LAST TIME: The variational method.

Want to estimate ground state energy for some H

Method:

① Choose trial state with some arbitrary parameters

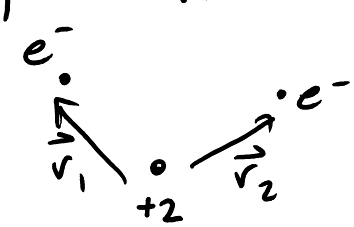
$$|\psi(a_i)\rangle$$

② Normalize: $\langle\psi(a_i)|\psi(a_i)\rangle = 1$

③ Evaluate $E_\psi(a_i) = \langle\psi(a_i)|\,H\,|\psi(a_i)\rangle$

④ Minimize over $a_i \longrightarrow E^{\psi}_{min}$

Example: Helium atom



$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)$$

$$= H_1 + H_2 + V_{ee}$$

Single electron: similar to H atom: $\psi_{100}(\vec{r}) = \sqrt{\frac{Z^3}{\pi a^3}}\, e^{-Zr/a}$

$Z=2$

$$E = -13.6\,\text{eV} \cdot Z^2$$

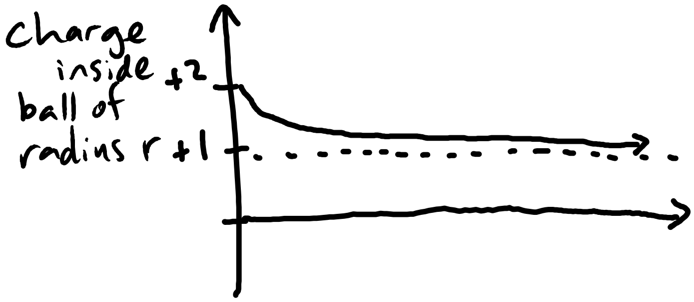
If no V_{ee}:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) \qquad E = -13.6\,\text{eV} \cdot 2^2 \times 2 = -109\,\text{eV}$$

↳ if we use this as variational wavefn, get

$$\langle\psi|H_1 + H_2 + V_{ee}|\psi\rangle = -75\,\text{eV}$$

BUT: with single electron:



- 1st electron partly screens charge of nucleus.

$\therefore$ try $\psi_{100}^{Z}(\vec{r}_1)\,\psi_{100}^{Z}(\vec{r}_2)$ with Z arbitrary

$$E_0 \leq \langle \psi_Z | H_1^{Z=2} + H_2^{Z=2} + V_{ee} | \psi_Z \rangle$$

$$= \langle \psi_Z | H_1^{Z} + H_2^{Z} | \psi_Z \rangle + \langle \psi_Z | (H_1^{Z=2} - H_1^{Z}) + (H_2^{Z=2} - H_2^{Z}) | \psi_Z \rangle + \langle \psi_Z | V_{ee} | \psi_Z \rangle$$

$$= (-13.6\,\mathrm{eV}) Z^2 \cdot 2 + 2 \cdot \int d\vec{r}\, \psi_{100}^{Z}(r) \cdot \frac{e^2}{4\pi\varepsilon_0} \frac{Z-2}{r}$$

$$+ \int d\vec{r}_1\, d\vec{r}_2 \left(\psi_{100}^{Z}(r_1)\psi_{100}^{Z}(r_2)\right)^2 \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

$$= 13.6\,\mathrm{eV}\left(2Z^2 - \frac{27}{4} Z\right)$$

minimize: $Z = 1.69$ $\quad \langle H \rangle = -77.5\,\mathrm{eV}$

experimental: $-78.95\,\mathrm{eV}$

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improve by trying more parameters

e.g. $\psi^{Z_1}(\vec{r}_1)\psi^{Z_2}(\vec{r}_2) + \psi^{Z_2}(\vec{r}_1)\psi^{Z_1}(\vec{r}_2)$ gives $-78.218\,\mathrm{eV}$