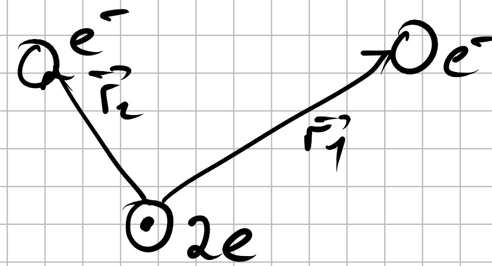
Helium atom



$$\hat H = \underbrace{\frac{\hat p_1^2}{2m_e} - \frac{Ze^2}{|\vec r_1|}}_{\hat H_1} + \underbrace{\frac{\hat p^2}{2m_e} - \frac{Ze^2}{|\vec r_2|}}_{\hat H_2} + \underbrace{\frac{e^2}{|\vec r_1 - \vec r_2|}}_{\hat H_{int}} = \hat H_1 + \hat H_2 + \hat H_{int}$$

non interacting electrons around nucleus with charge $Ze = 2e$

electrons repulsion term

Measurements show that $E_{ground} = -78.975\,eV$

$$\boxed{\text{This problem does not have exact solution !!!}}$$

How can we aproach this problem ?

Method 1: neglect the interaction

$$\hat{H} = \underbrace{\hat{H}_1(\vec{r}_1, \vec{p}_1) + \hat{H}_2(\vec{r}_2, \vec{p}_2)}_{\text{independent}}$$

ground state ψ for single electron

$$\Rightarrow \psi_g(\vec{r}_1, \vec{r}_2) = \psi_{10}(\vec{r}_1) \cdot \psi_{10}(\vec{r}_2)$$

n, ℓ quantum numbers

$$E_g = E_{g_1} + E_{g_2} = 2 \underset{2^2}{\underset{\parallel}{Z^2}} \cdot \underbrace{E_g(z=1)}_{\text{ground energy of Hydrogen}} = 8 \cdot (-13{,}6\,eV) = -108.8\,eV$$

way bigger than $-79\,eV$

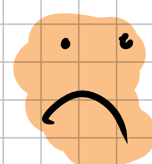
nice try but no banana :(

Method 2: treat $\hat{H}_{int} = \dfrac{e^2}{|\vec{r}_1 - \vec{r}_2|}$ as perturbation

This is possible to do mathematicly
but <u>$\hat{H}_{int}$ is not a perturbation</u>

Distance between electrons $\sim$ distance to the nucleus so $\dfrac{Ze^2}{r_{1,2}} \sim \dfrac{e^2}{|\vec{r}_1 - \vec{r}_2|}$

So we cannot use our perturbations formalism



Method 3: Variational method $\langle \psi_{any} | H | \psi_{any} \rangle \geq E_g$

We will use guess / anzatz $\psi_a = \underbrace{\psi_{10}(r_1)}_{\text{ground states for single electron}} \psi_{10}(r_2)$

It is nice since, it is eigen for the "most" of $\hat{H}$

$$\psi_{10}(r) = \sqrt{\frac{1}{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$\langle \psi_a | \hat{H} | \psi_a \rangle = \langle \psi_{10}(r_1), \psi_{10}(r_2) | \hat{H}_1 + \hat{H}_2 + \hat{H}_{int} | \psi_{10}(r_1), \psi_{10}(r_2) \rangle$$

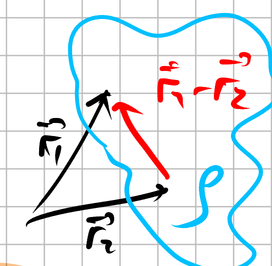
$$= \langle H_1 \rangle + \langle H_2 \rangle + \langle H_{int} \rangle = \underbrace{+Z^2(-13.6\,eV)}_{\langle H_1 \rangle} \underbrace{+Z^2(-13.6\,eV)}_{\langle H_2 \rangle} + \langle H_{int} \rangle$$

we need to work on it

$$\langle H_{int} \rangle = \iint \psi_{10}(r_1)\, \psi_{10}(r_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_{10}(r_1)\, \psi_{10}(r_2)\, d^3r_1\, d^3r_2$$

= / Note that we can think about $e\, \psi^*_{00}(r)\, \psi_{00}(r) = \rho(r)$ density of charge

than $\langle H_{int} \rangle$ can be interpreted as $\dfrac{\rho(r_1)\rho(r_2)}{|\vec{r}_1 - \vec{r}_2|}$



i.e. potential energy of charge distribution

Back to the task

$$\langle M_{int} \rangle = \left(\frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 \right)^2 e^2 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \underbrace{\int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2}_{(2\pi)^2} \int_0^{\pi} \underbrace{\sin\theta_1 \, d\theta_1}_{\substack{2 \\ \text{see} \\ \text{below}}} \int_0^{\pi} \sin\theta_2 \, d\theta_2 \, \cdot$$

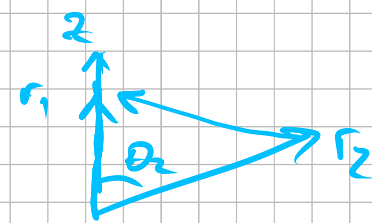
$$\cdot \frac{1}{|\vec{r}_1 - \vec{r}_2|} \cdot e^{-2Zr_1/a_0} e^{-2Zr_2/a_0} =$$

$=$ Let's direct $\vec{r}_1$ along 'z'

then $|\vec{r}_1 - \vec{r}_2|^2 =$

$= r_1^2 + r_2^2 + 2 r_1 r_2 \cos\theta$

in this case $\int_0^{\pi} \sin\theta_1 \, d\theta_1 = 2$



Let's work on intermediate

$$\int_0^{\pi} \frac{\sin\theta_2 \, d\theta^{\,= d(-\cos\theta)}}{\sqrt{r_1^2 + r_2^2 + 2 r_1 r_2 \cos\theta}} = \int_{-1}^{1} \frac{dt}{\sqrt{r_1^2 + r_2^2 + 2 r_1 r_2 t}} = \left. \frac{\sqrt{r_1^2 + r_2^2 + 2 r_1 r_2 t}}{r_1 r_2} \right|_{-1}^{1}$$

$$= \frac{\sqrt{(r_1 + r_2)^2} - \sqrt{(r_1 - r_2)^2}}{r_1 r_2} = \frac{r_1 + r_2 - |r_1 - r_2|}{r_1 r_2}$$

notice no squares

$$\langle H_{int}\rangle = \left(\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3\right)^2 e^2 \cdot 8\pi^2 \int r_1\,dr_1 \int r_2\,dr_2 \underbrace{\left(r_1+r_2-|r_1-r_2|\right)}_{\substack{r_2<r_1\,:\;2r_2 \\ r_2>r_1\,:\;2r_1}} \cdot e^{-2Zr_1/a_0}\, e^{-2Zr_2/a_0}$$

$$= \left(\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3\right)^2 e^2\, 8\pi^2 \int e^{-2Zr_1/a_0}\, r_1\,dr_1 \cdot 2 \cdot \left[\underbrace{\int_0^{r_1} r_2^2\, e^{-2Zr_2/a_0}\,dr_2 + r_1 \int_{r_1}^{\infty} r_2\, e^{-2Zr_2/a_0}\,dr_2}_{\text{boring can be taken by parts} \Rightarrow \text{HW}}\right]$$

$$= -Z \cdot \frac{5}{4}\, \underbrace{E_g(Z=1)}_{\frac{e^2}{2a_0}} = \frac{5}{2}\cdot 13.6\,\text{eV} = 34\,\text{eV}$$

$$\boxed{\langle H\rangle = 2\langle H_1\rangle + \langle H_{int}\rangle = -109\,\text{eV} + 34\,\text{eV} = -75\,\text{eV}}$$

still 4eV away from experimental

Method 4 — Use variable parameter in variational method

Recall that we used

$$\psi(r_1, r_2) = \psi_{10}(r_1)\, \psi_{10}(r_2) = \frac{Z^3}{\pi a^3} \; e^{-Z(r_1+r_2)/a_0}$$

We will use 'Z' as a tuning parameter (it as if one electron "screened" the nucleus charge for the other one.

We can do whatever we want with ψ, but we are not alowed to change $\hat{H}$

We will do a bit of treakery to $\hat{H}$

* 1st: we plug $Z = 2$ for the

$$\hat{H} = \frac{\hat{p}_1^2}{2m} - \frac{2e^2}{r_1} + \frac{\hat{p}_2^2}{2m} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

* we add and subtract $\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)$ where Z is tunable now

thus $\hat{H}$ unchanged

$$\Rightarrow \langle \hat{H} \rangle = \left\langle \frac{p_1^2}{2m} - \frac{Ze^2}{r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_2} \right\rangle + \quad \langle \hat{H}_2 \rangle$$

$$+ \left\langle (Z-2)\frac{e^2}{r_1} + (Z-2)\frac{e^2}{r_2} \right\rangle + \quad (Z-2)e^2\left(\left\langle \frac{1}{r_1} \right\rangle + \left\langle \frac{1}{r_2} \right\rangle\right)$$

$$+ \left\langle \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right\rangle \quad \langle \hat{H}_{int} \rangle$$

$\langle H_2 \rangle$, $\langle H_{int} \rangle$ } we know we just did them

$$\langle H_2 \rangle = 2Z^2 E_g(Z=1) - Z \cdot \frac{5}{4} E_g(Z=1)$$

but we also know $\left\langle \frac{1}{r} \right\rangle$ with Hellmann - Feynman theorem

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a} \quad , \quad \frac{e^2}{2a} = E_g(Z=1)$$

two $\left\langle \frac{1}{r} \right\rangle$

$$\langle \hat{H} \rangle = 2Z^2 E_g(Z=1) - Z \cdot \frac{5}{4} E_g(Z=1) + (Z-2)\, 2Z \cdot 2 \cdot E_g(Z=1)$$

$$= \left[2Z^2 - 4Z(Z-2) - \frac{5}{4}Z \right] \underbrace{E_g(Z=1)}_{\text{ground energy of Hydrogen}}$$

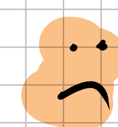
$$f(z) = -2z^2 + \frac{27}{4} z$$

$$f'(z) = -4z + \frac{27}{4} = 0$$

$$z = \frac{27}{16} \approx 1.69$$ ← Can be thought as effective charge of nucleus

$$\Rightarrow \boxed{\langle \hat{H} \rangle = \frac{1}{2}\left(\frac{3}{2}\right)^6 E_g(z=1) = -77.5\ \text{eV}}$$

Closer but still not matching -79 eV



At this point we leave He alone
The estimate can be improved but it requires a search for better anzatz / guess.