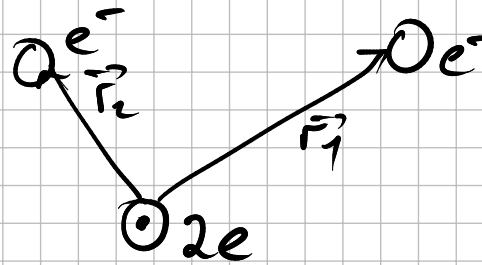


# Helium atom



$$\hat{H} = \underbrace{\frac{\hat{p}_1^2}{2m_e} - \frac{ze^2}{|\vec{r}_1|}}_{\hat{H}_1} + \underbrace{\frac{\hat{p}_2^2}{2m_e} - \frac{ze^2}{|\vec{r}_2|}}_{\hat{H}_2} + \underbrace{\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}}_{\hat{H}_{int}} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{int}$$

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

electrons  
repulsion  
term

Measurements show that  $E_{\text{ground}} = -78.575 \text{ eV}$

This problem does not have  
exact solution !!!

How can we approach this problem?

Method 1: neglect the interaction

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

↑ independent ↑

$$\Rightarrow \Psi(\vec{r}_1, \vec{r}_2) = \Psi_{1,0}(\vec{r}_1) \cdot \Psi_{1,0}(\vec{r}_2)$$

ground state  
ψ for single electron  
↑  
↑ quantum numbers

$$E_g = E_{g1} + E_{g2} = 2 \cdot \frac{1}{2^2} \cdot E_g(z=1) = 8 \cdot (-13.6 \text{ eV}) = -108.8 \text{ eV}$$

ground energy of Hydrogen

way bigger than -79 eV

nice try but no banana ☹️

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

This is possible to do mathematically  
but  $\hat{H}_{int}$  is not a perturbation

Distance between electrons  $\sim$  distance  
to the nucleus so  $\frac{ze^2}{r_{12}} \sim \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$

so we cannot use our perturbations formalism



### Method 3: Variational method $\langle \Psi_{\text{ansatz}} | \hat{H} | \Psi_{\text{ansatz}} \rangle \geq E_g$

We will use guess / ansatz  $\Psi_a = \Psi_{10}(r_1) \Psi_{10}(r_2)$

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

↑ ground states for single electron

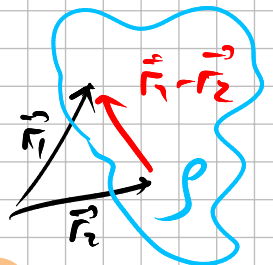
$$\Psi_{10}(r) = \sqrt{\frac{1}{\pi}} \left(\frac{z}{a_0}\right)^{3/2} e^{-zr/a_0}$$

$$\begin{aligned} \langle \Psi_a | \hat{H} | \Psi_a \rangle &= \langle \Psi_{10}(r_1), \Psi_{10}(r_2) | \hat{H}_1 + \hat{H}_2 + \hat{H}_{\text{int}} | \Psi_{10}(r_1), \Psi_{10}(r_2) \rangle \\ &= \langle H_1 \rangle + \langle H_2 \rangle + \langle H_{\text{int}} \rangle = \underbrace{+z^2(-13.6\text{eV})}_{\langle H_1 \rangle} + \underbrace{+z^2(-13.6\text{eV})}_{\langle H_2 \rangle} + \langle H_{\text{int}} \rangle \end{aligned}$$

↑ we need to work on it

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

= / Note that we can think about  $e \Psi_{10}^*(r) \Psi_{10}(r) = \rho(r)$  density of charge  
than  $\langle H_{\text{int}} \rangle$  can be interpreted as  $\frac{\rho(r_1)\rho(r_2)}{|\vec{r}_1 - \vec{r}_2|}$   
i.e. potential energy of charge distribution

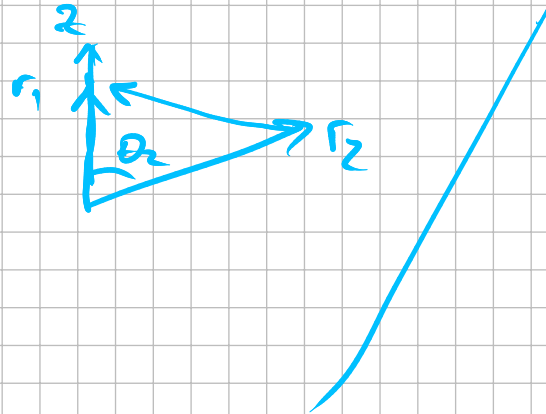


Back to the task

$$\langle \text{Mint} \rangle = \left( \frac{1}{\pi} \left( \frac{z}{a_0} \right)^3 \right)^2 e^2 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \underbrace{\int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2}_{(2\pi)^2} \int_0^\pi \underbrace{\sin\theta_1 d\theta_1}_2 \int_0^\pi \frac{\sin\theta_2 d\theta_2}{|\vec{r}_1 - \vec{r}_2|} \times$$

$$\times \frac{1}{|\vec{r}_1 - \vec{r}_2|} \cdot e^{-2zr_1/a_0} e^{-2zr_2/a_0} =$$

Let's direct  $\vec{r}_1$  along 'z'  
 then  $|\vec{r}_1 - \vec{r}_2|^2 =$   
 $= r_1^2 + r_2^2 + 2r_1r_2 \cos\theta$   
 in this case  $\int_0^\pi \sin\theta_1 d\theta_1 = 2$



Let's work on intermediate

$$\int_0^\pi \frac{\sin\theta_2 d\theta_2}{\sqrt{r_1^2 + r_2^2 + 2r_1r_2 \cos\theta}} = \int_{-1}^1 \frac{dt}{\sqrt{r_1^2 + r_2^2 + 2r_1r_2 t}} = \frac{\sqrt{r_1^2 + r_2^2 + 2r_1r_2 t}}{r_1 r_2} \Big|_{-1}^1$$

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

$$\langle M_{int} \rangle = \left( \frac{1}{\pi} \left( \frac{z}{a_0} \right)^3 \right)^2 e^2 \cdot 8\pi^2 \int r_1 dr_1 \int r_2 dr_2 \underbrace{(r_1 + r_2 - |r_1 - r_2|)}_{\substack{r_2 < r_1 : 2r_2 \\ r_2 > r_1 : 2r_1}} \cdot e^{-2zr_1/a_0} e^{-2zr_2/a_0}$$

notice NO squares

$$= \left( \frac{1}{\pi} \left( \frac{z}{a_0} \right)^3 \right)^2 e^2 8\pi^2 \int e^{-2zr_1/a_0} r_1 dr_1 \cdot 2 \cdot \left[ \int_0^{r_1} r_2^2 e^{-2zr_2/a_0} 2r_2 + r_1 \int_{r_1}^{\infty} r_2 e^{-2zr_2/a_0} dr_2 \right]$$

broring can be taken by parts  $\Rightarrow$  MW

$$= -z \cdot \frac{5}{4} E_0 (z=1) = \frac{5}{2} \cdot 13.6 \text{ eV} = 34 \text{ eV}$$

$\leq \frac{e^2}{2a_0}$

$$\langle M \rangle = 2\langle M_i \rangle + \langle M_{int} \rangle = -109 \text{ eV} + 34 \text{ eV} = -75 \text{ eV}$$

still 4 eV 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 is as if one electron "screened" the nucleus  
charge for the other one).

We can do whatever we want with  $\Psi$   
but we are not allowed to change  $\hat{H}$

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

\* 1st: we plug  $z=2$  for He

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

\* we add and subtract  $\left(\frac{z}{r_1} + \frac{z}{r_2}\right)$  thus  $\hat{H}$   
where  $z$  is tunable now unchanged

$$\Rightarrow \langle \hat{H} \rangle = \left\langle \frac{p_1^2}{2m} - \frac{ze^2}{r_1} + \frac{p_2^2}{2m} - \frac{ze^2}{r_2} \right\rangle + \left\langle (z-2) \frac{e^2}{r_1} + (z-2) \frac{e^2}{r_2} \right\rangle + \left\langle \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right\rangle$$

$\left. \begin{array}{l} \langle \hat{H}_2 \rangle \\ (z-2)e^2 \left( \langle \frac{1}{r_1} \rangle + \langle \frac{1}{r_2} \rangle \right) \end{array} \right\} \langle \hat{H}_{int} \rangle$

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

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

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

$$\langle \frac{1}{r} \rangle = \frac{z}{a}, \quad \frac{e^2}{2a} = E_J(z=1)$$

$$\langle \hat{H} \rangle = 2z^2 E_J(z=1) - z \cdot \frac{5}{4} E_J(z=1) + (z-2) \overset{\text{two } \langle \frac{1}{r} \rangle}{2z \cdot 2 \cdot E_J(z=1)}$$

$$= \left[ 2z^2 - 4z(z-2) - \frac{5}{4}z \right] E_J(z=1)$$

ground energy of Hydrogen



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

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

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

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

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 ansatz / guess.