Orbitaler

Mån Lv7

{ Obs! Ingen föreläsning Mån Lv 2 (Lp2 !) }

Spinnorbitaler $\chi_m(1) = \chi_m(\mathbf{x}_1)$

där $\mathbf{x}_1 = [\underbrace{x_1 \; y_1 \; z_1}_{\mathbf{r}_1} \; w_1] = [\mathbf{r}_1 \; w_1]$

$$\langle \chi_m | \chi_n \rangle = \delta_{mn} = \begin{cases} 0 & \text{om } m \neq n \\ 1 & \text{om } m = n \end{cases}$$

dvs ON-bas!

Rumsorbitaler $\phi_a(1) = \phi_a(\mathbf{r}_1)$

{ Boken ψ ; Levine ϕ }

Slutet skal (closed shell) - lika ~~mag~~ många uppspinns-elektroner som nedspinnselektroner!

Spinnfunktionerna $\begin{cases} \alpha(w_1) \\ \beta(w_1) \end{cases} \Rightarrow \begin{matrix} \langle \alpha | \beta \rangle = 0 \\ \langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \end{matrix}$

$\chi_m = \phi_a \cdot \alpha$

$\chi_n = \phi_a \beta$

Låt $\phi_a \alpha = \phi_a$, $\phi_a \beta = \bar{\phi}_a$ $\Rightarrow$ $\begin{cases} \langle \phi_a | \phi_a \rangle = 1 = \langle \phi_a | \phi_b \rangle \\ \langle \phi_a | \bar{\phi}_a \rangle = 0 \neq \langle \phi_a | \phi_b \rangle \end{cases}$

Enklaste N-elektronvågfunktionen

$$|\tilde{\Phi}\rangle^{HP} = \chi_m(1)\cdot\chi_n(2)\cdot\ldots\cdot\chi_w(N)$$ Hartree produkt

Men! Detta bryter mot Pauli principen !! ⌒

→ Enklaste korrekta N-elektronvåg fkn. : Slaterdeterminant

Ex. 2 elektroner:

$$|\tilde{\Phi}\rangle^{\text{Slater}} = \frac{1}{\sqrt{2}}\left(\chi_m(1)\chi_n(2) - \chi_m(2)\chi_n(1)\right)$$

N-elektroner:

antal koordinatbyten

$$|\tilde{\Phi}\rangle = (N!)^{-\frac{1}{2}} \sum_{k=1}^{N!} (-1)^{P_k} \mathcal{P}_k\{\chi_m(1)\chi_n(2)\cdots\chi_w(N)\}$$

summerar antal permutationer

permutationsoperator (byter elektron koordinater!)

$$= \underbrace{|\chi_m(1)\chi_n(2)\cdots\rangle}_{\text{Slater determinant}}$$

{ Atomenheter s.42 }

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum\sum\frac{Z_c}{|r_{ic}|}}_{\sum_i^N \hat{h}(i) = N\hat{h}(i)} + \sum_{i=1}\sum_{j>i}\underbrace{r_{ij}^{-1}}_{\text{avstånd mellan elektron } i \text{ och } j}$$

1-Elektronoperator

2-elektronoperator

$$\langle \tilde{\Phi} | \tilde{\Phi} \rangle = 1 \qquad \tilde{E} = \langle \tilde{\Phi} | \hat{H} | \tilde{\Phi} \rangle$$

$$\langle \tilde{\Phi} | \tilde{\Phi} \rangle = (N!)^{-1} \sum \sum (-1)^{P_k} (-1)^{P_l} \int dx_1 dx_2 \cdots dx_N \, P_k \{ \chi_m(1) \chi_n(2) \cdots \} P_l \{ \chi_m(2) \chi_n(1) \}$$

$$\langle \chi_m | \chi_n \rangle = 0 \qquad m \neq n$$

$$\langle \chi_m | \chi_n \rangle = 1 \qquad m = n$$

$$= (N!)^{-1} \sum_{k=1}^{N!} (-1)^{2P_k} \cdot 1 = (N!)^{-1} N! = 1$$

$$N \langle \tilde{\Phi} | h_{(1)} | \tilde{\Phi} \rangle = \left[(N-1)! \right]^{-1} \sum (-1)^{2P_k} \int P_k \{ \chi_m(1) \cdots \} \hat{h}_{(1)} P_k \{ \chi_m(1) \cdots \}$$

$$= \frac{(N-1)!}{[(N-1)!]} \sum_{m=1}^{N} \int dx_1 \, \chi_m^* h_{(1)} \chi_m = \langle m | \hat{h} | m \rangle$$

Finns att läsa om i boken!

$$\tilde{E} = \langle \tilde{\Phi} | \hat{H} | \tilde{\Phi} \rangle = \sum_m^N \langle m | \hat{h} | m \rangle + \frac{1}{2} \sum_m^N \sum_{n=m} \langle mn | mn \rangle - \langle mn | nm \rangle$$

$$\underset{1\,2\;1\,2}{\langle mn | mn \rangle} = \int dx_1 dx_2 \, \chi_m^*(1) \chi_n^*(2) \, r_{12}^{-1} \, \chi_m(1) \chi_n(2)$$

$$\underset{1\,1\;2\,2}{[mm | nn]} = \int dx_1 dx_2 \, \chi_m^*(1) \chi_m(1) \, r_{12}^{-1} \, \chi_n^*(2) \chi_n(2)$$

Closed shell

$$\sum_{m=1}^{N} \Longrightarrow \sum_{a=1}^{N/2} + \sum_{\bar{a}=1}^{N/2}$$

$\langle a|h|a\rangle$

$\langle \bar{a}|h|\bar{a}\rangle$

Va?! Vad händer??

$$\sum_{m}^{N}\sum_{n}^{N} = \sum_{a}^{N/2}\sum_{b}^{N/2} + \sum_{\bar{a}}\sum_{b} + \sum_{a}\sum_{\bar{b}} + \sum_{\bar{a}}\sum_{\bar{b}}$$

$$\hookrightarrow \overset{N}{E} = 2\sum^{N/2} (a|h|a) + \sum_{a}^{N/2}\sum_{b}^{N/2} 2(aa|bb) - (ab|ab)$$

rums-orbitaler