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 (<u>many</u> 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 <u>lower</u> than constituting parts?

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

minima at infinity $\Rightarrow$ no bound state

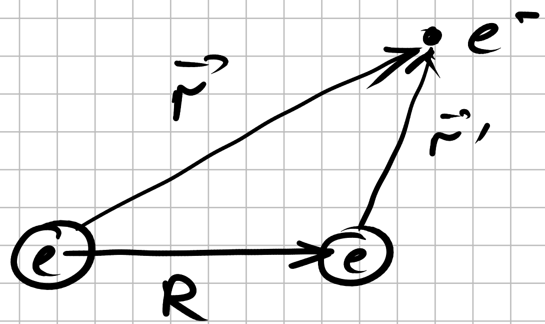
localized minima $\Longrightarrow$ bound state exist

Hydrogen molecule ion

this is the next "easiest" case

Born-Oppenheimer approximation

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



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

nucleus repulsion for any ψ

R is constant in our model!

$$\left\langle \frac{e^2}{R} \right\rangle = \frac{e^2}{R} = \frac{e^2}{a_0}\,\frac{a_0}{R}$$

$$= -\frac{2a_0}{R}\cdot E_g(z=1)$$

Hydrogen grond energy

As usual, the art is in chosing good anzatz ψ.

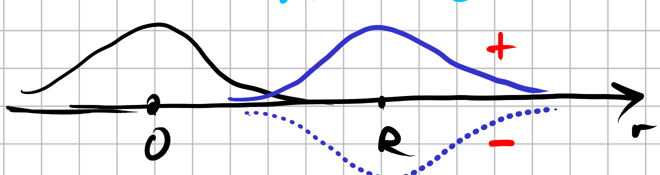
We will use

$$\psi = C\left(\psi_{10}(r) \pm \psi_{10}(r')\right), \qquad \vec{r}\,' = \vec{r} - \vec{R}$$

Hydrogen grond level eigen state

n l

right now it is unclear which + or − is better. But if we think that two nuclei repel each other $\Longrightarrow$ 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

$$\langle\psi|\psi\rangle = c^2\left(\overbrace{\langle\psi_{10}(r)|\psi_{10}(r)\rangle}^{=1} + \overbrace{\langle\psi_{10}(r')|\psi_{10}(r')\rangle}^{=1} + \pm 2\langle\psi_{10}(r)|\psi_{10}(r')\rangle\right)$$

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

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

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

$$\boxed{\begin{aligned} I &= e^{-R/a}\left[1 + \left(\frac{R}{a}\right) + \frac{1}{3}\left(\frac{R}{a}\right)^2\right] \\ c^2 &= \frac{1}{2(1 \pm I)} \end{aligned}}$$

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

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

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

prime   no prime

Similarly

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

$$\langle\psi|H_T|\psi\rangle = \langle\psi|H_T|\underbrace{C(\psi_{10}(r) \pm \psi_{10}(r'))}_{\psi}\rangle =$$

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

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

'' ← variable relabel → ''

$$\langle\psi_{10}(r')|\frac{1}{r}|\psi_{10}(r')\rangle \pm \langle\psi_{10}(r')|\frac{1}{r'}|\psi_{10}(r)\rangle\Big]$$

$< E_g(z=1)$

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

$$\boxed{\begin{aligned} D &= \frac{a}{R} - \left(1 + \frac{a}{R}\right)e^{-2R/a} \\ X &= \left(1 + \frac{R}{a}\right)e^{-R/a} \end{aligned}}$$

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

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

λ_{min} for $(+)$ case $\frac{R}{a} = 2.4 \Rightarrow R = 1.3\,\mathring{A}$

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

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