$$\hat{H}(H_2^+) \neq \underbrace{\frac{\vec{p}^{\,2}}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R}}_{\hat{H}_{e^-}} + K_{nuclei}$$

$$K_{nuclei} = \frac{\vec{p}_A^{\,2}}{2m_H} + \frac{\vec{p}_B^{\,2}}{2m_H}$$

the nuclei move (rotate and vibrate)

How could we possibly neglect that?

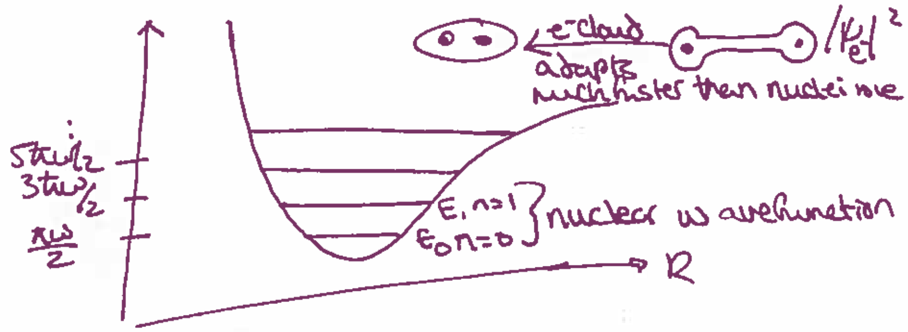
For the harmonic oscillator

$$E = \hbar\sqrt{\frac{k}{m}}\left(n+\tfrac{1}{2}\right) \sim \frac{1}{\sqrt{m}} \implies \text{generally true for any particle}$$

$$\implies \frac{K_{nuclei}}{K_{e^-}} \sim \sqrt{\frac{m_e}{m_n}} \sim \sqrt{\frac{1}{1836}} \sim \frac{1}{43}$$ % error is small

so $\left\langle \frac{\vec{p}_{A,B}^{\,2}}{2m_H} \right\rangle \sim \frac{1}{43}\left\langle \frac{\vec{p}^{\,2}}{2m_e} \right\rangle \implies$ Can solve e^- by keeping a fixed R

$$E(R) = \langle \psi_0 | \hat{H}_{e^-} | \psi_0 \rangle$$



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1) Delete the small $\hat{K}_{nuc}$ and solve

$$\hat{H}_e\,\psi_0(\vec{r}_1, \vec{r}_2 \ldots) = E(R)\,\psi_0(\vec{r}_1, \vec{r}_2 \ldots$$

e.g. ground

2) Take $E(R)$ as the potential energy within which nuclei move and let

$\hat{H}_{nuc} = \hat{K}_{nuc} + E(R)$ to solve

$$\hat{H}_{nuc}\,\chi_n(R) = E_n\,\chi_n(R)$$

$\psi_{tot}(\vec{r}_1, \vec{r}_2 \ldots \vec{R}_1, \vec{R}_2 \ldots) \approx \psi_n(\vec{r}_1 \ldots) \cdot \chi_n(R_1 \ldots) \cdot Y_{JM_J}(\theta, \varphi)$

n=0 is e⁻ groundstate

n=0 is the nuclear ground state

$E_{tot} = E_{elec} + E_{nuc} \approx E_n$

schrödinger eq. #2 ~~also~~ already includes E(R) of electrons

(see handout)