Ro-vibrational spectra of diatomic molecules

Mittwoch, 2. Februar 2022 16:10

Rotational & vibrational excitations

Born-Oppenheimer approx → e^- faster → see before
nuclear d.o.f. are treated separately

⇒ total w.f. separates into

- w.f. of electronic states $\Psi^0_{\{k\}}(\{\vec{r}_i\}, \{\vec{R}_i\})$

electronic quantum numbers

e^- coordinates

nucl. coordinates $\hat{=}$ parameters

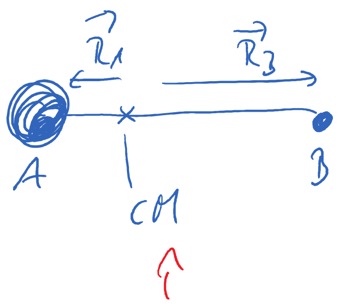
- w.f. of nuclear coordinates $\xi(\vec{R}_i)$

$$\Rightarrow \text{total w.f.} = \Psi_{\{k\}}(\{\vec{r}_i\}, \{\vec{R}_i\}) = \xi(\vec{R}_i) \cdot \Psi^0_{\{k\}}(\{\vec{r}_i\}, \{\vec{R}_i\})$$

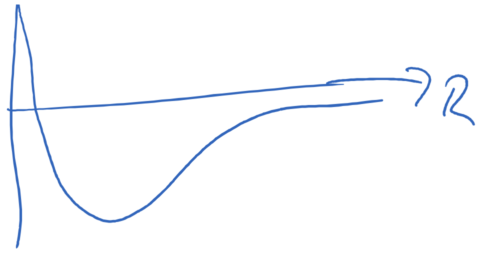
e^- w.f. ⇒ done ✓

now: S.E. for the nuclei

$$\left(\frac{-\hbar^2}{2M_A}\Delta_A + \frac{-\hbar^2}{2M_B}\Delta_B + \underbrace{E_{pot}\{\{\vec{R}_j\};\{k\}\}}\right)\xi(\{\vec{R}_j\}) = E\,\xi(\{\vec{R}_j\})$$



these are the potential curves we looked at before



→ Into CM system:

$$\left(\frac{-\hbar^2}{2M}\Delta + E_{pot}(R,u)\right)\xi(\vec{R}) = E\,\psi(\vec{R})$$

$$M = \frac{M_A \cdot M_B}{M_A + M_B}$$ reduced mass

⇒ system becomes rotationally symmetric

⇒ spherical coordinates $\xi(R,\theta,\varphi) = S(R)\cdot Y(\theta,\phi)$

á la H atom !!!

angular part $Y(\theta,\phi)$ → quantum numbers

atom: l, m_l

molecules: J, m_J

radial part: 1D S.E. for R

$$\left\{\underbrace{\cancel{\frac{d}{R^2 dR}\left(R^2\frac{d}{dR}\right)}}_{=0 \text{ for } R=\text{const}} + \frac{2M}{\hbar^2}\left[E - E_{pot} - \frac{J(J+1)\hbar^2}{2MR^2}\right]\right\}S(R) = 0$$

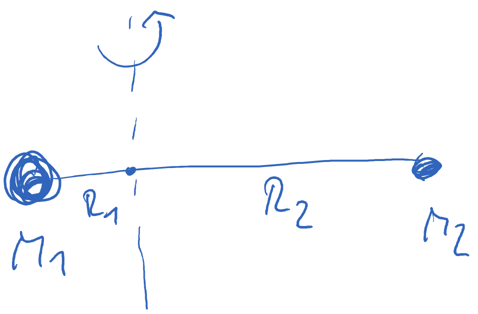
trivial if R = const

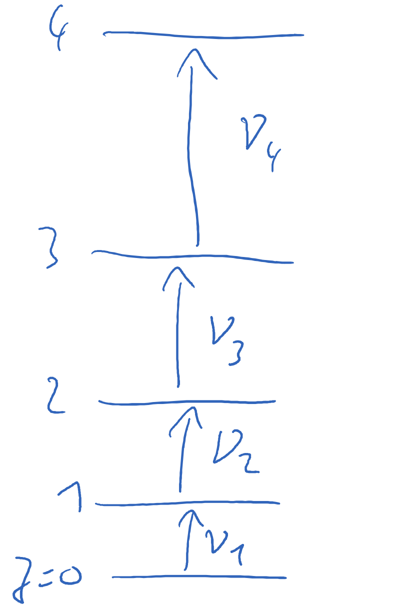
$E = E_{tot} = E_{kin} + E_{pot}$

↳ no vibration, only rotation

≙ rigid rotor

$$E_{kin} = E_{rot} = \frac{J(J+1)\hbar^2}{2MR^2}$$

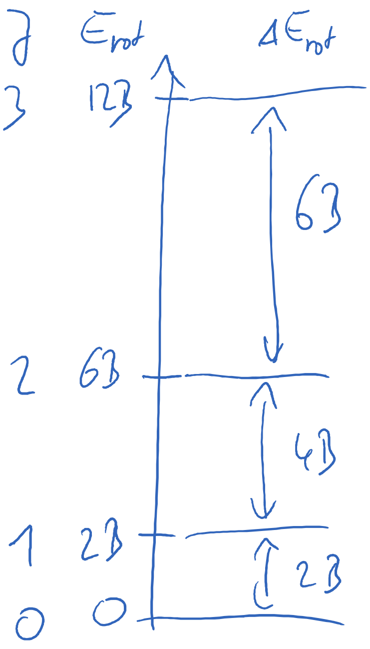




<u>not</u> equidistant!

$$\Delta E = E(J+1) - E(J) =$$

$$= \frac{1}{2MR^2}\,2(J+1) \equiv 2B_e(J+1)$$



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Schwingungskonstanten für zweiatomige Moleküle

Molekül	$\omega_e = \frac{\hbar\omega}{hc}[cm^{-1}]$	$\hbar\omega\,[eV]$
H_2	4395	0.55
Li_2	351	0.044
N_2	2359	0.296
O_2	1580	0.198
NO	1904	0.239
I_2	214	0.027
ICl	384	0.048
HCl	2990	0.376

Rotationskonstanten

Molekül	B_e (meV)
H_2	7,64
Li_2	0,085
N_2	0,253
O_2	0,182
NO	0,22
I_2	0,005
ICl	0,014
HCl	1,33

$B_e \approx$ meV

$T \approx 300\,K = RT$

≙ thermal energies $\boxed{kT = 25\,meV}$

⇒ at RT: molecules rotate at quite high quantum numbers

Vibrations $\rightarrow$ tomorrow