Modern Physics WS 21/22 Sören Bieling

Problem Sheet 8

$dV = r^2 dr \sin\theta \, d\theta \, d\varphi$

Ex. 8.1: H-atom: Orthogonality of the wave fct.

$$\boxed{\Psi_{n,l,m}(r,\theta,\varphi) = R_{n,l}(r)\, Y_{l,m}(\theta,\varphi)}$$

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \qquad Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\, e^{\pm i\varphi}\sin\theta$$

a)

$\langle 0,0|1,0\rangle$:
$$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi} \frac{1}{\sqrt{4\pi}}\cdot\sqrt{\frac{3}{4\pi}}\cos\theta \sin\theta \, d\theta \, d\varphi = \frac{\sqrt{3}}{\cancel{4\pi}}\cancel{2\pi}\int_{\theta=0}^{\pi}\cos\theta\sin\theta\, d\theta = \sqrt{\frac{3}{4}}\left[\frac{1}{2}\sin^2\theta\right]_0^{\pi} = \underline{\underline{0}}$$

$\langle 0,0|1,\pm1\rangle$:
$$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi} \frac{1}{\sqrt{4\pi}}\cdot\mp\sqrt{\frac{3}{8\pi}}\, e^{\pm i\varphi}\sin\theta\sin\theta\, d\theta\, d\varphi = \mp\frac{1}{4\pi}\sqrt{\frac{3}{2}}\underbrace{\int_{\varphi=0}^{2\pi} e^{\pm i\varphi}d\varphi}_{\substack{2\pi\text{ - periodic fct.}\\ \int\ldots\to 0}}\underbrace{\int_{\theta=0}^{\pi}\sin^2\theta\, d\theta}_{\pi/2} = \underline{\underline{0}}$$

$\langle 1,0|1,\pm1\rangle$:
$$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\sqrt{\frac{3}{4\pi}}\cos\theta\cdot\mp\sqrt{\frac{3}{8\pi}}\, e^{\pm i\varphi}\sin\theta\sin\theta\, d\theta\, d\varphi$$
$$= \mp\frac{3}{4\pi}\cdot\frac{1}{\sqrt{2}}\underbrace{\int_{\varphi=0}^{2\pi} e^{\pm i\varphi}d\varphi}_{\substack{=0\\ \text{as above}}}\underbrace{\int_{\theta=0}^{\pi}\sin^2\theta\cos\theta\, d\theta}_{=\left[\frac{1}{3}\sin^3\theta\right]_0^{\pi}=0} = \underline{\underline{0}}$$

$\langle 0,0|0,0\rangle$:
$$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\frac{1}{\sqrt{4\pi}}\frac{1}{\sqrt{4\pi}}\sin\theta\, d\theta\, d\varphi = \frac{1}{4\pi}\underbrace{\int_{\varphi}^{2\pi} d\varphi}_{2\pi}\int_{\theta=0}^{\pi}\sin\theta\, d\theta = \frac{1}{2}\underbrace{\left[-\cos\theta\right]_0^{\pi}}_{1-(-1)} = \underline{\underline{1}}$$

$\langle 1,0|1,0\rangle$:
$$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\sqrt{\frac{3}{4\pi}}\cos\theta\cdot\sqrt{\frac{3}{4\pi}}\cos\theta\sin\theta\, d\theta\, d\varphi = \frac{3}{4\pi}\underbrace{\int_{\varphi=0}^{2\pi} d\varphi}_{2\pi}\underbrace{\int_{\theta=0}^{\pi}\cos^2\theta\sin\theta\, d\theta}_{=\left[-\frac{1}{3}\cos^3\theta\right]_0^{\pi}} = \frac{3}{2}\cdot\left[\frac{1}{3}-\left(-\frac{1}{3}\right)\right] = \underline{\underline{1}}$$

complex conjugate!

$\langle 1,\pm1|1,\pm1\rangle$:
$$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\mp\sqrt{\frac{3}{8\pi}}\, e^{\mp i\varphi}\sin\theta\cdot\mp\sqrt{\frac{3}{8\pi}}\, e^{\pm i\varphi}\sin\theta\sin\theta\, d\theta\, d\varphi$$
$$= \mp\frac{3}{8\pi}\underbrace{\int_{\varphi=0}^{2\pi} e^{\mp i\varphi\pm i\varphi}d\varphi}_{\int_{\varphi=0}^{2\pi} e^0 d\varphi = 2\pi}\underbrace{\int_{\theta=0}^{\pi}\sin^3\theta\, d\theta}_{\text{see hint}} = \frac{3}{4}\cdot\frac{1}{12}\left[\cos(3\theta) - 9\cos\theta\right]_0^{\pi} = \frac{1}{16}\left[-1+9-1+9\right] = \underline{\underline{1}}$$

$\Longrightarrow$ equation (2) from Ex. 8.1 a) checked ✓

Ex. 8.1 b) 1s: $R_{10}(r) = \frac{2}{(a_0)^{3/2}} \cdot e^{-\frac{r}{a_0}}$ 2s: $R_{20}(r) = \frac{2}{(2a_0)^{3/2}} \cdot \left(1-\frac{r}{2a_0}\right) e^{-\frac{r}{2a_0}}$

1. $\langle 1,0|1,0\rangle$: $\int_0^\infty \underbrace{\frac{4}{(a_0)^3} e^{-\frac{2r}{a_0}} r^2\, dr}_{\text{use hint 2: } \alpha=\frac{2}{a_0},\ n=2} = \frac{4}{a_0^3}\ \frac{2!}{\left(\frac{2}{a_0}\right)^3} = \underline{\underline{1}}$

$(a-b)^2 = a^2 - 2ab + b^2$

2. $\langle 2,0|2,0\rangle$: $\int_0^\infty \frac{4}{8a_0^3}\left(1-\frac{r}{2a_0}\right)^2 e^{-\frac{2r}{2a_0}} r^2\, dr$

$$= \frac{4}{(2a_0)^3}\Big[\underbrace{\int_0^\infty e^{-\frac{r}{a_0}} r^2\, dr}_{\text{use hint2: } n=2\ \ \alpha=\frac{1}{a_0}} - \underbrace{\int_0^\infty e^{-\frac{r}{a_0}} \frac{r}{a_0} r^2\, dr}_{n=3\ \ \alpha=\frac{1}{a_0}} + \underbrace{\int_0^\infty e^{-\frac{r}{a_0}} \frac{r^2}{(2a_0)^2} r^2\, dr}_{n=4\ \ \alpha=\frac{1}{a_0}}\Big]$$

$$= \frac{4}{(2a_0)^3}\left[\frac{2!}{\left(\frac{1}{a_0}\right)^3} - \frac{1}{a_0}\ \frac{3!}{\left(\frac{1}{a_0}\right)^4} + \frac{1}{(2a_0)^2}\ \frac{4!}{\left(\frac{1}{a_0}\right)^5}\right]$$

$$= \frac{4}{8a_0^3}\left[2a_0^3 - \cancel{6a_0^3} + \cancel{6a_0^3}\right] = \underline{\underline{1}}$$

3. $\langle 1,0|2,0\rangle$: $\int_0^\infty \frac{4}{2^{3/2} a_0^3}\left(1-\frac{r}{2a_0}\right) e^{-\frac{3r}{2a_0}} r^2\, dr$

$$= \frac{\sqrt{2}}{a_0^3}\Big[\underbrace{\int_0^\infty e^{-\frac{3r}{2a_0}} r^2\, dr}_{n=2\ \ \alpha=\frac{3}{2a_0}} - \frac{1}{2a_0}\underbrace{\int_0^\infty e^{-\frac{3r}{2a_0}} r^3\, dr}_{n=3\ \ \alpha=\frac{3}{2a_0}}\Big] = \frac{\sqrt{2}}{a_0^3}\left[\frac{2!}{\left(\frac{3}{2a_0}\right)^3} - \frac{1}{2a_0}\ \frac{3!}{\left(\frac{3}{2a_0}\right)^4}\right]$$

$$= \frac{\sqrt{2}}{a_0^3}\Big[\underbrace{\frac{16}{27}a_0^3 - \frac{\cancel{3}\cdot 16}{\cancel{81}\ 27} a_0^3}_{=0}\Big] = \underline{\underline{0}}$$

Ex. 8.2: $\Psi_{2p_x}(r,\theta,\varphi) = R_{21}(r)\, Y_{1,+1}(\theta,\varphi)$ with $R_{21}(r) = \frac{1}{(2a_0)^{3/2}}\ \frac{r}{\sqrt{3}\, a_0}\ e^{-\frac{r}{2a_0}}$

$|2,1,+1\rangle \hat{=} 2p_x$

a) $\int_{\theta=90°-30°}^{90°+30°} \dots$

$$P_{(\pm 30° \text{ of x-y plane})} = \int_{r=0}^{\infty}\int_{\theta=60°}^{120°}\int_{\varphi=0}^{2\pi} R^*_{21}(r)\, Y^*_{1,+1}(\theta,\varphi)\, R_{21}(r)\, Y_{1,+1}(\theta,\varphi)\, r^2 dr \sin\theta\, d\theta\, d\varphi$$

$60° = \frac{\pi}{3}$

$120° = \frac{2}{3}\pi$

$$= \underbrace{\int_{r=0}^{\infty} R^*_{21}(r)\, R_{21}(r)\, r^2\, dr}_{=1 \text{ (Ex. 8.1 b) Hint1)}} \cdot \frac{3}{8\pi} \underbrace{\int_0^{2\pi} e^{-i\varphi} e^{+i\varphi}\, d\varphi}_{2\pi} \cdot \underbrace{\int_{\theta=60°}^{120°} \sin^2\theta \sin\theta\, d\theta}_{\text{Ex. 8.1a) Hint}}$$

$$= \frac{3}{4}\cdot\frac{1}{\cancel{12}_{4}}\Big[\cos(3\theta) - 9\cos\theta\Big]_{60°}^{120°} = \frac{1}{16}\Big[\underbrace{1}_{1} - \underbrace{9\cdot\left(-\tfrac{1}{2}\right)}_{+\frac{9}{2}} - \Big[\underbrace{(-1)}_{+1} - \underbrace{9\cdot\tfrac{1}{2}}_{+\frac{9}{2}}\Big]\Big]$$

$$= \frac{11}{16} \approx \underline{\underline{68{,}75\,\%}}$$

b) $\int_{r=2a_0}^{6a_0} \dots$

$$P_{(2a_0 < r < 6a_0)} = \int_{r=2a_0}^{6a_0} R^*_{21}(r)\, R_{21}(r)\, r^2\, dr \underbrace{\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} Y^*_{1,+1}(\theta,\varphi)\, Y_{1,+1}(\theta,\varphi) \sin\theta\, d\theta\, d\varphi}_{=1 \text{ from Ex. 8.1 a)}}$$

$$= \frac{1}{(2a_0)^3}\ \frac{1}{3a_0^2}\int_{r=2a_0}^{6a_0} e^{-\frac{2r}{2a_0}} r^2 r^2\, dr = \left\{\begin{array}{l}\text{can be calculated analytically,}\\ \text{by 4-fold integration by parts,}\\ \text{but very long ... looked it up}\\ \text{in Wolfram Alpha / Mathematica}\end{array}\right\} = \frac{7e^4 - 115}{e^6} \approx 66{,}23\,\%$$

or Bronstein Integration Book.

c) $$P_{(a)+b))} = \underbrace{\int_{r=2a_0}^{6a_0} R^*_{21}(r)\, R_{21}(r)\, r^2\, dr}_{b)} \underbrace{\int_{\theta=60°}^{120°}\int_{\varphi=0}^{2\pi} Y^*_{1,+1}(\theta,\varphi)\, Y_{1,+1}(\theta,\varphi) \sin\theta\, d\theta\, d\varphi}_{a)} = 68{,}75\% \cdot 66{,}23\% = \underline{45{,}53\%}$$

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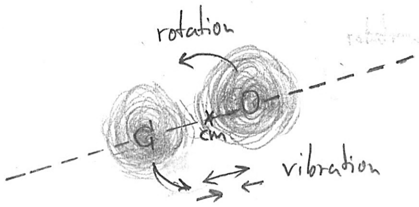
Ex. 8.3:



a) rotation frozen out $\Rightarrow$ only vibration possible → harmonic oscillator potential

$$i\hbar \frac{\partial}{\partial t} \Psi_{(x,t)} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2} D x^2\right)\Psi_{(x,t)}$$

b) possible vibration energy levels?

$$E_v = \hbar\omega\left(v + \tfrac{1}{2}\right) \qquad v \in \mathbb{N}_0$$

c) $\lambda = 4{,}7\ \mu m$ $\qquad \omega = \sqrt{\frac{D}{m}} = \sqrt{\frac{D}{\mu}}$ $\qquad m \to \mu$ reduced mass $\qquad \mu = \frac{m_C m_O}{m_C + m_O}$ $\qquad m_C = 12u$, $m_O = 16u$

In the C-O Mol. case

$= 6{,}857\ u$

$$\omega = 2\pi f = 2\pi\frac{c}{\lambda}$$

$$D = \mu\omega^2 = \mu\left(2\pi\frac{c}{\lambda}\right)^2 = 1829\ \frac{kg}{s^2}$$

d) vibrations frozen out $\Rightarrow$ only rotation possible. $\qquad$ bond length = 100 pm

rotation energy eigenvalues: $\qquad E_{rot} = \frac{\hbar^2 l(l+1)}{2I} \qquad I = \mu r^2 \qquad l \in \mathbb{N}_0$

$$= 305\,\mu eV \cdot l(l+1)$$

$$\Delta E_{rot\ l+1 \leftrightarrow l} = E_{l+1} - E_l = \frac{\hbar^2}{2\mu r^2}\Big((l+1)(l+2) - l(l+1)\Big)$$

$$= \frac{\hbar^2}{2\mu r^2}\left(l^2 + 3l + 2 - l^2 - l\right)$$

$$= \frac{\hbar^2}{2\mu r^2}\, 2(l+1) \overset{!}{=} \frac{hc}{\lambda}$$

$$\lambda_{l \to l+1} = \frac{hc \cdot 2\mu r^2}{\hbar^2 \cdot 2(l+1)}$$

$$= \frac{2{,}034\ mm}{l+1}$$