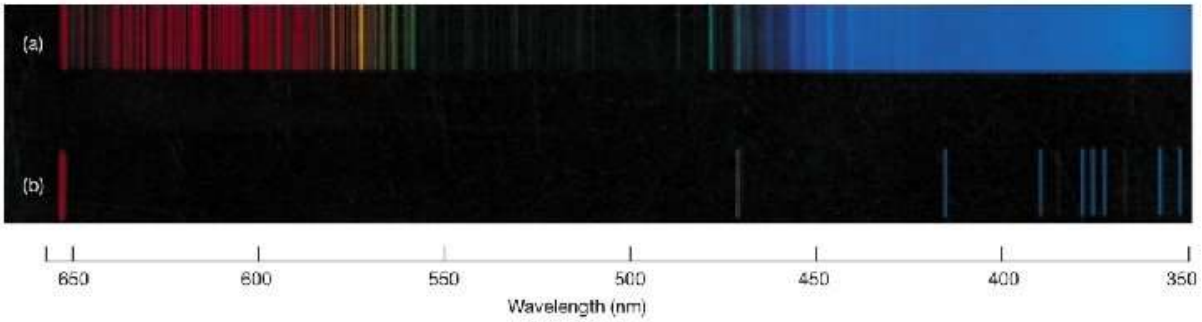
Molecular physics

Molecules

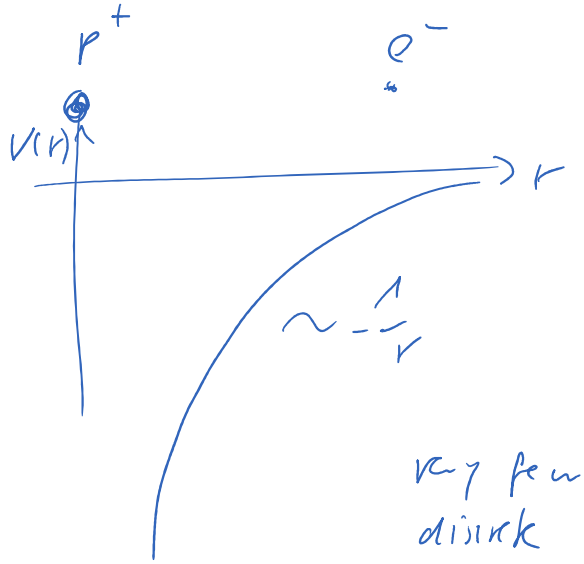
Molecular spectra are much more complex than atomic spectra, even for hydrogen:

(a) Molecular hydrogen **(b) Atomic hydrogen**



H-atom

simple

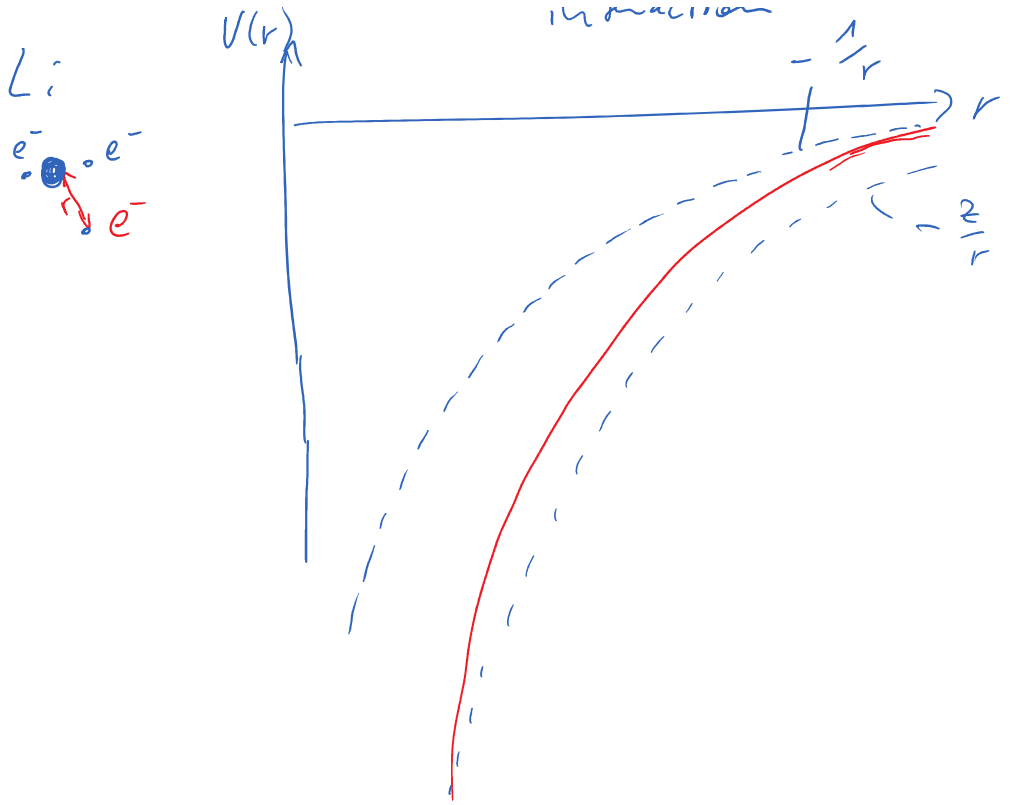


very few distinct wavelengths

He atom

He gets complicated by e-e interaction

Li:



what's the difference between

He and H_2^+

2 Coulomb centers, from heavy particles

→ scale separation

e^- excitation

e^- excitation

nuclear motion

⇓

rotations & vibrations

e^- excitation

large ratio $\frac{m_e}{M_{nucl.}}$

M_{nucl}

2 diatomic molecules H_2^+, H_2,

O_2, N_2, CO

others may be more important: H_2O, CO_2, CH_4, ...

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

enables most important approximation in molecular physics

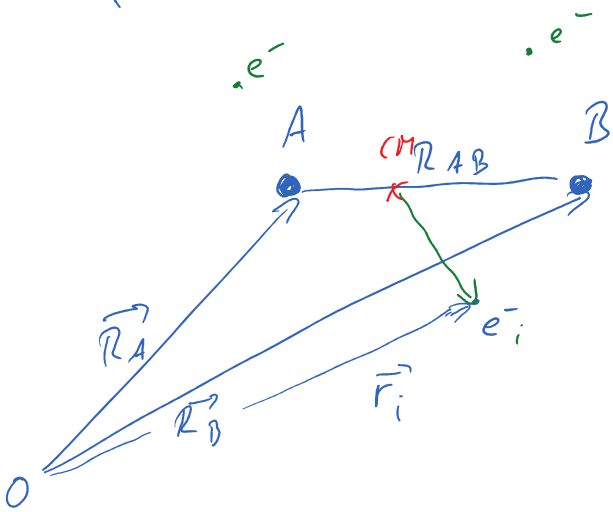
↳ Born–Oppenheimer approximation

Coulomb force acts on e^- & nuclei

but e^- velocities are much faster

snapshot: fixed positions of nuclei

(nuclear motion is much slower, electrons rearrange quickly)



typical $R_{AB} \sim 0.07 \dots 0.2$ nm

O_2: 0.12 nm

Hamiltonian: center of mass system

kin. energy: $T_n = -\frac{m_e}{2M} \nabla_R^2$

kin. energy : $T_n = -\frac{m_e}{2M}\nabla^2_R$ ← R_{AB} internuclear distance

$T_e = \sum_{i=1}^{N}\left(-\frac{m_e}{2}\nabla^2_{r_i}\right)$ ← electron coordinates

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

Coulomb potential

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

... SE ...

Molecules have

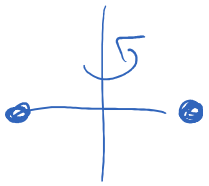
- electronic excitation a la atoms

energy $W_e \approx 5\,eV$ a la atoms

- vibrations

energy $W_v = 0.5\,eV$ $\lambda \simeq 3\,\mu m$

- rotations



energy $W_r \sim 10\,meV$

μwave transitions