EXAMPLE: $2\bar{e}$: f_1, f_2

$(x_1 x_2) = -(x_2, x_1)$

$x \equiv (\bar{r}, \sigma)$

NOTA BENE: IF $f_1 \equiv 1s, f_2 \equiv 2s \Rightarrow$ EXCITED STATE OF He ATOM

$s_1 = s_2 = 1/2$: $m_s = \frac{1}{2}$ $\alpha(\sigma)$ $(\overset{+}{f}_1, \overset{+}{f}_2, \uparrow)$

$= -\frac{1}{2}$ $\beta(\sigma)$ $(\bar{f}_1, \bar{f}_2, \downarrow)$

S $\chi_1 = N_1 \alpha(1)\alpha(2)$ $\uparrow \; \uparrow$

S $\chi_2 = N_2 \beta(1)\beta(2)$ $\downarrow \; \downarrow$

S $\chi_3 = N_3 \{\alpha(1)\beta(2) + \alpha(2)\beta(1)\}$ $\uparrow \; \downarrow \; + \; \downarrow \; \uparrow$

A $\chi_4 = N_4 \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$ $\uparrow \; \downarrow \; - \; \downarrow \; \uparrow$

$$\Phi_S = \frac{1}{\sqrt{2}}\{f_1(1)f_2(2) + f_1(2)f_2(1)\}$$

$$\Phi_A = \frac{1}{\sqrt{2}}\{f_1(1)f_2(2) - f_1(2)f_2(1)\}$$

SEPARATION VALID ONLY FOR $2\bar{e}$!!!

$$\Psi(\bar{r}\sigma) \equiv \Psi_A(\bar{r}\sigma)$$

ORBITAL PART	SPIN FUNCTION	$\Psi_A(\bar{r}\sigma)$
S	A	$\Psi_1 = \Phi_S \chi_4$
A	S	$\underbrace{\Phi_A \chi_1}_{\Psi_2}$ $\underbrace{\Phi_A \chi_2}_{\Psi_3}$ $\underbrace{\Phi_A \chi_3}_{\Psi_4}$

$$\Psi_1(\bar{r}\sigma) = \underbrace{\frac{1}{\sqrt{2}}\{f_1(1)f_2(2) + f_1(2)f_2(1)\}}_{S} \underbrace{N_4\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}}_{A} =$$

$$= a\{\overset{+}{f}_1(1)\bar{f}_2(2) - \bar{f}_1(1)\overset{+}{f}_2(2) + \bar{f}_1(2)\overset{+}{f}_2(1) - \overset{+}{f}_1(2)\bar{f}_2(1)\} =$$

$$= a\{\overset{+}{f}_1(1)\bar{f}_2(2) - \overset{+}{f}_1(2)\bar{f}_2(1) \quad + \bar{f}_1(2)\overset{+}{f}_2(1) - \bar{f}_1(1)\overset{+}{f}_2(2)\} =$$

$$= a\left\{\begin{vmatrix} \overset{+}{f}_1(1) & \overset{+}{f}_1(2) \\ \bar{f}_2(1) & \bar{f}_2(2) \end{vmatrix} - \begin{vmatrix} \bar{f}_1(1) & \bar{f}_1(2) \\ \overset{+}{f}_2(1) & \overset{+}{f}_2(2) \end{vmatrix}\right\} = a\{|\overset{+}{f}_1(1)\bar{f}_2(2)| - |\bar{f}_1(1)\overset{+}{f}_2(2)|\}$$

LINEAR COMBINATION OF SLATER DETERMINANTS

Ψ_2? Ψ_3? Ψ_4?

ARE THESE FUNCTIONS OF GOOD SYMMETRY?

THEY ARE ANTISYMMETRIC BUT $[H, \hat{J}] = 0$!

MATRIX ELEMENTS

$\hat{F} = \sum_i^N \hat{f}(i)$ ONE-PARTICLE OPERATORS

$\hat{G} = \sum_{i<j}^N \hat{g}(ij)$ TWO-PARTICLE OPERATORS

$\Phi = |\psi_1(1)\psi_2(2)\ldots\psi_i(i)\ldots\psi_N(N)| \equiv$

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \ldots & \psi_i(1) & \ldots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & & \psi_i(2) & & \psi_N(2) \\ \vdots & \vdots & & \vdots & & \vdots \\ \psi_1(i) & \psi_2(i) & & \psi_i(i) & & \psi_N(i) \\ \vdots & \vdots & & \vdots & & \vdots \\ \psi_1(N) & \psi_2(N) & & \psi_i(N) & & \psi_N(N) \end{vmatrix} \begin{array}{l} \sum_i \quad \sum_{i<j} \\ \leftarrow \hat{f}(1) \\ \leftarrow \hat{f}(2) \\ \vdots \\ \leftarrow \hat{f}(i) \\ \vdots \\ \leftarrow \hat{f}(N) \end{array} \begin{array}{l} \\ \hat{g}(12) \\ \hat{g}(23) \\ \vdots \end{array}$$

N X N

EXPANSION BY MINORS ("LAPLACIAN EXPANSION")

BRA: $\frac{1}{\sqrt{N}} \frac{1}{\sqrt{(N-1)!}} \sum_k^N (-1)^{1+k} \psi_k(1) \mathbb{D}_k^1(N-1)$

$\langle \psi_i | \psi_k \rangle = \delta_{ik}$

KET: $\frac{1}{\sqrt{N}} \frac{1}{\sqrt{(N-1)!}} \sum_l^N (-1)^{1+l} \psi_l(1) \mathbb{D}_l^1(N-1)$

$$\langle \Phi | \hat{F} | \Phi \rangle_{1,2,\ldots N} = \sum_{i=1}^N \frac{1}{N} \frac{1}{(N-1)!} \sum_{kl} (-1)^{2+k+l} \langle \psi_k(1) | f(i) | \psi_l(1) \rangle_1 \times$$

$$\langle \mathbb{D}_k^1(N-1) | \mathbb{D}_l^1(N-1) \rangle_{2,3,\ldots N} = \delta(kl)$$

$$= N \cdot \frac{1}{N} \sum_k^N \langle \psi_k(1) | f(1) | \psi_k(1) \rangle \Rightarrow$$

$$\langle \Phi | \hat{F} | \Phi \rangle = \sum_k \langle \psi_k(1) | f(1) | \psi_k(1) \rangle$$

$$\Phi(1\ldots N) = \frac{1}{\sqrt{N!}} \sum_{k,l} (1)^{1+2+k+l} \begin{vmatrix} \psi_k(1) & \psi_l(1) \\ \psi_k(2) & \psi_l(2) \end{vmatrix} \mathbb{D}_{kl}^{12}(N-2)$$

$$\Downarrow$$

$$\frac{1}{\sqrt{N!}} = \frac{1}{\sqrt{N(N-1)(N-2)!}} = \frac{1}{\sqrt{(N-2)!}} \cdot \frac{1}{\sqrt{2}} \cdot \sqrt{\frac{2}{N(N-1)}}$$

NUMBER OF PAIRS $\frac{N(N-1)}{2} = \binom{N}{2}$

$$\langle\Phi|G|\Phi\rangle = \sum_{i<j}\langle\Phi|\hat g(ij)|\Phi\rangle = \frac{N(N-1)}{2}\langle\Phi|\hat g(12)|\Phi\rangle =$$

$$= \frac{N\cancel{(N-1)}}{\cancel{2}}\underbrace{\frac{\cancel{2}}{\cancel{N}(N-1)}\frac{1}{(N-2)!}\frac{1}{2}}_{\frac{1}{N!}}\sum_{kl}\sum_{rs}(-1)^{1+2+k+l+1+2+r+s}$$

$$\left\langle\begin{vmatrix}\psi_k(1) & \psi_l(1)\\ \psi_k(2) & \psi_l(2)\end{vmatrix}\middle|\hat g(12)\middle|\begin{vmatrix}\psi_r(1) & \psi_s(1)\\ \psi_r(2) & \psi_s(2)\end{vmatrix}\right\rangle\langle \mathbb{D}^{12}_{kl}(N-2)|\mathbb{D}^{12}_{rs}(N-2)\rangle_{3,\dots N}$$

$\delta(kr)\,\delta(ls)$

$$= \frac{1}{2}\sum_{kl}^{N}\left\langle\begin{vmatrix}\psi_k(1) & \psi_l(1)\\ \psi_k(2) & \psi_l(2)\end{vmatrix}\middle|\hat g(12)\middle|\begin{vmatrix}\psi_k(1) & \psi_l(1)\\ \psi_k(2) & \psi_l(2)\end{vmatrix}\right\rangle =$$

$$= \frac{1}{2}\sum_{kl}^{N}\langle\psi_k(1)\psi_l(2)-\psi_l(1)\psi_k(2)|g(12)|\psi_k(1)\psi_l(2)-\psi_l(1)\psi_k(2)\rangle =$$

$$= \frac{1}{2}\sum_{kl}\Big\{\langle\psi_k(1)\psi_l(2)|g(12)|\psi_k(1)\psi_l(2)\rangle + \langle\psi_l(1)\psi_k(2)|g(12)|\psi_l(1)\psi_k(2)\rangle$$

$$- \langle\psi_k(1)\psi_l(2)|g(12)|\psi_l(1)\psi_k(2)\rangle - \langle\psi_l(1)\psi_k(2)|g(12)|\psi_k(1)\psi_l(2)\rangle$$

$\langle \overset{(1)}{k}\overset{(2)}{l}|g|\overset{(1)}{k}\overset{(2)}{l}\rangle$ „DIRECT"

$-\langle \overset{(1)}{k}\overset{(2)}{l}|g|\overset{(1)}{l}\overset{(2)}{k}\rangle$ „EXCHANGE"

CAUSED BY ANTISYMMETRY!
(PURELY QUANTUM EFFECT)

$$\langle\Phi|G|\Phi\rangle = \sum_{kl}\{\langle kl|g|kl\rangle - \langle kl|g|lk\rangle\}$$

IF G = COULOMB INTERACTION:

$$\langle \overset{1}{k}\overset{2}{l}||\overset{1}{k}\overset{2}{l}\rangle - \langle \overset{1}{k}\overset{2}{l}||\overset{1}{l}\overset{2}{k}\rangle \equiv \langle \overset{1}{k}\overset{2}{l}||\overset{1}{k}\overset{2}{l}\rangle_A$$

$$\langle \underset{1}{k}\underset{1}{k}||\underset{2}{l}\underset{2}{l}\rangle - \langle \underset{1}{k}\underset{1}{l}||\underset{2}{l}\underset{2}{k}\rangle \equiv \langle \underset{1}{k}\underset{1}{k}||\underset{2}{l}\underset{2}{l}\rangle_A$$

NON-DIAGONAL MATRIX ELEMENTS

$$\Phi_1 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_m(1) & \dots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & & \psi_m(2) & & \psi_N(2) \\ \vdots & \vdots & & \vdots & & \vdots \\ \psi_1(N) & \psi_2(N) & & \psi_m(N) & & \psi_N(N) \end{vmatrix}$$

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

$$\langle \psi_i | \chi \rangle = 0$$

$$\Phi_2 = \frac{1}{\sqrt{N!}} \begin{array}{c} \begin{array}{cccccc} & & & m. & & \end{array} \\ \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \chi(1) & \dots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & & \chi(2) & & \psi_N(2) \\ \vdots & \vdots & & \vdots & & \vdots \\ \psi_1(N) & \psi_2(N) & & \chi(N) & & \psi_N(N) \end{vmatrix} \end{array}$$

$$\langle \Phi_1 | \hat{F} | \Phi_2 \rangle = \sum_i \langle \Phi_1 | f(i) | \Phi_2 \rangle$$

ELIMINATE m. COLUMN ON BOTH SIDES

$\mathbb{D}^1_m(N-1)$ OF Φ_1 $=$ $\mathbb{D}^1_m(N-1)$ OF Φ_2

$$\langle \Phi_1 | \hat{F} | \Phi_2 \rangle = \langle \psi_m(1) | f(1) | \chi(1) \rangle$$

$$\langle \Phi_1 | \hat{G} | \Phi_2 \rangle = \sum_{i<j} \langle \Phi_1 | g(ij) | \Phi_2 \rangle$$

ELIMINATE TWO COLUMNS : ONE HAS TO BE m !!!

$$\langle \mathbb{D}^{12}_{km}(N-2) \,|\, \mathbb{D}^{12}_{rm}(N-2) \rangle$$

$$\delta(k,r)$$

$$\langle \Phi_1 | G | \Phi_2 \rangle = \frac{1}{2} \sum_r \left\langle \begin{vmatrix} \psi_r(1) & \psi_m(1) \\ \psi_r(2) & \psi_m(2) \end{vmatrix} \middle| g(12) \middle| \begin{vmatrix} \psi_r(1) & \chi(1) \\ \psi_r(2) & \chi(2) \end{vmatrix} \right\rangle$$

$$\langle \Phi_1 | G | \Phi_2 \rangle = \sum_r \left\{ \langle r\, m | g | r\, \chi \rangle - \langle r\, m | g | \chi\, r \rangle \right\}$$

$\langle \Phi_1 | \hat{F} | \Phi_2 \rangle = 0$ FOR TWO (OR MORE) DIFFERENT FUNCTIONS IN COLUMNS m AND n ON BOTH SIDES

$$\langle \Phi_1 | G | \Phi_2 \rangle = \langle m\, n | g | \chi_1 \chi_2 \rangle - \langle m\, n | g | \chi_2 \chi_1 \rangle$$

$$\left\langle \begin{vmatrix} \psi_1(1) \dots & \psi_m(1) \dots & \psi_m(1) \dots & \psi_N(1) \\ \psi_1(2) \dots & \psi_m(2) \dots & \psi_n(2) \dots & \psi_N(2) \\ \vdots & & & \\ \psi_1(N) \dots & \psi_m(N) \dots & \psi_n(N) \dots & \psi_N(N) \end{vmatrix} \middle| g(12) \middle| \begin{array}{c} \begin{array}{cccc} & m. & n. & \end{array} \\ \begin{vmatrix} \psi_1(1) \dots & \chi_1(1) \dots & \chi_2(1) \dots & \psi_N(1) \\ \psi_1(2) \dots & \chi_1(2) \dots & \chi_2(2) \dots & \psi_N(2) \\ \vdots & & & \\ \psi_1(N) \dots & \chi_1(N) \dots & \chi_2(N) \dots & \psi_N(N) \end{vmatrix} \end{array} \right\rangle$$

THEY HAVE TO BE ELIMINATED