1

$3e^-$

$$H = \begin{array}{ccc} c_1 & c_2 & c_3 \\ \end{array}$$
$$H = \begin{bmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{bmatrix}$$

identiteettimatriisi $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$$\det \left| H - \varepsilon I \right| = 0$$

$$\det \begin{bmatrix} \alpha - \varepsilon & \beta & 0 \\ \beta & \alpha - \varepsilon & \beta \\ 0 & \beta & \alpha - \varepsilon \end{bmatrix} =$$

$$(\alpha - \varepsilon)\left[(\alpha - \varepsilon)(\alpha - \varepsilon) - \beta \cdot \beta\right]$$
$$+ \beta\left[\beta 0 - \beta(\alpha - \varepsilon)\right]$$
$$+ 0 \cdot \left[\beta \cdot \beta - (\alpha - \varepsilon) \cdot 0\right] =$$
$$(\alpha - \varepsilon)^3 - (\alpha - \varepsilon)\beta^2 - \beta^2(\alpha - \varepsilon) =$$
$$(\alpha - \varepsilon)\left[(\alpha - \varepsilon)^2 - 2\beta^2\right]$$

$$\Rightarrow (\alpha - \varepsilon)\left[(\alpha - \varepsilon)^2 - 2\beta^2\right] = 0$$

$$\Rightarrow \alpha - \varepsilon) = 0 \quad \text{tai} \quad \left[(\alpha - \varepsilon)^2 - 2\beta^2\right] = 0$$

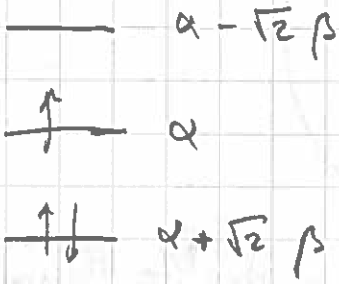
$$\Rightarrow \varepsilon = \alpha$$

$$\Rightarrow (\alpha - \varepsilon)^2 = 2\beta^2$$

$$\Rightarrow \begin{cases} \alpha - \varepsilon = \sqrt{2}\beta \\ \text{tai} \\ \alpha - \varepsilon = -\sqrt{2}\beta \end{cases}$$

$$\Rightarrow \begin{cases} \varepsilon = \alpha - \sqrt{2}\beta \\ \text{tai} \\ \varepsilon = \alpha + \sqrt{2}\beta \end{cases}$$

$\epsilon = \alpha + \sqrt{2}\beta,\ \alpha,\ \alpha - \sqrt{2}\beta$



α on negatiivinen koska $2p_z$ on sidottu

β on negatiivinen eli vuorovaikutus on attraktiivinen

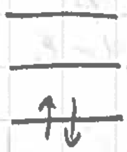
radikaalin energia:

$E = (\alpha + \sqrt{2}\beta)2 + \alpha = 3\alpha + 2\sqrt{2}\beta$

sidosenergia $\Delta E = 3\alpha + 2\sqrt{2}\beta - 3\cdot\alpha = \underline{\underline{2\sqrt{2}\beta}}$

↑ atomien energiat

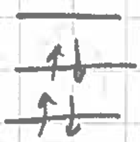
kationi:



$E = 2\alpha + 2\sqrt{2}\beta$

$\Delta E = 2\alpha + 2\sqrt{2}\beta - 2\cdot\alpha = \underline{\underline{2\sqrt{2}\beta}}$

anioni:



$E = 4\cdot\alpha + 2\sqrt{2}\beta$

$\Delta E = 4\cdot\alpha + 2\sqrt{2}\beta - 4\alpha = \underline{\underline{2\sqrt{2}\beta}}$

Kaikki sitoutuneet yhtä paljon!

2 $\quad \psi_1 = \frac{1}{\sqrt{2}}(\phi_A + \phi_B) \qquad \psi_2 = \frac{1}{\sqrt{2}}(\phi_A - \phi_B)$

$$C = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

$$C^{-1} = \frac{1}{\det C}\,\frac{1}{\sqrt{2}}\begin{pmatrix} -1 & -1 \\ -1 & 1 \end{pmatrix}$$ ⇐ wikipedia tai vast

$$\det C = \frac{1}{2}(-1-1) = -1$$

$$C^{-1} = \frac{1}{-1}\,\frac{1}{\sqrt{2}}\begin{pmatrix} -1 & -1 \\ -1 & 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

tarkistetaan

$$C\,C^{-1} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix} 1+1 & 1-1 \\ 1-1 & 1+1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \text{ ok}$$

$$C^{-1} H C = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} \alpha+\beta & \alpha-\beta \\ \alpha+\beta & \beta-\alpha \end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix} 2(\alpha+\beta) & 0 \\ 0 & 2(\alpha-\beta) \end{pmatrix} = \begin{pmatrix} \alpha+\beta & 0 \\ 0 & \alpha-\beta \end{pmatrix}$$

ψ_1 ja ψ_2 ovat molekyylin orbitaaleja ominaisenergioilla $\alpha+\beta$ ja $\alpha-\beta$.

(5) $H^{35}Cl$ $m_1 = 1u,\ m_2 = 35u$.

a) $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} = \frac{35}{36} u$

$R = 127{,}5 \cdot 10^{-12} m$

b) $I = \mu R^2 = \frac{35}{36} u \cdot \left(127{,}5 \cdot 10^{-12} m\right)^2$

$= \frac{35}{36} \cdot 1{,}6605 \cdot 10^{-27} kg \left(127{,}5 \cdot 10^{-12} m\right)^2$

$= 2{,}62 \cdot 10^{-47}\ kg\, m^2$

c) $E_\ell = \frac{\hbar^2}{2I}\ \ell(\ell+1)$

$E_1 - E_0 = \frac{\hbar^2}{2I} 1(1+1) - 0$

$= \frac{\hbar^2}{I} = \frac{\left(1{,}05457 \cdot 10^{-34} m^2 kg/s\right)^2}{2{,}62 \cdot 10^{-47}\ kg\, m^2}$

$= 4{,}24 \cdot 10^{-22} \left(\frac{kg\, m^2}{s^2}\right) = J$

$= 21{,}3\ cm^{-1}$

$\lambda = 469\ \mu m$

$\nu = 639\ GHz$

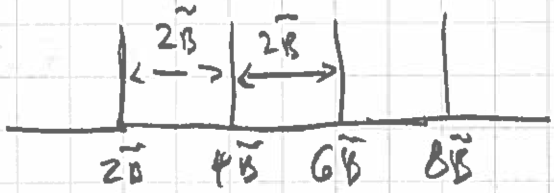
(4) $\tilde{B} = 298 \cdot 10^9\ Hz$ $\quad NH_3$

Katso myös kirjan esimerkki !!

$$\tilde{F}(J,K) = \tilde{B}J(J+1) + (\tilde{A}-\tilde{B})K^2$$

valintasäännöt $\quad \Delta J = \pm 1$ ja $\Delta K = 0$

$$\Delta\tilde{F}(J+1 \leftarrow J,\ K \leftarrow K) = \tilde{B}(J+1)(J+2) - BJ(J+1)$$
$$= 2\tilde{B}(J+1)$$



$$\Delta\tilde{\nu} = 2\tilde{B} = 596 \cdot 10^9\ Hz$$
$$= 19{,}9\ cm^{-1}$$
$$= 0{,}503\ mm$$

Kirjasta $\quad I_\perp = m_H(1-\cos\theta)R^2 + \frac{m_H m_N}{3m_H + m_N}(1+2\cos\theta)R^2$

$$I_\parallel = 2m_H(1-\cos\theta)R^2$$

$\theta = 106{,}78^\circ \qquad R = 101{,}4\ pm$

$\cos\theta = -0{,}2887$

$I_\perp = 4{,}4005 \cdot 10^{-47}\ kg\ m^2$

$I_\parallel = 2{,}7945 \cdot 10^{-47}\ kg\ m^2$

$B = \frac{\hbar^2}{2I_\perp}$

$= 1{,}989 \cdot 10^{-22}$

$\tilde{B} = 10{,}018\ cm^{-1}$

$2\tilde{B} = 20{,}0\ cm^{-1}$

ok

5

$$G(v) = \left(v+\tfrac{1}{2}\right)\tilde{\nu} - \left(v+1/2\right)^2 x_e \tilde{\nu}$$

$$\Delta G(v+1 \leftarrow v) = G(v+1) - G(v)$$

$$= \left(v+\tfrac{3}{2}\right)\tilde{\nu} - \left(v+3/2\right)^2 x_e \tilde{\nu}$$

$$- \left[\left(v+\tfrac{1}{2}\right)\tilde{\nu} - \left(v+\tfrac{1}{2}\right)^2 x_e \tilde{\nu}\right]$$

$$\tilde{\nu} - \left[\left(v^2 + 2\tfrac{3}{2}v + \tfrac{9}{4}\right)x_e\tilde{\nu} - \left(v^2 + 2\tfrac{1}{2}v + \tfrac{1}{4}\right)x_e\tilde{\nu}\right]$$

$$= \tilde{\nu} - \left[(2v+2)x_e\tilde{\nu}\right]$$

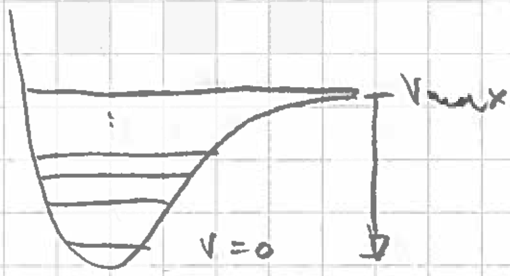
$$= \tilde{\nu}\left(1 - 2(v+1)x_e\right)$$

dissociation:

$$\Delta G(v+1 \leftarrow v) = 0$$
$$= \tilde{\nu}\left(1-2(v+1)x_e\right)$$

$$\Rightarrow 1 - 2(v_{max}+1)x_e = 0$$

$$\Rightarrow v_{max} = \frac{1}{2x_e} - 1$$



$$\tilde{D} = G(v_{max}) - G(0)$$

$$= \left(\frac{1}{2x_e} - 1 + \frac{1}{2}\right)\tilde{\nu} - \left(\frac{1}{2x_e} - 1 + 1/2\right)^2 x_e\tilde{\nu}$$
$$- \left(\frac{1}{2}\tilde{\nu} - \frac{1}{4}x_e\tilde{\nu}\right)$$

$$= \frac{\tilde{\nu}}{x_e}\left[\frac{1}{2} - \frac{1}{2}x_e - \left(\frac{1}{2} - \frac{1}{2}x_e\right)^2\right] - \left[\frac{1}{2}\tilde{\nu} - \frac{1}{4}x_e\tilde{\nu}\right]$$

$$= \frac{\tilde{\nu}}{4x_e}\left[2 - 2x - 1 + 2\,e - e^2\right] - \left[\frac{1}{2}\tilde{\nu} - \frac{1}{4}x_e\tilde{\nu}\right]$$

$$\tilde{D} = \frac{\tilde{\nu}}{4x_e}\left[1 - x_e^2\right] - \frac{1}{2}\tilde{\nu} + \frac{1}{4}x_e\tilde{\nu}$$

$$= \frac{\tilde{\nu}}{4x_e}\left(1 - x_e^2\right) - \frac{1}{2}\tilde{\nu} + \frac{1}{4}x_e\tilde{\nu} \approx \frac{\tilde{\nu}}{4x_e}$$

$x_e \ll 1$