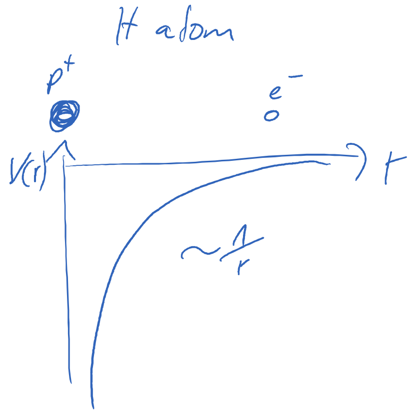
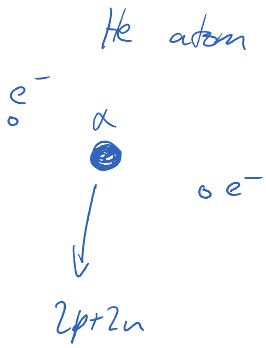
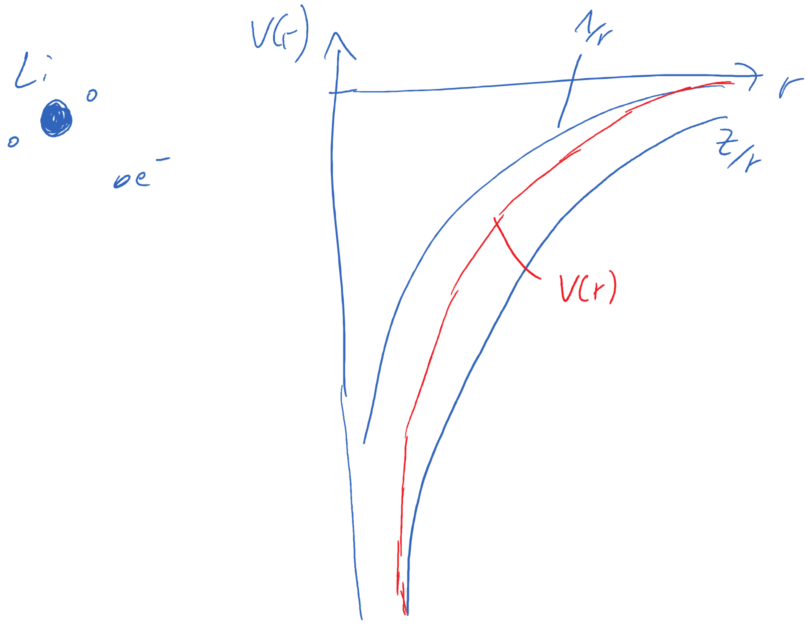
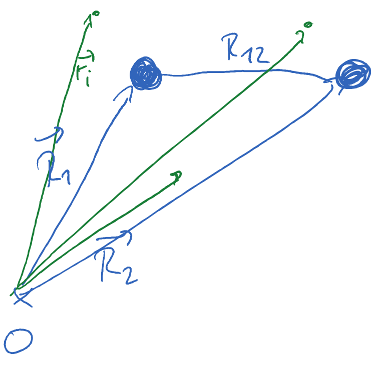
Molecular physics







molecules (diatomic) H_2, CO, H_2^+, N_2, O_2, ...



CO_2, H_2O, CH_4

<u>large ratio</u> of mass between nuclei & electrons

$$\frac{m_e}{M} \approx 10^{-3} \dots 10^{-5}$$

$\Rightarrow$ enables most <u>important approximation</u> in mol. phys.

Coulomb force acts on all

e^- velocities are <u>much faster</u>

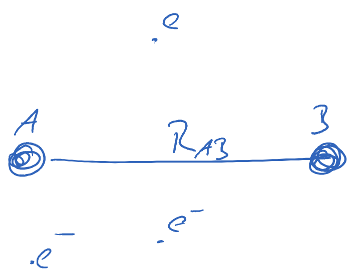
$\rightarrow$ <u>nuclei</u> stay essentially <u>fixed</u>

typical internuclear distances $R_{AB} \sim 0.075\,nm \dots 0.18\,nm$

O_2: $0.12\,nm$

N_2: $0.11\,nm$

Hamiltonian: center-of-mass



<u>kin. energy</u>

$$\hat{T}_n = -\frac{m_e}{2M} \nabla_R^2 \leftarrow R_{AB} \text{ internuclear distance}$$

$$\hat{T}_e = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_{r_i}^2\right)$$

$\uparrow$ electron coordinates

reduced mass

$$\bar{M} = \frac{M_A \cdot M_B}{M_A + M_B} \qquad \left(\frac{1}{\bar{M}} = \frac{1}{M_A} + \frac{1}{M_B} \right)$$

Coulomb potential

$$V(\vec{r}, \vec{R}) = -\sum_{i=1}^{N} \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} - \sum_{i=1}^{N} \frac{Z_B}{|\vec{r}_i - \vec{R}_B|} + \sum_{\substack{i,k=1 \\ i<k}}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_k|} + \frac{Z_A Z_B}{R}$$

Total $\hat{H} = \hat{T}_n(\vec{R}) + \hat{T}_e(\vec{r}) + V(\vec{r}, \vec{R})$

all nuclear coordinates

all electrons

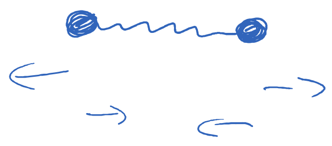
S.E. $\hat{H} \Psi(\vec{r}, \vec{R}) = W \Psi(\vec{r}, \vec{R})$ $\rightarrow$ Hertel Schulz

Molecules have

- electronic excitations

  à la atoms

- vibrational excitations



- rotational excitations

- electronic energy

  electron orbitals $\langle r \rangle \approx R_{AB}$ bond length

  $\hookrightarrow a_{Bohr}$

  uncertainty principle : $p = \frac{\hbar}{\langle r \rangle}$ momentum

  $$\langle \hat{T}_r \rangle = \frac{p^2}{2m_e}$$

  Virial theorem :

  for $\frac{1}{r}$ potentials $\quad 2\langle \hat{T}_r \rangle = -\langle V_e \rangle$

  kin. pot. energy

  $\rightarrow$ binding energy of e^- in molecule

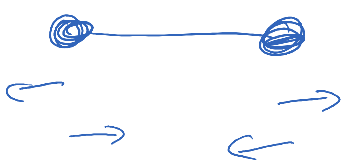
  $$W_e = \langle \hat{T}_r \rangle + \langle V_e \rangle = -\langle \hat{T}_r \rangle = \frac{p^2}{2m_e} = -\frac{\hbar^2}{2m_e \langle r \rangle^2} \approx \underline{\underline{5\,eV}}$$

  $\hat{=}$ e^- in atoms $\qquad \hat{=}$ optical (UV-vis-NIR) transitions

- vibrational energy

  harmonic oscillator : $F = -k \cdot R$

  $$\omega_v = \sqrt{\frac{k}{M}}$$



  consider force on electron ~ same

$u \sim$ same

$$\omega_e = \sqrt{\frac{u}{m_e}}$$

estimate $\Rightarrow$ $$W_v = \sqrt{\frac{m_e}{\bar{M}}} \cdot W_e \lesssim 0.1\,eV$$

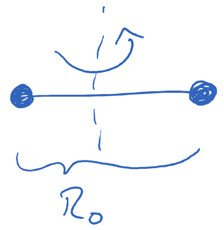
$\Rightarrow$ infrared transitions

HCl : $W_v \sim 0.37\,eV$

$$\lambda = 3.33\,\mu m$$

wavenumber $\bar{\nu} = \frac{1}{\lambda} = 3000\,cm^{-1}$

- rotational energies



ang. mom. op $\hat{N}$

rotational quantum number N

$$\langle \hat{N}^2 \rangle = 2\hbar^2$$

moment of inertia $I_0 = \bar{M} R_0^2 = \bar{M} \langle r^2 \rangle$

$$W_N = \frac{\langle \hat{N}^2 \rangle}{2MR^2} \simeq \frac{\hbar^2}{\bar{M} \langle r^2 \rangle} = \frac{m_e}{\bar{M}} W_e$$

$$\simeq 10^{-3} \dots 10^{-4}\, W_e \simeq 1 \dots 10\, meV$$

for IR & μwave transitions $\bar{\nu} = 1\,cm^{-1} \dots 10\,cm^{-1}$