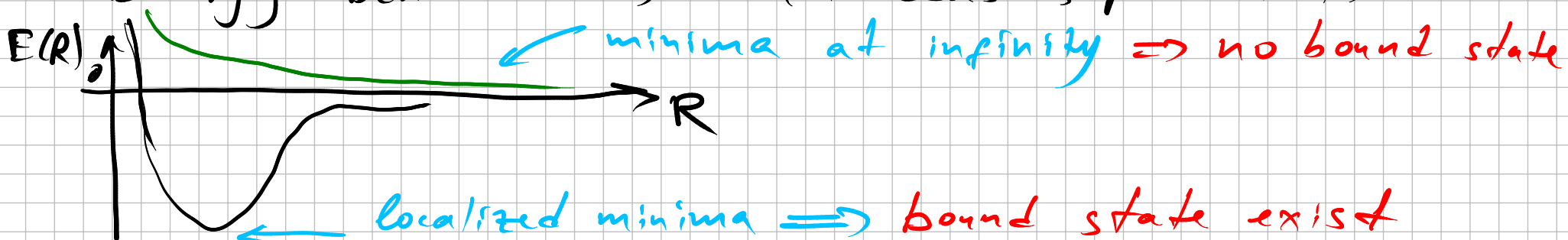


Molecules (at least simple ones)

We saw that there is no analytical solution for He (1 nucleus and 2 electrons), so there is little hope to have solutions for a general molecule (many electrons and at least two nucleus).

So in general we would be concern with a question: can the system bound?
i.e. is combined ground state energy lower
than constituting parts?

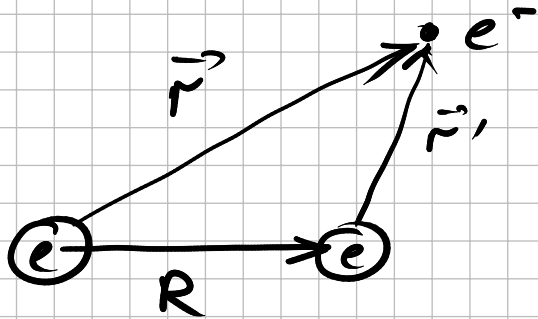
If we somehow can predict the ground level Energy behavior vs R (nucleus separation)



Hydrogen molecule ion

this is the next "easier" case

Born-Oppenheimer approximation



Nucleus are heavy \Rightarrow slow so we will disregard their relative motion with respect to the center of mass.

$$\hat{H} = \frac{p^2}{2m_e} - \frac{e^2}{r} - \frac{e^2}{r'} + \frac{e^2}{R}$$

As usual, the art is in choosing good ansatz ψ .

We will use

$$\psi = c (\psi_{10}(r) \pm \psi_{10}(r'))$$

nucleus repulsion for any ψ

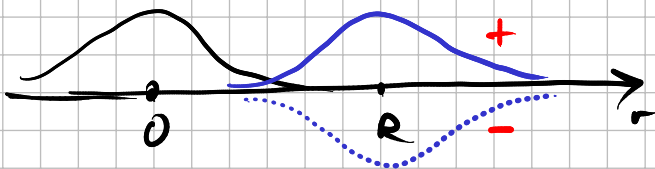
R is constant in our model

$$\left\langle \frac{e^2}{R} \right\rangle = \frac{e^2}{R} = \frac{e^2}{a_0} \frac{a_0}{R} = -2 \frac{a_0}{R} \cdot E_g(z=1)$$

Hydrogen ground level eigen state

Hydrogen ground energy

$$\vec{r}' = \vec{r}_0 - \vec{R}$$



right now it is unclear which + or - is better. But if we think that two nuclei repel each other \Rightarrow we need electron in between, so '+' is more promising

Ψ in the form of $(\psi_{10}(r) + \psi_{10}(r'))$ is what quantum chemist call a linear combination of atomic orbitals (LCAO).

Our 1st task to normalize Ψ

$$\langle \Psi | \Psi \rangle = c^2 \left(\langle \psi_{10}(r) | \psi_{10}(r) \rangle + \langle \psi_{10}(r') | \psi_{10}(r') \rangle + \pm 2 \langle \psi_{10}(r) | \psi_{10}(r') \rangle \right)$$

$$= c^2 2 \left(1 \pm \underbrace{\langle \psi_{10}(r) | \psi_{10}(r') \rangle}_{\text{overlap integral which we label } I} \right)$$

overlap integral which we label I

$$\text{Recall } \psi_{10}(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

Calculation of I is tedious (see Ch.8 Griffiths)

$$I = e^{-R/a} \left[1 + \left(\frac{R}{a} \right) + \frac{1}{3} \left(\frac{R}{a} \right)^2 \right]$$

$$c^2 = \frac{1}{2(1 \pm I)}$$

Next we need the expectation value of truncated \hat{H}_T (no nucleus repulsion) $\frac{p^2}{2m} - \frac{e^2}{r} - \frac{e^2}{r'}$

Observe that

$$\hat{H}_T |\psi_{10}(r)\rangle = \left(\underbrace{\frac{p^2}{2m} - \frac{e^2}{r}}_{\hat{H} \text{ of } H_{\text{hydrogen}}} - \frac{e^2}{r'} \right) |\psi_{10}(r)\rangle =$$

$$= \underbrace{E_g(z=1)}_{\text{ground energy of Hydrogen}} |\psi_{10}(r)\rangle - \frac{e^2}{r'} |\psi_{10}(r)\rangle$$

↑ no prime
↑ prime

Similarly

$$\hat{H}_T |\psi_{10}(r')\rangle = E_g(z=1) |\psi_{10}(r')\rangle - \frac{e^2}{r} |\psi_{10}(r')\rangle$$

$$\langle \psi | \hat{H}_T | \psi \rangle = \langle \psi | \hat{H}_T | c (\underbrace{\psi_{10}(r) \pm \psi_{10}(r')}_{\psi}) \rangle =$$

$$= E_g(z=1) - c^2 e^2 \left(\langle \psi_{10}(r) \pm \psi_{10}(r') | \left(\frac{1}{r'} |\psi_{10}(r)\rangle \pm \frac{1}{r} |\psi_{10}(r')\rangle \right) \right)$$

$$= E_g(z=1) - c^2 e^2 \left[\begin{aligned} &\langle \psi_{10}(r) | \frac{1}{r'} |\psi_{10}(r)\rangle \pm \langle \psi_{10}(r) | \frac{1}{r} |\psi_{10}(r')\rangle \\ &\langle \psi_{10}(r') | \frac{1}{r} |\psi_{10}(r')\rangle \pm \langle \psi_{10}(r') | \frac{1}{r'} |\psi_{10}(r)\rangle \end{aligned} \right]$$

!! ← variable relabel → !!

$$\langle H_T \rangle = E_g(z=1) - \frac{2C^2 2e^2}{2a} \left[\underbrace{a \langle \Psi_{10}(r) | \frac{1}{r} | \Psi_{10}(r) \rangle}_{D\text{-direct integral}} \pm \underbrace{a \langle \Psi_{10}(r) | \frac{1}{r} | \Psi_{10}(r') \rangle}_{X\text{-exchange integral}} \right]$$

$= E_g(z=1)$

$$D = \frac{a}{R} - \left(1 + \frac{a}{R}\right) e^{-2R/a}$$

$$X = \left(1 + \frac{R}{a}\right) e^{-R/a}$$

$$\langle H \rangle = \langle H_T \rangle - \underbrace{\frac{2a}{R} E_g(z=1)}_{\text{nuclear repulsion}} = \left[\left(1 + 2 \frac{D \pm X}{1 \pm I}\right) - \frac{2a}{R} \right] E_g(z=1)$$

notice that we can introduce unitless parameter $\lambda = \frac{R}{a}$ and search for minimum

$$\lambda_{\min} \text{ for } (+) \text{ case } \frac{R}{a} = 2.4 \Rightarrow R = 1.3 \text{ \AA}$$

$$\langle H \rangle - E_g(z=1) = 1.8 \text{ eV}$$

https://quantummechanics.ucsd.edu/ph130a/130_notes/node398.html

