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$s_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle$$

$$\boxed{s_z = \frac{1}{2} \sigma_z}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$s_z |\beta\rangle = -\frac{1}{2} |\beta\rangle$$

$$s_+ |\alpha\rangle = 0 \quad s_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad s_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$$s_+ |\beta\rangle = |\alpha\rangle$$

$$s_+ s_- = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

$$s_+ s_- - s_z + s_z^2 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} - \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \frac{1}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} =$$

$$= \begin{pmatrix} 3/4 & 0 \\ 0 & 3/4 \end{pmatrix} = s^2$$

E2.35

$$[A, H] = 0$$

$$H|\Phi\rangle = E|\Phi\rangle$$

$$A H |\Phi\rangle - H A |\Phi\rangle = 0$$

Since $|\Phi\rangle$ is energetically non-degenerate
 $A|\Phi\rangle$ should be

$$A|\Phi\rangle = \alpha|\Phi\rangle$$

$$E(A|\Phi\rangle) = H(A|\Phi\rangle)$$

↑
eigenvector

This means that
 $|\Phi\rangle$ is the eigenvector
of A .

E2.36

$$\langle \psi_1 | [A, H] | \psi_2 \rangle = 0 = \langle \psi_1 | AH |\psi_2 \rangle - \langle \psi_1 | HA |\psi_2 \rangle$$

$$= \alpha_1 \langle \psi_1 | H | \psi_2 \rangle - \alpha_2 \langle \psi_1 | H | \psi_2 \rangle$$

$$\text{Since } \alpha_1 \neq \alpha_2, \quad \langle \psi_1 | H | \psi_2 \rangle = 0.$$

E2.37

$$\mathcal{L}_z |x_i x_j \dots x_k\rangle = \underbrace{\frac{1}{2} (N^\alpha - N^\beta)}_{M_S} |x_i \dots x_k\rangle$$

$$\mathcal{L}_z |x_i x_j \dots x_k\rangle = \frac{1}{\sqrt{N!}} \sum_i^{N!} (-)^{P_i} \mathcal{L}_z P_i \{x_i \dots x_k\} =$$

$$\mathcal{L}_z P_i = P_i \mathcal{L}_z$$

$$= \frac{1}{\sqrt{N!}} \sum_i^{N!} (-)^{P_i} P_i \{ \mathcal{L}_z x_i \dots x_k \}$$

$$\mathcal{L}_z x_i \dots x_k = \sum_{i=1}^N S_z(i) x_i \dots x_k = \underbrace{\frac{1}{2} (N^\alpha - N^\beta)}_{M_S} x_i \dots x_k$$

E 3.1

$$\begin{aligned}
 & \langle x_i | f | x_j \rangle = \langle x_i | h | x_j \rangle + \\
 & + \sum_b \int d\bar{x}_1 \chi_i^*(x_1) \int d\bar{x}_2 \chi_b^*(2) r_{12}^{-1} (1 - P_{12}) \chi_b(2) \chi_j(1) \\
 & = \langle x_i | h | x_j \rangle + \sum_b \int d\bar{x}_1 \int d\bar{x}_2 \chi_i^*(1) \chi_j(1) \frac{1}{r_{12}} \chi_b^*(2) \chi_b(2) - \\
 & - \sum_b \int d\bar{x}_1 \int d\bar{x}_2 \chi_i^*(1) \chi_b(1) \frac{1}{r_{12}} \chi_b^*(2) \chi_j(2) = \\
 & = \langle x_i | h | x_j \rangle + \sum_b [ij|bb] - [ib|bj] = \\
 & = \langle x_i | h | x_j \rangle + \sum_b \underbrace{\langle ib|jb \rangle}_{\langle ib||jb \rangle} - \langle ib|bj \rangle
 \end{aligned}$$

E 3.3 $E_0[\{x_\alpha\}] = \sum_a [a|h|a] + \frac{1}{2} \sum_{ab} [aa|bb] - [ab|ba]$

$$\begin{aligned}
 \delta E_0 &= \sum_a [\delta x_\alpha | h | x_\alpha] + [x_\alpha | h | \delta x_\alpha] + \\
 &+ \frac{1}{2} \sum \sum [\delta x_\alpha x_\alpha | x_\beta x_\beta] + [x_\alpha \delta x_\alpha | x_\beta x_\beta] + \\
 &+ [x_\alpha x_\alpha | \delta x_\beta x_\beta] + [x_\alpha x_\alpha | x_\beta \delta x_\beta] - \\
 &- \frac{1}{2} \sum \sum [\delta x_\alpha x_\beta | x_\beta x_\alpha] + [x_\alpha \delta x_\beta | x_\beta x_\alpha] + [x_\alpha x_\beta | \delta x_\beta x_\alpha] \\
 &+ [x_\alpha x_\beta | \delta x_\alpha]
 \end{aligned}$$

$$\begin{aligned}
 [x_\alpha x_\alpha | \delta x_\beta x_\beta] &= \underset{\substack{a=b \\ b=a}}{[x_\beta x_\beta | \delta x_\alpha x_\alpha]} = \iint d\bar{x}_1 d\bar{x}_2 \chi_a^*(x_1) \chi_a(x_1) \frac{1}{r_{12}} \chi_b(\bar{x}_2) \chi_b(\bar{x}_2) \\
 r_{12}^{-1} \delta x_a^*(x_2) \chi_a(x_2) &= \iint d\bar{x}_1 d\bar{x}_2 \delta \chi_a^*(x_1) \chi_a(x_1) \frac{1}{r_{12}} \chi_b(\bar{x}_2) \chi_b(\bar{x}_2)
 \end{aligned}$$

$$\sum_{a,b} [\delta \chi_a \chi_a | \delta \chi_b \chi_b] = \sum_b [\delta \chi_a \chi_a | \chi_b \chi_b]$$

Similarly,

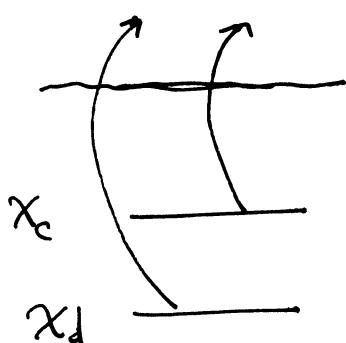
$$\sum_b [\delta \chi_a \chi_b | \chi_b \chi_a] = \sum_a [\chi_a \chi_b | \delta \chi_b \chi_a]$$

$$\delta E_0 = \sum_a [\delta \chi_a | h | \chi_a] + \sum_b [\delta \chi_a \chi_a | \chi_b \chi_b] - [\delta \chi_a \chi_b | \chi_b \chi_a]$$

+ c.c.

E 3.5

$$^N E_0 = \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_{a,b} \langle a b | h | a b \rangle$$



$$^{N-2} E_0 = \sum_{\substack{a \neq c \\ a \neq d}} \langle a | h | a \rangle + \frac{1}{2} \sum_{\substack{a, b \neq c \\ a, b \neq d}} \langle a b | h | a b \rangle$$

$$IP_2 = {}^{N-2} E_0 - {}^N E_0 = \\ = - \langle c | h | c \rangle - \langle d | h | d \rangle -$$

$$- \frac{1}{2} \sum_a \langle a c | h | a c \rangle - \frac{1}{2} \sum_b \langle c b | h | c b \rangle -$$

$$- \frac{1}{2} \sum_a \langle a d | h | a d \rangle - \frac{1}{2} \sum_b \langle d b | h | d b \rangle + \langle c d | h | c d \rangle =$$

$$= - \langle c | h | c \rangle - \langle d | h | d \rangle - \sum_b \langle c b | h | c b \rangle - \sum_b \langle d b | h | d b \rangle$$

$$+ \langle c d | h | c d \rangle = - \varepsilon_c - \varepsilon_d + \langle c d | h | c d \rangle$$

E 3.7

$$H_0 = \sum_{i=1}^n f(i)$$

$$P_{ij} H_0 = (f(1) + f(2) + \dots + \underbrace{f(i) + \dots + f(j)}_{\uparrow} + \dots) = \\ = H_0 P_{ij}$$

$$[P_{ij}, H_0] = 0$$

$$H_0 |\Psi_0\rangle = \frac{1}{\sqrt{N!}} \sum_i^{N!} (-)^{p_i} p_i \{ H_0 \chi_i \dots \chi_k \}$$

$$H_0 \chi_i \dots \chi_k = \sum f(i) \chi_i \dots \chi_k =$$

$$= f(i) \underbrace{\chi_i(1) \dots}_{\varepsilon_i} + \chi_i(1) \chi_m(3) \dots \chi_k(N) \underbrace{f(j) \chi_j(2) + \dots}_{\varepsilon_j} \\ = \sum (\varepsilon_i + \varepsilon_j + \dots + \varepsilon_k) \chi_i(1) \dots \chi_k(N)$$

$$H_0 |\Psi_0\rangle = (\varepsilon_i + \varepsilon_j + \dots + \varepsilon_k) |\Psi_0\rangle$$

E 3.8

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \langle \Psi_0 | H_0 | \Psi_0 \rangle + \langle \Psi_0 | V | \Psi_0 \rangle$$

$\sum_a \varepsilon_a$

$$= E_0^{(0)} + E_0^{(1)}, \quad E_0^{(0)} = \sum_a \varepsilon_a$$

$$\langle \Psi_0 | \sum_{i < j} \frac{1}{r_{ij}} - \sum_i V^{HF} | \Psi_0 \rangle =$$

$$= \frac{1}{2} \sum_{a,b} \langle ab || ab \rangle - \sum_a \langle a | V^{HF} | a \rangle =$$

$$\text{According to E 3.1, } \langle a | V^{HF} | a \rangle = \sum_b \langle ab || ab \rangle$$

$$= \frac{1}{2} \sum_{a,b} \langle ab || ab \rangle - \sum_{ab} \langle ab || ab \rangle = -\frac{1}{2} \sum \langle ab || ab \rangle$$

$$E_0 = \sum \langle ah | ah \rangle + \sum_{ab} \langle ab || ab \rangle - \frac{1}{2} \sum \langle ab || ab \rangle$$

$$E_0 = \sum \langle ah | ah \rangle + \frac{1}{2} \sum_{a,b} \langle ab || ab \rangle$$

E 3.9

$$\varepsilon_i = \langle x_i | h | x_i \rangle + \sum_b \langle x_i | h_b | x_i x_b \rangle$$

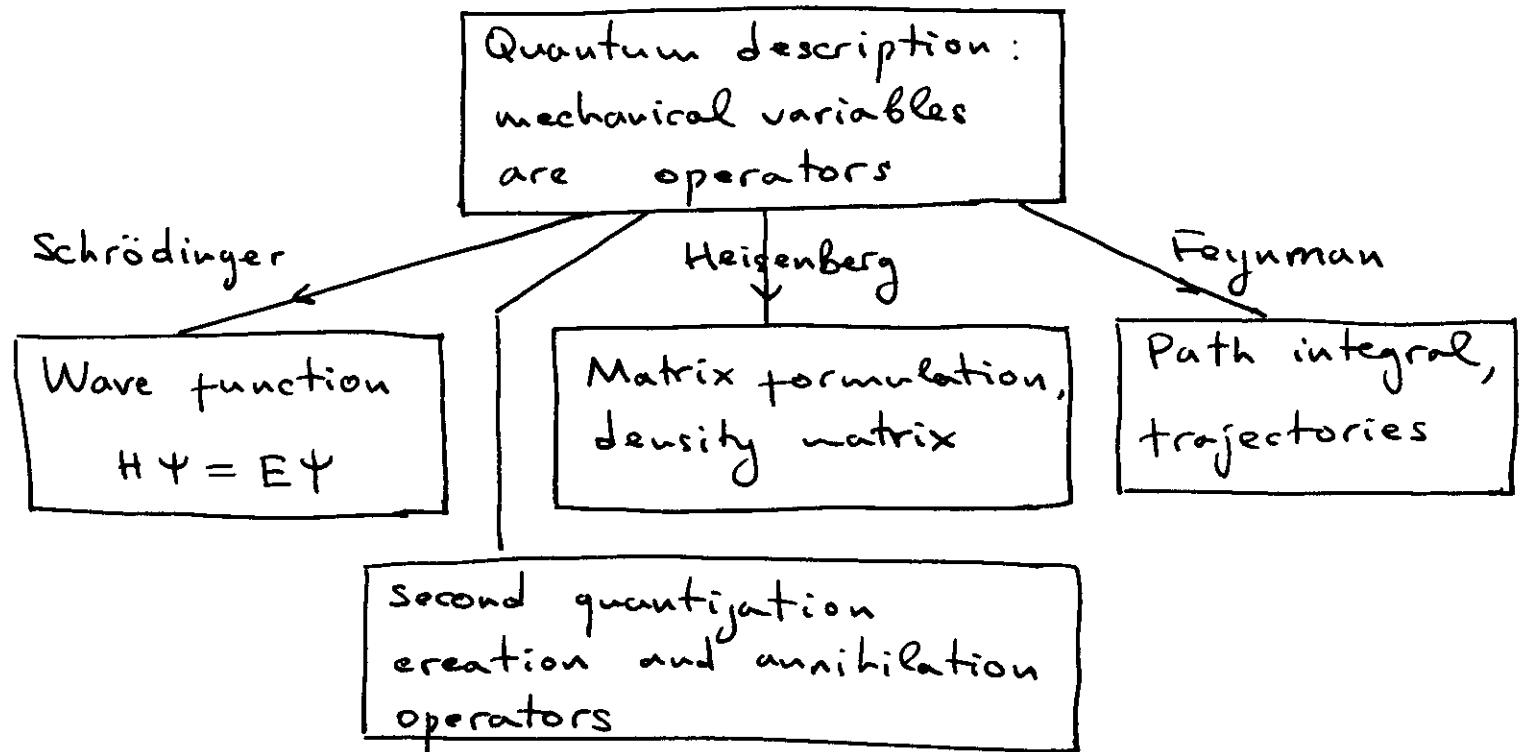
$$\sum_b = \sum_b^{N/2} + \sum_b^{N/2}$$

$$\begin{aligned}\varepsilon_i &= (\psi_i | h | \psi_i) + \sum_b^{N/2} [\psi_i \psi_i | \psi_b \psi_b] - [\psi_i \psi_b] \psi_i \psi_b \\ &\quad + \sum_b^{N/2} [t_i \psi_i | \bar{\psi}_b \bar{\psi}_b] - [t_i \bar{\psi}_b] \psi_i \bar{\psi}_b\end{aligned}$$

$$\varepsilon_i = (\psi_i | h | \psi_i) + \sum_b^{N/2} 2[t_i \psi_i | \psi_b t_b] - [t_i t_b] \psi_i \psi_b$$

$$\varepsilon_i = h_{ii} + \sum_b^{N/2} [2J_{ib} - K_{ib}]$$

Foundations of quantum mechanics



Schrödinger equation → { One-particle problems,
simple collisions in gas phase
small molecules

Matrix formulation → { Large molecules in the gas phase,
weak coupling to collective
excitation of condense media

Second quantization → { Many-electron problems
with well-defined basis sets;
solid-state chemistry /physics

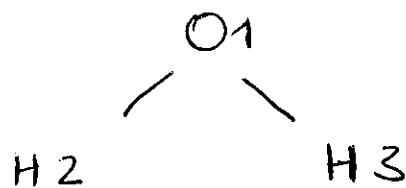
Path integrals → { strong coupling between
quantum modes and
collective excitations of
disordered systems

Building a Z-matrix

- ①. Draw a molecule
- ②. Assign one atom #1
- ③. From the first atom, assign all other atoms a sequential number.
- ④. Starting from #1, list the atoms you numbered one right under the other.
- ⑤. Atom #1 is placed in the origin of your coordinate system.
- ⑥. Atom #2 is defined by its bond length to atom #1
- ⑦. For atom #3 you need to define a bond angle between #3 and atoms #1 and #2.
- ⑧. To identify atom #4 and all other atoms, you must include a bond length, bond angle, and a dihedral angle

Dihedral angle = angle between an atom and the plane created by three other atoms

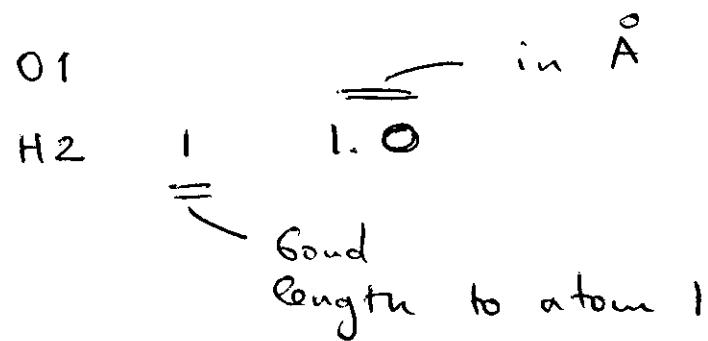
Z-Matrix : Water molecule



1. Label the oxygen as atom O1

O1

2. Indicate the bond length to atom 1

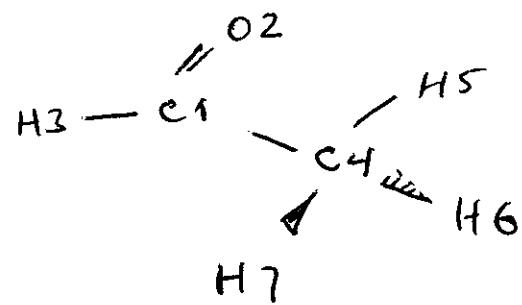


3. Indicate the bond length to atom 1 and the angle between 2, 1, and 3

O1



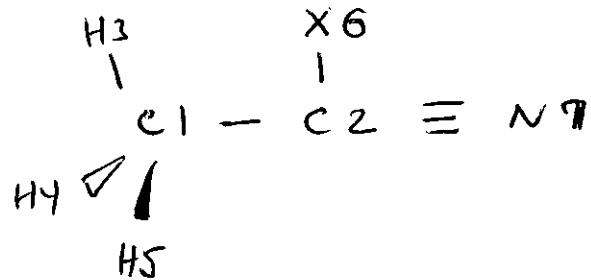
Z-matrix : Acetaldehyde



	C1	O2	H3	C4	H5	H6	H7
C1		1.20					
O2	1						
H3	1	1.0	2		120.0		
C4	1	1.50	2	120.0	3	180.0	
H5	4	1.0	1	110.0	2	0.0	
H6	4	1.0	1	110.0	2	120.0	
H7	4	1.0	1	110.0	2	-120.0	

Z-matrix: Methyl Cyanide

Using a dummy atom:



C1

C2 1 1.50

H3 1 1.0 2 110.0

H4 1 1.0 2 110.0 3 120.0

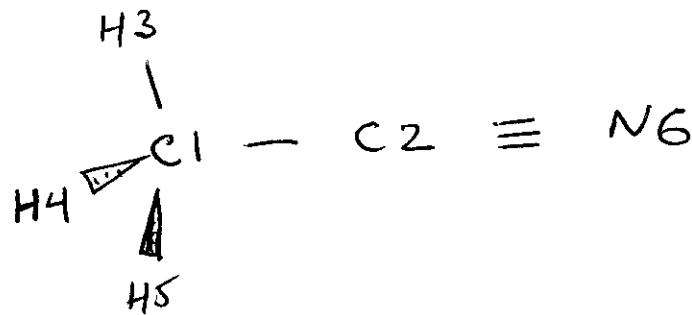
H5 1 1.0 2 110.0 3 -120.0

X6 2 1.0 1 90.0 3 0.0

N7 2 1.2 6 90.0 4 180.0

Z-matrix: Methyl Cyanide

Ignoring the connecting atom



C1

C2 1 1.50

H3 1 1.0 2 110.0

H4 1 1.0 2 110.0 3 120.0

H5 1 1.0 2 110.0 3 -120.0

N6 1 2.7 3 110.0 2 0.0

8 example.inp

```
$CTRL SCFTYP=RHF RUNTYP=OPTIMIZE COORD=ZMT NZVAR=0 PLTORB=.TRUE. $END
$BASIS GBASIS=STO NGAUSS=3 $END
$GUESS GUESS=HUCKEL $END
$DATA
Water calculation by D. Matyushov
Cnv 2

01
H2    1      R1
H3    1      R1    2      A1

R1=1.00
A1=104.0
$END
```

Z-matrix construction

Rules:

- ① One atom per line
- ② Each atom is specified in terms of atoms already defined, i.e. relative to atoms above
- ③ Distances are always positive, angles are in the range $0 - 180^\circ$, torsional angles are in the range $-180^\circ - 180^\circ$ or $0^\circ - 360^\circ$.

Typical bond lengths (\AA):

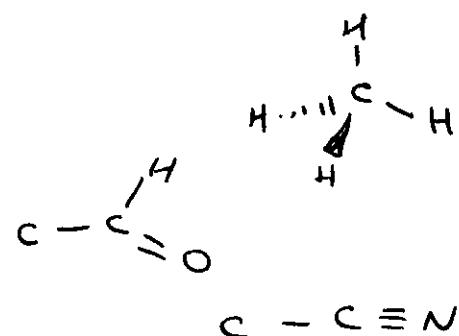
C-H : 1.10	A-B	$\text{A,B} = \text{C,O,N}$: 1.40 - 1.50
O-H : 1.00	A=B	$\text{A,B} = \text{C,O,N}$: 1.20 - 1.30
N-H : 1.00	$\text{A}\equiv\text{B}$	$\text{A,B} = \text{C,N}$: 1.20
S-H : 1.40	A-B	A=C, B=S,P : 1.80
P-H : 1.40		

Typical angles:

sp^3 hybridization : 110°

$\Rightarrow \text{sp}^2$ hybridization : 120°

sp hybridization : 180°



Torsional angles:

around sp^3 atoms : 120°

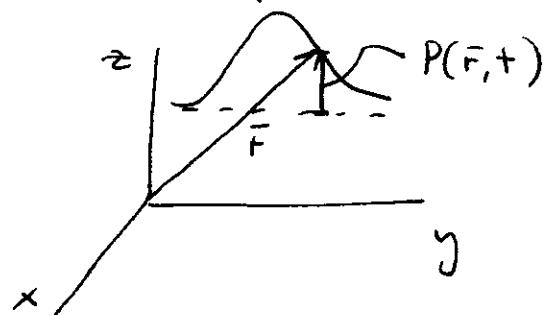
around sp^2 atoms : 180°

Schrödinger formulation

Dynamics of a quantum particle is considered as propagation of a wave package with the intensity at point \vec{r} equal to the squared wave amplitude

$$P(\vec{r}, t) = |\Psi(\vec{r}, t)|^2$$

probability to find a particle at point \vec{r} at time t



The dynamics of the wave amplitude is defined by the Schrödinger equation

$$H\Psi(\vec{r}, t) = \hat{E}\Psi(\vec{r}, t), \quad \hat{E} = i\hbar \frac{\partial}{\partial t}$$

Planck constant

The Hamiltonian H is the sum of the kinetic and potential energies

$$H = K + V, \quad K = \frac{\vec{p}^2}{2m}, \quad V = V(\vec{r})$$

In quantum mechanics, \vec{p} (momentum) is an operator

$$\vec{p} = i\hbar \nabla_{\vec{r}}$$

gradient operator

$$\nabla_{\vec{r}} = \vec{i}_x \frac{\partial}{\partial x} + \vec{i}_y \frac{\partial}{\partial y} + \vec{i}_z \frac{\partial}{\partial z}$$

Kinetic energy:

$$K = -\frac{\hbar^2}{2m} \nabla^2$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Cartesian coordinates

$$\nabla_r^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}$$

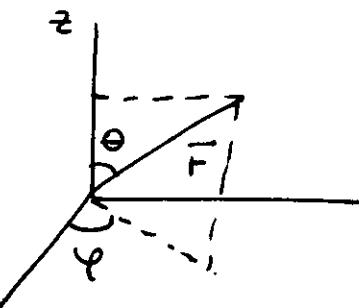
polar coordinates, spherical symmetry

$$\nabla^2 = \nabla_r^2 + \nabla_\theta^2$$

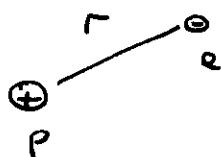
$$\nabla_\theta^2 = \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \frac{1}{r^2}$$

$$\nabla_\theta^2 \psi(r) = 0$$

$$\nabla_r^2 \psi(r) = \text{#A}$$



Hydrogen atom:



$$H = \underbrace{-\frac{\hbar^2}{2m} (\nabla_r^2 + \nabla_\theta^2)}_K - \underbrace{\frac{e^2}{4\pi\epsilon_0 r}}_{U(r)}$$

e is the elementary electron charge
 ϵ_0 is the vacuum permittivity

Atomic units

a.u

Dimensionless spacial coordinates

$$x, y, z \rightarrow a_0 x', a_0 y', a_0 z'$$

↑
dimensionless

a_0 is the unit length equal to 0.52918 \AA , the radius of the first orbit of the Bohr model of hydrogen atom.

$$\frac{\hbar^2}{mea_0^2} = \frac{e^2}{4\pi\epsilon_0 a_0^2} = \varepsilon_a$$

o the atomic unit of energy called the Hartree.

The hydrogen atom Hamiltonian becomes

$$H = \varepsilon_a \left[-\frac{1}{2} (\nabla')^2 - \frac{1}{r'} \right]$$

Symbol	Quantity	Value in a.u.
m_e	Electron mass	1
e	Electron charge	1
\hbar	$\hbar/2\pi$	1
a_0	Bohr radius	1
ε_a	Hartree	1
c	Speed of light	137.036
μ	dipole moment	$1 = 2.5418 D$

$$\varepsilon_a = 27.211 \text{ eV}$$

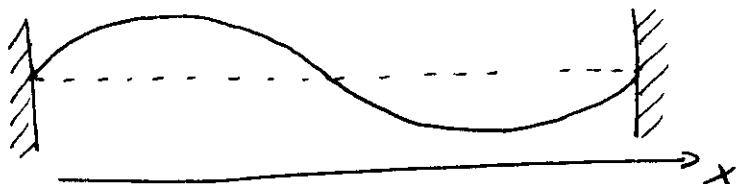
$$a_0 = 0.52918 \text{ \AA}$$

Stationary solution of the Schrödinger equation

$$H \Psi(r, t) = \hat{E} \Psi(r, t), \quad \hat{E} = i\hbar \frac{\partial}{\partial t}$$

For a stationary solution, the spacial part of the wave function does not depend on time

$$\Psi(\vec{r}, t) = \Psi(\vec{r}) e^{-iEt/\hbar}$$



A stationary wave between two walls is a stationary solution

Normalization

$$\int \Psi^*(\vec{r}) \Psi(\vec{r}) d\vec{r} = 1$$

normalization of probability,
the probability to find a quantum object at any place is equal to one.

Spectrum of energies

$$\varepsilon_N = \Psi_N(\vec{r})$$

$$H \Psi_i(\vec{r}) = \varepsilon_i \Psi_i(\vec{r})$$

$$\vdots$$

$$\varepsilon_3 = \Psi_3(\vec{r})$$

$$\varepsilon_2 = \Psi_2(\vec{r})$$

$$\varepsilon_1 = \Psi_1(\vec{r})$$

If the set $\{\Psi_1(\vec{r}), \dots, \Psi_N(\vec{r})\}$ makes a complete set of all solutions of the Schrödinger equation, it is called the complete basis.

eigenvalue

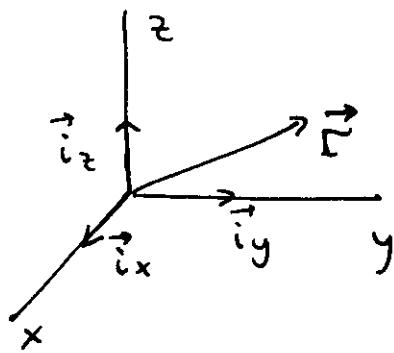
eigenstate

Bra and ket notations (1.1.4 so)

A quantum mechanical system in the stationary state ψ is denoted by a ket vector $|\psi\rangle$

$$|\Psi(\vec{r})\rangle \equiv |\psi\rangle$$

The notation can be generalized to any state characterized by N basis vectors



$$\vec{r} = a_x \vec{i}_x + a_y \vec{i}_y + a_z \vec{i}_z$$

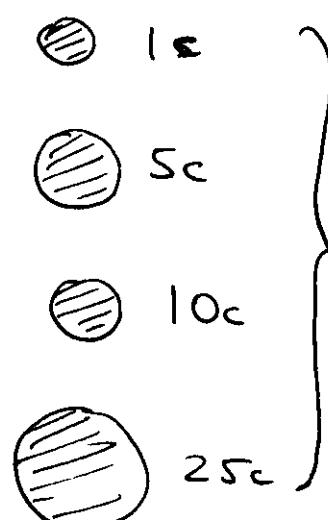
$$|r\rangle = \sum_{i=1}^3 a_i |i\rangle$$

↑
state ↑
basis vectors

N -dimensional vector :

$$|a\rangle = \sum_{i=1}^N |i\rangle a_i$$

Example:



$$|35c\rangle = 1 \cdot |10c\rangle + 1 \cdot |25c\rangle$$

↑ ↑
 $a(10c)$ $a(25c)$

$$|44c\rangle = 1 \cdot |25c\rangle + 1 \cdot |10c\rangle +$$

$$+ 1 \cdot |5c\rangle + 4 \cdot |1c\rangle$$

↑ ↑
 $a(5c)$ $a(1c)$

- ! Any amount of charge can be expanded !
- over the basis ket vectors of charge !

When you know the basis set, you just need to care about the expansion coefficient and use the matrix notation for a vector

$$\vec{a} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} \quad 35c = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 1 \end{pmatrix} \quad 44c = \begin{pmatrix} 4 \\ -1 \\ 1 \\ 1 \end{pmatrix}$$

Vectors can be complex. The adjoint vector is defined by the row matrix

$$\vec{a}^* = (a_1^* \ a_2^* \ \dots \ a_N^*)$$

\vec{a}^* is the matrix representation of the bra vector $\langle a |$ Bra and ket form the scalar product

$$\boxed{\langle a | B \rangle = \sum_{i=1}^N a_i^* b_i}, \quad \langle a | a \rangle = \sum_{i=1}^N |a_i|^2$$

Basis expansion: $\langle a | = \sum_{i=1}^N a_i^* \langle i |$

$$\langle a | B \rangle = \sum_{i,j=1}^N a_i^* \langle i | j \rangle b_j$$

For an orthonormal set:

$$\langle i | j \rangle = \begin{cases} 1 & \text{when } i=j \\ 0 & \text{when } i \neq j \end{cases} \quad \} \quad \langle i | j \rangle = \delta_{ij}$$

δ_{ij} is the Kronecker symbol.

Operators

Transition from state $|a\rangle$ to state $|b\rangle$

$$O|a\rangle = |b\rangle$$

operator

An operator is completely determined if we know what it does to the basis $|i\rangle$!

$$O|i\rangle = \sum_j |j\rangle O_{ji}$$

$$O_{ji} = \langle j | O | i \rangle$$

An operator is completely defined by its matrix

$$\hat{O} = \begin{pmatrix} O_{11} & O_{12} & O_{13} & \cdots \\ O_{21} & O_{22} & & \\ O_{31} & & \ddots & \\ \vdots & & & \end{pmatrix}$$

Adjoint operator O^+ changes bra $\langle a |$ into bra $\langle b |$

$$\langle a | O^+ = \langle b |$$

An operator is Hermitian when it is self-adjoint

$$O = O^+$$

$$\langle a | O | b \rangle = \langle a | O^+ | b \rangle = \langle b | O | a \rangle^*$$

All operators corresponding to observable quantities are hermitian

Properties of Hermitian operators

$$O|\alpha\rangle = \omega_\alpha |\alpha\rangle$$

↑ ↑
eigenvector eigenvalue

- ①. if $O = O^+$ $\omega_\alpha = \omega_\alpha^*$
- ②. if $\omega_\alpha \neq \omega_\beta$ and $O = O^+$, $\langle \alpha | \beta \rangle = 0$
- ③. if $\omega_\alpha = \omega_\beta$ and $|\alpha\rangle \neq |\beta\rangle$, the two states are degenerate
- ④. Degenerate eigenvectors can always be chosen to be orthogonal

$|1\rangle, |2\rangle$ are degenerate states, $\langle 1|2 \rangle = s$

$$|1'\rangle = |1\rangle \quad \langle 1'|2 \rangle = a + b s = 0$$

$$|2'\rangle = a|1\rangle + b|2\rangle \quad \langle 2'|2' \rangle = a^2 + b^2 + 2ab s = 1$$

$$|2'\rangle = \frac{s}{\sqrt{1-s^2}}|1\rangle - \frac{1}{\sqrt{1-s^2}}|2\rangle$$

Eigenvectors $\{|\alpha\rangle\}$ of a Hermitian operator can be chosen to form an orthonormal set

$$\langle \alpha | \beta \rangle = \delta_{\alpha\beta}$$

Change of Basis

What is the relationship between two complete orthonormal basis sets $\{|i\rangle\}$ and $\{|\alpha\rangle\}$?

$$\langle i|j \rangle = \delta_{ij}$$

$$\langle \alpha | \beta \rangle = \delta_{\alpha \beta}$$

$$\sum_i |i\rangle \langle i| = 1$$

$$\sum_{\alpha} |\alpha\rangle \langle \alpha| = 1$$

Use the projection operator!

$$|\alpha\rangle = \sum_i |i\rangle \langle i|\alpha \rangle = \sum_i |i\rangle v_{i\alpha}$$

$v_{i\alpha}$ are the elements of a transformation matrix $\overset{\leftrightarrow}{U}$

$$|i\rangle = \sum_{\alpha} |\alpha\rangle \langle \alpha| i\rangle = \sum_{\alpha} |\alpha\rangle v_{i\alpha}^* = \sum_{\alpha} |\alpha\rangle (\overset{\leftrightarrow}{U}^+)^{di}$$

$\overset{\leftrightarrow}{U}^+$ is the adjoint of matrix $\overset{\leftrightarrow}{U}$.

$\overset{\leftrightarrow}{U}$ is unitary

$$\overset{\leftrightarrow}{U}^+ \overset{\leftrightarrow}{U} = \overset{\leftrightarrow}{U} \overset{\leftrightarrow}{U}^+ = \overset{\leftrightarrow}{I}$$

All transformations between orthonormal basis sets are performed by unitary transformations.

Change of operators

How do the operators change under unitary transformations of the basis set?

$$O|i\rangle = \sum |j\rangle O_{ji} \quad O|\alpha\rangle = \sum |\beta\rangle \overset{\leftrightarrow}{S}_\alpha{}^\beta$$

↑ what is the relationship
between $\overset{\leftrightarrow}{O}$ and $\overset{\leftrightarrow}{S}_\alpha$? ↑

$$\Omega_{\alpha\beta} = \langle \alpha | O | \beta \rangle = \sum_{i,j} \langle \alpha | i \rangle \langle i | O | j \rangle \langle j | \beta \rangle$$

$$= \sum (U^+)_\alpha{}^i O_{ij} U_j{}^\beta$$

In matrix notation:

$$\overset{\leftrightarrow}{S} = \overset{\leftrightarrow}{U}^+ \overset{\leftrightarrow}{O} \overset{\leftrightarrow}{U}$$

Why is it important? Because for any Hermitian operator it is always possible to find a unitary transformation U that makes $\overset{\leftrightarrow}{S}$ diagonal

$$(\overset{\leftrightarrow}{S})_{\alpha\beta} = \omega_\alpha \delta_{\alpha\beta}$$

or

$$\overset{\leftrightarrow}{S} = \overset{\leftarrow}{I} \overset{\rightarrow}{\omega}$$

$$\vec{\omega} = \begin{pmatrix} \omega_1 \\ \omega_2 \\ \vdots \\ \omega_N \end{pmatrix}$$

Eigenfunctions and operators

Consider an infinite set of functions $\{\Psi_i(x), i=1, 2, \dots\}$ such that they satisfy the orthonormality condition

$$\int_{x_1}^{x_2} dx \Psi_i^*(x) \Psi_j(x) = \delta_{ij}$$

If any function $\psi(x)$ can be expressed as a linear combination of the set of functions $\{\Psi_i\}$

$$\psi(x) = \sum_i \Psi_i(x) a_i$$

the set $\{\Psi_i\}$ is complete. For a complete basis set

$$\sum_i \Psi_i(x) \Psi_i^*(x') = \delta(x - x')$$

Dirac delta function

$\delta(x - x')$ is a generalization of δ_{ij}

$$a(x) = \int dx' \delta(x - x') a(x') , \quad \int \delta(x - x') dx' = 1$$

Definition:

$$\delta(x) = \lim_{\varepsilon \rightarrow 0} \delta_\varepsilon(x)$$

$$\delta_\varepsilon(x) = \frac{1}{2\varepsilon} , \quad -\varepsilon \leq x \leq \varepsilon$$

$$= 0 , \quad x < -\varepsilon , \quad x > \varepsilon$$

The eigenvalue problem

$$\langle \beta | \mathbf{O} | \alpha \rangle = \omega_\alpha \delta_{\alpha\beta}$$

unknown unknown

$$k = \sum_{i=1}^n l_i c_i$$

$$\vec{c} = \begin{pmatrix} c_1 \\ \vdots \\ c_N \end{pmatrix}$$

$$\underbrace{\begin{pmatrix} O_{11} & O_{12} & \dots & O_{1N} \\ O_{21} & & & \\ \vdots & & & \\ O_{N1} & \dots & \dots & O_{NN} \end{pmatrix}}_{\text{matrix}} \begin{pmatrix} c_1 \\ \vdots \\ c_N \end{pmatrix} = \omega \begin{pmatrix} c_1 \\ \vdots \\ c_N \end{pmatrix}$$

$$\det(\hat{\mathbf{O}} - \omega \hat{\mathbf{I}}) = 0 \quad (\text{Sec. 1.1.3})$$

$$\underbrace{\det}_{\substack{\text{"secular} \\ \text{determinant}}} \left(\begin{pmatrix} 1 & & 0 \\ & \ddots & \\ 0 & \cdots & 1 \end{pmatrix} \right)$$

For each ω_α

$$\hat{\mathbf{O}} \vec{c}_\alpha = \omega_\alpha \vec{c}_\alpha$$

gives the vector of
the eigenvalue ω_α

Projection operator

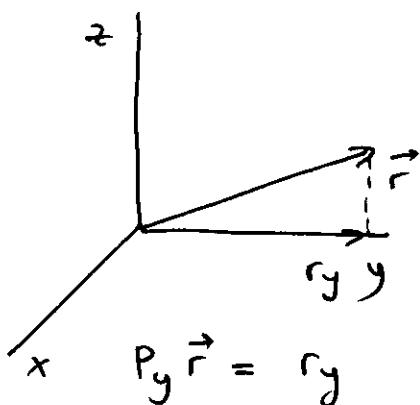
Definition:

$$P_i = |i\rangle\langle i|$$

$$\Psi = \sum |j\rangle \alpha_j$$

$$P_i \Psi = |i\rangle\langle i| \sum |j\rangle \alpha_j$$

$$= |i\rangle \sum_j \delta_{ij} \alpha_j = \alpha_i |i\rangle$$



P_i gives the projection of a state on the basis component $|i\rangle$

Most important property:

$$\sum P_i = \sum |i\rangle\langle i| = I$$

is the unitary operator

Product of two operators:

$$\begin{aligned} \langle i | A B | j \rangle &= \sum_k \langle i | A | k \rangle \langle k | B | j \rangle \\ &= \sum_k A_{ik} B_{kj} \end{aligned}$$

$$\overleftrightarrow{(AB)} = \overleftrightarrow{A} \overleftrightarrow{B}$$

matrix of the product
of operators is
the product of operator
matrices

Matrix formulation of quantum mechanics

$$\psi_i(x) \equiv |i\rangle, \quad \psi_i^*(x) \equiv \langle i|$$

$$\psi(x) \equiv |\psi\rangle, \quad \psi^*(x) \equiv \langle \psi|$$

$$|\psi(x)\rangle = \sum_i \psi_i(x) a_i \quad \text{is equivalent to} \quad |\psi\rangle = \sum_i |i\rangle a_i$$

$$\langle a | b \rangle = \int dx a^*(x) b(x)$$

$$1 = \sum_i |i\rangle \langle i|$$

The Schrödinger equation is an eigenvalue problem: one needs to find a function $\psi(x)$ (eigenvector) which generates the energy E (eigenvalue) according to the relation

$$H\psi = E\psi$$

If one expands ψ in a complete basis $\{\psi_i\}$, one gets

$$H \sum \psi_i(x) a_i = E \sum \psi_i(x) a_i$$

or

$$H \sum |i\rangle a_i = E \sum |i\rangle a_i$$

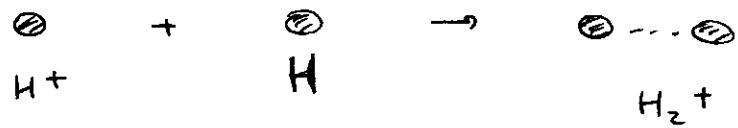
This is equivalent to the matrix equation

$$\hat{H} \vec{a} = E \vec{a}$$

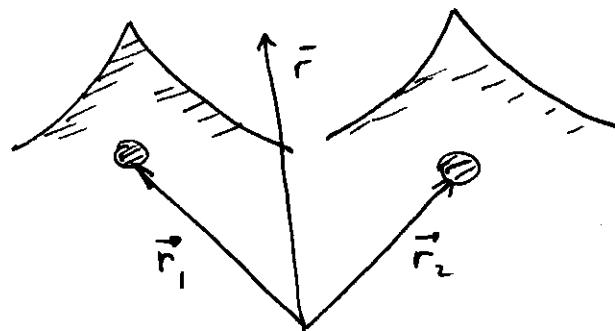
$$\hat{H} = \begin{pmatrix} H_{11} & H_{12} & H_{13} & \dots \\ H_{21} & - & - & - \\ H_{31} & & - & - \\ \vdots & & & \ddots \end{pmatrix}$$

Two-state problem

Example: A hydrogen cation molecule



Assume that two 1s states form a complete basis set for the hydrogen cation molecule.



$$|\Psi_1\rangle = |1s(\vec{r} - \vec{r}_1)\rangle$$

$$|\Psi_2\rangle = |1s(\vec{r} - \vec{r}_2)\rangle$$

$$H = -\frac{1}{2} \nabla^2 - \frac{1}{|\vec{r} - \vec{r}_1|} - \frac{1}{|\vec{r} - \vec{r}_2|}$$

Instead of solving the Schrödinger equation, one can rely on the matrix formulation. The matrix of the Hamiltonian

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \quad H_{11} = \langle \Psi_1 | H | \Psi_1 \rangle$$

$$= \int \Psi_1^*(\vec{r}) \left[-\frac{1}{2} \nabla^2 - \frac{1}{|\vec{r} - \vec{r}_1|} - \frac{1}{|\vec{r} - \vec{r}_2|} \right] \Psi_1 d\vec{r}$$

fully defines the problem of calculating the energy spectrum of H_2^+ .

Two-state problem. Secular equation

Energies of a two-state system are found as solutions of the secular equation

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

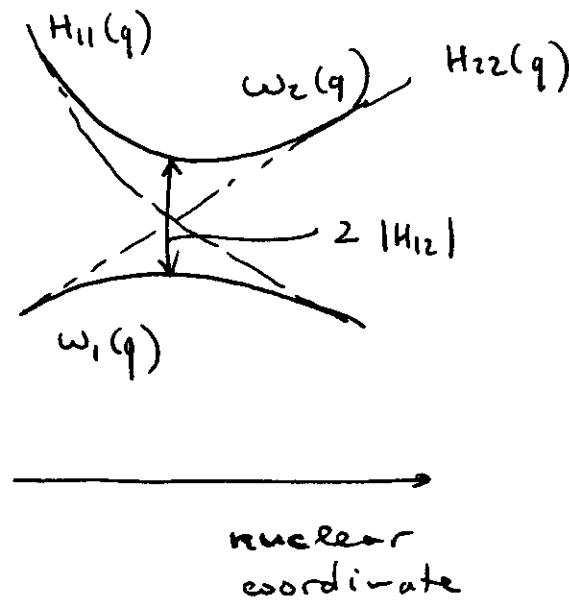
$$\omega^2 - \omega (H_{11} + H_{22}) + H_{11}H_{22} - H_{12}H_{21} = 0$$

$$\omega_1 = \bar{H} - \frac{1}{2} \Delta \omega, \quad \bar{H} = \frac{1}{2} (H_{11} + H_{22})$$

$$\omega_2 = \bar{H} + \frac{1}{2} \Delta \omega \quad \Delta \omega = \sqrt{(H_{22} - H_{11})^2 + 4 H_{12} H_{21}}$$

For a real Hamiltonian, $H_{12}^* = H_{21}$ and $H_{12} H_{21} = |H_{12}|^2$

Avoided adiabatic crossing



or adiabatic ($|H_{12}|/kT \gg 1$) chemical reactions.

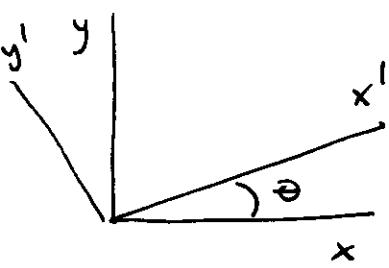
Two molecular terms that cross in the two-state "diabatic" basis do not cross when the Hamiltonian matrix is diagonalized. Depending on the magnitude of $|H_{12}|$, one considers diabatic ($|H_{12}|/kT \ll 1$)

Two-state problem: matrix diagonalization

The eigenvalue problem can be solved by diagonalizing the matrix H

$$\overset{\leftrightarrow}{U}^+ \overset{\leftrightarrow}{H} \overset{\leftrightarrow}{U} = \begin{pmatrix} w_1 & 0 \\ 0 & w_2 \end{pmatrix}$$

Any two-dimensional unitary transformation can be represented by rotation of the basis set



$$U = \begin{pmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{pmatrix}$$

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = U \begin{pmatrix} x \\ y \end{pmatrix} \quad x' = \cos \theta x + \sin \theta y \\ y' = \sin \theta x - \cos \theta y$$

$$\overset{\leftrightarrow}{U}^+ \overset{\leftrightarrow}{H} \overset{\leftrightarrow}{U} = \begin{pmatrix} H_{11} \cos^2 \theta + H_{22} \sin^2 \theta & \frac{1}{2} (H_{11} - H_{22}) \sin 2\theta - H_{12} \cos 2\theta \\ \frac{1}{2} (H_{11} - H_{22}) \sin 2\theta - H_{12} \cos 2\theta & H_{11} \sin^2 \theta + H_{22} \cos^2 \theta - H_{12} \sin 2\theta \end{pmatrix}$$

$$\frac{1}{2} (H_{11} - H_{22}) \sin 2\theta - H_{12} \cos 2\theta;$$

$$\boxed{\theta_0 = \frac{1}{2} \tan^{-1} \frac{2H_{12}}{H_{11} - H_{22}}}$$

Eigenvectors :

$$\vec{c}_1 = \begin{pmatrix} \cos \theta_0 \\ \sin \theta_0 \end{pmatrix}$$

$$\vec{c}_2 = \begin{pmatrix} \sin \theta_0 \\ -\cos \theta_0 \end{pmatrix}$$

The variational principle

The variational principle states that an approximate wave function has an energy which is above or equal to the exact energy. The equality holds only if the wave function is exact.

ψ_i and E_i are exact eigenstates and eigenvalues of the Schrödinger equation

$$H \psi_i = E_i \psi_i, \quad i=0, 1, 2, \dots$$

Let's assume that E_0 is the lowest eigenvalue

$$E_0 < E_1 < E_2 \dots$$

For an approximate function

$$|\Phi\rangle = \sum_i |\psi_i\rangle a_i$$

the energy is calculated as

$$W = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\sum a_i^2 E_i}{\sum a_i^2}$$

$$W - E_0 = \frac{\sum a_i^2 (E_i - E_0)}{\sum a_i^2}$$

Since $a_i^2 > 0$ and $E_i - E_0 > 0$,

$$W - E_0 > 0$$

$$W > E_0$$

The linear variational problem

A complete basis generally consists of an infinite set of functions ψ_i , $i = 1, 2, 3, \dots$. If a finite set ψ_1, \dots, ψ_n is chosen, an arbitrary state $|\Psi\rangle$ can be only approximately expanded in ψ_i

$$|\Psi\rangle = \sum_{i=1}^n |\psi_i\rangle c_i$$

In this case, however, the problem of calculating the coefficients c_i is that of linear algebra

$$\langle \psi | \psi \rangle = \sum_{i,j=1}^n c_i c_j \langle \psi_i | \psi_j \rangle = \sum c_i^2 = 1$$

$$\langle \psi | H | \psi \rangle = \sum_{i,j=1}^n c_i \langle \psi_i | H | \psi_j \rangle c_j = \sum c_i c_j H_{ij}$$

The problem of finding c_i can be solved by minimizing $\langle \psi | H | \psi \rangle$:

$$\frac{\partial}{\partial c_k} \langle \psi | H | \psi \rangle = 0, \quad k = 1, 2, \dots, n$$

One should remember, however, that c_1, \dots, c_n are not independent, since $\sum_{i=1}^n c_i^2 = 1$. The problem is solved by Lagrange's method of undetermined multipliers.

The Lagrange function

$$\mathcal{L}(c_1, \dots, c_N, E) = \sum c_i c_j H_{ij} - E \left(\sum c_i^2 - 1 \right)$$

is minimized by finding c_1, \dots, c_{N-1}

$$\frac{\partial \mathcal{L}}{\partial c_i} = 0, \quad i = 1, \dots, N-1$$

The Lagrange multiplier E is chosen so that

$$\frac{\partial \mathcal{L}}{\partial c_N} = 0$$

The equation for coefficients becomes

$$\sum H_{ij} c_j - E c_i = 0$$

$$\boxed{\vec{H}\vec{c} = E\vec{c}}$$

The variation problem is reduced to the standard eigenvalue problem.

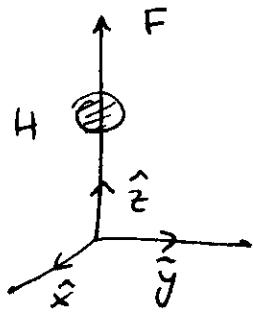
$$\vec{H}\vec{c}^\alpha = E_\alpha \vec{c}^\alpha, \quad \alpha = 0, 1, \dots, N-1$$

$$(\vec{c}^\alpha)^+ (\vec{c}^\beta) = \sum c_i^\alpha c_i^\beta = \delta_{\alpha\beta}$$

The lowest energy E_0 in the spectrum E_α is the best variational approximation for the ground state energy.

Exercise 1.22

$$\left(-\frac{1}{2} \nabla^2 - \frac{1}{r} + Fr \cos\theta\right) |\Phi\rangle = (H_0 + Fr \cos\theta) |\Phi\rangle = \epsilon(F) |\Phi\rangle$$



$$|\Phi\rangle = c_1 |1s\rangle + c_2 |2p_z\rangle$$

$$|1s\rangle = \frac{1}{\sqrt{\pi}} e^{-r}$$

$$|2p_z\rangle = \frac{1}{\sqrt{32\pi}} r e^{-r/2} \cos\theta$$

Electronic levels of the hydrogen atom:

$$H_0 |n\rangle = -\frac{1}{2n^2} |n\rangle$$

$$H_0 = -\frac{1}{2} \nabla^2 - \frac{1}{r}$$

$$\langle 1s | H | 1s \rangle = -\frac{1}{2}$$

$$\langle 2p_z | H | 2p_z \rangle = -\frac{1}{8}$$

$$H_{12} = \frac{F}{\sqrt{32\pi/2}} \int_0^\infty 4\pi r^2 dr \ r^2 e^{-3r/2} \underbrace{\int \frac{ds}{4\pi} \cos^2\theta}_{\text{Angular part}}$$

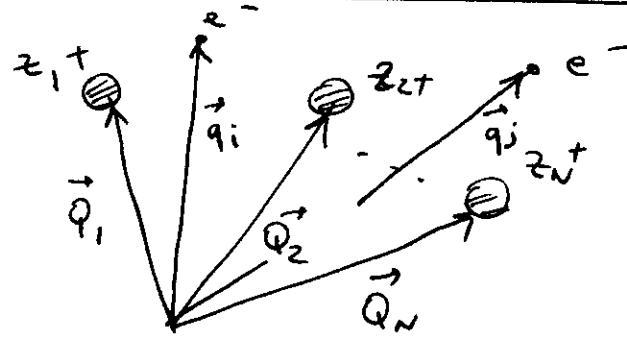
$$= \frac{F}{3\sqrt{2}} \int_0^a r^4 e^{-3r/2} dr = \frac{8F}{r_2} \left(\frac{2}{3}\right)^5 \frac{1}{8}$$

$$\omega_1 = \frac{H_{11} + H_{22}}{2} - \frac{1}{2} \sqrt{\Delta H^2 + 4|H_{12}|^2} = E(0) - \frac{|H_{12}|^2}{|\Delta H|} =$$

$$= E(0) - \frac{\alpha}{2} F^2, \quad \underline{\underline{\alpha = 64 \cdot 4 \cdot \left(\frac{2}{3}\right)^5 = 296}}$$

$$|\Delta H| = \frac{3}{8}$$

Vibronic coupling in polyatomic molecules



Schrödinger equation: $H(qQ) \psi(qQ) = \varepsilon \psi(qQ)$

$$H(qQ) = T(q) + T(Q) + U(qQ) + V(Q)$$

$$T(q) = -\frac{1}{2} \sum_{i=1}^M \nabla_i^2, \quad T(Q) = -\frac{1}{2} \sum_{i=1}^N \frac{1}{m_i} \nabla_{Q_i}^2$$

$$U(qQ) = - \sum_{ij} \frac{z_i z_j}{|\vec{r}_i - \vec{R}_j|} + \frac{1}{2} \sum_{ij} \frac{1}{r_{ij}}$$

↑ Coulomb attraction of electrons to nuclei ↑ Coulomb repulsion between the electrons

$$V(Q) = \frac{1}{2} \sum_{ij} \frac{z_i z_j}{Q_{ij}}$$

Split the Hamiltonian into the electronic and nuclear components

$$H = H_e + H_n$$

$$H_e(qQ) = T(q) + U(qQ)$$

depends on q and Q

$$H_n = T(Q) + V(Q)$$

depends only on Q

Born-Huang (BH) procedure

$$H_e(qQ) \Psi_n(qQ) = E_n(Q) \Psi_n(qQ)$$

$$\Phi_i(qQ) = \sum_n \Psi_n(qQ) \chi_{ni}(Q) \iff |\Phi_i\rangle = \sum_n |\Psi_n\rangle a_n$$

$$[H_e(qQ) + H_u(Q)] \sum_n \Psi_n(qQ) \chi_{ni}(Q) = \varepsilon_i \sum_n \Psi_n(qQ) \chi_{ni}(Q)$$

The main problem arises with calculating

$$T(Q) \Psi_n(qQ) \chi_{ni}(Q) =$$

$$= \Psi_n T(Q) \chi_{ni} + \chi_{ni} T(Q) \Psi_n - \hbar^2 \sum_k \frac{\partial \Psi_n}{\partial Q_k} \frac{\partial \chi_{ni}}{\partial Q_k}$$

$$\left. \begin{aligned} & \sum_n \left(\{ \Psi_n(qQ) [T(Q) + V(Q) + E_n(Q)] + [T(Q) \Psi_n] \} \chi_{ni} \right. \\ & \quad \left. - \hbar^2 \sum_k \frac{\partial \Psi_n}{\partial Q_k} \frac{\partial \chi_{ni}}{\partial Q_k} \right) = \varepsilon_i \sum_n \Psi_n \chi_{ni} \end{aligned} \right\}$$

multiply by Ψ_n and integrate over q

$$\begin{aligned} & [T(Q) + V(Q) + E_n(Q) + \langle n | T | n \rangle - \varepsilon_i] \chi_{ni} + \\ & + \sum_{m \neq n} \left[\langle n | T | m \rangle - \hbar^2 \sum_k \langle n | \frac{\partial}{\partial Q_k} | m \rangle \frac{\partial}{\partial Q_k} \right] \chi_{mi} = 0 \end{aligned}$$

BH adiabatic approximation:

$$\langle u | T(Q) | l_m \rangle = 0 \quad (m \neq n) \quad (1)$$

$$\langle u | \frac{\partial}{\partial Q_e} | l_m \rangle = 0 \quad (2)$$

$$\psi_{ni}^A(qQ) = \psi_n(qQ) \chi_{ni}^A(Q)$$

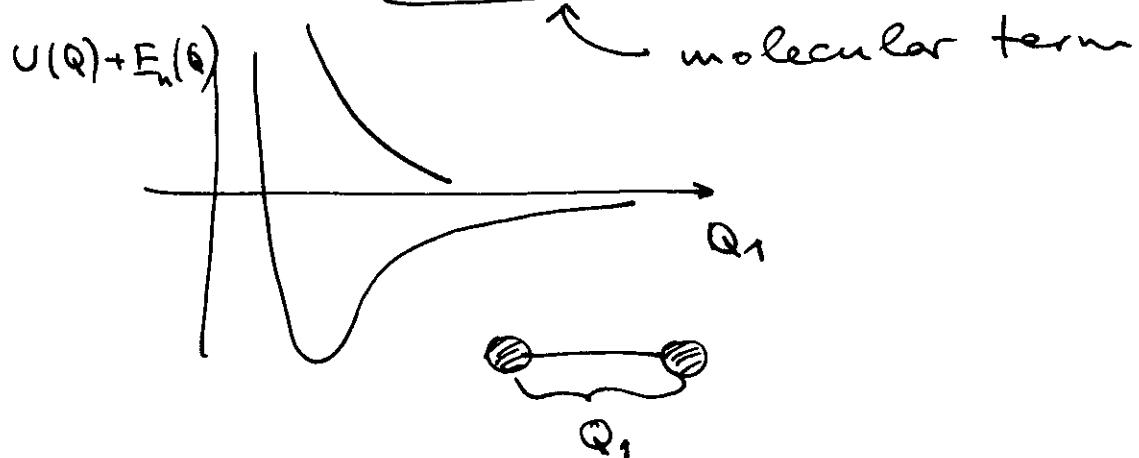
Born-Oppenheimer approximation (BO):

BO approximation assumes (1) + (2) +

$$\langle u | T(Q) | u \rangle = 0 \quad (3)$$

$$\psi_{ni}^{BO}(qQ) = \psi_n(qQ) \chi_{ni}^{BO}(Q)$$

$$[T(Q) + U(Q) + E_n(Q) - \varepsilon_{ni}^{BO}] \chi_{ni}^{BO}(Q) = 0$$



Crude adiabatic approximation

$$\Psi_i(qQ) = \sum t_n(qQ_0) \chi_{ni}(Q)$$

↑
ground state equilibrium
structure

$$H_e(qQ_0) \Psi_i(qQ_0) = E_n(Q_0) \Psi_i(qQ_0)$$

$$H_e(qQ) = H_e(qQ_0) + \Delta U(qQ)$$

$$[T(Q) + U(Q) + E_n(Q_0) + \langle n | \Delta U | n \rangle - \varepsilon_i] \chi_{ni}(Q)$$

$$+ \sum_{m \neq n} \langle n | \Delta U | m \rangle \chi_{mi}(Q) = 0$$

$$\boxed{\langle n | \Delta U | m \rangle = 0}$$

↑ CA assumption

The most frequently used adiabatic approximations

CA BO

BH

Vibronic wavefunction

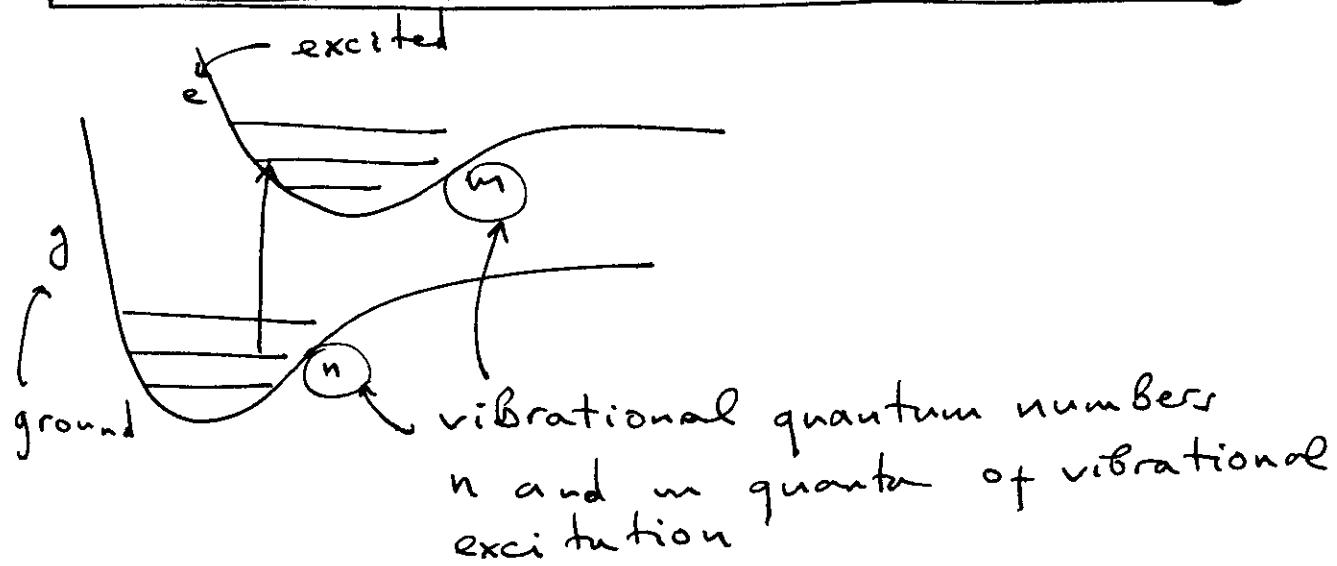
$$\Psi_{ui}^{CA}(qQ) = \Psi_u(qQ) \chi_{ui}^{CA}(Q) \quad \Psi_u^{BO}(qQ) = \Psi_u(qQ) \chi_{ui}^{BO}(Q) \quad \Psi_{ui}^A(qQ) = \Psi_u(qQ) \chi_{ui}^A(Q)$$

Electrostatic Screening eq.

$$\begin{aligned} & [\Pi(q) + U(qQ_0)] \Psi(qQ_0) = E_u(qQ_0) \quad [\Pi(q) + U(qQ)] \Psi(qQ) \\ & \Psi(qQ_0) \quad = \quad E_u(qQ) \Psi(qQ) \end{aligned}$$

$$\begin{aligned} & \text{Vibrational Schrödinger eq.} \quad [\Pi(Q) + U(Q) + E_u(Q)] \quad [\Pi(Q) + U(Q) + E_u(Q)] \\ & \quad + \langle u | \delta U(qQ) | u \rangle \] \chi_{ui}^{CA}(Q) \quad \chi_u^{BO}(Q) = \sum_{ui} \chi_{ui}^{BO}(Q) \\ & \quad + \langle u | \Pi(Q) | u \rangle \] \chi_{ui}^A(Q) \quad = \varepsilon_{ui}^A \chi_{ui}^A(Q) \end{aligned}$$

Vibronic transitions & Transition moments



$$M_{gn, em} = \langle g_n(q, Q) | \hat{\mu} | e_m(q, Q) \rangle$$

↑
transition dipole $\mu = \mu(q) + \mu(Q)$

$$M_{gn, em} = \langle g | e \rangle \langle n(Q) | \mu(Q) | m(Q) \rangle$$

" "

$$+ \langle n(Q) | \langle g(q, Q) | \mu(q) | e(q, Q) \rangle | m(Q) \rangle$$

[]

$M_{ge}(Q)$
electronic transition dipole

Condon approximation : $M_{ge}(Q) = M_{ge}$ \rightarrow independent of Q

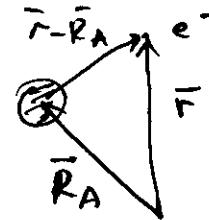
$$M_{gnem} = M_{ge} \langle n(Q) | m(Q) \rangle$$

Basis sets

Two types of basis set functions have found common use:

(1) Slater-type orbitals (STOs)

$$\phi_{1s}^{SF}(\mathbf{r}, \mathbf{r} - \vec{R}_A) = \left(\frac{\pi^3}{\pi}\right)^{1/2} e^{-\beta |\mathbf{r} - \vec{R}_A|}$$



(2) Gaussian-type functions (GFs):

$$\phi_{1s}^{GF}(\alpha, \mathbf{r} - \vec{R}_A) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp[-\alpha |\mathbf{r} - \vec{R}_A|^2]$$

The orbital exponents ($\beta, \alpha > 0$) determine the diffuseness or "size" of the basis functions.

Advantage of GFs is in their computational efficiency.

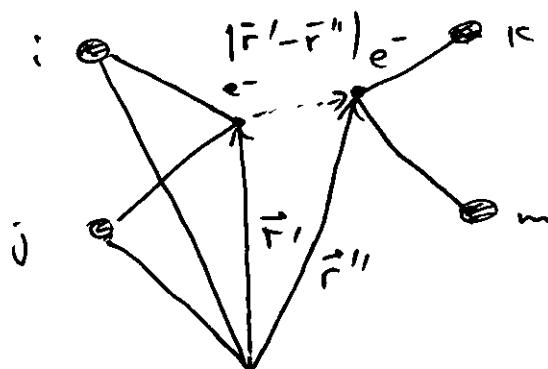
Electron repulsion integrals:

$$|\Phi^{MO}\rangle = \sum_i |\Phi^{AO}\rangle c_i, \quad \rho^{MO}(\mathbf{r}) = |\Phi^{MO}(\mathbf{r})|^2 = \sum_{i,j} c_i c_j \Phi_i^{AO}(\mathbf{r})^* \Phi_j^{AO}(\mathbf{r})$$

Coulomb repulsion $\int \rho(\mathbf{r}') \frac{1}{|\mathbf{r}' - \mathbf{r}''|} \rho(\mathbf{r}'') d\mathbf{r}' d\mathbf{r}''$

includes

$$c_i c_j c_k c_m \int (\Phi_i^{AO})^* (\Phi_j^{AO})^* \frac{1}{r} \Phi_k^{AO} \Phi_m^{AO} d\mathbf{r}' d\mathbf{r}''$$



four-center
integral

Gaussian algebra

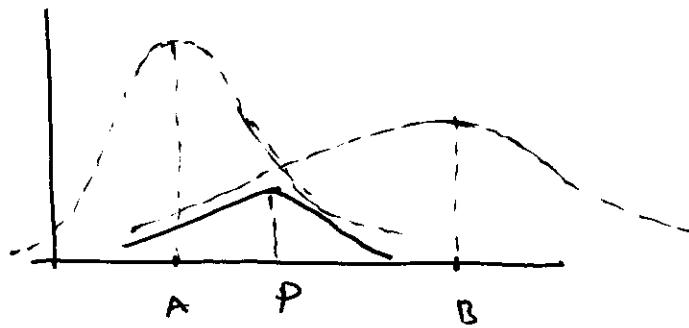
Product of two Gaussians:

$$\Phi_{IS}^{GF}(\alpha, \vec{r} - \vec{R}_A) \Phi_{IS}^{GF}(\beta, \vec{r} - \vec{R}_B) = K_{AB} \Phi_{IS}^{GF}(\rho, \vec{r} - \vec{R}_\rho)$$

$$K_{AB} = \left(\frac{2\alpha\beta}{(\alpha+\beta)\pi} \right)^{3/4} \exp \left[-\frac{\alpha\beta}{\alpha+\beta} |\vec{R}_A - \vec{R}_B|^2 \right]$$

$$\rho = \alpha + \beta, \quad \vec{R}_\rho = \frac{\alpha \vec{R}_A + \beta \vec{R}_B}{\alpha + \beta}$$

Homework:
derive this equation



The product of two
Gaussians is a Gaussian

$$(\mu_A \nu_B | \lambda_C \lambda_D) = \int (\Phi_A^{AO})^* \Phi_B^{AO} \frac{1}{|\vec{r}' - \vec{r}''|} (\Phi_C^{AO})^* \Phi_D^{AO} d\vec{r}' d\vec{r}''$$

$$= K_{AB} K_{CD} \int d\vec{r}' d\vec{r}'' \Phi_{IS}^{GF}(\rho, \vec{r}' - \vec{R}_\rho) \frac{1}{|\vec{r}' - \vec{r}''|} \Phi_{IS}^{GF}(q, \vec{r}'' - \vec{R}_Q)$$

This integral is evaluated analytically
(see Appendix A, SO)

Overlap and kinetic energy

unnormalized
Gaussians

Overlap :

$$(A|B) = \langle A|B \rangle = \int d\vec{r} \hat{g}_{1s}(\vec{r} - \bar{R}_A) \hat{g}_{1s}(\vec{r} - \bar{R}_B)$$

$$= K_{AB} \int d\vec{r} e^{-\rho|\vec{r}-\bar{R}_P|^2} = 4\pi K_{AB} \underbrace{\int_0^{\infty} r^2 dr e^{-\rho r^2}}_{(\pi/\rho)^{3/2}/4\pi}$$

$$(A|B) = \left(\frac{\pi}{\alpha+\beta} \right)^{3/2} \exp \left[- \frac{\alpha\rho}{\alpha+\beta} |\bar{R}_A - \bar{R}_B|^2 \right]$$

Kinetic energy :

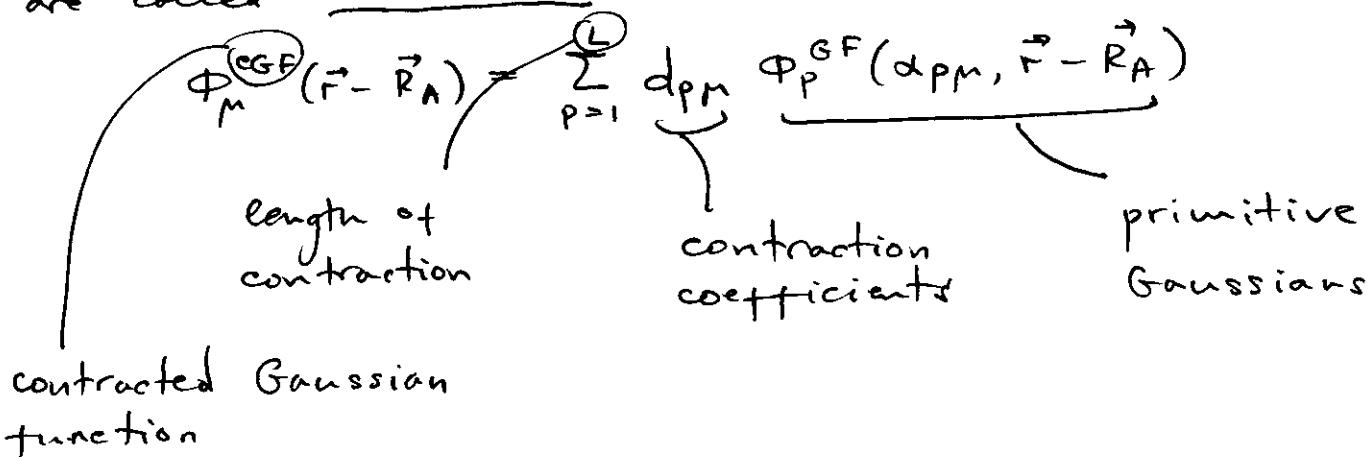
$$\langle A + \frac{1}{2} \nabla^2 | B \rangle = \int d\vec{r} \hat{g}_{1s}(\vec{r} - \bar{R}_A) \left(-\frac{1}{2} \nabla^2 \right) g_{1s}(\vec{r} - \bar{R}_B)$$

$$= \frac{\alpha\rho}{\alpha+\beta} \left(\frac{\pi}{\alpha+\beta} \right)^{3/2} \left[3 - \frac{2\alpha\rho}{\alpha+\beta} |\bar{R}_A - \bar{R}_B|^2 \right] e^{-\frac{\alpha\rho}{\alpha+\beta} |\bar{R}_A - \bar{R}_B|^2}$$

prove at home

STO-LG procedure

Fixed linear combinations of primitive Gaussians are used as basis functions. These linear combinations are called contractions:



STO-LG is a procedure that approximates a Slater orbital by L primitive Gaussians

$$\Phi_{1s}^{CGF} (\zeta = 1.0, \text{STO-1G}) = \Phi_{1s}^{GF} (\alpha_{11})$$

$$\Phi_{1s}^{CGF} (\zeta = 1.0, \text{STO-3G}) = d_{13} \Phi_{1s}^{GF} (\alpha_{13}) + d_{23} \Phi_{1s}^{GF} (\alpha_{23}) + d_{33} \Phi_{1s}^{GF} (\alpha_{33})$$

The coefficients d_{13} , d_{23} , d_{33} are found by minimizing the overlap integral

$$S = \langle \Phi_{1s}^{SF} | \Phi_{1s}^{CGF} \rangle$$

$$\Phi_{1s}^{CGF} (\zeta = 1.0, \text{STO-3G}) = 0.444635 \Phi_{1s}^{GF} (0.109818)$$

$$+ 0.535328 \Phi_{1s}^{GF} (0.405771) + 0.154329 \Phi_{1s}^{GF} (2.22766)$$

Homework: Compare the radial distribution function $4\pi r^2 |\Phi_{1s}(r)|^2$ in STO-3G and SF for 1s orbital of H.

Polyatomic Basis contraction

s, p, d atomic orbitals are given as linear combinations of Gaussian primitives

$$\phi_{\mu}^{\text{EGF}}(\vec{r} - \vec{R}_A) = \sum_{p=1}^L d_{p\mu} g_p(\alpha_{p\mu}, \vec{r} - \vec{R}_A)$$

$$g_{1s}(\alpha, \vec{r}) = (8\alpha^3/\pi^3)^{1/4} e^{-\alpha r^2}$$

$$g_{2p_x}(\alpha, \vec{r}) = (128\alpha^5/\pi^3)^{1/4} \times e^{-\alpha r^2}$$

$$g_{3d_{xy}}(\alpha, \vec{r}) = (2048\alpha^7/\pi^3)^{1/4} \times y e^{-\alpha r^2}$$

Contraction is commonly defined from atomic SCF calculations.

(4s) basis:

$$\Psi_{1s} = \alpha_1 g_{1s}(\alpha_1, \vec{r}) + \alpha_2 g_{1s}(\alpha_2, \vec{r}) + \alpha_3 g_{1s}(\alpha_3, \vec{r}) + \alpha_4 g_{1s}(\alpha_4, \vec{r}); \quad \{\alpha_1, \dots, \alpha_4, \alpha_1, \dots, \alpha_4\}$$

(4s)/[2s] contraction:

$$\Phi_1(\vec{r}) = g_{1s}(\alpha_1, \vec{r})$$

$$\Phi_2(\vec{r}) = N [\alpha_2 g_{1s}(\alpha_2, \vec{r}) + \alpha_3 g_{1s}(\alpha_3, \vec{r}) + \alpha_4 g_{1s}(\alpha_4, \vec{r})]$$

↑ normalization constant

(4s) is an uncontracted basis set
 [2s] is a contracted basis set

Minimal Basis sets: STO-3G

1s, 2s, and 2p Slater functions are expanded in a set of primitive Gaussians

$$\Phi_{1s}^{\text{CGF}} (\zeta = 1.0) = \sum_{i=1}^3 d_{i,1s} g_{1s}(d_{i,1s})$$

$$\Phi_{2s}^{\text{CGF}} (\zeta = 1.0) = \sum_{i=1}^3 d_{i,2s} g_{1s}(d_{i,2s})$$

$$\Phi_{2p}^{\text{CGF}} (\zeta = 1.0) = \sum_{i=1}^3 d_{i,2p} g_{2p}(d_{i,2p})$$

α_{1s}	d_{1s}	α_{2sp}	d_{2s}	d_{2p}
0.109818	0.444635	0.0751386	0.700115	0.391957
0.405771	0.53528	0.231031	0.399572	0.607684
2.22766	0.154329	0.904203	-0.0999872	0.155916

* 2s and 2p orbitals have equal exponents α_{2sp} ; this allows to treat $4^4 = 256$ integrals as one radial integral.

Scaling:

The contraction exponent for fitting a Slater function with orbital exponent ζ is

$$\alpha = \alpha(\zeta = 1.0) \times \zeta^2$$

Best ζ 's:

Atom	ζ_{1s}	ζ_{2sp}
H	1.24	-
Li	2.69	0.75
Be	3.63	1.10
B	4.68	1.45
C	5.67	1.72
N	6.67	1.95
O	7.66	2.25
F	8.65	2.55

Double zeta basis sets: 4-31 G

Double zeta basis sets use two STO functions for each of the minimal basis functions:

$$(\text{H}): \Phi_{1s}^{\text{SF}}(z', \vec{r}), \Phi_{1s}^{\text{SF}}(z'', \vec{r})$$

Example:



P_x and P_y are involved in π -Bonds. They are more diffuse than P_z orbital.

4 - 31 G

core orbitals are contracted into four Gaussians

$$\Phi_{1s} = \sum_{i=1}^4 d_{i,1s} g_{1s}(d_{i,1s}, \vec{r})$$

valence functions are contractions of three and one primitive Gaussians

$$\Phi'_{2s}(\vec{r}) = \sum_{i=1}^3 d'_{i,2s} g_{1s}(d'_{i,2s}, \vec{r})$$

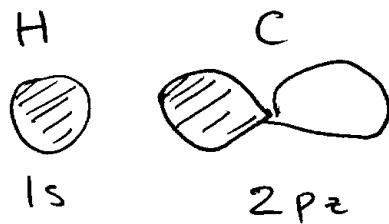
$$\Phi''_{2s}(\vec{r}) = g_{1s}(d''_{2s}, \vec{r})$$

$$\Phi'_{2p}(\vec{r}) = \sum_{i=1}^3 d'_{i,2p} g_{2p}(d'_{i,2p}, \vec{r})$$

$$\Phi''_{2p}(\vec{r}) = g_{2p}(d''_{2p}, \vec{r})$$

Polarized basis sets: 6-31G* and 6-31G**

Higher angular momentum functions (d and f) are called polarization function.



Empty p-orbitals are used to polarize s-orbitals, d-orbitals are used to polarize p-orbitals, ...

If only 1s is present on H, it does not describe the polarization of the bond in the perpendicular direction. One needs p-orbitals on H!

- When a basis has one * it means that d-type functions are added to heavy atoms
- Two ** means that p-type functions are added to hydrogen.

6-31G

inner-shell functions are contractions of 6 Gaussians

valence functions are contractions of three and one Gaussians

Diffuse Functions

Diffuse functions are large-size versions of s- and p-type functions. They allow orbitals to occupy a larger region of space. Basis sets with diffuse functions are important for systems where electrons are relatively far from the nucleus: molecules with lone pairs, anions, systems with excited states, etc.

GAUSSIAN: G-31 + G(d), G-31++G(d)

↑
double plus adds diffuse function to the hydrogen atoms as well

In GAMESS, \$BASIS group is responsible for the choice of basis sets.

NDFUNC = 1, 2, 3 ← adds d-functions to heavy atoms
(polarization functions)

DIFFSP = .TRUE. ← adds diffuse sp shell to heavy atoms

DIFFS = .TRUE. ← diffuse s shell to hydrogens

Spin variables

Electron has a magnetic moment that can have two projections on an external magnetic field. The spin is then said to be "up" and "down". Two states of the electron spin can be characterized by two vectors

$$\text{"up"} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{"down"} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

These correspond to spin populations of the two states split by an external magnetic field

$$H \uparrow \longrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad + \quad \text{"down"} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Any spin state of an electron can be described as a linear combination of two basis states

$$\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = c_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + c_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Here c_1^2 and c_2^2 are populations of the spin states that are proportional to the intensity of a spectral signal measuring the splitting.

The basis of two states $\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ is

orthonormal, $\begin{pmatrix} 1 \\ 0 \end{pmatrix}^T \begin{pmatrix} 1 \\ 0 \end{pmatrix} = (10) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1$

$$\begin{pmatrix} 0 \\ 1 \end{pmatrix}^T \begin{pmatrix} 1 \\ 0 \end{pmatrix} = (01) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0$$

Antisymmetry or Pauli Exclusion Principle

In order to provide a uniform description for both the spatial and spin components of electronic states, one introduces two spin states

$$\alpha(\omega) \quad \text{and} \quad \beta(\omega),$$

↑ ↑
 spin up spin down

ω is some spin variable, which is not specified.

Scalar product rules:

$$\int d\omega \alpha^*(\omega) \alpha(\omega) = \int d\omega \beta^*(\omega) \beta(\omega) = 1$$

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$

$$\int d\omega \alpha^*(\omega) \beta(\omega) = \int d\omega \beta^*(\omega) \alpha(\omega) = 0$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$

An electron is described by four coordinates

$$\vec{x} = \{\vec{r}, \omega\}$$

The wave function for an N -electron system is a function of $\vec{x}_1, \dots, \vec{x}_N$

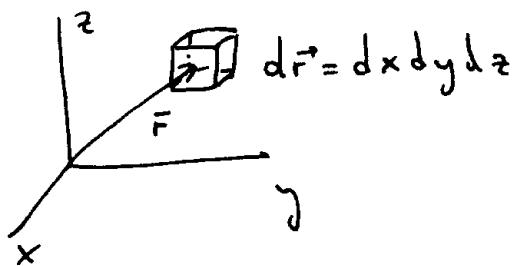
$$|\Phi_N\rangle = \Phi(\vec{x}_1, \dots, \vec{x}_N)$$

A many-electron wave function must be antisymmetric in respect to the interchange of the coordinate \vec{x} of any two electrons

$$\Phi(\vec{x}_1, \dots, \vec{x}_N) = -\Phi(\vec{x}_1, \dots, \vec{x}_N)$$

Spin orbitals and spatial orbitals

A spatial orbital refers to the wave function $\Psi_i(\vec{r})$ which describes the spatial distribution of an electron as $|\Psi_i(\vec{r})|^2 d\vec{r}$



$|\Psi_i(\vec{r})|^2 d\vec{r} \rightarrow$ the probability to find an electron in the i th state in the element of volume $d\vec{r} = dx dy dz$.

Orthonormal set: $\int \Psi_i^*(\vec{r}) \Psi_j(\vec{r}) d\vec{r} = \delta_{ij}$

From each spatial orbital, $\Psi(\vec{r})$, one can form two different spin orbitals

$$\chi(\vec{r}) = \begin{cases} \Psi(\vec{r}) \alpha(\omega) & \uparrow \\ \Psi(\vec{r}) \beta(\omega) & \downarrow \end{cases}$$

spatial-spin coordinates

spin functions

For a set of K spatial functions $\Psi_1(\vec{r}), \dots, \Psi_K(\vec{r})$, one can form a set of $2K$ spin orbitals $\{\chi_i\} = \{\chi_1, \dots, \chi_{2K}\}$.

$$\langle \chi_i | \chi_j \rangle = \delta_{ij}$$

Hartree Products

Approximation of non-interacting electrons. If electrons do not interact, each of them has its own Hamiltonian and the Hamiltonian of N electrons is the sum of one-electron Hamiltonians

$$H = \sum_{i=1}^N h(i)$$

$$h(i) \chi_i(\vec{x}_i) = \varepsilon_j \chi_j(\vec{x}_i)$$

↑ ↑
ith electron one-electron
 energy spectrum
↓ ↓
jth eigenfunction

$$\begin{array}{c} \overline{\varepsilon_j} \\ | \\ \overline{\varepsilon_3} \\ | \\ \overline{\varepsilon_2} \\ | \\ \overline{\varepsilon_1} \\ \text{one} \\ \text{electron} \end{array}$$

N electrons:

$\varepsilon_1 +$	—	—	—	—	...
	—	—	—	—	...
	—	—	$+ \varepsilon_3$	—	...
	$+ \varepsilon_2$	—	—	$+ \varepsilon_2$...
	$\brace{ }$				

$$E = \varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_k$$

The eigenfunction of N independent electrons is the product of one-electron eigenfunctions

$$\Psi^{HP}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \chi_1(\vec{x}_1) \chi_2(\vec{x}_2) \dots \chi_m(\vec{x}_N)$$

↑
Hartree product

Slater determinants

The Hartree product does not satisfy the antisymmetry principle.

2-electron problem:

$$\Psi_{12}^{\text{HP}}(\bar{x}_1, \bar{x}_2) = \chi_i(\bar{x}_1) \chi_j(\bar{x}_2)$$

$$\Psi_{21}^{\text{HP}}(\bar{x}_1, \bar{x}_2) = \chi_i(\bar{x}_2) \chi_j(\bar{x}_1)$$

These two Hartree products distinguish between electrons by specifying which electron occupies which orbital.

The linear combination

$$\Psi(\bar{x}_1, \bar{x}_2) = \frac{1}{\sqrt{2}} [\chi_i(\bar{x}_1) \chi_j(\bar{x}_2) - \chi_j(\bar{x}_1) \chi_i(\bar{x}_2)]$$

does not distinguish between the electrons and is antisymmetric:

$$\Psi(\bar{x}_1, \bar{x}_2) = -\Psi(\bar{x}_2, \bar{x}_1)$$

$$\Psi(\bar{x}_1, \bar{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(\bar{x}_1) & \chi_j(\bar{x}_1) \\ \chi_i(\bar{x}_2) & \chi_j(\bar{x}_2) \end{vmatrix}$$

Slater determinant

For N electrons:

$$\Psi(\bar{x}_1, \bar{x}_2, \bar{x}_3, \dots, \bar{x}_N) = \frac{1}{\sqrt{N!}}$$

$$\begin{vmatrix} \chi_i(\bar{x}_1) & \chi_j(\bar{x}_1) & \dots & \chi_k(\bar{x}_1) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(\bar{x}_N) & \chi_j(\bar{x}_N) & \dots & \chi_k(\bar{x}_N) \end{vmatrix}$$

Slater determinants

A short-hand notation (including the normalization constant)

$$\Psi(\bar{x}_1 \dots \bar{x}_N) = \underbrace{|x_i(\bar{x}_1) x_j(\bar{x}_2) \dots x_k(\bar{x}_N)\rangle}_{N \text{ functions}}$$

Antisymmetry property

$$| \dots x_m \dots x_n \dots \rangle = \underset{\text{exchange}}{\overset{\curvearrowleft}{(-1)}} | \dots x_n \dots x_m \dots \rangle$$

General definition:

$$|x_i x_j \dots x_k\rangle = \frac{1}{\sqrt{N!}} \sum_{n=1}^{N!} (-1)^{P_n} P_n \{ x_i(1) x_j(2) \dots x_k(N) \}$$

total number of permutations P_n $\overbrace{}$
 number of simple interchanges required to obtain the n th permutation
 operator that generates the n th permutation of electron labels
 $1, 2, \dots, N$

Example:

$$\begin{aligned}
 & |x_i(1) x_j(2) x_k(3)\rangle = \frac{1}{\sqrt{6}} [x_i(1) x_j(2) x_k(3) - \\
 & - x_i(1) x_j(3) x_k(2) - x_i(2) x_j(1) x_k(3) + x_i(3) x_j(1) x_k(2) \\
 & + x_i(2) x_j(3) x_k(1) - x_i(3) x_j(2) x_k(1)]
 \end{aligned}$$

Exercise 2.5 Calculate $\langle K | L \rangle$ for two-electron slater determinants

$$|K\rangle = |\chi_i \chi_j\rangle$$

$$|L\rangle = |\chi_e \chi_e\rangle$$

$$\langle K | L \rangle = \frac{1}{r^2} \sum_{n=1}^2 (-1)^{p_n} \int P_n \{ \chi_i^*(1) \chi_j^*(2) \} \frac{1}{r^2} \sum_{m=1}^2 (-1)^{p_m}$$

$$P_m \{ \chi_e(1) \chi_e(2) \} d\vec{x}_1 d\vec{x}_2 =$$

$$= \frac{1}{2} \sum_{n,m=1}^2 (-1)^{p_n + p_m} P_n P_m \{ \underbrace{\int \chi_i^*(1) \chi_j^*(2)}_{\text{---}} \underbrace{\chi_e(1) \chi_e(2)}_{\text{---}} d\vec{x}_1 d\vec{x}_2 \}$$

$$P_n, P_m = 1, 0$$

$$= \frac{1}{2} [2\delta_{ik}\delta_{je} - 2\delta_{ic}\delta_{jk}] = \delta_{ik}\delta_{je} - \delta_{ie}\delta_{jk}$$

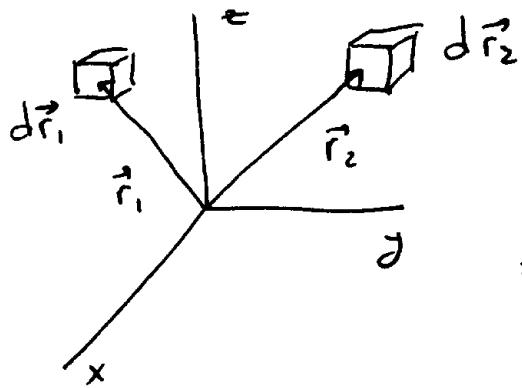
$$\langle K | L \rangle = 1, \quad i=k, j=e$$

$$\langle K | L \rangle = -1, \quad i=e, j=k$$

Exchange correlation

A Slater determinant incorporates exchange correlation, that is the motion of two electrons with parallel spins is correlated. The motion of electrons with opposite spins remains uncorrelated.

2 electrons :



$$P(\bar{r}_1, \bar{r}_2) d\bar{r}_1 d\bar{r}_2 =$$

$$= d\bar{r}_1 d\bar{r}_2 \int dw_1 dw_2 |\langle \chi_1(\bar{x}_1) \chi_2(\bar{x}_2) \rangle|^2$$

$$= \frac{d\bar{r}_1 d\bar{r}_2}{2} \int dw_1 dw_2 [\Psi_1(\bar{r}_1) \alpha(w_1) \Psi_2(\bar{r}_2) \beta(w_2)$$

$$- \Psi_1(\bar{r}_2) \alpha(w_2) \Psi_2(\bar{r}_1) \beta(w_1)]^2$$

$$= \frac{d\bar{r}_1 d\bar{r}_2}{2} [|\Psi_1(\bar{r}_1)|^2 |\Psi_2(\bar{r}_2)|^2 + |\Psi_1(\bar{r}_2)|^2 |\Psi_2(\bar{r}_1)|^2]$$

$$\text{if } \Psi_1 = \Psi_2, \quad P(\bar{r}_1, \bar{r}_2) d\bar{r}_1 d\bar{r}_2 = |\Psi(\bar{r}_1)|^2 |\Psi(\bar{r}_2)|^2 \underbrace{d\bar{r}_1 d\bar{r}_2}_{\text{probability of finding two electrons at points } \bar{r}_1 \text{ and } \bar{r}_2 \Rightarrow \text{the product of}}$$

probability of finding two electrons at points \bar{r}_1 and $\bar{r}_2 \Rightarrow$ the product of

Same spin :

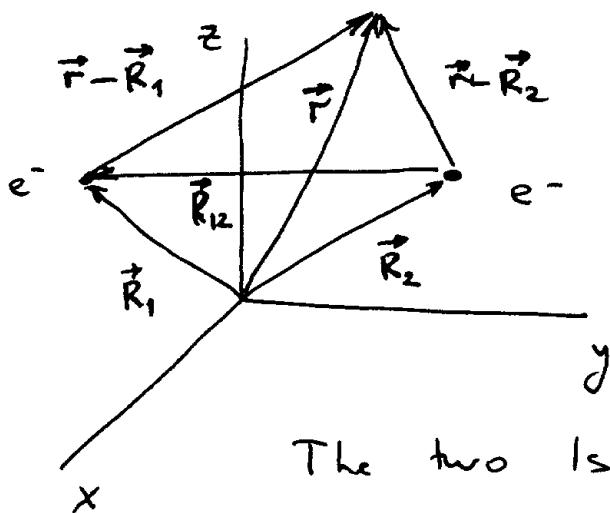
$$\chi_1(\bar{x}_1) = +_1(\bar{r}_1) \alpha(w_1)$$

$$\chi_2(\bar{x}_2) = +_2(\bar{r}_2) \alpha(w_2)$$

$$P(\bar{r}_1, \bar{r}_2) = \frac{1}{2} \{ |\Psi_1(\bar{r}_1)|^2 |\Psi_2(\bar{r}_2)|^2 + |+_1(\bar{r}_2)|^2 |+_2(\bar{r}_1)|^2 \} -$$

$$- [+_1^*(\bar{r}_1) +_2(\bar{r}_1) +_2^*(\bar{r}_2) +_1(\bar{r}_2) + +_1(\bar{r}_1) +_2^*(\bar{r}_1) +_2(\bar{r}_2) +_1^*(\bar{r}_2)]$$

The minimal basis H₂ model



Slater 1s orbital:

$$\Phi(F - \vec{R}) = (8^3/\pi)^{1/2} e^{-S(F - \vec{R})}$$

Gaussian 1s orbital:

$$\Phi(F - \vec{R}) = (\alpha/\pi)^{1/4} e^{-\alpha|F - \vec{R}|^2}$$

The two 1s orbitals overlap

$$S_{12} = \int dF \Phi_1^*(F) \Phi_2(F)$$

From two localized AO's, one can form two delocalized MO's

$$\Psi_g = \frac{1}{\sqrt{2(1+S_{12})}} (\Phi_1 + \Phi_2) \leftarrow \text{gerade symmetry}$$

$$\Psi_u = \frac{1}{\sqrt{2(1-S_{12})}} (\Phi_1 - \Phi_2) \leftarrow \text{ungerade symmetry}$$

$$X_1 = \Psi_g \alpha \Leftarrow \Psi_g \quad X_3 \quad \quad \quad X_4$$

$$X_2 = \Psi_g \beta \Leftarrow \bar{\Psi}_g$$

$$X_3 = \Psi_u \alpha \Leftarrow \Psi_u \quad X_1 \not\propto \quad \not\propto X_2$$

$$X_4 = \Psi_u \beta \Leftarrow \bar{\Psi}_u$$

Ground state wave function

$$|\Psi_0\rangle = |X_1, X_2\rangle = |\Psi_g \bar{\Psi}_g\rangle$$

Hartree-Fock approximation: Concepts

The Hartree-Fock method is a variational procedure on N-electron Slater determinants:

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle, \quad |\Psi_0\rangle = |x_1, x_2, \dots, x_N\rangle$$

$$\frac{\delta}{\delta x_a} \left[\langle \Psi_0 | H | \Psi_0 \rangle - \sum_{a,b=1}^N \epsilon_{ab} (\langle x_a | x_b \rangle - \delta_{ab}) \right] = 0$$

The variational procedure leads to the HF equation

$$f(i) x(\vec{x}_i) = \epsilon x(x_i)$$

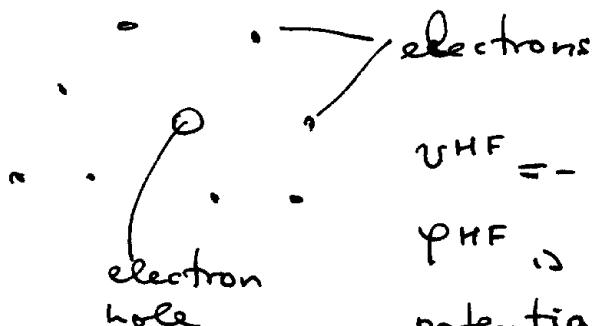
This equation finds the spin orbital of a single electron in the field of the nuclei and $N-1$ electrons in the system

$$f(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{z_A}{r_{Ai}} + v^{HF}(i)$$

kinetic energy
of the i th electron

attraction
to the nuclei

average energy of
interaction with
 $N-1$ electrons

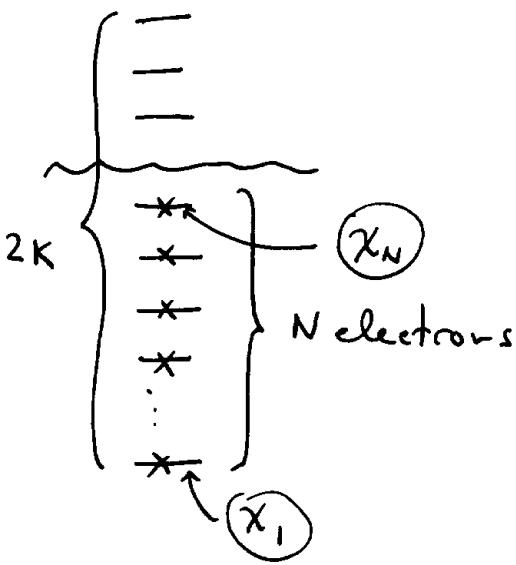


$$v^{HF} = -e \varphi^{HF}$$

φ^{HF} is the potential of $N-1$ electrons at the position of the i th electron

The HF equation is a nonlinear mean-field equation depending on the states of other electrons in the system. The procedure for solving the HF equation is called the self-consistent-field (SCF) method.

Excited determinants



The ground state of a system of N electrons is the Slater determinant

$$|\Psi_0\rangle = |x_1 x_2 \dots x_N\rangle$$

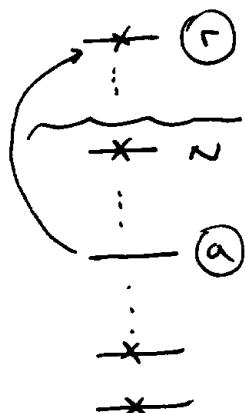
which leads to the lowest energy in the matrix element

$$\langle \Psi_0 | H | \Psi_0 \rangle$$

when variation is performed over the spin orbitals x_i .

Excited determinants can be formed from $2K > N$ states.

Excitations to virtual states $r > N$ can be used to form excited determinants. An excitation from state \underline{a} of the ground state determinant to \underline{r} virtual state creates a hole in \underline{a} and excitation \underline{r}



$$|\Psi_0\rangle = |x_1 x_2 \dots x_a x_b \dots x_N\rangle$$

spin orbital \underline{r}
is created

$$|\Psi_{\underline{a}}^{\underline{r}}\rangle = |x_1 x_2 \dots x_r x_b \dots x_N\rangle$$

spin orbital
 \underline{a} is removed

A doubly excited determinant:

$$|\Psi_{ab}^{rs}\rangle = |x_1 x_2 \dots x_r x_s \dots x_N\rangle$$

$\underline{a} \quad \underline{b}$

Exact wavefunction and CI

The exact wave function for the ground and excited states of an N -electron problem can be written as a linear of all possible Slater determinants formed from a complete set of spin orbitals $\{\psi_i\}$

$$|\Phi\rangle = c_0 |\Psi_0\rangle + \sum_{ra} c_a^r |\Psi_a^r\rangle + \sum_{\substack{acb \\ rcs}} c_{abc}^{rs} |\Psi_{abc}^{rs}\rangle + \dots$$

all unique pairs of excitations

The infinite set

$$\{|\Psi_i\rangle\} = \{|\Psi_0\rangle, |\Psi_a^r\rangle, |\Psi_{abc}^{rs}\rangle, \dots\}$$

is a complete set for the expansion of any N -electron wave function.

The procedure of forming all excited spin orbitals is called configuration interaction (CI). The lowest eigenvalue (Σ_0) of the Hamiltonian obtained on the basis $\{|\Psi_i\rangle\}$ is the exact nonrelativistic ground state energy of the system within the BO approximation.

The difference

$$E_{\text{corr}} = \Sigma_0 - E_0$$

is called the correlation energy (motion of opposite spin electrons is not correlated within the HF theory).

Full CI

If the basis of spin orbitals is finite

$$\{\chi_i \mid i = 1, 2, \dots, 2k\}$$

then $\binom{2k}{N}$ determinants formed from these spin orbitals do not form a complete N -electron basis. The procedure of incorporating all excited state determinants formed from a finite basis set is called full CI.

H_2 molecule: minimal basis of 4 spin orbitals
 $\chi_1 \chi_2 \chi_3 \chi_4$

ground state

$$|\Psi_0\rangle = |\chi_1 \chi_2\rangle = |\Psi_g \bar{\Psi}_g\rangle \quad \begin{array}{c} \text{—} \\ \uparrow \downarrow \end{array} \quad \begin{array}{c} u \\ g \end{array}$$

singly excited determinants

$$|\Psi_1^1\rangle = |2\bar{1}\rangle \quad \begin{array}{c} \uparrow \\ \downarrow \end{array} \quad \begin{array}{c} u \\ g \end{array}$$

$$|\Psi_1^{\bar{1}}\rangle = |\bar{2}1\rangle \quad \begin{array}{c} \downarrow \\ \uparrow \end{array} \quad \begin{array}{c} u \\ g \end{array}$$

$$|\Psi_{\bar{1}}^{\bar{1}}\rangle = |1\bar{2}\rangle \quad \begin{array}{c} \uparrow \\ \uparrow \end{array} \quad \begin{array}{c} u \\ g \end{array}$$

$$|\Psi_{\bar{1}}^{\bar{2}}\rangle = |1\bar{2}\rangle \quad \begin{array}{c} \uparrow \\ \uparrow \end{array} \quad \begin{array}{c} u \\ g \end{array}$$

doubly excited determinant

$$|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |2\bar{2}\rangle \quad \begin{array}{c} \text{—} \\ \uparrow \downarrow \end{array} \quad \begin{array}{c} u \\ g \end{array}$$

Homework: Write $|\Psi_1^1\rangle$ and $|\Psi_{1\bar{1}}^{2\bar{2}}\rangle$ in terms of atomic and spin wave functions.

due on Mon. Lecture

Operators and determinants

All electronic structure theories involve evaluation of matrix elements between determinants. Our problem is to evaluate

$\langle K \mid O \mid L \rangle$

for an operator O , i.e. to reduce it to matrix elements over spatial basis functions.

H₂ molecule: electronic Hamiltonian (BO approximation)

$$H = h(1) + h(2) + \frac{1}{r_{12}}$$

atom Hamiltonians

electron-electron
repulsion

$$O_1 = h(1) + h(2)$$

(1) + h(2) one-electron operators

$$\frac{1}{r_{12}} = O_2$$

two-electron operator

$$\langle \psi_0 | h(1) | \psi_0 \rangle = \int d\bar{x}_1 d\bar{x}_2 \frac{1}{\sqrt{2}} [\chi_1(\bar{x}_1) \chi_2(\bar{x}_2) - \chi_2(\bar{x}_1) \chi_1(\bar{x}_2)]^*$$

$$x \cdot h(\vec{r}_1) \frac{1}{r_2^2} [x_1(\vec{x}_1) x_2(\vec{x}_2) - x_2(\vec{x}_1) x_1(\vec{x}_2)]$$

$$\langle \psi_0 | 10, 14 \rangle = \langle 11 \downarrow 11 \rangle + \langle 21 \downarrow 12 \rangle$$

$$\langle \Psi_0 | O_2 | \Psi_0 \rangle = \int d\bar{x}_1 d\bar{x}_2 \frac{1}{r_{12}} [\chi_1(\bar{x}_1) \chi_2(\bar{x}_2) - \chi_2(\bar{x}_1) \chi_1(\bar{x}_2)]^*$$

$$x \frac{1}{r_{12}} \frac{1}{r_{21}} [\chi_1(\bar{x}_1) \chi_2(\bar{x}_2) - \chi_2(\bar{x}_1) \chi_1(\bar{x}_2)]$$

$$= \int d\bar{x}_1 d\bar{x}_2 \left[\chi_1^*(\bar{x}_1) \chi_2^*(\bar{x}_2) \frac{1}{r_{12}} \chi_1(\bar{x}_1) \chi_2(x_2) - \chi_1^*(\bar{x}_1) \chi_2^*(x_2) \frac{1}{r_{12}} \chi_1(\bar{x}_2) \chi_2(\bar{x}_1) \right]$$

$$= \langle 12|12 \rangle - \langle 12|21 \rangle$$

$$\langle \psi_0 | H | \psi_0 \rangle = \langle 1|H|1\rangle + \langle 2|H|2\rangle + \langle 12|H|2\rangle - \langle 12|H|1\rangle$$

Notations for one- and two-electron integrals

"One- and two-electron integrals" are in fact one- and two-electron matrix elements.

Notations:

spin orbitals

$$\langle ij|kl \rangle = \int d\bar{x}_1 d\bar{x}_2 \chi_i^*(\bar{x}_1) \chi_j^*(\bar{x}_2) r_{12}^{-1} \chi_k(\bar{x}_1) \chi_l(\bar{x}_2) = [ijk|l] \quad \begin{matrix} \nearrow \\ \text{physicists' notation} \end{matrix} \quad \begin{matrix} \nearrow \\ \text{chemists' notation} \end{matrix}$$

$$\langle i|h|j \rangle = [ih|j] = \int d\bar{x}_1 \chi_i^*(\bar{x}_1) h(\bar{r}_1) \chi_j(\bar{x}_1)$$

$$\begin{aligned} \langle ij||kl \rangle &= \langle ij|kl \rangle - \langle ij|lk \rangle \\ &= \int d\bar{x}_1 d\bar{x}_2 \chi_i^*(\bar{x}_1) \chi_j^*(\bar{x}_2) (1 - P_{12}) \chi_k(\bar{x}_1) \chi_l(\bar{x}_2) \end{aligned}$$

spatial orbitals

$$(i|h|j) = h_{ij} = (\psi_i|h|\psi_j) = \int d\bar{r}_1 \psi_i^*(\bar{r}_1) h(\bar{r}_1) \psi_j(\bar{r}_1)$$

$$(ij|kl) = (\psi_i t_j | \psi_k \psi_l) = \int d\bar{r}_1 d\bar{r}_2 \psi_i^*(\bar{r}_1) t_j(\bar{r}_1) r_{12}^{-1} \psi_k^*(\bar{r}_2) \psi_l(\bar{r}_2)$$

$$J_{ij} = (ii|jj) \leftarrow \text{Coulomb integral}$$

$$K_{ij} = (ij|ji) \leftarrow \text{Exchange integral}$$

Classification

One-electron operator

$$O_1 = \sum_i h(i)$$

Two-electron operator

$$O_2 = \sum_{i=1}^N \sum_{\substack{j=1 \\ j>i}}^N v(i,j) \equiv \sum_{j>i} v(i,j)$$

Rules to calculate

$$\langle K | O | L \rangle$$

depend on two factors:

- ①. whether O is one- or two-electron
- ②. the degree to which the two determinant $|K\rangle$ and $|L\rangle$ differ

Three cases:

①. $|K\rangle = |L\rangle$

②. $|K\rangle$ and $|L\rangle$ differ by one spin orbital

$$|K\rangle = |x_1 \dots x_a \dots x_n\rangle \quad |L\rangle = |x_1 \dots x_p \dots x_n\rangle$$

③. $|K\rangle$ and $|L\rangle$ differ by two spin orbitals

$$|K\rangle = |x_1 \dots x_a x_b \dots x_n\rangle$$

$$|L\rangle = |x_1 \dots x_p x_q \dots x_n\rangle$$

Rules for matrix elements

$$O_1 = \sum_{i=1}^N h(i)$$

① $|K\rangle = |L\rangle = | \dots mn \dots \rangle$

$$\langle K | O_1 | L \rangle = \sum_m \langle m | h | m \rangle$$

② $|K\rangle = | \dots mn \dots \rangle$

$$|L\rangle = | \dots pq \dots \rangle$$

$$\langle K | O_1 | L \rangle = \langle m l | h | p \rangle = [m l h | p]$$

③ $|K\rangle = | \dots mn \dots \rangle$

$$|L\rangle = | \dots pq \dots \rangle$$

$$\langle K | O_1 | L \rangle = 0$$

$$O_2 = \sum_{j>i} r_{ij}^{-1}$$

① $\langle K | O_2 | K \rangle = \frac{1}{2} \sum_{m,n=1}^N \langle mn || mn \rangle$

② $\langle K | O_2 | L \rangle = \sum_{n=1}^N \langle mn || pn \rangle$

③ $\langle K | O_2 | L \rangle = \langle mn || pq \rangle$

Ground-state energy

$$\langle \Psi_0 | O_1 | \Psi_0 \rangle = \sum_{a=1}^N \langle a | h | a \rangle$$

$$\langle \Psi_0 | O_2 | \Psi_0 \rangle = \frac{1}{2} \sum_{a,b=1}^N \langle ab || ab \rangle = \frac{1}{2} \sum_{a,b=1}^N [\langle ab | ba \rangle - \langle ab | ab \rangle]$$

For a general molecular Hamiltonian, its diagonal matrix element is

$$\begin{aligned} \langle k | H | k \rangle &= \sum_{m=1}^N \langle m | h | m \rangle + \sum_{m=1}^N \sum_{n>m} \langle m h | m n \rangle \\ &= \sum_{m=1}^N [m | h | m] + \sum_{m=1}^N \sum_{n>m} ([m m | m n] - [m n | m m]) \end{aligned}$$

The ground-state energy

$$\begin{aligned} E_0 &= \sum_{a=1}^N [a | h | a] + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [[aa | bb] - [ab | ba]] \\ &= \sum_{a=1}^N \langle a | h | a \rangle + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N \langle ab || ab \rangle \\ &= \sum_{a=1}^N \langle a | h | a \rangle + \sum_{a=1}^N \sum_{b>a} \langle ab || ab \rangle \end{aligned}$$

Each occupied spin orbital contributes a term $\langle a | h | a \rangle$ to the energy, and every unique pair of occupied spin orbitals x_i, x_j contribute a term $\langle ij || ij \rangle$ to the energy.

Exercises 2.9, 2.12

Full CI calculation of H₂:

$$\{|\Psi\rangle\} = |\Psi_0\rangle, \underbrace{|\Psi_1^2\rangle, |\Psi_1^{\bar{2}}\rangle, \dots, |\Psi_{\bar{1}}^{\bar{2}}\rangle}_{\substack{\text{single excitation} \\ \text{"u"} \\ \text{ungerade}}} \quad |\Psi_{12}^{3Y}\rangle \leftarrow \underbrace{\text{two-electron}}_{\substack{\text{"g"} \\ \text{gerade}}} \text{excitation}$$

ground state "g"
 "g" ungerade "g" gerade

Because of symmetry:

$$|\Psi_0\rangle = c_0|\Psi_0\rangle + c_1|\Psi_{12}^{3Y}\rangle = c_0|x_1x_2\rangle + c_1|x_3x_4\rangle$$

In order to find coefficients c_0 and c_1 , one needs
to build the Hamiltonian matrix

$$\langle x_1x_2 | H | x_1x_2 \rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12||12\rangle$$

$$\langle x_3x_4 | H | x_3x_4 \rangle = \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34||34\rangle$$

$$\langle x_1x_2 | H | x_3x_4 \rangle = \langle 12||34\rangle$$

$$H = \begin{pmatrix} & \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12||12\rangle & \langle 12||34\rangle \\ & & \\ \langle 34||12\rangle & & \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34||34\rangle \end{pmatrix}$$

Exercise 2.14

Calculate the ionization energy for an N -electron system

$$IP = {}^N E_0 - {}^{N-1} E_0$$

$${}^N E_0 = \langle {}^N \Psi_0 | H | {}^N \Psi_0 \rangle, \quad {}^{N-1} E_0 = \langle {}^{N-1} \Psi_0 | H | {}^{N-1} \Psi_0 \rangle$$

$${}^N E_0 = \sum_{a=1}^N \langle a | h | a \rangle + \sum_{a < b=1}^N \langle ab || ab \rangle$$

$${}^{N-1} E_0 = \sum_{a=1}^{N-1} \langle a | h | a \rangle + \sum_{a < b=1}^{N-1} \langle ab || ab \rangle$$



:

:

x_3 —

x_2 —

x_1 —

$${}^N E_0 - {}^{N-1} E_0 = \langle \alpha | h | \alpha \rangle + \sum_{b=1}^N \langle \alpha b || \alpha b \rangle$$

Transition from spin orbitals to spatial orbitals

Spin orbitals $\alpha(\omega)$, $\beta(\omega)$ must be integrated out for computational purposes

H₂ model:

$$E_0 = \langle \chi_1 | h | \chi_1 \rangle + \langle \chi_2 | h | \chi_2 \rangle + \langle \chi_1 \chi_2 | \chi_1 \chi_2 \rangle - \langle \chi_1 \chi_2 | \chi_2 \chi_1 \rangle$$

$$\chi_1 = \Psi_g(\vec{r}) \alpha(\omega)$$

$$\chi_2 = \Psi_g(\vec{r}) \beta(\omega)$$

$$\begin{aligned} \langle \chi_1 | h | \chi_1 \rangle &= \int d\vec{r}_1 d\omega_1 \Psi_g^*(\vec{r}_1) \alpha(\omega_1) h(\vec{r}_1) \Psi_g(\vec{r}_1) \alpha(\omega_1) \\ &= (\Psi_g | h | \Psi_g) \end{aligned}$$

One-electron contribution:

$$\langle \chi_1 | h | \chi_1 \rangle + \langle \chi_2 | h | \chi_2 \rangle = \underbrace{2 (\Psi_g | h | \Psi_g)}_{\text{two electrons with opposite spins}}$$

$$\begin{aligned} \langle \chi_1 \chi_2 | \chi_1 \chi_2 \rangle &= \int \Psi_g^*(\vec{r}_1) \alpha(\omega_1) \Psi_g^*(\vec{r}_2) \beta(\omega_2) \frac{1}{r_{12}} \Psi_g(\vec{r}_1) \alpha(\omega_1) \\ &\quad \Psi_g(\vec{r}_2) \beta(\omega_2) d\vec{r}_1 d\vec{r}_2 d\omega_1 d\omega_2 \\ &= (\Psi_g \Psi_g | \Psi_g \Psi_g) \end{aligned}$$

$$\langle \chi_1 \chi_2 | \chi_2 \chi_1 \rangle = 0$$

$$E_0(H_2) = 2 (\Psi_g | h | \Psi_g) + (\Psi_g \Psi_g | \Psi_g \Psi_g)$$

Closed-shell restricted HF

The spatial orbitals are restricted to be the same for α and β spins: electrons occupy states in pairs

$$|\Psi_0\rangle = |\Psi_1 \bar{\Psi}_1 \Psi_2 \bar{\Psi}_2 \dots \Psi_{N/2} \bar{\Psi}_{N/2}\rangle$$

$$\begin{matrix} \uparrow\downarrow & \Psi_{N/2} \\ \vdots & \end{matrix} \quad \sum_a^N \Psi_a = \sum_a^{N/2} \Psi_a + \sum_a^{N/2} \bar{\Psi}_a$$

$$\begin{matrix} \uparrow\downarrow & \Psi_a \\ \vdots & \end{matrix} \quad \sum_a^N \sum_b^N \chi_a \chi_b = \sum_a^{N/2} (\Psi_a + \bar{\Psi}_a) \sum_b^{N/2} (\Psi_b + \bar{\Psi}_b)$$

$$\begin{matrix} \uparrow\downarrow & \Psi_2 \\ \vdots & \end{matrix} \quad = \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} (\Psi_a \Psi_b + \Psi_a \bar{\Psi}_b + \bar{\Psi}_a \Psi_b + \bar{\Psi}_a \bar{\Psi}_b)$$

$$\begin{matrix} \uparrow\downarrow & \Psi_1 \\ \vdots & \end{matrix} \quad \sum_a^N \sum_b^N = \sum_a^{N/2} \sum_b^{N/2} + \sum_a^{N/2} \sum_b^{N/2} + \sum_a^{N/2} \sum_b^{N/2} + \sum_a^{N/2} \sum_b^{N/2}$$

$$\frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N ([aa|bb] - [ab|ba]) =$$

$$= \frac{1}{2} \left\{ \sum_a^{N/2} \sum_b^{N/2} ([aa|bb] - [ab|ba]) + \sum_a^{N/2} \sum_b^{N/2} ([a\bar{a}|\bar{b}\bar{b}] - [\bar{a}\bar{b}|\bar{b}\bar{a}]) \right.$$

$$+ \left. \sum_a^{N/2} \sum_b^{N/2} ([\bar{a}\bar{a}|bb] - [\bar{a}\bar{b}|ba]) + \sum_a^{N/2} \sum_b^{N/2} ([\bar{a}\bar{a}|\bar{b}\bar{b}] - [\bar{a}\bar{b}|\bar{b}\bar{a}]) \right)$$

$$= \sum_a^{N/2} \sum_b^{N/2} [2(\Psi_a \Psi_a | \Psi_b \Psi_b) - (\Psi_a \Psi_a | \Psi_b \Psi_b)]$$

$$E_0 = 2 \sum_a^{N/2} (\Psi_a | h(\Psi_a)) + \sum_a^{N/2} \sum_b^{N/2} [2(\Psi_a \Psi_a | \Psi_b \Psi_b) - (\Psi_a \Psi_a | \Psi_b \Psi_b)]$$

Exercise 2.17

Show that the full CI matrix of H_2 has the form

$$\overset{\leftrightarrow}{H} = \begin{pmatrix} 2(11\hbar 11) + (11111) & (12112) \\ (21121) & 2(2\hbar 12) + (22122) \end{pmatrix}$$

Off-diagonal terms:

$$\langle 12|34 \rangle = \langle \psi_g^* \bar{\psi}_g | \psi_u \bar{\psi}_u \rangle =$$

$$= \int \psi_g^*(\bar{r}_1) \alpha(\omega_1) \psi_g^*(\bar{r}_2) \beta(\omega_2) \frac{1}{r_{12}} \psi_u(\bar{r}_1) \alpha(\omega_1) \psi_u(\bar{r}_2) \beta(\omega_2) \frac{d\bar{r}_1 d\bar{r}_2}{d\omega_1 d\omega_2}$$

$$= (g_u | g_u)$$

$$\langle 12|43 \rangle = 0$$

$$\overset{\leftrightarrow}{H} = \begin{pmatrix} 2(g1\hbar1g) + (gg|gg) & (gu|gu) \\ (ug|ug) & 2(u1\hbar1u) + (uu|uu) \end{pmatrix}$$

Coulomb and exchange integrals

$$(aa|bb) = \int d\vec{r}_1 d\vec{r}_2 |\Psi_a(\vec{r}_1)|^2 r_{12}^{-1} |\Psi_b(\vec{r}_2)|^2$$

electronic density
at point \vec{r}_1

represents coulomb repulsion between the charge clouds $|\Psi_a(\vec{r}_1)|^2$ and $|\Psi_b(\vec{r}_1)|^2$.

This integral is called a coulomb integral and is denoted as

$$J_{ij} = (iiljj) = \langle ij | ij \rangle$$

The integral

$$(ab|ba) = \int d\vec{r}_1 d\vec{r}_2 \Psi_a^*(\vec{r}_1) \Psi_b(\vec{r}_1) r_{12}^{-1} \Psi_b^*(\vec{r}_2) \Psi_a(\vec{r}_2)$$

does not have a simple classical interpretation. It appears as a result of the requirement of wave functions being antisymmetric.

$$K_{ij} = (ijlji) = \langle ij | ji \rangle$$

is called an exchange integral.

$$E_0 = 2 \sum_a h_{aa} + \sum_{ab} [2J_{ab} - K_{ab}]$$

$\uparrow\downarrow$ vs $\uparrow\uparrow$

Parallel spins try to avoid each other. Antiparallel spins can be at the same point of space.

The repulsion between antiparallel spins should be higher:

$$E(\uparrow\downarrow) = [\psi_1 | h | \psi_1] + [\bar{\psi}_2 | h | \bar{\psi}_2] +$$

$$+ [\psi_1 \psi_1 | \bar{\psi}_2 \bar{\psi}_2] - [\psi_1 \bar{\psi}_2 | \bar{\psi}_2 \psi_1]$$

$\int d\alpha d\omega = 1 \qquad \qquad \int d\beta d\omega = 0$

$$= h_{11} + h_{22} + J_{12}$$

$$E(\uparrow\uparrow) = [\psi_1 | h | \psi_1] + [\psi_2 | h | \psi_2] +$$
$$+ [\psi_1 \psi_1 | \psi_2 \psi_2] - [\psi_1 \psi_2 | \psi_2 \psi_1]$$

$$= h_{11} + h_{22} + J_{12} - K_{12}$$

$E(\uparrow\uparrow) < E(\uparrow\downarrow)$

Rules for Determinantal Energies

- An electron (irrespective of its spin) in spatial orbital Ψ_i contributes the term h_{ii} to the energy

$$\langle \chi_i | h | \chi_i \rangle = h_{ii}$$

$$\begin{matrix} \downarrow & \downarrow \\ \{\alpha \Psi_i & \alpha \Psi_i \\ \beta \Psi_i & \beta \Psi_i \} \end{matrix}$$

- Each unique pair of electrons (irrespective of their spin) in spatial orbitals Ψ_i and Ψ_j contributes the term J_{ij} to the energy.
- Each unique pair of electrons with parallel spins in spatial orbitals Ψ_i and Ψ_j contributes the term $-k_{ij}$ to the energy.

$$\chi_i = \Psi_i \alpha \quad \chi_j = \Psi_j \beta$$

$$\langle ij || ij \rangle = [\Psi_i \Psi_i | \bar{\Psi}_j \bar{\Psi}_j] - [\Psi_i \bar{\Psi}_j | \bar{\Psi}_j \Psi_j] = J_{ij}$$

$$\chi_i = \Psi_i \beta \quad \chi_j = \Psi_j \beta$$

$$\langle ij || ij \rangle = [\bar{\Psi}_i \bar{\Psi}_i | \bar{\Psi}_j \bar{\Psi}_j] - [\bar{\Psi}_i \bar{\Psi}_j | \bar{\Psi}_j \Psi_i] = J_{ij} - k_{ij}$$

Atomic functions representation of $|\Psi_1^z\rangle$ and $|\Psi_{1\bar{1}}^{z\bar{z}}\rangle$

$$|\Psi_1^z\rangle = |\Psi_u \bar{\Psi}_g\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \Psi_u(1)\alpha(1) & \Psi_g(1)\beta(1) \\ \Psi_u(2)\alpha(2) & \Psi_g(2)\beta(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} [\Psi_u(1)\Psi_g(2)\alpha(1)\beta(2) - \Psi_g(1)\Psi_u(2)\alpha(2)\beta(1)] =$$

$$= \frac{1}{2\sqrt{2}} \left[(\Phi_A(1) - \Phi_B(1))(\Phi_A(2) + \Phi_B(2)) \beta(2)\alpha(1) - \right.$$

$$\left. - (\Phi_A(1) + \Phi_B(1))(\Phi_A(2) - \Phi_B(2)) \beta(1)\alpha(2) \right] \frac{1}{\sqrt{1-s^2}}$$

$$|\Psi_{1\bar{1}}^{z\bar{z}}\rangle = |\Psi_u \bar{\Psi}_u\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \Psi_u(1)\alpha(1) & \Psi_u(1)\beta(1) \\ \Psi_u(2)\alpha(2) & \Psi_u(2)\beta(2) \end{vmatrix} =$$

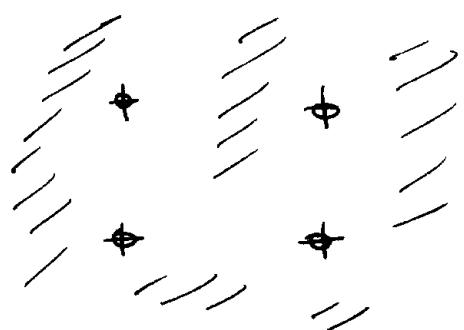
$$= \frac{1}{\sqrt{2}} [\Psi_u(1)\Psi_u(2)\alpha(1)\beta(2) - \Psi_u(1)\Psi_u(2)\alpha(2)\beta(1)]$$

$$= \frac{1}{\sqrt{2}} \Psi_u(1)\Psi_u(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

$$= \frac{1}{2\sqrt{2}(1-s^2)} (\Phi_A(1) - \Phi_B(1))(\Phi_A(2) - \Phi_B(2)) (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

$$= \frac{1}{2\sqrt{2}(1-s^2)} (\Phi_A(1) - \Phi_B(1))(\Phi_A(2) - \Phi_B(2)) [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

Electron gas of metals



n_0 — is the density of electrons in the metal

volume per electron = $1/n_0$

Average radius of an electron in Bohr radii :

$$r_s = \left(\frac{3}{4\pi n_0 a_0^3} \right)^{1/3}$$

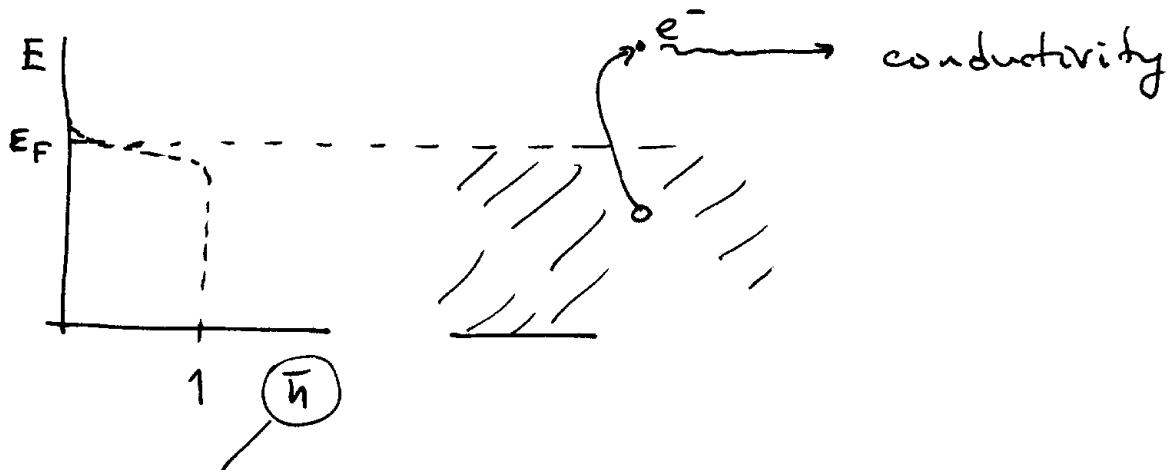
$$\frac{4\pi}{3} (r_s a_0)^3 = \frac{1}{n_0}$$

The density of electrons directly defines the Fermi wave vector

$$k_0 = \frac{k_F^2}{3\pi^2}, \quad k_F a_0 = \frac{1.9192}{r_s}$$

Fermi energy

$$E_F = \frac{1.8416}{r_s^2} \text{ a.u.}$$



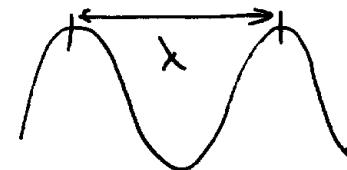
Fermi distribution
of electrons

Electronic energy

Wave functions of conduction electrons are plane waves:

$$\psi = e^{ikx}, \quad k = \frac{2\pi}{\lambda}$$

wavevector



$$\langle \psi_k | -\frac{1}{2} \nabla^2 | \psi_k \rangle = \frac{k^2}{2} \leftarrow \begin{matrix} \text{kinetic energy matrix} \\ \text{element} \end{matrix}$$

Since the kinetic energy is an one-electron operator, the total kinetic energy of N electrons is the sum of individual kinetic energies

$$E_K = (2V) \int \frac{d^3k}{(2\pi)^3} \frac{k^2}{2} = \frac{1}{2\pi^2} \frac{k_F^5}{5} = \frac{3}{5} E_F \frac{N}{V}$$

two spins

total number
of electrons

$$\frac{E_K}{N} = \frac{3}{5} E_F = \frac{1.105}{r_s^2} \text{ a.u.}$$

Coulomb interactions

$$NE_c = \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{[\rho_e(\vec{r}_1) - \rho_i] [\rho_e(\vec{r}_2) - \rho_i]}{|\vec{r}_1 - \vec{r}_2|} = 0$$

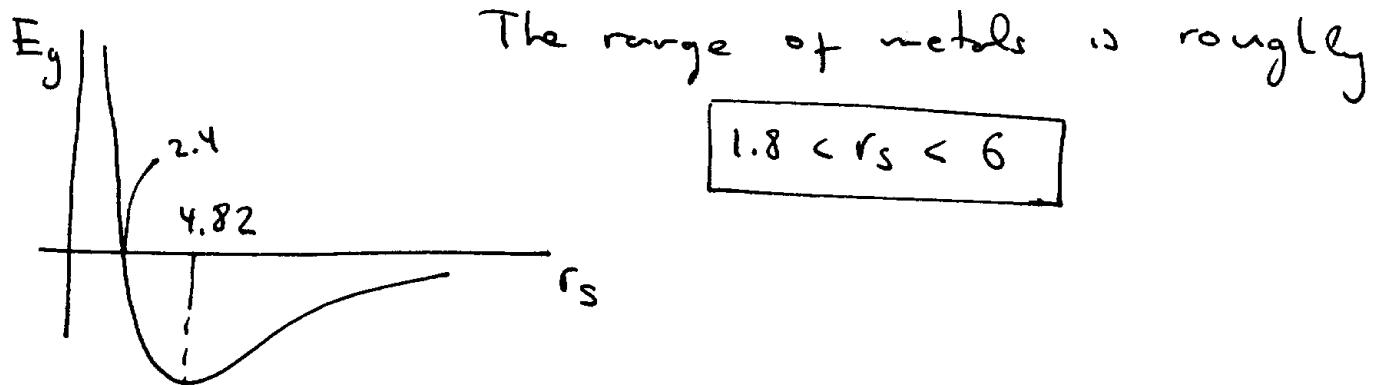
- The Coulomb interaction energy cancels out by the direct interaction with the positive background.

Exchange energy

$$E_{\text{ex}} = - \frac{3}{4} \frac{e^2 k_F}{\pi} = - \frac{3}{2\pi} (k_F a_0) \frac{e^2}{2a_0} = - \frac{0.458}{r_s} \text{ a.u.}$$

Total energy:

$$E_g = \left(\frac{1.105}{r_s^2} - \frac{0.458}{r_s} \right) \text{ a.u.} \quad \text{||} \leftarrow \begin{array}{l} \text{HF level of} \\ \text{theory for } E_g \end{array}$$



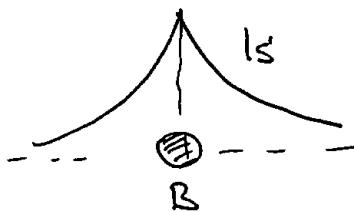
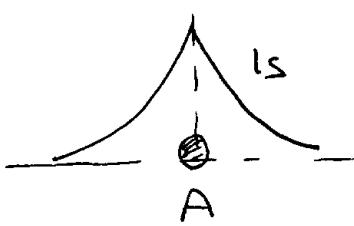
One needs to include the correlation energy

$$E_c = -0.047 + 0.0311 \ln(r_s)$$

'Exact' ground energy:

$$E_g' = \frac{1.105}{r_s^2} - \frac{0.458}{r_s} - 0.047 + 0.0311 \ln(r_s)$$

Full CI calculation of H₂ energy



$$\Phi_A = \left(\frac{\gamma^3}{\pi}\right)^{1/2} e^{-\delta|\vec{r} - \vec{R}_A|}$$

$$\Phi_B = \left(\frac{\gamma^3}{\pi}\right)^{1/2} e^{-\delta|\vec{r} - \vec{R}_B|}$$

For 1s of H, $\underline{\gamma = 1}$. Let us consider an equilibrium separation of $R = 1.40 \text{ a.u.}$ and calculate the atomic integrals.

①. Atomic wave function integrals

at $R = 1.40 \text{ a.u.}$

$$\langle \Phi_A | \Phi_B \rangle = S = 0.753$$

$$\langle \Phi_A | h | \Phi_A \rangle = -1.110 \text{ a.u.}$$

$$\langle \Phi_A | h | \Phi_B \rangle = -0.968 \text{ a.u.}$$

$$h = -\frac{1}{2} \nabla^2 - \frac{1}{r} - \frac{1}{|\vec{r} - \vec{R}|}$$

\vec{R} is the vector connecting two H nuclei

$$\langle \Phi_A \Phi_A | \Phi_A \Phi_A \rangle = \int |\Phi_A(\vec{r}_1)|^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} |\Phi_A(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 = 0.625 \text{ a.u.}$$

$$\langle \Phi_A \Phi_A | \Phi_B \Phi_B \rangle = 0.504 \text{ a.u.} \quad \leftarrow \text{Coulomb}$$

$$\langle \Phi_A \Phi_B | \Phi_A \Phi_B \rangle = 0.323 \text{ a.u.} \quad \leftarrow \text{Exchange}$$

$$\langle \Phi_A \Phi_A | \Phi_A \Phi_B \rangle = 0.426 \text{ a.u.}$$

②. Molecular orbitals (spatial)

$$\Psi_g = \frac{1}{\sqrt{2+2S}} (\Phi_A + \Phi_B)$$

$$\Psi_u = \frac{1}{\sqrt{2-2S}} (\Phi_A - \Phi_B)$$

③. Matrix elements

$$\begin{aligned} \langle \Psi_g | h | \Psi_g \rangle &= \frac{1}{2+2S} \left(\langle \Phi_A | h | \Phi_A \rangle \cdot 2 + 2 \cdot \langle \Phi_A | h | \Phi_B \rangle \right) \\ &= -1.185 \text{ a.u.} \end{aligned}$$

$$\langle \Psi_g | h | \Psi_u \rangle = 0$$

$$\begin{aligned} \langle \Psi_u | h | \Psi_u \rangle &= \frac{1}{2-2S} \left(2 \langle \Phi_A | h | \Phi_B \rangle - 2 \langle \Phi_A | h | \Phi_B \rangle \right) \\ &= -0.575 \text{ a.u.} \end{aligned}$$

④. Determinantal energies

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = 2 \langle \Psi_g | h | \Psi_g \rangle + (gg | gg)$$

$$\begin{aligned} (gg | gg) &= \frac{1}{(2+2S)^2} \langle (\Phi_A + \Phi_B)(\Phi_A + \Phi_B) | \frac{1}{r} | (\Phi_A + \Phi_B)(\Phi_A + \Phi_B) \rangle \\ &= 0.566 \text{ a.u.} \end{aligned}$$

$$\begin{aligned} (gu | gu) &= \frac{1}{4-4S^2} \langle (\Phi_A + \Phi_B)(\Phi_A - \Phi_B) | \frac{1}{r} | (\Phi_A + \Phi_B)(\Phi_A - \Phi_B) \rangle \\ &= 0.140 \text{ a.u.} \end{aligned}$$

The ground-state electronic energy

$$E_0 = 2 \times (-1.185) + 0.566 = -1.804 \text{ a.u.}$$

The Born-Oppenheimer energy

$$E^{BO} = E_0 + \frac{1}{R} = -1.090 \text{ a.u.}$$

Excited-state energy

$$\begin{aligned} \langle \psi_{12}^{34} | H | \psi_{12}^{34} \rangle &= 2 \langle \psi_u | h | \psi_u \rangle + \epsilon_{uu}(uu) \\ &= -0.568 \text{ a.u.} \end{aligned}$$

Off-diagonal term:

$$\begin{aligned} \langle \psi_0 | H | \psi_{12}^{34} \rangle &= \langle 12 | 134 \rangle = \langle 12 | 24 \rangle - \langle 12 | 43 \rangle \\ &= \underbrace{\langle \psi_g \bar{\psi}_g | \psi_u \bar{\psi}_u \rangle}_{1} - \underbrace{\langle \psi_g \bar{\psi}_g | \bar{\psi}_u \psi_u \rangle}_{0} \\ &= \int \psi_g^* \psi_g^* \frac{1}{r_{12}} \psi_u \psi_u = (gu | gu) = 0.140 \text{ a.u.} \end{aligned}$$

$$\overset{\leftrightarrow}{H} = \begin{pmatrix} -1.804 & 0.140 \\ 0.140 & -0.568 \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

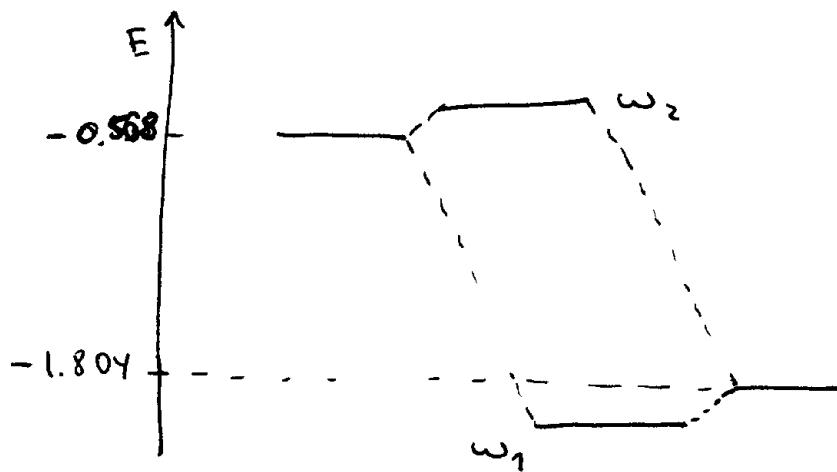
⑤ Eigenvalues

$$\omega_1 = \bar{H} - \frac{\Delta\omega}{2} = -1.837 \text{ a.u.}$$

$$\bar{H} = \frac{1}{2} (-1.804 - 0.568) = -1.186 \text{ a.u.}$$

$$\Delta\omega = \sqrt{(\Delta H)^2 + 4(H_{12})^2} = \sqrt{(1.84 - 0.568)^2 + 4 \cdot 0.14^2} = 1.302$$

$$\omega_2 = \bar{H} + \frac{\Delta\omega}{2} = -0.535$$



⑥ Correlation energy

By definition, correlation energy is the difference between the HF solution based on a single determinant and the eigenvalue obtained from a multideterminant expansion.

$$E_{\text{corr}} = \omega_1 - E_0 = -1.837 + 1.804 = -0.033 \text{ a.u.}$$

Spin operators

Spin angular momentum: $\vec{s} = s_x \hat{i}_x + s_y \hat{i}_y + s_z \hat{i}_z$

Squared magnitude: $s^2 = \vec{s} \cdot \vec{s} = s_x^2 + s_y^2 + s_z^2$

Commutation relations:

$$[s_x, s_y] = i s_z, \quad [s_y, s_z] = i s_x, \quad [s_z, s_x] = i s_y$$

The complete set of states can be taken to be simultaneous eigenfunctions of s^2 and s_z
 $([s^2, s_z] = 0)$

$$s^2 |s, m\rangle = s(s+1) |s, m\rangle$$

$$s_z |s, m\rangle = m |s, m\rangle$$

$$|\alpha\rangle \equiv |\frac{1}{2}, \frac{1}{2}\rangle \quad s^2 |\alpha\rangle = \frac{3}{4} |\alpha\rangle, \quad s^2 |\beta\rangle = \frac{3}{4} |\beta\rangle$$

$$|\beta\rangle \equiv |\frac{1}{2}, -\frac{1}{2}\rangle \quad s_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle, \quad s_z |\beta\rangle = -\frac{1}{2} |\beta\rangle$$

$|\alpha\rangle$ and $|\beta\rangle$ are not eigenvalues of s_x and s_y

$$s_x |\alpha\rangle = \frac{1}{2} |\beta\rangle \quad s_x |\beta\rangle = \frac{1}{2} |\alpha\rangle$$

$$s_y |\alpha\rangle = \frac{i}{2} |\beta\rangle \quad s_y |\beta\rangle = -\frac{i}{2} |\alpha\rangle$$

Step-up and step-down operators:

$$s_+ = s_x + i s_y$$

$$s_- = s_x - i s_y$$

$$s_+ |\alpha\rangle = 0 \quad s_- |\beta\rangle = |\beta\rangle$$

$$s_+ |\beta\rangle = |\alpha\rangle \quad s_- |\beta\rangle = 0$$

Spin-adapted configurations

The Hamiltonian of a non-relativistic system does not depend on spin coordinates,

$$[H, \vec{L}^2] = 0 = [H, L_z]$$

where

$$\vec{L} = \sum_{i=1}^N \vec{s}(i)$$

\rightarrow the total spin of the system of N electrons.

The exact eigenfunctions of the Hamiltonian must be also eigenfunctions of the two spin operators

$$\vec{L}^2 |\phi\rangle = \langle \vec{s}(s+1) | \phi \rangle$$

$$L_z |\phi\rangle = \langle M_s | \phi \rangle$$

total spin
z-projection

$s = 0 \leftarrow$ singlet

$s = \frac{1}{2} \leftarrow$ doublet

$s = 1 \leftarrow$ triplet

Any single determinant is an eigenfunction of L_z :

$$L_z |x_i x_j \dots x_k\rangle = \frac{1}{2} (\underset{\text{number of ups}}{\uparrow} N^U - \underset{\text{number of downs}}{\downarrow} N^D) = M_s |x_i \dots x_k\rangle$$

Closed- and open-shell determinants

Restricted determinant \leftarrow states with spin "up" and "down" have equal energies

Closed-shell determinant \leftarrow each spatial orbital is doubly occupied

Open-shell determinant \leftarrow there are spatial orbitals that contain single electrons

$\uparrow \cdots \downarrow \quad \uparrow \cdots -$

$\uparrow \cdots \downarrow \quad \uparrow \cdots \uparrow$
closed-shell open-shell

$$\nabla^2 |\Psi_i \bar{\Psi}_i \dots \rangle = 0 (0+1) |\Psi_i \bar{\Psi}_i \dots \rangle = 0 \quad (*)$$

(closed-shell determinants are eigenstates of the total spin squared)

Exercise 2.38. Prove Eq. (*).

$$\nabla^2 = \nabla_- \nabla_+ + \nabla_z + \nabla_z^2, \quad \nabla_z |\Psi_i \bar{\Psi}_i \dots \rangle = (N_\alpha - N_\beta) |\dots \rangle = 0$$

$$\nabla_+ |\Psi_i \bar{\Psi}_i \dots \rangle = \sum_i s_+(i) |\Psi_i \bar{\Psi}_i \dots \rangle \quad \nabla_z^2 |\Psi_i \bar{\Psi}_i \dots \rangle = 0$$

$$= \sum_i |\underbrace{\Psi_i \bar{\Psi}_i \dots}_{\text{same spin-orbitals}} \rangle = 0$$

same spin-orbitals

$$|\dots \rangle = 0$$

Spin-adapted linear combinations

- * Single determinants are not necessarily eigenfunctions of \mathcal{L}^2 .
- * Open-shell determinants with parallel spins are eigenfunctions of \mathcal{L}^2

\uparrow_b

\uparrow_a

$$\mathcal{L}^2 = \mathcal{L}_- \mathcal{L}_+ + \mathcal{L}_z + \mathcal{L}_z^2$$

$$\mathcal{L}_z |\psi_i \bar{\psi}_i \dots \psi_a \bar{\psi}_a \uparrow_b \uparrow_a \rangle = M_S |\psi_i \bar{\psi}_i \dots \psi_a \bar{\psi}_a \uparrow_b \uparrow_a \rangle$$

total projection of the spin on the z-axis

$$\mathcal{L}_z^2 |\psi_i \dots \rangle = (M_S)^2 |\psi_i \dots \rangle$$

$$\mathcal{L}_+ |\psi_i \bar{\psi}_i \dots \psi_a \bar{\psi}_a \uparrow_b \uparrow_a \rangle = \frac{1}{\sqrt{N!}} \sum_n (-1)^{P_n} \mathcal{L}_+ \Psi_n \{ \psi_i \dots \bar{\psi}_a \uparrow_b \uparrow_a \}$$

$$= \frac{1}{\sqrt{N!}} \sum_n (-1)^{P_n} \sum_i s_+(i) \Psi_n \{ \psi_i \dots \bar{\psi}_a \uparrow_b \uparrow_a \} = 0$$

$$s_+(\alpha) \uparrow_\alpha = 0 \quad s_+(i) \uparrow_i \bar{\psi}_i = 0$$

$$s_+(b) \uparrow_b = 0$$

$$\mathcal{L}^2 |\psi_i \bar{\psi}_i \dots \psi_a \bar{\psi}_a \uparrow_b \uparrow_a \rangle = M_S(M_S+1) |\psi_i \bar{\psi}_i \dots \psi_a \bar{\psi}_a \uparrow_b \uparrow_a \rangle$$

$$M_S = 1 \quad \text{and}$$

$$\mathcal{L}^2 |\psi_i \bar{\psi}_i \dots \psi_a \bar{\psi}_a \uparrow_b \uparrow_a \rangle = 2 |\psi_i \bar{\psi}_i \dots \psi_a \bar{\psi}_a \uparrow_b \uparrow_a \rangle$$

| $\psi_i \bar{\psi}_i \dots \psi_a \bar{\psi}_a \uparrow_b \uparrow_a \rangle$ is a triplet and is an eigenfunction of \mathcal{L}^2

\uparrow_B
 \downarrow_a

Open-shell singlets are not eigenfunctions of L^2 .

However, by taking appropriate linear combinations of singlet determinants, one can form spin-adapted configurations, which are eigenfunctions of L^2 .

$$H_2 \text{ minimal basis: } |\Psi_1^2\rangle = |z\bar{z}\rangle$$

Singlet:

$$|\Psi_1^2\rangle = |\Psi_{\bar{z}}^2\rangle - |\Psi_z^2\rangle$$

$$\begin{aligned} |\Psi_1^2\rangle &= \frac{1}{\sqrt{2}} (|\Psi_{\bar{z}}^2\rangle - |\Psi_z^2\rangle) = \\ &= \frac{1}{2} \left[\begin{vmatrix} \psi_g(1)\alpha(1) & \psi_u(1)\beta(1) \\ \psi_g(2)\alpha(2) & \psi_u(2)\beta(2) \end{vmatrix} - \begin{vmatrix} \psi_g(1)\beta(1) & \psi_u(1)\alpha(1) \\ \psi_g(2)\beta(2) & \psi_u(2)\alpha(2) \end{vmatrix} \right] \\ &= \frac{1}{2} [\psi_g(1)\psi_u(2) + \psi_u(1)\psi_g(2)] (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \end{aligned}$$

$$|\Psi_1^2\rangle = \frac{1}{\sqrt{2}} (|\Psi_{\bar{z}}^2\rangle + |\Psi_z^2\rangle) =$$

$$= \frac{1}{2} [\psi_g(1)\psi_u(2) - \psi_u(1)\psi_g(2)] (\alpha(1)\beta(2) + \beta(1)\alpha(2))$$

Exercise 2.39. Using $\mathcal{L}^2 = \mathcal{L}_- \mathcal{L}_+ + \mathcal{L}_z + \mathcal{L}_z^2$
 show that $|{}^1\Psi_1^2\rangle$ is a singlet and $|{}^3\Psi_1^2\rangle$ is
 a triplet.

$$\mathcal{L}_z \frac{1}{\sqrt{2}} (|{}^1\Psi_1^2\rangle \pm |{}^3\Psi_1^2\rangle) = \frac{1}{\sqrt{2}} (\mathcal{L}_z |{}^1\Psi_1^2\rangle \pm \mathcal{L}_z |{}^3\Psi_1^2\rangle) = 0$$

$$(\mathcal{L}_z + \mathcal{L}_z^2) |{}^1,3\Psi_1^2\rangle = 0$$

$|{}^1\Psi_1^2\rangle$:

$$\mathcal{L}_- \mathcal{L}_+ (\alpha(1)\beta(2) - \beta(1)\alpha(2)) =$$

$$= (s_-(1) + s_-(2))(s_+(1) + s_+(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2)) =$$

$$= (s_-(1) + s_-(2)) [\alpha(1)\alpha(2) - \alpha(1)\alpha(2)] = 0$$

$$\boxed{\mathcal{L}^2 |{}^1\Psi_1^2\rangle = 0}$$

$$\underline{|{}^3\Psi_1^2\rangle}: \quad \mathcal{L}_- \mathcal{L}_+ (\alpha(1)\beta(2) + \beta(1)\alpha(2)) =$$

$$= (s_-(1) + s_-(2))(s_+(1) + s_+(2))(\alpha(1)\beta(2) + \beta(1)\alpha(2))$$

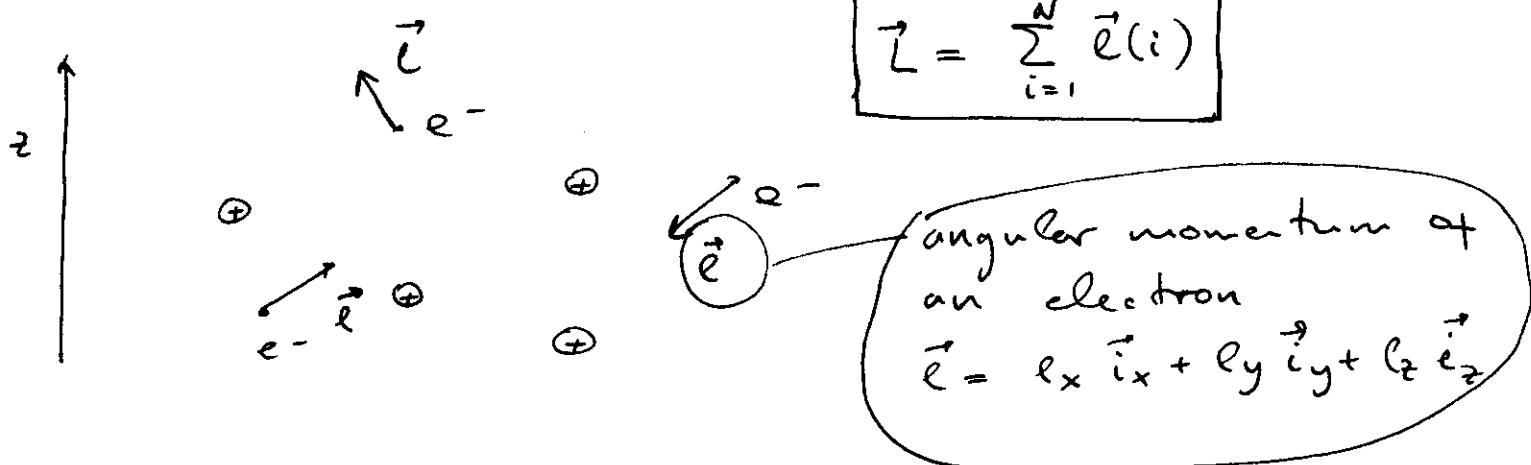
$$= (s_-(1) + s_-(2)) (\alpha(1)\alpha(2) + \alpha(1)\alpha(2)) =$$

$$= 2 (\alpha(1)\beta(2) + \beta(1)\alpha(2))$$

$s(s+1), s=1$

$$\boxed{\mathcal{L}^2 |{}^3\Psi_1^2\rangle = 2 |{}^3\Psi_1^2\rangle}$$

Molecular terms: Some classification



Projection of the total angular momentum on a molecular axis (usually z) is a "good" quantum number ($[L_z, H] = 0$). The algebraic sum of all angular momentum projections makes M_L :

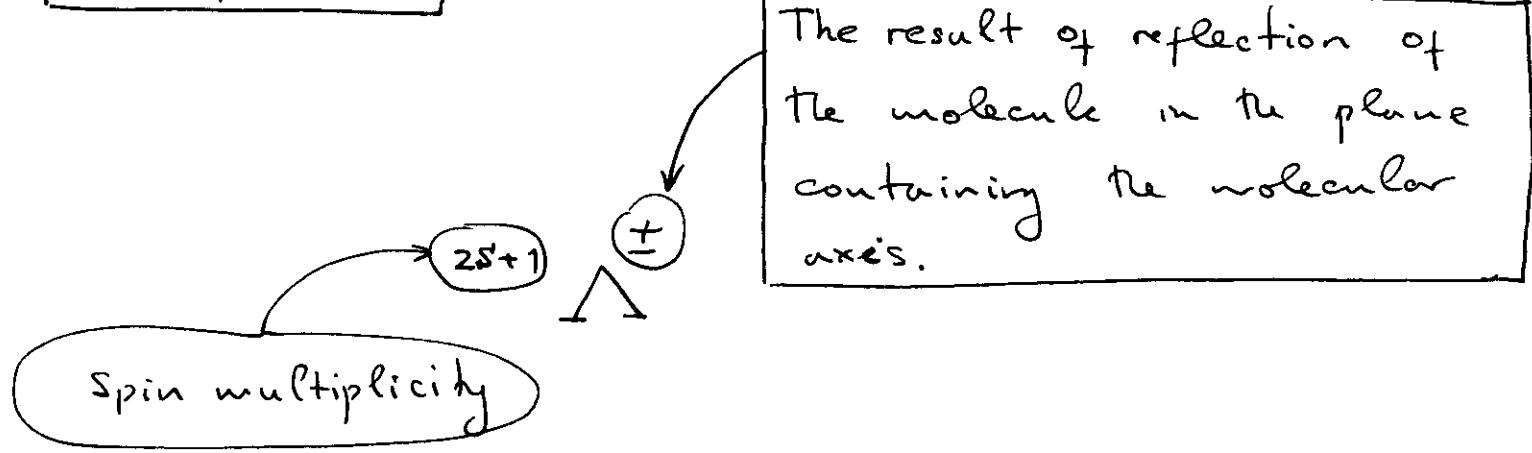
$$M_L = \sum_{i=1}^N m(i) = \sum_{i=1}^N \frac{l_z(i)}{\hbar}$$

The absolute value of M_L

$$\Delta = |M_L|$$

is used to classify molecular terms

Classification



H₂ molecule: When only 1s orbitals are included, the angular momentum of the molecule is zero. Only Σ states exist.

Electronic terms of H₂:

$$\Psi_0 = |\Psi_g \bar{\Psi}_g\rangle \leftarrow {}^1\Sigma_g^+$$

$$|\Psi_1^{\bar{2}}\rangle = |\bar{\Psi}_g \bar{\Psi}_u\rangle \leftarrow {}^3\Sigma_u^+ \quad (m_s = -1)$$

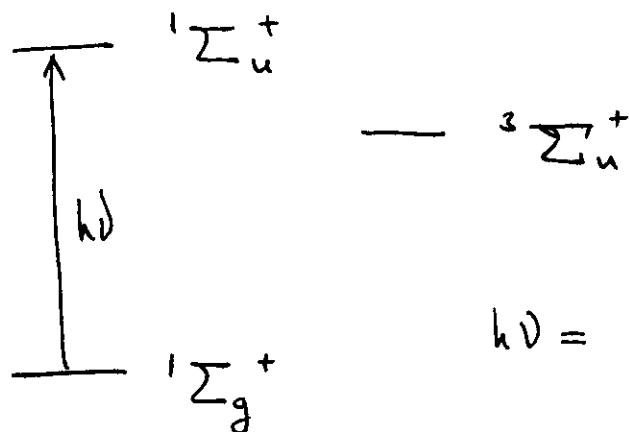
$$|\Psi_1^2\rangle = |\Psi_g \Psi_u\rangle \leftarrow {}^3\Sigma_u^+ \quad (m_s = +1)$$

$$|{}^1\Psi_1^2\rangle = \frac{1}{\sqrt{2}} (|\Psi_1^{\bar{2}}\rangle - |\Psi_1^2\rangle) \leftarrow {}^1\Sigma_u^+$$

$$|{}^3\Psi_1^2\rangle = \frac{1}{\sqrt{2}} (|\Psi_1^{\bar{2}}\rangle + |\Psi_1^2\rangle) \leftarrow {}^3\Sigma_u^+$$

$$|\Psi_{12}^{34}\rangle = |\Psi_{1T}^{2\bar{2}}\rangle = |\Psi_u \bar{\Psi}_u\rangle \leftarrow {}^1\Sigma_g^+$$

${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ transition in H_2



$$\begin{aligned} h\nu &= E({}^1\Sigma_u^+) - E({}^1\Sigma_g^+) \\ &= (g|u|g) + (u|u|u) + (gg|uu) \\ &\quad + (gu|ug) - 2(g|u|g) - (gg|gg) \end{aligned}$$

$$h\nu = \underbrace{(u|h|u) - (g|h|g)}_{\text{one-electron contribution}} + \underbrace{(gg|uu) + (gu|ug) - (gg|gg)}_{\text{two-electron contribution}}$$

$$= +1.185 - 0.575 + 0.558 + 0.140 - 0.566$$

$$= 0.602 \text{ a.u.} = 16.4 \text{ eV}$$

Exercise 2.40

$$\text{Show that : } E_s = \langle {}^1\Psi_1^2 | H | {}^1\Psi_1^2 \rangle = h_{11} + h_{22} + J_{12} + K_{12}$$

$$E_T = \langle {}^3\Psi_1^2 | H | {}^3\Psi_1^2 \rangle = h_{11} + h_{22} + J_{12} - K_{12}$$

$$E_s = \frac{1}{2} \left(\langle \Psi_1^{\bar{2}} | H | \Psi_1^{\bar{2}} \rangle + \langle \Psi_1^2 | H | \Psi_1^2 \rangle - \langle \Psi_1^{\bar{2}} | H | \Psi_1^2 \rangle - \langle \Psi_1^2 | H | \Psi_1^{\bar{2}} \rangle \right)$$

$$= \frac{1}{2} \left((g|hg) + (u|hu) + (gg|uu) + (gl|hg) + (ul|hu) \right. \\ \left. + (gg|uu) - \langle \Psi_g \bar{\Psi}_u || \bar{\Psi}_g \Psi_u \rangle - \langle \bar{\Psi}_g \Psi_u || \Psi_g \bar{\Psi}_u \rangle \right)$$

$$= (g|hg) + (u|hu) + (gg|uu) + (gu|ug)$$

$$\langle \Psi_g \bar{\Psi}_u || \bar{\Psi}_g \Psi_u \rangle = \underbrace{\langle \Psi_g \bar{\Psi}_u | \bar{\Psi}_g \Psi_u \rangle}_{\circ} - \langle \Psi_g \bar{\Psi}_u | \Psi_u \bar{\Psi}_g \rangle = \\ = (gu|ug)$$

$$E_s = (g|hg) + (u|hu) + (gg|uu) + (gu|ug)$$

$$E_T = (g|hg) + (u|hu) + (gg|uu) - (gu|ug)$$



intersystem
crossing

Triplet energy is lower than singlet energy by
2 (gu|ug)

One can in principle measure exchange integrals by means of spectroscopy !

Dipolar transitions

External electromagnetic field polarizes the electronic density of a molecule. This polarization creates an induced dipole moment, which is coupled to the field with the energy

$$H_{\text{int}} = - \hat{\vec{\mu}} \cdot \vec{E}$$

↓ ↑
 dipole moment operator electric field

The off-diagonal matrix element $\langle \psi_{\text{in}} | H_{\text{int}} | \psi_{\text{fin}} \rangle$ mixes the initial, ψ_{in} , and final, ψ_{fin} , wavefunctions:

$$\langle \psi_{\text{in}} | H_{\text{int}} | \psi_{\text{fin}} \rangle = - \langle \psi_{\text{in}} | \hat{\vec{\mu}} | \psi_{\text{fin}} \rangle \cdot \vec{E}$$

Transition dipole:

$$\langle \psi_{\text{in}} | H_{\text{int}} | \psi_{\text{fin}} \rangle = (\psi_{\text{in}} | \hat{\vec{\mu}} | \psi_{\text{fin}}) (\chi_{\text{in}} | \chi_{\text{fin}})$$

electronic wave functions nuclear wave functions

The absorption cross section $\beta(\omega)$ is proportional to the transition dipole averaged over the vibrational excitations of the molecule.

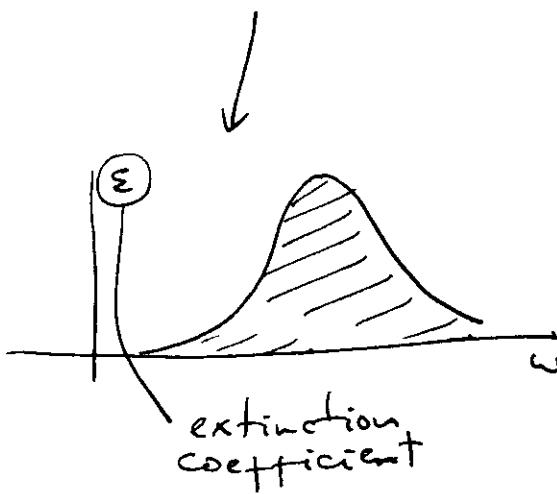
Dipolar, spin-allowed transitions

$$\beta(\omega) \propto |(\phi_{in} | \hat{\mu} | \phi_{fin})|^2 \langle (X_{in} | X_{fin})^2 \rangle$$

↑
Franck-Condon factor of
optical transitions

The total absorption intensity is defined by the transition dipole

$$\int \beta(\omega) d\omega = \text{Const} \times |(\phi_{in} | \hat{\mu} | \phi_{fin})|^2$$



Transition dipole defines the
intensity of optical transi-
tions

For a transition dipole to be non-zero, the total spins of the initial and final states should be equal and ϕ_{in} and ϕ_{fin} should have different symmetry with respect to inversion

$$|\langle g | \hat{\mu} | u \rangle \neq 0|$$

$$\langle g | \hat{\mu} | g \rangle = \langle u | \hat{\mu} | u \rangle = 0$$

Mit

$$M_{if} = \langle \Psi_g \bar{\Psi}_g | z(1) + z(2) | \Psi_i^2 \rangle$$

$$= \frac{1}{2\sqrt{2}} \langle \Psi_g(1) \Psi_g(2) (\alpha(1)\beta(2) - \alpha(2)\beta(1)) | z(1) + z(2) |$$
$$(\psi_g(1)\psi_u(2) + \psi_u(1)\psi_g(2)) (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \rangle$$

$$\langle \alpha(1)\beta(2) - \alpha(2)\beta(1) | \alpha(1)\beta(2) - \beta(1)\alpha(2) \rangle = 2$$

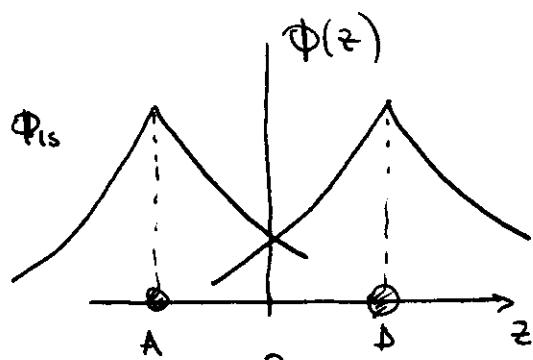
$$= \frac{1}{\sqrt{2}} \langle \psi_g(1) \psi_g(2) | z(1) + z(2) | \psi_g(1) \psi_u(2) + \psi_u(1) \psi_g(2) \rangle$$

$$= \sqrt{2} \langle \psi_g | z | \psi_u \rangle = \underline{1.505 \text{ a.u.}}$$

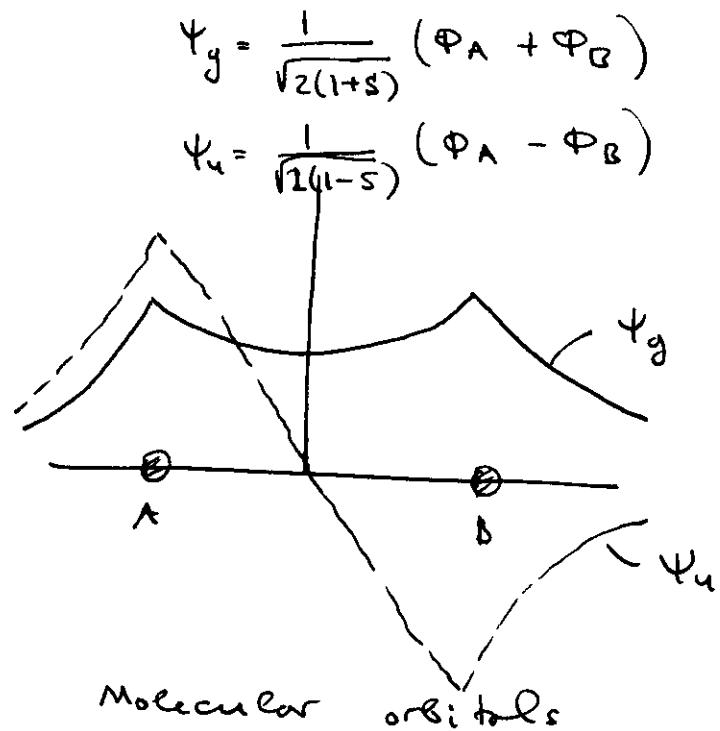
The oscillator strength

$$f_{if} = \frac{2}{3} M_{if}^2 (E_f - E_i) = 0.909$$

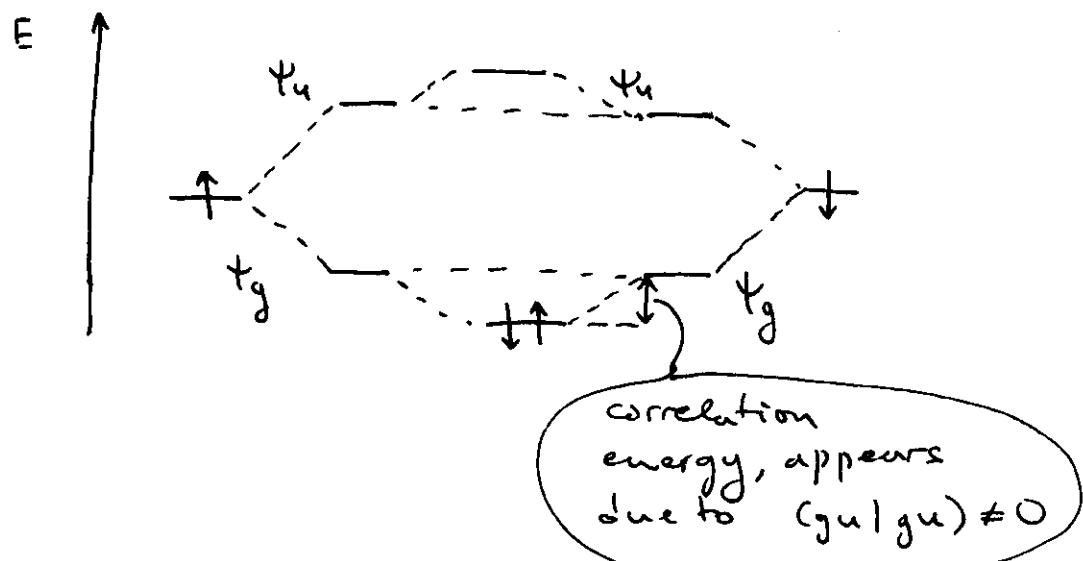
H_2 : gerade configuration



Atomic orbitals



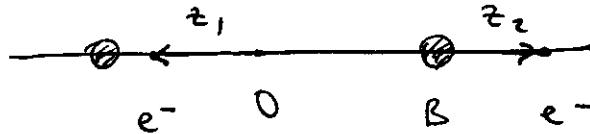
Molecular orbitals



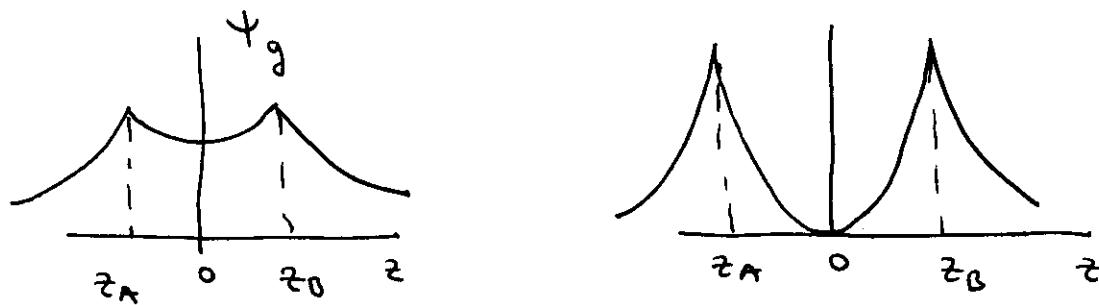
$$|{}^1\Sigma_g^+ \rangle_1 = 0.994 |\psi_g \bar{\psi}_g \rangle - 0.1106 |\psi_u \bar{\psi}_u \rangle$$

$$|{}^1\Sigma_g^+ \rangle_2 = 0.1106 |\psi_g \bar{\psi}_g \rangle + 0.994 |\psi_u \bar{\psi}_u \rangle$$

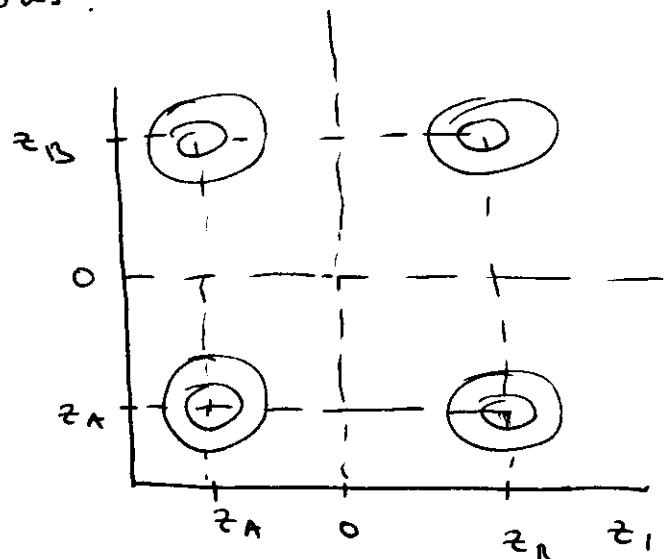
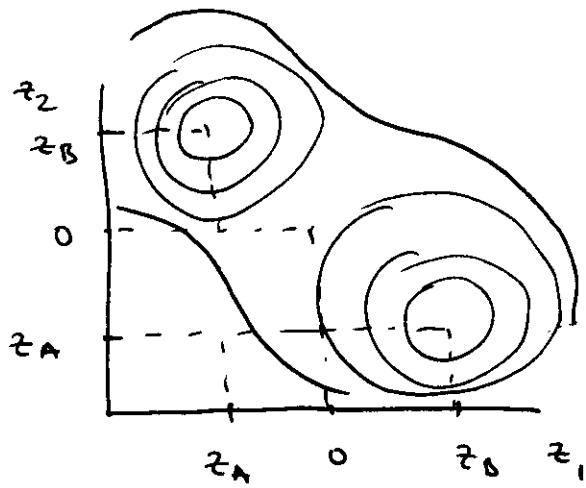
Gerade configuration: Contour plot



One-electron wave functions:



Two-electron wave functions:



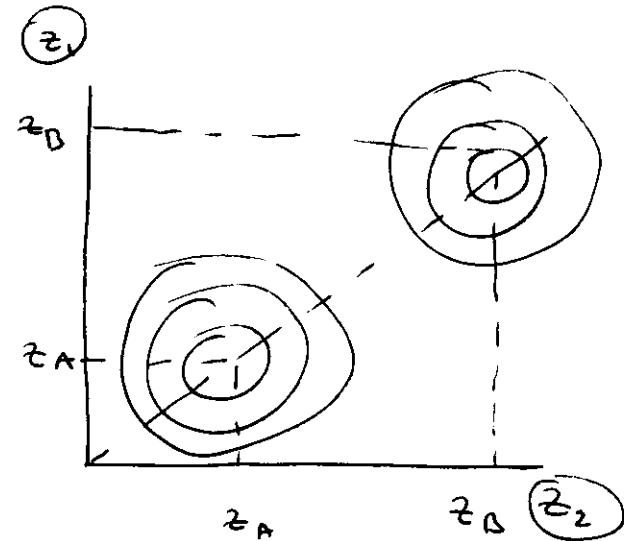
$^1\Sigma_g^+$ ground configuration
Bonding two-electron orbital

$^1\Sigma_g^+$ excited state
antibonding two-electron orbital

H_2 : singlet

$$|^1\text{I}_{\text{u}}^+ \rangle = \frac{1}{2} \left[\underbrace{\Psi_{\text{g}}(1)\Psi_{\text{u}}(2) + \Psi_{\text{u}}(1)\Psi_{\text{g}}(2)}_{\text{symmetric linear combination of spatial wave functions}} \right] \left[\underbrace{\alpha(1)\beta(2) - \beta(1)\alpha(2)}_{\text{antisymmetric linear combination of spin wave functions}} \right]$$

$$\underbrace{\Psi_{\text{g}}(z)\Psi_{\text{u}}(-z) + \Psi_{\text{u}}(z)\Psi_{\text{g}}(-z)}_{\text{the singlet wave function vanishes when the electrons are located exactly opposite to each other}} = 0$$



The two-electron density has maximum when both electrons are localized on the same nucleus

Singlets are ionically correlated

H_2 : triplet states

$$|{}^3\Sigma_u^+ \rangle = \frac{1}{\sqrt{2}} [\Psi_g(1)\Psi_u(2) - \Psi_g(2)\Psi_u(1)]$$

antisymmetric combination of spatial wave functions

$$\alpha(1)\alpha(2)$$

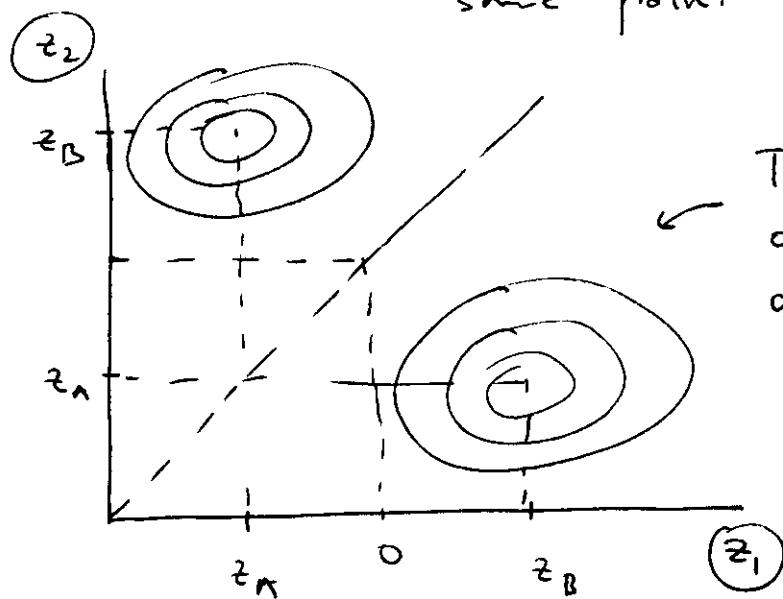
$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\beta(1)\beta(2)$$

symmetric combination of spin wave functions

$$\Psi_g(z)\Psi_u(z) - \Psi_g(z)\Psi_u(z) = 0$$

two electrons with parallel spin cannot be found at the same point in space



Two-electron density function on the molecular axis

The maximum electronic density corresponds to two electrons localized on different nuclei

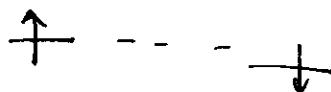
The triplet state is covalently correlated

Unrestricted determinants

Restricted
determinants



Unrestricted
determinants



(Li) : $|\psi_{1s} \bar{\psi}_{1s} \psi_{2s} \rangle$

RHF

$|\psi_{1s}^\alpha \bar{\psi}_{1s}^\beta \psi_{2s}^\gamma \rangle$

UHF

unrestricted determinant

Unrestricted determinants are not orthonormal:

$$\langle \psi_i^\alpha | \psi_j^\alpha \rangle = \delta_{ij}$$

$$\langle \psi_i^\alpha | \psi_j^\beta \rangle = \delta_{ij}$$

$$\langle \psi_i^\alpha | \psi_j^\beta \rangle = S_{ij}^{\alpha\beta} \leftarrow \boxed{\text{overlap integral}}$$

Unrestricted determinants are not eigenfunctions of L^2 .

They cannot be spin-adapted by combining a small number of unrestricted determinants.

Exercise 2.41

② For the determinant $|k\rangle = |\Psi_1^\alpha \bar{\Psi}_1^\rho\rangle$ show that $|k\rangle$ is an eigenstate of \mathcal{L}^2 only if $\Psi_1^\alpha = \Psi_1^\rho$.

$$\mathcal{L}^2 |\Psi_1^\alpha \bar{\Psi}_1^\rho\rangle = (\mathcal{L}_z + \mathcal{L}_z^2 + \mathcal{L}_- \mathcal{L}_+) |\Psi_1^\alpha \bar{\Psi}_1^\rho\rangle$$

$$|\Psi_1^\alpha \bar{\Psi}_1^\rho\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \Psi_1^\alpha(1) \alpha(1) & \Psi_1^\rho(1) \rho(1) \\ \Psi_1^\alpha(2) \alpha(2) & \Psi_1^\rho(2) \rho(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} [\Psi_1^\alpha(1) \alpha(1) \Psi_1^\rho(2) \rho(2) - \Psi_1^\rho(1) \Psi_1^\alpha(2) \rho(1) \alpha(2)]$$

$$\mathcal{L}_z = S_z(1) + S_z(2)$$

$$\mathcal{L}_z |\Psi_1^\alpha \bar{\Psi}_1^\rho\rangle = 0$$

$$\mathcal{L}_+ |\Psi_1^\alpha \bar{\Psi}_1^\rho\rangle = \frac{1}{\sqrt{2}} \left[\frac{1}{2} \Psi_1^\alpha(1) \Psi_1^\rho(2) \alpha(1) \alpha(2) + \frac{1}{2} \Psi_1^\alpha(1) \Psi_1^\rho(2) \alpha(1) \alpha(2) \right]$$

$$- \Psi_1^\rho(1) \Psi_1^\alpha(2) \alpha(1) \alpha(2)]$$

$$= \frac{1}{\sqrt{2}} \alpha(1) \alpha(2) \underbrace{[\Psi_1^\alpha(1) \Psi_1^\rho(2) - \Psi_1^\rho(1) \Psi_1^\alpha(2)]}_{\Psi_1^\alpha = \Psi_1^\rho}$$

(8) Show that

$$\langle k | \mathcal{L}^2 | k \rangle = 1 - |S_{11}^{\alpha\beta}|^2$$

$$\mathcal{L}_- \mathcal{L}_+ |\psi_1^\alpha \bar{\psi}_1^\beta\rangle =$$

$$= (s_-(1) + s_-(2)) \frac{1}{r_2} \alpha(1) \alpha(2) [+\alpha(1) \psi_1^\beta(2) - \psi_1^\beta(1) \psi_1^\alpha(2)]$$

$$= \frac{1}{r_2} (\alpha(1) \beta(2) + \beta(1) \alpha(2)) [+\alpha(1) \psi_1^\beta(2) - \psi_1^\beta(1) \psi_1^\alpha(2)]$$

$$\langle k | \mathcal{L}_- \mathcal{L}_+ | k \rangle =$$

$$= \frac{1}{2} \left\langle \psi_1^\alpha(1) \psi_1^\beta(2) \alpha(1) \beta(2) - \psi_1^\beta(1) \psi_1^\alpha(2) \beta(1) \alpha(2) \right|$$

$$\left(\alpha(1) \beta(2) + \beta(1) \alpha(2) \right) [+\alpha(1) \psi_1^\beta(2) - \psi_1^\beta(1) \psi_1^\alpha(2)] \rangle =$$

$$= 1 - |S_{11}^{\alpha\beta}|^2$$

$$\langle \psi_1^\alpha(1) \psi_1^\beta(2) \alpha(1) \beta(2) | \alpha(1) \beta(2) [+\alpha(1) \psi_1^\beta(2) - \psi_1^\beta(1) \psi_1^\alpha(2)] \rangle$$

$$= \langle +\alpha(1) \psi_1^\beta(2) | \psi_1^\alpha(1) \psi_1^\beta(2) \rangle - \langle +\alpha(1) | \psi_1^\beta(1) \rangle \langle \psi_1^\beta(2) | \psi_1^\alpha(1) \rangle$$

1
||

The expectation values of \mathcal{L}^2
for unrestricted determinants
are always too large!

$$\begin{array}{ccc} \downarrow & & \downarrow \\ S_{11}^{\alpha\beta} & & (S_{11}^{\alpha\beta})^* \\ \searrow & & \swarrow \\ & & |S_{11}^{\alpha\beta}|^2 \end{array}$$

Hartree - Fock Theory

Theory of molecular orbitals is a concept

HF theory is a quantitative realization of the MO theory

$$\left\{ \begin{array}{l} N\text{-electron} \\ \text{wave function} \end{array} \right\} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \dots & \chi_N(1) \\ \vdots & & \vdots \\ \chi_1(N) & \dots & \chi_N(N) \end{vmatrix}$$

Matrix formulation

$$[CI] \rightarrow \hat{H} = \begin{vmatrix} \langle \psi_1^1 | H | \psi_1^1 \rangle & \dots & \langle \psi_N^1 | H | \psi_N^1 \rangle \\ \vdots & & \vdots \\ \langle \psi_1^k | H | \psi_1^k \rangle & \dots & \langle \psi_N^k | H | \psi_N^k \rangle \end{vmatrix}$$

$$[HF] \rightarrow E_0 = \langle \psi_0 | H | \psi_0 \rangle$$

$$\frac{\delta E_0}{\delta \psi_0} = 0$$

variation principle,
HF equations

$$[\text{SCF}] \quad \chi = \sum c_j \Phi_j^{AO}$$

↑ molecular orbital ↑ atomic orbitals

Gaussian contraction

$$\Phi_j^{AO} = \sum_{k=1}^M d_k^j g_k^j()$$

↓ spatial coordinates

$$\delta \mathcal{L} = \sum_{a=1}^N \int d\vec{x}_1 8\chi_a^*(1) \left[h(1)\chi_a(1) + \sum_{b=1}^N (J_b(1) - K_b(1))\chi_a(1) - \sum_{b=1}^N \epsilon_{ba}\chi_b(1) \right] + \text{e.c.} = 0$$

Since $\delta \chi_a$ is arbitrary, one gets

$$\boxed{\left[h(1) + \sum_b (J_b(1) - K_b(1)) \right] \chi_a(1) = \sum_b \epsilon_{ba} \chi_b(1)}$$

one-particle operator

$$h(1) = -\frac{1}{2}\nabla_1^2 - \sum_A \frac{z_A}{r_{1A}}$$

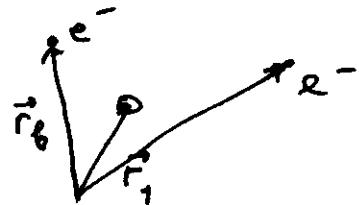
Coulomb operator

$$J_b(1) = \int d\vec{x}_2 |\chi_b(2)| \frac{1}{r_{12}}$$

$\sum_b J_b(1)$ represents the average local potential at \vec{r}_1 arising from all $N-1$ electrons

Exchange operator:

$$K_b(1)\chi_a(1) =$$



$$= \left[\int d\vec{x}_2 \chi_b^*(2) \frac{1}{r_{12}} \chi_a(2) \right] \chi_b(1)$$

Unlike the Coulomb operator, the exchange operator is nonlocal; when it acts on $\chi_a(1)$, the result arises from an integral over $\chi_a(2)$.

Derivation of the HF equations

HF equations search for the variational minimum of the ground-state energy

$$E_0 = \langle \psi_0 | H | \psi_0 \rangle = \sum_b [b | h | b] + \sum_{a>b} [a a | B B] - [a b | B a]$$

$J_{ab} = \int |\Psi_a(\vec{r}_1)|^2 \frac{1}{r_{12}} |\Psi_b(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2$
 $K_{ab} = \int \Psi_a^*(\vec{r}_1) \Psi_b(\vec{r}_1) \frac{1}{r_{12}} \Psi_b^*(\vec{r}_2) \Psi_a(\vec{r}_1) d\vec{r}_1 d\vec{r}_2$

Method of Lagrange multipliers:

①. Lagrange functional

$$\int d\vec{r}_1 d\omega_1 \chi_a^*(1) \chi_b(1) = [a | b] = \delta_{ab}$$

$$\mathcal{L}[\{\chi_a\}] = E_0[\{\chi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} ([a | b]) - \delta_{ab}$$

$$\textcircled{2}. \quad \delta \mathcal{L} = \delta E_0 - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} \delta [a | b] = 0$$

$$\begin{aligned} \delta \mathcal{L} = & \sum_{a=1}^N [\delta \chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N \left([\delta \chi_a \chi_a | \chi_b \chi_b] - \right. \\ & \left. [\delta \chi_a \chi_b | \chi_b \chi_a] \right) - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} [\delta \chi_a | \chi_b] + \\ & + \text{complex conjugate} \end{aligned}$$

The Fock operator

The HF equation:

$$[h(i) + \sum_{b \neq a} J_b(i) - \sum_{b \neq a} K_b(i)] \chi_a(i) = \varepsilon_a \chi_a(i)$$

When $b = a$

$$J_b \chi_a = J_a \chi_a = \int d\vec{r}_1 | \chi_a(\vec{r}_1) |^2 \frac{1}{r_{12}} \chi_a(2)$$

$$K_a \chi_a = \int d\vec{r}_1 | \chi_a(\vec{r}_1) |^2 \frac{1}{r_{12}} \chi_a(2)$$

$$J_a \chi_a - K_a \chi_a = 0$$

The Fock operator:

$$f(i) = h(i) + \sum_b [J_b(i) - K_b(i)]$$

The HF equation:

$$f |\chi_a\rangle = \varepsilon_a |\chi_a\rangle$$

and $f(i)$ is the sum of a core-Hamiltonian operator $h(i)$ and an effective one-electron potential

$$v^{HF}(i) = \sum_b [J_b(i) - K_b(i)]$$

The Canonical HF equations

Unitary transformation of spin orbitals:

$$\chi_a' = \sum_b \chi_b U_{ba}, \quad \underbrace{U^+ U = 1}_{\text{unitary}}$$

The Slater determinant:

$$|\Psi_0\rangle = \frac{1}{\sqrt{N!}} \det(\tilde{A}), \quad \tilde{A} = \begin{pmatrix} \chi_1(1) & \dots & \chi_N(1) \\ \vdots & & \vdots \\ \chi_1(N) & \dots & \chi_N(N) \end{pmatrix}$$

Under unitary transformations

$$\tilde{A}' = A U = \begin{pmatrix} \chi_1(1) & \dots & \chi_N(1) \\ \vdots & & \vdots \\ \chi_1(N) & \dots & \chi_N(N) \end{pmatrix} \begin{pmatrix} U_{11} & \dots & U_{1N} \\ \vdots & & \vdots \\ U_{N1} & \dots & U_{NN} \end{pmatrix}$$

$$\det(AU) = \det(A) \det(U), \quad \det(U) = e^{i\phi}$$

Under unitary transformations, the transformed determinant $|\Psi_0'\rangle$ may differ from $|\Psi_0\rangle$ only by a phase factor.

Spin orbitals that make the total energy stationary are not unique.

The method of Lagrange multipliers leads to the HF equation in the form

$$f |x_a\rangle = \sum_b \varepsilon_{ba} |x_b\rangle$$

The Lagrange multipliers transform under the unitary transformations of $\{x_a\}$ as

$$\tilde{\Sigma}' = \tilde{U}^+ \tilde{\Sigma} \tilde{U},$$

that is

$$\varepsilon'_{ab} = \sum_{d,c} (U^+)^{ad} \varepsilon_{dc} (U)_{cb}$$

It is always possible to find a unitary matrix \tilde{U} that diagonalizes $\tilde{\Sigma}$. The unique set of spin orbitals obtained from a solution of the diagonalization problem is called the set of canonical spin orbitals. The form of HF equations

$$f |x_a\rangle = \varepsilon_a |x_a\rangle$$

is called the canonical HF equations.

Homework: Full CI solution for the ground-state wavefunction of H_2

$$\tilde{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} = \begin{pmatrix} -1.804 & 0.140 \\ 0.140 & -0.568 \end{pmatrix}$$

$$\vec{c}_1 = \begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix}$$

$$\tan 2\theta = \frac{2H_{12}}{\Delta H} = \frac{2H_{12}}{H_{22} - H_{11}}.$$

$$\theta = \frac{1}{2} \tan^{-1} \frac{0.28}{1.236}$$

$$\vec{c}_2 = \begin{pmatrix} \sin\theta \\ -\cos\theta \end{pmatrix}$$

$$\cos\theta = 0.994$$

$$\sin\theta = 0.111$$

$$\Psi_1(\text{CI}) = 0.994 |\Psi_0\rangle + 0.111 |\Psi_{12}^{34}\rangle$$

$$\Psi_2(\text{CI}) = 0.111 |\Psi_0\rangle - 0.994 |\Psi_{12}^{34}\rangle$$

Orbital energies

Fock operator is a Hermitian operator with the eigenstate x_i and the eigenvalue ε_i :

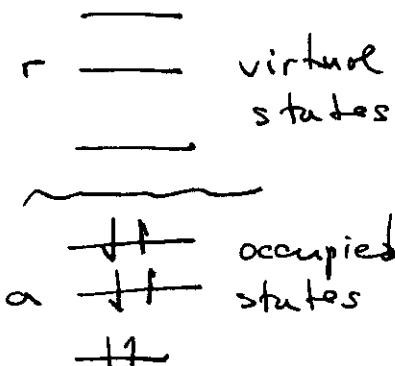
$$f|x_i\rangle = \varepsilon_i|x_i\rangle$$

$$\langle x_i | f | x_j \rangle = \varepsilon_i \delta_{ij}$$

Exercise 3.1

$$\varepsilon_i = \langle x_i | h + \sum_b (J_b - k_b) | x_i \rangle =$$

$$= \langle i | h | i \rangle + \sum_b \langle i b | i b \rangle$$



For a within the occupied shell

$$\varepsilon_a = \langle a | h | a \rangle + \sum_{b \neq a} (\langle ab | ab \rangle - \langle ba | ba \rangle)$$

For r within the virtual states shell

$$\varepsilon_r = \langle r | h | r \rangle + \sum_{b=1}^{\infty} (\langle rb | rb \rangle - \langle br | br \rangle)$$

Total energy of the occupied shell

$$\sum_{a=1}^n \varepsilon_a = \sum \langle a | h | a \rangle + \sum_a \sum_b \langle ab | ab \rangle$$

$$\neq E_o = \sum \langle a | h | a \rangle + \frac{1}{2} \sum_a \sum_b \langle ab | ab \rangle$$

Total energy of the state $|4o\rangle$ is not just the sum of the orbital energies!

Koopmans' Theorem

$$IP = {}^{N-1}E_c - {}^N E_0$$

electron \rightarrow
removed from X_c

$$EA = {}^N E_0 - {}^{N+1} E^r$$

electron \rightarrow placed
on X_r

$${}^N E_0 = \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_a \sum_b \langle a b | | a b \rangle$$

$${}^{N-1} E_c = \sum_{a \neq c} \langle a | h | a \rangle + \frac{1}{2} \sum_{a \neq c} \sum_{b \neq c} \langle a b | | a b \rangle$$

$$\begin{aligned} IP &= - \langle e | h | c \rangle - \frac{1}{2} \sum_a \langle a c | | a c \rangle - \frac{1}{2} \sum_a \langle c a | | c a \rangle \\ &= - \langle e | h | c \rangle - \sum_a \langle c a | | c a \rangle = - \varepsilon_c \end{aligned}$$

$${}^{N+1} E^r = \langle r | h | r \rangle + \sum_b \langle r b | | r b \rangle$$

$$EA = - \varepsilon_r$$

IPs for $H_2 O$

IB₂ IB₁

Koopmans' 0.7002 0.4895

FCI 0.6836 0.4350

$$PI = - \varepsilon_c$$

$$EA = - \varepsilon_r$$

This is a "frozen orbital" approximation neglecting relaxation of orbitals in the $(N \pm 1)$ states.

Brillouin's theorem

One-excitation corrections to the ground-state energy:

$$|\Psi_0\rangle = c_0 |\Psi_0\rangle + c_a' |\Psi_a'\rangle$$

$$\begin{pmatrix} \langle \Psi_0 | H | \Psi_0 \rangle & \langle \Psi_0 | H | \Psi_a' \rangle \\ \langle \Psi_a' | H | \Psi_0 \rangle & \langle \Psi_a' | H | \Psi_a' \rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_a' \end{pmatrix} = E_0' \begin{pmatrix} c_0 \\ c_a' \end{pmatrix}$$

new eigenenergy

The mixing of the ground-state energy with single excitations depends on $\langle \Psi_a' | H | \Psi_0 \rangle$

$$\langle \Psi_a' | H | \Psi_0 \rangle = \langle a | h(r) | r \rangle + \sum_b \langle a b | h(r) | b \rangle$$

$$= \langle x_{af} | x_r \rangle$$

Exercise 3.1

Since x_a and x_r are eigenstates of f ,

$$\langle x_a | f | x_r \rangle = 0$$

and

$$\begin{pmatrix} E_0 & 0 \\ 0 & \langle \Psi_a' | H | \Psi_a' \rangle \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = E_0 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

The HF ground state is stable toward singlet excitations.

Brillouin's theorem: Singly excited determinants $|\Psi_a'\rangle$ do not interact directly with a reference HF determinant $|\Psi_0\rangle$: $\langle \Psi_0 | H | \Psi_a' \rangle = 0$.

The HF Hamiltonian

Two basic approaches can be used to find a solution of the N -electron problem:

Searching for
the best approximate
wave function

Searching for the best
approximate
Hamiltonian

The HF Hamiltonian:

$$H_0 = \sum_{i=1}^N f(i)$$

$$\begin{aligned} H_0 |\Psi_0\rangle &= \sum_{i=1}^N f(i) \frac{1}{\sqrt{N!}} \sum (-1)^{P_n} P_n \{x_i(1) \dots x_k(N)\} \\ &= \sum_{i=1}^N \frac{1}{\sqrt{N!}} \sum (-1)^{P_n} P_n \{x_i(1) \dots f(i)x_{\alpha}(1) \dots x_k(N)\} \\ &\quad \underbrace{\qquad}_{\text{Ex } x_{\alpha}(i)} \\ &= \sum_a \varepsilon_a |H_0\rangle \end{aligned}$$

$|\Psi_0\rangle$ is the exact eigenstate of the HF Hamiltonian

The perturbation to the HF Hamiltonian is the difference between the exact Hamiltonian and H_0

$$\overline{V} = \overline{H - H_0} = \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N V^{HF}(i)$$

Möller-Plesset (MP) perturbation approaches

In perturbation approaches, one uses the complete set of eigenfunctions obtained for H_0 to build corrections to the energy due to the perturbation V

$$\varepsilon_0 = E_0^{(0)} + E_0^{(1)} + \dots$$

If one can calculate the infinite series, it gives the exact ground-state energy. The first order correction is

$$E_0 = \underbrace{\sum_a \varepsilon_a}_{\text{eigenvalue of } H_0} + \underbrace{\langle \psi_0 | V | \psi_0 \rangle}_{\text{first order correction}}$$

$$\langle \psi_0 | V | \psi_0 \rangle = \langle \psi_0 | \sum_{j>i} r_{ji}^{-1} - \sum_i \sum_B [k_s(i) - k_s(i)] | \psi_0 \rangle$$

$$\langle \psi_0 | \sum_{j>i} r_{ji}^{-1} | \psi_0 \rangle = \frac{1}{2} \sum_{ab} \langle ab || ab \rangle$$

$$\langle \psi_0 | V^{\text{HF}} | \psi_0 \rangle = \sum_{ab} \langle ab || ab \rangle$$

$$\begin{aligned} \langle \psi_0 | V | \psi_0 \rangle &= \frac{1}{2} \sum_{ab} \langle ab || ab \rangle - \sum_{ab} \langle ab || ab \rangle \\ &= -\frac{1}{2} \sum_{ab} \langle ab || ab \rangle \end{aligned}$$

$$E_0 = \sum_a \langle a | h(a) \rangle + \sum_{ab} \langle ab || ab \rangle - \frac{1}{2} \sum_{ab} \langle ab || ab \rangle$$

Permutation operator

Coulomb operator:

$$J_B^{(1)} \chi_a(1) = \left[\int d\vec{x}_2 |\chi_b(2)|^2 \frac{1}{r_{12}} \right] \chi_a(1)$$

Exchange operator:

$$K_B(1) \chi_a(1) = \left[\int d\vec{x}_2 \chi_b^*(2) \chi_a(2) \frac{1}{r_{12}} \right] \chi_b(1)$$

Permutation operator:

$$K_B(1) \chi_a(1) = \left[\int d\vec{x}_2 \chi_b^*(2) \frac{1}{r_{12}} P_{12} \chi_b(2) \right] \chi_a(1)$$

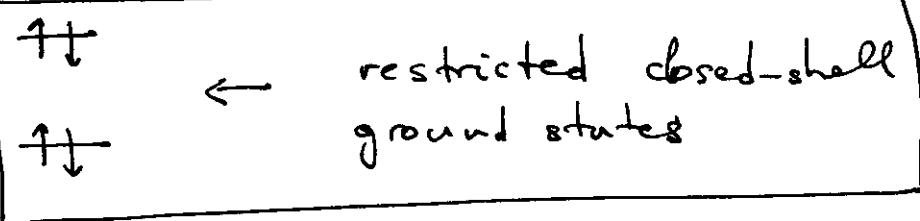
The permutation operator exchanges electrons 1 and 2:

$$P_{12} \chi_b(2) \chi_a(1) = \chi_b(1) \chi_a(2)$$

In terms of the permutation operator, the HF effective potential is

$$v^{HF}(1) = \sum_b \int d\vec{x}_2 \chi_b^*(2) r_{12}^{-1} (1 - P_{12}) \chi_b(2)$$

RHF



$$\chi_i(\vec{x}) = \begin{cases} \psi_j(\vec{r}) \alpha(\omega) \\ \psi_j(\vec{r}) \beta(\omega) \end{cases}$$

HF equation:

$$[h(r_1) + \sum_b \int d\vec{x}_2 \Psi_b(x_2) r_{12}^{-1} (1 - P_{12}) \chi_b(x_2)] \Psi_j(\vec{r}_1) \alpha(\omega_1) = \varepsilon_j \Psi_j(\vec{r}_1) \alpha(\omega_1)$$

Closed-shell Fock operator:

$$f(\vec{r}_1) = \int d\omega_1 \alpha^*(\omega_1) f(\vec{x}_1) \alpha(\omega_1) = \langle \alpha | f | \alpha \rangle$$

$$f(\vec{r}_1) \Psi_j(\vec{r}_1) = h(\vec{r}_1) \Psi_j(\vec{r}_1) + \sum_b \int d\omega_1 d\vec{x}_2 \alpha^*(\omega_1) |\chi_b(x_2)|^2 \frac{1}{r_{12}} \alpha(\omega_1) \Psi_j(\vec{r}_1)$$

$$- \sum_b \int d\omega_1 d\vec{x}_2 \alpha^*(\omega_1) \chi_b^*(2) r_{12}^{-1} \chi_b(1) \alpha(\omega_2) \Psi_j(\vec{r}_2)$$

$$\sum_b \rightarrow \sum_b^{N/2} + \sum_z^{N/2}$$

$$f(\vec{r}_1) = h(\vec{r}_1) + \sum_a^{N/2} \int d\vec{r}_2 \Psi_a^*(\vec{r}_2) (2 - P_{12}) r_{12}^{-1} \Psi_a(\vec{r}_2)$$

$$f(1) = h(1) + \sum_a^{N/2} [2 J_a(1) - K_a(1)]$$

Rules for calculating closed-shell energies

Total energy :

$$E_0 = 2 \sum_{a=1}^{n/2} h_{aa} + \sum_{a,b}^{n/2} [2J_{ab} - K_{ab}]$$

††

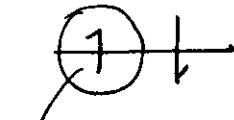
- * each electron contributes $h_{aa} = \langle a | h | a \rangle$
- * each unique pair of electrons contributes a Coulomb term J_{ab}
- * each unique pair of antiparallel spins contributes $-K_{ab}$

Orbital energy :

$$\varepsilon_i = \langle i | h | i \rangle + \sum_b^{n/2} [2J_{ib} - K_{ib}]$$

—†—

- * circle an electron for which you need to calculate its orbital energy.



ε_i :

- * $\langle i | h | i \rangle$
- * add up all Coulomb interactions
- * subtract all exchange interactions of the circled electrons with spins parallel to it.

The Roothaan Equations

HF equation:

Linear combination of basis functions:

$$f(\vec{r}_i) \Psi_i(\vec{r}_i) = \varepsilon_i \Psi_i(\vec{r}_i) \quad \leftarrow \Psi_i(\vec{r}_i) = \sum_j c_{ji} \Phi_j$$

x
 $\langle \Phi_m |$

$$\sum c_{ji} (\Phi_m | f(i) | \Phi_j) = \varepsilon_i \sum_j c_{ji} (\Phi_m | \Phi_j)$$

spatial matrix element

①. The overlap matrix:

$$S_{\mu\nu} = \langle \Phi_\mu | \Phi_\nu \rangle, \quad S = \begin{pmatrix} 1 & S_{12} & \dots & S_{1K} \\ S_{21} & 1 & & \vdots \\ \vdots & & 1 & \ddots \\ S_{K1} & \dots & \ddots & 1 \end{pmatrix}$$

②. The Fock matrix:

$$F_{\mu\nu} = \langle \Phi_\mu | f | \Phi_\nu \rangle$$

The HF equation becomes a matrix multiplication problem

$$\sum_j F_{\mu\nu} c_{ji} = \varepsilon_i \sum_j S_{\mu\nu} c_{ji}$$

Roothaan equations:

$$\tilde{F} \tilde{C} = \tilde{S} \tilde{C} \tilde{\varepsilon}$$

$$\tilde{\varepsilon} = \begin{pmatrix} \varepsilon_1 & & 0 \\ & \ddots & \\ 0 & & \ddots \end{pmatrix}$$

Expression for the Fock matrix

$$F_{\mu\nu} = (\Phi_\mu | f | \Phi_\nu) =$$

$$= (h_\mu | h_\nu) + \sum_{a=1}^{N/2} \left[2 \int |\Phi_a|^2 \frac{1}{r_{12}} \Phi_a^*(1) \Phi_\nu(1) d\vec{r}_1 d\vec{r}_2 \right]$$

$$- \left[\Phi_a^*(2) \Phi_j(2) \frac{1}{r_{12}} \Phi_\mu^*(1) \Phi_a(1) d\vec{r}_1 d\vec{r}_2 \right]$$

$$= (h_\mu | h_\nu) + \sum_{a=1}^{N/2} [2(\alpha a | \mu\nu) - (\alpha j | \mu a)]$$

$$\boxed{F_{\mu\nu} = h_{\mu\nu} + \sum_{a=1}^{N/2} [2(\alpha a | \mu\nu) - (\alpha j | \mu a)]}$$

Example : F-matrix for the Ba atom

$\Phi_{2s} \uparrow\uparrow \quad F_{11} = h_{11} + (11|11) + 2(11|22) - (21|12)$

$\Phi_{1s} \uparrow\uparrow \quad F_{22} = h_{22} + (22|22) + 2(22|11) - (12|21)$

$$F_{12} = h_{12} + (11|12) + (22|12)$$

$$F = \begin{pmatrix} h_{11} + (11|11) + 2(11|22) - (21|12) & h_{12} + (11|12) + (22|12) \\ h_{21} + (22|21) + (11|21) & h_{22} + (22|22) + 2(22|11) - (12|21) \end{pmatrix}$$

Fock matrix in terms of $P_{\mu\nu}$

$$F_{\mu\nu} = \langle \mu | h | \nu \rangle + \sum_a^{\text{N/2}} [2(\mu\nu|aa) - (\mu a|a\nu)]$$



$$\langle \mu | -\frac{1}{2}\nabla^2 - \sum_A \frac{z_A}{|\vec{r} - \vec{R}_A|} | \nu \rangle = H_{\mu\nu}^{\text{core}}$$

↑
atomic
orbitals

core-Hamiltonian
matrix

$$H_{\mu\nu}^{\text{core}} = T_{\mu\nu} + V_{\mu\nu}^{\text{molecular}}$$

$$\int d\vec{r}_1 \Phi_{\mu}^{*}(\vec{r}_1) \left[-\frac{1}{2} \nabla_1^2 \right] \Phi_{\nu}(\vec{r}_1)$$

$$\int d\vec{r}_1 \Phi_{\mu}^{*}(\vec{r}_1) \left[- \sum_A \frac{z_A}{|\vec{r}_1 - \vec{R}_A|} \right] \Phi_{\nu}(\vec{r}_1)$$

With the linear expansion of molecular
orbitals in atomic orbitals

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda\delta} P_{\lambda\delta} \left[(\mu\nu|\lambda\delta) - \frac{1}{2} (\mu\lambda|\delta\nu) \right]$$

density matrix

atomic integrals

Density matrix

The total electronic density for a closed-shell molecule

$$\rho(\vec{r}) = 2 \sum_{\alpha=1}^{N/2} |\Psi_{\alpha}(\vec{r})|^2$$

$$\int d\vec{r} \rho(\vec{r}) = 2 \sum_{\alpha=1}^{N/2} 1 = N$$

Basis expansion:

$$\begin{aligned} \rho(\vec{r}) &= 2 \sum_{\alpha=1}^{N/2} \Psi_{\alpha}^*(\vec{r}) \Psi_{\alpha}(\vec{r}) = 2 \sum_{\alpha,\nu}^{N/2} C_{\nu\alpha}^* \Phi_{\nu}^*(\vec{r}) \sum_{\mu} C_{\mu\alpha} \Phi_{\mu}(\vec{r}) \\ &= \sum_{\mu\nu} \left[2 \sum_{\alpha}^{N/2} C_{\mu\alpha} C_{\nu\alpha}^* \right] \Phi_{\mu}(\vec{r}) \Phi_{\nu}^*(\vec{r}) \end{aligned}$$

Density matrix:

$$P_{\mu\nu} = 2 \sum_{\alpha=1}^{N/2} C_{\mu\alpha} C_{\nu\alpha}^*$$

summation over occupied molecular orbitals

Fock operator representation:

$$f(\vec{r}_1) = h(\vec{r}_1) + \frac{1}{2} \sum_{\lambda\delta} P_{\lambda\delta} \left[\int d\vec{r}_2 \Phi_{\delta}^*(\vec{r}_2) (2 - \Phi_{1\lambda}) r_{12}^{-1} \Phi_{\lambda}(\vec{r}_2) \right]$$

Example: Density matrix of the minimal basis
H₂ molecule

— u Two molecular orbitals: "g" and "u".

~~H₂~~ g Only "g" is occupied

$$\Psi_g = \frac{1}{\sqrt{2(1+s)}} (\phi_A + \phi_B)$$

$$\Psi_u = \frac{1}{\sqrt{2(1-s)}} (\phi_A - \phi_B)$$

$$c_{Ag} = \frac{1}{\sqrt{2(1+s)}}, \quad c_{Bg} = \frac{1}{\sqrt{2(1-s)}}$$

$$P_{AA} = 2 \sum_{a=g} \frac{1}{\sqrt{2(1+s)}} \times \frac{1}{\sqrt{2(1+s)}} = \frac{1}{1+s}$$

$$P_{AB} = 2 c_{Ag} c_{Bg}^* = \frac{1}{1+s}$$

$$P_{BA} = P_{AB}$$

$$P_{BB} = P_{AA}$$

$$\overset{\leftrightarrow}{P} = \begin{pmatrix} \frac{1}{1+s} & \frac{1}{1+s} \\ \frac{1}{1+s} & \frac{1}{1+s} \end{pmatrix} = \frac{1}{1+s} \overset{\leftrightarrow}{I}$$

Exercise 3.25

Fock matrix for H₂

$$\overleftrightarrow{P} = \frac{1}{1+s} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum P_{\lambda\delta} [(\mu\nu|\beta\lambda) - \frac{1}{2} (\mu\lambda|\beta\nu)]$$

$$\mu, \nu = A, B$$

$$F_{AA} = H_{AA}^{\text{core}} + \frac{1}{1+s} \sum_{\lambda, \delta = A, B} [(\AA|\beta\lambda) - \frac{1}{2} (\A\lambda|\beta\A)]$$

$$\begin{aligned} &= H_{AA}^{\text{core}} + \frac{1}{1+s} \left[(\AA|AA) + (\AA|BB) + (\AA|AB) \right. \\ &\quad \left. + (\AA|BA) - \frac{1}{2} (\AA|AA) - \frac{1}{2} (\AB|BA) - \right. \\ &\quad \left. - \frac{1}{2} (\AA|BA) - \frac{1}{2} (\AB|BA) \right] \\ &= H_{AA}^{\text{core}} + \frac{1}{1+s} \left[\frac{1}{2} (\AA|AA) + (\AA|BB) + (\AA|AB) \right. \\ &\quad \left. - \frac{1}{2} (\AB|BA) \right] \end{aligned}$$

Homework : show that

$$\begin{aligned} F_{AB} &= H_{AB}^{\text{core}} + \frac{1}{1+s} \left[-\frac{1}{2} (\AA|BD) + (\AA|AB) \right. \\ &\quad \left. + \frac{3}{2} (\AB|AB) \right] \end{aligned}$$

Exercise 3.23

Eigenstates for H_2^+

$$\overset{\leftrightarrow}{H}^{\text{core}} \overset{\leftrightarrow}{C} = \overset{\leftrightarrow}{S} \overset{\leftrightarrow}{C} \overset{\leftrightarrow}{\Sigma} \quad \leftarrow \text{Roothaan equations}$$

$$\overset{\leftrightarrow}{S} \overset{\leftrightarrow}{C} \overset{\leftrightarrow}{\Sigma} = \begin{pmatrix} 1 & s \\ -s & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2(1+s)}} & \frac{1}{\sqrt{2(1-s)}} \\ \frac{1}{\sqrt{2(1+s)}} & -\frac{1}{\sqrt{2(1-s)}} \end{pmatrix} \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} =$$

$$= \frac{1}{\sqrt{2}} \begin{pmatrix} \sqrt{1+s} & \sqrt{1-s} \\ \sqrt{1+s} & \sqrt{1-s} \end{pmatrix} \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix}$$

$$= \frac{1}{\sqrt{2}} \begin{pmatrix} \varepsilon_1 \sqrt{1+s} & \varepsilon_2 \sqrt{1-s} \\ \varepsilon_1 \sqrt{1-s} & \varepsilon_2 \sqrt{1-s} \end{pmatrix}$$

$$\overset{\leftrightarrow}{H}^{\text{core}} \overset{\leftrightarrow}{C} = \begin{pmatrix} \overset{\text{core}}{H_{11}} & \overset{\text{core}}{H_{12}} \\ \overset{\text{core}}{H_{21}} & \overset{\text{core}}{H_{22}} \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} \frac{1}{\sqrt{1+s}} & \frac{1}{\sqrt{1-s}} \\ \frac{1}{\sqrt{1+s}} & -\frac{1}{\sqrt{1-s}} \end{pmatrix}$$

$$= \frac{1}{\sqrt{2}} \begin{pmatrix} \frac{\overset{\text{core}}{(H_{11} + H_{12})}}{\sqrt{1+s}} & \frac{\overset{\text{core}}{(H_{11} - H_{12})}}{\sqrt{1-s}} \\ \frac{\overset{\text{core}}{H_{22} + H_{12}}}{\sqrt{1+s}} & \frac{\overset{\text{core}}{H_{22} - H_{12}}}{\sqrt{1-s}} \end{pmatrix}$$

$$\boxed{\varepsilon_1 = \frac{\overset{\text{core}}{H_{11}} + \overset{\text{core}}{H_{12}}}{1 + s}}$$

$$\boxed{\varepsilon_2 = \frac{\overset{\text{core}}{H_{11}} - \overset{\text{core}}{H_{12}}}{1 - s}}$$

Exercise 3.26

Eigenenergies of H₂

$$\hat{F} \hat{C} = \hat{S} \hat{C} \hat{\Sigma}$$

$$\varepsilon_1 = \frac{F_{11} + F_{12}}{1 + S}$$

$$\varepsilon_2 = \frac{F_{11} - F_{12}}{1 - S}$$

$$F_{11} = (\Phi_A | h | \Phi_A) + \frac{1}{1 + S_{AB}} \left[\frac{1}{2} (\Phi_A \Phi_A | \Phi_A \Phi_A) + (\Phi_A \Phi_A | \Phi_B \Phi_B) + (\Phi_A \Phi_A | \Phi_A \Phi_B) - \frac{1}{2} (\Phi_A \Phi_B | \Phi_A \Phi_B) \right]$$

$$= -1.110 + \frac{1}{1 + 0.753} [0.5 \cdot 0.625 + 0.504 + 0.426 - 0.5 \cdot 0.323] = -0.493 \text{ a.u.}$$

$$F_{12} = (\Phi_A | h | \Phi_B) + \frac{1}{1 + S_{AB}} \left[-\frac{1}{2} (\Phi_A \Phi_A | \Phi_B \Phi_B) + (\Phi_A \Phi_A | \Phi_A \Phi_B) + \frac{3}{4} (\Phi_A \Phi_B | \Phi_A \Phi_B) \right] = -0.968 + \frac{1}{1 + 0.753} [-0.5 \cdot 0.504 + 0.426 + 0.75 \cdot 0.323] = -0.731 \text{ a.u.}$$

$$\boxed{\varepsilon_1 = -0.698 \text{ a.u.}} \quad \leftarrow \quad \boxed{PI = 19 \text{ eV}} \quad (15.9 \text{ eV exp}),$$

$$\boxed{\varepsilon_2 = 0.136 \text{ a.u.}} \quad \leftarrow \quad \boxed{EA = -3.69 \text{ eV}}$$

Diagonalizing the overlap matrix

2-state problem:

$$\hat{S} = \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix}$$

Since \hat{S} is Hermitian, there is a unitary transformation that diagonalizes it.

the basis set is normalized
but not orthonormalized

$$\hat{U}^\dagger \hat{S} \hat{U} = \hat{D} \leftarrow \hat{D} \text{ is a diagonal matrix}$$

$$\begin{aligned} & \begin{pmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{pmatrix} \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix} \begin{pmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{pmatrix} \\ &= \begin{pmatrix} 1 + 2s \cos \theta \sin \theta & s(\sin^2 \theta - \cos^2 \theta) \\ s(\sin^2 \theta - \cos^2 \theta) & 1 - 2s \sin \theta \cos \theta \end{pmatrix} \underset{\theta = \frac{\pi}{4}}{=} \begin{pmatrix} 1+s & 0 \\ 0 & 1-s \end{pmatrix} \end{aligned}$$

Can we find a matrix that makes the basis set orthonormal?

$$\Phi'_\mu = \sum_v X_{\lambda\mu} \Phi_v \quad \langle \Phi'_\mu | \Phi'_v \rangle = \delta_{\mu\nu}$$

$$\sum_{\lambda, \nu} \langle \Phi_\lambda | X_{\lambda\mu}^* X_{\lambda\nu} | \Phi_\nu \rangle = \delta_{\mu\nu} \quad \sum_{\lambda, \nu} X_{\lambda\mu}^* S_{\lambda\lambda} X_{\nu\nu} = \delta_{\mu\nu}$$

$$\boxed{\hat{X}^\dagger \hat{S} \hat{X} = \hat{I}}$$

\hat{X} is a non-unitary transformation.

Symmetric orthogonalization

$$\overset{\leftrightarrow}{X} = \overset{\leftrightarrow}{S}^{-\frac{1}{2}} = \overset{\leftrightarrow}{U} \overset{\leftrightarrow}{S}^{-\frac{1}{2}} \overset{\leftrightarrow}{U}^+, \quad \overset{\leftrightarrow}{U}^+ \overset{\leftrightarrow}{S} \overset{\leftrightarrow}{U} = \overset{\leftrightarrow}{S}$$

In order to obtain $\overset{\leftrightarrow}{X}$ you do two steps:

① diagonalize $\overset{\leftrightarrow}{S}$

② unidiagonalize the square root of $\overset{\leftrightarrow}{S}^{-1}$, $\overset{\leftrightarrow}{S}^{-\frac{1}{2}}$

$$\overset{\leftrightarrow}{S} = \begin{pmatrix} 1+s & 0 \\ 0 & 1-s \end{pmatrix}, \quad \overset{\leftrightarrow}{S}^{\frac{1}{2}} = \begin{pmatrix} \sqrt{1+s} & 0 \\ 0 & \sqrt{1-s} \end{pmatrix}$$

$$\overset{\leftrightarrow}{S}^{-\frac{1}{2}} = \begin{pmatrix} \frac{1}{\sqrt{1+s}} & 0 \\ 0 & \frac{1}{\sqrt{1-s}} \end{pmatrix}$$

$$\overset{\leftrightarrow}{X} = \begin{pmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{1+s}} & 0 \\ 0 & \frac{1}{\sqrt{1-s}} \end{pmatrix} \begin{pmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{pmatrix}$$

$$= \begin{pmatrix} \frac{\cos \theta}{\sqrt{1+s}} & \frac{\sin \theta}{\sqrt{1-s}} \\ \frac{\sin \theta}{\sqrt{1+s}} & -\frac{\cos \theta}{\sqrt{1-s}} \end{pmatrix} \begin{pmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{pmatrix}$$

$$= \begin{pmatrix} \frac{\cos^2 \theta}{\sqrt{1+s}} + \frac{\sin^2 \theta}{\sqrt{1-s}} & \cos \theta \sin \theta \left(\frac{1}{\sqrt{1+s}} - \frac{1}{\sqrt{1-s}} \right) \\ \cos \theta \sin \theta \left(\frac{1}{\sqrt{1+s}} - \frac{1}{\sqrt{1-s}} \right) & \frac{\sin^2 \theta}{\sqrt{1+s}} + \frac{\cos^2 \theta}{\sqrt{1-s}} \end{pmatrix} = \begin{pmatrix} \frac{1}{2\sqrt{1+s}} + \frac{1}{2\sqrt{1-s}} & \frac{1}{2} \left(\frac{1}{\sqrt{1+s}} - \frac{1}{\sqrt{1-s}} \right) \\ \dots & \dots \end{pmatrix}$$

$\theta = \frac{\pi}{4}$

Canonical orthogonalization

$$\tilde{X} = \tilde{U} \tilde{S}^{-1/2}$$

$$\begin{aligned} X^+ S X &= (\tilde{U} \tilde{S}^{-1/2})^+ \tilde{S} \tilde{U} \tilde{S}^{-1/2} = \\ &= \tilde{S}^{-1/2} \tilde{U}^+ + \tilde{S} \tilde{U} \tilde{S}^{-1/2} = \tilde{S}^{-1/2} \tilde{S} \tilde{S}^{-1/2} = \tilde{I} \end{aligned}$$

Transformation of Roothaan equations:

$$\tilde{C}' = \tilde{X}^{-1} \tilde{C}, \quad \tilde{C} = \tilde{X} \tilde{C}'$$

$$\tilde{X}^+ \times \tilde{F} \tilde{X} \tilde{C}' = \tilde{S} \tilde{X} \tilde{C}' \tilde{\varepsilon}$$

$$\hookrightarrow (\tilde{X}^+ \tilde{F} \tilde{X}) \tilde{C}' = (\tilde{X}^+ \tilde{S} \tilde{X}) \tilde{C}' \tilde{\varepsilon}$$

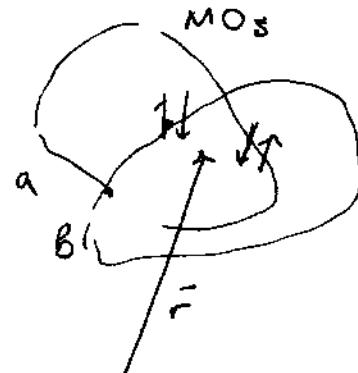
$$\boxed{\tilde{F}' \tilde{C}' = \tilde{C}' \tilde{\varepsilon}}$$

Population analysis

Electronic density at point \vec{r}

$$\rho(\vec{r}) = \sum_a |\Psi_a(\vec{r})|^2 = \sum_{\mu} \Phi_\mu^*(\vec{r}) \Phi_\mu(\vec{r}) \times$$

$$\times \underbrace{\sum_a c_{va}^* c_{ma}}_{P_{\mu\nu} \leftarrow \text{density matrix}}$$



$$\rho(\vec{r}) = \sum_{\mu\nu} P_{\mu\nu} \Phi_\nu^*(\vec{r}) \Phi_\mu(\vec{r})$$

The total number of electrons:

$$N = \int \rho(\vec{r}) d\vec{r} = \frac{N}{V} \cdot V = \sum_{\mu\nu} P_{\mu\nu} S_{\mu\nu} = \sum_{\mu} (\overleftrightarrow{P} \cdot \overleftrightarrow{S})_{\mu\mu}$$

The sum over μ can be split into sums over atomic wave functions

$$N = \sum_A \sum_{\mu \in A} \underbrace{(\overleftrightarrow{P} \cdot \overleftrightarrow{S})_{\mu\mu}}_{\text{electronic density on the atom A}}$$

$$q_A = Z_A - \sum_{\mu \in A} (\overleftrightarrow{P} \cdot \overleftrightarrow{S})_{\mu\mu}$$

Mulliken population analysis

Example: H₂ molecule



$$\vec{P} = \frac{1}{1+s} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad \text{AA} \quad \text{AB}$$

↑
BB

$$\vec{S} = \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix}$$

$$q_A = 1 - (\vec{P} \cdot \vec{S})_{11} = 1 - \frac{1}{1+s} \times (1+s) = 0$$

$$q_B = 1 - (\vec{P} \cdot \vec{S})_{22} = 0$$

Lödwin population

A symmetrically orthogonalized set is used in the Lödwin population analysis

$$p(\vec{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu}^{-1} \Phi_{\mu}'(\vec{r}) \Phi_{\nu}'(\vec{r})^*$$

$$\Phi_{\mu}'(\vec{r}) = \sum_{\nu} (S^{-1/2})_{\mu\nu} \Phi_{\nu}(r)$$

q_A = z_A - \sum_{\mu \in A} (\vec{S}^{1/2} \vec{P} \vec{S}^{1/2})_{\mu\mu}

SCF procedure

Fix a set of nuclear coordinates $\{\vec{R}_A\}$

← adiabatic approximation

Calculate the molecular integrals and overlaps
 $H_{\mu\nu}^{\text{core}}, (\mu\nu|\lambda\zeta), S_{\mu\nu}$

← for a given atomic basis $\{\Phi_i\}$

Diagonalize the overlap matrix and obtain a transformation matrix X

← symmetric or canonical diagonalization

Build the G matrix from the density matrix and the core integrals

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + G_{\mu\nu}$$

$$G_{\mu\nu} = \sum_{\lambda\zeta} P_{\lambda\zeta} [(\mu\nu|\lambda\zeta) - \frac{1}{2}(\mu\lambda|\lambda\zeta)]$$

Calculate $F' = X^+ F X$

Diagonalize F' to obtain C' and ϵ

Calculate $C = XC'$
and form a new matrix P

test

out

Energy in the SCF

Ground-state energy

$$E_0 = 2 \sum_a^{N/2} h_{aa} + \sum_a^{N/2} \sum_b^{N/2} [2J_{ab} - K_{ab}]$$

Molecular orbital energies

$$\varepsilon_a = f_{aa} = h_{aa} + \sum_b^{N/2} [2J_{ab} - K_{ab}]$$

$$E_0 = \sum_a^{N/2} (h_{aa} + f_{aa}) = \sum_a^{N/2} (h_{aa} + \varepsilon_a)$$

sum over occupied molecular orbitals

At each stage of the SCF procedure,

$$E_0 = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\mu\nu} (H_{\mu\nu}^{\text{core}} + F_{\mu\nu})$$

Double- ζ calculation of the ground-state energy of He

Problem: Using the SCF procedure with the double- ζ basis set calculate the ground-state energy of He.

$$\Psi_{1s} = c_1 \Phi_{1s}^{(1)} + c_2 \Phi_{1s}^{(2)}, \quad \Phi_{1s}^{(i)} = \left(\frac{\zeta_i^2}{\pi}\right)^{1/2} e^{-\zeta_i r}$$

$$\zeta_1 = 1.45, \quad \zeta_2 = 2.91$$

①. Atomic integrals

$$h_{ii} = \zeta_i (\zeta_i/2 - z_A) \quad \leftarrow \text{Homework 1}$$

↑
nuclear
charge

$$\langle 1|2 \rangle = \frac{8(\zeta_1 \zeta_2)^{3/2}}{(\zeta_1 + \zeta_2)^3} \quad \langle 11|11 \rangle = \frac{5}{8} \zeta_1$$

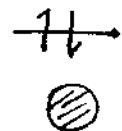
$$h_{12} = -\frac{4(\zeta_1 \zeta_2)^{3/2}}{(\zeta_1 + \zeta_2)^2} \left(2 - \frac{\zeta_1 \zeta_2}{\zeta_1 + \zeta_2}\right) \quad \langle 12|12 \rangle = \frac{20(\zeta_1 \zeta_2)^2}{(-\zeta_1 + \zeta_2)^5}$$

$$\langle 11|12 \rangle = \frac{16(\zeta_1^3 \zeta_2)^{3/2}}{(3\zeta_1 + \zeta_2)^4} \left[\frac{12\zeta_1 + 8\zeta_2}{(\zeta_1 + \zeta_2)^2} + \frac{9\zeta_1 + \zeta_2}{2\zeta_1^2} \right] \quad \langle 11|22 \rangle = \frac{\zeta_1^3 \zeta_2 (-\zeta_1 + 4\zeta_2) + \zeta_1 \zeta_2^3 (\zeta_2 + 4\zeta_1)}{(-\zeta_1 + \zeta_2)^4}$$

②. Zero-order approximation:

both electrons have the same energy

$$\boxed{\Psi_{1s} = \Phi_{1s}^{(1)}}$$



$$z_A = 2$$

$$\left. \begin{array}{l} c_1 = 1 \\ c_2 = 0 \end{array} \right\} \quad P_{11}^{(0)} = 1 \quad P_{12}^{(0)} = 0 \quad P_{22}^{(0)} = 0$$

③. Fock matrix

$$F_{11}^{(0)} = h_{11} + \sum_{p=1}^2 \sum_{s=1}^2 P_{ps}^{(0)} \left[(11|ps) - \frac{1}{2} (1s|p1) \right]$$

$$= h_{11} + (11|11) = \frac{1.45^2}{2} - 2.9 + \frac{5}{8} \times 1.45 = - 0.943$$

$$F_{12}^{(0)} = h_{12} + \sum_{p=1}^2 \sum_{s=1}^2 P_{ps}^{(0)} \left[(12|ps) - \frac{1}{2} (1s|p2) \right]$$

$$= h_{12} + 2 \left[(12|11) - \frac{1}{2} (11|12) \right] = h_{12} + (11|12)$$

$$h_{12} = - 0.583 \text{ a.u.} \quad (11|12) = 1.18259$$

$$(11|12) = 0.963 \quad (12|12) = 0.9536$$

$$F_{22}^{(0)} = h_{22} + 2 \left[(22|11) - \frac{1}{2} (12|21) \right] =$$

$$= h_{22} + 2(22|11) - (12|21) = - 0.174$$

$$(11|11) = 0.9063$$

$$F^{(0)} = \begin{pmatrix} -0.943 & -0.980 \\ -0.980 & -0.174 \end{pmatrix}$$

④. Diagonalization

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

$$\varepsilon_1^{(1)} = -0.976 \text{ a.u.} \quad \varepsilon_2^{(1)} = 2.725 \text{ a.u.}$$

over the occupied molecular orbitals

$$E = \sum_k (\varepsilon_k + \langle k | h | k \rangle)$$

$$\Psi_{1s}^{(1)} = 0.851 \Phi_{1s}^{(1)} + 0.173 \Phi_{1s}^{(2)}$$

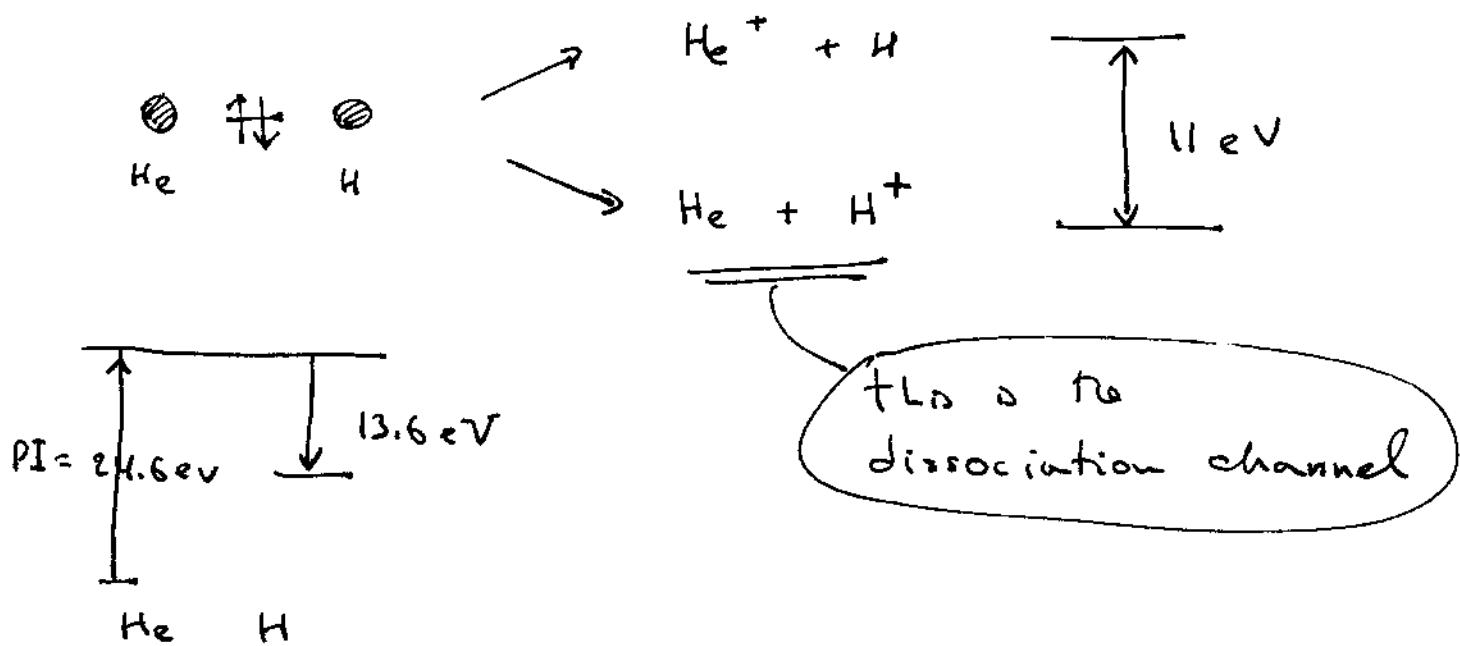
$$\langle \Psi_{1s}^{(1)} | h | \Psi_{1s}^{(1)} \rangle = -1.942 \text{ a.u.}$$

$$E^{(1)} = -2.917 \text{ a.u.}$$

$$E^{(0)} = h_{11} + h_{22} + (11|11) = -2.528 \text{ a.u.}$$

$$E^{(1)} < E^{(0)}$$

SCF calculation of HeH^+



①. Calculation of overlap and atomic integrals

②. Zero-order Fock matrix

③. Orthogonalization

$$\Phi_{\mu}' = \sum x_{\mu} \Phi_{\mu}$$

④. New Fock matrix and a new density matrix.

ATOMIC BASIS SET

THE CONTRACTED PRIMITIVE FUNCTIONS HAVE BEEN UNNORMALIZED
THE CONTRACTED BASIS FUNCTIONS ARE NOW NORMALIZED TO UNITY

SHELL TYPE PRIMITIVE	EXONENT	CONTRACTION COEFFICIENTS
----------------------	---------	--------------------------

HE

1	S	1	6.3624214	0.154328967295
1	S	2	1.1589230	0.535328142282
1	S	3	0.3136498	0.444634542185

\leftarrow STO $s = 2.012$
Text : $s = 2.0925$

H

2	S	4	3.4252509	0.154328967295
2	S	5	0.6239137	0.535328142282
2	S	6	0.1688554	0.444634542185

\leftarrow STO $s = 1.24$

TOTAL NUMBER OF BASIS SET SHELLS = 2

NUMBER OF CARTESIAN GAUSSIAN BASIS FUNCTIONS = 2

NUMBER OF ELECTRONS = 2

CHARGE OF MOLECULE = 1

SPIN MULTIPLICITY = 1

NUMBER OF OCCUPIED ORBITALS (ALPHA) = 1

NUMBER OF OCCUPIED ORBITALS (BETA) = 1

TOTAL NUMBER OF ATOMS = 2

THE NUCLEAR REPULSION ENERGY IS 0.7233149935

THIS MOLECULE IS RECOGNIZED AS BEING LINEAR.

The best atom value
for $s \alpha$

$\underline{\underline{s = 1.6875}} \quad \leftarrow H_2$

RHF SCF CALCULATION

NUCLEAR ENERGY = 0.7233149935
MAXIT = 30 NPUNCH= 2
EXTRAP=T DAMP=F SHIFT=F RSTRCT=F DIIS=F DEM=F SOSCF=F
DENSITY CONV= 1.00E-05
MEMORY REQUIRED FOR RHF STEP= 30056 WORDS.

ITER EX DEM TOTAL ENERGY E CHANGE DENSITY CHANGE DIIS
ERROR

*** START OF DEBUG OUTPUT FOR ITERATION 1
SKELETON FOCK MATRIX

1 2
1 HE 1 S 0.956420
2 H 2 S 0.011005 0.682899

SYMMETRIZED FOCK OPERATOR

1 2
1 HE 1 S 0.956420
2 H 2 S 0.011005 0.682899

EHF1 = -2.640887344145 EHF2 = -4.252335838397 EHF =
-3.446611591271

TOTAL FOCK OPERATOR

1 2
1 HE 1 S -1.336846
2 H 2 S -0.411672 -0.503570

LAGRANGE MULTIPLIER MATRIX

1
1 -2.6408873
2 0.4142118

NEW ORBITALS

1 2
-1.3661 -0.3818

1 HE 1 S 0.952536 0.357919
2 H 2 S 0.175539 -1.002306

NEW DENSITY MATRIX

1 2
1 HE 1 S 1.814650
2 H 2 S 0.334414 0.061628

*** END OF DEBUG OUTPUT FOR ITERATION 1
1 0 0 -2.723296598 -2.723296598 0.359269588 0.000000000

$$C = \begin{pmatrix} 0.952 & 0.3579 \\ 0.1755 & -1.0023 \end{pmatrix}$$

$$P = \begin{pmatrix} 1.8147 & 0.3344 \\ 0.3344 & 0.0616 \end{pmatrix}$$

*** START OF DEBUG OUTPUT FOR ITERATION 6
EHF1 = -2.547305609696 EHF2 = -4.549712794320 EHF =
-3.548509202008
TOTAL FOCK OPERATOR

1 2

1 HE 1 S -1.260230
2 H 2 S -0.337461 -0.500738

Text:

NEW DENSITY MATRIX

1 2

$P_{11} = 1.2861 \quad P_{22} = 0.2269$

$P_{12} = 0.5402$

1 HE 1 S 1.875959
2 H 2 S 0.247218 0.032579
*** END OF DEBUG OUTPUT FOR ITERATION 6
6 1 0 -2.825194209 -0.000001244 0.000000373 0.000000000

MULLIKEN AND LOWDIN POPULATION ANALYSES

MULLIKEN ATOMIC POPULATION IN EACH MOLECULAR ORBITAL

1

2.000000

1 1.921690
2 0.078310

----- POPULATIONS IN EACH AO -----

MULLIKEN LOWDIN

1 HE 1 S 1.92169 1.90578
2 H 2 S 0.07831 0.09422

----- MULLIKEN ATOMIC OVERLAP POPULATIONS ----- (OFF-DIAGONAL ELEMENTS NEED TO BE MULTIPLIED BY 2)

1 2
1 1.8759586
2 0.0457312 0.0325790

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS

ATOM	MULL.POP.	CHARGE	LOW.POP.	CHARGE
1 HE	1.921690	0.078310	1.905783	0.094217
2 H	0.078310	0.921690	0.094217	0.905783

FINAL RHF ENERGY IS -2.8251942085 AFTER 7 ITERATIONS

EIGENVECTORS

	1	2			
	-1.2737	-0.4204			
A1	A1				
1	HE	1	S	0.968493	-0.312173
2	H	2	S	0.127630	1.009525
..... END OF RHF CALCULATION					

ITER	EX DEM	TOTAL ENERGY	E CHANGE	DENSITY CHANGE	DIIS	
					ERROR	
1	0	0	-2.723296598	-2.723296598	0.359269588	0.000000000
2	1	0	-2.822334922	-0.099038324	0.063548092	0.000000000
3	2	0	-2.824996269	-0.002661348	0.016988799	0.000000000
4	3	0	-2.825178750	-0.000182481	0.004765644	0.000000000
5	0	0	-2.825192964	-0.000014214	0.001892722	0.000000000
6	1	0	-2.825194209	-0.000001244	0.000000373	0.000000000
7	2	0	-2.825194209	0.000000000	0.000000107	0.000000000

2 ELECTRON INTEGRALS

THE -PK- OPTION IS OFF, THE INTEGRALS ARE NOT IN SUPERMATRIX FORM.

STORING 15000 INTEGRALS/RECORD ON DISK, USING 16 BYTES/INTEGRAL.

TWO ELECTRON INTEGRAL EVALUATION REQUIRES 59659 WORDS OF MEMORY.

II,JST,KST,LST = 1 1 1 1 NREC = 1 INTLOC = 1

II,JST,KST,LST = 2 1 1 1 NREC = 1 INTLOC = 2

(1111) → 1 1 1 1 1.000 1 0.105571294007E+01 2 1 1 1 1.000 1 0.127484278495E+00

2 (2111)

(2211) → 2 1 1 1.000 1 0.357490342139E+00

2 1 2 1 1.000 257 0.223391768097E-01 2 2 2 1 1.000 1 0.947758034106E-01

2 (2112)

(2421)

(22122) = 0.774606

```
$CONTRL SCFTYP=RHF COORD=ZMT ICHARG=1 NZVAR=0 RUNTYP=TRUDGE $END  
$BASIS GBASIS=STO NGAUSS=3 $END  
$GUESS GUESS=HUCKEL $END  
$DATA
```

HeH calculation by D. Matyushov
Cnv 4

He
H 1 R1

R1=1.4632
\$END
\$TRUDGE OPTMIZ=BASIS NPAR=3
IEX(1)=1 IEX(2)=2 IEX(3)=3 \$END

ATOMIC BASIS SET

THE CONTRACTED PRIMITIVE FUNCTIONS HAVE BEEN UNNORMALIZED
THE CONTRACTED BASIS FUNCTIONS ARE NOW NORMALIZED TO UNITY

SHELL TYPE	PRIMITIVE	EXPONENT	CONTRACTION COEFFICIENTS
------------	-----------	----------	--------------------------

HE

1	S	1	6.3624214	0.154328967295
1	S	2	1.1589230	0.535328142282
1	S	3	0.3136498	0.444634542185

H

2	S	4	3.4252509	0.154328967295
2	S	5	0.6239137	0.535328142282
2	S	6	0.1688554	0.444634542185

----- TRUDGE RESTART DATA AT NSTEP 0 -----
\$TRUDGE OPTIMIZE=BASIS NPAR= 3
IEX(1)= 1, 2, 3,
F(1)= 6.362421, 1.158923, 0.313650,
\$END

FINAL RHF ENERGY IS -2.8251942085 AFTER 7 ITERATIONS

STRUDGE OPTIMIZE=BASIS NPAR= 3
IEX(1)= 1, 2, 3,
F(1)= 9.641588, 1.395252, 0.303863,
\$END

FINAL RHF ENERGY IS -2.8412097309 AFTER 2 ITERATIONS

```
*****  
***** NEW INPUT FILE FOR HeH *****  
*****  
$CONTRL SCFTYP=RHF ICHARG=1 NZVAR=0 $END  
$GUESS GUESS=HUCKEL $END  
$DATA  
HeH calculation by D. Matyushov  
Cnv 4
```

Helium 2
S 3
1 9.641588 0.154328967295
2 1.395252 0.535328142282
3 0.303863 0.444634542185

Hydrogen 1 0. 0. 1.4632
S 3
1 3.4252509 0.154328967295
2 0.6239137 0.535328142282
3 0.1688554 0.444634542185

END

\$CONTROL SCFTYP=RHF RUNIYP=SURFACE COORD=ZMT NZVAR=0 PLTORB=.TRUE. \$END
 \$BASIS GBASIS=STO NGAUSS=3 \$END
 \$GUESS GUESS=HUCKEL \$END
 \$SURF IVEC1(1)=2,1 IGRP1=1 ORIG1=1. DISP1=0.1 NDTSP1=20 \$END
 \$DATA

Water dissociation by D. Matyushov

Cnv 2

C1
 H2 1 R1
 H3 1 R1 2 A1

R1=1.00

A1=104.48

\$END

1 O1	8.953261	-0.953261	8.930288	-0.930288
2 H2	0.693704	0.306296	0.706545	0.293455
3 H2	0.353035	0.646965	0.363167	0.636833

COORD 1= 1.000 COORD 2= 0.000

HAS ENERGY VALUE -76.134894

1 C1	8.906858	-0.906858	8.891231	-0.891231
2 H2	0.700455	0.299545	0.711805	0.288195
3 H2	0.392688	0.607312	0.396964	0.603036

COORD 1= 1.100 COORD 2= 0.000

HAS ENERGY VALUE -75.811870

$\Delta E = 51.97 \text{ eV}$

1 C1	8.856301	-0.856301	8.846321	-0.846321
2 H2	0.708936	0.291064	0.718752	0.281248
3 H2	0.434763	0.565237	0.434926	0.565074

COORD 1= 1.200 COORD 2= 0.000

HAS ENERGY VALUE -75.508727

1 O1	8.116302	-0.116302	8.116645	-0.116645
2 H2	0.949858	0.050142	0.950478	0.049522
3 H2	0.933839	0.066161	0.932877	0.067123

COORD 1= 2.400 COORD 2= 0.000

HAS ENERGY VALUE -74.166006

1 C1	8.033485	-0.033485	8.033580	-0.033580
2 H2	0.985660	0.014340	0.985852	0.014148
3 H2	0.980855	0.019145	0.980568	0.019432

COORD 1= 2.700 COORD 2= 0.000

HAS ENERGY VALUE -74.192304

1 C1	8.011840	-0.011840	8.011871	-0.011871
2 H2	0.995044	0.004956	0.995119	0.004881
3 H2	0.993117	0.006883	0.993010	0.006990

COORD 1= 2.900 COORD 2= 0.000

HAS ENERGY VALUE -74.220418

$D_e(\text{exp}) = 125.9 \text{ kcal/mol} = 5.46 \text{ eV}$

\$CCTRL SCFTYP=RHF COORD=ZMI ICHARG=1 NZVAR=3 RUNTYP=SURFACE \$END
 \$BASIS GBASIS=STO NGAUSS=3 \$END
 \$GUESS GUESS=HUCKEL \$END
 \$SURF IVEC1(1)=2,1 TGRP1=1 ORIG1=0. DISP1=0.2 NDISP1=10 \$END
 \$DATA

HeH calculation by D. Matyushov
Chv 4

Re
H 1 R1

R1=1.5
\$END

COORD 1= 0.000 COORD 2= 0.000
HAS ENERGY VALUE -2.631665

COORD 1= 0.200 COORD 2= 0.000
HAS ENERGY VALUE -2.820617

COORD 1= 0.400 COORD 2= 0.000
HAS ENERGY VALUE -2.854844

COORD 1= 0.600 COORD 2= 0.000
HAS ENERGY VALUE -2.847716

COORD 1= 0.800 COORD 2= 0.000
HAS ENERGY VALUE -2.834468

COORD 1= 1.000 COORD 2= 0.000
HAS ENERGY VALUE -2.823450

COORD 1= 1.200 COORD 2= 0.000
HAS ENERGY VALUE -2.816188

COORD 1= 1.400 COORD 2= 0.000
HAS ENERGY VALUE -2.812008

COORD 1= 1.600 COORD 2= 0.000
HAS ENERGY VALUE -2.809814

	R/Å	E(r)/eV
COORD 1= 0.000 COORD 2= 0.000 HAS ENERGY VALUE -2.631665	0.5	4.79
COORD 1= 0.200 COORD 2= 0.000 HAS ENERGY VALUE -2.820617	0.7	0.349
COORD 1= 0.400 COORD 2= 0.000 HAS ENERGY VALUE -2.854844	0.9	-1.258
COORD 1= 0.600 COORD 2= 0.000 HAS ENERGY VALUE -2.847716	1.1	-1.086
COORD 1= 0.800 COORD 2= 0.000 HAS ENERGY VALUE -2.834468	1.3	-0.727
COORD 1= 1.000 COORD 2= 0.000 HAS ENERGY VALUE -2.823450	1.5	-0.426
COORD 1= 1.200 COORD 2= 0.000 HAS ENERGY VALUE -2.816188	1.7	-0.229
COORD 1= 1.400 COORD 2= 0.000 HAS ENERGY VALUE -2.812008	1.9	-0.115
COORD 1= 1.600 COORD 2= 0.000 HAS ENERGY VALUE -2.809814	2.1	-0.0552

\$DATA

He calculation by D. Matyushov

C1 0
HE 2.0 0.0000000000 0.0000000000 0.0000000000
STO 3

SEND

--- OPEN SHELL ORBITALS -- GENERATED AT Wed Feb 20 14:52:53 2002

He calculation by D. Matyushov

E(UHF)= -2.8377839566, E(NUC)= 0.0000000000, 2 ITERS

\$VEC

1 1 1.00000000E+00

1 1 1.00000000E+00

SEND

POPULATION ANALYSIS

HE 2.00000 0.00000 2.00000 0.00000
MOMENTS AT POINT 1 X,Y,Z= 0.000000 0.000000 0.000000
DIPOLE C.000000 0.000000 0.000000

HOMEWORK SET (Due on March 6th, 6:00 PM)

Problem 1. Run an RHF 6-31G calculation of HeH^+ (GAMESS) at $R = 1.4632$ a.u. and list the C-matrix of the Roothaan equation corresponding to the converged SCF procedure.

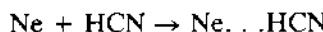
Problem 2. Calculate the first-order orbital energies of He within the minimal-basis double-zeta SCF procedure using the symmetric diagonalization of the overlap matrix (see lecture notes for the atomic integrals).

Problem 3. Run a UHF STO 3G calculation of Li using GAMESS and determine the spin density matrix

$$\mathbf{P}^S = \mathbf{P}^\alpha - \mathbf{P}^\beta$$

Plot the dependence of the spin density on the radius-vector r from the nucleus.

dispersion forces which owe their existence to the instantaneous interactions between the electrons. Thus for van der Waals molecules such as

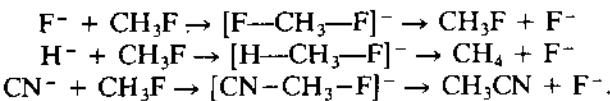


SCF calculations should be regarded as somewhat suspect and they are totally suspect for studies at large internuclear separation of systems like $\text{He}\dots\text{He}$.

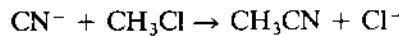
Table 3.9 Dissociation energies for a selection of alkali halides. SCF calculations using large polarised Dunning basis sets. The dissociation process is molecules \rightarrow ions not molecule \rightarrow neutral atoms. (Thermodynamic data refer to the latter process.)

Molecule	$R(\text{X}-\text{Y})(\text{pm})$		$D_e(\text{kJ mol}^{-1})$	
	Calculation	Experiment	Calculation	Experiment
LiF	156.9	156.4	771.3	770.3
LiCl	202.4	202.1	628.3	641.4
LiBr	220.0	217.0	595.9	618.4
NaF	192.7	192.6	643.5	643.9
NaCl	242.1	236.1	537.9	554.8
NaBr	253.9	250.2	519.2	534.3
KF	224.9	217.1	570.0	582.4
KCl	266.7	266.7	471.8	493.7
KBr	293.5	282.1	453.0	475.3

A number of studies have been concerned with mapping out the minimum energy pathway between closed-shell reactants and products in elementary $S_{\text{N}}2$ reactions such as



Thus for example Duke and Bader used an extended basis set augmented with diffuse s and p primitives together with polarisation functions for the first reaction, and they predict a barrier of 31 kJ mol^{-1} with the intermediate complex having D_{3h} symmetry. Bohme *et al* were able to observe experimentally a barrier in the reaction



of about 21 kJ mol^{-1} , suggesting that such theoretically predicted barriers do exist. The calculated energy barrier is not the same quantity as the energy of activation, however.

UHF

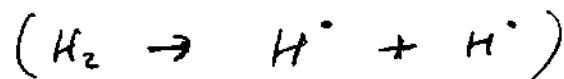
Open-shell orbitals
(unpaired electrons)

Restricted S_{center}
determinants:
electrons occupy
orbitals in pairs

Unrestricted S_{center}
determinants:
"up" and "down"
have different energies

Where do you use UHF?

- × unpaired electrons
- × even for closed-shell molecules, RHF
 - ↳ inappropriate at long distances for molecules that dissociate in open-shell species



Unrestricted spin orbitals:

$$\chi_j(\vec{r}) = \begin{cases} \psi_j^{\alpha}(\vec{r}) \alpha(\omega) \\ \psi_j^{\beta}(\vec{r}) \beta(\omega) \end{cases}$$

α and β show that spatial wave functions are different for "up" and "down"

UHF equations

The general HF equation

$$\underbrace{f(i) \chi_i(i)}_{\downarrow} = \varepsilon_i \chi_i(i)$$

$$f(i) \psi_i^\alpha = \varepsilon_i^\alpha \psi_i^\alpha$$

$$\downarrow$$

$$f^\alpha(i) \psi_i^\alpha(i) = \varepsilon_i^\alpha \psi_i^\alpha(i)$$

$$f(i) \psi_i^\beta = \varepsilon_i^\beta \psi_i^\beta$$

$$\downarrow$$

$$f^\beta(i) \psi_i^\beta(i) = \varepsilon_i^\beta \psi_i^\beta(i)$$

$$f^\alpha(i) = \langle \alpha | f | \alpha \rangle$$

$$f^\beta(i) = \langle \beta | f | \beta \rangle$$

$$= \int d\omega_1 \alpha^*(\omega_1) f(r_1 \omega_1) \alpha(\omega_1)$$

$$= \int d\omega_1 \beta^*(\omega_1) f(r_1 \omega_1) \beta(\omega_1)$$

$$\underline{\psi_i^\alpha}$$

$$\underline{\psi_i^\beta}$$

—

+

+

+

$$f^\alpha(i) = h(i) + \sum_a^{N_\alpha} [J_a^\alpha(i) - K_a^\alpha(i)] + \sum_a^{N_\beta} J_a^\beta(i)$$

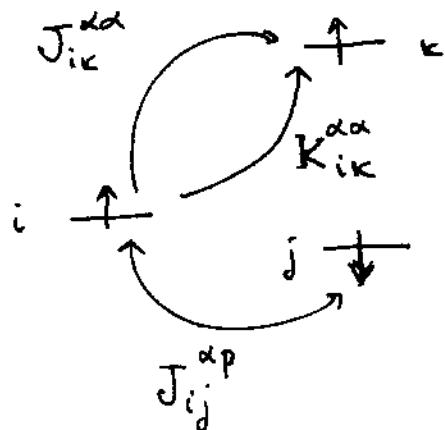
$$f^\beta(i) = h(i) + \sum_a^{N_\beta} [J_a^\beta(i) - K_a^\beta(i)] + \sum_a^{N_\alpha} J_a^\alpha(i)$$

Matrix elements

$$h_{ii}^{\alpha} = (\Psi_i^{\alpha} | h | \Psi_i^{\alpha}) \quad h_{ii}^{\beta} = (\Psi_i^{\beta} | h | \Psi_i^{\beta})$$

$$J_{ij}^{\alpha\beta} = (\Psi_i^{\alpha} | J_j^{\beta} | \Psi_i^{\alpha}) = (\Psi_i^{\alpha} \Psi_i^{\alpha} | \Psi_j^{\beta} \Psi_j^{\beta})$$

$$J_{ij}^{\alpha\alpha} = (\Psi_i^{\alpha} | J_j^{\alpha} | \Psi_i^{\alpha}) = (\Psi_i^{\alpha} \Psi_i^{\alpha} | \Psi_j^{\alpha} \Psi_j^{\alpha})$$



The ground-state energy

$$E_0 = \sum_a^{N_\alpha} h_{aa}^{\alpha} + \sum_a^{N_\beta} h_{aa}^{\beta} + \frac{1}{2} \sum_a^{N_\alpha} \sum_b^{N_\alpha} [J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}] \\ + \frac{1}{2} \sum_{a=1}^{N_\beta} \sum_b^{N_\beta} [J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}] + \underbrace{\sum_a^{N_\alpha} \sum_b^{N_\beta} J_{ab}^{\alpha\beta}}$$

eliminates
double counting,

at $a=b$, $J_{aa} - K_{aa} = 0$
and the self-energy
term disappears

$$\frac{1}{2} \sum_a \sum_c = \sum_a \sum_{b \neq a}$$

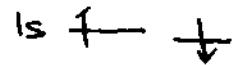
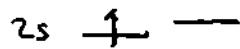
Pople-Nesbet equations

Basis expansion of unrestricted MOs:

$$\Psi_i^\alpha = \sum_{\mu=1}^k c_{\mu i}^\alpha \phi_\mu, \quad i = 1, 2, \dots, k$$

$$\Psi_i^\beta = \sum_{\mu=1}^k c_{\mu i}^\beta \phi_\mu, \quad i = 1, 2, \dots, k \quad \text{number of basis set functions}$$

Example: Li in STO 3G



$$\Psi^\alpha = c_1^\alpha \phi_{1s} + c_2^\alpha \phi_{2s} + c_3^\alpha \phi_{2p_x}$$

$$+ c_4^\alpha \phi_{2p_y} + c_5^\alpha \phi_{2p_z}$$

$$\Psi^\beta = c_1^\beta \phi_{1s} + c_2^\beta \phi_{2s} + c_3^\beta \phi_{2p_x} + c_4^\beta \phi_{2p_y} + c_5^\beta \phi_{2p_z}$$

Each set $\{\Psi_i^\alpha\}$ and $\{\Psi_i^\beta\}$ forms an orthonormal set:

$$f^\alpha(i) \Psi_i^\alpha = \varepsilon_i^\alpha \Psi_i^\alpha \quad \langle \Psi_i^\alpha | \Psi_j^\alpha \rangle = \delta_{ij}$$

$$f^\beta(i) \Psi_i^\beta = \varepsilon_i^\beta \Psi_i^\beta \quad \langle \Psi_i^\beta | \Psi_j^\beta \rangle = \delta_{ij}$$

The α - and β - sets are not orthogonal

$$\langle \Psi_j^\alpha | \Psi_k^\beta \rangle \neq \delta_{jk}$$

$$\overset{\leftrightarrow}{F} \overset{\leftrightarrow}{C} \overset{\leftrightarrow}{C}^\alpha = \overset{\leftrightarrow}{S} \overset{\leftrightarrow}{C} \overset{\leftrightarrow}{C} \overset{\leftrightarrow}{\varepsilon}^\alpha$$

$$\overset{\leftrightarrow}{F} \overset{\leftrightarrow}{P} \overset{\leftrightarrow}{C} \overset{\leftrightarrow}{P} = \overset{\leftrightarrow}{S} \overset{\leftrightarrow}{C} \overset{\leftrightarrow}{P} \overset{\leftrightarrow}{\varepsilon}^\beta$$

← Pople-Nesbet equations

Unrestricted density matrix

$$\rho^\alpha(\vec{r}) = \sum_a^{N_\alpha} |\psi_a^\alpha(\vec{r})|^2$$

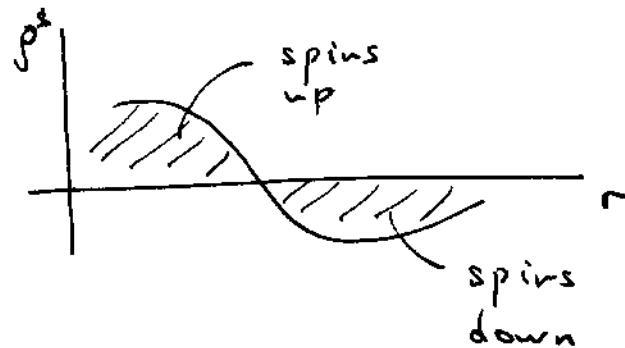
(density of "up" spins)

$$\rho^\beta(\vec{r}) = \sum_a^{N_\beta} |\psi_a^\beta(\vec{r})|^2$$

(density of "down" spins)

$$\rho^T(\vec{r}) = \rho^\alpha(\vec{r}) + \rho^\beta(\vec{r}) \quad \leftarrow \text{total charge density}$$

$$\rho^S(\vec{r}) = \rho^\alpha(\vec{r}) - \rho^\beta(\vec{r}) \quad \leftarrow \text{spin density}$$



Exercise 3.36 Show that $\int \rho^S(r) d\vec{r} = 2 \langle \hat{\sigma}_z \rangle$

$$\hat{\sigma}_z |x_1 \dots x_e\rangle = \frac{1}{2} (N_\alpha - N_\beta) |x_1 \dots x_e\rangle$$

$$\langle x_1 \dots x_e | \hat{\sigma}_z |x_1 \dots x_e\rangle = \frac{1}{2} (N_\alpha - N_\beta) =$$

$$= \frac{1}{2} \int \rho^\alpha(\vec{r}) d\vec{r} - \frac{1}{2} \int \rho^\beta(\vec{r}) d\vec{r}$$

"Up" and "down" density matrices

$$\rho^\alpha(\vec{r}) = \sum_a |\Psi_a^\alpha(\vec{r})|^2 = \sum_{\mu\nu} \Phi_\mu(\vec{r}) \Phi_\nu^*(\vec{r}) \sum_a^{N_\alpha} C_{\mu a}^\alpha (C_{\nu a}^\alpha)^*$$

summation over all basis functions, irrespective whether occupied or not

sum over occupied orbitals with spin up

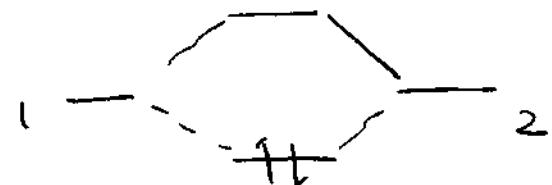
$$\rho^P = \sum_{\mu\nu} \Phi_\mu(\vec{r}) \Phi_\nu^*(\vec{r}) \sum_a^{N_P} C_{\mu a}^P (C_{\nu a}^P)^*$$

$$P_{\mu\nu}^\alpha = \sum_a^{N_\alpha} C_{\mu a}^\alpha (C_{\nu a}^\alpha)^* \leftarrow \text{"up" density matrix}$$

$$P_{\mu\nu}^P = \sum_a^{N_P} C_{\mu a}^P (C_{\nu a}^P)^* \leftarrow \text{"down" density matrix}$$

Example : H₂

$$\Psi_g = \frac{1}{\sqrt{2(1+s)}} (\Phi_1 + \Phi_2)$$



$$\Psi_u = \frac{1}{\sqrt{2(1-s)}} (\Phi_1 - \Phi_2)$$

$$\tilde{C}^\alpha = \tilde{C}^P = \begin{pmatrix} \frac{1}{\sqrt{2(1+s)}} & \frac{1}{\sqrt{2(1-s)}} \\ \frac{1}{\sqrt{2(1+s)}} & -\frac{1}{\sqrt{2(1-s)}} \end{pmatrix} \quad \begin{aligned} C_{2g} &= \frac{1}{\sqrt{2(1+s)}} \\ C_{1g} &= \frac{1}{\sqrt{2(1-s)}} \end{aligned}$$

$$\tilde{\rho}^\alpha = \tilde{\rho}^P = C_{\mu g} (\psi_g)^* = \frac{1}{2(1+s)} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

Total and spin density matrices

Total density matrix:

$$\overleftrightarrow{P}^T = \overleftrightarrow{P}^\alpha + \overleftrightarrow{P}^\beta$$

Spin density matrix:

$$\overleftrightarrow{P}^S = \overleftrightarrow{P}^\alpha - \overleftrightarrow{P}^\beta$$

Exercise 3.38. Show that for $O_1 = \sum_{i=1}^n h(i)$

$$\langle O_1 \rangle = \sum_m \sum_\nu P_{\mu\nu}^T (\nu | h | m)$$

$$\langle O_1 \rangle = \sum_a \langle a | h | a \rangle = \sum_a^{N_\alpha} \langle \Psi_a^\alpha | h | \Psi_a^\alpha \rangle + \sum_a^{N_\beta} \langle \Psi_a^\beta | h | \Psi_a^\beta \rangle$$

$$= \sum_a^{N_\alpha} \sum_{\mu,\nu} (C_{\nu a}^\alpha)^* C_{\mu a}^\alpha (\Phi_\nu | h | \Phi_\mu)$$

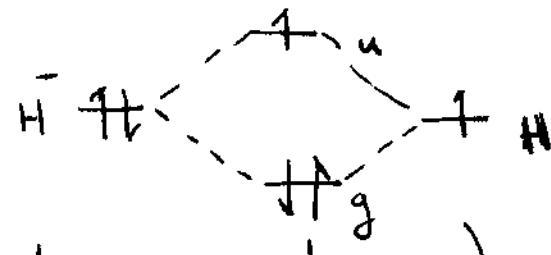
$$+ \sum_a^{N_\beta} \sum_{\mu,\nu} (C_{\nu a}^\beta)^* C_{\mu a}^\beta (\Phi_\nu | h | \Phi_\mu) =$$

$$= \sum_{\mu,\nu} (\nu | h | \mu) \underbrace{\sum_a \left[(C_{\nu a}^\alpha)^* C_{\mu a}^\alpha + (C_{\nu a}^\beta)^* C_{\mu a}^\beta \right]}_{P_{\mu\nu}^T}$$

$$P_{\mu\nu}^T$$

$$= \sum_{\mu,\nu} P_{\mu\nu}^T (\nu | h | \mu)$$

Example : H_2^-



$$\tilde{c}^\alpha = \tilde{c}^p = \begin{pmatrix} \frac{1}{\sqrt{2(1+s)}} & \frac{1}{\sqrt{2(1-s)}} \\ \frac{1}{\sqrt{2(1+s)}} & -\frac{1}{\sqrt{2(1-s)}} \end{pmatrix}$$

$$P_{\mu\nu}^p = C_{\mu g} C_{gj}^*, \quad \tilde{P}^p = \frac{1}{2(1+s)} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$P_{\mu\nu}^\alpha = C_{\mu g} C_{gj}^* + C_{\mu u} C_{ju}^*$$

$$\tilde{P}^\alpha = \frac{1}{2(1+s)} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} + \frac{1}{2(1-s)} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

Spin matrix :

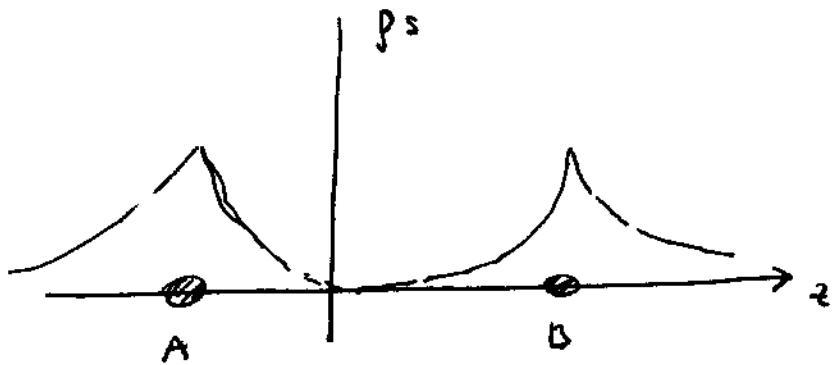
$$\tilde{P}^s = \tilde{P}^\alpha - \tilde{P}^p = \frac{1}{2(1-s)} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

Spin density:

$$\rho^s(\vec{r}) = \sum_{\mu, \nu} P_{\mu, \nu}^s \Phi_\mu(\vec{r}) \Phi_\nu^*(\vec{r})$$

$$\mu, \nu = 1, 2, \quad \Phi_{\mu, \nu} = \Phi_{A, B}(\vec{r})$$

$$\begin{aligned} \rho^s(\vec{r}) &= \frac{1}{2(1-s)} \left[\Phi_A(\vec{r})^2 + \Phi_B(\vec{r})^2 - 2\Phi_A(\vec{r})\Phi_B(\vec{r}) \right] \\ &= \frac{1}{2(1-s)} \left[\Phi_A(\vec{r}) - \Phi_B(\vec{r}) \right]^2 \end{aligned}$$



{ This is the procedure to be used for the }
{ homework set ! }

H₂ dissociation

Minimal basis set ground-state energy (Ex. 3.27):

$$E_0 = \frac{1}{1+s} \left(F_{11} + H_{11}^{\text{core}} + F_{12} + H_{12}^{\text{core}} \right)$$

$$E_0 = \frac{1}{2} \sum_{\mu, \nu} P_{\mu\nu} \left(H_{\mu\nu}^{\text{core}} + F_{\mu\nu} \right)$$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda, \delta} P_{\lambda\delta} \left[(\mu\nu | \delta\lambda) - \frac{1}{2} (\mu\lambda | \delta\nu) \right]$$

The density matrix:

$$\hat{P} = \frac{1}{1+s} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$\begin{aligned} F_{11} &= H_{11}^{\text{core}} + \frac{1}{1+s} \left[\frac{1}{2} (\Phi_A \Phi_A | \Phi_A \Phi_A) + (\Phi_A \Phi_A | \Phi_B \Phi_B) \right. \\ &\quad \left. + (\Phi_A \Phi_B | \Phi_A \Phi_B) - \frac{1}{2} (\Phi_A \Phi_B | \Phi_B \Phi_A) \right] \rightarrow \\ &\rightarrow H_{11}^{\text{core}} + \frac{1}{2(1+s)} (\Phi_A \Phi_A | \Phi_A \Phi_A) \rightarrow H_{11}^{\text{core}} + \frac{1}{2} (\Phi_A \Phi_A | \Phi_A \Phi_A) \end{aligned}$$

$$F_{12} \rightarrow H_{12}^{\text{core}} \rightarrow 0$$

$$E_0 \xrightarrow[R \rightarrow \infty]{} 2 H_{11}^{\text{core}} + \underline{\frac{1}{2} (\Phi_A \Phi_A | \Phi_A \Phi_A)}$$

spurious term, result of
the RKF assumption

RHF calculation of H₂:

```
$CTRL SCFTYP=RHF MULT=1 NZVAR=0 RUNTYP=SURFACE COORD=ZMT $END
$BASIS GBASIS=STO NGAUSS=3 $END
$GUESS GUESS=HUCKEL $END
$SURF IVEC1(1)=2,1 IGRP1=1 ORIG1=0.5 DISP1=0.1 NDISP1=20      $END
$DATA
```

H2 calculation by D. Matyushov

Cnv 4

H1

H2 1 0.7

```
$END
```

ROHF calculations of H₂:

```
$CTRL SCFTYP=ROHF MULT=1 NZVAR=0 RUNTYP=SURFACE COORD=ZMT $END
$BASIS GBASIS=STO NGAUSS=3 $END
$GUESS GUESS=HUCKEL $END
$SURF IVEC1(1)=2,1 IGRP1=1 ORIG1=0.3 DISP1=0.1 NDISP1=20      $END
$SCF NCO=0 NSETO=2 NO(1)=1,1 $END
$DATA
```

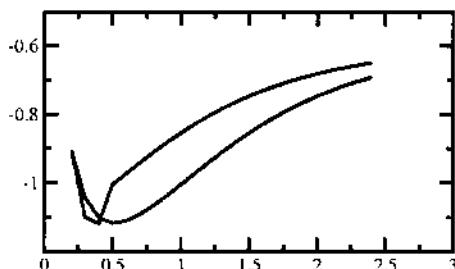
H2 calculation by D. Matyushov

Cnv 4

H1

H2 1 0.3

```
$END
```



RHF calculation of the H₂ dissociation curve.

Table 1: Calculations of the H₂ dissociation curve by RHF and ROHF methods.

<i>R</i>	RHF	ROHF	UHF
0.5	-1.005107	-1.110850	-1.117349
0.6	-0.973111		
0.7	-0.941481	-1.066109	
0.8	-0.910874	-1.036539	-1.066109
0.9	-0.881732		
1.0	-0.854338	-0.973111	-1.005107
1.1	-0.828848		
1.2	-0.805333	-0.910874	-0.941481
1.3	-0.783793		-0.910874
1.4	-0.764178	-0.854338	-0.881732
1.5	-0.746401		
1.6	-0.730353		-0.828848
1.7	-0.715910	-0.783793	-0.805333
1.8	-0.702944		-0.783793
1.9	-0.691328	-0.746401	-0.764178
2.0	-0.680941	-0.730353	-0.746401
2.1	-0.671669		-0.730353
2.2	-0.663405	-0.702944	
2.3	-0.656048		
2.4	-0.649506		-0.691328

Solutions of the unrestricted SCF equations

Fock matrices :

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda, \beta} \left[P_{\lambda z}^T(\mu\nu) | \beta\lambda \rangle - P_{\lambda z}^{\alpha}(\mu\lambda) | \beta\lambda \rangle \right]$$

$$F_{\mu\nu}^{\beta} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda, \beta} \left[P_{\lambda z}^T(\mu\nu) | \beta\lambda \rangle - P_{\lambda z}^{\alpha}(\mu\lambda) | \beta\lambda \rangle \right]$$

In the Pople-Nesbet equations

$$\tilde{F}^{\alpha} \tilde{C}^{\alpha} = \tilde{S} \tilde{C}^{\alpha} \tilde{\xi}^{\alpha}$$

$$\tilde{F}^{\beta} \tilde{C}^{\beta} = \tilde{S} \tilde{C}^{\beta} \tilde{\xi}^{\beta}$$

\tilde{F}^{α} and \tilde{F}^{β} depend on both \tilde{P}^{α} and \tilde{P}^{β} .
The two set of equations are coupled.

When $N^{\alpha} = N^{\beta}$, a restricted solution of the Roothaan equation is a solution to the unrestricted Pople-Nesbet equations. The initial guess for the density matrix should be close to the unrestricted electronic configuration in order to avoid the SCF procedure to converge to the RHF solution.

Calculation of the spin density and hyperfine coupling constants for methyl radical (Sec. 3.8.6).

```
$CONTRL SCFTYP=UHF RUNTYP=OPTIMIZE MULT=2 $END
$SYSTEM MEMORY=200000 $END
$BASIS GBASIS=N311 NDFUNC=3 NPFUNC=3 DIFFS=.FALSE. $END
$ELDENS IEDEN=1 $END
$DATA
CH_3 calculation by D. Matyushov
Dnh 3
```

```
C 6
H 1 1.1 0. 0.
$END
```

ATOMIC BASIS SET

THE CONTRACTED PRIMITIVE FUNCTIONS HAVE BEEN UNNORMALIZED
THE CONTRACTED BASIS FUNCTIONS ARE NOW NORMALIZED TO UNITY

SHELL TYPE	PRIMITIVE	EXONENT	CONTRACTION COEFFICIENTS	
<hr/>				
C				
1	S 1	4563.2400000	0.001966650249	
1	S 2	682.0240000	0.015230601932	
1	S 3	154.9730000	0.076126909656	
1	S 4	44.4553000	0.260801033080	
1	S 5	13.0290000	0.616462078191	
1	S 6	1.8277300	0.221006028032	
2	L 7	20.9642000	0.114660080729	0.040248692673
2	L 8	4.8033100	0.919999647749	0.237593956746
2	L 9	1.4593300	-0.003030682134	0.815853851473
3	L 10	0.4834560	1.000000000000	1.000000000000
4	L 11	0.1455850	1.000000000000	1.000000000000

5	D	12	2.5040000	1.000000000000
6	D	13	0.6260000	1.000000000000
7	D	14	0.1565000	1.000000000000

H

20	S	15	33.8650000	0.025493814541
20	S	16	5.0947900	0.190373108582
20	S	17	1.1587900	0.852161486043
21	S	18	0.3258400	1.000000000000
22	S	19	0.1027410	1.000000000000
23	P	20	3.0000000	1.000000000000
24	P	21	0.7500000	1.000000000000
25	P	22	0.1875000	1.000000000000

MULLIKEN AND LOWDIN POPULATION ANALYSES

MULLIKEN ATOMIC POPULATION IN EACH MOLECULAR ORBITAL
ALPHA ORBITALS

	1	2	3	4	5
	1.000000	1.000000	1.000000	1.000000	1.000000
1	0.999965	0.593110	0.558675	0.558675	0.963450
2	0.000012	0.135630	0.075027	0.219189	0.012183
3	0.000012	0.135630	0.075027	0.219189	0.012183
4	0.000012	0.135630	0.291271	0.002946	0.012183

MULLIKEN ATOMIC POPULATION IN EACH MOLECULAR ORBITAL
BETA ORBITALS

	1	2	3	4
	1.000000	1.000000	1.000000	1.000000
1	1.000011	0.486664	0.450999	0.450999
2	-0.000004	0.171112	0.091167	0.274834
3	-0.000004	0.171112	0.091167	0.274834
4	-0.000004	0.171112	0.366667	-0.000666

ATOMIC SPIN POPULATION (ALPHA MINUS BETA)

ATOM	MULL.POP.	LOW.POP.
1 C	1.285203	0.832162
2 H	-0.095068	0.056135
3 H	-0.095068	0.056135
4 H	-0.095068	0.055569

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS

ATOM	MULL.POP.	CHARGE	LOW.POP.	CHARGE
1 C	6.062547	-0.062547	5.881415	0.118585
2 H	0.979151	0.020849	1.034886	-0.034886
3 H	0.979151	0.020849	1.034886	-0.034886
4 H	0.979151	0.020849	1.048813	-0.048813

Spin density and electron density. Electron density is the density of all the electrons on a given atom.

ATOMIC SPIN DENSITY AT THE NUCLEUS (A.U.)

	SPIN DENS	ALPHA DENS	BETA DENS
1 C	6.0	0.1247201	59.77990
2 H	1.0	-0.0262756	0.20125
3 H	1.0	-0.0262756	0.20125

4 H 1.0 -0.0262756 0.20125 0.22753

ELECTRON DENSITY

POINT	X	Y	Z	DENSITY (A.U.)
	(BOHR)			
1	0.00000	0.00000	0.00000	119.435089
2	-1.01196	1.75277	0.00000	0.428779
3	-1.01196	-1.75277	0.00000	0.428779
4	2.02392	0.00000	0.00000	0.428779

SCF spin densities and hyperfine coupling constants for the methyl radical
(6-31G**))

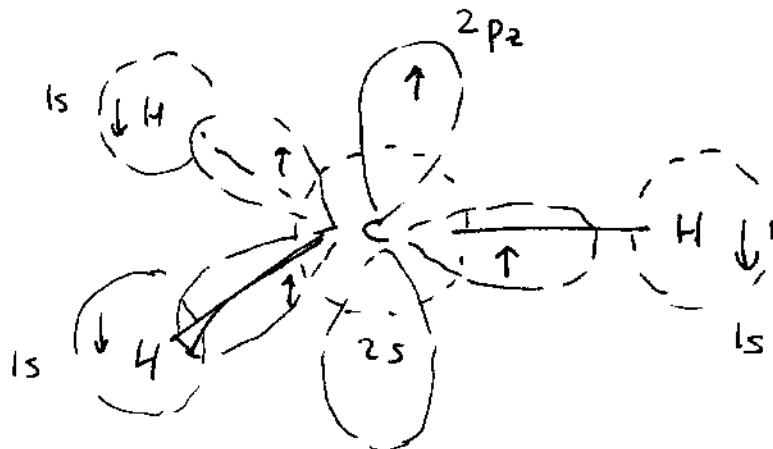
C	H	Spin density (a.u.)	Coupling constant (G)
		α_c	α_H
0.1247	-0.0263	+49.9	-41.86
Exp.		+38.3	-23.0

$$\alpha^H(G) = 1592 \rho^S(\vec{R}_H)$$

$$\alpha^C(G) = 400.3 \rho^S(\vec{R}_C)$$

Hund's rules

- * electrons tend to have parallel spins on the same atom.
- * spins of electrons on orbitals that form chemical bonds tend to be antiparallel.



The essence of ESR

Electron

Electron angular momentum:

$$\underline{S} = \sqrt{s(s+1)} \underline{\hbar} = \frac{\sqrt{3}}{2} \underline{\hbar}$$

electron spin quantum number

$$s = 1/2$$

$$S_z = m_s \underline{\hbar}, \quad m_s = \pm 1/2$$

Electron magnetic dipole moment:

$$\underline{\mu}_s = -g_e \underline{m}_e \underline{S}/\hbar$$

$$\underline{g_e} = 2.00232$$

$$m_e = \frac{e\hbar}{2m_ec} \quad \text{Bohr magneton}$$

electron mass speed of light

Landé g-factor

Nucleus

Nuclear spin angular momentum: $\underline{I} = \sqrt{i(i+1)} \underline{\hbar}$

Nuclear magnetic dipole moment: $I_z = m_I \underline{\hbar}$

$$\underline{\mu}_I = -g_N m_N \underline{I}/\hbar$$

$$m_I = -i, \dots, 0, \dots, i$$

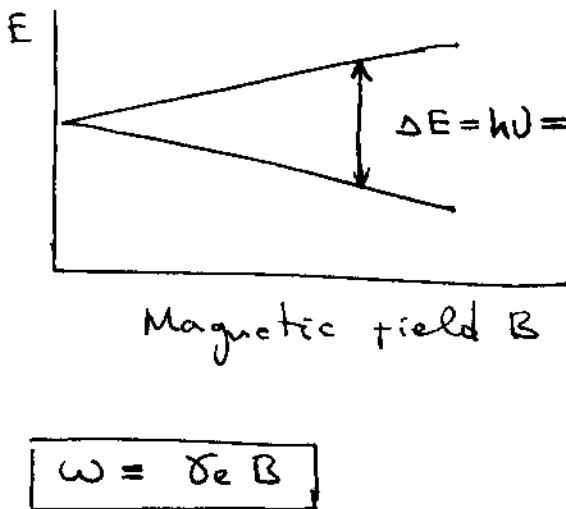
$$\underline{M}_N = \frac{e\hbar}{2m_Nc}$$

$$g_N = 5.5856 \quad \text{for a proton}$$

nuclear magneton

ESR hyperfine coupling constants

Zeeman energy:



$$E = -M_z B =$$

$$= g e M_e m_s B$$

$$= \gamma_e B M_z$$

\equiv

$$\gamma_e = \frac{e}{2 M_e c}$$

γ_e is the gyromagnetic ratio

The interaction of an unpaired electron with a magnetic nucleus is called nuclear hyperfine interaction.

$$E = g e M_e m_s B + \sum_i a_i m_s M_i$$

sum over the
magnetic
nuclei

hyperfine coupling
constant

For isotropic systems with one electron, the interaction energy is given by the Fermi equation

$$E_{iso} = -\frac{8\pi}{3} |F(0)|^2 M_e z M_N z$$

electronic density
on the nucleus

Hyperfine coupling constants: Hydrogen atom

Fermi (isotropic) interaction:

$$H_{iso} = \frac{8\pi}{3} g_e g_N \mu_e \mu_N g^s(r) \hat{S}_z \hat{I}_z = h A_0 S_z I_z$$

Total interaction Hamiltonian:

$$H_{int} = g_e \mu_e B S_z + h A_0 S_z I_z$$

Spin states for the hydrogen atom:

$$|\alpha_e \alpha_n\rangle \quad |\beta_e \alpha_n\rangle \quad |\alpha_e \beta_n\rangle \quad |\beta_e \beta_n\rangle$$

$$S_z |\alpha_e \beta_n\rangle = \frac{1}{2} |\alpha_e \beta_n\rangle \quad I_z |\alpha_e \beta_n\rangle = -\frac{1}{2} |\alpha_e \beta_n\rangle$$

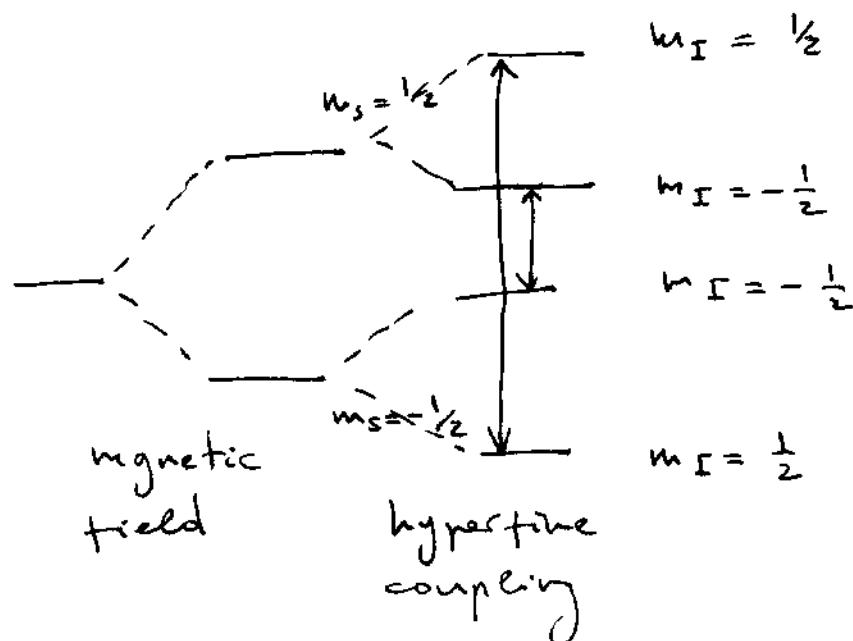
$$W(\alpha_e \alpha_n) = \frac{1}{2} g_e \mu_e B + \frac{1}{4} h A_0$$

$$W(\alpha_e \beta_n) = \frac{1}{2} g_e \mu_e B - \frac{1}{4} h A_0$$

$$W(\beta_e \alpha_n) = -\frac{1}{2} g_e \mu_e B - \frac{1}{4} h A_0$$

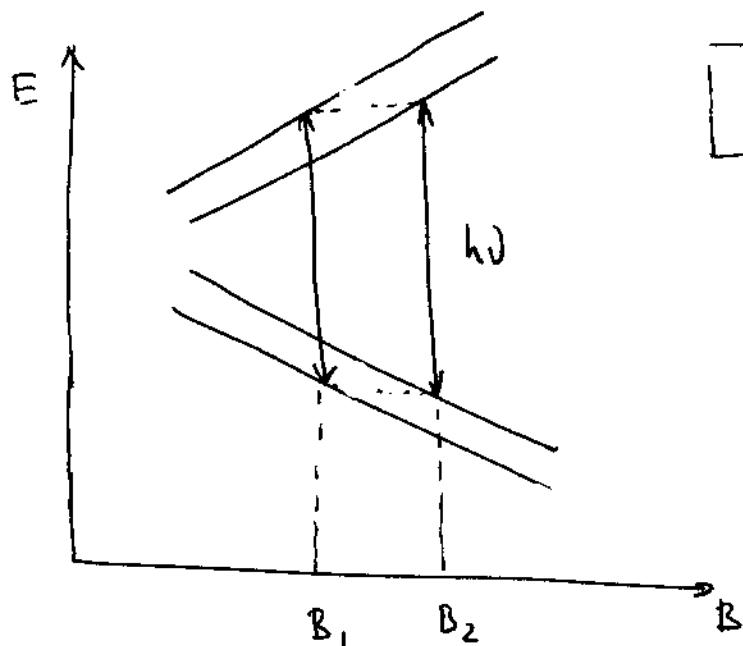
$$W(\beta_e \beta_n) = -\frac{1}{2} g_e \mu_e B + \frac{1}{4} h A_0$$

electron-nuclear
interaction energies



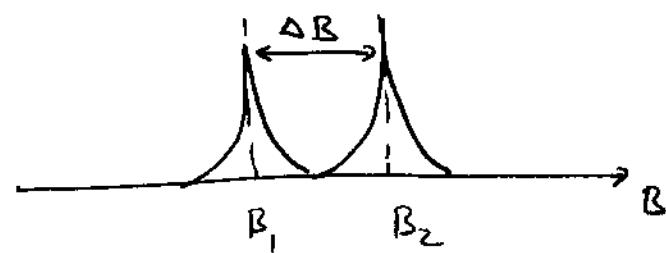
Experimental measurement of
the coupling constants

Zeeman energies for an unpaired electron
interacting with the proton



$$\Delta B = \frac{8\pi}{3} \frac{g_N \mu_N}{h} S_H^z$$

spin density on
the proton



The dissociation problem and its unrestricted solution

There may exist two solutions to the Pople-Nesbet equations at $N^* = N^F$. The restricted solution of Roothaan's equations is necessarily a solution of Pople-Nesbet equations.

H₂ dissociation problem. Minimal Basis set.

$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{2(1+s)}} (\Phi_1 + \Phi_2) \\ \Psi_2 &= \frac{1}{\sqrt{2(1-s)}} (\Phi_1 - \Phi_2) \end{aligned} \quad \rightarrow \quad \begin{cases} \Psi_1^\alpha = \cos\theta \Psi_1 + \sin\theta \Psi_2 \\ \Psi_1^\beta = \cos\theta \Psi_1 - \sin\theta \Psi_2 \\ \Psi_2^\alpha = -\sin\theta \Psi_1 + \cos\theta \Psi_2 \\ \Psi_2^\beta = \sin\theta \Psi_1 + \cos\theta \Psi_2 \end{cases}$$

since this is a unitary transformation,

$$\langle \Psi_1^\alpha | \Psi_2^\alpha \rangle = 0$$

$$\langle \Psi_1^\beta | \Psi_2^\beta \rangle = 0$$

$$\quad .$$

$$\begin{pmatrix} \Psi_1^\alpha \\ \Psi_2^\alpha \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}$$

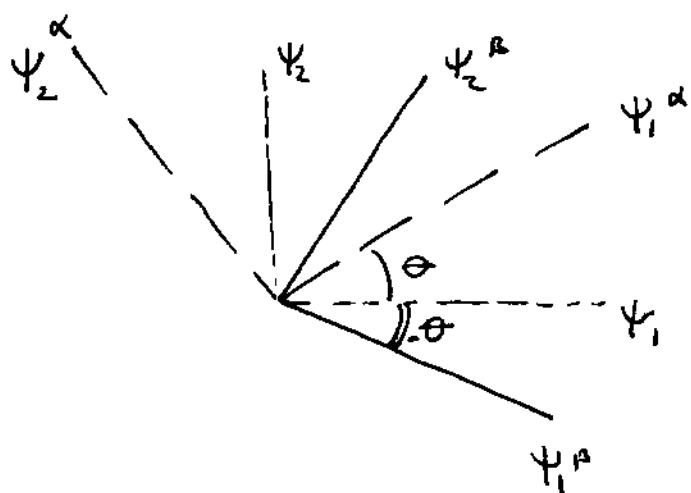
$$\begin{pmatrix} \Psi_1^\beta \\ \Psi_2^\beta \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}$$

The rotation of the basis set on some angle θ eliminates gerade or ungerade symmetry for the spatial orbitals and creates more freedom in relocating the electronic density

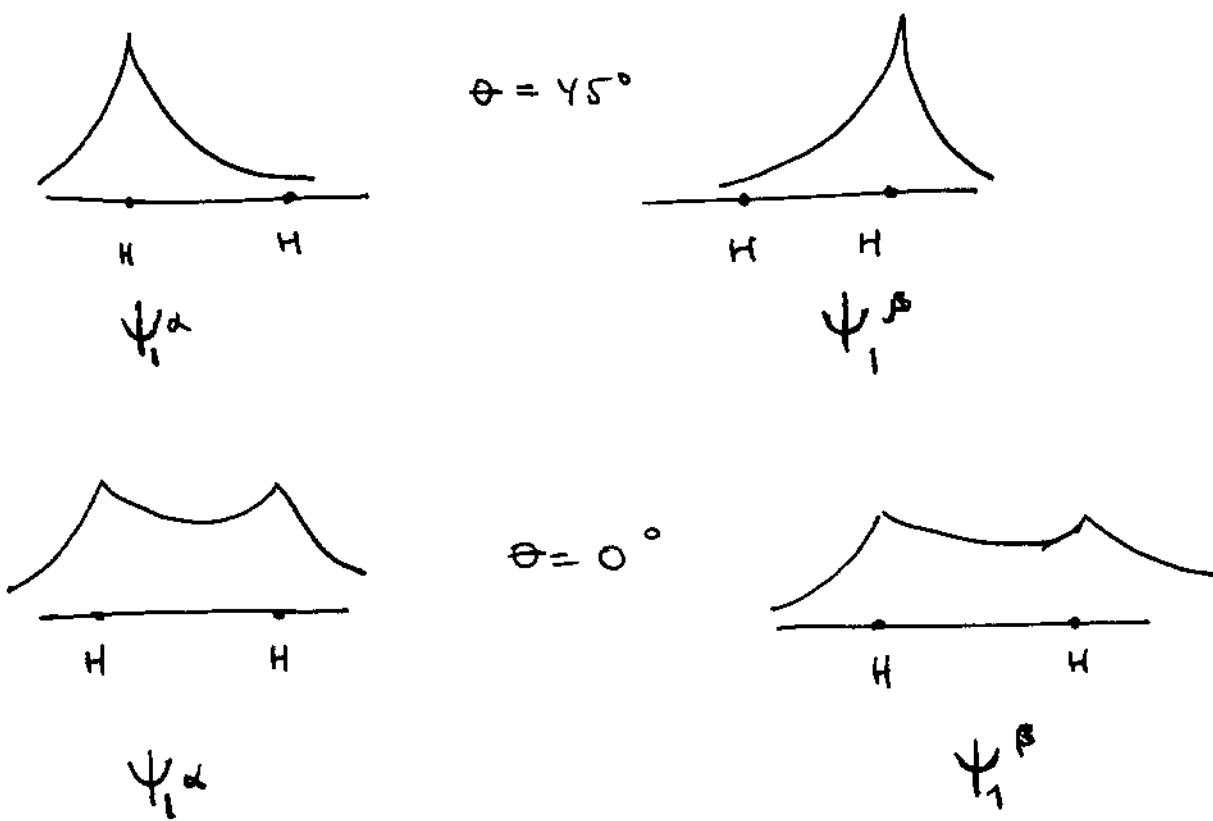
$$\Psi_1^\alpha = c_1 \Phi_1 + c_2 \Phi_2$$

$$\Psi_1^\beta = c_2 \Phi_1 + c_1 \Phi_2$$

The basis set $\{\psi^\alpha\}$ is obtained by rotation on angle θ ;
 the basis $\{\psi^\beta\}$ comes from rotation on angle $-\theta$:



In going from $\theta = 0^\circ$ to $\theta = 45^\circ$ the electronic density changes from localization to delocalization



Ground-state energy:

$$E_0 = h_{11}^\alpha + h_{11}^\beta + J_{11}^{\alpha\beta}$$

$$= 2 \cos^2 \theta h_{11} + 2 \sin^2 \theta h_{22} + \cos^4 \theta J_{11}$$

$$+ \sin^4 \theta J_{22} + 2 \sin^2 \theta \cos^2 \theta (J_{12} - 2K_{12})$$

$$\frac{\partial E_0}{\partial \theta} = 0 = A \cdot B,$$

$$A = (\cos \theta \sin \theta)$$

$$B = h_{22} - h_{11} + \sin^2 \theta J_{22} - \cos^2 \theta J_{11}$$

$$+ (\cos^2 \theta - \sin^2 \theta) (J_{12} - 2K_{12})$$

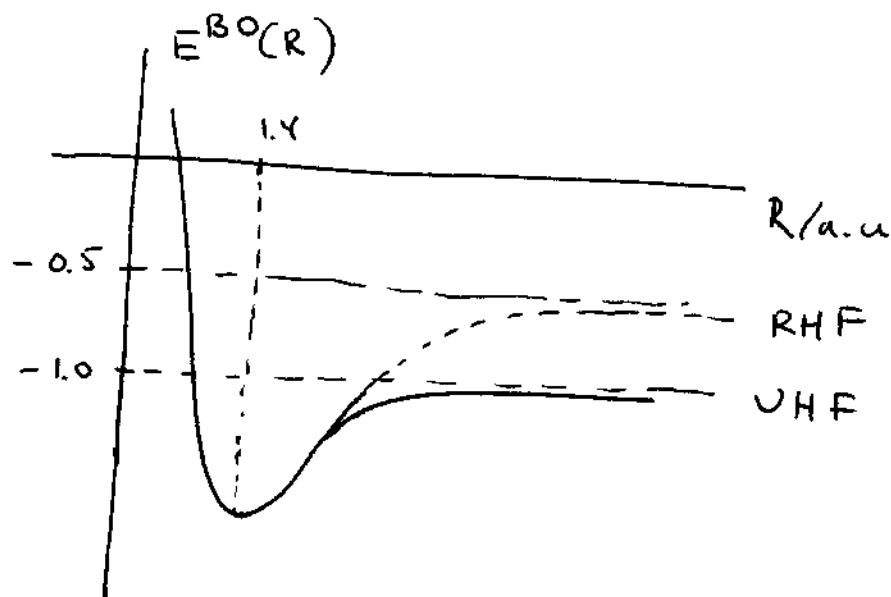
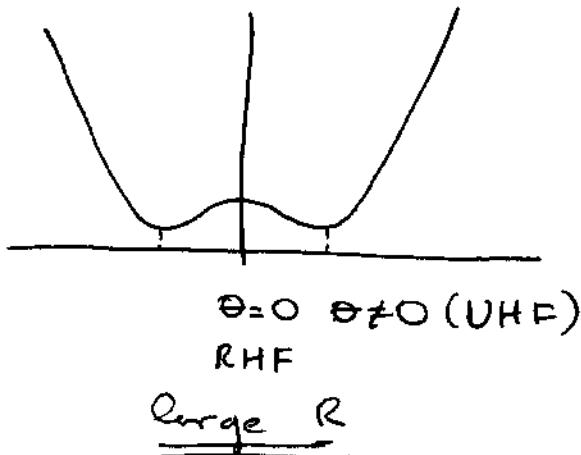
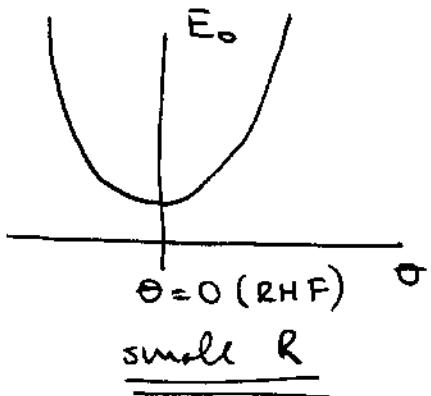
①. $A=0 \leftarrow$ RHF solution, $\theta=0$ corresponds to a delocalized electronic configuration

②. $B=0$ has a solution if

$$\cos^2 \theta = \underline{\underline{\gamma}} < 1$$

$$\gamma = \frac{h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}}$$

Homework: Exercise 3.43. Show that no UHF solution exists at $R=1.4$ a.u. and show that an UHF solution of $\theta=39.5^\circ$ exists at $R=4.0$ a.u.



Spin contamination problem

Final state of H_2

$$\lim_{R \rightarrow \infty} |\Psi_0\rangle = |\Phi_1(1) \bar{\Phi}_2(2)\rangle + \begin{matrix} + \\ H \end{matrix}$$

The state $|\Phi_1(1) \bar{\Phi}_2(2)\rangle$ is not an eigenstate of the L^2 operator; $L^2 |\Phi_1(1) \bar{\Phi}_2(2)\rangle \neq 0$

A spin-adapted linear combination

$$|\Psi_0\rangle = \frac{1}{\sqrt{2}} [|\Phi_1(1) \bar{\Phi}_2(2)\rangle + |\bar{\Phi}_1(2) \Phi_2(1)\rangle]$$

should be a correct singlet state

The UHF solution for the ground state:

$$|\Psi_0\rangle = \cos^2 \theta |\Psi_1 \bar{\Psi}_1\rangle - \sin^2 \theta |\Psi_2 \bar{\Psi}_2\rangle$$

$$-\frac{\sin \theta \cos \theta}{\sqrt{2}} |{}^3\Psi_1^2\rangle$$

if $\theta \neq 0$, the ground state of singlet is contaminated with the triplet state

At $R \rightarrow \infty$, $\theta = 45^\circ$

$$|\Psi_0\rangle \xrightarrow[R \rightarrow \infty]{} \frac{1}{2} [|\Psi_1 \bar{\Psi}_1\rangle - |\Psi_2 \bar{\Psi}_2\rangle - \overbrace{(\sqrt{2}) |{}^3\Psi_1^2\rangle}^{-1}]$$

misprint in the textbook

Selection rules (high-field magnetic dipole transitions)

The transition probability between states $|m_s m_I\rangle$ and $|m'_s m'_I\rangle$ is proportional to

$$|\langle m'_s m'_I | H' | m_s m_I \rangle|^2$$

with

$$H' = - \underbrace{\vec{\mu} \cdot \vec{B}}_{\substack{\text{magnetic} \\ \text{dipole} \\ \text{operator}}} = g_e \mu_e \vec{S} \cdot \vec{B} = g_e \mu_e B S_z$$

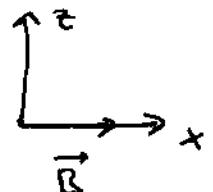
\vec{B}

$$\langle m'_s m'_I | H' | m_s m_I \rangle = g_e \mu_e B m_s \langle m'_s | m_s \rangle \langle m'_I | m_I \rangle$$

$$\Delta m_s = 0, \Delta m_I = 0$$

$$\vec{B} \parallel z$$

$$H' = g_e \mu_e B S_x$$



$$\langle m'_s m'_I | H' | m_s m_I \rangle = \frac{g_e \mu_e B}{2} \langle m'_s m'_I | (S^+ + S^-) | m_s m_I \rangle$$

$$\Delta m_s = \pm 1, \Delta m_I = 0$$

$$\vec{B} \parallel x$$

These selection rules are valid only if $|m_s m_I\rangle$ are eigenstates of the Hamiltonian. This approximation is valid if

$$g_e \mu_e H \gg \hbar A_0$$

i.e. for strong magnetic fields only.

Hyperfine Interaction in the Hydrogen Atom

Spin Hamiltonian:

$$H = g \mu_e \vec{B} \cdot \vec{S} + h A_0 \vec{S} \cdot \vec{I} - g_N M_N \vec{B} \cdot \vec{I}$$

$\vec{B} \parallel z$:

$$H = g \mu_e B S_z - g_N M_N B I_z + h A_0 [S_z I_z + \frac{1}{2} (S_+ I_- + S_- I_+)]$$

$|msm_I\rangle$ Basis: $|1s\alpha\alpha\rangle |1s\beta\beta\rangle$
 $|1p\alpha\alpha\rangle |1p\beta\beta\rangle$

this component makes the Hamiltonian matrix non-diagonal in the $|msm_I\rangle$ basis

$$S_+ I_- |1p\alpha\alpha\rangle \approx |1s\beta\beta\rangle$$

The Hamiltonian matrix becomes:

$$\text{H} = \begin{pmatrix} \frac{1}{2} g \mu_e B + \frac{1}{2} h A_0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} g \mu_e B - \frac{1}{2} h A_0 & \frac{1}{2} h A_0 & 0 \\ 0 & \frac{1}{2} h A_0 & -\frac{1}{2} g \mu_e B - \frac{1}{2} h A_0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} g \mu_e B + \frac{1}{2} h A_0 + \frac{1}{2} g_N M_N B \end{pmatrix}$$

Wave functions and allowed transitions
for the hydrogen atom at arbitrary B

One needs to define the basis set that diagonalizes the Hamiltonian matrix:

$$|F, M_F\rangle$$



$$F = |S+I|, |S+I-1|, \dots |S-I|$$

$$F = 0, 1$$

$$|1,1\rangle = |\alpha e \alpha n\rangle \quad |1,-1\rangle = |\beta e \beta n\rangle$$

$$|1,0\rangle = \cos\omega |\alpha e \beta n\rangle + \sin\omega |\beta e \alpha n\rangle$$

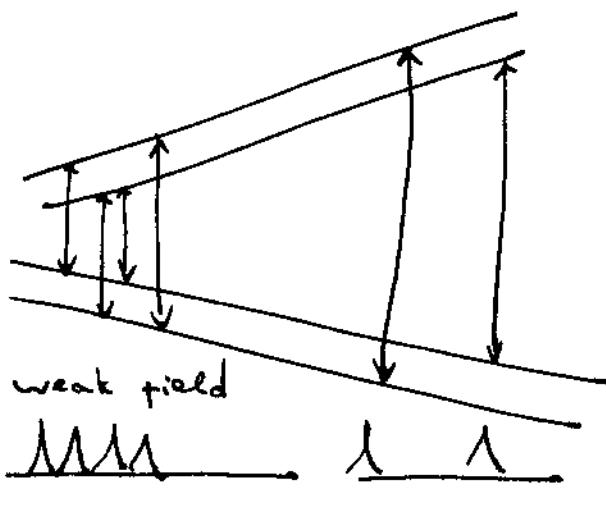
$$|0,0\rangle = -\sin\omega |\alpha e \beta n\rangle + \cos\omega |\beta e \alpha n\rangle$$

$$\tan 2\omega = \frac{hA_0}{(g_e \mu_e + g_n \mu_n)B}$$

$$B \rightarrow \infty, \quad |1,0\rangle \rightarrow |\alpha e \beta n\rangle \quad |0,0\rangle \rightarrow |\beta e \alpha n\rangle$$

$$B \rightarrow 0 \quad |1,0\rangle = \frac{1}{\sqrt{2}} [|\alpha e \beta n\rangle + |\beta e \alpha n\rangle]$$

$$|0,0\rangle = \frac{1}{\sqrt{2}} [|\alpha e \beta n\rangle - |\beta e \alpha n\rangle]$$



Four transitions are observed in weak magnetic fields and only two in strong magnetic fields.

Homework

Derive Breit-Rabi equations (1931) for the energies of electronic states of hydrogen in the external magnetic field (diagonalization of the 4×4 Hamiltonian matrix). Find the hyperfine splitting in zero external magnetic field.

DFT: concepts

- * For a system of N electrons, the wave mechanics searches for a N -electron wave function

$$\Psi_N(\vec{x}_1, \dots, \vec{x}_N)$$

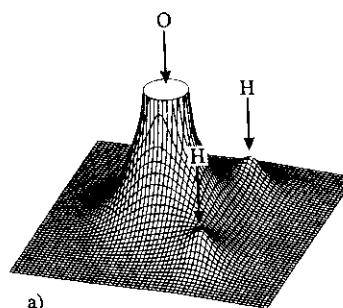
which is a function of $4N$ variables.

- * The matrix formulation of quantum mechanics eliminates the necessity to solve the differential wave propagation equation for each of $4N$ variables, but does not reduce the dimensionality of the problem.
- * The density-functional approach tries to reduce the problem dimensionality from $\underline{4N}$ to $\underline{8}$ suggesting that a two-electron matrix $p(\vec{r}_1, \vec{r}_2) \rightarrow$ sufficient for describing systems with pairwise interactions.

$$p(\vec{r}) = N \int \dots \int |\Psi_N(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\vec{x}_1 d\vec{x}_2 \dots d\vec{x}_N$$

$$p(\vec{r}) \rightarrow 0, |\vec{r}| \rightarrow \infty$$

$$\int p(\vec{r}) d\vec{r} = N$$



Representations of the electron density of the water molecule: (a) relief map showing values of $p(r)$ projected onto the plane, which contains the nuclei (large values near the oxygen atom are cut out); (b) three-dimensional molecular shape represented by an envelope of constant electron density (0.001 a.u.).

Asymptotic properties:

$$\lim_{r_A \rightarrow 0} \left[\frac{\partial}{\partial r} + 2z_A \right] p(\vec{r}) = 0$$

$$p(\vec{r}) \propto \exp [-2\sqrt{2I} |\vec{r}|]$$

ionization potential

Density matrix and the HF theory

Fock matrix (HF formulation):

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda\beta} P_{\lambda\beta} [(\mu\nu|\beta\lambda) - \frac{1}{2}(\mu\lambda|\beta\nu)]$$

In the matrix formulation, all space integration is absorbed into the atomic integrals. $P_{\lambda\beta}$ is the matrix of the spatial density matrix

$$\rho(\vec{r}\vec{r}') = 2 \sum_{i=1}^{n/2} \psi_i(\vec{r}) \psi_i^*(\vec{r}')$$

HF ground-state energy in terms of $\rho(\vec{r}\vec{r}')$:

$$E_{\text{HF}}[\rho] = T[\rho] + \int \rho(\vec{r}) \underline{U(\vec{r})} d\vec{r} + J[\rho] - K[\rho]$$

potential of the nuclei

$$T[\rho] = \int -\frac{1}{2} \nabla_i^2 \rho(\vec{r}_i\vec{r}_i) \Big|_{\vec{r}_i=\vec{r}_e} d\vec{r}_i \leftarrow \text{kinetic energy}$$

$$J[\rho] = \frac{1}{2} \int \rho(\vec{r}_i) \frac{1}{r_{i2}} \rho(\vec{r}_2) d\vec{r}_i d\vec{r}_e \leftarrow \text{Coulomb repulsion}$$

$$K[\rho] = \frac{1}{4} \int |\rho(\vec{r}_i\vec{r}_j)|^2 \frac{1}{r_{ij}} d\vec{r}_i d\vec{r}_j \leftarrow \text{Exchange interaction}$$

The main question the DFT approach addresses is how to express the kinetic energy, exchange, and correlation terms in terms of the diagonal elements of the density matrix

$$\boxed{\rho(\vec{r}) = \rho(\vec{r},\vec{r}') \Big|_{\vec{r}=\vec{r}'}}$$

Exchange - correlation hole

The pair density

$$p_2(\vec{x}_1, \vec{x}_2) = N(N-1) \dots \int |\Psi(\vec{x}_1, \dots, \vec{x}_N)|^2 d\vec{x}_3 \dots d\vec{x}_N$$

↑
the probability to find two
electrons at coordinates \vec{r}_1
and \vec{r}_2 with spins \vec{s}_1 and \vec{s}_2

$$p_2(\vec{x}_1, \vec{x}_1) = 0 \leftarrow \begin{array}{l} \text{Pauli exclusion principle} \\ (\text{exchange or Fermi correlation}) \end{array}$$

$$p_2(\vec{x}_1, \vec{x}_2) = p(\vec{x}_1)p(\vec{x}_2) + p(\vec{x}_1) h_{xc}(\vec{x}_1, \vec{x}_2)$$

\nearrow
exchange - correlation hole

$$\int h_{xc}(\vec{x}_1, \vec{x}_2) d\vec{x}_2 = -1$$

The electron-electron interaction energy:

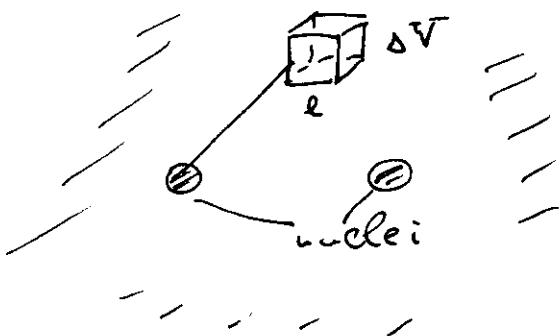
$$E_{ee} = \frac{1}{2} \iint \frac{p_2(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 = J[p] +$$

\nearrow
Coulomb integral

$$+ \frac{1}{2} \int \frac{p(\vec{r}_1) h_{xc}(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

\nearrow
Exchange + correlation term

The Thomas - Fermi model (1927)



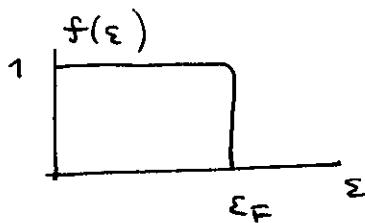
Assumptions:

- * electrons are distributed with the total electronic density $\rho(r)$
- * there is an effective potential determined by the nuclear field and the electronic distribution

The total energy of electrons in the cell of $\Delta V = \ell^3$:

$$\Delta E = 2 \int \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon$$

Fermi-Dirac distribution



$$f(\varepsilon) = \begin{cases} 1, & \varepsilon < \varepsilon_F \\ 0, & \varepsilon > \varepsilon_F \end{cases}$$

number of energy levels between ε and $\varepsilon + d\varepsilon$

$$g(\varepsilon) = 4\pi \left(\frac{2m}{\hbar^2}\right)^2 \ell^3$$

$$\Delta E = \frac{8\pi}{3} \left(\frac{2m}{\hbar^2}\right)^{3/2} \ell^3 \varepsilon_F^{5/2}$$

$$\Delta N = 2 \int f(\varepsilon) g(\varepsilon) d\varepsilon = \frac{8\pi}{3} \left(\frac{2m}{\hbar^2}\right)^{3/2} \ell^3 \varepsilon_F^{3/2}$$

$$\Delta E = \frac{3}{5} \Delta N \varepsilon_F = \frac{3\hbar^2}{10m} \left(\frac{3}{8\pi}\right)^{2/3} \ell^3 \left(\frac{\Delta N}{\ell^3}\right)^{5/3}$$

$p(r)$

$$I_{TF}[\rho] = C_F \int \rho^{5/3}(r) d\vec{r},$$

$$C_F = \frac{3}{10} (3\pi^2)^{2/3} = 2.891 \text{ a.u.}$$

Thomas - Fermi energy Functional

$$E_{TF} [\rho(\vec{r})] = C_F \int \rho^{5/3}(\vec{r}) d\vec{r} - \sum_A z_A \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{R}_A|} d\vec{r}$$

$$+ \frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2$$

The variational principle for the ground state :

$$\delta [E_{TF} [\rho] - \mu_{TF} (\int \rho(\vec{r}) d\vec{r} - N)] = 0$$

$$\mu_{TF} = \frac{5}{3} C_F \overline{\rho^{2/3}(\vec{r})} - \overline{\Phi(\vec{r})}$$

$\underbrace{\quad}_{\text{effective electrostatic potential}}$

Poisson equation : $\Delta \Phi = 4\pi \rho(r)$

$$\frac{5}{3} C_F \times \frac{2}{3} \frac{1}{\rho^{1/3}} \Delta \rho = 4\pi \rho$$

$$\boxed{\Delta \rho = \frac{36\pi}{10C_F} \rho^{4/3}}$$

Thomas - Fermi equation

Dirac exchange energy

For an uniform electron gas

$$\rho(\vec{r}_1, \vec{r}_2) = \frac{2}{V} \sum_{\text{occupied } \vec{k}} e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)} = \frac{1}{4\pi^3} \int e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)} d\vec{k}$$

$$= \frac{1}{\pi^2} \int_0^{k_F} dk k^2 \frac{\sin kr_{12}}{kr_{12}}$$

at $r_{12} \rightarrow 0$ one gets $\rho(\vec{r}) = \frac{(k_F(\vec{r}))^3}{3\pi^2}$

$$\rho(\vec{r}_1, \vec{r}_2) = 3\rho(\vec{r}_1) \frac{j_1(k_F r_{12})}{k_F r_{12}}$$

$$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}$$

spherical Bessel function
of the first order

$$K_D[\rho] = \frac{1}{4} \iint \frac{(\rho(\vec{r}_1, \vec{r}_2))^2}{r_{12}} d\vec{r}_1 d\vec{r}_{12}$$

$$= g\pi \int \frac{\rho(\vec{r})^2 d\vec{r}}{k_F^2} \underbrace{\int_0^\infty j_1(x)^2 \frac{dx}{x}}_{= 1/4}$$

$$= \frac{g\pi}{4} \int \frac{\rho(\vec{r})^2 d\vec{r}}{k_F^2}$$

$$= C_x \int \rho^{4/3} d\vec{r}, \quad C_x = \frac{3}{4} \left(\frac{2}{\pi}\right)^{1/2}$$

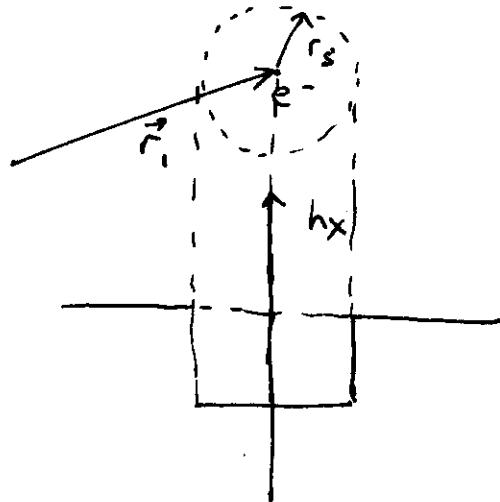
$$K_D[\rho] = C_x \int \rho^{4/3} d\vec{r} \quad \leftarrow \text{Dirac exchange term}$$

Slater's approximation for HF exchange

$$K[\rho] = -\frac{1}{2} \iint \frac{\rho(\vec{r}_1) h_x(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

only exchange, no correlation

Slater's construction:



wigner-seitz radius

$$r_s = \left(\frac{3}{4\pi} \right)^{1/3} \rho(\vec{r}_1)^{-1/3}$$

$$h_x(r) = \begin{cases} -\frac{3}{4\pi r_s^3}, & r \leq r_s \\ 0, & r > r_s \end{cases}$$

$$\begin{aligned} K[\rho] &= -\frac{1}{2} \int \rho(\vec{r}_1) d\vec{r}_1 \int_0^{r_s} -\frac{3}{4\pi r_s^3} \frac{4\pi r_{12}^2 dr_{12}}{r_{12}} \\ &= \frac{3}{4} \left(+ \left(\frac{4\pi}{3} \right)^{1/3} \right) \int \rho(\vec{r}_1)^{4/3} d\vec{r}_1 \end{aligned}$$

$$K[\rho] = + \frac{9}{8} \left(\frac{3}{\pi} \right)^{1/3} \propto \int \rho(\vec{r})^{4/3} d\vec{r}$$

Hartree-Fock-Slater model

DFT Calculation of H₂ dissociation

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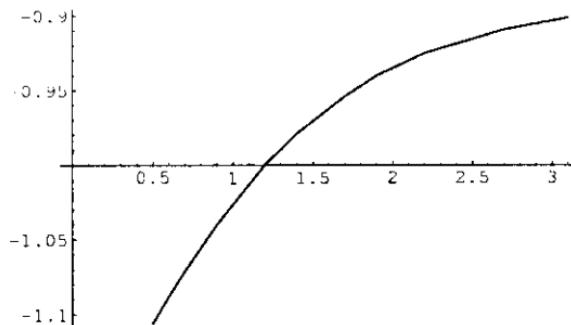
H2 calculation by D. Matyushov

Cnv 4

H1

H2 1 0.7

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$END
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The Thomas - Fermi - Dirac model

$$E_{TFD}[p] = C_F \int p(\vec{r})^{5/3} d\vec{r} + \int p(\vec{r}) v(\vec{r}) d\vec{r}$$

$$+ J[p] = C_X \int p(\vec{r})^{4/3} d\vec{r}$$

$$\mu_{TFD} = \frac{\delta E_{TFD}[p]}{\delta p} = \frac{5}{3} C_F p^{2/3}(\vec{r}) - \frac{4}{3} C_X p^{1/3}(\vec{r}) - \underbrace{\Phi(r)}_{\text{classical electrostatic potential}}$$

Poisson equation:

$$\Delta \Phi = \left(\frac{10}{9} C_F p^{1/3} - \frac{4}{9} C_X p^{-2/3} \right) \Delta p = 4\pi p$$

Thomas-Fermi solution

TF energy of a neutral atom:

$$E_{TF} = -0.7687 Z^{7/3}$$

↖ nuclear charge

TFD model is even worse:

$$E_{TFD} \approx -0.7687 Z^{7/3} - 0.221 Z^{5/3}$$

Energies of Neutral Atoms ($-E/Z^{7/3}$)

Atom (Z)	Hartree-Fock Energy ^a	Modified Thomas-Fermi Model ^b
He (2)	0.5678	0.4397
Ne (10)	0.5967	0.5763
Ar (18)	0.6204	0.6110
Kr (36)	0.6431	0.6439
Xe (54)	0.6562	0.6599
Rn (86)	0.6698	0.6745

^a In conventional Thomas-Fermi theory, the energy is given by (6.2.25) of the text: $-E/Z^{7/3} = 0.7687$.

^b Model of §6.4 of text (Parr and Ghosh 1986).

At $r \rightarrow 0$, $p(r) \propto r^{3/2}$ $\int r^2 p(r) dr = \infty$

By imposing the constraint

$$\int e^{-2kr} r^2 p(r) dr = \text{finite}$$

one can obtain a much better solution (see Table).

The bottom line \Rightarrow that the TF model can be substantially improved if the density in the functional \Rightarrow picked up from a "right" set of solutions.

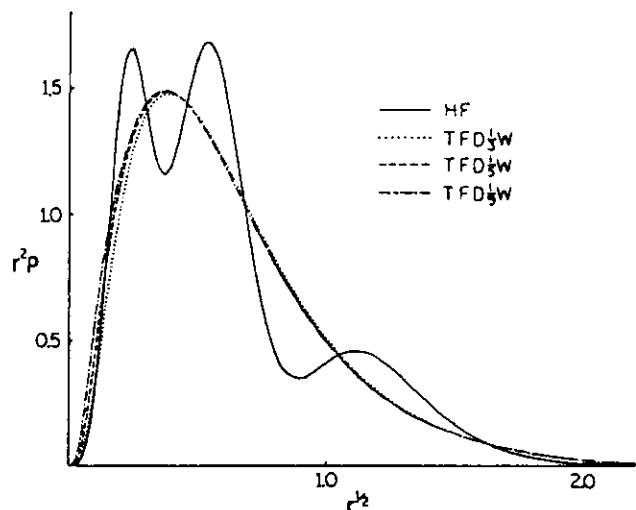
The Thomas-Fermi-Dirac-Weizsäcker model

Weizsäcker correction to the TF kinetic energy

$$T_W[\rho] = \frac{1}{8} \frac{\hbar^2}{m} \int \frac{|\nabla \rho|^2}{\rho} d\vec{r}$$

TFDW functional:

$$E_{TFD-\lambda W}[\rho] = C_F \int \rho^{5/3}(\vec{r}) d\vec{r} + \lambda \frac{1}{8} \int \frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})} d\vec{r} \\ + \int \rho(\vec{r}) V(\vec{r}) d\vec{r} + J[\rho] - C_X \int \rho^{4/3}(\vec{r}) d\vec{r}$$



Electron density for argon from various models (after Yang 1986.)

Atomic Energies from Various TFD- λ W Models (a.u.)^{a,b,c}

	TF	TFD	TFD $\frac{1}{9}$ W	TFD $\frac{1}{6}$ W	TFD(0.186)W	TFD $\frac{1}{3}$ W	TFD $\frac{1}{3}$ W	TFDW	HF
Ne	-165.61	-176.3	-139.91	-132.53	-130.33	-128.83	-117.09	-86.43	-128.55
Ar	-652.72	-680.7	-561.98	-537.34	-529.94	-524.91	-485.00	-378.51	-526.82
Kr	-3289.50	-3377.9	-2898.54	-2796.95	-2766.29	-2745.60	-2578.10	-2132.19	-2752.05
Xe	-8472.46	-8646.1	-7563.13	-7330.95	-7260.72	-7213.92	-6827.59	-5828.96	-7232.13

^a Values for TFD, TFD $\frac{1}{9}$ W, and TFDW from Tomishima and Yonei (1966); HF results from Clementi and Roetti (1974).

^b TF results from (6.2.23) of the text.

^c TFD $\frac{1}{9}$ W, TFD $\frac{1}{6}$ W, TFD(0.186)W, TFD $\frac{1}{3}$ W results. From Yang (1986).

The Hohenberg - Kohn theorem (1964)

$\therefore \therefore \therefore \therefore \therefore$ N electrons



$$v(\vec{r}) = - \sum_A \frac{z_A}{r_A}$$

External potential $v(r)$

+

N electrons

||

Ground state

Hohenberg & Kohn: {The external potential $v(\vec{r})$ is determined within an additive constant by the electron density $p(\vec{r})$.}

$$H = T + v_{ee} + v \quad \langle \psi | H | \psi \rangle = E_0$$

$$H' = T + v_{ee} + v' \quad \langle \psi' | H' | \psi' \rangle = E'_0$$

$$\begin{aligned} \psi' \rightarrow E_0 < \langle \psi' | H' | \psi' \rangle &= \langle \psi' | H' | \psi' \rangle + \int p(\vec{r}) [v - v'] d\vec{r} \\ &= E'_0 + \int p(\vec{r}) [v - v'] d\vec{r} \end{aligned}$$

$$\psi \rightarrow E'_0 < \langle \psi | H' | \psi \rangle = E_0 - \int p(\vec{r}) (v - v') d\vec{r}$$

$E_0 + E'_0 < E_0 + E'_0$ || ← there is no density $p(\vec{r})$ corresponding to v and v'

HK variational principle

$$\langle \Psi | H | \Psi \rangle = \underbrace{\int d\vec{r} \rho(\vec{r}) v(\vec{r})}_{\text{field of the nuclei}} + \underbrace{F_{HK}[\rho]}_{N \text{ electrons at a given density}}$$

$F_{HK}[\rho]$ is a universal functional for a gas of N electrons. If the form of $F_{HF}[\rho]$ were known, the variational principle would provide an exact solution for the ground-state electron density.

HK variational principle: For a trial density $\tilde{\rho}(\vec{r})$ such that $\tilde{\rho}(r) \geq 0$ and $\int \tilde{\rho}(\vec{r}) d\vec{r} = N$

$$E_0 \leq E_V[\tilde{\rho}]$$

$$\delta \left[E_V[\rho] - \mu \left(\int \rho(\vec{r}) d\vec{r} - N \right) \right] = 0$$

$$\downarrow$$

$$E_V[\rho] = F_{HK}[\rho] + \int \rho(\vec{r}) v(\vec{r}) d\vec{r}$$

$$\mu = v(\vec{r}) + \frac{\delta F_{HK}[\rho]}{\delta \rho(\vec{r})}$$

$\overline{\int}$
chemical potential

Kohn-Sham approach

HF method: a single Slater determinant is an exact wave function of an N -electron system

$$T_{HF} = \langle \Psi | - \sum_i \frac{1}{2} \nabla_i^2 | \Psi \rangle = - \frac{1}{2} \sum_i \langle \Psi_i | \nabla^2 | \Psi_i \rangle$$

A Slater determinant is an exact wave function of a fictitious system of N non-interacting electrons

$$E_{HF} = \min_{\Psi} \langle \Psi | T + V_{HF} | \Psi \rangle$$

KS method: Set up a reference system of non-interacting electrons moving in an effective external potential V_s

$$H_s = - \frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_s(r_i)$$

Since electrons do not interact, the ground state wave function is represented by a Slater determinant

$$|\Theta_s\rangle = |\varphi_1 \dots \varphi_N\rangle$$

The KS orbitals are

$$f^{KS} \varphi_i = \varepsilon_i \varphi_i \quad f^{KS} = - \frac{1}{2} \nabla^2 + V_s(\vec{r})$$

The potential V_s is chosen to reproduce the real density of interacting electrons

$$\rho_s(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2 = \rho_0(\vec{r})$$

The Kohn-Sham Equations

The non-interacting reference kinetic energy

$$T_s = -\frac{1}{2} \sum_{i=1}^N \langle \varphi_i | \nabla_i^2 | \varphi_i \rangle$$

The KS functional

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

The exchange-correlation energy

$$E_{xc}[\rho] = \underbrace{(T[\rho] - T_s[\rho])}_{\text{the error in calculating the kinetic energy}} + \underbrace{(E_{xc}[\rho] - J[\rho])}_{\text{quantum effects of electron-electron interactions}}$$

The variational equations

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{eff}} \right) \varphi_i = \varepsilon_i \varphi_i$$

$$V_{\text{eff}} = \underbrace{\int \frac{\rho(\bar{r}_2)}{r_{12}} d\bar{r}_2}_{\delta E_{xc} / \delta \rho} + \underbrace{V_{xc}(\bar{r}_1)}_{=} - \sum_A \frac{z_A}{r_{1A}}$$

$$\frac{\delta E_{xc}}{\delta \rho}$$

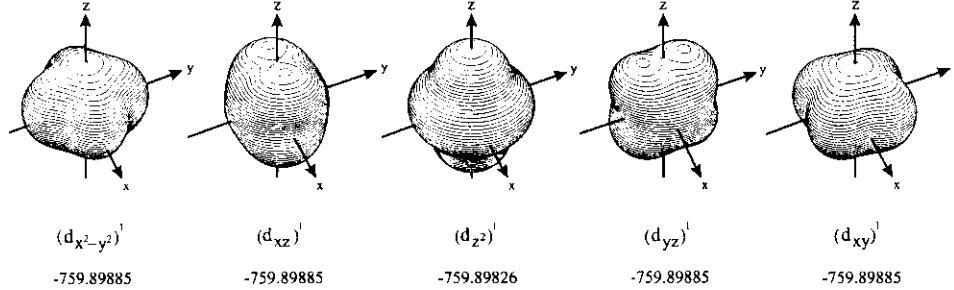
Features of the KS approach

- * In the HF approach, the approximation that a single Slater determinant is the wave function can never deliver the true solution.
The KS approach is in principle exact.
- * The main problem is to define the exchange-correlation functional. This functional is the universal functional for the non-Coulomb interactions of a free gas of electrons. As long as it is defined, it can be used for any atomic or molecular system.
- * The KS potential is local, i.e. $V_s(\vec{r})$ depends only on the coordinate \vec{r} and not on some other coordinate \vec{r}' . The exchange operator in the HF picture is non-local, it depends on the spin orbital in the whole space

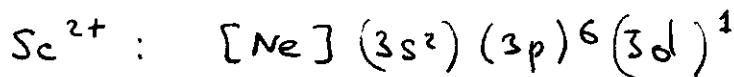
$$K_{\text{F}}(1) \chi_a(1) = \left[\int d\vec{r}_2 \chi_{\text{F}}^*(2) r_{12}^{-1} \chi_a(2) \right] \chi_{\text{F}}(1)$$

Problems: degenerate states

For states with degenerate atomic orbitals the electronic density is different, but the energies should be equal. Any approximate density functional thus faces the difficulty to deliver the same energy from different densities.



Isodensity surfaces (0.001 a.u.) of the d^1 -densities generated from integral orbital occupation of the five d-orbitals in Sc^{2+} by one electron in a DFT calculation. The shape of the density resulting from occupation of the d_{z^2} -orbital differs from the other four (which are identical to each other except for their orientation in space) and a slightly different total energy (given in a.u.) is assigned to this particular density.



The unrestricted KS approach

Functionals that explicitly depend on $p_{\alpha}(\vec{r})$ and $p_{\beta}(\vec{r})$ through the spin polarization parameter

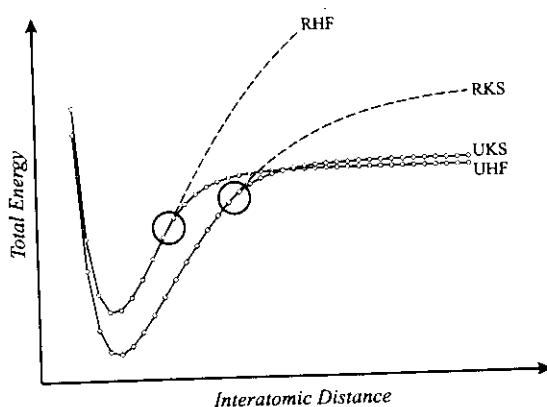
$$\delta = \frac{p_{\alpha} - p_{\beta}}{p_{\alpha} + p_{\beta}} = \frac{p^s}{p^T}$$

are employed to account for open-shell problems.

H₂ dissociation:



According to the molecular symmetry, the total spin density is zero. However, the spin density of each isolated atom is nonzero. If an approximate functional is used, the energy of a "supermolecule" at $R \rightarrow \infty$ does not correspond to $2E_H$.



H₂ potential curves computed within the restricted and unrestricted Hartree-Fock (RHF and UHF) and Kohn-Sham (RKS and UKS) formalisms.

A Slater determinant constructed from KS spin orbitals is not an eigenvalue of S^2 . The deviation of $\langle S^2 \rangle$ from the exact value is usually much less than for the HF.

The adiabatic connection

The KS exchange-correlation energy contains contributions from the non-classical electrostatic interactions and from the kinetic energy

$$E_{xc}[\rho] = \{T[\rho] - T_s[\rho]\} + E_{nl}[p]$$

In order to be able to generate XC functionals, the information about $\Delta T[\rho]$ must be folded into the exchange-correlation hole

$$H_\lambda = T + v^\lambda + \lambda \sum_{j>i} \frac{1}{r_{ij}}$$

$$\lambda = 0, \quad v^\lambda = V_s$$

$$\lambda = 1, \quad v^\lambda + \sum \frac{1}{r_{ij}} = \int \frac{p(\bar{r}_2)}{r_{12}} d\bar{r}_2 + V_{xc}(\bar{r}_1) - \sum \frac{z_A}{r_{iA}}$$

$$E_{\lambda=1} - E_{\lambda=0} = \int_0^1 d\lambda dE_\lambda$$

$$dE_\lambda = \int p(\bar{r}) dV^\lambda d\bar{r} + \frac{1}{2} d\lambda \iint \frac{p(\bar{r}_1)p(\bar{r}_2)}{r_{12}} d\bar{r}_1 d\bar{r}_2$$

$$+ \frac{1}{2} d\lambda \iint \frac{p(\bar{r}_1) h_{xc}^\lambda(\bar{r}_1, \bar{r}_2)}{r_{12}} d\bar{r}_1 d\bar{r}_2$$

$$E_{\lambda=1} - E_{\lambda=0} = \int p \Delta V d\bar{r} + J[\rho] +$$

$$+ \frac{1}{2} \iint d\bar{r}_1 d\bar{r}_2 \int_0^\lambda d\lambda \frac{p(\bar{r}_1) h_{xc}^\lambda(\bar{r}_1, \bar{r}_2)}{r_{12}}$$

At $\lambda = 0$

$$E_{\lambda=0} = T_s + \int \rho(r) V_s(r) dr$$

Coupling-strength integrated exchange-correlation hole:

$$\bar{h}_{xc}(\bar{r}_1, \bar{r}_2) = \int_0^\lambda h_{xc}(\bar{r}_1, \bar{r}_2) d\lambda$$

$$E_{\lambda=1} = T_s + \int \rho(r) U(r) dr + J[\rho]$$

$$+ \frac{1}{2} \iint dr_1 dr_2 \frac{\rho(\bar{r}_1) \bar{h}_{xc}(\bar{r}_1, \bar{r}_2)}{r_{12}}$$

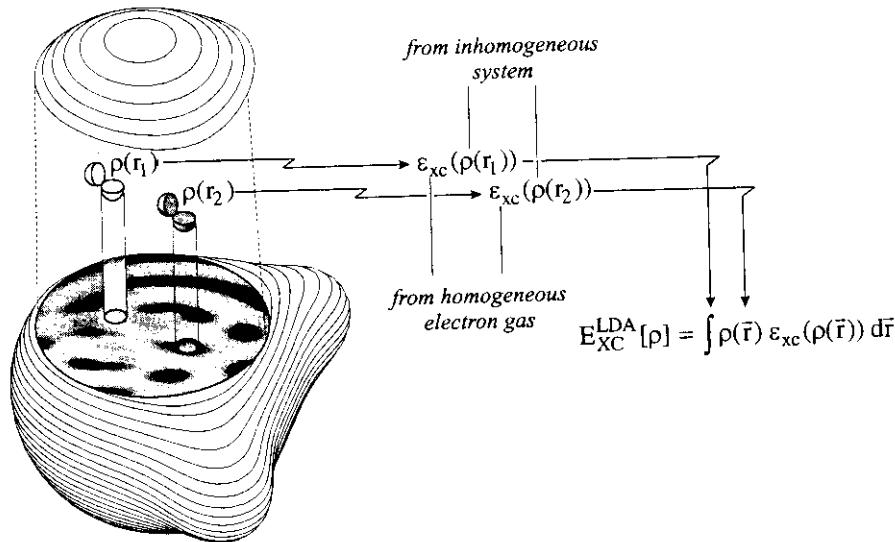
$$E_{xc} = \frac{1}{2} \iint dr_1 dr_2 \frac{\rho(\bar{r}_1) \bar{h}_{xc}(\bar{r}_1, \bar{r}_2)}{r_{12}}$$

The integration over the coupling parameter transfers the difference between T and T_s into the exchange-correlation hole.

Some Atoms ^a	
Atom	$T[\rho] - T_s[\rho]$ (eV)
H ⁻	0.8
He	1.0
Li ⁺	1.1
Be ²⁺	1.1
Li	1.7
Be	2.0

^a Values from Almbladh and Pedroza (1984).

Local density approximation



The exchange - correlation energy per particle in a uniform electron gas is split into exchange and correlation components

$$\epsilon_{xc}(\rho) = \epsilon_x(\rho) + \epsilon_c(\rho)$$

Bloch + Dirac :

$$\epsilon_x(\rho) = - \frac{3}{4\pi} \left(\frac{3}{\pi} \right)^{1/3} \rho^{4/3}$$

$$E_x = - \frac{3}{4\pi} \left(\frac{3}{\pi} \right)^{1/3} \int \rho^{4/3} d\bar{r} \quad \leftarrow \text{Slater exchange}$$

In GAMESS :

```
$DFT DFTTYP = SLATER $END
```

Local spin density approximation

$$E_{xc}^{LSD} = \int g(\vec{r}) \epsilon_{xc}(p_\alpha, p_\beta) d\vec{r}$$

\nearrow

$$p(\vec{r}) = p^T(\vec{r}) = p^\alpha(\vec{r}) + p^\beta(\vec{r})$$

If $p_\alpha \neq p_\beta$ (spin-polarized case), one employs the spin polarization parameter

$$\xi = \frac{p_\alpha - p_\beta}{p_\alpha + p_\beta} = \frac{p^s}{p^T}$$

$$DFTTYP = S \underbrace{VWN}_{\substack{\nearrow \\ \text{Vosko-Wilk-Nusair correlation}}} N$$

scater
exchange

$$\epsilon_c^{VWN} = \epsilon_c(r_s, 0) + \epsilon_c(r_s) \frac{f(\xi)}{f''(0)} [1 - \xi^4] +$$

$$+ [\epsilon_c(r_s, 1) - \epsilon_c(r_s, 0)] f(\xi) \xi^4$$

$$f(\xi) = \frac{(1+\xi)^{4/3} + (1-\xi)^{4/3} - 2}{2(2^{4/3} - 1)}$$

$\epsilon_c(r_s, \xi)$ see the handout.

GAMESS uses the VWN5 correlation that is parametrized to fit quantum MC simulations.

Features of the local density approximation

$$E_{xc} = \frac{1}{2} \iint \rho(\vec{r}_1) \frac{\bar{T}_{xc}(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

- * The exact exchange-correlation hole is a function of six variables and is anisotropic. However, the expression for the exchange-correlation energy includes a spherically averaged \bar{T}_{xc} , since r_{12}^{-1} does not depend on the angle and only on the distance between the two electrons.
- * It turns out that the LDA is not bad and often better than HF. This happens because the exchange-correlation hole of a uniform gas satisfies most of the fundamental relations established for the true hole.
- * The LDA hole is spherically symmetric, while the exact hole has a pronounced angular structure.
- * The LDA hole is a better approximation for the more homogeneous molecular density than for the more inhomogeneous density of atoms.

The Generalized Gradient Approximation

$$E_{xc}^{GGA} = E_x^{GGA} + E_c^{GGA}$$

$$E_{x,c}^{GGA} [\rho_a \rho_p] = \int f(\rho_a \rho_p \nabla \rho_a \nabla \rho_p) d\vec{r}$$

$$E_x^{GGA} = E_x^{LDA} - \sum_g \int F(s_g) \rho_g^{\gamma_3(F)} d\vec{r}$$

reduced density gradient

$$s_g(F) = \frac{|\nabla \rho_g(F)|}{\rho_g^{\gamma_3(F)}}$$

Becke Functional (B88):

$$F^B = \frac{\beta s_g^2}{1 + 6\beta s_g \sinh^{-1} s_g},$$

where β is an empirical parameter, $\beta = 0.0042$.

In GAMESS:

```
$DFT DFTTYPE = BECKE $END
```

A rational function of s_g :

DFTTYPE = PBE

↑ Perdew - Burke - Ernzerhof
exchange

Exchange + Correlation

In principle, each exchange functional could be combined with any of the correlation functionals, but only a few combinations are currently in use.

$$\epsilon_c^{\text{LYP}}(p_x p_p \sigma_{px} \sigma_{pp}) \leftarrow \text{see handout}$$

$$\text{DFTTYP} = \frac{\text{BLYP}}{\text{I}}$$

Becke exchange + LYP correlation

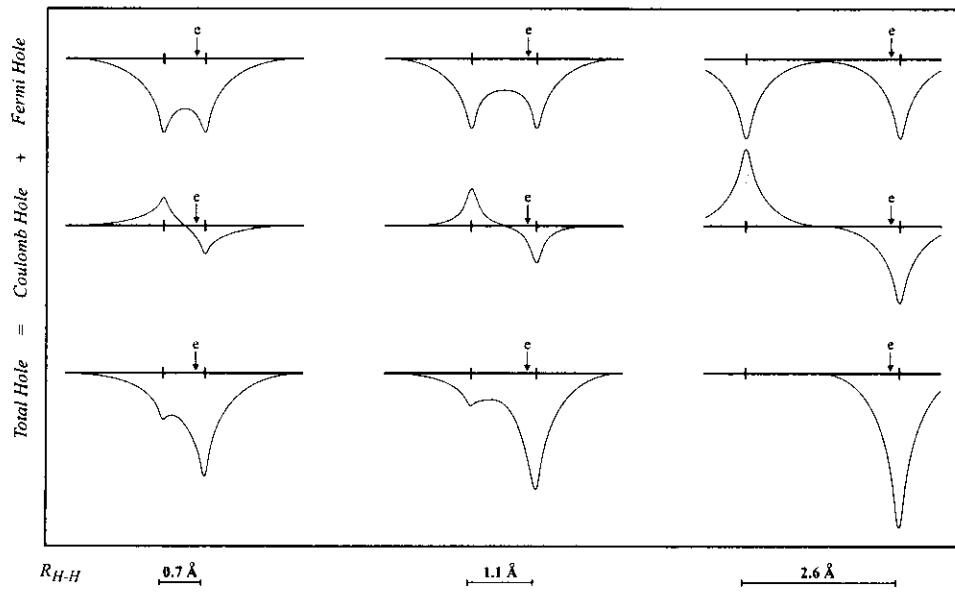
BVWN = Becke exchange + VWN5 correlation

SLYP = Slater exchange + LYP correlation

Hybrid functionals

The correlation energy is unknown, but the exchange energy can be calculated exactly in terms of the HF exchange operator

$$E_{xc} = E_x^{\text{exact}} + E_c^{\text{KS}}$$



Each component (x or c) taken separately is a poor representation of the real exchange-correlation hole. Therefore, calculating just one of them exactly does not help much.

Adiabatic connection formula

$$E_{xc} = \int_0^\lambda E_{xc}^{\lambda} d\lambda \quad (*)$$

at $\lambda=0$ we have an interaction-free system and

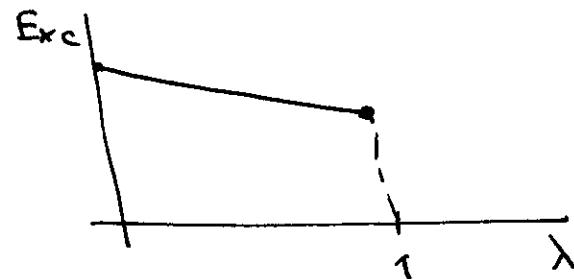
$$E_{xc}^{\lambda=0} = E_x^{\text{HF}}$$

at $\lambda=1$, the nonclassical contribution contains both exchange and correlation. They can be approximately calculated in the LDA.

The simplest approximation for the integral (*)

is

$$E_{xc} = \frac{1}{2} E_{xc}^{\lambda=0} + \frac{1}{2} E_{xc}^{\lambda=1}$$



Becke ('93) approximation:

$$E_{xc}^{B3} = E_{xc}^{\text{LSD}} + a (E_x^{\text{HF}} - E_x^{\text{LSD}}) + b E_x^{\text{R88}} + c E_c^{\text{PW91}}$$

Perdew & Wang '91

B3LYP:

$$E_{xc}^{\text{B3LYP}} = (1-a) E_x^{\text{LSD}} + a E_{xc}^{\lambda=0} + b E_x^{\text{R88}} + c E_c^{\text{LYP}}$$
$$+ (1-c) E_c^{\text{LSD}}$$

The basic machinery of DFT calculations

LCAO expansion of KS molecular orbitals

$$\varphi_i = \sum_{\lambda=1}^K c_{\lambda i} \Phi_{\lambda}$$

$$f^{ks} \varphi_i = \varepsilon_i \varphi_i$$

$$\int (\Phi_{\delta}^* f^{ks} \sum_{\lambda=1}^K c_{\lambda i} \Phi_{\lambda}) d\vec{r} = \varepsilon_i \sum c_{\lambda i} \langle \Phi_{\delta} | \Phi_{\lambda} \rangle$$

↓
 $F_{\delta \lambda}^{ks} = \int \Phi_{\delta}^* f^{ks} \Phi_{\lambda} d\vec{r}$
 overlap matrix element $S_{\delta \lambda}$

KS matrix

$$F^{ks} C = S C E$$

LCAO expansion matrix atomic overlap matrix eigenvalues matrix

$$F_{\mu\nu}^{ks} = \underbrace{-\frac{1}{2} \langle \Phi_{\mu} | \nabla^2 | \Phi_{\nu} \rangle}_{H_{\mu\nu}^{\text{core}}} + \underbrace{\sigma_{\mu\nu}}_{\text{need the charge density}} + \underbrace{J_{\mu\nu} + V_{xc}^{\mu\nu}}$$

$$\rho(\vec{r}) = \sum_{\mu\nu} \Phi_{\mu}(\vec{r}) \Phi_{\nu}^*(\vec{r}) \frac{\sum_i C_{\mu i} C_{\nu i}^*}{P_{\mu\nu}}$$

$$= \sum_{\mu,\nu} P_{\mu\nu} \Phi_{\mu}(\vec{r}) \Phi_{\nu}^*(\vec{r})$$

K^4 vs K^2M scaling of Coulomb integrals

HF relation for Coulomb integrals

$$J_{\mu\nu} = \sum_{\lambda_3}^K P_{\lambda_3} (\mu\nu | \lambda_3)$$

↑ number of integrals or K^4

DFT form for $J_{\mu\nu}$

$$J_{\mu\nu} = \int \Phi_\mu^* \Phi_\nu \frac{1}{r_{12}} \rho(\bar{r}_2) d\bar{r}_1 d\bar{r}_2$$

The density is expanded in terms of a separate atomic basis set

$$\rho(\bar{r}) = \sum_{k=1}^M c_k w_k(\bar{r})$$

$$J_{\mu\nu} = \sum_{k=1}^M c_k \iint \frac{\Phi_\mu(\bar{r}_1) \Phi_\nu(\bar{r}_1)^* w_k(\bar{r}_2)}{r_{12}} d\bar{r}_1 d\bar{r}_2$$

↑ number of integrals

$\propto K^2 M$

For small systems $M \approx K$ and scaling $\propto K^3$.

For extended systems, the integrals over the neighbours will survive and the integrals between atoms at large distances will disappear. The actual scaling $\propto K^2$.

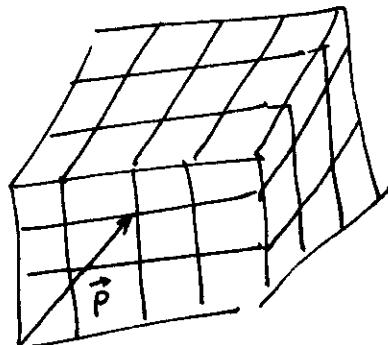
Exchange-correlation potential: Grid methods

GAMESS: METHOD = GRID (default)

Exchange-correlation matrix elements:

$$V_{\mu\nu}^{xc} = \int \Phi_{\mu}^*(\vec{r}) V_{xc}(\vec{r}) \Phi_{\nu}(\vec{r}) d\vec{r}$$

Since the function $V_{xc}[p]$ has often a very complex form, the integral is taken by summation on a 3D grid



$$V_{\mu\nu}^{xc} \approx \sum_{\vec{P}} \Phi_{\mu}^*(\vec{P}) V_{xc}(\vec{P}) \Phi_{\nu}(\vec{P}) W_{\vec{P}}$$

Grid-free techniques for exchange-correlation

S DFT METHOD = GRIDFREE #END

$$R_{\mu\nu} = \langle \psi | \rho(\vec{r}) | \psi \rangle = \sum_{\lambda, \zeta} p_{\lambda\zeta} \underbrace{\int \phi_\nu \phi_\lambda \phi_\mu^* \phi_\zeta^* d\vec{r}}_{\propto K^4}$$

$$\text{with } \rho(\vec{r}) = \sum_k c_k \omega_k(\vec{r})$$

$$R_{\mu\nu} = \underbrace{\sum_{\lambda} \sum_{\zeta} \sum_{\mu} \sum_{\nu} p_{\lambda\zeta} \int \phi_\mu^* \phi_\nu \omega_k d\vec{r}}_{\propto K^2 \cdot M} \times \int \phi_\zeta^* \phi_\lambda \omega_k d\vec{r}$$

The calculation of the exchange-correlation functional is performed by the diagonalization of the \hat{R} matrix

$$\begin{pmatrix} R_{11} & R_{12} & \dots \\ R_{21} & R_{22} & \dots \\ \dots & \dots & \dots \end{pmatrix} \xrightarrow{\text{diagonalize}} \begin{pmatrix} r_1 & & 0 \\ 0 & \ddots & \ddots \\ & & r_K \end{pmatrix}$$

$$E_{xc}(p) \xrightarrow{\rightarrow} \begin{pmatrix} E_{xc}(r_1) & & 0 \\ 0 & \ddots & \ddots \\ & \ddots & E_{xc}(r_K) \end{pmatrix} \xrightarrow{\text{anti-diagonalize}} \begin{pmatrix} E_{xc,11}' & \dots & \dots \\ \dots & \ddots & \ddots \\ \dots & \ddots & E_{xc,KK}' \end{pmatrix}$$

Performance

LDA :

Molecule	Binding energy (eV)			Bond Length (a_0)			Vibrational Frequency (cm^{-1})		
	LDA	HF	Exptl.	LDA	HF	Exptl.	LDA	HF	Exptl.
N ₂	7.8	5.3	9.8	2.16	2.01	2.07	2070	2730	2358
CO	9.6	7.9	11.2	2.22	2.08	2.13	2090	2131	2170

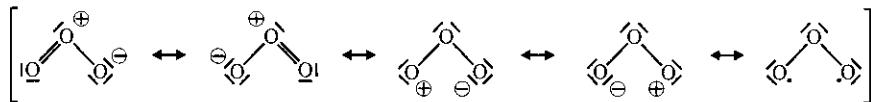


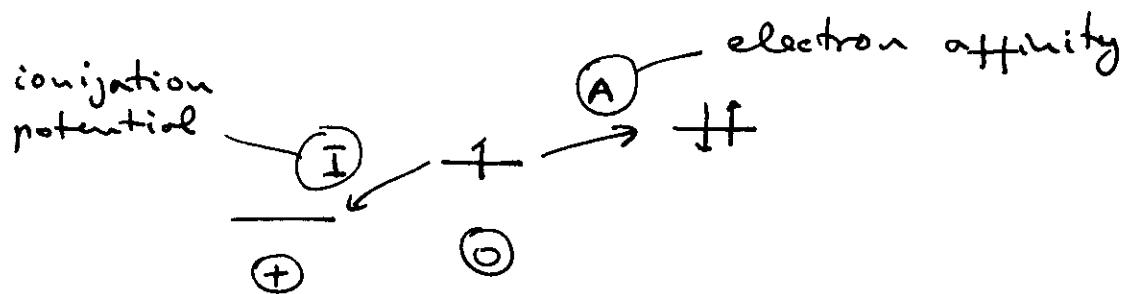
Figure 6-4. Resonance structures of O₃.

Table 6-1. Harmonic frequencies and experimental fundamentals for ozone [cm^{-1}]. Deviations from the experimental result [%] are given in parentheses.

Method	bending (a_1)	antisym. stretch (b_2)	sym. stretch (a_1)
Hartree-Fock	870 (+21.5)	1419 (+30.3)	1541 (+35.8)
MP2	747 (+4.3)	2211 (+203.0)	1170 (+3.1)
B3LYP	750 (+4.7)	1205 (+10.7)	1259 (+10.9)
<i>m</i> PW1PW	778 (+8.7)	1296 (+19.0)	1323 (+16.6)
BLYP	688 (-3.9)	991 (-9.0)	1135 (± 0)
BP	708 (-1.1)	1054 (-3.2)	1179 (+3.9)
Experiment	716	1089	1135

Chemical potential

Three-state system :



Energy : $E_0 + I$ E_0 $E_0 - A$

Electrons : $N_0 - 1$ N_0 $N_0 + 1$

Grand canonical partition function:

$$\begin{aligned} \Omega(\rho, \mu) &= \sum_i \sum_N e^{-\beta(E_i - \mu N)} \quad (\beta = 1/k_B T) \\ &= e^{-\beta(E_0 - \mu N_0)} + e^{-\beta(E_0 + I - \mu N_0 + M)} + e^{-\beta(E_0 - A - \mu N_0 - M)} \\ \bar{N} = N_0 &= \frac{1}{\beta} \left(\frac{\partial \ln \Omega}{\partial \mu} \right)_\beta = N_0 + \frac{e^{\beta(A+M)} - e^{-\beta(I+M)}}{1 + e^{\beta(A+M)} + e^{-\beta(I+M)}} \end{aligned}$$

$$\boxed{\mu = -\frac{I+A}{2}}$$

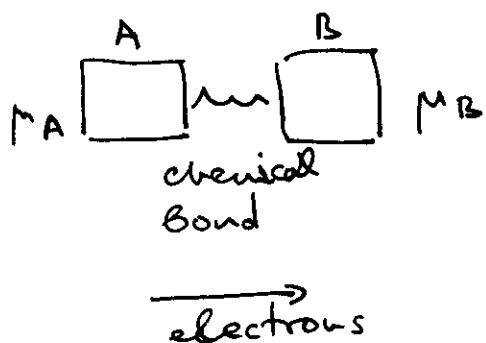
$$\underline{\chi_M = \frac{I+A}{2}} \leftarrow \text{Nulliken's (1934) formula for electronegativity}$$

Electronegativity plays the same role in DFT models that the energy plays in the wave-function theory

Electronegativity equalization

The Sanderson principle of electronegativity equilibration (1951):

When atoms or other chemical groups of different chemical potential unite to form a molecule with its own characteristic chemical potential, their chemical potentials should equalize.



$$\left(\frac{\partial E}{\partial N}\right)_V = \mu \leftarrow \begin{matrix} \text{chemical} \\ \text{potential} \end{matrix}$$

$$\left(\frac{\partial^2 E}{\partial N^2}\right)_V = 2\gamma \leftarrow \begin{matrix} \text{hardness} \end{matrix}$$

$$\mu_A > \mu_B$$

$$E_A = E_A^\circ + \mu_A^\circ \Delta N + \gamma_A \Delta N^2 + \dots$$

$$E_B = E_B^\circ - \mu_B^\circ \Delta N + \gamma_B \Delta N^2 + \dots$$

$$\left. \frac{\partial (E_A + E_B)}{\partial \Delta N} \right|_{\Delta N=0} = 0 \quad \boxed{\mu_A = \mu_B}$$

$$\mu_A = \mu_A^\circ + 2\gamma_A \Delta N$$

$$\mu_B = \mu_B^\circ - 2\gamma_B \Delta N$$

The total transfer of electron density in bond formation

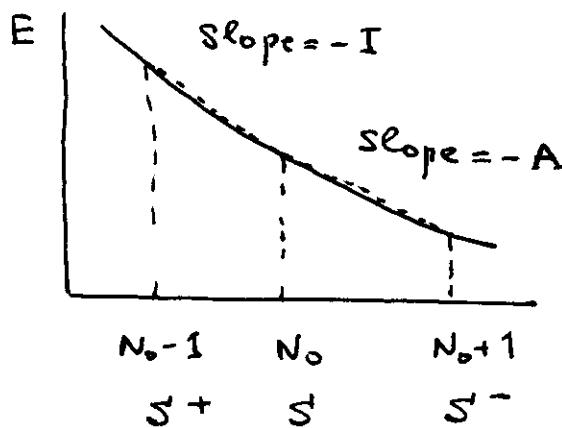
$$\rightarrow \boxed{\Delta N = \frac{\mu_B^\circ - \mu_A^\circ}{2(\gamma_A + \gamma_B)}}$$

Electronegativity

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_V$$

electronegativity is negative of the chemical potential at $T=0$

Hardness & Softness



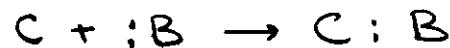
$$\text{average slope} = -\frac{I+A}{2}$$

$$\begin{aligned} \text{curvature} &= \frac{\partial^2 E}{\partial N^2} = \\ &= -\frac{1}{DN} \left(\frac{\partial E}{\partial N} \Big|_{N=N_0+1} - \frac{\partial E}{\partial N} \Big|_{N=N_0-1} \right) \\ &= -\frac{A}{2} + \frac{I}{2} = \frac{I-A}{2} \end{aligned}$$

$$\gamma = \frac{I-A}{2}$$

$$\text{softness } s = \gamma/2$$

Acid-Base reactions



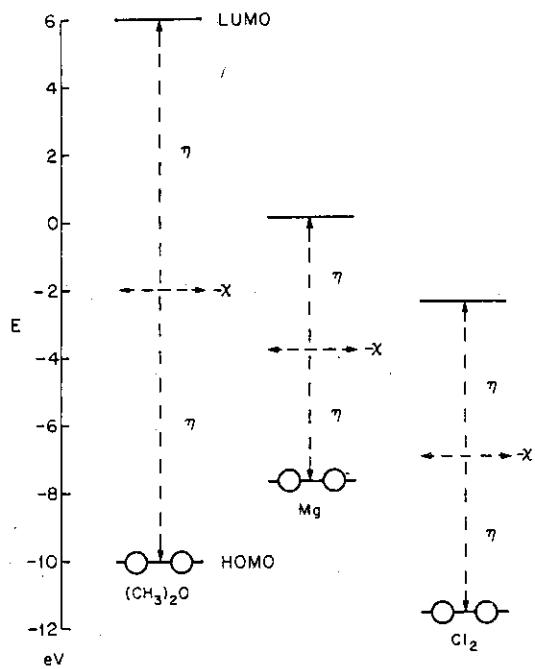
electronegativity drives electron transfer

$$\frac{\Delta N}{\gamma} = \frac{x_C - x_B}{2(\gamma_C + \gamma_B)}$$

amount of charge transferred

hardness parameter acts as a resistance

Polarity of the Chemical Bond



- * Hard molecules have a large HOMO-LUMO gap
- * Soft molecules have a small HOMO-LUMO gap
- * Soft acids and bases are those with high polarizability

HSAB principle: Hard bases prefer to coordinate with hard acids, and soft bases to soft acids.

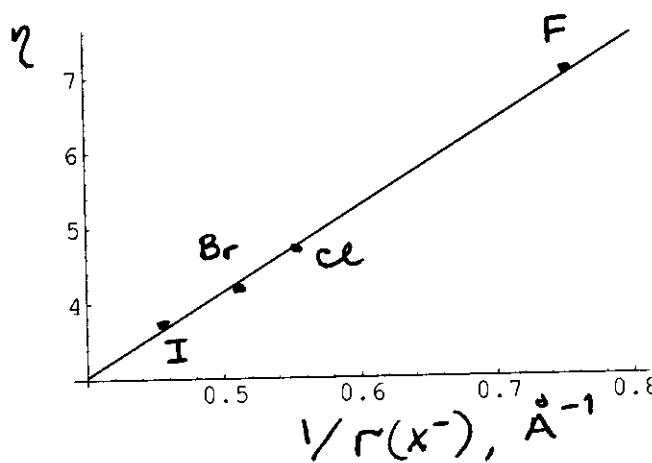
Polarity of chemical bond:

One parameter is not sufficient to decide how much charge is transferred. To characterize the bond polarity, one needs both electronegativity and hardness.

Hardness / Softness

Hardness characterizes the mean interelectronic repulsion of two electrons on the same orbit.

The Coulomb repulsion is inversely proportional to the size of the valence orbital:



- * Softness is a local parameter; various parts of a molecule are not equally soft
- * Local softness:

$$S(F) = S_{\text{pHOMO}}(F) \leftarrow \text{nucleophilic attack}$$

$$S(F) = S_{\text{pLUMO}}(F) \leftarrow \text{electrophilic attack}$$

Of two different sites with similar disposition for reacting, the reagent prefers the one associated with the maximum response of the system's chemical potential.

Configuration interaction (CI)

← Chapter 4.

The method of CI allows to calculate the correlation energy:

$$E_{\text{corr}} = \underbrace{\varepsilon_0}_{\text{exact ground state energy}} - \underbrace{E_0}_{\text{HF ground state energy}}$$

The basic idea of CI:

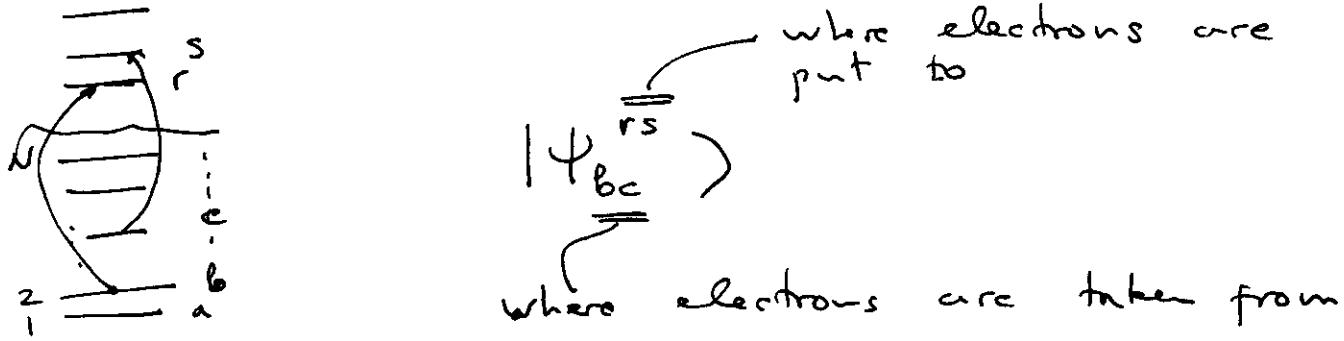
represent the wave function as a linear combination of the ground and excited Slater determinants + diagonalize the Hamiltonian matrix in terms of N-electron matrix elements.

For a set of K basis functions there are

$$\binom{2K}{N} = \frac{(2K)!}{(2K-N)! N!}$$

different Slater determinants. Full CI (FCI) includes all determinants and is computationally impossible even for small molecules. One has to truncate the expansion and use a limited set of N-electron functions. If determinant differ from two by at most two spin orbitals, this approximation is called SDCI (singly and doubly excited CI).

Excited determinants



Full CI wave function:

$$\begin{aligned}
 |\Phi_0\rangle &= c_0 |\Psi_0\rangle + \sum_{\text{ar}} c_a^r |\Psi_a^r\rangle + \sum_{\substack{a < b \\ r < s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle \\
 &+ \sum_{\substack{a < b < c \\ r < s < t}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \dots \\
 &= c_0 |\Psi_0\rangle + \left(\frac{1}{1!}\right)^2 \sum c_a^r |\Psi_a^r\rangle + \frac{1}{(2!)^2} \sum_{abrs} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \dots
 \end{aligned}$$

$$c_{ab}^{rs} = -c_{ba}^{sr} = c_{ba}^{sr}$$

$$= c_0 |\Psi_0\rangle + c_s |S\rangle + c_D |D\rangle + c_T |T\rangle + c_Q |Q\rangle + \dots$$

\uparrow single excitations \uparrow double excitations

- * $\langle \Psi_0 | H | S \rangle = 0 \leftarrow \text{Brillouin's theorem}$
(there is no coupling between the HF ground state and single excitations)
- * There is no coupling between $|\Psi_0\rangle$ and triples and quadruples.
- * Single excitations do not mix directly with $|\Psi_0\rangle$, they mix indirectly through interactions with doubles.

Full CI matrix and correlation energy

	$ 1\psi_0\rangle$	$ 1s\rangle$	$ 1D\rangle$	$ 1T\rangle$	$ 1Q\rangle$
$\langle \psi_0 $	E_0	0	$\langle \psi_0 H 1D \rangle$	0	0
$\langle s $		$\langle s H s \rangle$	$\langle s H D \rangle$	$\langle s H T \rangle$	0
$\langle D $			$\langle D H D \rangle$	$\langle D H T \rangle$	$\langle D H Q \rangle$
$\langle T $				$\langle T H T \rangle$	

Intermediate normalized form:

$$|\Phi_0\rangle = |\psi_0\rangle + \sum c_c^+ |\psi_c^+\rangle + \sum_{\substack{c < d \\ t < u}}^{tu} c_{cd}^{tu} |\psi_{cd}^{tu}\rangle + \dots$$

$$\langle \psi_0 | \Phi_0 \rangle = 1 \quad \langle \Phi_0 | \Phi_0 \rangle = 1 + \sum (c_c^+)^2 + \dots > 1$$

Linear variation method:

$$H |\Phi_0\rangle = E_0 |\Phi_0\rangle$$

$$\langle \psi_0 | (H - E_0) |\Phi_0 \rangle = (E_0 - E_0) \langle \psi_0 | \Phi_0 \rangle = E_{corr}$$

$$\langle \psi_0 | (H - E_0) |\Phi_0 \rangle = \langle \psi_0 | H - E_0 \left(|\psi_0\rangle + \sum c_c^+ |\psi_c^+\rangle + \sum_{\substack{c < d \\ t < u}}^{tu} c_{cd}^{tu} |\psi_{cd}^{tu}\rangle + \dots \right)$$

$$E_{corr} = \sum c_{ab}^{rs} \langle \psi_0 | H | \psi_{ab}^{rs} \rangle$$

The correlation energy is determined solely by the coefficient of the double excitations of the intermediate normalized CI function.

Full CI for the minimal basis H_2

$$|\Psi_0\rangle = |\Psi_0\rangle + c_{1\bar{1}}^2 |\bar{\Psi}_1|^2 \rangle + c_{1\bar{1}}^{2\bar{2}} |\bar{2}\bar{2}\rangle$$

$\frac{1}{\sqrt{2}} (|1\bar{2}\rangle + |2\bar{1}\rangle)$ spin-adapted singlet
of "u" symmetry

$$|\Psi_0\rangle = |\Psi_0\rangle + c_{1\bar{1}}^{2\bar{2}} |\bar{2}\bar{2}\rangle = |\Psi_0\rangle + c_{1\bar{1}}^{2\bar{2}} |\bar{\Psi}_{1\bar{1}}^{2\bar{2}}\rangle$$

$$\overset{\leftrightarrow}{H} = \begin{pmatrix} \langle \Psi_0 | H | \Psi_0 \rangle & \langle \Psi_0 | H | \Psi_{1\bar{1}}^{2\bar{2}} \rangle \\ \langle \bar{\Psi}_{1\bar{1}}^{2\bar{2}} | H | \Psi_0 \rangle & \langle \bar{\Psi}_{1\bar{1}}^{2\bar{2}} | H | \Psi_{1\bar{1}}^{2\bar{2}} \rangle \end{pmatrix}$$

$$\langle \Psi_0 | H | \Psi_0 \rangle = E_0 = 2h_{11} + J_{11} = \varepsilon_1 + h_{11}$$

$$\langle \Psi_0 | H | \Psi_{1\bar{1}}^{2\bar{2}} \rangle = \langle 1\bar{1} || 2\bar{2} \rangle = K_{12}$$

$$\langle \bar{\Psi}_{1\bar{1}}^{2\bar{2}} | H | \bar{\Psi}_{1\bar{1}}^{2\bar{2}} \rangle = 2h_{22} + J_{22} = 2\varepsilon_2 - 4J_{12} + J_{22} + 2K_{12}$$

$$(H - E_0) (|\Psi_0\rangle + c |\bar{\Psi}_{1\bar{1}}^{2\bar{2}}\rangle) = E_{\text{corr}} (|\Psi_0\rangle + c |\bar{\Psi}_{1\bar{1}}^{2\bar{2}}\rangle)$$

$$E_{\text{corr}} = c K_{12}$$

$$K_{12} + \frac{2\Delta}{\underline{\underline{c}}} c = c E_{\text{corr}}$$

$$\langle \bar{\Psi}_{1\bar{1}}^{2\bar{2}} | H | \bar{\Psi}_{1\bar{1}}^{2\bar{2}} \rangle - E_0 = 2(h_{22} - h_{11}) + J_{22} - J_{11}$$

$$E_{\text{corr}} = \Delta - (\Delta^2 + K_{12}^2)^{1/2}$$

$$\varepsilon_0 = E_0 + E_{\text{corr}} = 2h_{11} + J_{11} + \Delta - (\Delta^2 + K_{12}^2)^{1/2}$$

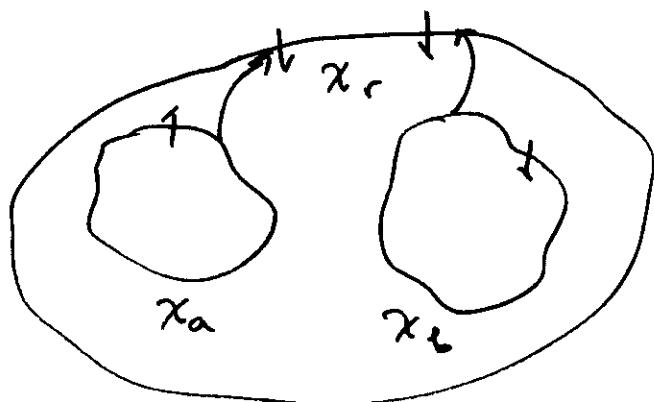
How do electrons correlate? (not exact)

- * Electron correlation energy accounts for the effects of mutual polarization of molecular orbitals in a molecule
- * How do electrons correlate? Through the virtual excited states!

$$E_{\text{corr}} = \sum_{a \in B} \sum_{rs} c_{ab}^{rs} \langle \psi_0 | H | \psi_{ab}^{rs} \rangle$$

$$= \sum_{a \in B} e_{ab}$$

$e_{ab} = \sum_{rs} c_{ab}^{rs} \langle \psi_0 | H | \psi_{ab}^{rs} \rangle$ ← pair correlation energy, gives the correlation energy between a pair of HF MO orbitals.



Molecular orbitals "feel" each other through virtual excitations to empty MOs. Since electrons "see" each other in the excited states, this correlation is transferred in some additional optimization of the ground state electronic configuration resulting in lower total energy.

Full CI/6-31G calculations of the H₂ dissociation

```
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$CIDET GROUP=C1 NCORE=0 NACT=2 NELS=2 $END
$SURF IVEC1(1)=2,1 IGRP1=1 ORIG1=0.4 DISP1=0.2 NDISP1=20      $END
$GUESS GUESS=MOREAD NORB=22 $END
$DATA
```

H2 calculation by D. Matyushov

Cnv 4

H1

H2 1 0.7

\$END

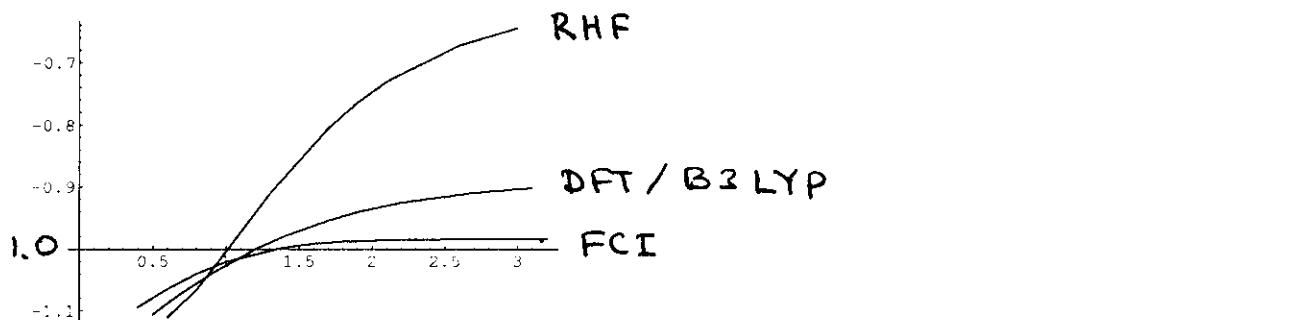
--- CLOSED SHELL ORBITALS --- GENERATED AT Mon Apr 1 16:31:36 2002

H2 calculation by D. Matyushov

E(RHF)= -1.1320819378, E(NUC)= 0.7131768858, 6 ITERS

\$VEC

1	1	3.13526480E-01	2.73282378E-01	0.00000000E+00	0.00000000E+00	2.52775521E-01
1	2	0.00000000E+00	0.00000000E+00	1.32489768E-02	0.00000000E+00	0.00000000E+00
1	3	2.10037994E-02	3.13526480E-01	2.73282378E-01	0.00000000E+00	0.00000000E+00
1	4	-2.52775521E-03	0.00000000E+00	0.00000000E+00	-1.32489768E-02	0.00000000E+00
1	5	0.00000000E+00	-2.10037994E-02			
2	1	-1.55072326E-01	-3.08850056E+00	0.00000000E+00	0.00000000E+00	-2.61213349E-01



Doubly excited CI (DCI)

The intermediate normalized DCI trial function:

$$|\Psi_{\text{DCI}}\rangle = |\Psi_0\rangle + \sum_{\substack{c \in d \\ t \in u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle$$

$$(H - E_0) [|\Psi_0\rangle + \sum_{\substack{c \in d \\ t \in u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle] = E_{\text{corr}} [|\Psi_0\rangle + \sum_{\substack{c \in d \\ t \in u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle]$$

$$\langle \Psi_0 | : \sum c_{cd}^{tu} \langle \Psi_0 | H | \Psi_{cd}^{tu} \rangle = E_{\text{corr}}$$

$$\langle \Psi_{ab}^{rs} | : \langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle + \sum c_{cd}^{tu} \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle = c_{ab}^{rs} E_{\text{corr}}$$

Matrices:

$$(\overleftrightarrow{B})_{rasb} = \langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle$$

$$(\overleftrightarrow{D})_{rasb, tcd} = \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle$$

$$(\overleftrightarrow{C})_{rasb} = c_{ab}^{rs}$$

$$\overleftrightarrow{B}^+ \overleftrightarrow{C} = E_{\text{corr}}$$

$$\overleftrightarrow{B} + \overleftrightarrow{D} \overleftrightarrow{C} = \overleftrightarrow{C} E_{\text{corr}}$$

$$\begin{pmatrix} \overleftrightarrow{0} & \overleftrightarrow{B}^+ \\ \overleftrightarrow{B} & \overleftrightarrow{D} \end{pmatrix} \begin{pmatrix} \overleftrightarrow{1} \\ \overleftrightarrow{C} \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} \overleftrightarrow{1} \\ \overleftrightarrow{C} \end{pmatrix}$$

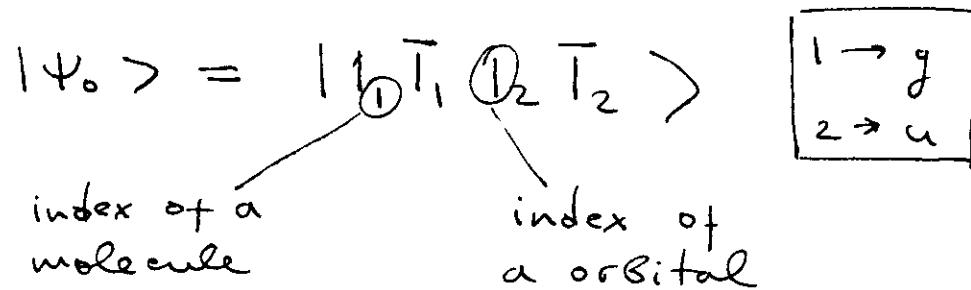
4.6. Truncated CI and the size consistency problem

Size consistency: the energy of a many-particle system
 is proportional to the number of particles N in the limit $N \rightarrow \infty$

Full CI is size-consistent: the energy of two non-interacting molecular fragments is the sum of energies of each fragment!

Any truncated CI does not have the property of size consistency.

Two non-interacting H_2 molecules:



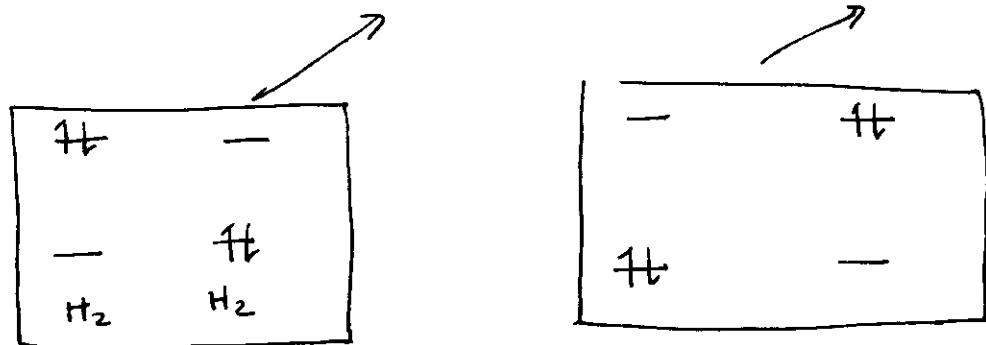
$$|1_1\rangle = \frac{1}{\sqrt{2(1+s)}} (\Phi_1^1 + \Phi_2^1)$$

$$|2_1\rangle = \frac{1}{\sqrt{2(1-s)}} (\Phi_1^1 - \Phi_2^1)$$

DCI on H₂

Dimer of two H₂ molecules

$$|\Phi_0\rangle = |\Psi_0\rangle + c_1 |2_1 \bar{2}_1 1_2 \bar{1}_2\rangle + c_2 |1_1 \bar{1}_1 2_2 \bar{2}_2\rangle$$



DCI means that only one double excitation is allowed.
Quadruple excitations are not considered.

Exercise 4.10.

$\begin{array}{c} + \\ - \end{array}$ $|1_1 \bar{1}_1 2_1 \bar{2}_1\rangle$ does not mix
with $|\Phi_0\rangle$

$\begin{array}{c} + \\ - \end{array}$

$$\underbrace{\langle 1_1 \bar{1}_1 2_1 \bar{2}_1 |}_{\text{"0}} \underbrace{|2_1 \bar{2}_1 1_2 \bar{1}_2\rangle}_{\text{"0}} = 0$$

$$\underbrace{\langle 1_1 \bar{1}_1 2_1 \bar{2}_1 |}_{\text{"0}} \underbrace{|1_1 \bar{1}_1 2_2 \bar{2}_2\rangle}_{\text{"0}} = 0$$

This matrix element is zero

Because two H₂ molecules
are supposed to be separated
by $R \rightarrow \infty$.

Matrix elements:

$$\begin{aligned} \langle \psi_0 | H | 2, \bar{2}_1, 1_2 \bar{1}_2 \rangle &= \langle \psi_0 | H | \Psi_{1, \bar{1}_1}^{2, \bar{2}_1} \rangle = \langle 1\bar{1}_1 | 2, \bar{2}_1 \rangle \\ &= \int \underbrace{\psi_1^*(1) \alpha^*(1)}_{\text{1''}} \underbrace{\psi_1^*(2) \beta^*(2)}_{\text{2''}} \frac{1}{r_{12}} \underbrace{\psi_2(1) \alpha(1) \psi_2(2) \beta(2)}_{\text{1''}} d\bar{x}_1 d\bar{x}_2 \\ &= \int \psi_1^*(1) \psi_2(1) \frac{1}{r_{12}} \psi_1^*(2) \psi_2(2) d\bar{r}_1 d\bar{r}_2 = (12 | 12) = K_{12} \end{aligned}$$

$$\langle \Psi_{1, \bar{1}_1}^{2, \bar{2}_1} | H | \Psi_{1, \bar{1}_1}^{2, \bar{2}_1} \rangle = 2 h_{22} + J_{22}$$

↓↓

—

$$\langle \Psi_{1, \bar{1}_1}^{2, \bar{2}_1} | (H - E_0) | \Psi_{1, \bar{1}_1}^{2, \bar{2}_1} \rangle = 2\Delta = 2h_{22} + J_{22} - E_0$$

Hamiltonian matrix:

$$\overset{\leftrightarrow}{H} - E_0 \vec{1} = \begin{pmatrix} 0 & K_{12} & K_{12} \\ K_{12} & 2\Delta & 0 \\ K_{12} & 0 & 2\Delta \end{pmatrix} \quad \vec{c} = \begin{pmatrix} 1 \\ c_1 \\ c_2 \end{pmatrix}$$

$$(\overset{\leftrightarrow}{H} - E_0 \vec{1}) \vec{c} = {}^2 E_{\text{corr}} (\text{DCI}) \vec{c}$$

Secular equation:

from symmetry $c_1 = c_2 = c$

$$2K_{12}c = {}^2E_{\text{corr}}(\text{DCI})$$

$$K_{12} + 2\Delta c = {}^1E_{\text{corr}}(\text{DCI})c$$

$$({}^2E_{\text{corr}})^2 - 2\Delta({}^1E_{\text{corr}}) - 2K_{12}^2 = 0$$

$$\boxed{{}^2E_{\text{corr}}(\text{DCI}) = \Delta - (\Delta^2 + 2K_{12}^2)^{\frac{1}{2}}}$$

$${}^2E_{\text{corr}}(\text{exact}) = 2{}^1E_{\text{corr}} = 2\Delta - 2(\Delta^2 + K_{12}^2)^{\frac{1}{2}}$$

- * Information about excited states is kept in the ground-state energy in terms of the correlation energy
- * If the spectrum of system excitations is limited, some electron-electron correlation becomes lost; the correlation energy loses its size-consistency

N DCI H_2 molecules

$$|\Phi_0\rangle = |\Psi_0\rangle + c \sum_{i=1}^N |\Psi_{i\bar{i}}^{z_i\bar{z}_i}\rangle$$

$$\hat{H} - E_0 \hat{1} = \begin{pmatrix} 0 & K_{12} & \dots & \dots & K_{12} \\ K_{12} & 2\Delta & & & 0 \\ \vdots & & \ddots & & \vdots \\ \vdots & 0 & & \ddots & 2\Delta \\ K_{12} & & & & 0 \end{pmatrix}$$

$$(\hat{H} - E_0 \hat{1}) \vec{c} = {}^N E_{\text{corr(DCI)}} \vec{c}, \quad \vec{c} = \begin{pmatrix} 1 \\ c \\ \vdots \\ c \end{pmatrix}$$

$$CNK_{12} = {}^N E_{\text{corr}}$$

$$K_{12} + 2\Delta c = {}^N E_{\text{corr}} c$$

$$({}^N E_{\text{corr}})^2 - 2\Delta({}^N E_{\text{corr}}) - N K_{12}^2 = 0$$

$${}^N E_{\text{corr}} = \Delta - (\Delta^2 + N K_{12}^2)^{1/2}$$

, at $N \gg 1$

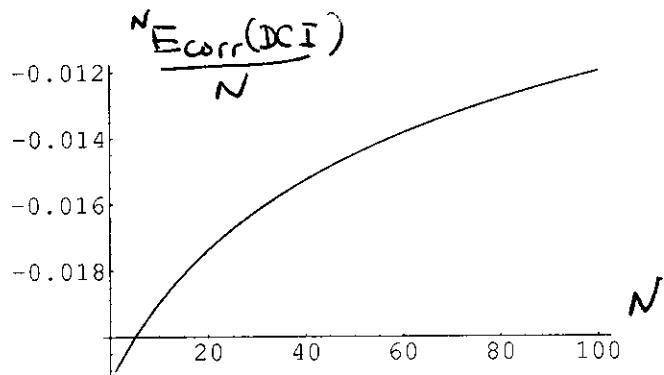
$${}^N E_{\text{corr}} \approx -N^{1/2} K_{12}$$

Exercise 4.11

with STO-3G H_2 integrals
calculate

$$\frac{{}^N E_{\text{corr(DCI)}}}{N}$$

$$\lim_{N \rightarrow \infty} \frac{{}^N E_{\text{corr}}}{N} = 0$$



Exercise 4.14 (Davidson correction)

A simple prescription to correct for size inconsistency of the DCI is given by the Davidson correction

$$E_{\text{corr}} = E_{\text{corr}}(\text{DCI}) + \Delta E_{\text{Davidson}}$$

$$\Delta E_{\text{Davidson}} = (1 - c_0^2) \Delta E_{\text{corr}}(\text{DCI})$$

c_0 is the coefficient in front of $|\psi_0\rangle$ in the normalized DCI wave function

$$|\Phi_0\rangle = c_0 |\psi_0\rangle + c_0 \sum c_{cd}^{tu} |\psi_{cd}^{tu}\rangle$$

a. N^2 expansion of ${}^N E_{\text{corr}}(\text{DCI})$

$${}^N E_{\text{corr}}(\text{DCI}) = \Delta - (\Delta^2 + N K_{12}^2)^{1/2}$$

$$\text{if } N K_{12}^2 / \Delta^2 < 1$$

$${}^N E_{\text{corr}}(\text{DCI}) = - \frac{N K_{12}^2}{2 \Delta} + \frac{N^2 K_{12}^4}{8 \Delta^3}$$

$${}^N E_{\text{corr}}(\text{exact}) = N [\Delta - (\Delta^2 + K_{12}^2)^{1/2}] \simeq - \frac{N K_{12}^2}{2 \Delta}$$

$\frac{K_{12}}{\Delta} < 1$

b. For N independent H_2 molecules

$$|\Phi_0\rangle = |\Psi_0\rangle + c \sum_i |z_i \bar{z}_i\rangle$$

$$\langle \Phi_0 | \Phi_0 \rangle = 1 + c^2 N = A^2$$

$\frac{1}{\sqrt{A}} |\Phi_0\rangle \rightarrow$ a normalized wave function

$$|\Phi_0\rangle = \frac{1}{\sqrt{1+c^2N}} |\Psi_0\rangle + \frac{c}{\sqrt{1+c^2N}} \sum_i |z_i \bar{z}_i\rangle$$

$$1 - c_0^2 = \frac{N c^2}{1 + N c^2}$$

$$c = \frac{K_{12}}{N E_{\text{corr}}(\text{DCI}) - 2\Delta} \approx - \frac{K_{12}}{2\Delta}$$

$$E_{\text{corr}}(\text{DCI}) - 2\Delta = -\Delta - (\Delta^2 + N K_{12}^2)^{1/2} \approx -2\Delta$$

$$\Delta E_{\text{Davidson}} \approx - \underbrace{\frac{N K_{12}^2}{2\Delta}}_{N E_{\text{corr}}(\text{DCI})} \times \underbrace{\frac{N K_{12}^2}{\Delta^2}}_{N c^2} \approx - \frac{N^2 K_{12}^4}{8\Delta^3}$$

$$E_{\text{corr}} = E_{\text{corr}}(\text{DCI}) + \Delta E_{\text{Davidson}}$$

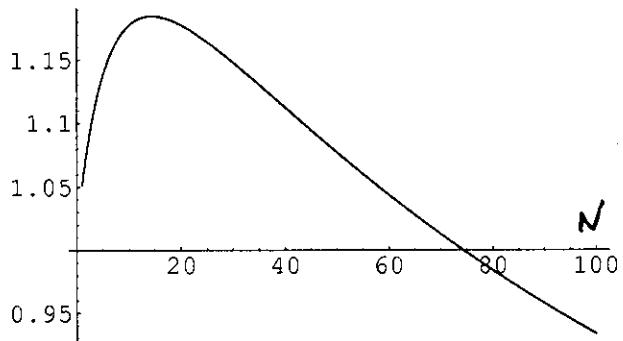
$$= - \frac{N K_{12}^2}{2\Delta} + O(N^3)$$

The Davidson correction exactly cancels the terms proportional to N^2

e.

$$\frac{^N E_{\text{corr}} (\text{DCI}) + \Delta E_{\text{Davidson}}}{^N E_{\text{corr}} (\text{exact})}$$

J_{ij} and k_{12} at $R = 1.4 \text{ a.u.}$ are taken from
Appendix D: $\Delta = 0.27$, $k_{12} = 0.18$



Water calculation using full CI

```
$CONTRL CITYP=ALDET SCFTYP=RHF NZVAR=0 MULT=1 $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=3 NPFUNC=3 DIFFS=.TRUE. $END
$CIDET GROUP=C2v NCORE=1 NACT=5 NELS=8 NSTATE=2 $END
$GUESS GUESS=MOREAD NORB=51 $END
$DATA
```

Water calculation by D. Matyushov

Cnv 2

O1	8.0	0.0000000000	0.0000000000	-0.0380492824
H2	1.0	0.7494524065	0.0000000000	0.5313335789

\$END

--- OPTIMIZED RHF MO-S --- GENERATED AT Mon Apr 1 13:42:27 2002

E= -76.0333603854, E(NUC)= 9.3487379618

\$VEC

1	1	9.95200165E-01	1.22624608E-02	0.00000000E+00	0.00000000E+00	1.50108411E-01
1	2-2	1.15196702E-03	0.00000000E+00	0.00000000E+00	-1.14753906E-03	3.43951592E-01
1	3	3.39846908E-03	3.42719182E-03	0.00000000E+00	0.00000000E+00	0.00000000E+00
1	4-6	4.28761377E-04	-7.73371882E-04	-6.59068704E-04	0.00000000E+00	0.00000000E+00
1	5	0.00000000E+00	8.77985460E-05	1.94968864E-04	-1.79248609E-04	0.00000000E+00
1	6	0.00000000E+00	0.00000000E+00	1.25349693E-04	9.26652456E-04	-1.42025097E-04
1	7-8	7.2577935E-06	0.00000000E+00	3.02172606E-05	-3.57216918E-04	0.00000000E+00

STATE 1 ENERGY= -76.0334136120 S= 0.00 SZ= 0.00 SPACE SYM=A1

STATE 2 ENERGY= -75.6138205412 S= 1.00 SZ= 0.00 SPACE SYM=A1

ELECTROSTATIC MOMENTS

POINT	1	X	Y	Z (BOHR)	CHARGE
		0.000000	0.000000	0.048515	0.00 (A.U.)
DX	DY	DZ	/D/ (DEBYE)		
0.000000	0.000000	1.929358	1.929358		

Water calculation using SDCI

```
$CTRL CITYP=GUGA SCFTYP=RHF NZVAR=0 MULT=1 $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=3 NPFUNC=3 DIFFS=.TRUE. $END
$CIDRT GROUP=C2v NFZC=1 NDOC=4 NVAL=3 IEXCIT=2 $END
$GUGDIA NSTATE = 2 $END
$GUESS GUESS=MOREAD NORB=51 $END
$DATA
```

Water calculation by D. Matyushov

Cnv 2

O1	8.0	0.0000000000	0.0000000000	-0.0380492824
H2	1.0	0.7494524065	0.0000000000	0.5313335789

\$END

--- OPTIMIZED RHF MO-S --- GENERATED AT Mon Apr 1 13:42:27 2002

E= -76.0333603854, E(NUC)= 9.3487379618

\$VEC

1	1	9.95200165E-01	1.22624608E-02	0.00000000E+00	0.00000000E+00	1.50108411E-03
1	2-2	1.15196702E-03	0.00000000E+00	0.00000000E+00	-1.14753906E-03	3.43951592E-03
1	3	3.39846908E-03	3.42719182E-03	0.00000000E+00	0.00000000E+00	0.00000000E+00
1	4-6	4.28761377E-04	-7.73371882E-04	-6.59068704E-04	0.00000000E+00	0.00000000E+00

STATE # 1 ENERGY = -76.036682352

CSF	COEF	OCCUPANCY (IGNORING CORE)
---	----	-----
1	0.998968	2222000

STATE # 2 ENERGY = -75.638199483

CSF	COEF	OCCUPANCY (IGNORING CORE)
---	----	-----
8	0.224976	2212001
19	0.962301	2212100
28	0.113902	2202101
33	0.052688	2202200

COSQ= 0.997937 EREF= -76.033360 E-E(REF)= 0.003322 E(Q)= 0.000007
GIVES A E(SD+Q) ESTIMATE OF -76.0366892213

ELECTROSTATIC MOMENTS

POINT	1	X	Y	Z (BOHR)	CHARGE
		0.000000	0.000000	0.048515	0.00 (A.U.)
DX		DY	DZ	/D/	(DEBYE)
0.000000	0.000000		1.884784	1.884784	

CI EIGENSTATE 1 TOTAL ENERGY = -76.0366823502

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

			1	2	3	4	5	
			2.0000	1.9999	1.9999	1.9994	1.9969	
1	0	1	S	-0.995200	0.213153	0.000000	0.000000	-0.052097
2	0	1	S	-0.012262	-0.437569	0.000000	0.000000	0.086907
3	0	1	X	0.000000	0.000000	0.000000	-0.505534	0.000000
4	0	1	Y	0.000000	0.000000	-0.638990	0.000000	0.000000
5	0	1	Z	-0.001501	0.219271	0.000000	0.000000	0.520190
6	0	1	S	0.002152	-0.525081	0.000000	0.000000	-0.146926
7	0	1	X	0.000000	0.000000	0.000000	-0.275574	0.000000
8	0	1	Y	0.000000	0.000000	-0.453661	0.000000	0.000000
9	0	1	Z	0.001148	0.156733	0.000000	0.000000	0.286728
10	0	1	XX	-0.003440	-0.021027	0.000000	0.000000	0.005942
11	0	1	YY	-0.003398	-0.018891	0.000000	0.000000	-0.001302
12	0	1	ZZ	-0.003427	-0.018288	0.000000	0.000000	0.007123
13	0	1	XY	0.000000	0.000000	0.000000	0.000000	0.000000
14	0	1	XZ	0.000000	0.000000	0.000000	-0.009901	0.000000
15	0	1	YZ	0.000000	0.000000	-0.003172	0.000000	0.000000
16	0	1	XX	0.000629	-0.026119	0.000000	0.000000	-0.003531
17	0	1	YY	0.000773	-0.024863	0.000000	0.000000	-0.008071

18	0	1	ZZ	0.000659	-0.011939	0.000000	0.000000	0.021973
19	0	1	XY	0.000000	0.000000	0.000000	0.000000	0.000000
20	0	1	XZ	0.000000	0.000000	0.000000	-0.024277	0.000000
21	0	1	YZ	0.000000	0.000000	-0.020601	0.000000	0.000000
22	0	1	XX	-0.000088	-0.019931	0.000000	0.000000	-0.063485
23	0	1	YY	-0.000195	-0.016823	0.000000	0.000000	-0.044526
24	0	1	ZZ	0.000179	-0.005722	0.000000	0.000000	-0.028325
25	0	1	XY	0.000000	0.000000	0.000000	0.000000	0.000000
26	0	1	XZ	0.000000	0.000000	0.000000	-0.014327	0.000000

RENORMALIZED DAVIDSON CORRECTION FOR 1-REFERENCE CI.

COSQ= 0.997937 EREF= -76.033360 E-E(REF)= 0.003322 E(Q)= 0.000007

GIVES A E(SD+Q) ESTIMATE OF -76.0366892192

Exercise 4.15

Intermediate normalization

$$|\Phi_0\rangle = |\Psi_0\rangle + c |2\bar{2}\rangle$$

$$c = E_{\text{corr}}/\kappa_{12} = \frac{\Delta}{\kappa_{12}} - \frac{(\Delta^2 + \kappa_{12}^{-2})^{1/2}}{\kappa_{12}}$$

$$\langle \Phi_0 | \Phi_0 \rangle = 1 + c^2$$

Normalization:

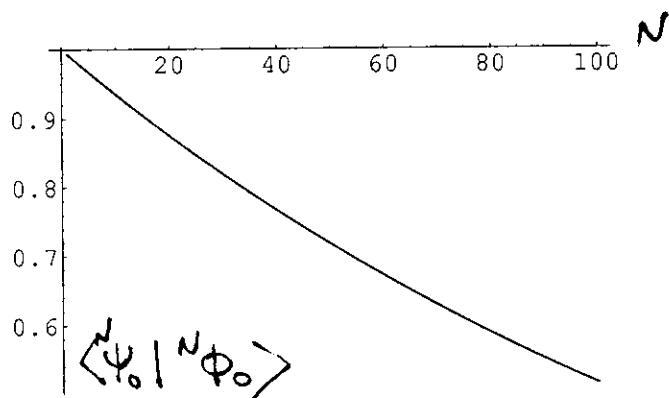
$$|\Phi_0\rangle = \frac{1}{\sqrt{1+c^2}} |\Psi_0\rangle + \frac{c}{\sqrt{1+c^2}} |2\bar{2}\rangle$$

For N independent H_2 molecules

$$|\Phi_0\rangle = \prod_{i=1}^N \left[\frac{1}{\sqrt{1+c^2}} |1_i\bar{1}_i\rangle + \frac{c}{\sqrt{1+c^2}} |2_i\bar{2}_i\rangle \right]$$

$$|\Psi_0\rangle = \prod_{i=1}^N |1_i\bar{1}_i\rangle$$

$$\begin{aligned} \langle \Psi_0 | {}^N \Phi_0 \rangle &= \prod_{i,j=1}^N \left[\frac{1}{\sqrt{1+c^2}} \langle 1_j\bar{1}_j | 1_i\bar{1}_i \rangle + \frac{c}{\sqrt{1+c^2}} \langle 1_j\bar{1}_j | 2_i\bar{2}_i \rangle \right] \\ &= (1+c^2)^{-N/2} = e^{-\frac{N}{2} \ln(1+c^2)} \xrightarrow[N \rightarrow \infty]{} 0 \end{aligned}$$



4.4. Natural orbitals

The CI expansion is based on canonical HF orbitals and turns out to be rather slowly convergent.

Can one find a one-electron basis for which the CI expansion converges more rapidly than it does with the HF Basis?

This problem is solved with the set of natural orbitals.

One-electron density matrix

$$\gamma(\bar{x}, \bar{x}') = N \int d\bar{x}_2 \dots d\bar{x}_N \Phi(\bar{x}, \bar{x}_2 \dots \bar{x}_N) \Phi^*(\bar{x}', \bar{x}_2, \dots \bar{x}_N)$$

The diagonal element of $\gamma(\bar{x}, \bar{x}')$ is the electronic density

$$\rho(\bar{x}) = \gamma(\bar{x}, \bar{x})$$

$\gamma(\bar{x}, \bar{x}')$ can be expanded in the orthonormal basis set of HF spin orbitals $\{\chi_i\}$

$$\gamma(\bar{x}, \bar{x}') = \sum_i \chi_i(\bar{x}) \chi_i(\bar{x}') \gamma_{ij}$$

$$\gamma_{ij} = \langle i | \gamma | j \rangle$$

Exercise 4.6

$$O_1 = \sum_{i=1}^n h(i)$$

a. Show that

$$\langle \Phi | O_1 | \Phi \rangle = \int dx_1 [h(x_1) \delta(x_1, x_1')]_{x_1' = x_1}$$

$$\begin{aligned} \langle \Phi | O_1 | \Phi \rangle &= \sum_i \int \Phi^*(\bar{x}_1 \dots \bar{x}_N) h(i) \Phi(\bar{x}_1 \dots \bar{x}_N) d\bar{x}_1 \dots d\bar{x}_N \\ &= \sum_i \int d\bar{x}_i h(i) \underbrace{\int \Phi^*(\bar{x}_1 \dots \bar{x}_i' \dots \bar{x}_N) \Phi^*(\bar{x}_1 \dots \bar{x}_i \dots \bar{x}_N) d\bar{x}_i'}_{N^{-1} \delta(\bar{x}_i' \bar{x}_i)} \Big|_{\bar{x}_i' = \bar{x}_i} \\ &= \sum_i \int d\bar{x}_i N^{-1} [h(i) \delta(\bar{x}_i' \bar{x}_i)]_{\bar{x}_i' = \bar{x}_i} \end{aligned}$$

$$\delta(\bar{x}_i' \bar{x}_i) = \delta(\bar{x}_i \bar{x}_i)$$

$$= \int d\bar{x}_i [h(i) \delta(\bar{x}_i' \bar{x}_i)]_{\bar{x}_i' = \bar{x}_i}$$

b. Show that $\langle \Phi | O_1 | \Phi \rangle = \text{Tr}(h \delta)$

$$h_{ij} = \langle i | h | j \rangle$$

$$\begin{aligned} \text{Tr}(h \delta) &= \sum_{i,j} h_{ij} \delta_{ji} = \sum_{i,j} \int \chi_i^*(\bar{x}_i) h(\bar{x}_i) \chi_j(\bar{x}_i) d\bar{x}_i \\ &\quad \int \chi_j^*(\bar{x}_2) \delta(\bar{x}_2, \bar{x}_3) \chi_i(\bar{x}_3) d\bar{x}_2 d\bar{x}_3 = \\ &= \int d\bar{x}_1 d\bar{x}_2 d\bar{x}_3 \underbrace{\sum_i \chi_i^*(\bar{x}_1) \chi_i(\bar{x}_3)}_{\delta(\bar{x}_1 - \bar{x}_3)} h(\bar{x}_1) \underbrace{\sum_j \chi_j^*(\bar{x}_2) \chi_j(\bar{x}_1)}_{\delta(\bar{x}_2 - \bar{x}_1)} \delta(\bar{x}_2, \bar{x}_3) = \\ &= \int d\bar{x}_1 [h(\bar{x}_1) \delta(\bar{x}_2, \bar{x}_1)]_{\bar{x}_2 = \bar{x}_1} = \langle \Phi | O_1 | \Phi \rangle \end{aligned}$$

HF basis set

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \{ \chi_a(1) \chi_b(2) \dots \chi(N) \}$$

$$\delta_{ij}^{\text{HF}} = \int d\bar{x}_i d\bar{x}'_j \chi_i^*(\bar{x}_i) \chi_j(\bar{x}'_j) N \frac{1}{N!}$$

$$\int \sum_P (-1)^P P \{ \chi_a^*(1) \chi_s^*(2) \dots \} \sum_{P'} (-1)^{P' P} \{ \chi_r(1) \chi_s(2) \dots \} \\ d\bar{x}_2 \dots d\bar{x}_N =$$

$$= \sum_a \langle i | a \rangle \langle a | j \rangle = \delta_{ij}$$

$$\boxed{\delta_{ij}^{\text{HF}} = \delta_{ij}}$$

When $\Phi \neq \Psi_0$, the one-electron matrix is not diagonal. However, it is possible to define a unitary transformation that diagonalizes $\overleftrightarrow{\mathbf{U}}$

$$\chi_i = \sum_k \gamma_k (\mathbf{U}^+)_k i = \sum_k \gamma_k \mathbf{U}_{ik}^*$$

$$\mathbf{U}(\bar{x}, \bar{x}') = \sum_k \gamma_k(\bar{x}_i) \mathbf{U}_{ik}^* \delta_{ij} \mathbf{U}_{je} \gamma_e(\bar{x}'_e)$$

$$= \sum_k \gamma_k(\bar{x}_i) \gamma_e(\bar{x}'_e) \left(\sum_{ij} (\mathbf{U}^+)_k i \delta_{ij} \mathbf{U}_{je} \right)$$

$$\overleftrightarrow{\mathbf{U}}^+ \overleftrightarrow{\mathbf{U}} = \overleftrightarrow{\lambda} = \begin{pmatrix} \lambda_1 & 0 & & \\ & \lambda_2 & & \\ & & \ddots & \\ & 0 & & \lambda_n \end{pmatrix}$$

$$\delta(x_i, x'_i) = \sum \lambda_k \gamma_k(x_i) \gamma_k^*(x'_i)$$

↑
occupation number

Natural orbitals give the most rapidly convergent CI expansion. Small occupation numbers can be dropped from the expansion with the result of greater efficiency of calculations

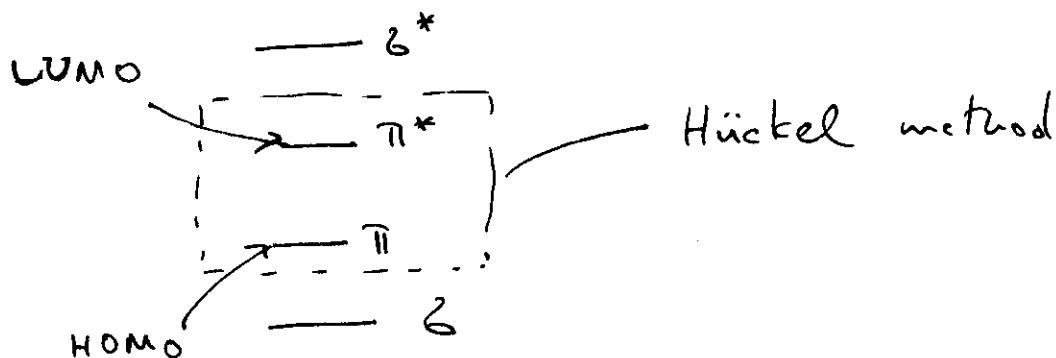
Example:

SDCI calculation of H₂O (51 MOs)

n(MO)	1	2	3	4	5
λ_n	2.000	1.999	1.999	1.999	1.999
6		7		8	
	0.0036		0.0003		0.0000

The Hückel method

For unsaturated hydrocarbons, the bonding σ -orbitals are below the bonding π -orbitals. Also, the antibonding σ -orbitals are above the antibonding π -orbitals. HOMOs and LUMOs are most important for reactivity and spectroscopy and only they are included in the Hückel method.



Assume we have a conjugated system of N p. atomic orbitals

$$\text{LCAO: } \psi_{\mathbf{k}} = \sum c_{\mu\mathbf{k}} p_{\mu} \quad \begin{matrix} \xleftarrow{\text{LCAO}} \\ \text{atomic P wave function} \end{matrix}$$

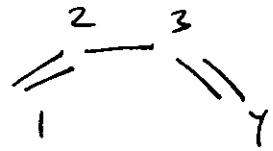
LCAO equation

$$\hat{H} \vec{c} = \vec{s} \vec{c} \vec{\varepsilon}$$

$$\vec{\varepsilon} = \begin{pmatrix} \varepsilon_1 & & & 0 \\ & \ddots & & \\ 0 & & \ddots & \varepsilon_N \end{pmatrix}$$

$$\vec{s} = \begin{pmatrix} 1 & s_{12} & s_{13} & \dots \\ s_{21} & 1 & & \\ \vdots & & \ddots & \dots \end{pmatrix}$$

Example : Butadiene



$$\Psi = \alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3 + \alpha_4 p_4$$

Secular equation

$$\left| \begin{array}{cccc} H_{11} - E & H_{12} - ES_{12} & H_{13} - ES'_{13} & H_{14} - ES'_{14} \\ H_{21} - ES'_{21} & H_{22} - E & - & - \\ H_{31} - ES'_{31} & & - & - \\ H_{41} - ES'_{41} & & & - \end{array} \right| = 0$$

Hückel theory approximations:

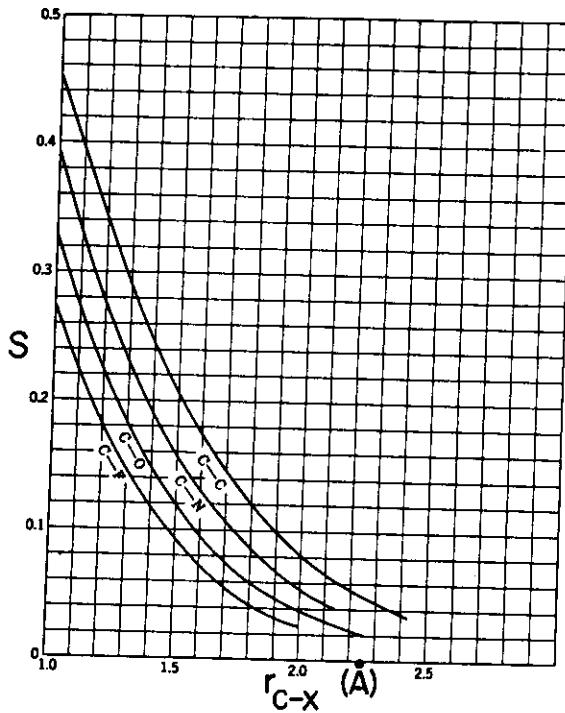
$$H_{ii} = \alpha$$

$$H_{ij} = \beta \delta_{ij}, i \neq j$$

$$S_{ij} = \delta_{ij}$$

$$x = \frac{\alpha - E}{\beta}$$

$$\left| \begin{array}{cccc} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{array} \right|$$



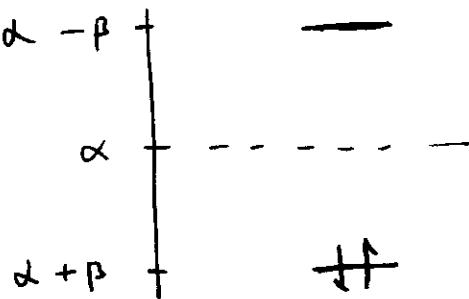
Ethylene :

$$1 = 2$$

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 = \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix}$$

$$x = \pm 1$$

$$E = \alpha \pm \beta$$



Butadiene :

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

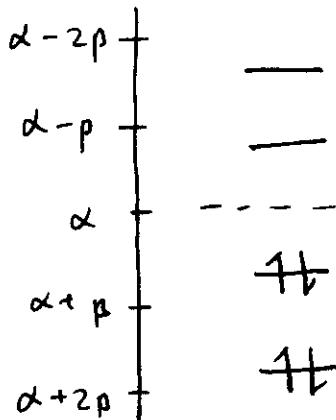
$$x = \pm \left(\frac{3 \pm \sqrt{5}}{2} \right)^{1/2}$$

$$E_1 = \alpha + 1.62\beta$$

$$E_2 = \alpha + 0.62\beta$$

$$E_3 = \alpha - 0.62\beta$$

$$E_4 = \alpha - 1.62\beta$$



Annulenes: $N = 4j + 2$

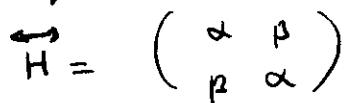
$$\varepsilon_0 = 2 \sum_{i=-\nu}^{+\nu} \varepsilon_i = N\alpha + \frac{4\beta}{\sin \frac{\pi}{N}}$$

Benzene: $N = 6, n = 3, j = 1$

$$\varepsilon_0 = 6\alpha + 8\beta$$

In the zeroth-order approximation, each double bond is separate from all other double bonds.

For this ethylene unit



and

$$\varepsilon_1^{(0)} = \alpha + \beta$$

$$\varepsilon_1^{(0)*} = \alpha - \beta$$

$$E_0 = n(2\alpha + 2\beta) = \alpha N + N\beta$$

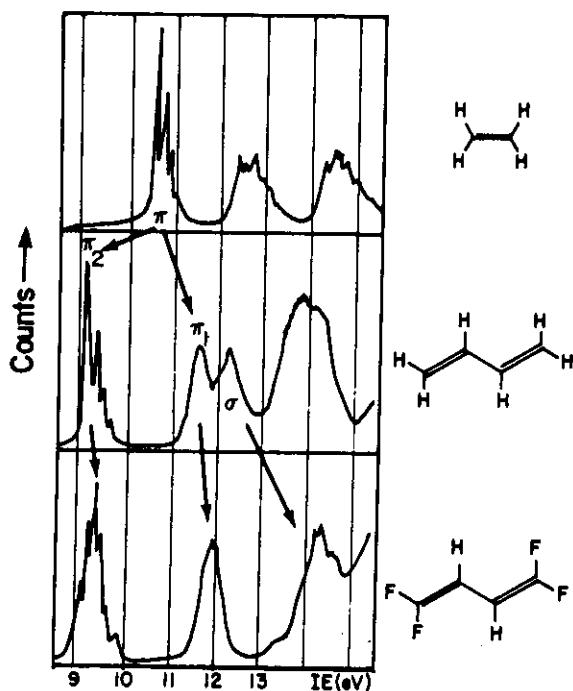
The resonance energy is defined as the difference between the exact energy of the polyene and the energy of n localized and noninteracting double bonds (ethylene units)

$$E_R = \varepsilon_0 - E_0 = \frac{4\beta}{\sin \frac{\pi}{N}} - N\beta \xrightarrow[N \rightarrow \infty]{} \underline{0.2732N\beta}$$

For Benzene:

$$E_R = \frac{4\beta}{\sin \frac{\pi}{6}} - 6\beta = \underline{\underline{2\beta}}$$

PES spectra of ethylene, butadiene, and 1,1,4,4-tetrafluorobutadiene:



Hückel solution for energies:

$$\Psi_p = \sum c_{pm} p_m$$

$$c_{km} = A \sin(km)$$

$$c_{km} = c_{k(N+m)}$$

$$k = \frac{2\pi p}{N}$$

$$\langle \Psi_p | \Psi_p \rangle = 1 = \sum_m |c_{pm}|^2 =$$

$$= A^2 \sum_m \sin^2 \frac{2\pi pm}{N} = \frac{A^2 N}{2}$$

$$c_{pm} = \sqrt{\frac{2}{N}} \sin \frac{2\pi pm}{N}$$

Hückel secular equation

$$c_{p(m-1)} + x c_{pm} + c_{p(m+1)} = 0$$

$$\sin \frac{2\pi p}{N}(m-1) + \sin \frac{2\pi p}{N}(m+1) = \\ = -x \sin \frac{2\pi pm}{N}$$

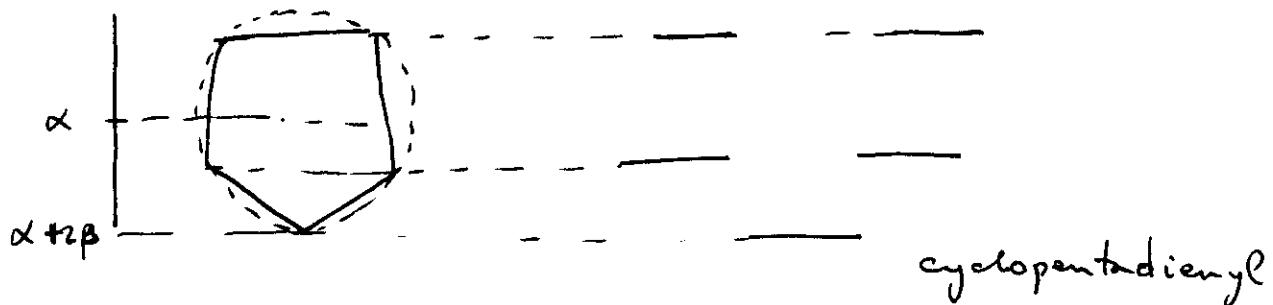
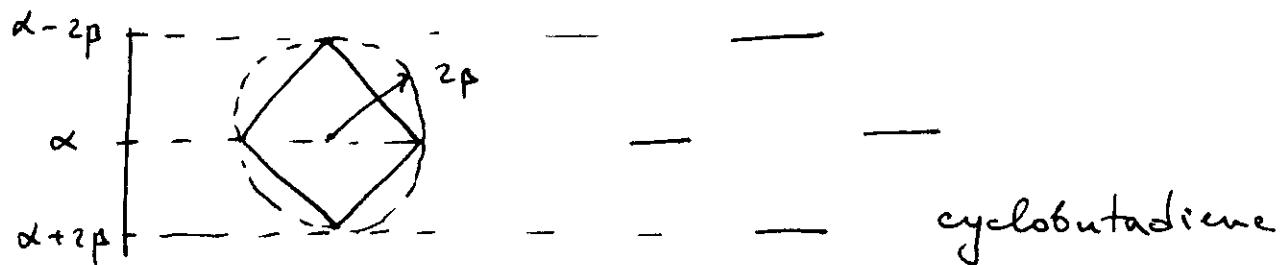
$$x = -2 \cos \frac{2\pi p}{N}$$

$$\epsilon_p = \alpha + 2\beta \cos \frac{2\pi p}{N}$$

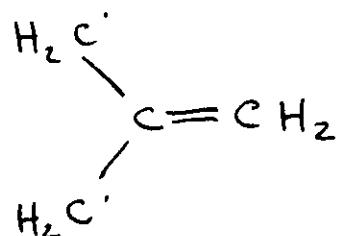
Hückel orbital energies

Geometric shortcut:

- * draw the cyclic compound so that one of the vertices points downward inside a circle of radius 2β .
- * Hückel pi energy levels come at the energies where the vertices intersect the circle:



Homework problem: Using Hückel theory, determine the energies of four pi orbitals of trimethylmethane



Exercise 4.3

$$c = \frac{k_{12}}{E_{\text{corr}} - 2\Delta} = - \frac{k_{12}}{\Delta + (\Delta^2 + k_{12}^2)^{1/2}}$$

$$\begin{aligned}\Delta &= \varepsilon_2 - \varepsilon_1 + \frac{1}{2} (J_{11} + J_{22} - 4J_{12} + 2k_{12}) \\ &= 0.6703 + 0.5782 + \frac{1}{2} (0.6746 + 0.6975) - 2 \cdot 0.6636 + \\ &\quad + 0.1813 = 0.789\end{aligned}$$

At $R \rightarrow \infty$ $J_{11}, J_{22}, k_{12}, J_{12} \rightarrow \frac{1}{2}(11/11)$, $\Delta \rightarrow 0$

$$c \rightarrow - \frac{k_{12}}{\Delta + (\Delta^2 + k_{12}^2)^{1/2}} \xrightarrow[\Delta \rightarrow 0]{} -\frac{1}{2}$$

At $R \rightarrow \infty$

$$\begin{aligned}|\Phi_0\rangle &= |\Psi_0\rangle - |\Psi_{1\bar{1}}^{2\bar{2}}\rangle = \\ &= \frac{1}{\sqrt{2}} (\Psi_g(1)\Psi_g(2) - \Psi_u(1)\Psi_u(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2))\end{aligned}$$

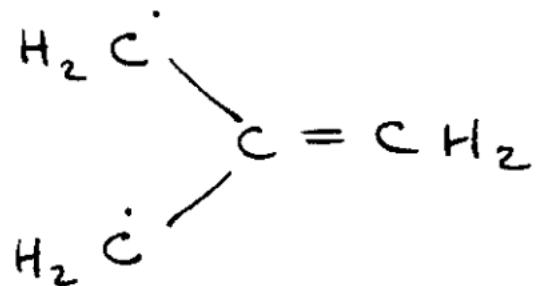
At $R \rightarrow \infty$ $s \rightarrow 0$ and

$$\Psi_g(1)\Psi_g(2) - \Psi_u(1)\Psi_u(2) = \Phi_1(1)\Phi_2(2) + \Phi_1(2)\Phi_2(1)$$

$$\begin{aligned}|\Phi_0\rangle &= \frac{1}{\sqrt{2}} (\Phi_1(1)\Phi_2(2) + \Phi_1(2)\Phi_2(1))(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\ &= \frac{1}{\sqrt{2}} (|\Phi_1\bar{\Phi}_2\rangle + |\Phi_2\bar{\Phi}_1\rangle)\end{aligned}$$

Homework problem:

Using Hückel theory, determine the energies of four π orbitals of trimethylmethane :



Perturbation theories

CI is a variational procedure (as well as HF) :

$$E_0 \leq E_0^{\text{HF}} [\tilde{\Psi}] + E_{\text{corr}}^{\text{CI}} [\tilde{\Psi}]$$

! only FCI is size-consistent

Perturbation theory (PT) is not variational; the approximate energy may fall below the exact energy. However, the PT is fully size-consistent no matter at which term it is truncated.

PT:

$$\boxed{\text{Total Hamiltonian}} = \boxed{\text{zero-order part}} + \boxed{\text{perturbation}}$$

$$H = H_0 + V$$

"Perturbation" is understood in a sense that V does not strongly affect a property of interest compared to its value generated by H_0 .

This scheme of calculating energies is referred to as the Rayleigh - Schrödinger PT (RSPT).

The Møller - Plesset PT (MPPT or MP) is based on using the HF Hamiltonian as H_0 .

$$H^{\text{HF}} = H_0 = \sum_a f(a) \quad \sum_a \varepsilon_a = E_0^{(0)} \neq E_0^{\text{HF}}$$

$$H_0 |\Psi_0\rangle = \sum_a \varepsilon_a |\Psi_0\rangle \quad E_0^{\text{HF}} = E_0^{(0)} + \langle \Psi_0 | V | \Psi_0 \rangle$$

RSPT

RSPT is a procedure to systematically improve the eigenfunctions and eigenvalues of H by summing series in the matrix elements of the perturbation V

$$H |\Phi_i\rangle = \varepsilon_i |\Phi_i\rangle$$

↖ ↑
unknown

$$H_0 |\Psi_i^{(0)}\rangle = E_i^{(0)} |\Psi_i^{(0)}\rangle \quad |\Psi_i^{(0)}\rangle = |i\rangle$$

↑ ↑
known

λ -scaling:

$$H = H_0 + \lambda V$$

$$\varepsilon_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots$$

$$|\Phi_i\rangle = |i\rangle + \lambda |\Psi_i^{(1)}\rangle + \lambda^2 |\Psi_i^{(2)}\rangle + \dots$$

Intermediate normalization:

$$\begin{cases} \langle i | i \rangle = 1 \\ \langle i | \Phi_i \rangle = 1 \end{cases} \Rightarrow \langle i | \Psi_i^{(n)} \rangle = 0$$

$$(H_0 + \lambda V) (|i\rangle + \lambda |\Psi_i^{(1)}\rangle + \lambda^2 |\Psi_i^{(2)}\rangle + \dots) = (E_i^{(0)} + \lambda E_i^{(1)} + \dots) (|i\rangle + \lambda |\Psi_i^{(1)}\rangle + \dots)$$

$$n=0 \quad H_0 |i\rangle = E_i^{(0)} |i\rangle$$

$$n=1 \quad H_0 |\Psi_i^{(1)}\rangle + V |i\rangle = E_i^{(0)} |\Psi_i^{(1)}\rangle + E_i^{(1)} |i\rangle$$

$$n=2 \quad H_0 |\Psi_i^{(1)}\rangle + V |\Psi_i^{(1)}\rangle = E_i^{(0)} |\Psi_i^{(2)}\rangle + E_i^{(1)} |\Psi_i^{(1)}\rangle + E_i^{(2)} |i\rangle$$

n -th order energies:

$$E_i^{(0)} = \langle i | H_0 | i \rangle$$

$$E_i^{(1)} = \langle i | V | i \rangle$$

$$E_i^{(2)} = \langle i | V | \Psi_i^{(1)} \rangle$$

$$E_i^{(3)} = \langle i | V | \Psi_i^{(2)} \rangle$$

one needs higher order wave functions for $n \geq 2$

$|\Psi_i^{(1)}\rangle$ and $E_i^{(1)}$:

$$(E_i^{(0)} - H_0) |\Psi_i^{(1)}\rangle = (V - \langle i | V | i \rangle) |i\rangle$$

$$|\Psi_i^{(1)}\rangle = \sum_n c_n^{(1)} |n\rangle = \sum_n |n\rangle \langle n | \Psi_i^{(1)} \rangle$$

state $|i\rangle$ is not included into the sum

$$(E_i^{(0)} - E_n^{(0)}) \langle n | \Psi_i^{(1)} \rangle = \langle n | V | i \rangle$$

$$c_n^{(1)}$$

$$|\Psi_i^{(1)}\rangle = \sum' \frac{\langle n | V | i \rangle}{E_i^{(0)} - E_n^{(0)}} |n\rangle$$

$$E_i^{(1)} = \langle i | V | \Psi_i^{(1)} \rangle = \sum' \frac{|\langle n | V | i \rangle|^2}{E_i^{(0)} - E_n^{(0)}}$$

$|\Psi_i^{(2)}\rangle$ and $E_i^{(2)}$:

$$(E_i^{(0)} - E_n^{(0)}) \langle n | \Psi_i^{(2)} \rangle = \langle n | V | \Psi_i^{(1)} \rangle - E_i^{(1)} \langle n | \Psi_i^{(1)} \rangle$$

$$\downarrow \\ C_n^{(2)}$$

$$E_i^{(2)} = \sum_n' \langle i | V | n \rangle \langle n | \Psi_i^{(2)} \rangle =$$

$$= \sum_n' \frac{\langle i | V | n \rangle \langle n | V | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}} - E_i^{(1)} \sum_n' \frac{\langle i | V | n \rangle \langle n | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}}$$

$$= \sum_{n,m} \frac{\langle i | V | n \rangle \langle n | V | m \rangle \langle m | V | i \rangle}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} - E_i^{(1)} \sum_n' \frac{K_i |V|_n|^2}{(E_i^{(0)} - E_n^{(0)})^2}$$

$$\langle n | \Psi_i^{(2)} \rangle = \frac{\langle n | V | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}} - E_i^{(1)} \frac{\langle n | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}}$$

$$= \sum_m' \frac{V_{nm} \langle m | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}} - V_{ii} \frac{V_{ni}}{(E_i^{(0)} - E_n^{(0)})^2}$$

$$= \sum_m' \frac{V_{nm} V_{ni}}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} - \frac{V_{ii} V_{ni}}{(E_i^{(0)} - E_n^{(0)})^2}$$

$$|\Psi_i^{(2)}\rangle = \sum' |n\rangle \langle n | \Psi_i^{(2)} \rangle$$

Two-state problem

$$H = H_0 + \lambda V, \quad H_0 |1\rangle = E_1^{(0)} |1\rangle$$

$$H |\Phi\rangle = \varepsilon |\Phi\rangle \quad H_0 |2\rangle = E_2^{(0)} |2\rangle$$

$$|\Phi\rangle = c_1 |1\rangle + c_2 |2\rangle$$

$$\tilde{H} \vec{c} = \varepsilon \vec{c}, \quad \tilde{H} = \begin{pmatrix} E_1^{(0)} + \lambda V_{11} & \lambda V_{12} \\ \lambda V_{21} & E_2^{(0)} + \lambda V_{22} \end{pmatrix}$$

The lower eigenvalue (ground state):

$$\varepsilon_1 = \bar{E} - \frac{1}{2} \sqrt{\Delta E^2 + 4\lambda^2 |V_{12}|^2}$$

$$\bar{E} = \frac{1}{2} (E_1^{(0)} + E_2^{(0)} + \lambda V_{11} + \lambda V_{22})$$

$$\Delta E = E_2^{(0)} - \bar{E}_1^{(0)} + \lambda (V_{22} - V_{11})$$

Expansion into a series in λ :

$$\varepsilon_1 = \varepsilon_1^{(0)} + \lambda \varepsilon_1^{(1)} + \lambda^2 \varepsilon_1^{(2)} + \dots$$

$$\varepsilon_1^{(0)} = E_1^{(0)} \quad (\text{if } E_1^{(0)} < E_2^{(0)})$$

$$\varepsilon_1^{(1)} = V_{11}$$

$$\varepsilon_1^{(2)} = \frac{|V_{12}|^2}{E_1^{(0)} - E_2^{(0)}}$$

Diagrammatic representation of the PT

Diagrammatic representation: a one-to-one correspondence between the mathematical expressions for perturbation terms and a set of pictures drawn in a well-defined way.

Rules for drawing the diagrams:

Symbol	Meaning	Name
.	\checkmark	dot
\downarrow	$ 1\rangle$	hole line
\uparrow	$ 2\rangle$	particle line
\nearrow	$\langle \text{label of line 1} V \text{label of line out} \rangle$	matrix element

- * draw n dots vertically ordered : :
- * connect all dots by a continuous line, so that each dot has one line passing through it
- * connect the dots in all possible distinct ways.
Two diagrams are equivalent if each and every dot is connected to an identical pair of dots in both diagrams.

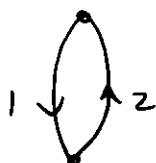
* draw arrows on each of the connecting lines in all possible ways so that each dot has a line going into it and a line coming out of it.

* lines going down are labeled with 1 and lines going up are labeled with 2.

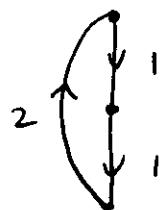
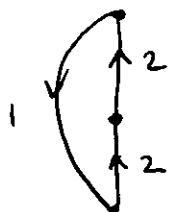
* circular lines are hole lines



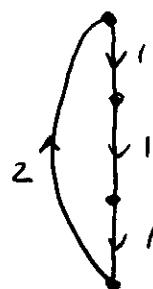
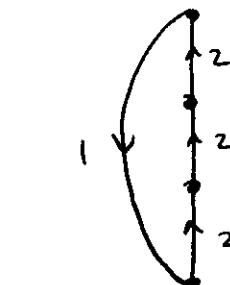
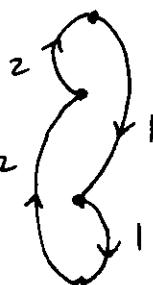
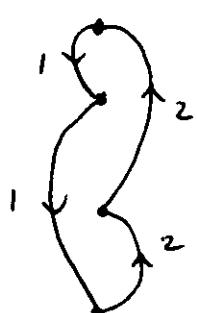
$$n = 1$$



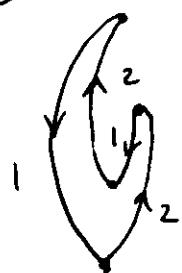
$$n = 2$$



$$n = 3$$



$$n = 4$$



Translation rules: Diagrams \rightarrow Algebraic expressions

* Each dot contributes a factor

$\langle \text{label of line in } |V| \text{ label of line out} \rangle$

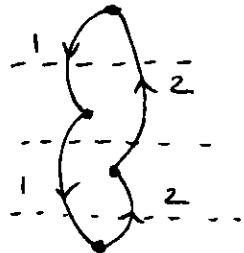
to the numerator.

* Each pair of adjacent dots contributes the factor

$$\sum E_{\text{hole}}^{(0)} - \sum E_{\text{particle}}^{(0)}$$

↙ →

runs over the labels of all hole
and particle lines crossing an imaginary
horizontal line separating the two
adjacent dots



* The overall sign of the expression is

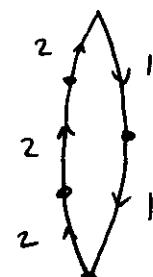
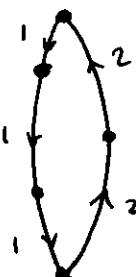
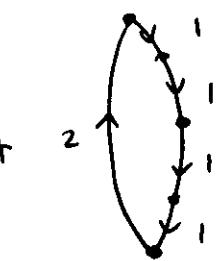
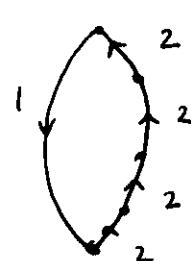
$$(-1)^{h+1}$$

number of hole lines

Exercise 6.1

Evaluate all fifth-order horizontal line crosses particle line.

diagrams for which an imaginary only one hole and one

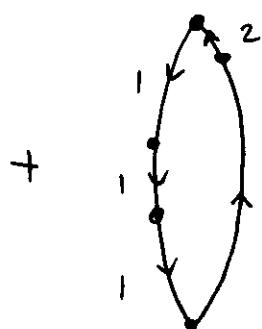


1

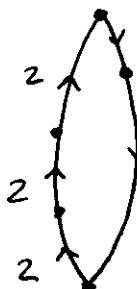
2

3

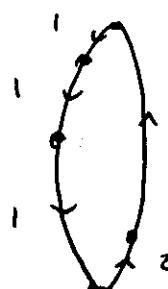
4



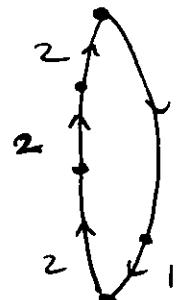
5



6



7



8

$$1 = \frac{|V_{12}|^2 V_{22}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$

$$2 = - \frac{|V_{12}|^2 V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$

$$3 = \frac{|V_{12}|^2 V_{22} V_{11}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

$$4 = - \frac{|V_{12}|^2 V_{22}^2 V_{11}}{(E_1^{(0)} - E_2^{(0)})^4}$$

$$5 = \frac{|V_{12}|^2 V_{22} V_{11}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

$$6 = - \frac{|V_{12}|^2 V_{11} V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

$$7 = \frac{|V_{12}|^2 V_{11} V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

$$8 = - \frac{|V_{12}|^2 V_{11} V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

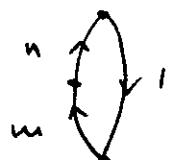
Diagrammatic PT for N states

Perturbation expansion for the lowest eigenvalue (ground state) of an N -state system:
one has one hole and $N-1$ particle states

The diagram



can be labeled as



$$m, n = 2, 3, \dots, N$$

In order to obtain an algebraic equation for an N -state system, sum the expression over all particle indices

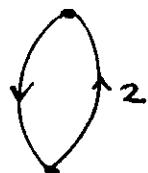
$$\text{Diagram with indices } m \text{ and } n = \sum_n' \frac{V_{1n} V_{n1}}{E_1^{(0)} - E_n^{(0)}}$$

$$\begin{aligned} \text{Diagram with indices } m \text{ and } n + \text{Diagram with indices } n \text{ and } m &= \sum_{n,m}' \frac{V_{1m} V_{mn} V_{n1}}{(E_1^{(0)} - E_m^{(0)})(E_1^{(0)} - E_n^{(0)})} - \\ &- \sum_n' \frac{V_{11} V_{1n} V_{n1}}{(E_1^{(0)} - E_n^{(0)})^2} \end{aligned}$$

Summation of sub-classes of diagrams

Summation of certain classes of diagrams to infinite order allows one to renormalize (shift) the energies in denominators of perturbation expansion terms.

Second-order term:



$$\Delta = \left[\begin{array}{c} 1 \\ | \\ \text{loop} \\ | \\ 2 \end{array} \right] + \left[\begin{array}{c} 1 \\ | \\ \text{loop} \\ | \\ 2 \\ + \\ 1 \\ | \\ \text{loop} \\ | \\ 2 \end{array} \right]$$

$$+ \left[\begin{array}{c} 1 \\ | \\ \text{loop} \\ | \\ 2 \\ + \\ 1 \\ | \\ \text{loop} \\ | \\ 2 \\ + \\ 1 \\ | \\ \text{loop} \\ | \\ 2 \\ + \\ 1 \\ | \\ \text{loop} \\ | \\ 2 \end{array} \right] + \dots$$

Δ is generated by adding dots to the second-order diagram in all possible ways.

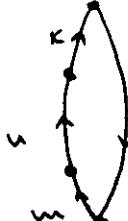
$$\Delta = \frac{|V_{12}|^2}{E_1^{(0)} - E_2^{(0)}} \left[1 + \frac{V_{22} - V_{11}}{E_1^{(0)} - E_2^{(0)}} + \frac{(V_{22} - V_{11})^2}{(E_1^{(0)} - E_2^{(0)})^2} + \dots \right]$$

$$1 + x + x^2 + x^3 + \dots = \frac{1}{1-x}$$

$$\Delta = \frac{|V_{12}|^2}{E_1^{(0)} - E_2^{(0)}} \frac{1}{1 - \frac{V_{22} - V_{11}}{E_1^{(0)} - E_2^{(0)}}} = \frac{|V_{12}|^2}{(E_1^{(0)} + V_{11}) - (E_2^{(0)} + V_{22})}$$

$$= \frac{|V_{12}|^2}{E_1^{\text{HF}} - E_2^{\text{HF}}} \quad \text{HF energy level } H_0 = H^{\text{HF}}$$

Exercise 6.2

I 

$$I = \sum'_{u, m, n, k} \frac{V_{im} V_{mn} V_{ni} V_{ki}}{(E_i^{(0)} - E_m^{(0)}) (E_i^{(0)} - E_n^{(0)}) (E_i^{(0)} - E_k^{(0)})}$$

II 

$$II = \sum'_n \frac{|V_{ii}|^2 |V_{in}|^2}{(E_i^{(0)} - E_n^{(0)})^3}$$

III 

$$III = - \sum'_{u, m} \frac{V_{iu} V_{um} V_{mi} V_{ii}}{(E_i^{(0)} - E_m^{(0)})^2 (E_i^{(0)} - E_u^{(0)})}$$

IV 

$$IV = - \sum'_{u, m} \frac{V_{iu} V_{um} V_{ni} V_{ii}}{(E_i^{(0)} - E_m^{(0)})^2 (E_i^{(0)} - E_u^{(0)})}$$

V 

$$V = - \sum'_{u, m} \frac{|V_{in}|^2 |V_{im}|^2}{(E_i^{(0)} - E_n^{(0)}) (E_i^{(0)} - E_m^{(0)}) (2E_i^{(0)} - E_n^{(0)} - E_m^{(0)})}$$

VI 

$$VI = - \sum'_{u, m} \frac{|V_{in}|^2 |V_{im}|^2}{(E_i^{(0)} - E_n^{(0)})^2 (2E_i^{(0)} - E_n^{(0)} - E_m^{(0)})}$$

$$V + VI = - \sum'_{n,m} \frac{|V_{in}|^2 |V_{im}|^2}{(E_i^{(0)} - E_n^{(0)})(2E_i^{(0)} - E_n^{(0)} - E_m^{(0)})} \left(\frac{1}{E_i^{(0)} - E_n^{(0)}} + \frac{1}{E_i^{(0)} - E_m^{(0)}} \right)$$

$$= - \sum'_{n,m} \frac{|V_{in}|^2 |V_{im}|^2}{(E_i^{(0)} - E_n^{(0)})^2 (E_i^{(0)} - E_m^{(0)})}$$

$$E^{(4)} = \sum' \left[\frac{V_{in} V_{nm} V_{mk} V_{ki}}{(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_k^{(0)})} + \right.$$

$$\left. + \frac{|V_{in}|^2 V_{ii}^2}{(E_i^{(0)} - E_n^{(0)})^3} - \frac{|V_{in}|^2 |V_{nm}|^2 + V_{ii} (V_{in} V_{nm} V_{ni} + V_{in} V_{nn} V_{ni})}{(E_i^{(0)} - E_n^{(0)})^2 (E_i^{(0)} - E_m^{(0)})} \right]$$

Perturbation expression :

$$E^{(4)} = \sum' \frac{V_{in} \langle u | V | \Psi_i^{(2)} \rangle}{E_i^{(0)} - E_n^{(0)}} - E_i^{(2)} \sum \frac{V_{in} \langle u | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}} -$$

$$- E_i^{(1)} \sum \frac{V_{in} \langle u | \Psi_i^{(2)} \rangle}{E_i^{(0)} - E_n^{(0)}} =$$

$$\langle u | \Psi_i^{(2)} \rangle = \frac{\langle u | V | \Psi^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}} - \frac{E_i^{(1)}}{E_i^{(0)} - E_n^{(0)}} \langle u | \Psi_i^{(1)} \rangle$$

$$= \sum' \frac{V_{in} V_{nm} V_{mk}}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} \langle u | \Psi_i^{(1)} \rangle - \sum' \frac{V_{in} V_{nm} V_{ii} \langle u | \Psi_i^{(1)} \rangle}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})}$$

$$- \sum' \frac{V_{in} V_{mk} V_{ii}}{(E_i^{(0)} - E_n^{(0)})^2} \langle u | \Psi_i^{(1)} \rangle + \sum' \frac{V_{ii}^2 V_{in}}{(E_i^{(0)} - E_n^{(0)})^2} \langle u | \Psi_i^{(1)} \rangle$$

$$- \sum \frac{V_{in} |V_{in}|^2}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} \langle u | \Psi_i^{(1)} \rangle =$$

$$\boxed{\langle n | \Psi_i^{(0)} \rangle = \frac{V_{ni}}{E_i^{(0)} - E_n^{(0)}}}$$

$$E_i^{(n)} = \sum' \frac{V_{in} V_{nn} V_{nn} V_{ni}}{(E_i^{(0)} - E_n^{(0)}) (E_i^{(0)} - E_n^{(0)}) (E_i^{(0)} - E_c^{(0)})} + \sum' \frac{|V_{in}|^2 |V_{ii}|^2}{(E_i^{(0)} - E_n^{(0)})^3}$$

$$- \sum' \frac{V_{in} V_{in} V_{nn} V_{ni}}{(E_i^{(0)} - E_n^{(0)})^2 (E_i^{(0)} - E_c^{(0)})} - \sum' \frac{V_{ii} V_{in} V_{nn} V_{ni}}{(E_i^{(0)} - E_n^{(0)}) (E_i^{(0)} - E_n^{(0)})^2}$$

$$- \sum' \frac{|V_{in}|^2 |V_{in}|^2}{(E_i^{(0)} - E_n^{(0)}) (E_i^{(0)} - E_n^{(0)})^2}$$

Dispersion (van der Waals or London) forces



Interaction between virtual dipole moments:

$$V = - \mu_1^\alpha \mu_2^\beta \nabla_\alpha \nabla_\beta \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

$$E^{(2)} = \frac{\langle 1, 1_2 | V | 2, 2_2 \rangle \langle 2, 2_2 | V | 1, 1_2 \rangle}{E_1^{(1)} + E_1^{(2)} - E_2^{(1)} - E_2^{(2)}} =$$

$$= - \frac{\langle 1 | \mu_1^\alpha | 1_2 \rangle \langle 1 | \mu_2^\beta | 2 \rangle \langle 2 | \mu_1^\delta | 1 \rangle \langle 2 | \mu_2^\gamma | 1 \rangle}{\Delta E_1 + \Delta E_2} \times$$

$$\nabla_\alpha \nabla_\beta \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad \nabla_\gamma \nabla_\delta \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

In the assumption of isotropic polarizabilities:

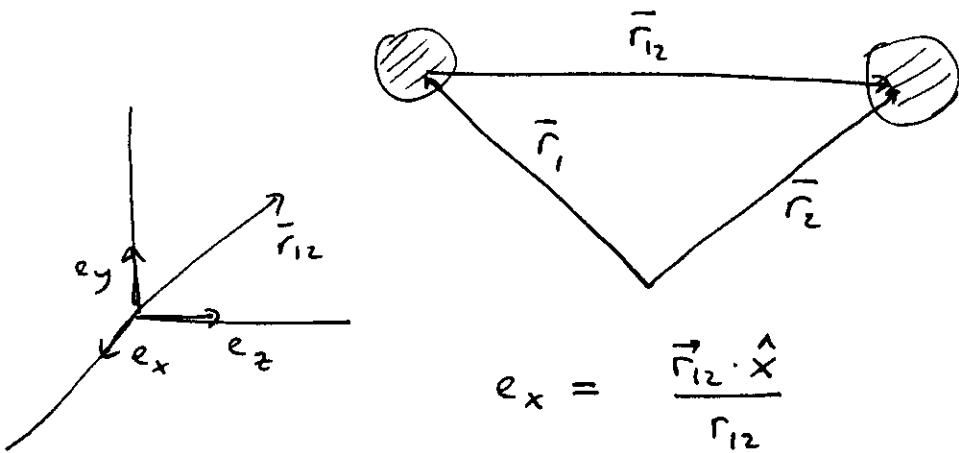
$$\alpha_1^{\alpha\beta} = 2 \frac{\langle 1 | \mu_1^\alpha | 1_2 \rangle \langle 2 | \mu_2^\beta | 1 \rangle}{\Delta E_1} \quad \delta_{\alpha\beta} = \alpha_1 \delta_{\alpha\beta}$$

$$E^{(2)} = - \frac{\alpha_1 \Delta E_1}{2} \quad \frac{\alpha_2 \Delta E_2}{2} \quad \frac{1}{\Delta E_1 + \Delta E_2} \times$$

$$\times \sum_{\alpha\beta\gamma\delta} \nabla_\alpha \nabla_\beta \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad \nabla_\gamma \nabla_\delta \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad \delta_{\alpha\gamma} \delta_{\beta\delta}$$

$$\sum_{\alpha \neq \beta} \nabla_{\alpha} \nabla_{\beta} \frac{1}{|\bar{r}_1 - \bar{r}_2|} \quad \nabla_{\alpha} \nabla_{\beta} \frac{1}{|\bar{r}_1 - \bar{r}_2|} =$$

$$= \sum_{\alpha \neq \beta} \frac{(3e_{\alpha} e_{\beta} - \delta_{\alpha \beta})(3e_{\alpha} e_{\beta} - \delta_{\alpha \beta})}{r_{12}^6} =$$



$$= \frac{6}{r_{12}^6}$$

$$E^{(2)} = - \frac{\alpha_1 \alpha_2}{4} \frac{\Delta E_1 \Delta E_2}{\Delta E_1 + \Delta E_2} \frac{6}{r_{12}^6} =$$

$$= - \frac{3}{2} \frac{\frac{I_1 I_2}{I_1 + I_2}}{\frac{I_1 + I_2}{I_1 + I_2}} \frac{1}{r_{12}^6}$$

ionization potential

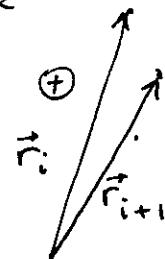
Perturbation equation for molecular polarizability

$$H = H_0 - \vec{\mu} \cdot \vec{E}_0$$

external electric field

dipole operator $\vec{\mu}$

$$\vec{\mu} = \sum_i e_i \vec{r}_i$$



Second-order perturbation expansion:

$$\varepsilon = \varepsilon_1^{(0)} + \varepsilon_1^{(1)} + \varepsilon_1^{(2)}$$

$$H_0 |\Phi_n\rangle = E_n^{(0)} |\Phi_n\rangle$$

$$\varepsilon = E_1^{(0)} - \langle 1 | \vec{\mu} \cdot \vec{E}_0 | 1 \rangle + \sum' \frac{\langle 1 | \vec{\mu} \cdot \vec{E}_0 | n \rangle \langle n | \vec{\mu} \cdot \vec{E}_0 | 1 \rangle}{E_1^{(0)} - E_n^{(0)}}$$

$$= E_1^{(0)} - \vec{\mu}_1 \cdot \vec{E}_0 - \sum' \frac{\vec{\mu}_{1n} \cdot \vec{E}_0 \vec{\mu}_{n1}}{\Delta E_{n1}}$$

$$\boxed{E_n^{(0)} - E_1^{(0)}}$$

$$\vec{\mu}_{1n} \cdot \vec{E}_0 = \sum_{\alpha} \mu_{1n}^{\alpha} E_0^{\alpha}$$

\uparrow

$$\mu_{1n}^x E_0^x + \mu_{1n}^y E_0^y + \mu_{1n}^z E_0^z$$

$$\varepsilon = E_1^{(0)} - \sum_{\alpha} \mu_1^{\alpha} E_0^{\alpha} - \sum_{\alpha \beta} E_0^{\alpha} E_0^{\beta} \sum_n' \frac{\mu_{1n}^{\alpha} \mu_{n1}^{\beta}}{\Delta E_{n1}}$$

Dipole moment:

$$\mu^{\alpha} = - \frac{\partial \varepsilon}{\partial E_0^{\alpha}} = \mu_1^{\alpha} + \underbrace{2 \sum_n' \frac{\mu_{1n}^{\alpha} \mu_{n1}^{\beta}}{\Delta E_{n1}} E_0^{\beta}}_{\delta \mu_{1n}^{\alpha}}$$

Polarizability tensor:

$$\alpha^{\alpha\beta} = - \left(\frac{\partial^2 \epsilon}{\partial E_0^\alpha \partial E_0^\beta} \right) \Big|_{E_0=0}$$

$$\boxed{\alpha^{\alpha\beta} = 2 \sum' \frac{M_{in}^\alpha M_{ni}^\beta}{\Delta E_{ni}^{(0)}}}$$

Example: Highly anisotropic polarizability of a two-atom molecule

$\alpha = \begin{pmatrix} 0 & 0 & 0 & M_{in} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha_{zz} & 0 \end{pmatrix}$

$$\alpha_{zz} = 2 \sum' \frac{|M_{in}|^2}{\Delta E_{ni}^{(0)}}$$

Two-state polarizability

$$2 - E_2^{(0)}$$

$$\alpha_1 = \frac{2 |M_{12}|^2}{E_2^{(0)} - E_1^{(0)}} = \frac{2 |M_{12}|^2}{\Delta E_{21}^{(0)}}$$

$$1 - E_1^{(0)}$$

$$\alpha_2 = -\alpha_1 = - \frac{2 |M_{12}|^2}{\Delta E_{21}^{(0)}}$$

Two-state problem:

$$E_2^{(0)} \quad \text{---}$$

$$H = H_0 - \vec{\mu} \cdot \vec{E}_0$$

$$H_0 |\Phi_1\rangle = E_1^{(0)} |\Phi_1\rangle$$

$$E_1^{(0)} \quad \text{---}$$

$$H_0 |\Phi_2\rangle = E_2^{(0)} |\Phi_2\rangle$$

$$\varepsilon = \bar{E} - \frac{1}{2} \Delta E, \quad \bar{E} = \frac{E_1^{(0)} + E_2^{(0)}}{2} - \frac{\vec{\mu}_1 + \vec{\mu}_2}{2} \cdot \vec{E}_0$$

$$\Delta E = \sqrt{(\Delta E_{21}^{(0)} - \Delta \vec{\mu} \cdot \vec{E}_0)^2 + 4 |\vec{\mu}_{12} \cdot \vec{E}_0|^2}$$

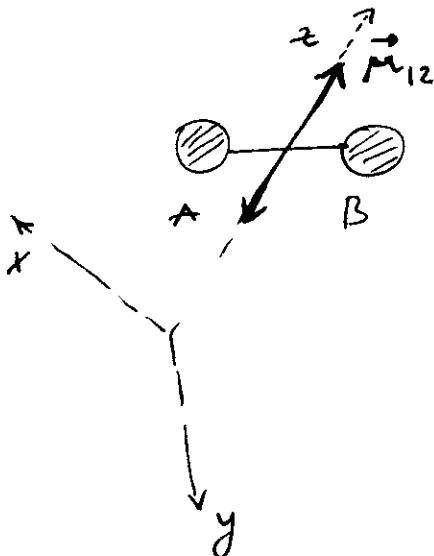
$$\alpha^{\alpha\beta} = - \left. \left(\frac{\partial^2 \varepsilon}{\partial E_0^\alpha \partial E_0^\beta} \right) \right|_{E_0=0} = \frac{1}{2} \left. \left(\frac{\partial^2 \Delta E}{\partial E_0^\alpha \partial E_0^\beta} \right) \right|_{E_0=0}$$

$$= \frac{1}{4 \Delta E} \frac{\partial}{\partial E_0^\alpha} \left(8 \mu_{12}^\beta \vec{\mu}_{12} \cdot \vec{E}_0 - 2 (\Delta E_{21}^{(0)} - \Delta \vec{\mu} \cdot \vec{E}_0) \Delta \mu^\alpha \right)$$

$$= \frac{2 \mu_{12}^\alpha \mu_{12}^\beta + \Delta \mu^\alpha \Delta \mu^\beta / 2}{\Delta E}$$

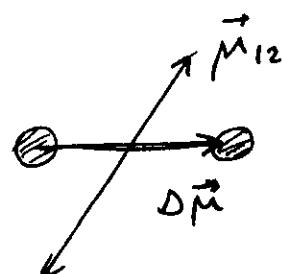
$$\boxed{\alpha^{\alpha\beta} = \frac{2 \mu_{12}^\alpha \mu_{12}^\beta + \Delta \mu^\alpha \Delta \mu^\beta / 2}{\Delta E}}$$

$$\underline{\Delta \mu = 0}$$



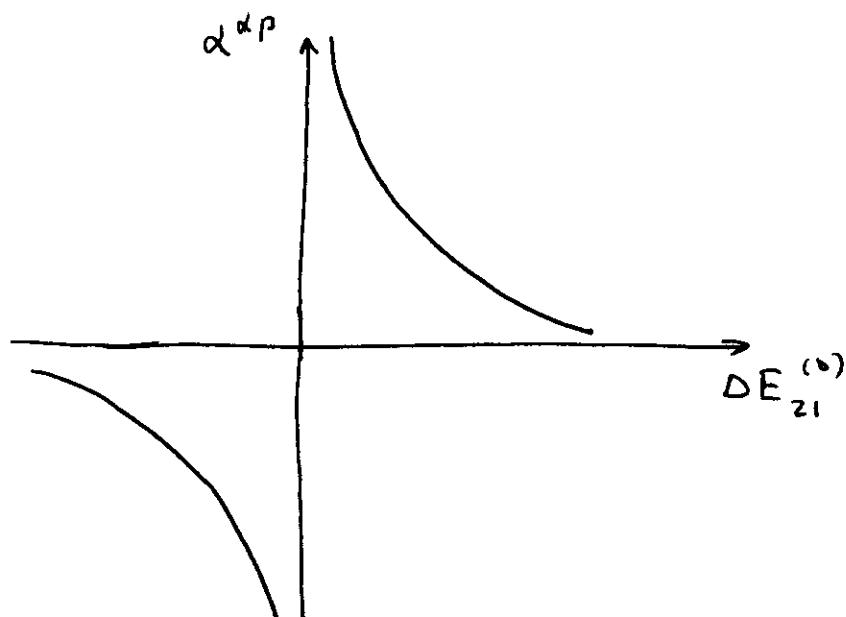
$$\alpha_{zz} = \frac{2 |\mu_{12}|^2}{\Delta E_{21}^{(0)}}$$

$\Delta \mu \neq 0$, Tensor polarizability



$$\alpha^{\alpha\beta} = \frac{2 \mu_{12}^{\alpha} \mu_{12}^{\beta} + \Delta \mu^{\alpha} \Delta \mu^{\beta} / 2}{\Delta E_{21}^{(0)}}$$

Dependence on ΔE



Orbital PT: One-particle perturbations

One-particle unperturbed Hamiltonian + one-particle perturbation:

$$H_0 = \sum_i h_0(i)$$

$$V = \sum_i v(i)$$

Unperturbed solution:

$$h_0 \chi_i^{(0)} = \varepsilon_i^{(0)} \chi_i^{(0)} \quad |\Psi_0\rangle = |\chi_1^{(0)} \dots \chi_a^{(0)} \dots \chi_N^{(0)}\rangle$$

$$H_0 |\Psi_0\rangle = \sum_a \varepsilon_a^{(0)} |\Psi_0\rangle$$

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_a \varepsilon_a^{(0)} + \sum_a v_{aa}$$

Exact solution:

$$(h_0 + V) \chi_i = \varepsilon_i \chi_i \quad |\Psi_0\rangle = |\chi_1 \dots \chi_a \dots \chi_N\rangle$$

$$H |\Psi_0\rangle = \sum_a \varepsilon_a |\Psi_0\rangle$$

$$\boxed{\varepsilon_0 = \sum_a \varepsilon_a}$$

exact ground state energy

$$\varepsilon_a = \varepsilon_a^{(0)} + \langle a | v | a \rangle + \sum_i' \frac{\langle a | v | i \rangle \langle i | v | a \rangle}{\varepsilon_a^{(0)} - \varepsilon_i^{(0)}} + \dots$$

Total ground state energy:

$$\varepsilon_0 = \sum_a \varepsilon_a = \sum_a \varepsilon_a^{(0)} + \sum_a v_{aa} + \sum_{ar} \frac{v_{ar} v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}$$

$$+ \sum_{\substack{a, b \\ a \neq b}} \frac{v_{ab} v_{ba}}{\varepsilon_a^{(0)} - \varepsilon_b^{(0)}} = 0$$

Diagrammatic technique for orbital PT

- * dots represent one-particle perturbations
- * sum the expression over all particle and hole indices

$$E_0^{(1)} = \text{---}^a = \sum_a v_{aa}$$

$$E_0^{(2)} = \text{---}^a \text{---}^r = \sum_{ar} \frac{v_{ar} v_{ra}}{\epsilon_a^{(0)} - \epsilon_r^{(0)}}$$

$$E_0^{(3)} = \text{---}^r \text{---}^a + \text{---}^a \text{---}^r =$$

$$= \sum_{ars} \frac{v_{as} v_{sr} v_{ra}}{(\epsilon_a^{(0)} - \epsilon_s^{(0)})(\epsilon_a^{(0)} - \epsilon_r^{(0)})} - \sum_{abr} \frac{v_{ra} v_{ab} v_{er}}{(\epsilon_a^{(0)} - \epsilon_r^{(0)})(\epsilon_b^{(0)} - \epsilon_r^{(0)})}$$

- * hole lines are labeled by a, b, \dots
particle lines are r, s, \dots

- * for a closed-shell system,

$$\sum^N = 2 \sum^{N/2}$$

PT solution:

$$E_0^{(0)} = \sum \varepsilon_a^{(0)} = 2 \sum_a^{N/2} \varepsilon_a^{(0)}$$

$$E_0^{(1)} = \sum u_{aa} = 2 \sum_a^{N/2} u_{aa}$$

$$E_0^{(2)} = \sum_{ar} \frac{u_{ar} u_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}} = 2 \sum_{ar}^{N/2} \frac{u_{ar} u_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}$$

Exercise 6.3

Derive

$$E_0^{(2)} = \sum_{ar} \frac{u_{ar} u_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}$$

from the general expression of the RSPT

$$E_0^{(2)} = \sum_n \left| \frac{\langle \Psi_0 | \sum_i v(i) | n \rangle}{E_0^{(0)} - E_n^{(0)}} \right|^2$$

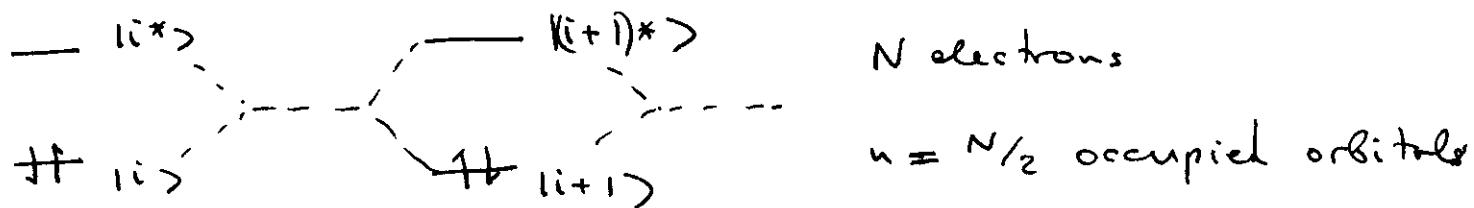
$$|n\rangle = |\chi_1^{(0)} \dots \chi_{a-1}^{(0)} \chi_r^{(0)} \chi_{a+1}^{(0)} \dots \chi_N^{(0)}\rangle$$

$$\langle \Psi_0 | \sum_i v(i) | n \rangle = u_{ar}$$

$$E_0^{(0)} - E_n^{(0)} = \varepsilon_a^{(0)} - \varepsilon_r^{(0)}$$

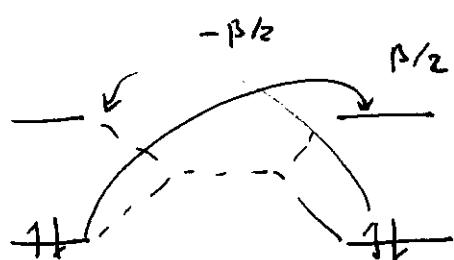
$$E_0^{(2)} = \sum_{ar} \frac{u_{ar} u_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}$$

Perturbation theory for polyenes



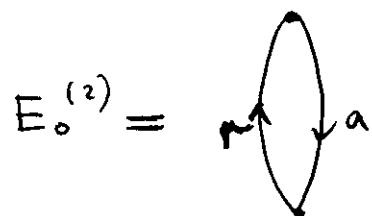
$$h_0 |ii\rangle = (\alpha + \beta) |ii\rangle \quad \langle ii|v|i\pm 1\rangle^* = \pm \beta/2$$

$$h_0 |ii^*\rangle = (\alpha - \beta) |ii^*\rangle \quad \langle ii^*|v|i\pm 1\rangle = \beta/2$$



$$\langle ii^*|v|i\pm 1\rangle^* = -\beta/2$$

$$E_0^{(0)} = N\alpha + N\beta$$



$$E_0^{(1)} = \sum_a \langle a|v|a\rangle = 0$$

$$E_0^{(2)} = 2 \sum_{a,r}^{N/2} \underbrace{\frac{v_{ar} v_{ra}}{\epsilon_a^{(0)} - \epsilon_r^{(0)}}}_{2\beta} = \frac{1}{\beta} \sum_{a=1}^n \left[\langle a|v|(a+1)^*\rangle \langle (a+1)^*|v|a\rangle \right]$$

$$+ \langle a|v|(a-1)^*\rangle \langle (a-1)^*|v|a\rangle] =$$

$$= \frac{1}{\beta} \sum_{a=1}^n \left(\frac{R^2}{4} + \frac{\beta^2}{4} \right) = 0.25 N \beta$$

$\nearrow g_1 \%$

$$E_R (N \rightarrow \infty) = 0.2732 N \beta$$

$$E_0^{(1)} = \begin{array}{c} \text{Diagram of two loops: one clockwise (a) and one counter-clockwise (r).} \\ \text{Loop a: } s \rightarrow a \rightarrow s \\ \text{Loop r: } a \rightarrow r \rightarrow a \end{array} =$$

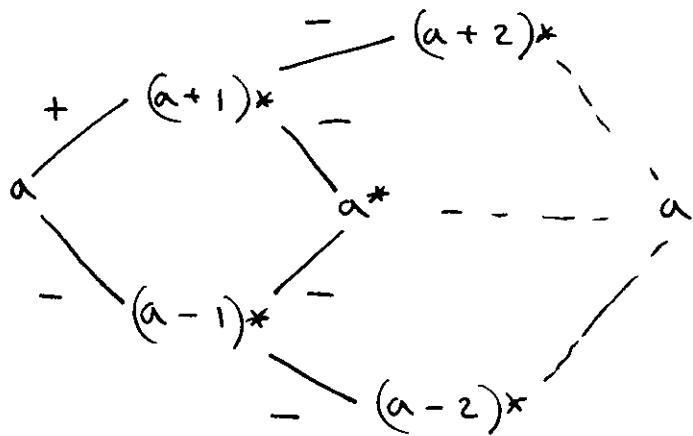
$$= \sum_{ars} \frac{U_{as} U_{sr} U_{ra}}{(E_a^{(0)} - E_s^{(0)})(E_a^{(0)} - E_r^{(0)})} - \sum_{abr} \frac{U_{br} U_{ra} U_{ab}}{(E_a^{(0)} - E_r^{(0)})(E_b^{(0)} - E_r^{(0)})}$$

$$= \frac{2}{4\beta^2} A + \frac{2}{4\beta^2} B = 0$$

$$A = \sum_{ars} U_{as} U_{sr} U_{ra}$$

$$E_0^{(1)} = 0$$

$$a \rightarrow s^* \rightarrow r^* \rightarrow a$$



- * start at 'a' on the left and go to "a" on the right by all possible paths
- * assign to each path a number corresponding to the product of matrix element with their signs.
- * add all the paths.

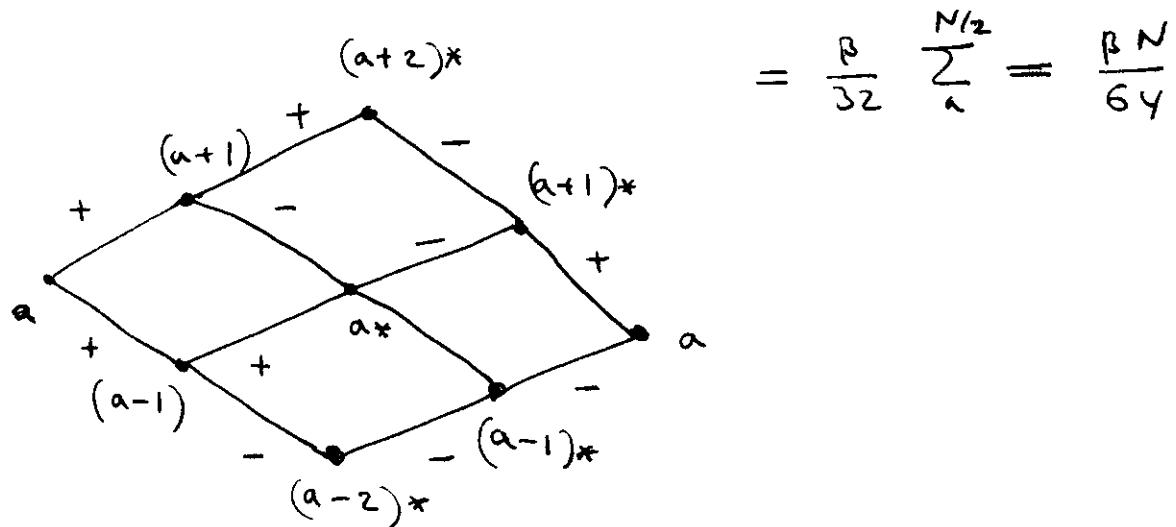
$$E_0^{(4)} =$$

+

+

Exercise 6.7

$$\begin{aligned}
 & \text{Diagram of a loop with vertices } a, b, s, r \text{ and arrows } a \rightarrow b \rightarrow s \rightarrow r \rightarrow a \\
 & = - \sum_{abrs} \frac{U_{ab} U_{bs} U_{sr} U_{ra}}{(\varepsilon_b^{(0)} - \varepsilon_s^{(0)}) (\varepsilon_b^{(0)} - \varepsilon_r^{(0)}) (\varepsilon_a^{(0)} - \varepsilon_r^{(0)})} \\
 & = - \frac{2}{(2\beta)^3} \left[(+) + (+) + (-) + (-) + (-) + (-) \right]
 \end{aligned}$$



$$= - \sum \frac{\text{Var } V_{rb} V_{bs} V_{sa}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}) (\varepsilon_s^{(0)} - \varepsilon_a^{(0)}) (\varepsilon_a^{(0)} + \varepsilon_b^{(0)} - \varepsilon_r^{(0)} - \varepsilon_s^{(0)})}$$

$$= - 2 \cdot \frac{1}{2\beta \cdot 2\beta \cdot 4\beta} \cdot A = - \frac{12\beta N}{16 \times 16^2} = - \frac{3\beta N}{128}$$

$$A =$$

$$= \frac{6\beta^4}{16}$$

$$E_0^{(4)} = 4 \cdot \frac{\beta N}{64} - 2 \cdot \frac{3\beta N}{128} = \frac{3\beta N}{64}$$

$$E_0^{(2)} + E_0^{(4)} = \left(\frac{1}{4} + \frac{1}{64}\right) \beta N = 0.2656 N \beta \quad \xrightarrow{97\%}$$

$E_R(\text{exact}) \xrightarrow[N \rightarrow \infty]{} 0.2732 N \beta$

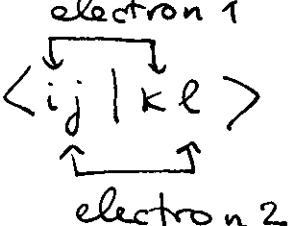
Møller-Plesset PT:

$$H_0 = \sum_i f(i) = \sum_i [h(i) + v^{HF}(i)]$$

$$V = \sum_{i < j} r_{ij}^{-1} - \sum_i v^{HF}(i)$$

Two-electron integrals:

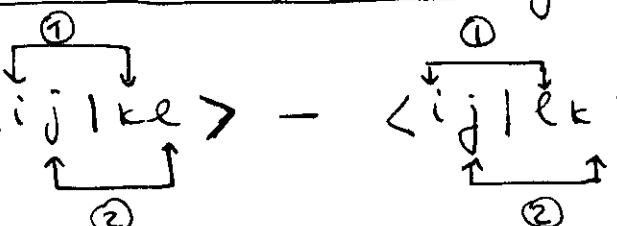
$$\langle ij | kl \rangle = \langle \chi_i(1) \chi_j(2) | r_{ij}^{-1} | \chi_k(1) \chi_l(2) \rangle$$

electron 1


placement in the Dirac bra or ket gives the electron number

Antisymmetric two-electron integral:

$$\langle ij || kl \rangle = \langle \overset{\textcircled{1}}{ij} | \overset{\textcircled{1}}{kl} \rangle - \langle \overset{\textcircled{1}}{ij} | \overset{\textcircled{2}}{lk} \rangle$$



Selection rules:

$$\langle t_0 | \sum_{i < j} r_{ij}^{-1} | t_{rs}^{\text{rs}} \rangle = \langle ab || rs \rangle$$

$$v^{HF}(i) \chi_j(i) = \sum_b \langle b | r_i^{-1} | b \rangle \chi_j(i) - \sum_b \langle b | r_i^{-1} | j \rangle \chi_b(i)$$

$$\begin{aligned} \langle \chi_k(i) | v^{HF}(i) | \chi_j(i) \rangle &= \sum_b \langle b_k | b_j \rangle - \sum_b \langle b_k | j b \rangle \\ &= \sum_b \langle b_k || b_j \rangle \end{aligned}$$

PT expansion

Zeroth-order contribution:

$$E_0^{(0)} = \sum_a \varepsilon_a$$

First-order contribution:

$$\begin{aligned} E_0^{(1)} &= \langle \Psi_0 | V | \Psi_0 \rangle = \frac{1}{2} \langle \Psi_0 | \sum_{i \neq j} r_{ij}^{-1} | \Psi_0 \rangle - \langle \Psi_0 | \sum_i v^{\text{HF}}(i) | \Psi_0 \rangle \\ &= \frac{1}{2} \sum_{ab} \langle ab || ab \rangle - \sum_a \langle a | v^{\text{HF}} | a \rangle \\ &= \frac{1}{2} \sum_{ab} \langle ab || ab \rangle - \sum_{ab} \langle ab || ab \rangle = -\frac{1}{2} \sum_{ab} \langle ab || ab \rangle \end{aligned}$$

$$E_0^{(1)} + E_0^{(0)} = \sum \varepsilon_a - \frac{1}{2} \sum \langle ab || ab \rangle = E_0^{\text{HF}}$$

The first term in the correlation energy comes from $E_0^{(2)}$:

$$E_0^{(2)} = \sum_n' \frac{|\langle \Psi_0 | V | n \rangle|^2}{E_0^{(0)} - E_n^{(0)}}$$

excitation of the
N-electron system
p. 72, Table 2.6

$$\langle \Psi_0 | V | \Psi_a^r \rangle = \langle \Psi_0 | \sum_{i < j} \frac{1}{r_{ij}} | \Psi_a^r \rangle - \langle \Psi_0 | \sum_i v^{\text{HF}}(i) | \Psi_a^r \rangle$$

$$= \sum_b \langle ab || rb \rangle - \sum_b \langle ab || rb \rangle = 0$$

$$\langle \Psi_0 | V | \underbrace{\Psi_{ab...c}^{\text{vs...}}}_{n>3} \rangle = 0$$

$\langle \Psi_0 | V | n \rangle \neq 0$
only for double excitations

MP2

$$E_c^{(2)} = \sum_{\substack{a < b \\ r < s}} \frac{|\langle \psi_0 | \sum_i c_{ij}^{-1} | \Psi_{rs}^{\tau_j} \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \sum_{\substack{a < b \\ r < s}} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

$$E_c^{(2)} = \sum_{a < b} e_{ab},$$

$$e_{ab} = e_{ab}^{\text{FO}} = \sum_{r < s} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

The MP2 correlation energy coincides with the first order I EPA

$$E_c^{(2)} = \frac{1}{4} \sum_{abrs} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

For H_2 : $a = g, u$

$$\langle gg || gg \rangle = \langle uu || uu \rangle = 0$$

$$E_c^{(2)} = \frac{|\langle g\bar{g} || u\bar{u} \rangle|^2}{2\varepsilon_g - 2\varepsilon_u} = \frac{|\langle g\bar{g} | u\bar{u} \rangle|^2}{2(\varepsilon_g - \varepsilon_u)} = \frac{K_{gu}^2}{2(\varepsilon_g - \varepsilon_u)}$$

$$E_c^{(2)} (1.4 \text{ a.u.}) = \underline{-0.0134} \quad \leftarrow \text{MP2}$$

$$E_{\text{corr}} = \Delta - (\Delta^2 + K_{12}^2)^{\frac{1}{2}} = \underline{-0.022} \quad \leftarrow \text{exact}$$

↑
0.7389

RHF/MP2 calculation of H₂O:

Input File:

```
$CTRL MPLEVL=2 SCFTYP=RHF NZVAR=0 RUNTYP=OPTIMIZE MULT=1 $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=3 NPFUNC=3 DIFFS=.TRUE. $END
$GUESS GUESS=MOREAD NORB=51 $END
$DATA
```

Water/MP2 calculation by D. Matyushov

Cnv 2

```
01      8.0    0.0000000000    0.0000000000   -0.0380492824
H2      1.0    0.7494524065    0.0000000000    0.5313335789
```

\$END

--- OPTIMIZED RHF MO-S --- GENERATED AT Mon Apr 1 13:42:27 2002

E= -76.0333603854, E(NUC)= 9.3487379618

\$VEC

```
1  1 9.95200165E-01 1.22624608E-02 0.00000000E+00 0.00000000E+00 1.50108411E-
1  2-2.15196702E-03 0.00000000E+00 0.00000000E+00-1.14753906E-03 3.43951592E-
```

```
.....
```

51 1-6.28513683E-01 7.42230715E+00 0.00000000E+00 0.00000000E+00-7.07472522E-
51 2 5.93044374E+00 0.00000000E+00 0.00000000E+00-1.53497510E-01-3.06786682E-
51 3-3.05733085E+00-3.05824806E+00 0.00000000E+00 0.00000000E+00 0.00000000E-
51 4-3.39414171E+00-3.27199912E+00-3.35953110E+00 0.00000000E+00 0.00000000E-
51 5 0.00000000E+00-8.12835216E-01-7.36673476E-01-7.46974817E-01 0.00000000E-
51 6 0.00000000E+00 0.00000000E+00 1.25641112E-01 1.34809863E-01 1.25086230E-
51 7-1.42320876E-01 0.00000000E+00 9.59903200E-02 2.02972582E-01 0.00000000E-
51 8-1.26127921E-01-4.66826502E-02 0.00000000E+00 1.23749975E-03 1.25641112E-
51 9 1.34809863E-01 1.25086230E-01 1.42320876E-01 0.00000000E+00 9.59903200E-
51 10-2.02972582E-01 0.00000000E+00-1.26127921E-01 4.66826502E-02 0.00000000E-
51 11 1.23749975E-03

\$END

Results:

RHF-MP2 GRADIENT

PROGRAM WRITTEN BY A.MARQUEZ, S.MALUENDES, M.DUPUIS,
AND S.P.WEBB

RESULTS OF MOLLER-PLESSET 2ND ORDER CORRECTION ARE

E(0)= -76.0326330624
E(1)= 0.0
E(2)= -0.2294088808
E(MP2)= -76.2620419432

INTERNUCLEAR DISTANCES (ANGS.)

	O1	H2	H2
1 O1	0.0000000	0.9588196 *	0.9588196 *
2 H2	0.9588196 *	0.0000000	1.5038634 *
3 H2	0.9588196 *	1.5038634 *	0.0000000

ELECTROSTATIC MOMENTS

POINT	1	X	Y	Z (BOHR)	CHARGE
		0.000000	0.000000	0.021740	0.00 (A.U.)
DX	DY	DZ	/D/ (DEBYE)		
0.000000	0.000000	1.846839	1.846839		

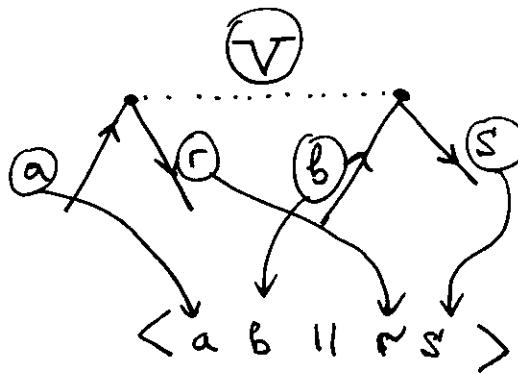
Goldstone diagrams

The matrix elements entering the MPPT are of the form

$$\langle ab \parallel cd \rangle$$

4 spin orbitals

The Goldstone diagrams represent the perturbation by two elements connected by a dotted line



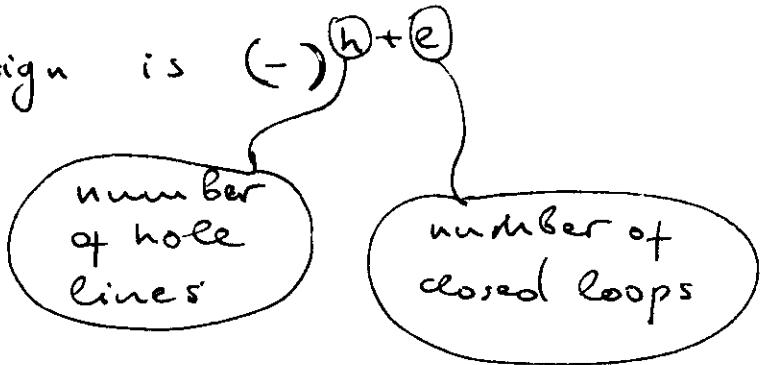
$$\langle \text{left-in right-in} \parallel \text{left-out right-out} \rangle$$

* each pair of adjacent interaction lines (---) contributes the denominator factor

$$\sum \epsilon_{\text{hole}} - \sum \epsilon_{\text{particle}}$$

$$\frac{1}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

- * sum the expression over all particles and Lorex
- * the overall sign is $(-)^{h+e}$



- * diagrams that have a mirror plane symmetry are multiplied by $\frac{1}{2}$

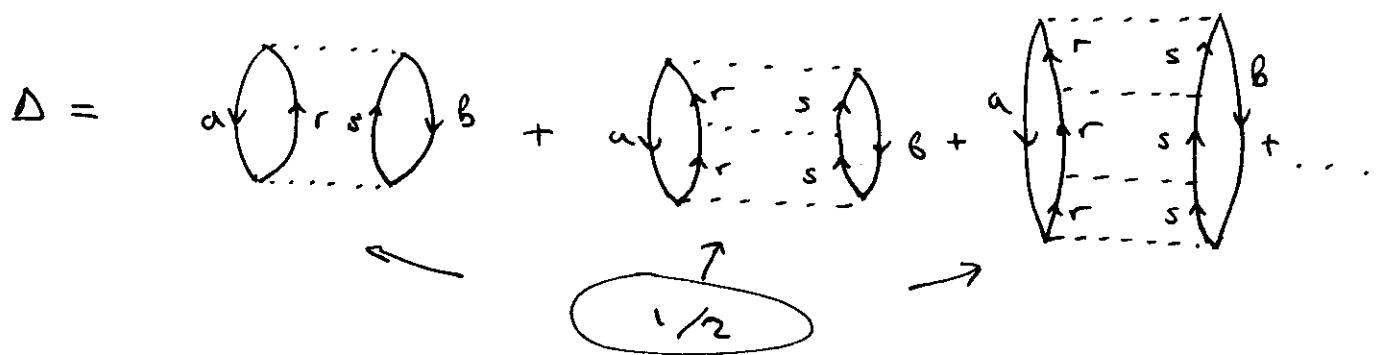
$$\frac{1}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = (-)^{2+2} \frac{1}{2} \sum_{abrs} \frac{\langle ab | rs \rangle \langle rs | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

- * for closed-shell systems, a summation over spin orbitals is equal to 2^e a summation over spatial orbitals, i.e.

$$\sum^n = (2)^e \sum^{N/2}$$

Summation of diagrams

Diagrams forming geometric series can be summed to infinite order. These diagrams are formed by adding dots to the second order diagram in such a way that labels in and out are the same:



$$\Delta = \frac{1}{2} \frac{|\langle r_s | ab \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \left[1 + \frac{\langle rs | rs \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} + \left(\frac{\langle rs | rs \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right)^2 + \dots \right]$$

$$= \frac{1}{2} \frac{|\langle rs | ab \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s - \langle rs | rs \rangle}$$

As a result of this re-summation, one gets the Epstein-Nesbet pair correlation energy (IEPA)

$$E_{\text{corr}}(\text{EN}) = -\frac{1}{4} \sum_{abrs} \frac{|\langle ab | rs \rangle|^2}{\langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{ab}^{rs} \rangle}$$

MP2 with infinite-order corrections is equivalent to IEPA.

Features of MPPT

- * MP2 is a K^5 method. MP2 typically accounts for $\sim 80-90\%$ of the correlation energy, and it is the most economical method for including electron correlation.
- * MP3 scales as K^6 and typically gets $\sim 90-95\%$ of the correlation energy
- * The second order correction for the wave function

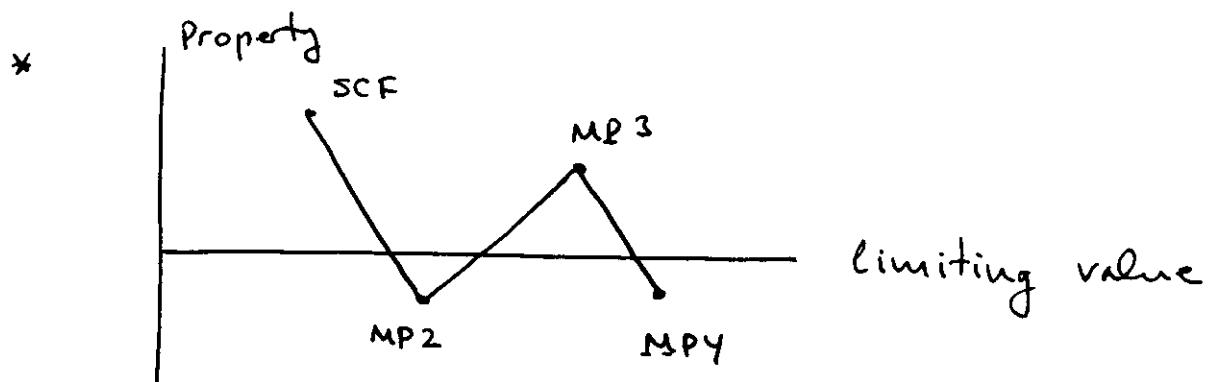
$$\langle n | \psi_i^{(2)} \rangle = \sum_m \frac{\langle n | V | m \rangle \langle m | \psi_i^{(1)} \rangle}{E_i^{(0)} - E_m^{(0)}} - E_i^{(1)} \frac{\langle n | \psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}}$$

\downarrow

$$\langle n | V | m \rangle \langle m | V | i \rangle$$

if $i=0$, $|m\rangle = |\Psi_{08}^{rs}\rangle$, $|n\rangle$ may be a singlet, triplet, or quadruplet

- * MP4 scales as K^7 (MP4(SDQ) as K^6)
- * MPPT is size consistent



MP2 typically overshoots the correlation effect, but often gives a better result than MP3

7.1 Definition of Green's functions

Green's functions are defined to provide a universal algorithm for solving inhomogeneous matrix and differential equations.

$$\overset{\leftrightarrow}{H} \vec{a} = 0$$

↑
homogeneous
equation

$$\overset{\leftrightarrow}{H} \vec{B} = \vec{C}$$

↓
inhomogeneous
equation

Matrix equation :

$$(E \overset{\leftrightarrow}{I} - \overset{\leftrightarrow}{H}_0) \vec{a} = \vec{b} \quad \leftarrow \text{arbitrary vector}$$

$$\vec{a} = \overset{\leftrightarrow}{G}_0 \vec{b}, \quad \overset{\leftrightarrow}{G}_0 = (E \overset{\leftrightarrow}{I} - \overset{\leftrightarrow}{H}_0)^{-1}$$

$$\downarrow a_i = \sum_j (G_0)_{ij} b_j$$

V is a unitary transformation such that

$$\overset{\leftrightarrow}{V}^+ \overset{\leftrightarrow}{H}_0 \overset{\leftrightarrow}{V} = \overset{\leftrightarrow}{E}_0 = \begin{pmatrix} E_1 & & & \\ & E_2 & & \\ & & \ddots & \\ & & & E_N \end{pmatrix}$$

$$\overset{\leftrightarrow}{H}_0 = \overset{\leftrightarrow}{V} \overset{\leftrightarrow}{E}_0 \overset{\leftrightarrow}{V}^+$$

$$(E \overset{\leftrightarrow}{I} - \overset{\leftrightarrow}{H}_0)^{-1} = (E \overset{\leftrightarrow}{I} - \overset{\leftrightarrow}{V} \overset{\leftrightarrow}{E}_0 \overset{\leftrightarrow}{V}^+)^{-1} =$$

$$= [V(E \overset{\leftrightarrow}{I} - \overset{\leftrightarrow}{E}_0)V^+]^{-1} = V^+ (E \overset{\leftrightarrow}{I} - \overset{\leftrightarrow}{E}_0)^{-1} V$$

For a unitary transformation to diagonalize matrix H_0 , $\overset{\leftrightarrow}{U}$ should be composed of the eigen-vectors

$$\overset{\leftrightarrow}{U} = (\vec{c}_1 \vec{c}_2 \dots \vec{c}_N) = \begin{pmatrix} c_{11} & \dots & c_{1N} \\ c_{21} & & c_{2N} \\ c_{31} & & \vdots \\ \vdots & & \end{pmatrix}$$

where

$$\overset{\leftrightarrow}{H}_0 \vec{c}^\alpha = E_\alpha \vec{c}^\alpha \quad \alpha = 1, 2, \dots, N$$

$$(\overset{\leftrightarrow}{U}^+ (E \overset{\leftrightarrow}{I} - \overset{\leftrightarrow}{H}_0)^{-1} \overset{\leftrightarrow}{U})_{ij} = \sum_{\alpha} \frac{\vec{c}_i^\alpha (\vec{c}_j^\alpha)^*}{E - E_\alpha} = \underline{\underline{(\overset{\leftrightarrow}{G}_0)_{ij}}}$$

$(\overset{\leftrightarrow}{G}_0)_{ij}$ has a pole ($(\overset{\leftrightarrow}{G}_0)_{ij} \rightarrow \infty$) at $E = E_\alpha$

E 7.1 $\overset{\leftrightarrow}{H} = \overset{\leftrightarrow}{H}_0 + \overset{\leftrightarrow}{V}$

$$G(E) = (E \overset{\leftrightarrow}{I} - \overset{\leftrightarrow}{H}_0 - \overset{\leftrightarrow}{V})^{-1}$$

$$(E \overset{\leftrightarrow}{I} - \overset{\leftrightarrow}{H}_0 - \overset{\leftrightarrow}{V})^{-1} (E \overset{\leftrightarrow}{I} - \overset{\leftrightarrow}{H}_0 - \overset{\leftrightarrow}{V}) = 1$$

$$\overset{\leftrightarrow}{G}(E) (E \overset{\leftrightarrow}{I} - H_0) = 1 + \overset{\leftrightarrow}{V} \overset{\leftrightarrow}{G}(E)$$

$\overset{\nearrow}{G_0(E)} \overset{-1}{-}$

$$\overset{\leftrightarrow}{G}(E) = \overset{\leftrightarrow}{G}_0(E) + G_0(E) V G(E)$$

Inhomogeneous Schrödinger equation

$$(E - H_0) a(x) = b(x)$$

$$H_0 \psi_\alpha(x) = E_\alpha^{(0)} \psi_\alpha(x)$$

$$a(x) = \sum \alpha_\alpha \psi_\alpha(x)$$

$$b(x) = \sum b_\alpha \psi_\alpha(x)$$

$$\sum \alpha_\alpha (E - E_\alpha^{(0)}) \psi_\alpha(x) = \sum b_\alpha \psi_\alpha(x)$$

$$\langle \psi_\beta | \quad \alpha_\beta (E - E_\beta^{(0)}) = b_\beta$$

$$a(x) = \sum_\alpha \frac{b_\alpha}{E - E_\alpha^{(0)}} \psi_\alpha(x)$$

$$b_\alpha = \langle \psi_\alpha | b \rangle = \int dx' \psi_\alpha^*(x') b(x')$$

$$a(x) = \int dx' b(x') \left[\sum_\alpha \frac{\psi_\alpha(x) \psi_\alpha^*(x')}{E - E_\alpha^{(0)}} \right]$$

Green's function:

$$G_0(x, x', E) = \sum_\alpha \frac{\psi_\alpha(x) \psi_\alpha^*(x')}{E - E_\alpha^{(0)}}$$

$$a(x) = \int dx' G_0(x, x', E) b(x')$$

Differential equation for the Green's function:

$$b(x) = \delta(x - x')$$

$$a(x) = \int dx'' G_0(x, x'', E) \delta(x' - x'') = G_0(x, x', E)$$

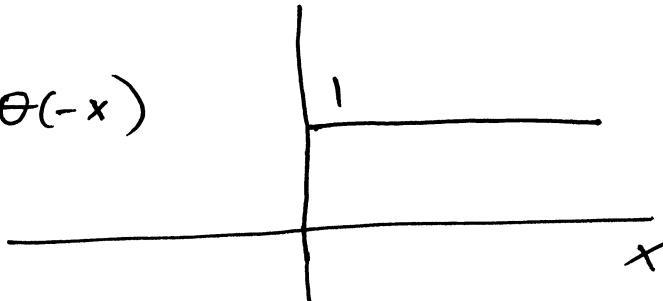
$$\boxed{(E - H_0) G_0(x, x', E) = \delta(x - x')}$$

E 7.2

$$\frac{d^2}{dx^2} a(x) = b(x)$$

a) $\frac{d^2}{dx^2} |x| - ?$

$$\frac{d}{dx} |x| = \Theta(x) - \Theta(-x)$$



$$\frac{d^2|x|}{dx^2} = \begin{cases} \infty, & x=0 \\ 0, & x \neq 0 \end{cases}$$

$$\frac{d^2|x|}{dx^2} \propto \delta(x) \quad \frac{d^2|x|}{dx^2} = c \delta(x)$$

$$-\int_{-\infty}^{\infty} c \delta(x) dx = c = -\int_{-\infty}^{\infty} \frac{d^2|x|}{dx^2} dx = \left. \frac{d|x|}{dx} \right|_{-\infty}^{\infty} = 2$$

$$c = 2$$

b, c) $\frac{d^2}{dx^2} \left(\frac{1}{2} |x - x'| \right) = \delta(x - x')$

$$a(x) = \frac{1}{2} \int_a^b b(x') dx' / |x - x'|$$

Integral equation for G

$$H = H_0 + V \quad (E - H_0 - V) G(x x' E) = \delta(x - x')$$

$$(E - H_0) G = \delta(x - x') + V G$$

$$\uparrow G_0^{-1}$$

$$G = \int dx'' G_0(x x'' E) [\delta(x'' - x') + V(x'') G(x'' x' E)]$$

$$G(x x' E) = G_0(x x' E) + \int dx'' G_0(x x'' E) V(x'') G(x'' x' E)$$

in the matrix
form (E 7.1)

$$G = G_0 + G_0 V G$$

Operator equation for G

$$\mathcal{L}_0(E) = (E - H_0)^{-1}$$

$$\mathcal{L}(E) = (E - H_0 - V)^{-1}$$

$$\mathcal{L}(E)^{-1} = E - H_0 - V = \mathcal{L}_0(E)^{-1} - V$$

$$\mathcal{L}_0(E) \times \mathcal{L}(E)^{-1} = \mathcal{L}_0(E)^{-1} - V \times \mathcal{L}(E)$$

$$\mathcal{L}_0(E) = \mathcal{L}(E) - \mathcal{L}_0 V \mathcal{L}$$

$$\mathcal{L}(E) = \mathcal{L}_0(E) + \mathcal{L}_0 V \mathcal{L}$$

Eigenstates of the attractive δ -potential

$$V(x) = -\delta(x)$$

$$\left(E + \frac{1}{2} \frac{d^2}{dx^2}\right) G_0(x, x', E) = \delta(x - x')$$

$$G_0(x, x', E) = \frac{1}{i\sqrt{2E}} \exp[i\sqrt{2E}|x - x'|]$$

$$\begin{aligned} \frac{d^2}{dx^2} G_0 &= \frac{d}{dx} \left(\frac{1}{i\sqrt{2E}} i\sqrt{2E} \frac{d}{dx} |x - x'| e^{i\sqrt{2E}|x - x'|} \right) = \\ &= \frac{d^2}{dx^2} |x - x'| e^{i\sqrt{2E}|x - x'|} + i\sqrt{2E} \left(\frac{d}{dx} |x - x'| \right)^2 e^{i\sqrt{2E}|x - x'|} \end{aligned}$$

$$\left(\frac{d}{dx} |x - x'| \right)^2 = 1 \quad \frac{d^2}{dx^2} |x - x'| = 2\delta(x - x')$$

$$\begin{aligned} \frac{1}{2} \frac{d^2}{dx^2} G_0 &= \delta(x - x') e^{i\sqrt{2E}|x - x'|} - E G_0(x, x', E) \\ \hookrightarrow \left(E + \frac{1}{2} \frac{d^2}{dx^2} G_0 \right) &= \delta(x - x') \end{aligned}$$

$$\begin{aligned} G(x, x', E) &= G_0(x, x', E) - \int dx'' G_0(x, x'', E) \delta(x'') G(x'', x', E) = \\ &= G_0(x, x', E) - G_0(x, 0, E) G(0, x', E) \end{aligned}$$

$$G(0, x', E) = \frac{G_0(0, x', E)}{1 + G_0(0, 0, E)}$$

$$G(x, x', E) = G_0(x, x', E) - \frac{G_0(x, 0, E) G_0(0, x', E)}{1 + G_0(0, 0, E)}$$

$$1 + G_0(00|E) = 1 + \frac{1}{i\sqrt{2E}} = 0 \quad \text{at} \quad E = -\frac{1}{2}$$

$E = -\frac{1}{2}$ is the eigenvalue of the Schrödinger equation defining the energy of the bound state

E 7.4 $\Phi_n(x) \Phi_n(x')^* = \lim_{E \rightarrow E_n} (E - E_n) G(x|x'|E)$

For the bound state in $-\delta(x)$ potential:

$$\begin{aligned} \lim_{E \rightarrow E_0 = -\frac{1}{2}} G(x|x'|E) &= -G_0(x|0|-\frac{1}{2}) G_0(0|x'|\frac{1}{2}) \times \\ &\times \underbrace{\frac{E + \frac{1}{2}}{1 + \frac{1}{i\sqrt{2E}}}}_{\rightarrow E} \rightarrow \frac{(1 + \frac{1}{i\sqrt{2E}})(1 - \frac{1}{i\sqrt{2E}})}{1 + \frac{1}{i\sqrt{2E}}} = \\ &= -\frac{1}{2} \times 2 = -1 \end{aligned}$$

$$|\Phi_0(x)|^2 = + \left(\frac{1}{i\sqrt{2E}}\right)^2 \exp[i\sqrt{2E} \times 2|x|] = \exp(-2|x|)$$

$$E = -\frac{1}{2}$$

$$\boxed{\Phi_0(x) = \exp(-|x|)}$$

7.6 Time-dependent Schrödinger equation

$$i \frac{\partial \Phi(x,t)}{\partial t} = H \Phi(x,t)$$

a) $i \frac{\partial G(x,x',t)}{\partial t} = H G(x,x',t) , \quad G(x,x',0) = \delta(x-x')$

Show that ($\Phi(x,0) = \psi(x)$)

$$\Phi(x,t) = \int dx' G(x,x',t) \psi(x')$$

$$i \frac{\partial \Phi(x,t)}{\partial t} = \int dx' i \frac{\partial G(x,x',t)}{\partial t} \psi(x') = \int dx' H G(x,x',t) \psi(x')$$

$$= H \int dx' G(x,x',t) \psi(x') = H \Phi(x,t)$$

at $t=0$ $\Psi(x) = \Phi(x,0) = \int dx' \delta(x-x') \psi(x') = \psi(x)$

b) $G(x,x',E) = \lim_{\epsilon \rightarrow 0} (-i) \int_0^{\infty} dt e^{iEt - \epsilon t} G(x,x',t)$

$$\lim_{\epsilon \rightarrow 0} (-i) \int_0^{\infty} dt e^{iEt - \epsilon t} i \frac{\partial G(x,x',t)}{\partial t} =$$

$$= \lim_{\epsilon \rightarrow 0} G(x,x',t) e^{iEt - \epsilon t} \Big|_0^{\infty} - \lim_{\epsilon \rightarrow 0} \int_0^{\infty} (iE - \epsilon) e^{iEt - \epsilon t} G(x,x',t) dt$$

$$= -\delta(x-x') + E G(x,x',E) = \lim_{\epsilon \rightarrow 0} (-i) \int_0^{\infty} dt H G(x,x',t) e^{iEt - \epsilon t}$$

$$= H G(x,x',E)$$

HW: 7.6(c)

$$(E - H) G(x,x',E) = \delta(x-x')$$

7.2 The one-particle many-body Green's function

$$H_0 = \sum_i f(i)$$

↑
HF Hamiltonian

$f \chi_i(\vec{x}) = \varepsilon_i \chi_i(\vec{x})$

Fock operator for i th MO

spin-orbital

HF Green's function (HFGF):

$$G_0(\vec{x} \vec{x}' E) = \sum_i \frac{\chi_i(\vec{x}) \chi_i^*(\vec{x}')}{E - \varepsilon_i}$$

$$G_0(\vec{x} \vec{x}' E) = \sum_a \frac{\chi_a(\vec{x}) \chi_a^*(\vec{x}')}{E - \varepsilon_a} + \sum_r \frac{\chi_r(\vec{x}) \chi_r^*(\vec{x}')}{E - \varepsilon_r}$$

$$(G_0)_{ij} = \langle \chi_i | G_0 | \chi_j \rangle = \frac{\delta_{ij}}{E - \varepsilon_i}$$

$$\overset{\leftrightarrow}{G}_0 = \begin{pmatrix} E - \varepsilon_1 & & & \\ & E - \varepsilon_2 & & 0 \\ & & \ddots & \\ 0 & & & E - \varepsilon_n \end{pmatrix} = (E \vec{1} - \vec{\varepsilon})^{-1}$$

$$\vec{\varepsilon} = \begin{pmatrix} \varepsilon_1 & & 0 \\ \varepsilon_2 & \ddots & \\ 0 & & \varepsilon_n \end{pmatrix}$$

$$\det(E \vec{1} - \vec{\varepsilon}) = \prod_i (E - \varepsilon_i) = 0$$

This condition defines the spectrum of eigenstates of the HF Hamiltonian

IP and EA

$$- \text{IP} = \varepsilon_c = \langle {}^N\psi_0 | H | {}^N\psi_0 \rangle - \langle {}^{N-1}\psi_c | H | {}^{N-1}\psi_c \rangle$$

$$- \text{EA} = \varepsilon_r = \langle {}^{N+1}\psi^r | H | {}^{N+1}\psi^r \rangle - \langle {}^N\psi_0 | H | {}^N\psi_0 \rangle$$

$${}^{N-1}E_r(c) = \langle {}^{N-1}\psi_c | H | {}^{N-1}\psi_c \rangle + {}^{N-1}E_{\text{corr}}(c)$$

${}^{N-1}E_r(c)$ is the relaxation energy indicating that the HF solution for the system of $N-1$ electrons is different from the HF solution for N electrons.

Correlation energy: $\overset{N}{\varepsilon}_0 = {}^N E_0 + {}^N E_{\text{corr}}$

$$\overset{N-1}{\varepsilon}_0(c) = {}^{N-1}E_0(c) + {}^{N-1}E_{\text{corr}}(c)$$

$$- \text{IP} = \overset{N}{\varepsilon}_0 - {}^{N-1}\varepsilon_0(c) = {}^N E_0 - {}^{N-1}E_0(c) + {}^N E_{\text{corr}} - {}^{N-1}E_{\text{corr}}(c)$$

$$= \varepsilon_c - {}^{N-1}E_r(c) + ({}^N E_{\text{corr}} - {}^{N-1}E_{\text{corr}}(c))$$



Koopman's theorem

7.2.1 The Self-Energy

The idea of self-energy is akin to the main idea of DFT: one wants to keep a one-particle description with the effective potential to be determined from approximate theories. The advantage compared to the DFT is that HF is retained as the zero-order solution so that exchange effects are taken into account exactly. Only correlation contribution needs evaluation.

For the Hamiltonian

$$H = H_0 + V$$

GF:

$$\tilde{L}(E) = \tilde{\mathcal{L}}_0(E) + \tilde{\mathcal{L}}_0(E) V \tilde{\mathcal{L}}(E)$$

↑ ↑ ↑
 exact HF GF perturbation
 Green's
function

Dyson equation:

$$\tilde{G}(E) = \tilde{G}_0(E) + \tilde{G}_0(E) \tilde{\Sigma}(E) \tilde{G}(E)$$

↗ ↑ ↑
 matrix of matrix self-energy
 the exact GF of HF GF

7.2.2 The solution of the Dyson equation

$\Sigma(E)$

depends on the total exact energy of the system
 This indicates the many-body character of
 the problem. Analogously to the DFT, if
 $\Sigma(E)$ is known, the problem is solved exactly.

$$(\tilde{G}_0(E))^{-1} \times \underbrace{\tilde{G}(E) = \tilde{G}_0(E) + \tilde{G}_0(E) \Sigma(E) \tilde{G}(E) \times (\tilde{G}(E))^{-1}}_{\text{Dyson equation}}$$

$$\tilde{G}_0(E)^{-1} = \tilde{G}(E)^{-1} + \Sigma(E)$$

$$G(E) = (G_0(E)^{-1} - \Sigma(E))^{-1}$$

$$\tilde{G}(E) = \frac{1}{E \mathbb{1} - \tilde{\epsilon} - \tilde{\Sigma}(E)}$$

$\tilde{G}(E)$ preserves the form of a one-particle Green's function (cf. to $\tilde{G}_0(E) = (E \mathbb{1} - \tilde{\epsilon})^{-1}$).
 The roots of the equation

$$\det [E \mathbb{1} - \tilde{\epsilon} - \tilde{\Sigma}(E)] = 0$$

define the exact energy levels of the many-electron system.

Energy levels

$$\det [E \vec{I} - \vec{\Sigma} - \vec{\Sigma}(E)] = 0$$

If one assumes that $\Sigma(E)_{ij} = \Sigma(E)_{ii} \delta_{ij}$, then

$$\prod_i (E - \varepsilon_i - \Sigma_{ii}(E)) = 0$$

$$E = \varepsilon_i + \Sigma_{ii}(E)$$

ε_i MO energy correction to
the MO energy

First order correction: $E = \varepsilon_i + \Sigma_{ii}(\varepsilon_i)$

$$\vec{\Sigma}(E) = \Sigma^{(2)}(E) + \Sigma^{(s)}(E) + \dots$$

\downarrow \uparrow
perturbation terms for the
self-energy

$$\Sigma_{ij}^{(2)}(E) = \frac{1}{2} \sum_{ars} \frac{\langle r_s || i_a \rangle \langle j_a || r_s \rangle}{E + \varepsilon_a - \varepsilon_r - \varepsilon_s} + \frac{1}{2} \sum_{sbr} \frac{\langle s_b || i_r \rangle \langle j_r || s_b \rangle}{E + \varepsilon_r - \varepsilon_a - \varepsilon_b}$$

GF theory and H₂

$$^2 \text{---} \varepsilon_2 \quad \varepsilon_2 = h_{22} + 2J_{12} - K_{12}$$

H₂

$$^1 \text{---} \varepsilon_1 \quad \varepsilon_1 = h_{11} + J_{11}$$

$$^2E_0 = 2h_{11} + J_{11} = 2\varepsilon_1 - J_{11}$$

$$^2E_{\text{corr}} = \Delta - (\Delta^2 + K_{12}^2)^{1/2}$$

$$\Delta = (c_2 - \varepsilon_1) + \frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12}$$

H₂⁺

^2 ---

$$^1E_0 = h_{11} \quad ^1\varepsilon_0 = h_{11}$$

1 +

$$\begin{aligned} -\text{IP} &= ^2\varepsilon_0 - ^1\varepsilon_0 = 2\varepsilon_1 - J_{11} - h_{11} + ^1E_{\text{corr}} \\ &= \varepsilon_1 + ^N E_{\text{corr}} \end{aligned}$$

Sel + energy : $r, s = 2$

$\alpha, \beta = 1$

$$\begin{aligned} \Sigma_{11}^{(2)}(E) &= \frac{1}{2} \times 2 \frac{\langle 21||11\rangle \langle 11||22\rangle}{E + \varepsilon_1 - 2\varepsilon_2} + \frac{1}{2} \frac{\langle 11||12\rangle \langle 12||11\rangle}{E + \varepsilon_2 - 2\varepsilon_1} \\ &= \frac{K_{12}^2}{E + \varepsilon_1 - 2\varepsilon_2} \end{aligned}$$

$$\Sigma_{12}^{(2)}(E) = \Sigma_{21}^{(2)}(E) = 0$$

$$\Sigma_{22}^{(2)}(E) = \frac{K_{12}^2}{E + \varepsilon_2 - 2\varepsilon_1}$$

↑
HW (show this)!!

Energy levels:

$$E - \varepsilon_1 - \Sigma_{11}(E) = 0$$

$$E - \varepsilon_1 - \frac{K_{12}^2}{E - \varepsilon_1 + 2(\varepsilon_1 - \varepsilon_2)} = 0$$

The lowest-order correction ($E = \varepsilon_1$):

$$E = \varepsilon_1 + \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \quad (\text{MP2, p. 353, eq 6.77})$$

$$\varepsilon_{11}^{\pm} = \varepsilon_1 + \left[(\varepsilon_2 - \varepsilon_1) \pm \left((\varepsilon_2 - \varepsilon_1)^2 + K_{12}^2 \right)^{1/2} \right]$$

$$\begin{aligned} \varepsilon_{11}^- &= \varepsilon_1 + \left[(\varepsilon_2 - \varepsilon_1) - \left(\Delta\varepsilon^2 + K_{12}^2 \right)^{1/2} \right] = \\ &= \varepsilon_1 + E_0^{(2)} + \frac{K_{12}^4}{8 \Delta\varepsilon^3} + \dots \end{aligned} \quad (*)$$

Compare ε_{11}^- to

$${}^2E_{\text{corr}} = \Delta - \left(\Delta^2 + K_{12}^2 \right)^{1/2}$$

In eq (*) Δ is replaced with $\varepsilon_2 - \varepsilon_1 = \Delta\varepsilon$

GF theory of HeH⁺

$\varepsilon_2 \longrightarrow f|1\rangle = \varepsilon_1 |1\rangle$
 $\varepsilon_1 \not\longrightarrow f|2\rangle = \varepsilon_2 |2\rangle$
 $\langle 1|f|2\rangle = 0$

Two electrons:

$$^2\varepsilon_0 = ^2E_0 + ^2E_{\text{corr}} = 2h_{11} + J_{11} + ^2E_{\text{corr}}$$

One electron:

$$^1\varepsilon_0 = h_{11} + \underline{\overline{^1E_R}}$$

orbital relaxation energy accounts
for difference between HF states
for 2 electrons and one electron.

$$\begin{aligned} -\text{IP} &= ^2\varepsilon_0 - ^1\varepsilon_0 = 2h_{11} + J_{11} + ^2E_{\text{corr}} - h_{11} - \underline{\overline{^1E_R}} = \\ &= \varepsilon_1 + \underbrace{^2E_{\text{corr}} - ^1E_R}_{\text{correction to Koopman's IP}} \end{aligned}$$

$$[^1E_R] : \varepsilon_1 \longrightarrow |2\rangle \quad \left. \right\} h_{12} \neq 0$$

$$\varepsilon_1 \not\longrightarrow |1\rangle \quad h_{12} = -\langle 1|12\rangle$$

$$\begin{aligned} f_{\mu\nu} &= h_{\mu\nu} + \sum_{a=1}^{N/2} 2(\mu\nu|aa) - (\mu a|a\nu) = \\ &= h_{12} + 2(12|11) - (11|12) = h_{12} + (12|11) \end{aligned}$$

$\mu=1$
 $\nu=2$

Secular equation for $'E_R$:

$$\begin{pmatrix} h_{11} & -\langle 11112 \rangle \\ -\langle 11112 \rangle & h_{22} \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = 'E_0 \begin{pmatrix} 1 \\ c \end{pmatrix}$$

$$h_{11} - c \langle 11112 \rangle = 'E_0 \quad c = \frac{h_{11} - 'E_0}{\langle 11112 \rangle}$$

$$-\langle 11112 \rangle + ch_{22} = c'E_0$$

$$-\langle 11112 \rangle^2 + h_{22}(h_{11} - 'E_0) = 'E_0(h_{11} - 'E_0)$$

$$-\langle 11112 \rangle^2 = -'E_R(h_{22} - h_{11} - 'E_R)$$

$$-\langle 11112 \rangle^2 = 'E_R(h_{22} - h_{11} - 'E_R)$$

$$\varepsilon_2 = h_{22} + 2J_{12} - K_{12}$$

$$\varepsilon_1 = h_{11} + J_{11}$$

$$h_{22} - h_{11} = \varepsilon_2 - \varepsilon_1 - 2J_{12} + K_{12} + J_{11}$$

$$'E_R = \frac{\langle 11112 \rangle^2}{\varepsilon_1 - \varepsilon_2 - (J_{11} - 2J_{12} + K_{12}) + 'E_R}$$

E.7.11

Zero-order approximation:

$${}^1E_R^{(2)} = \frac{\langle 11112 \rangle^2}{\varepsilon_1 - \varepsilon_2}$$

$$\varepsilon_1' = \varepsilon_1 + {}^2E_{corr} - \frac{\langle 11112 \rangle^2}{\varepsilon_1 - \varepsilon_2}$$

^
0 v
 0

GF Theory:

$$\begin{aligned} \Sigma_{ij}^{(2)} &= \sum_{ars}^{N/2} \frac{\langle rs|ia\rangle (2\langle ja|rs\rangle - \langle aj|rs\rangle)}{E + \varepsilon_a - \varepsilon_r - \varepsilon_s} \\ &+ \sum_{abr}^{N/2} \frac{\langle ab|ir\rangle (2\langle jr|ab\rangle - \langle rj|ab\rangle)}{E + \varepsilon_r - \varepsilon_a - \varepsilon_b} \end{aligned}$$

$$\underline{r=s=2}, \quad \underline{a=b=1}$$

$$\begin{aligned} \Sigma_{11}^{(2)} &= \frac{\langle 22|11\rangle (2\langle 11122\rangle - \langle 11122\rangle)}{E + \varepsilon_1 - 2\varepsilon_2} + \\ &+ \frac{\langle 11112\rangle (2\langle 12111\rangle - \langle 21111\rangle)}{E + \varepsilon_2 - 2\varepsilon_1} \\ &= \frac{k_{12}^2}{E + \varepsilon_1 - 2\varepsilon_2} + \frac{|\langle 11112\rangle|^2}{E + \varepsilon_2 - 2\varepsilon_1} \end{aligned}$$

Zero-order self-energy:

$$\varepsilon_1' = \varepsilon_1 + \sum_{11}^{(2)}(\varepsilon_1) = \varepsilon_1 + \underbrace{\frac{k_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}}_{2E_{\text{corr}}^{(2)}} - \underbrace{\frac{|\langle 11|12 \rangle|^2}{\varepsilon_1 - \varepsilon_2}}_{1E_R^{(2)}}$$

The GF energy includes both the correlation energy in the N -electron system and relaxation energy in the $(N-1)$ -electron system.

$$E = \varepsilon_1' = \varepsilon_1 + \frac{k_{12}^2}{E + \varepsilon_1 - 2\varepsilon_2} + \frac{|\langle 11|12 \rangle|^2}{E + \varepsilon_2 - 2\varepsilon_1}$$

$$E(E + \varepsilon_1 - 2\varepsilon_2)(E + \varepsilon_2 - 2\varepsilon_1) = \varepsilon_1(E + \varepsilon_1 - 2\varepsilon_2)(E + \varepsilon_2 - 2\varepsilon_1) \\ + k_{12}(E + \varepsilon_2 - 2\varepsilon_1) + |\langle 11|12 \rangle|^2(E + \varepsilon_1 - 2\varepsilon_2)$$

This is the polynomial equation of the third order. The lowest-energy root will give the ground-state energy.

HOMEWORK SET II

- ①. Calculate the dissociation curve of H_2 using B3LYP/6-31G.
- ②. Calculate singlet-triplet energy gap in CH_2 ($\text{exp} = 9.4 \text{ kcal/mol}$) using SLATER, SLYP, B3LYP with 6-31G or higher.
- ③. Calculate the dipole moment of LiCl based on the parameters given in the table and the interionic distance of 2.02 \AA .

Table III. Experimental Parameters for Atoms (eV)

atom	I^a	A^b	χ	η
H	13.60	0.75	7.18	6.43
Li	5.39	0.62	3.01	2.39
Be	9.3	0.4	4.9	4.5
B	8.3	0.28	4.29	4.01
C	11.26	1.27	6.27	5.00
N	14.53	0.07	7.30	7.23
O	13.62	1.46	7.54	6.08
F	17.42	3.40	10.41	7.01
Na	5.14	0.55	2.85	2.30
Mg	7.65	-0.15	3.75	3.90
Al	5.99	0.46	3.23	2.77
Si	8.15	1.39	4.77	3.38
P	10.49	0.74	5.62	4.88
S	10.36	2.08	6.22	4.14
Cl	12.97	3.62	8.30	4.68
K	4.34	0.50	2.42	1.92
Ca	6.1	-1.8	2.2	4.0
Sc	6.54	0.14	3.34	3.20
Ti	6.82	0.08	3.45	3.37
V	6.7	0.5	3.6	3.1
Cr	6.77	0.66	3.72	3.06
Mn	7.44	0	3.72	3.72
Fe	7.87	0.25	4.06	3.81
Co	7.8	0.7	4.3	3.6
Ni	7.64	1.15	4.40	3.25
Cu	7.73	1.23	4.48	3.25
Zn	9.39	-0.49	4.45	4.94
Ga	6.0	0.3	3.2	2.9
Ge	7.9	1.2	4.6	3.4
As	9.8	0.8	5.3	4.5
Se	9.75	2.02	5.89	3.87
Br	11.81	3.36	7.59	4.22
Rb	4.18	0.49	2.34	1.85
Sr	5.7	-1.7	2.0	3.7
Y	6.38	0	3.19	3.19
Zr	6.84	0.43	3.64	3.21
Nb	6.9	1.0	4.0	3.0
Mo	7.10	0.75	3.9	3.1
Ru	7.4	1.5	4.5	3.0
Rh	7.46	1.14	4.30	3.16
Pd	8.34	0.56	4.45	3.89
Ag	7.58	1.30	4.44	3.14
Cd	8.99	-0.33	4.33	4.66
In	5.8	0.3	3.1	2.8
Sn	7.34	1.25	4.30	3.05
Sb	8.64	1.05	4.85	3.80
Te	9.01	1.97	5.49	3.52
I	10.45	3.06	6.76	3.69
Cs	3.89	0.47	2.18	1.71
Ba	5.2	-0.5	2.4	2.9
La	5.6	0.5	3.1	2.6
Hf	6.7	-0.8	3.8	3.0
Ta	7.89	0.32	4.11	3.79
W	7.98	0.82	4.40	3.58
Re	7.88	0.15	4.02	3.87
Os	8.7	1.1	4.9	3.8
Ir	9.1	1.6	5.4	3.8
Pt	9.0	2.1	5.6	3.5
Au	9.23	2.31	5.77	3.46
Hg	10.44	-0.63	4.91	5.54
Tl	6.1	0.3	3.2	2.9
Pb	7.42	0.37	3.90	3.53
Bi	8.42	0.95	4.69	3.74

^aReference 52. ^bHotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* 1985, 14, 731.

HOMEWORK 3

- ①. Using molecular integrals for H_2 in Appendix D calculate the energy of the triplet state $E ({}^3\Sigma_u^+)$ at $R = 2.0$ a.u.
- ②. Calculate the ionization potential of N_2 using Koopman's theorem and by doing SDCI on N_2 and N_2^+ . For SDCI use results of RHF as input in MOREAD. The basis set is G-31 + G(3d).
- ③. E 4.12 (p. 266 in SO).

HOMEWORK SET (Due on Dec. 8, 5:00 PM)

Problem 1. Using the perturbation formula for molecular polarizability calculate the xx , yy , and zz component of the polarizability arising from the transition between the ground state of water and first singlet excited state. Use GAMESS with the input file shown below to obtain the transition dipole moments and energies. The input is taken from exam14.inp from GAMESS distribution (you can find the file in the upper directory from your home: `cd ..`). Find the experimental values of the water polarizability and argue why does the calculated value differ from experiment.

```
! CI transition moments. Water, using RHF/STO-3G MOs.
! All orbitals are occupied, transition is 1-1A1 to 2-1A1.
!
! E(STATE 1)= -75.0101113548, E(STATE 2)= -74.3945819375
! Dipole LENGTH is <Q>=0.392614
! Dipole VELOCITY is <d/dQ>=0.368205
!
$CTRL SCFTYP=NONE CITYP=GUGA RUNTYP=TRANSITN UNITS=BOHR $END
$SYSTEM TIMLIM=1 MEMORY=150000 $END
$BASIS GBASIS=STO NGAUSS=3 $END
! standard SD-CI calculation
$DRT1 GROUP=C2V IEXCIT=2 NFZC=1 NDOC=4 NVAL=2 $END
$TRANST NFZC=1 IROOTS(1)=2 $END
$DATA
WATER MOLECULE...STO-3G...TRANSITION MOMENT
CNV      2

OXYGEN      8.0    0.0    0.0      0.0
HYDROGEN    1.0    0.0    1.428   -1.096
$END

--- RHF ORBITALS --- GENERATED AT 09:24:04      18-FEB-88
WATER MOLECULE...STO-3G...TRANSITION MOMENT
E(RHF)= -74.9620539825, E(NUC)=      9.2384802989,      8 ITERS
$VEC1
1  1  9.94117078E-01 2.66680164E-02 0.00000000E+00 0.00000000E+00-4.37663441E-03
1  2-6.02779209E-03-6.02779209E-03
```

```
2 1-2.32646075E-01 8.31899807E-01 0.00000000E+00 0.00000000E+00-1.30711442E-0
2 2 1.59112113E-01 1.59112113E-01
3 1 0.00000000E+00 0.00000000E+00 0.00000000E+00 6.05977383E-01 0.00000000E+0
3 2-4.44410026E-01 4.44410026E-01
4 1-1.03107214E-01 5.36888546E-01 0.00000000E+00 0.00000000E+00 7.79238006E-0
4 2-2.75438667E-01-2.75438667E-01
5 1 0.00000000E+00 0.00000000E+00-1.00000000E+00 0.00000000E+00 0.00000000E+0
5 2 0.00000000E+00 0.00000000E+00
6 1-1.33255319E-01 8.93987858E-01 0.00000000E+00 0.00000000E+00-7.40007314E-0
6 2-8.01069824E-01-8.01069824E-01
7 1 0.00000000E+00 0.00000000E+00 0.00000000E+00-9.94651519E-01 0.00000000E+0
7 2-8.42653177E-01 8.42653177E-01
$END
```

Problem 2. Exercise 6.2.