PHYS 4410

Quantum Mechanics 2

Spring 2023

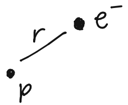
Lecture 22

The helium atom

March 13

$\boxed{1}$ Review hydrogen atom:

$$H = \frac{\vec{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$$



In chemistry: natural to work in dimensionless units:

$$\left[\frac{e^2}{4\pi\varepsilon_0}\right] = \underset{\text{energy}}{[E]}\cdot\underset{\text{length}}{[L]} \qquad [m] = \underset{\text{mass}}{[M]} \qquad [\hbar] = [E]\cdot\underset{\text{time}}{[T]}$$

$$\hookrightarrow \frac{[L]}{[T]} = \frac{e^2}{4\pi\varepsilon_0\hbar} \, .$$

$$[E] = [M]\frac{[L]^2}{[T]^2} = \frac{me^4}{\underbrace{(4\pi\varepsilon_0\hbar)^2}_{\to 1}} = \underbrace{2\times 13.6\,\text{eV}}_{\text{g.s. of H}}$$

$$\sim 4\times10^{-18}\,\text{J}$$

$$[L] = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \simeq 5\times10^{-11}\,\text{m} \quad \text{(Bohr radius)}$$

Work in units w/ $[E]=[L]=[T]=1$

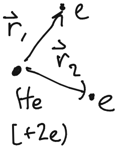
$$H = \frac{\vec{p}^2}{2} - \frac{1}{r} \mapsto \underbrace{-\frac{1}{2}\nabla^2 - \frac{Z}{r}}$$

$$\to H|\underbrace{n\ell m}_{\text{rot. sym.}}\rangle = -\frac{Z^2}{2n^2}|n\ell m\rangle$$

$n > \ell$, $|m| \le \ell$

$$\psi_{100} = \sqrt{\frac{Z^3}{\pi}}\, e^{-Zr}$$

2 Helium atom:



$$H = \underbrace{\left[\frac{\vec{p}_1^{\,2}}{2m} - \frac{2e^2}{4\pi\varepsilon_0 r_1}\right]}_{H_1} + \underbrace{\left[\frac{\vec{p}_2^{\,2}}{2m} - \frac{2e^2}{4\pi\varepsilon_0 r_2}\right]}_{H_2}$$

$$+ \underbrace{\frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}}_{V_{int}}$$

With $V_{int} = 0$, ground state is:

$$E = -Z^2 = -4$$

$$|\psi\rangle = \underset{1s}{\overset{n_1 l_1 m_1,\, n_2 l_2 m_2}{|100,100\rangle}} \otimes \underbrace{\overset{s_1 s_2}{\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}}}_{\text{spin singlet.}}$$

lower energy vs. $n=2$ (factor of 4)

Guess V_{int} doesn't change $\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}$ . . .

$\boxed{3}$ Try $(\psi_{100} \to \psi_0)$ $\psi(\vec{r}_1, \vec{r}_2) = \psi_0(\vec{r}_1)\,\psi_0(\vec{r}_2)$ [exact if $V_{int} = 0$].

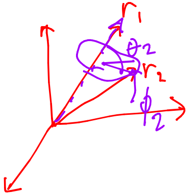
$\left[\otimes \frac{1}{\sqrt{2}}(\uparrow\downarrow\rangle - \downarrow\uparrow\rangle)\right]$ drops out

$$\langle\psi|\,H\psi\rangle = \langle\psi|H_1 + H_2 + V_{int}|\psi\rangle = \underset{\langle H_1\rangle}{-\frac{2^2}{2}} \underset{\langle H_2\rangle}{-\frac{2^2}{2}} + \underline{\langle\psi|V_{int}|\psi\rangle}$$

$$\underline{\int dV_1\,\underline{dV_2}\;|\psi_0(\vec{r}_1)|^2\,|\psi_0(\vec{r}_2)|^2 \boxed{\frac{1}{|\vec{r}_1 - \vec{r}_2|}}}$$

$$\psi_0(r_1) = \sqrt{\frac{8}{\pi}}\,e^{-2r} \to \sqrt{\frac{Z^3}{\pi}}\,e^{-Zr}$$

Annoying ... done as follows:



Do $\vec{r}_2$ integral first:

$$|\vec{r}_1 - \vec{r}_2| = \sqrt{(\vec{r}_1 - \vec{r}_2)\cdot(\vec{r}_1 - \vec{r}_2)}$$
$$= \sqrt{\underset{r_1\cdot r_1}{r_1^2} + \underset{r_2\cdot r_2}{r_2^2} \underset{-2r_1\cdot r_2}{-\,2r_1r_2\cos\theta_2}}$$

$$\int dV_2 = \int r_2^2\,dr_2\,\overset{-\sin\theta_2\,d\theta_2}{\overbrace{d[\cos\theta_2]}}\,d\phi_2 \to 2\pi\int\cdots\int_{-1}^{1} d\overset{u}{\cancel{[\cos\theta_2]}}\;\frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\,\overset{u}{\cancel{\cos\theta_2}}}}$$

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$$\int_{-1}^{1} \frac{du}{\sqrt{a-bu}} = -\frac{2}{b}(a-bu)^{1/2}\Big|_{-1}^{1} = \frac{2}{b}\Big[\underbrace{\underbrace{\sqrt{a+b}}_{r_1^2+r_2^2+2r_1r_2} - \sqrt{a-b}}_{\sqrt{(r_1+r_2)^2} - \sqrt{(r_1-r_2)^2}}\Big]$$

$$\underline{a = r_1^2+r_2^2}, \quad \underline{b = 2r_1r_2}$$

$$\langle\psi|V_{int}|\psi\rangle = \underbrace{\int dV_1}_{\int_0^\infty dr_1\, 4\pi r_1^2} \int_0^\infty dr_2\, r_2^2 \cdot \left(\frac{Z^3}{\pi}\right)^2 e^{-2Z(r_1+r_2)} \cdot \frac{2}{2r_1r_2}\, \underline{2\min(r_1,r_2)}$$

Step 1: $= 2\times \int_{r_1>r_2} = \int_{r_1>r_2} + \int_{r_2>r_1}$ since integrand is symmetric under $r_1 \leftrightarrow r_2$

$$\int_0^\infty dr\, e^{(c-a)r} = \frac{1}{a-c};$$

Taylor expand in c

Step 2: $$\int_0^\infty dr\cdot r^n e^{-ar} = \frac{n!}{a^{n+1}}$$

Combine: $\langle\psi|V_{int}|\psi\rangle = \frac{5}{8}Z$

5 Back to physics:

$$\langle\psi|H|\psi\rangle = -4 + \frac{5}{8}\overset{2}{\cancel{Z}} = -2.75 \quad (\times\, 2\times 13.6\ \text{eV})$$

$$\approx -75\ \text{eV} \qquad [\text{“true”} \approx \underbrace{-79\ \text{eV}}_{\approx -2.9}]$$

Do better: add one tunable parameter...

$$\psi(\vec{r}_1, \vec{r}_2; \alpha) = \frac{\alpha^3}{\pi} e^{-\alpha(r_1+r_2)} \quad (\alpha \text{ like effective } Z\ldots)$$

$$\langle\psi|H|\psi\rangle = \langle\psi|\Bigg(\underbrace{\left[\frac{\vec{p}_1^{\,2}}{2} - \frac{\alpha}{r_1}\right]} + \underbrace{\left[\frac{\vec{p}_2^{\,2}}{2} - \frac{\alpha}{r_2}\right]} - (2-\alpha)\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

$$+ \underbrace{\frac{1}{|\vec{r}_1 - \vec{r}_2|}}\Bigg)|\psi\rangle$$

$$= -2\cdot\frac{\alpha^2}{2} + \frac{5\alpha}{8}$$

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$$\left\langle \frac{1}{r_1} \right\rangle = \int dV_1\, dV_2\, |\psi_\alpha(r_1)\psi_\alpha(r_2)|^2 \frac{1}{r_1}$$

$$= \int_0^\infty dr_1\, 4\pi r_1^{\overset{1}{\cancel{2}}} \cdot \frac{\alpha^3}{\pi} e^{-2\alpha r_1} \cdot \cancel{\frac{1}{r_1}}$$

$$= \frac{4\cancel{\pi}\alpha^3}{\cancel{\pi}} \cdot \frac{1}{(2\alpha)^2} = \alpha$$

$$E_{trial}(\alpha) = -\alpha^2 + \frac{5}{8}\alpha - 2\alpha(2-\alpha) = \alpha^2 - \frac{27}{8}\alpha$$

prev: -2.75

$\uparrow$

$$\frac{dE_{trial}}{d\alpha} = 2\alpha - \frac{27}{8} = 0 \quad , \quad \text{so} \quad \alpha = \frac{27}{16} \rightsquigarrow E_{trial} \approx -2.85$$

$\downarrow$ true

-2.9

Physical interpret: $\alpha = \frac{27}{16}$ is "effective charge" seen by each electron.