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<u>Variatie rekening</u> : minimaliseer :

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$$

onder voorwaarde $\langle \Psi | \Psi \rangle - 1 = 0$

<u>He atoom:</u>

$$\Psi(x_1, x_2) = \phi(r_1)\,\phi(r_2)\, \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}$$

<u>Normering:</u>

$$(\Psi, \Psi) = 1 \qquad \left(\phi \otimes \phi \otimes \left(\frac{\alpha\otimes\beta - \beta\otimes\alpha}{\sqrt{2}}\right),\ \phi\otimes\phi\otimes \frac{\alpha\otimes\beta-\beta\otimes\alpha}{\sqrt{2}} \right) = 1$$

$$(\phi,\phi)(\phi,\phi)\cdot 1 = 1 \qquad \Rightarrow (\phi,\phi) = 1$$

<u>Hamiltoniaan</u>

$$\hat{H} = h(1) + h(2) + \hat{g}(1,2)$$

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle = \langle \phi\otimes\phi \,|\, h\otimes \hat{1} + \hat{1}\otimes h + \hat{g}(1,2) \,|\, \phi\otimes\phi \rangle$$

(spin komt niet voor in $\hat{H}$)

$$E[\Psi] = 2\langle \phi | h | \phi \rangle + \langle \phi\otimes\phi \,|\, \hat{g}(1,2) \,|\, \phi\otimes\phi \rangle$$

basis $\phi = \sum_i c_i \chi_i$

$$E[\underline{c}] = 2 \sum_{i'i} \langle \chi_{i'} | h | \chi_i \rangle c_{i'}^* c_i + \sum_{i'j'ij} \langle \chi_{i'} \otimes \chi_{j'}(2) | g(1,2) | \chi_i \otimes \chi_j \rangle c_{i'}^* c_{j'}^* c_i c_j$$

$$(\phi,\phi) = 1 \Rightarrow \sum_{i'i} S_{i'i}\, c_{i'}^* c_i = 1$$

Minimum $f(\underline{c})$ onder voorwaarden $g_i(\underline{c}) = 0$

- In omgeving $\underline{c} + \delta\underline{c}$ geldt:

$$f(\underline{c}+\delta\underline{c}) = f(\underline{c}) + \sum_i \frac{\partial f(\underline{c})}{\partial c_i}\delta c_i = f(\underline{c}) + \nabla f(\underline{c})\cdot\delta\underline{c}$$

$$g_i(\underline{c}+\delta\underline{c}) = g_i(\underline{c}) + \nabla g_i(\underline{c})\cdot\delta\underline{c}$$

- Beschouw alle $\underline{c}$ en $\delta\underline{c}$ die aan voorwaarden voldoen:

$$g_i(\underline{c}) = g_i(\underline{c}+\delta\underline{c}) = 0 \Rightarrow \nabla g_i(\underline{c})\cdot\delta\underline{c} = 0$$

- Voor <u>deze</u> $\underline{c}$'s en $\delta\underline{c}$'s moet in minimum gelden $f(\underline{c}+\delta\underline{c}) = f(\underline{c})$ oftewel $\nabla f(\underline{c})\cdot\delta\underline{c} = 0$
- Als dit moest kloppen voor alle $\delta\underline{c}$'s dan was enige oplossing $\nabla f(\underline{c}) = \underline{0}$
- Nu is echter voldoende als

$$\nabla f(\underline{c}) = \sum \lambda_i \nabla g_i(\underline{c}) \text{ want dan:}$$

$$\nabla f(\underline{c})\cdot\delta\underline{c} = \sum \lambda_i \nabla g_i(\underline{c})\cdot\delta\underline{c} = 0 \quad \Rightarrow \left\{ \begin{array}{l} g_i(\underline{c}) = 0 \\ \nabla[f(\underline{c}) - \sum \lambda_i g_i(\underline{c})] = 0 \end{array} \right.$$

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Probleempje: wat is $\frac{\partial}{\partial c} c^*$?

stel $f(z) = z^*$ $(z = x + iy)$

rond $z = 0$

$$f(0+h) = f'(0)\cdot h$$

$$h^* = f'(0)\cdot h$$

~~h reëel f'(0) = 1; h imag~~ $h = \varepsilon$ $\varepsilon \in \mathbb{R}$ $\Rightarrow f'(0) = 1$

$h = i\varepsilon$ $-i\varepsilon = f'(0)\, i\varepsilon \Rightarrow f'(0) = -1$

Dus apart differentiëren naar reële ~~en imag~~ gedeelte

Handiger ~~...~~ introduceer hulp functie

stel $f(c) = c^* c + c^* + c + 1$

introduceer ~~g(b,c) ...~~ met ~~...~~

~~stel c = x + iy~~ $g(b,c) = b\cdot c + b + c + 1 \Rightarrow f(c) = g(b,c)$ $b = x - iy$, $c = x + iy$

$$\frac{\partial f}{\partial x} = \frac{\partial}{\partial x} g(b,c) = \frac{\partial b}{\partial x}\frac{\partial g(b,c)}{\partial b} + \frac{\partial c}{\partial x}\frac{\partial g(b,c)}{\partial c}$$

$$\frac{\partial f}{\partial y} = \frac{\partial}{\partial y} g(b,c) = \frac{\partial b}{\partial y}\frac{\partial g(b,c)}{\partial b} + \frac{\partial c}{\partial y}\frac{\partial g(b,c)}{\partial c}$$

$$\begin{bmatrix}\frac{\partial f}{\partial x}\\ \frac{\partial f}{\partial y}\end{bmatrix} = \underbrace{\begin{bmatrix}1 & 1\\ -i & i\end{bmatrix}}_{\det 2i \neq 0}\begin{bmatrix}\frac{\partial g}{\partial b}\\ \frac{\partial g}{\partial c}\end{bmatrix}$$

→ schrijf $\frac{\partial g}{\partial b} \Rightarrow \frac{df}{dc^*}$

$\frac{\partial g}{\partial c} \rightarrow \frac{\partial f}{\partial c}$

$$\nabla E[c] = \lambda \nabla [\langle \psi | \psi \rangle - 1]$$

~~$\frac{\partial E[c]}{\partial c_k} = \sum_{i} c_i h$~~

$$\frac{\partial E}{\partial c_k^*} = 2\sum_i \langle \chi_k | h | \chi_i \rangle c_i + \sum_{i,j} \langle \chi_k \chi_j | g | \chi_i \chi_j \rangle c_j^* c_i c_j$$

$$+ \sum_{i,j} \langle \chi_i \chi_k | g | \chi_i \chi_j \rangle c_i^* c_i c_j$$

$$\sum_{i,j} \langle \chi_i \chi_k | g | \chi_i \chi_j \rangle c_i^* c_i c_j \Rightarrow$$

$$= \sum_{i,j} \langle \chi_k \chi_i | g | \chi_j \chi_i \rangle c_i^* c_i c_j = \sum_{i,j} \langle \chi_k \chi_j | g | \chi_i \chi_j \rangle c_j^* c_i c_j$$

$$\frac{\partial E}{\partial c_k^*} = \sum_i \Big[2\langle \chi_k | h | \chi_i \rangle + 2\sum_{j} \langle \chi_k \chi_j | g | \chi_i \chi_j \rangle c_j^* c_j \Big] c_i$$

$$\frac{\partial}{\partial c_k^*}\Big(\sum_{i,i} S_{ii} c_i^* c_i - 1\Big) = \sum_i S_{ki} c_i \Rightarrow F\underline{c} = \varepsilon S \underline{c}$$

$P_{1,2}\, \Psi(\underline{x}_1, \underline{x}_2) = \Psi(\underline{x}_2, \underline{x}_1)$

$(P_{1,2})^2\, \Psi(\underline{x}_1, \underline{x}_2) = \Psi(\underline{x}_1, \underline{x}_2)$

$$\left(P_{1,2}\, f(\underline{x}_1, \underline{x}_2), g(\underline{x}_1, \underline{x}_2)\right) = \iint f^*(\underline{x}_2, \underline{x}_1)\, g(\underline{x}_1, \underline{x}_2)\, d\underline{x}_1\, d\underline{x}_2$$

$$= \iint f^*(\underline{x}_1, \underline{x}_2)\, g(\underline{x}_2, \underline{x}_1)\, d\underline{x}_1\, d\underline{x}_2$$

$$= (f, P_{12}\, g)$$

Dus $P_{1,2}$ hermitisch. Ook $P_{1,2} H = H P_{1,2}$

Stel $H\Psi = E\Psi$ (E niet ontaard)

~~A P Ψ ...~~

~~$P_{1,2}$ ... P_{12}~~

$\hat{H} P \Psi = P \hat{H} \Psi = P E \Psi$

$\hat{H}(P\Psi) = E(P\Psi) \Rightarrow$ $P\Psi = \lambda \Psi$

$P^2 \Psi = \lambda^2 \Psi \Rightarrow \lambda = \pm 1$

Fermionen $\Rightarrow$ $\lambda = -1$

Golffunctie antisymmetrisch verwisseling coordinaten → Slater determinant

Def: determinant ~~D: $\mathbb{C}^{n\times n} \to \mathbb{C}$~~ $D(\underline{a}_1, \ldots, \underline{a}_n) \in \mathbb{C}$ $[\mathbb{C}^{n\times n} \to \mathbb{C}]$

$A = [\underline{a}_1\ \underline{a}_2 \ldots \underline{a}_n]$

1) Lineair $D(\underline{a}_1 \ldots \underline{a}_{n-1}, \underline{x} + \underline{y}) = D(\underline{a}_1 \ldots \underline{a}_{n-1}, \underline{x}) + D(\underline{a}_1 \ldots \underline{a}_{n-1}, \underline{y})$

$D(\underline{a}_1 \ldots \underline{a}_{n-1}, \lambda \underline{x}) = \lambda D(\underline{a}_1 \ldots \underline{a}_{n-1}, \underline{x})$

2) Antisymmetrisch verwisseling twee vector → determinant tegengesteld

3) $D(\underline{e}_1, \ldots \underline{e}_n) = 1$

Opm ~~soort verwisseling~~

1) Willekeurig permutatie van kolommen is serie verwisselingen

2) Ontbinding van permutatie in verwisselingen is niet uniek (denk aan sorteer algoritmen)

3) Permutaties zijn wel in te delen in ~~twee~~ permutaties die ontstaan door even aantal verwisseling en permutaties die ontstaan door oneven aantal verwisselingen

~~Ofteweel~~ De Pariteit: $\varepsilon_p = (-1)^P$ is wel uniek

Bewijs schrijf permutatie als $\begin{pmatrix} 1 & 2 & 3 & \cdots & n \\ i_1 & i_2 & i_3 & \cdots & i_n \end{pmatrix}$ met $i_k \neq i_l$ als $k \neq l$

b.v.

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 3 & 5 & 4 & 1 & 2 & 6 \end{pmatrix}$$

niet overlappend

- Ontbind in cycles:

b.v. $(1\,3\,4)(2\,5)(6)$

- Ontbinding is uniek

Bepaalt pariteit

$(1\,3\,4)\,(2\,5)$

$(-1)^{3+1}\,(-1)^{2+1} = (-1)^7 = -1$

- Dit klopt voor eenheids operator $(1)(2)(3)\cdots(n)$

$(-1)^{1+1}(-1)^{1+1}\cdots(-1)^{1+1} = 1$ even

- overlappende cycles:

niet overlappend:

$$(i_1, i_p)\,(i_1 \cdots i_p \cdots i_n) = (i_1 \cdots i_{p-1})\,(i_p \cdots i_n)$$

$$(-1)^{n+1} \qquad (-1)^{(p-1)+1}\,(-1)^{n-(p-1)+1} = (-1)^n$$

verwisseling $\rightarrow$ pariteit verandert

$$(i_1, j_1)\,(i_1 \cdots i_n)\,(j_1 \cdots j_m) = (i_1 \cdots i_n\, j_1 \cdots j_m)$$

$$(-1)^{n+1}\,(-1)^{m+1} \longrightarrow (-1)^{n+m+1}$$

$$(-1)^{n+m} \longrightarrow (-1)^{n+m+1}$$

q.e.d.

- Determinant is lineair in alle componenten
  - verwissel
  - lineair
  - vermenigvuldig

- twee gelijk geeft nul $D(a, a, a_3, \ldots a_n) = 0$

- Lineair afhankelijkheid geeft nul: $D\left(\sum_{i=2}^{n} \alpha_i a_i, a_2, \ldots a_n\right) = \sum_{i=2}^{n} \alpha_i\, D(a_i, a_2, \ldots a_n) = 0$

Uitschrijven determinant

$$D\left(\sum_{i_1} A_{i_1,1}\, e_{i_1}, \sum_{i_2} A_{i_2,2}\, e_{i_2} \ldots, \sum_{i_n} A_{i_n,n}\, e_{i_n}\right) =$$

$$= \sum_{i_1} \sum_{i_2} \cdots \sum_{i_n} A_{i_1,1}\, A_{i_2,2} \cdots A_{i_n,n}\, D(e_{i_1}, \ldots, e_{i_n})$$

$$= \sum_{\{i_1 \ldots i_n\}} A_{i_1,1} \cdots A_{i_n,n}\; \varepsilon\begin{pmatrix} 1 & 2 & \cdots & n \\ i_1 & i_2 & \cdots & i_n \end{pmatrix}$$

$$\Psi_{AS}(x_1 \ldots x_n) = \frac{1}{\sqrt{n!}} \sum_{i=1}^{n!} (-1)^{p} \hat{P}_i \, \psi_1(x_1) \ldots \psi_n(x_n)$$

$$\equiv \hat{A} \, \psi_1(x_1) \ldots \psi_n(x_n)$$

$\hat{A}$ is hermitisch $(\hat{A}f, g) = (f, \hat{A}g)$

- verwisseling is hermitisch
- permutatie ≡ serie verwisseling: $P = P_{i_1j_1} P_{i_2j_2} \cdots P_{i_nj_n}$

$$(P_{i_1j_1} \cdots P_{i_nj_n} f, g) = (f, P_{i_nj_n} P \cdots P_{i_1j_1} g)$$

- Algemeen $(Pf, g) = (f, P^{-1}g)$ (Verwisselen $P = P^{-1}$)
- $\varepsilon_{P^{-1}}^{(P^{-1})} = \varepsilon^{P}_{P}$
- $(\hat{A} f, g) = (f, A' g)$

$$A' g = \frac{1}{\sqrt{n!}} \sum_{k=1}^{n!} \varepsilon_{P_i}^{P} P_i^{-1}$$

Permutatie groep: stel $P_i^{-1} = P_j^{-1} \Rightarrow P_i = P_j$ $= (A = A')$

↓ alle inverse

$$\langle \hat{A} \psi_1 \otimes \cdots \otimes \psi_n | \hat{H} \hat{A} \, \psi_1 \otimes \cdots \psi_n \rangle = \langle \psi_1 \otimes \cdots \otimes \psi_n | \hat{A} H \hat{A} \Psi \rangle = \langle \psi_1 \otimes \cdots \psi_n | \hat{H} \hat{A}^2 \Psi \rangle$$

- $\varepsilon_k \hat{P}_k \hat{A} = \frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} \varepsilon_k \varepsilon_i \hat{P}_k \hat{P}_i$

stel $\hat{P}_k \hat{P}_i = \hat{P}_j \Rightarrow \varepsilon_k \varepsilon_i = \varepsilon_j$

$\hat{P}_k \hat{P}_i = \hat{P}_j \Rightarrow \hat{P}_k \hat{P}_i = \hat{P}_k \hat{P}_{i'} \Rightarrow \hat{P}_i = \hat{P}_{i'}$

dus $\varepsilon_k \hat{P}_k \hat{A} = \frac{1}{\sqrt{N!}} \sum_{j=1}^{N!} \varepsilon_j \hat{P}_j = \hat{A}$

- $\hat{A}^2 = \frac{1}{\sqrt{N!}} \sum_{k=1}^{N!} \varepsilon_k \hat{P}_k \hat{A} = \frac{1}{\sqrt{N!}} \cdot N! \hat{A} = \sqrt{N!} \hat{A}$

- Normering $(\hat{A}\psi, \hat{A}\psi) = (\psi, \hat{A}^2 \psi) = \sum_{i=1}^{n!} \varepsilon_{P_i} (\phi_1 \otimes \phi_2 \cdots \phi_n, \hat{P}_i \phi_1 \otimes \cdots \otimes \phi_n)$

$$= (\phi_1, \phi_1)(\phi_2, \phi_2) \ldots (\phi_n, \phi_n) = 1$$

- Eén electron operator $h = \sum_{i=1}^{N} h(i)$

$$(\hat{A}\psi, h \hat{A} \psi) = \sum_{i=1}^{N!} \sum_{j=1}^{N} \varepsilon_i (\phi_1 \otimes \cdots \phi_n, h(j) \hat{P}_i \phi_1 \otimes \cdots \otimes \phi_n) = \sum_{j=1}^{N} (\phi_j, h \phi_j)$$

- Twee electron operator

$$\frac{1}{2} \sum_{i \neq j} g(i, j)$$

$$\sum_{P} \varepsilon_P (\phi_1 \otimes \cdots \phi_n \mid \sum_{i \neq j} g(i,j)\, \varepsilon_P \hat{P}\, \phi_1 \otimes \cdots \otimes \phi_n)$$

$$= \frac{1}{2} \sum_{i \neq j} \sum_{P} \varepsilon_P (\phi_1 \otimes \cdots \phi_n, g(i,j) \hat{P}\, \phi_1 \otimes \cdots \phi_i \otimes \cdots \phi_j \otimes \cdots \phi_n)$$

$$\downarrow$$

$$1 - \hat{P}_{i,j}$$

$$= \frac{1}{2} \sum_{i \neq j} \langle \phi_i \phi_j \mid g \mid \phi_i \phi_j \rangle - \langle \phi_i \phi_j \mid g \mid \phi_j \phi_i \rangle$$