

- Variational Principle (L8, L10)
 - Symmetry adapted linear combination of atomic orbitals (L15; L16)
- Self-Consistent Field (L29 first half)
- Slater Determinants (L25; L26 (beginning))

Variational Principle

$$E_0 = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

$$E_\phi \geq E_0$$

$$\phi \rightarrow \psi_0 \Rightarrow E_\phi \rightarrow E_0$$

Justification:

$$\hat{H}\psi_i = E_i\psi_i$$
$$\phi = \sum_i c_i \psi_i ; \quad c_i = \langle \psi_i | \phi \rangle$$

$$\begin{aligned} \langle \hat{H} \rangle &= \langle \phi | \hat{H} | \phi \rangle \\ &= \sum_i |c_i|^2 E_i \\ &= |c_0|^2 E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 \cdots \\ &\geq |c_0|^2 E_0 + |c_1|^2 E_0 + |c_2|^2 E_0 \cdots \end{aligned}$$

Variational Calculation

$$E_0 = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

$$E_\phi \geq E_0$$

$$\phi \rightarrow \psi_0 \Rightarrow E_\phi \rightarrow E_0$$

Strategy:

$$\phi = \phi(\alpha)$$

$$E_\phi = E_\phi(\alpha)$$

$$\frac{dE_\phi(\alpha)}{d\alpha} = 0$$

$$\phi(\alpha_m); E_\phi(\alpha_m)$$

- Should satisfy boundary conditions
- Should be a well-behaved function

Linear Variational Principle

Let the trial function be, $\phi = c_1\psi_1 + c_2\psi_2$

$$E = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

$$\begin{aligned}\langle \phi | \phi \rangle &= \langle c_1\psi_1 + c_2\psi_2 | c_1\psi_1 + c_2\psi_2 \rangle \\ &= c_1^2 \langle \psi_1 | \psi_1 \rangle + c_2^2 \langle \psi_2 | \psi_2 \rangle + 2c_1c_2 \langle \psi_1 | \psi_2 \rangle\end{aligned}$$

$$\begin{aligned}\langle \phi | \hat{H} | \phi \rangle &= \langle c_1\psi_1 + c_2\psi_2 | \hat{H} | c_1\psi_1 + c_2\psi_2 \rangle \\ &= c_1^2 \langle \psi_1 | \hat{H} | \psi_1 \rangle + c_2^2 \langle \psi_2 | \hat{H} | \psi_2 \rangle + 2c_1c_2 \langle \psi_1 | \hat{H} | \psi_2 \rangle\end{aligned}$$

Linear Variational Principle

$$E(c_1, c_2) = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}}{c_1^2 S_{11} + c_2^2 S_{22} + 2c_1 c_2 S_{12}}$$

$$\frac{\partial E}{\partial c_1} = 0 \Rightarrow c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

$$\frac{\partial E}{\partial c_2} = 0 \Rightarrow c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

Linear Variational Principle

When the trial function is,

$$\phi = \sum_{i=1}^n c_i \psi_i$$

$$\begin{vmatrix} H_{11} - E & H_{12} & \dots & H_{1n} \\ H_{12} & H_{22} - E & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{1n} & H_{2n} & \dots & H_{nn} - E \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{vmatrix} = 0$$

Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

Diatomics

O: $1s^2 2s^2 2p^4$

- core orbitals are too compact and virtual orbitals are too diffused for significant overlap (constructive/destructive) between neighbouring atoms.

$$\phi = \sum_{i=1}^n c_i \psi_i$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - ES_{nn} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{vmatrix} = 0$$

	E	2 C _∞ [⊕]	...	∞ σ _v		
A ₁ =Σ ⁺	1	1	...	1	z	x ² + y ² , z ²
A ₂ =Σ ⁻	1	1	...	-1	R _z	
E ₁ =Π	2	2 cos(Φ)	...	0	(x, y), (R _x , R _y)	(xz, yz)
E ₂ =Δ	2	2 cos(2Φ)	...	0		(x ² - y ² , xy)
E ₃ =Φ	2	2 cos(3Φ)	...	0		
...		

$$\begin{aligned} \langle \psi_i | \hat{H} | \psi_j \rangle &= H_{ij} \neq 0 \\ \langle \psi_i | \psi_j \rangle &= S_{ij} \neq 0 \end{aligned}$$

Only when the atomic orbitals have same symmetry species in the point group of the molecule

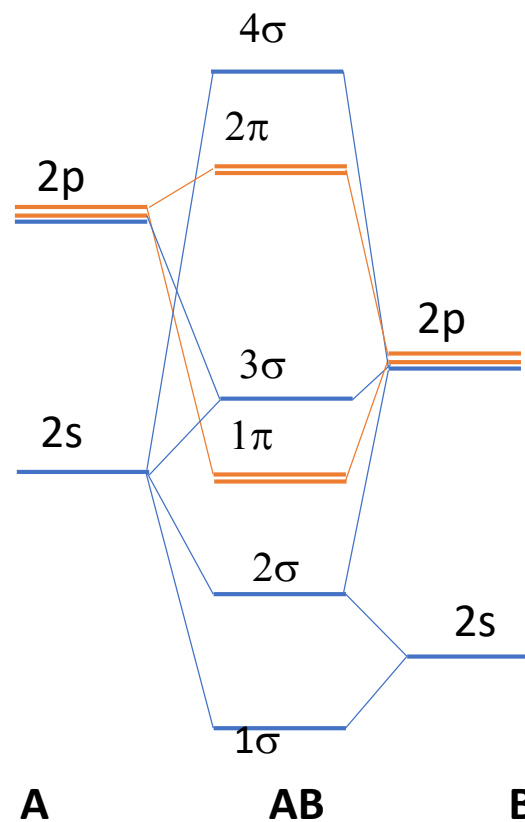
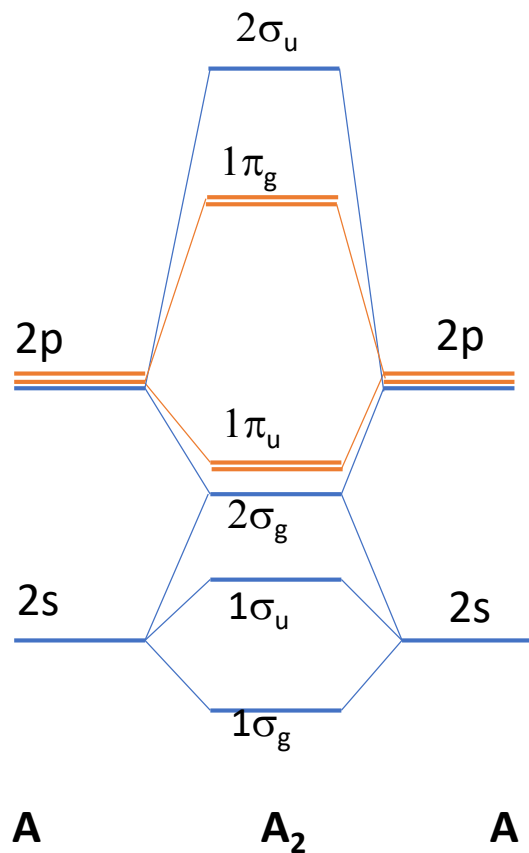
Σ : 2s 2p_z

Π : 2p_{x,y}

Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

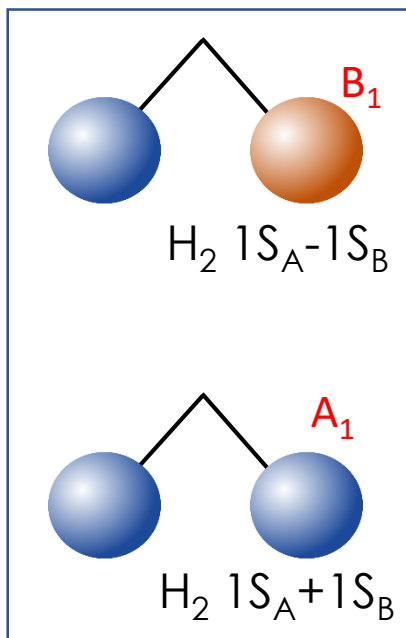
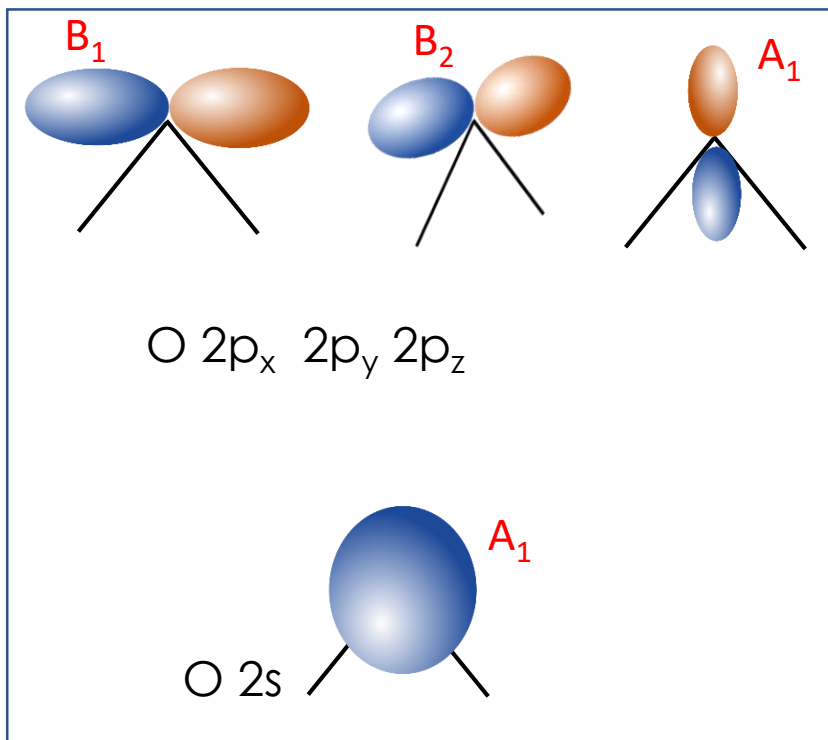
Diatomics



Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

Polyatomics: AH_2



$$\psi(A_1) = c_1\phi(\text{O}, 2s) + c_2\phi(\text{O}, 2p_z) + c_3\phi(\text{H}_2, 1s_A + 1s_B)$$

$$\psi(B_1) = c_1\phi(\text{O}, 2p_x) + c_2\phi(\text{H}_2, 1s_A - 1s_B)$$

$$\psi(B_2) = \phi(\text{O}, 2p_y)$$

z
x

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Linear Variational Principle in Chemical Bonding

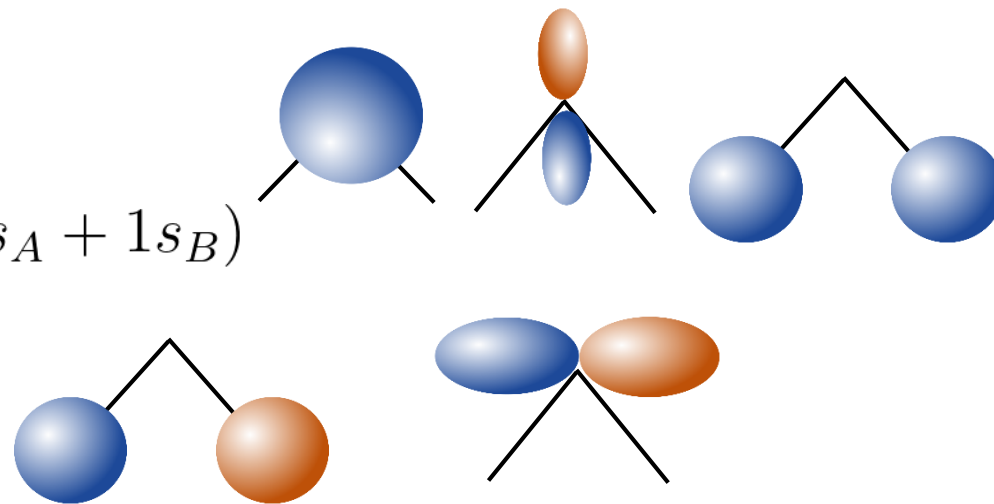
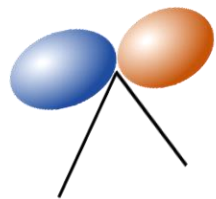
Symmetry Adapted Linear Combination of Atomic Orbitals

Polyatomics: AH₂

$$\psi(A_1) = c_1\phi(\text{O}, 2s) + c_2\phi(\text{O}, 2p_z) + c_3\phi(\text{H}_2, 1s_A + 1s_B)$$

$$\psi(B_1) = c_1\phi(\text{O}, 2p_x) + c_2\phi(\text{H}_2, 1s_A - 1s_B)$$

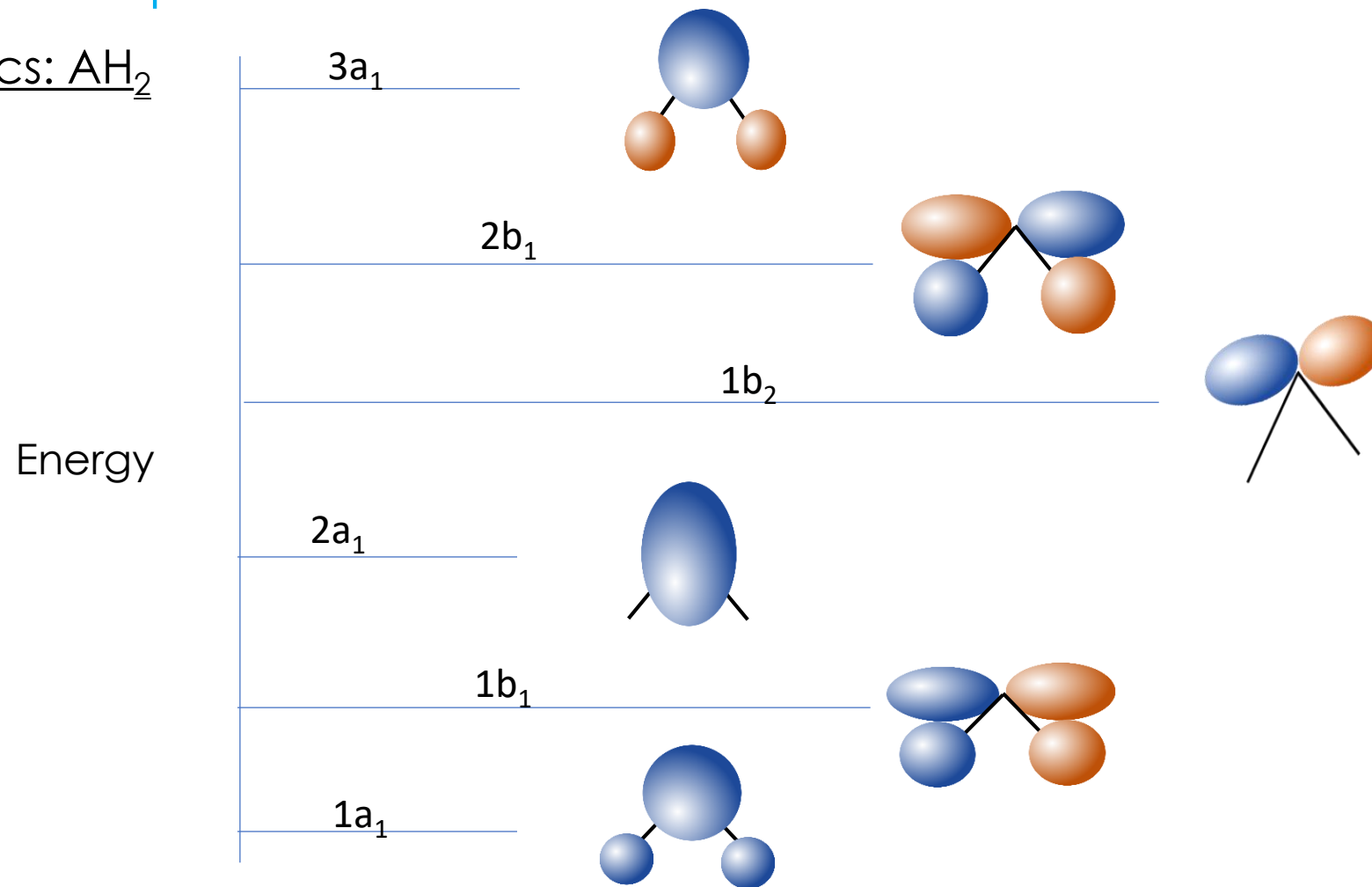
$$\psi(B_2) = \phi(\text{O}, 2p_y)$$



Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

Polyatomics: AH_2



Self-Consistent Field

For He atom

$$\begin{aligned}\hat{H} &= \sum_{i=1}^2 \left(-\frac{\nabla_i^2}{2} - \frac{2}{r_{iA}} \right) + \frac{1}{r_{12}} \\ &= \sum_{i=1}^2 \hat{h}_i + \frac{1}{r_{12}}\end{aligned}$$

$$\psi(1, 2) = \chi_a(1)\chi_b(2) \quad \text{Hartree Product}$$

$$\int \chi_b^*(2)\chi_b(2) dx_2 = p(2)$$

Interaction energy of electron 1 with the charge density (field) of electron 2:

$$U_1^{\text{eff}} = \frac{-e \cdot -ep(2)}{r_{12}} = \int \chi_b^*(2) \frac{1}{r_{12}} \chi_b(2) dx_2$$

New Hamiltonian for electron 1

$$\hat{H}_1^{\text{eff}} = \hat{h}_1 + U_1^{\text{eff}}$$

Self-Consistent Field

For He atom

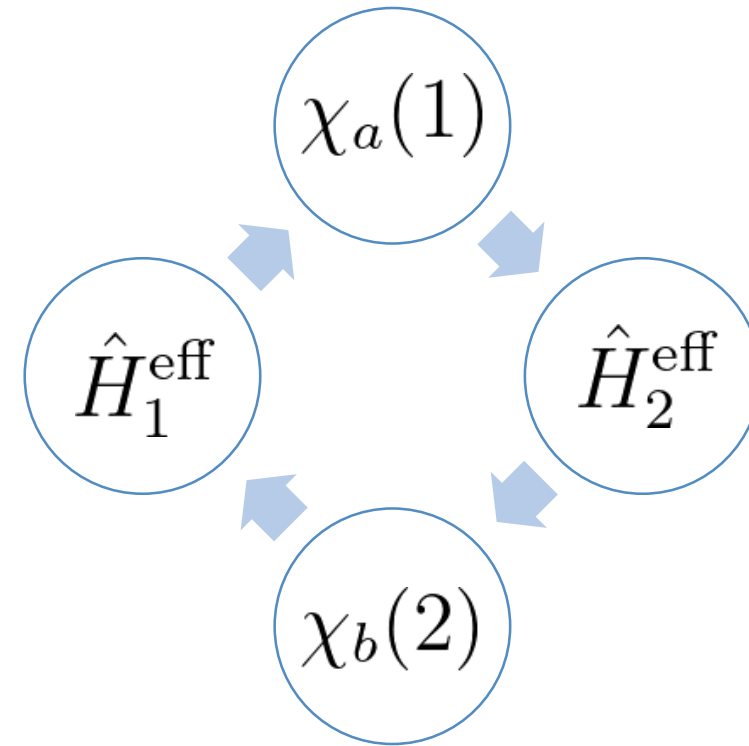
Effective one-electron Hamiltonian

$$\hat{H}_1^{\text{eff}} = \hat{h}_1 + \int \chi_b^*(2) \frac{1}{r_{12}} \chi_b(2) dx_2$$

$$\hat{H}_2^{\text{eff}} = \hat{h}_2 + \int \chi_a^*(1) \frac{1}{r_{12}} \chi_a(1) dx_1$$

$$\hat{H}_1^{\text{eff}} \chi_a(1) = \varepsilon_a \chi_a(1)$$

$$\hat{H}_2^{\text{eff}} \chi_b(2) = \varepsilon_b \chi_b(2)$$

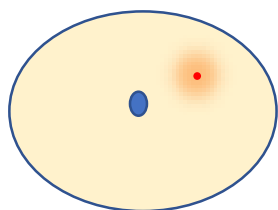
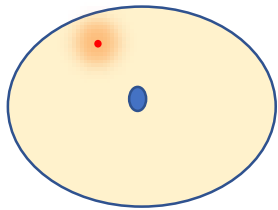
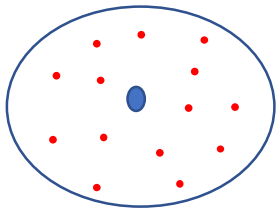


Iterative Solution

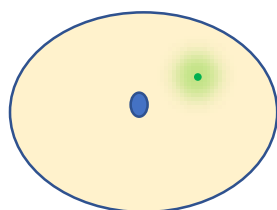
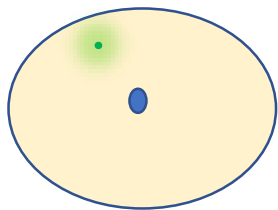
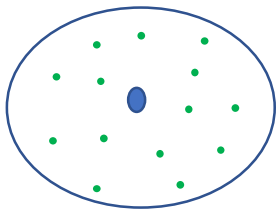
Self-Consistent Solution

Self-Consistent Field

For N-electron System

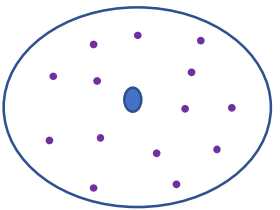


... .. repeat for each electron



... .. repeat for each electron

⋮
iterate the process till convergence (no change in spinorbitals)



Proposed by Hartree (Hartree's SCF)

Hartree-Fock SCF

SCF Scheme of Hartree, improved by Fock (and Slater)

$$\Phi_{\text{HP}}(1, 2, \dots, N) = \chi_1(1)\chi_2(2) \cdots \chi_a(i)\chi_b(j) \cdots \chi_N(N)$$

Hartree SCF

$$\Phi_{\text{SD}}(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} |\chi_1(1)\chi_2(2) \cdots \chi_a(i)\chi_b(j) \cdots \chi_N(N)|$$

Hartree-Fock SCF

- ❖ Find the *best* N-electron determinantal wavefunction (using variation method) that gives the lowest energy (for a given nuclear configuration) while making sure that the spinorbitals remain orthonormal.

Slater Determinant as Wavefunction

3 electronic system

$$\psi_1 = f(1)g(2)h(3)$$

$$\psi_2 = \hat{\mathcal{P}}_{12}\psi_1 = f(2)g(1)h(3)$$

$$\psi_3 = \hat{\mathcal{P}}_{13}\psi_1 = f(3)g(2)h(1)$$

$$\psi_4 = \hat{\mathcal{P}}_{23}\psi_1 = f(1)g(3)h(2)$$

$$\psi_5 = \hat{\mathcal{P}}_{12}\psi_3 = f(3)g(1)h(2)$$

$$\psi_6 = \hat{\mathcal{P}}_{12}\psi_4 = f(2)g(3)h(1)$$

f	g	h
1	2	3
1	3	2
2	1	3
2	3	1
3	1	2
3	2	1

$$\phi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 + c_5\psi_5 + c_6\psi_6 \quad \checkmark \text{ Indistinguishability Antisymmetric?}$$

$$c_2 = -c_1 \quad c_3 = -c_1 \quad c_5 = -c_3 = c_1$$

$$c_4 = -c_1 \quad c_6 = -c_4 = c_1$$

$$\phi = c_1 (\psi_1 - \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6)$$

Slater Determinant as wave function

3 electronic system

$$\phi = c_1 (\psi_1 - \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6)$$

Normalization

$$\int \phi^* \phi \, d\tau = 1$$

$$|c_1|^2 \left(\int \psi_1^* \psi_1 \, d\tau + \cdots + \int \psi_6^* \psi_6 \, d\tau \right) = 1$$

$$c_1 = \sqrt{1/6}$$

$$\psi_1 = f(1)g(2)h(3)$$

$$\psi_2 = \hat{\mathcal{P}}_{12}\psi_1 = f(2)g(1)h(3)$$

$$\psi_3 = \hat{\mathcal{P}}_{13}\psi_1 = f(3)g(2)h(1)$$

$$\psi_4 = \hat{\mathcal{P}}_{23}\psi_1 = f(1)g(3)h(2)$$

$$\psi_5 = \hat{\mathcal{P}}_{12}\psi_3 = f(3)g(1)h(2)$$

$$\psi_6 = \hat{\mathcal{P}}_{12}\psi_4 = f(2)g(3)h(1)$$

$$\sqrt{\frac{1}{N!}}$$

Slater Determinant as wave function

3 electronic system

$$\phi = \sqrt{1/6} (\psi_1 - \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6)$$

Slater determinant

$$\phi = \frac{1}{\sqrt{6}} \begin{vmatrix} f(1) & g(1) & h(1) \\ f(2) & g(2) & h(2) \\ f(3) & g(3) & h(3) \end{vmatrix}$$

$$\phi = \frac{1}{\sqrt{6}} \begin{vmatrix} f(1) & & \\ & g(2) & \\ & & h(3) \end{vmatrix} = \frac{1}{\sqrt{6}} \begin{vmatrix} f(1) & g(2) & h(3) \end{vmatrix}$$

$$\psi_1 = f(1)g(2)h(3)$$

$$\psi_2 = \hat{\mathcal{P}}_{12}\psi_1 = f(2)g(1)h(3)$$

$$\psi_3 = \hat{\mathcal{P}}_{13}\psi_1 = f(3)g(2)h(1)$$

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$$\psi_5 = \hat{\mathcal{P}}_{12}\psi_3 = f(3)g(1)h(2)$$

$$\psi_6 = \hat{\mathcal{P}}_{12}\psi_4 = f(2)g(3)h(1)$$

- Row -> Electron; Column -> spinorbital
- Antisymmetric with respect to electron exchange
- Obeys Pauli's exclusion principle

For N-electron System

$\psi_i(r)$ an orbital ; a **spatial** orbital

$$\int \psi_i^*(r) \psi_j(r) dr = \delta_{ij} \quad \text{Orthonormality of the spatial orbitals}$$

$\{\psi_i\}$ Complete set of orthonormal spatial orbitals $\{\psi_i | i = 1, 2, \dots, K\}$

$\alpha(\omega), \beta(\omega)$ One-electron spin functions

$$\begin{aligned} \chi(x) &= \psi_i(r) \alpha(\omega) \\ &= \psi_i(r) \beta(\omega) \end{aligned} \quad \text{spinorbitals}$$

Spinorbitals

$$\begin{aligned}\chi(x) &= \psi_i(r)\alpha(\omega) \\ &= \psi_i(r)\beta(\omega)\end{aligned}$$

spinorbitals

$$\{\psi_i | i = 1, 2, \dots, K\}$$

orbitals

$$\{\chi_i | i = 1, 2, \dots, 2K\}$$

spinorbitals

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

$$\chi_{2i}(x) = \psi_i(r)\beta(\omega) = \overline{\psi_i(x)}$$

$$\int \chi_i^*(x) \chi_j(x) dx = \delta_{ij}$$

Orthonormality of the spinorbitals

Wavefunction in terms of Slater determinant

N electronic system

$$\psi = \frac{1}{\sqrt{N!}} |\chi_i(1) \ \chi_j(2) \ \cdots \ \chi_k(N)|$$

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(1) & & & \\ & \chi_j(2) & & \\ & & \cdots & \\ & & & \chi_k(N) \end{vmatrix}$$

✓ indistinguishability of identical particles

✓ satisfies antisymmetry principle

✓ satisfies Pauli's exclusion principle

Uncorrelated wavefunction (?)

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(1) & \chi_j(1) & \cdots & \chi_k(1) \\ \chi_i(2) & \chi_j(2) & \cdots & \chi_k(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(N) & \chi_j(N) & \cdots & \chi_k(N) \end{vmatrix}$$

Wavefunction in terms of Spinorbitals (as Hartree Product)

$$\hat{H} = \sum_i^N \hat{h}_i$$

$$\hat{H}\psi = E\psi$$

$$\psi(1, 2, \dots, N) = \chi_i(1)\chi_j(2) \cdots \chi_k(N) \quad \text{Hartree Product}$$

$$\hat{h}_i\chi_j(i) = \varepsilon_j\chi_j(i)$$

$$E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k$$

$$\psi_{\text{HP}} = \psi(1, 2, \dots, N) = \chi_i(1)\chi_j(2) \cdots \chi_k(N)$$

$$|\psi_{\text{HP}}|^2 dx_1 dx_2 \cdots dx_N = |\chi_i(1)|^2 dx_1 |\chi_j(2)|^2 dx_2 \cdots |\chi_k(N)|^2 dx_N$$

- Uncorrelated/Independent-electron wavefunction
 - Does NOT satisfy indistinguishability of identical particles
 - Does NOT satisfy antisymmetry principle