Gremo na dipolni matrični element:

$$X_{12} = \int \psi_m^* \, x \, \psi_n \, dx \qquad\qquad y H_n(y) = \frac{1}{2} H_{n+1} + n H_{n-1}$$

$$= \frac{1 \quad a}{\sqrt{2^{n+m} n! m! \pi}\, \cancel{\alpha}} \int_{-\infty}^{\infty} \cancel{\alpha} dy \, e^{-y^2} H_m \frac{x}{a} H_n$$

$$= \frac{a}{\sqrt{2^{n+m} n! m! \pi}} \int_{-\infty}^{\infty} dy \, e^{-y^2} H_m \left(\frac{1}{2} H_{n+1} + n H_{n-1} \right)$$

$$= a \left(\frac{1 \cdot \sqrt{2(n+1)} \, \frac{1}{2}}{\sqrt{2^{n+1+m} (n+1)! m! \pi}} \int_{-\infty}^{\infty} dy \, e^{-y^2} H_{n+1} H_m \right.$$

$$\left. + \frac{n}{\sqrt{2^{n-1+m} (n-1)! m! \pi} \sqrt{2n}} \int_{-\infty}^{\infty} dy \, e^{-y^2} H_{n-1} H_m \right)$$

$$= a \left(\sqrt{\frac{n+1}{2}} \, \delta_{m\,n+1} + \sqrt{\frac{n}{2}} \, \delta_{m\,n-1} \right) = \frac{a}{\sqrt{2}} \left(\sqrt{n+1} \, \delta_{m\,n+1} + \sqrt{n} \, \delta_{m\,n-1} \right)$$

IZBIRNO PRAVILO : $\Delta n = \pm 1$; $\tau^{-1} \propto \left(\frac{X_{12}}{\hbar c} \right)^2$.

Na podoben način preverimo VIRIALNI TEOREM $\cancel{2}\langle T \rangle = \cancel{2}\langle V \rangle$

$$\langle V \rangle = \frac{1}{2} m \omega^2 \langle x^2 \rangle$$

$$\langle x^2 \rangle = ? \qquad x^2 H_n = \frac{1}{2} x H_{n+1} + x n H_{n-1} = \frac{1}{4} \cancelto{0}{H_{n+2}} + \frac{1}{2}(n+1) H_n + \frac{1}{2} n H_n + n(n-1) \cancelto{0}{H_{n-2}}$$

$$= \left(n + \frac{1}{2} \right) H_n$$

$$\Rightarrow \langle x^2 \rangle = a^2 \left(n + \frac{1}{2} \right) = \frac{\hbar}{m\omega} \left(n + \frac{1}{2} \right), \quad \langle V \rangle = \frac{1}{2} \hbar \omega \left(n + \frac{1}{2} \right)$$

$$\langle E \rangle = \langle T \rangle + \langle V \rangle = \hbar \omega \left(n + \frac{1}{2} \right)$$

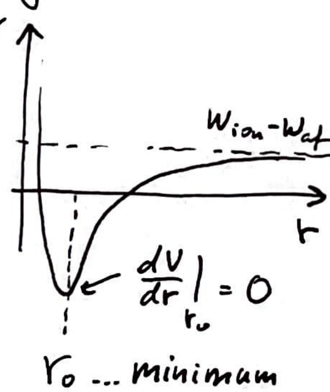
$$\Rightarrow \langle T \rangle = \frac{1}{2} \hbar \omega \left(n + \frac{1}{2} \right) \Rightarrow \langle T \rangle = \langle V \rangle . \checkmark$$

III/39 Vezavna energija molekule Na^+Cl^-

$$V_{odb} = \frac{C}{r^{35}} \quad , W_{ion} = 5{,}14\,eV \, , \quad W_{af} = 3{,}81\,eV$$

$$r_0 = 0{,}89\, r_0^{kristal} \, , M^{Na} = 23\,kg \, , M^{Cl} = 35\,kg \, , \rho^{NaCl} = 2160\,\frac{kg}{m^3}$$

Celotna vezavna energija je vsota ionizacijske, afinitete (z minusom), elektrostatske in odbojne energije



$$V(r_0) = W_{vez} = W_{ion} - W_{af} - \frac{\alpha\hbar c}{r_0} + \frac{C}{r_0^{35}}$$

Najprej določimo C iz minimizacije V

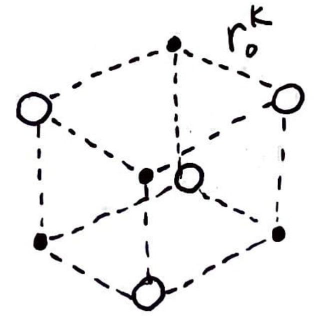
$$V(r) = W_{ion} - W_{af} - \frac{\alpha\hbar c}{r} + \frac{C}{r^{35}}$$

$$\frac{dV}{dr}(r_0) = \frac{\alpha\hbar c}{r_0^2} - \frac{35\,C}{r_0^{36}} = 0 \quad \Rightarrow \quad C = \frac{\alpha\hbar c}{35}\, r_0^{34} .$$

$$V(r) = W_{ion} - W_{af} - \frac{\alpha\hbar c}{r}\left(1 - \frac{1}{35}\left(\frac{r_0}{r}\right)^{34}\right)$$

Sedaj izračunajmo še r_0 v kristalu NaCl, če poznamo ρ in M:

V kubični rešetki se izmenjujeta Na in Cl:



$$V = (r_0^k)^3 \, , \quad \Sigma m = \frac{1}{8}(4m_{Cl} + 4m_{Na}) = \frac{1}{2}(m_{Cl} + m_{Na})$$

$$\rho = \frac{(35 + 23)\, m_p}{2\, r_0^{k\,3}}$$

Tako dobimo: $r_0^K = \sqrt[3]{\frac{29 m_p}{\rho}} = \sqrt[3]{\frac{29 \cdot 2 \cdot 10^{-27} kg}{2{,}2 \cdot 10^3 kg/(10^9 m)^3}} = 0{,}28$ nm.

In za molekulo velja $r_0 = 0{,}89\, r_0^K$

Sedaj dobimo vezavno energijo $W_{vez} = V(r_0)$

$$W_{vez} = W_{ion} - W_{af} - \frac{\alpha \hbar c}{r_0}\left(1 - \frac{1}{35}\right) =$$

$$= W_{ion} - W_{af} - 1.11\, \frac{\alpha \hbar c}{r_0^K}\, \frac{34}{35} = -\,\underline{\underline{4.16\, eV}}.$$

Nazadnje nas zanima popravek zaradi nihanja okoli ravnovesja. Tega dobimo z razvojem V do 2. reda:

$$V(r) \simeq V(r_0) + \underbrace{\frac{dV}{dr}\bigg|_{r_0}}_{\overset{\shortparallel}{0}}(r-r_0) + \frac{1}{2}\underbrace{\frac{d^2V}{dr^2}\bigg|_{r_0}}_{m\omega^2}(r-r_0)^2 + \dots$$

in $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$

m je reducirana masa $\frac{1}{m} = \frac{1}{m_{Na}} + \frac{1}{m_{Cl}} = \left(\frac{1}{23} + \frac{1}{35}\right)\frac{1}{m_p}$

$$\Rightarrow m = \frac{23 \cdot 35}{58}\, m_p.$$

$$\frac{d^2V}{dr^2}\bigg|_{r=r_0} = -\frac{2\alpha\hbar c}{r_0^3} + 36\,\frac{\alpha \hbar c\, r_0^{34}}{r_0^{37}} = \frac{\alpha\hbar c}{r_0^3}\cdot 34 = m\omega^2$$

$$\Rightarrow \omega = \sqrt{\frac{34\alpha\hbar c}{m r_0^3}} \quad \text{in} \quad E^{nih}_{n=0} = \hbar\omega\left(\overset{0}{\overset{\shortparallel}{n}} + \frac{1}{2}\right) = \frac{1}{2}\hbar\omega$$

$$= \frac{1}{2}\hbar\sqrt{\frac{34\alpha\hbar c \cdot 58}{23 \cdot 35\, m_p\, r_0^3}} = 0{,}047\, eV.$$

$$W_{vez} = W_{vez}^0 + E_{nih} = (-4{,}16 + 0{,}05)\, eV = -\,\underline{\underline{4{,}11\, eV}}.$$

III 138 Zanima nas nihajni prispevek eksponentnega potenciala. Ponovno razvijemo okoli ravnovesne lege in izvrednotimo za $n=0,1$.

$V_0 = 3\,\mathrm{eV}$

$a = 0{,}12\,\mathrm{nm}$

$M = 16$

$$V = V_0\left(e^{-\frac{2(r-r_0)}{a}} - 2e^{-\frac{r-r_0}{a}}\right)$$

$$\frac{1}{m} = \frac{1}{m_1} + \frac{1}{m_2} = \frac{\cancel{2}}{\cancel{16}m_p\,8}$$

$$m = 8m_p$$

• Pri $r=r_0$ je eksponent majhen in $e^x \sim 1 + x + \frac{x^2}{2} + \dots$

$$V \approx V_0\left(1 - 2\cancel{\frac{r-r_0}{a}} + \frac{2\cancel{4}}{\cancel{2}}\left(\frac{r-r_0}{a}\right)^2 - 2 + 2\cancel{\frac{r-r_0}{a}} - \left(\frac{r-r_0}{a}\right)^2 + \dots\right)$$

$$\simeq -V_0 + \underbrace{\frac{V_0}{a^2}}_{\frac{1}{2}m\omega^2}\underbrace{(r-r_0)^2}_{x^2} + \dots \qquad E_n = \hbar\omega\left(n+\tfrac{1}{2}\right), \quad n = 0,1,2\dots$$

$$\hbar\omega = \hbar\sqrt{\frac{2V_0}{\underset{8m_p}{\underset{\shortparallel}{m}}a^2}} = \frac{\hbar c}{2a}\sqrt{\frac{V_0}{m_pc^2}} \cong \frac{200\,\mathrm{eV\,nm}}{2\cdot 0{,}12\,\mathrm{nm}}\sqrt{\frac{3\,\mathrm{eV}}{4\,\mathrm{GeV}}} = \frac{100\sqrt{30}}{0{,}12\cdot 10^5}\,\mathrm{eV}$$

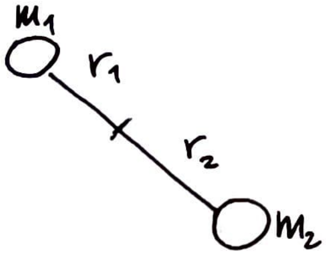
$$\doteq \underline{46\,\mathrm{meV}}.$$

Tako smo dobili $E_0 = \frac{1}{2}\hbar\omega = 23\,\mathrm{meV}$,

$E_1 = \frac{3}{2}\hbar\omega = 69\,\mathrm{meV}$.

III / 130 Rotacijski spekter molekule H_2, HD, D_2

$r_0 = 0{,}074$ nm



$r_0 = r_1 + r_2$

$m_1 r_1 = m_2 r_2$

$= m_2 (r_0 - r_1)$

$r_1 = r_0 \dfrac{m_2}{m_1 + m_2}$

$r_2 = r_0 \dfrac{m_1}{m_1 + m_2}$

KLASIČNO : $E_{rot} = \dfrac{p^2}{2J}$

KVANTNO : $\langle E_{rot} \rangle = \dfrac{\langle L^2 \rangle}{2J} = \dfrac{\hbar^2 l(l+1)}{2J}$

Vztrajnostni moment :

$$J = J_1 + J_2 = m_1 r_1^2 + m_2 r_2^2 = \left(\frac{m_1 m_2^2}{(m_1+m_2)^2} + \frac{m_2 m_1^2}{(m_1+m_2)^2} \right) r_0^2$$

$$= \frac{m_1 m_2}{m_1 + m_2} r_0^2 \quad , \quad \frac{1}{m} = \frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 + m_2}{m_1 m_2} \quad , \quad m = \frac{m_1 m_2}{m_1 + m_2}$$

$= m r_0^2$, kjer je m reducirana masa.

Poglejmo si prispevke za H_2, $\underset{pn}{HD}$ in D_2 , $m_{H_2} = 2 m_p$

$m_{HD} \cong 3 m_p$, $m_{D_2} \approx 4 m_p$

$$\langle E_{rot} \rangle = \frac{\hbar^2}{2 m r_0^2} l(l+1)$$

Reducirane mase so : $\dfrac{1}{m} = \dfrac{1}{m_p} + \dfrac{1}{m_p} = \dfrac{2}{m_p}$ za H_2 ,

$= \dfrac{1}{m_p} + \dfrac{1}{2m_p} = \dfrac{3}{2m_p}$ za HD ,

$= \dfrac{1}{2m_p} + \dfrac{1}{2m_p} = \dfrac{1}{m_p}$ za D_2 .

$$E_{rot}^{H_2} = \frac{\hbar^2 c^2}{\cancel{2} \frac{m_p}{\cancel{2}} c^2 r_0^2} l(l+1) \; , \; \frac{(200 \text{ eV nm})^2}{\text{GeV } (0{,}074 \text{ nm})^2} = \underline{\underline{7{,}6 \text{ meV}}}$$

$$\parallel$$

$$\frac{(\hbar c)^2}{m_p c^2 r_0^2}$$

Za osnovno stanje z $l=0$ smo dobili 0

$$H_2: \frac{\hbar c}{2mc^2 r_0^2} = \underline{7{,}6\ \mathrm{meV}}, \quad HD: \frac{\hbar c}{2\left(\frac{2}{3}m_p c^2\right)r_0^2} = \frac{3}{4}\frac{\hbar c}{m_p c^2 r_0^2} = \underline{5{,}6\ \mathrm{meV}}$$

$$\frac{\hbar c}{m_p c^2 r_0^2}$$

in

in na koncu še D_2: $\frac{\hbar c}{2(m_p c^2) r_0^2} = \underline{3{,}8\ \mathrm{meV}}$

Popravki za višja vzbujena stanja so tako: [meV]

l	$E_{rot}^{H_2}$	E_{rot}^{HD}	$E_{rot}^{D_2}$	degeneracija $(2l+1)$
0	0	0	0	1
1	15	11	7,5	3
2	45	33	23	5
3	90	66	45	7

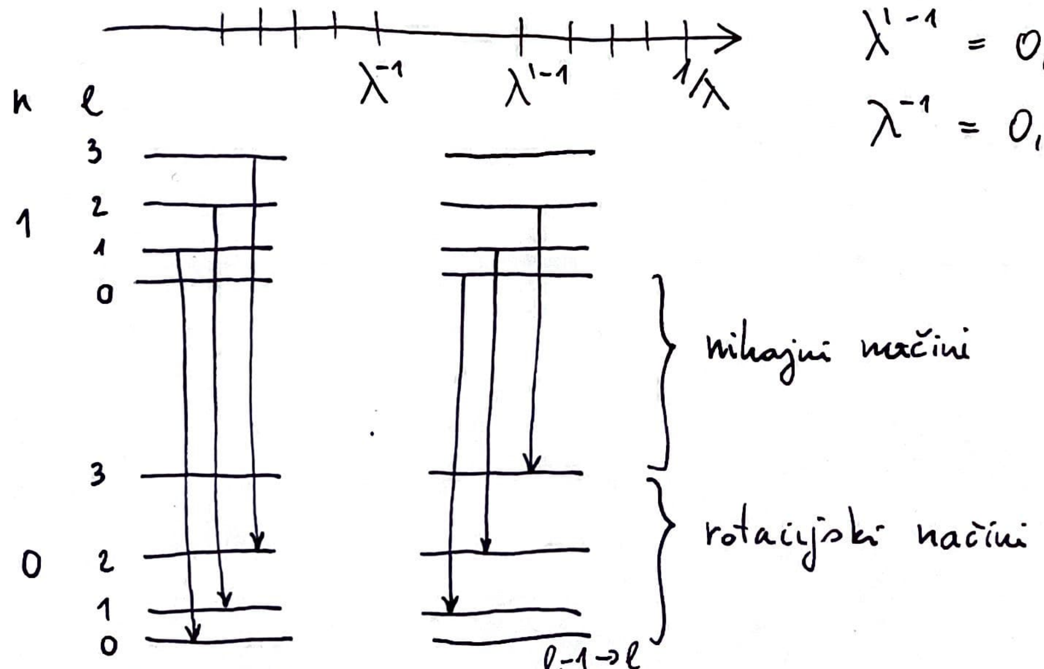
III /135 Vibracijsko-rotacijski spekter molekul

$$E = E_0 + E_{vib} + E_{rot} = E_0 + \hbar\omega\left(n+\tfrac{1}{2}\right) + \frac{\hbar^2}{2J}\,l(l+1)$$

$\Delta n = \pm 1$, $\Delta l = \pm 1$

$\lambda'^{-1} = 0{,}2907\ \mathrm{pm}^{-1}$

$\lambda^{-1} = 0{,}2866\ \mathrm{pm}^{-1}$



"R"-veja, $l+1 \to l$; "P"-veja, $l-1 \to l$

V R-veji preidemo iz $l+1 \to l$, zato velja:

$l=0,1,2$

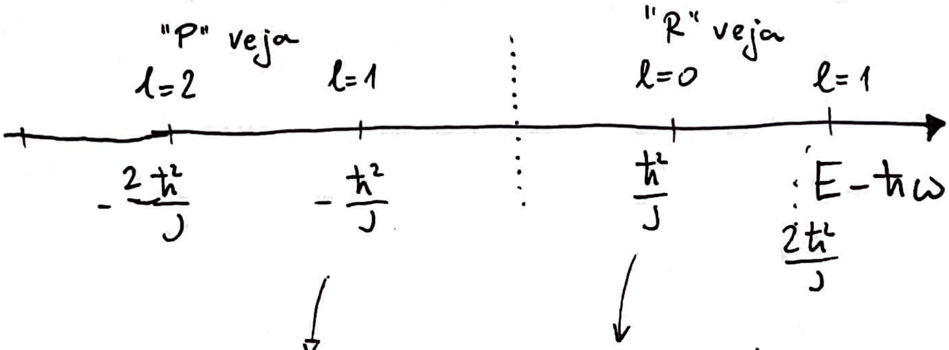
$$\Delta E_R = \hbar\omega + \frac{\hbar^2}{2J}\left((l+1)(l+2) - l(l+1)\right) = \hbar\omega + \frac{\hbar^2}{\cancel{2}J}(\cancel{2}l+\cancel{2}\,1)$$

$$\Delta E_P = \hbar\omega + \frac{\hbar^2}{2J}\left((l-1)l - l(l+1)\right) = \hbar\omega - \frac{\hbar^2}{J}l \,, \quad l=1,2,\ldots$$

$$\Delta E_R = \hbar\omega + \frac{\hbar^2}{J}(l+1),$$

$$\Delta E_P = \hbar\omega - \frac{\hbar^2}{J}l \,.$$

Poglejmo si, kako so razporejene energije fotonov



$$E_P = \frac{2\pi\hbar c}{\lambda} = \hbar\omega - \frac{\hbar^2}{J}, \quad E_R = \frac{2\pi\hbar c}{\lambda'} = \hbar\omega + \frac{\hbar^2}{J}.$$

Iz vsote in razlike E_R in E_P dobimo r_0 in k.

$$E_R - E_P = \frac{2\hbar^2}{J} = \frac{2\hbar^2}{mr_0^2}, \quad m = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{35}{36}m_p$$

$$= 2\pi\hbar c\left(\lambda^{-1} - \lambda'^{-1}\right).$$

$$\Rightarrow r_0^2 = \frac{\cancel{2}\hbar^{\cancel{2}}}{m\,\cancel{2\pi}\cancel{\hbar}c\left(\lambda^{-1}-\lambda'^{-1}\right)} \Rightarrow r_0 = \sqrt{\frac{\hbar c}{mc^2\left(\lambda^{-1}-\lambda'^{-1}\right)}} = \underline{0{,}13\ \mu m}.$$

$$E_R + E_P = 2\hbar\omega = 2\hbar\sqrt{\frac{k}{m}} = 2\pi\hbar c\left(\lambda^{-1}+\lambda'^{-1}\right)$$

$$\Rightarrow k = mc^2\pi^2\left(\lambda^{-1}+\lambda'^{-1}\right)^2 = 3\,\frac{keV}{nm^2} = 481\,\frac{N}{m}.$$