Opgaven week 4 2011 — Q.C. (1) Wk 4 2011

<u>Algemene formule spin orbitalen:</u>

$$\Phi = \sqrt{n!}\,\hat{A}\,\chi_1(1)\cdots\chi_n(n)$$

$$\langle \Phi | \hat{H} | \Phi \rangle = \sum_{i=1}^{n} h_{i,i} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} J_{i,j} - K_{i,j}$$

$$J_{i,j} = \iint \frac{\phi_i^*(1)\,\phi_j^*(2)\,\phi_i(1)\,\phi_j(2)}{r_{1,2}}\,d\tau_1\,d\tau_2$$

$$K_{i,j} = \iint \frac{\phi_i^*(1)\,\phi_j^*(2)\,\phi_j(1)\,\phi_i(2)}{r_{1,2}}\,d\tau_1\,d\tau_2$$

1) laat zien dat:

$J_{i,i} = K_{i,i}$ $\qquad h_{i,j} = h_{j,i}^*$

$J_{i,j}^* = J_{i,j}$

$K_{i,j}^* = K_{i,j}$

$J_{i,j} = J_{j,i}$

$K_{i,j} = K_{j,i}$

2) Bepaal uit algemene spinorbitaal formule:

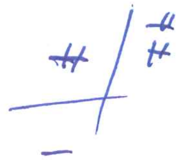
$\uparrow\downarrow$ $\qquad E = 2h_{1,1} + J_{1,1}$

$\uparrow\downarrow$

$\uparrow\downarrow$ $\qquad E = 2h_{1,1} + 2h_{2,2} + J_{1,1} + J_{2,2} + 4J_{1,2} - 2K_{1,2}$

3) ⇒ check ook met algemene ruimte orbitaal formule:

$$E = 2\sum_{k=1}^{n/2} h_{k,k} + \sum_{k=1}^{n/2}\sum_{l=1}^{n/2} 2J_{k,l} - K_{k,l}$$



4) check spinorbitaal formule → ruimte orbitaal formule

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Leidt Roothaan vgl af voor 2 elektron $\hat{H}$

$$\Phi = \frac{1}{\sqrt{2}} |\phi_1 \bar{\phi}_1|$$

$$\phi_1 = \sum_\lambda \chi_\lambda c_\lambda \qquad \text{reële coëfficiënt}$$

$$\langle \chi_\lambda | \chi_\mu \rangle = S_{\lambda\mu}$$

$$\varepsilon = 2 h_{1,1} + J_{1,1}$$

$$g(c) = \langle \phi_1 | \phi_1 \rangle - 1 = 0$$

Lagrange: $\underline{\nabla} f = \lambda \underline{\nabla} g$

Antwoord:

$$J_{1,1} = \sum_{\lambda\mu\nu\tau} c_\lambda c_\mu c_\nu c_\tau \langle \lambda\mu || \nu\tau \rangle$$

$$h_{1,1} = \sum_{\lambda\mu} c_\lambda c_\mu \langle \lambda | \hat{h} | \mu \rangle$$

$$g(c) = \sum_{\lambda,\mu} c_\lambda c_\mu S_{\lambda\mu} - 1 = 0$$

$$\boxed{\frac{\partial \varepsilon}{\partial c_\rho} = 2 \frac{\partial h_{1,1}}{\partial c_\rho} + \frac{\partial}{\partial c_\rho} J_{1,1} = \lambda \frac{\partial}{\partial c} g(c)}$$

$$\frac{\partial h_{1,1}}{\partial c_\rho} = \sum_{\lambda\mu} \left(\delta_{\lambda,\rho} c_\mu + c_\lambda \delta_{\mu,\rho} \right) h_{\lambda\mu}$$

$$= \sum_\mu c_\mu h_{\rho\mu} + \sum_\lambda c_\lambda h_{\lambda,\rho}$$

$$= 2 \sum_\mu h_{\rho\mu} c_\mu \qquad [h_{\lambda,\rho} = h^*_{\rho,\lambda} = h_{\rho,\lambda}]$$

(reëel)

[skip]

$$\frac{\partial J_{1,1}}{\partial c_\rho} = 4 \sum_{\mu\nu\tau} c_\mu \underbrace{c_\nu}_{\rho} c_\tau \langle \lambda\mu || \nu\tau \rangle$$

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$$\frac{\partial \xi}{\partial c_\rho} = 2 \sum_\mu S_{\rho\mu} c_\mu$$

$$4 \sum_\mu h_{\rho\mu} c_\mu + 4 \left[\sum_{\nu\tau} \langle \lambda\mu || \nu\tau \rangle c_\nu c_\tau \right] c_\mu = 2 \sum_\mu S_{\rho\mu} c_\mu \lambda$$

$\times \frac{1}{2}$

$$F_{\rho\mu} = h_{\rho\mu} + \sum_{\nu\tau} \langle \lambda\mu || \nu\tau \rangle c_\nu c_\tau$$

$$2 \sum_\mu F_{\rho\mu} c_\mu = \lambda \sum_\mu S_{\rho\mu} c_\mu$$

$$2 \underline{\underline{F}}\, \underline{c} = \lambda \underline{\underline{S}}\, \underline{c}$$