Aufgabe 55 Wasserstoffmolekül

i) $-\frac{\hbar^2}{2m}(\Delta_1+\Delta_2)\psi + e^2\left(\frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}}\right)\psi = E\psi$

$\hat{H}_{a1} = -\frac{\hbar^2}{2m}\Delta_1 - \frac{e^2}{r_{a1}}$; $\hat{H}_{a2} = \frac{-\hbar^2}{2m}\Delta_2 - \frac{e^2}{r_{a2}}$; $\hat{W}_{a1b2} = e^2\left(\frac{-1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}}\right)$

iii) $r_{12} \to \infty \Rightarrow W_{a1b2} \to 0$

Lösung $u(r_1, r_2) = \psi_a(\vec{r}_{a1})\,\psi_b(r_{b2})$

iV) $\hat{H}_{a2} = \frac{-\hbar^2}{2m}\Delta_2 - \frac{e^2}{r_{a2}}$ $\qquad \hat{W}_{a1b2} = -\frac{e^2}{r_{a1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{r_{12}} \xrightarrow{r_{12}\to\infty} 0$

$H_{b1} = -\frac{\hbar^2}{2m}\Delta_1 - \frac{e^2}{r_{b1}}$

Lösung $v(\vec{r}_1, \vec{r}_2) = \psi_b(\vec{r}_{b1})\,\psi_a(\vec{r}_{a2})$

Gesamtlösung: $\psi = a\,\psi_a(r_{a1})\psi_b(r_{b2}) + b\,\psi_b(r_{b1})\psi_a(r_{a2})$

mit $a^*a + b^*b = 1$

V)

H-Atome wechselwirken (ein bisschen)

$E = 2E_H + \varepsilon \qquad\qquad \psi = au + bv + \varepsilon$

Einsetzen in SGL, Annahme: φ, ε Wechselwirkungsterme klein $\to$ Produkte $\to 0$

$a(H_{a1} + H_{b2} + W_{a1b2})u + b(H_{a2} + H_{b1} + W_{a2b1})v + (H_{a1} + H_{b2})\varphi =$

$= 2E_1(au + bv) + \varepsilon(au + bv) + 2E_1\varphi$

$au + bv$ Lsg des ungestörten Systems

$\hookrightarrow aW_{a1b2}u + bW_{a2b1}v + (H_{a1} + H_{b2})\varphi = \varepsilon(bv + au) + 2E_1\varphi$

$\Leftrightarrow a(W_{a1b2} - \varepsilon)u + b(W_{a2b1} - \varepsilon)v + \underbrace{(H_{a1} + H_{b2} + 2E_1)\varphi = 0}$

für $a = b = 0$ löst u

Mit vertauschten Elektronen

$a(W_{a2b1} - \varepsilon)u + b(W_{a2b1} - \varepsilon)v + \underbrace{(H_{a2} + H_{b1} + 2E_1)\varphi = 0}$

für $a = b = 0$ löst v

$$\int_{\mathbb{R}^6} \left[a(H_{a1b2} - \varepsilon)u + b(H_{a2b1} - \varepsilon)v\right]^* u \, dV_1 dV_2 \qquad \mathrm{I}$$

$$\int_{\mathbb{R}^6} \left[a(H_{a1b2} - \varepsilon)u + b(H_{a2b1} - \varepsilon)v\right]^* v \, dV_1 dV_2 \qquad \mathrm{II}$$

VII)

$$K = -e^2 \int_{\mathbb{R}^3} \frac{|\psi_a(r_{a1})|^2}{r_{b2}} dV_1 - e^2 \int \frac{|\psi_b(r_{b2})|^2}{\cancel{r_b} r_{b2}} dV_2 + e^2 \int_{\mathbb{R}^6} \frac{|\psi_a(r_{a1})|^2 |\psi_b(r_{b2})|^2}{r_{12}} dV_1 dV_2$$

$$A = -e^2 \int \frac{\psi_a^*(r_{a1}) \psi_b(r_{b1})}{r_{b1}} dV_1 - e^2 \int \frac{\psi_a^*(r_{a2}) \psi_b(r_{b2})}{r_{a2}} dV_2$$

$$+ \int \frac{\psi_a^*(r_{a1}) \psi_b^*(r_{b2}) \psi_a(r_{a2}) \psi_b(r_{b1})}{r_{12}} dV_1 dV_2$$

$$S^2 = \int_{\mathbb{R}^6} u^* v \, dV_1 dV_2$$

$$\underline{\mathrm{I}} = \int a H_{a1b2} |u|^2 - a\varepsilon |u|^2 + b H_{a2b1} v^* u - b \varepsilon v^* u \, dV_1 dV_2 = 0$$

$$\underline{\mathrm{II}} = \int a H_{a1b2} u^* v - a \varepsilon u^* v + b H_{a2b1} |v|^2 - \varepsilon |v|^2 dV_1 dV_2$$

$$\Leftrightarrow (\varepsilon - K)a + (\varepsilon S^2 - A)b = 0$$

$$(\varepsilon S^2 - A)a + (\varepsilon - K)b = 0$$

$$\Rightarrow (\varepsilon - K)^2 - (\varepsilon S^2 - A)^2 \overset{!}{=} 0 \quad \Rightarrow \quad \varepsilon_1 = \frac{K - A}{1 - S^2}, \quad \varepsilon_2 = \frac{K + A}{1 + S^2}$$

$$E_{\text{symmetrisch}} = 2E_1 + \frac{K - A}{1 - S^2} \qquad E_{\text{antisymmetrisch}} = 2E_1 + \frac{K + A}{1 + S^2}$$