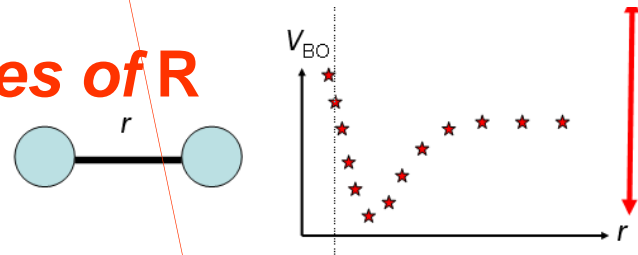


So we need to solve two Schrödinger equations:

(i)
$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) = E_{\text{el}}(\mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R})$$

must be solved for many values of R



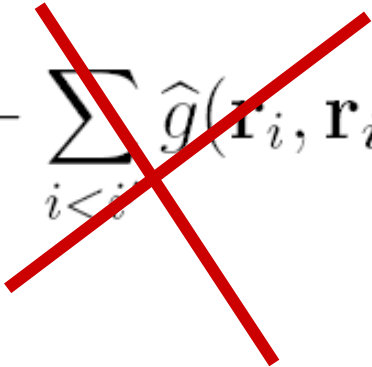
(ii)
$$\hat{H}_{\text{N}}(\mathbf{R}) = \hat{T}_{\text{N}}(\mathbf{R}) + \hat{V}_{\text{eff}}^m(\mathbf{R}) \quad \hat{V}_{\text{eff}}^m(\mathbf{R}) = E_{\text{el}}(\mathbf{R}) + V_{\text{NN}}(\mathbf{R}) = U(\mathbf{R})$$

$$\hat{H}_{\text{N}}(\mathbf{R})\chi_m(\mathbf{R}) = E\chi_m(\mathbf{R})$$

must only be solved once.

Nonrelativistic Hamiltonian (I)

$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}) = \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r})$$

$$= \sum_{i=1}^n \hat{h}(\mathbf{r}_i, \mathbf{p}_i) + \sum_{i < j} \hat{g}(\mathbf{r}_i, \mathbf{r}_j)$$


What would happen if there were no two-electron operators?

One-electron Schrödinger equation

$$\begin{aligned}\hat{h}(\mathbf{r}_1, \mathbf{p}_1)\chi_j(\mathbf{r}_1) &= \left\{ -\frac{1}{2} \left[\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right] \right. \\ &\quad \left. - \sum_{\alpha=1}^N \frac{C_\alpha}{\sqrt{(X_\alpha^{(0)} - x_1)^2 + (Y_\alpha^{(0)} - y_1)^2 + (Z_\alpha^{(0)} - z_1)^2}} \right\} \chi_j(\mathbf{r}_1) \\ &= \epsilon_j \chi_j(\mathbf{r}_1)\end{aligned}$$

orbital energy

(molecular) orbital

Same solutions for any one of the n electrons

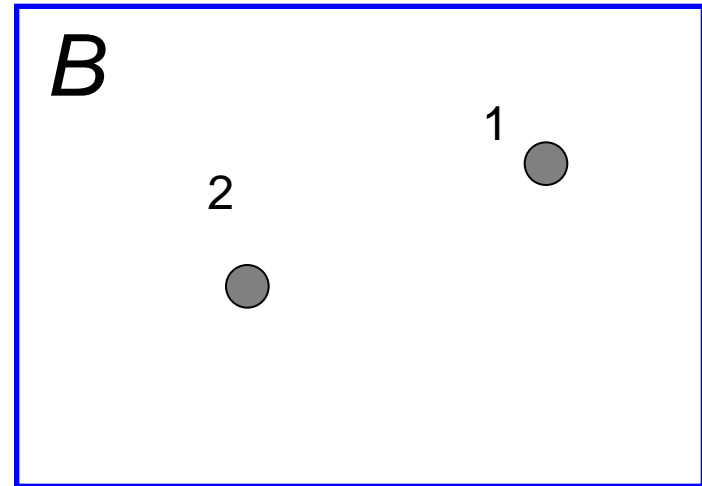
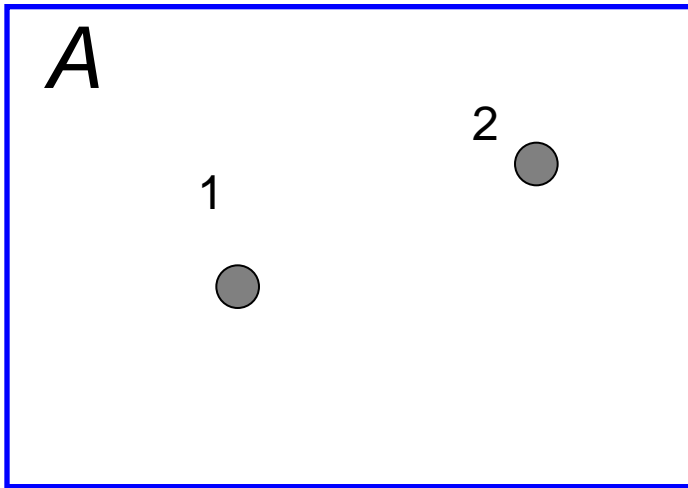
It seems that we can make an approximate n -electron wavefunction as the product of molecular orbitals:

$$\psi_{\text{product}}^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \chi_{j_1}(\mathbf{r}_1)\chi_{j_2}(\mathbf{r}_2)\chi_{j_3}(\mathbf{r}_3) \dots \chi_{j_n}(\mathbf{r}_n) = \prod_{i=1}^n \chi_{j_i}(\mathbf{r}_i)$$

$$\widehat{H}_{\text{elec}}^{(0)} \psi_{\text{product}}^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \left(\sum_{i=1}^n \epsilon_i \right) \psi_{\text{product}}^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$$

and the energy is the sum of the orbital energies
– there is a problem with this though!

However this theory does not generally give the same probability for the two situations:



but this is a *symmetry requirement* since all electrons are identical and *indistinguishable*

We can show that for n electrons, an acceptable wavefunction satisfies

$$\begin{aligned}\psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots, \underline{\mathbf{r}_j}, \dots, \underline{\mathbf{r}_i}, \dots, \mathbf{r}_n) &= e^{i\theta} \psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots, \underline{\mathbf{r}_i}, \dots, \underline{\mathbf{r}_j}, \dots, \mathbf{r}_n) \\ &= \pm \psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots, \underline{\mathbf{r}_i}, \dots, \underline{\mathbf{r}_j}, \dots, \mathbf{r}_n).\end{aligned}$$

If we interchange two electrons, the wavefunction stays the same (+) or it changes sign (-).

Can we somehow argue which sign applies?

Indistinguishability of electrons

In microscopic systems, particles of the same kind (e.g. electrons) cannot be distinguished experimentally. The probability density $\Psi^*\Psi$ in such many-particle systems must not depend on any arbitrary numbering of particles, a renumbering (exchange) of two particles must not alter $\Psi^*\Psi$.

Conclusion: Exchanging two particles of the same kind either leaves the corresponding many-particle wavefunction Ψ unchanged or its sign is altered. Wavefunctions are symmetric or antisymmetric with respect to the exchange of two particles of the same kind.

Empirical finding (Pauli principle): many-electron wavefunctions are antisymmetric with respect to the exchange of two electrons.

Pauli principle

All states of many-electron systems realized in nature are described by wavefunctions which are antisymmetric with respect to pairwise exchange of electrons.

In general:

fermions = particles with half-integer spin

bosons = particles with integer spin

All systems consisting of many fermions (bosons) of the same kind are described by wavefunctions which are antisymmetric (symmetric) with respect to pairwise exchange of fermions (bosons) of the same kind.

Example for fermions: **electron**, proton, neutron

Example for bosons: D nucleus, ^{12}C nucleus

An acceptable two-electron wavefunction is

$$\psi_{\text{asymm}(jk)}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \chi_j(\mathbf{r}_1)\chi_k(\mathbf{r}_2) - \chi_k(\mathbf{r}_1)\chi_j(\mathbf{r}_2) \} .$$

It can be written as a *determinant*

$$\psi_{\text{asymm}(jk)}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_j(\mathbf{r}_1) & \chi_k(\mathbf{r}_1) \\ \chi_j(\mathbf{r}_2) & \chi_k(\mathbf{r}_2) \end{vmatrix} .$$

For n electrons we can extend the determinant

$$\psi_{\text{determinant}}^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(\mathbf{r}_1) & \chi_2(\mathbf{r}_1) & \dots & \chi_n(\mathbf{r}_1) \\ \chi_1(\mathbf{r}_2) & \chi_2(\mathbf{r}_2) & \dots & \chi_n(\mathbf{r}_2) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_1(\mathbf{r}_n) & \chi_2(\mathbf{r}_n) & \dots & \chi_n(\mathbf{r}_n) \end{vmatrix}.$$

This function changes sign when we interchange two electrons but we can only use each χ_j once and so we are in trouble again!

To understand **the periodic system of elements** we need to be able to use each orbital twice!
 How can we fix that?

G	IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII			IB	II B	IIIA	IVA	VA	VIA	VIIA	0
1	1:1 H																	2:2 He
2	3:1 Li	4:2 Be										5:3 B	6:4 C	7:5 N	8:6 O	9:7 F	10:8 Ne	
3	11:1 Na	12:2 Mg										13:3 Al	14:4 Si	15:5 P	16:6 S	17:7 Cl	18:8 Ar	
4	19:1 K	20:2 Ca	21:2 Sc	22:2 Ti	23:2 V	24:1 Cr	25:2 Mn	26:2 Fe	27:2 Co	28:2 Ni	29:1 Cu	30:2 Zn	31:3 Ga	32:4 Ge	33:5 As	34:6 Se	35:7 Br	36:8 Kr
5	37:1 Rb	38:2 Sr	39:2 Y	40:2 Zr	41:1 Nb	42:1 Mo	43:2 Tc	44:1 Ru	45:1 Rh	46:0 Pd	47:1 Ag	48:2 Cd	49:3 In	50:4 Sn	51:5 Sb	52:6 Te	53:7 I	54:8 Xe
6	55:1 Cs	56:2 Ba	57:2 La	72:2 Hf	73:2 Ta	74:2 W	75:2 Re	76:2 Os	77:2 Ir	78:1 Pt	79:1 Au	80:2 Hg	81:3 Tl	82:4 Pb	83:5 Bi	84:6 Po	85:7 At	86:8 Rn
7	87:1 Fr	88:2 Ra	89:2 Ac	104:2 Rf	105:2 Ha	106:2 Sg	107:2 Ns	108:2 Hs	109:2 Mt	110:1 Ds	111:1 Rg	112:2 Uub	113 Lut	114 Uuq	115 Uu	116 Luh	117 Lus	118 Luo
8	119 Uue	120 Ubn	121 Ube	154 Upq	155 Up	156 Uph	157 Ups	158 Upo	159 Upe	160 Uhn	161 Uhu	162 Uhb	163 Uht	164 Uhq	165 Uh	166 Lhh	167 Uhs	168 Uho
6				50 Ce	59 Pr	50 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
7				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	
8			122 Ubb	123 Ubt	124 Ubc	125 Ubd	126 Ube	127 Ubf	128 Ubg	129 Ubh	130 Ubi	131 Ubj	132 Ubk	133 Ubl	134 Ubm	135 Ubn		
8	135 Utl	136 Uth	137 Uts	138 Utu	139 Utv	140 Utw	141 Utx	142 Uty	143 Utz	144 Uua	145 Uub	146 Uuc	147 Uud	148 Uue	149 Uuf	150 Uug	151 Uuh	152 Uui

Electron spin (I)

Experimental evidence:

The electron has an intrinsic angular momentum (spin angular momentum, spin) whose component in an arbitrarily chosen spatial direction (e.g. z direction) can adopt only two values:

$$s_z = +\frac{\hbar}{2} \quad \alpha\text{-spin}$$
$$s_z = -\frac{\hbar}{2} \quad \beta\text{-spin}$$

Spin orbitals:

For a complete description of an electron, we must use three spatial variables and one spin variable. The spin orbitals $\psi(\mathbf{r})|\sigma\rangle$ are products of a spatial orbital $\psi(\mathbf{r})$ and a spin eigenfunction $|\sigma\rangle$, i.e. $|\alpha\rangle$ or $|\beta\rangle$.

We use **Slater determinants** as zero-order wavefunctions

$$\begin{aligned}
 & \psi_{\text{determinant}}^{(0)}(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \dots, \mathbf{r}_n, \xi_n) \\
 &= \frac{1}{\sqrt{n!}} \begin{vmatrix}
 \chi_1(\mathbf{r}_1)\alpha(\xi_1) & \chi_1(\mathbf{r}_1)\beta(\xi_1) & \underbrace{\chi_2(\mathbf{r}_1)\alpha(\xi_1)} & \dots & \boxed{\chi_m(\mathbf{r}_1)\beta(\xi_1)} \\
 \chi_1(\mathbf{r}_2)\alpha(\xi_2) & \chi_1(\mathbf{r}_2)\beta(\xi_2) & \chi_2(\mathbf{r}_2)\alpha(\xi_2) & \dots & \chi_m(\mathbf{r}_2)\beta(\xi_2) \\
 \vdots & \vdots & \vdots & \vdots & \vdots \\
 \chi_1(\mathbf{r}_n)\alpha(\xi_n) & \chi_1(\mathbf{r}_n)\beta(\xi_n) & \chi_2(\mathbf{r}_n)\alpha(\xi_n) & \dots & \chi_m(\mathbf{r}_n)\beta(\xi_n)
 \end{vmatrix}
 \end{aligned}$$

spin orbital
space orbital

Change sign when two electrons are interchanged



Each space orbital can be used twice



Hartree-Fock (HF) calculation

=

Self-Consistent Field (SCF) calculation

Approximation:

Electronic wavefunction is taken to be one Slater determinant. We find „best“ Slater determinant

The electronic wavefunction is a Slater determinant

$$\begin{aligned} & \psi_{\text{determinant}}^{(0)}(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \dots, \mathbf{r}_n, \xi_n) \\ &= \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(\mathbf{r}_1)\alpha(\xi_1) & \chi_1(\mathbf{r}_1)\beta(\xi_1) & \chi_2(\mathbf{r}_1)\alpha(\xi_1) & \dots & \chi_m(\mathbf{r}_1)\beta(\xi_1) \\ \chi_1(\mathbf{r}_2)\alpha(\xi_2) & \chi_1(\mathbf{r}_2)\beta(\xi_2) & \chi_2(\mathbf{r}_2)\alpha(\xi_2) & \dots & \chi_m(\mathbf{r}_2)\beta(\xi_2) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \chi_1(\mathbf{r}_n)\alpha(\xi_n) & \chi_1(\mathbf{r}_n)\beta(\xi_n) & \chi_2(\mathbf{r}_n)\alpha(\xi_n) & \dots & \chi_m(\mathbf{r}_n)\beta(\xi_n) \end{vmatrix} \end{aligned}$$

Each space orbital is a linear combination of atomic orbitals (LCAO)

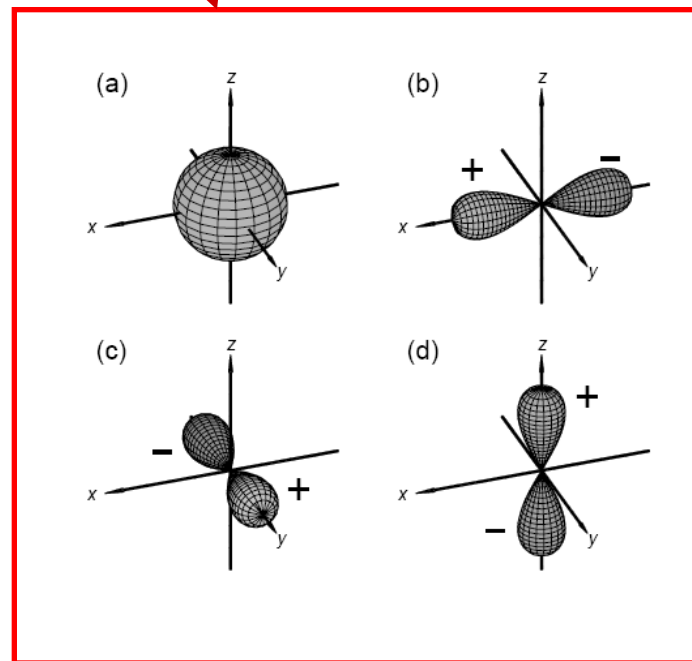
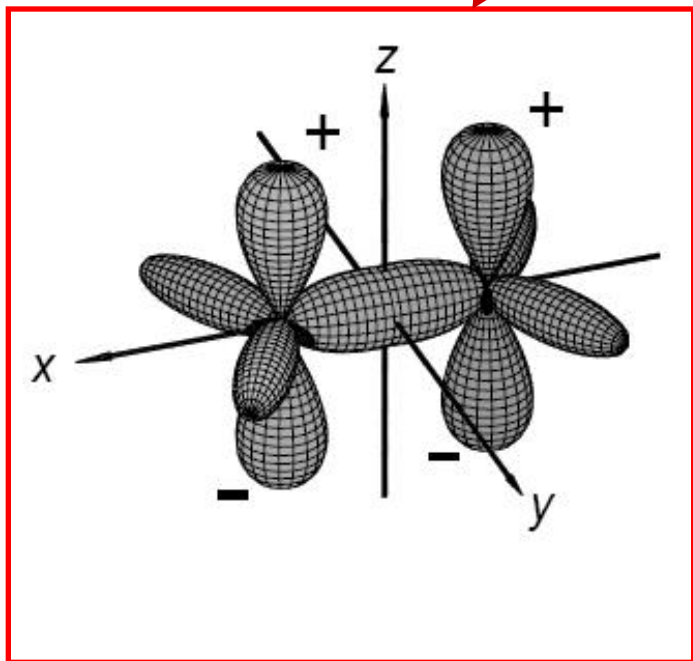
$$\chi_j(\mathbf{r}_i) = \sum_{\mu=1}^{N_{orb}} c_{\mu j} \phi_{\mu}(\mathbf{r}_i).$$

Linear combinations of atomic orbitals (LCAO)

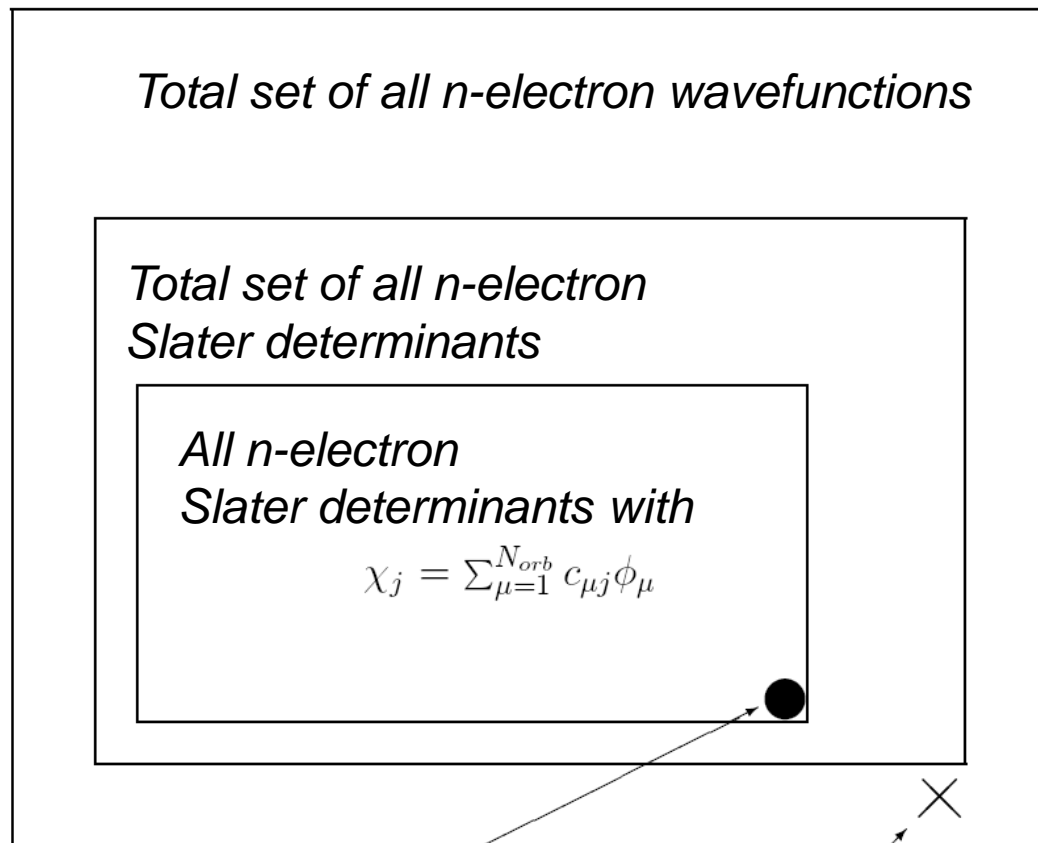
Molecular orbitals
(MO's)

$$\chi_j(\mathbf{r}_i) = \sum_{\mu=1}^{N_{orb}} c_{\mu j} \phi_{\mu}(\mathbf{r}_i).$$

Atomic orbitals
(AO's), 1s, 2s, 2p



Principle of Hartree-Fock calculation



Hartree-Fock (Roothaan-Hall) solution

Exact solution for electronic ground state

Principle of Hartree-Fock calculation

Wavefunction

$$\psi_{j,\alpha}(\mathbf{r}_i, \xi_i) = \chi_j(\mathbf{r}_i)\alpha(\xi_i)$$

or

$$\psi_{j,\beta}(\mathbf{r}_i, \xi_i) = \chi_j(\mathbf{r}_i)\beta(\xi_i)$$

$$\psi_{\text{det}}(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \dots, \mathbf{r}_n, \xi_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\mathbf{r}_1, \xi_1) & \psi_2(\mathbf{r}_1, \xi_1) & \psi_3(\mathbf{r}_1, \xi_1) & \dots & \psi_n(\mathbf{r}_1, \xi_1) \\ \psi_1(\mathbf{r}_2, \xi_2) & \psi_2(\mathbf{r}_2, \xi_2) & \psi_3(\mathbf{r}_2, \xi_2) & \dots & \psi_n(\mathbf{r}_2, \xi_2) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_1(\mathbf{r}_n, \xi_n) & \psi_2(\mathbf{r}_n, \xi_n) & \psi_3(\mathbf{r}_n, \xi_n) & \dots & \psi_n(\mathbf{r}_n, \xi_n) \end{vmatrix}$$

Hamiltonian

$$\widehat{H}_{\text{elec}} = \sum_{i=1}^n \widehat{h}(\mathbf{r}_i, \mathbf{p}_i) + \sum_{i < i'} \widehat{g}(\mathbf{r}_i, \mathbf{r}_{i'}).$$

Now use variation principle:

Derive expression for $\langle \psi_{\text{det}} | \widehat{H}_{\text{elec}} | \psi_{\text{det}} \rangle$

Determine LCAO's $\chi_j(\mathbf{r}_i) = \sum_{\mu=1}^{N_{\text{orb}}} c_{\mu j} \phi_{\mu}(\mathbf{r}_i)$. to minimize $\langle \psi_{\text{det}} | \widehat{H}_{\text{elec}} | \psi_{\text{det}} \rangle$

Expansion coefficients to be varied

Expectation value of Slater determinant

$$\langle \psi_{\text{det}} | \widehat{H}_{\text{elec}} | \psi_{\text{det}} \rangle = \sum_{j=1}^n h_j^{\circ} + \frac{1}{2} \sum_{j=1}^n \sum_{k=1}^n [J_{jk}^{\circ} - K_{jk}^{\circ}],$$

One-electron integral

$$h_j^{\circ} = \int \psi_j(\mathbf{r}_1, \xi_1)^* \widehat{h}(\mathbf{r}_1, \mathbf{p}_1) \psi_j(\mathbf{r}_1, \xi_1) dV_1 d\xi_1$$

Coulomb integral

$$J_{jk}^{\circ} = \int \int \psi_j(\mathbf{r}_1, \xi_1)^* \psi_k(\mathbf{r}_2, \xi_2)^* \widehat{g}(\mathbf{r}_1, \mathbf{r}_2) \psi_j(\mathbf{r}_1, \xi_1) \psi_k(\mathbf{r}_2, \xi_2) dV_1 d\xi_1 dV_2 d\xi_2$$

Exchange integral

$$K_{jk}^{\circ} = \int \int \psi_j(\mathbf{r}_1, \xi_1)^* \psi_k(\mathbf{r}_2, \xi_2)^* \widehat{g}(\mathbf{r}_1, \mathbf{r}_2) \psi_k(\mathbf{r}_1, \xi_1) \psi_j(\mathbf{r}_2, \xi_2) dV_1 d\xi_1 dV_2 d\xi_2$$

Spin functions?

Spin functions disappear from the expressions because of

$$\int \alpha(\xi_1)^* \alpha(\xi_1) d\xi_1 = \int \beta(\xi_1)^* \beta(\xi_1) d\xi_1 = 1$$

and

$$\int \alpha(\xi_1)^* \beta(\xi_1) d\xi_1 = \int \beta(\xi_1)^* \alpha(\xi_1) d\xi_1 = 0,$$

which we assume to be true!

Expectation value of Slater determinant

For closed shells (even number of electrons, each space orbital used twice)

$$\langle \psi_{\text{det}} | \widehat{H}_{\text{elec}} | \psi_{\text{det}} \rangle = \sum_{\mu=1}^{N_{\text{orb}}} \sum_{\nu=1}^{N_{\text{orb}}} P_{\mu\nu} \left(H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\lambda=1}^{N_{\text{orb}}} \sum_{\sigma=1}^{N_{\text{orb}}} P_{\lambda\sigma} \left\{ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\sigma | \lambda\nu) \right\} \right).$$

$$H_{\mu\nu}^{\text{core}} = \int \phi_{\mu}(\mathbf{r}_1)^* \widehat{h}(\mathbf{r}_1, \mathbf{p}_1) \phi_{\nu}(\mathbf{r}_1) dV_1 \quad \textit{Known completely!}$$

$$(\mu\nu | \lambda\sigma) = \int \int \frac{\phi_{\mu}(\mathbf{r}_1)^* \phi_{\lambda}(\mathbf{r}_2)^* \phi_{\nu}(\mathbf{r}_1) \phi_{\sigma}(\mathbf{r}_2)}{\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}} dV_1 dV_2. \quad \textit{Known completely!}$$

Density matrix, closed shells,
 $n=2m$ electrons, **UNKNOWN**

$$P_{\mu\nu} = 2 \sum_{j=1}^m c_{\mu j}^* c_{\nu j}$$