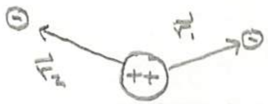
Helium

Classical model: $U = -\dfrac{Ze^2}{4\pi\epsilon_0 r_1} - \dfrac{Ze^2}{4\pi\epsilon_0 r_2} + \dfrac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$



ignoring the e^- interaction for a moment -

the energy of hydrogen $\sim e^4$, & here, we have Ze^2, so we get

$$\tilde{E} \sim 4E_H \quad \text{(for a single } e^-)$$

the Bohr radius for hydrogen has: $a \sim \frac{1}{e^2}$ so the natural length scale here is

$$\tilde{a} = a/2 \quad (e^2 \rightarrow 2e^2)$$

what should we use as our trial wavefunction? Ignoring the e^--e^- interaction,

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2)$$

the problem is seperable - this ψ will solve it, given single particle states ψ_a & ψ_b - how should we pick those?

$$\psi_0(\vec{r}_1, \vec{r}_2) = \tilde{\psi}_{100}(\vec{r}_1)\,\tilde{\psi}_{100}(\vec{r}_2)$$

(both in ground state) w/

$$\psi_{100}(\vec{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

the hydrogen ground state wavefunction.

send $a \rightarrow \tilde{a} = a/2$ to account for the 2^{nd} proton

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$$

$$\& \quad \hat{H}\psi(\vec{r}_1, \vec{r}_2) = \tilde{E}_1\psi + \tilde{E}_2\psi + \overbrace{\frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}}^{\equiv V_{ee}}\psi$$

$$= 8E_1\psi + V_{ee}\psi$$

the expectation value is

$$\langle\psi|\hat{H}|\psi\rangle = 8E_1 + \underbrace{\langle\psi|V_{ee}|\psi\rangle}_{= -5/2 E_1 \text{ (calc.)}}$$

so

$$\langle \hat{H} \rangle = 8E_1 - 5/2 E_1 \approx -75\,\text{eV}$$

the experimental value is: $E_{gs} \approx -79\,\text{eV}$.

Introducing a Parameter

The electrons "screen" the nucleus from each other

$\cdot e^-$ ← this e^- "sees" a central charge $< 2e$

Take the effective central charge to be Ze, w/

$$U = \frac{-Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}$$

we know how the energy & Bohr radius will scale here (in the absence of the $e^- - e^-$ interaction).

$$\tilde{E}_1 = Z^2 E_1 \quad \& \quad \tilde{a} = a/Z$$

Writing the full problem in a way that will make it easy to compute the expectation values:

$$\hat{H} = \left(\frac{\hat{p}_1^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_1}\right) + \left(\frac{\hat{p}_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\left[\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right]$$

& using

$$\psi = \frac{1}{\sqrt{\pi \tilde{a}^3}} e^{-r_1/\tilde{a}} \frac{1}{\sqrt{\pi \tilde{a}^3}} e^{-r_2/\tilde{a}} = \frac{Z^3}{\pi a^3} e^{-(r_1+r_2)\cdot Z/a}$$

we have:

$$\langle\psi|\hat{H}|\psi\rangle = 2Z^2E_1 + \frac{(Z-2)e^2}{4\pi\epsilon_0}\left[\langle\psi|\tfrac{1}{r_1}|\psi\rangle + \langle\psi|\tfrac{1}{r_2}|\psi\rangle\right] + \underbrace{\langle\psi|V_{ee}|\psi\rangle}_{= -\frac{5Z}{4}E_1}$$

we know the $\frac{1}{r}$ expectation values

$\left\langle \frac{1}{r} \right\rangle = \frac{1}{\tilde{a}} = \frac{Z}{a}$

$$= \left[-2Z^2 + (27/4)Z\right]E_1$$

& $\frac{d\langle \hat{H}\rangle}{dZ} = 0 \Rightarrow Z \approx 1.69$, w/ $\langle \hat{H}\rangle_{min} \approx -77.5\,eV$.

Comparison of Methods

We have a variety of ways to estimate the ground state energy of a quantum system:

- WKB

$$\frac{1}{\hbar}\int_0^a \sqrt{2m(E-U(\bar{x}))}\,d\bar{x} = n\pi \quad w/\ n=1.$$

- time-independent pert. theory

$$E^1_{g.s.} = \langle\psi_1^0|\hat{H}'|\psi_1^0\rangle$$

w/ $\hat{H}^0|\psi_1^0\rangle = E_1^0|\psi_1^0\rangle$ ← ground state energy.

$$E^2_{gs} = \sum_{j=2}^{\infty} \frac{|\langle\psi_j^0|\hat{H}'|\psi_1^0\rangle|^2}{E_1^0 - E_j^0}$$

- finite difference method

discretize $\left[-\frac{\hbar^2}{2m}\nabla^2 + U\right]\psi = E\psi$

to get the eigenvalue problem: $\mathbb{H}\vec{v} = E\vec{v}$ — find the min. e-val.

- Variational method

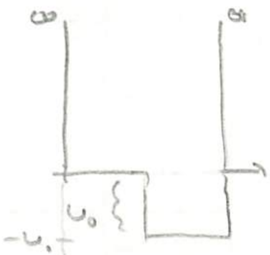
For some basis $|\psi_j\rangle$, let $H_{kj} \equiv \langle\psi_k|\hat{H}|\psi_j\rangle$ then solve the e-val prob. for the matrix $\mathbb{H}$.

$$\mathbb{H}\vec{c} = \lambda\vec{c} \quad \text{min. } \lambda \text{ is best bound.}$$

Example Problem

We want an example problem where we can compute all of these approx. easily — & for which we know the solution.

$$U(x) = \begin{cases} \infty & x<0,\ x>a \\ 0 & 0<x<a/2 \\ -U_0 & a/2<x<a \end{cases}$$



we can solve for the spectrum here by finding the roots of a transcendental eqn. (although that is still an approx...).

What do we expect? If you moved the whole "floor" down to $-U_0$:

$$-\frac{\hbar^2}{2m}\psi''(x) - U_0\psi = E\psi$$

has: $-\frac{\hbar^2}{2m}\psi''(x) = \overbrace{(E+U_0)}^{\equiv \tilde{E}}\psi$

so we'd end up w/:

$$\tilde{E} = \frac{j^2\pi^2\hbar^2}{2ma^2} \Rightarrow E = \frac{j^2\pi^2\hbar^2}{2ma^2} - U_0$$

(above the floor)

so we guess, for the ½-step,

$$E \cong \frac{j^2\pi^2\hbar^2}{2ma^2} - \frac{1}{2}U_0$$

using 1st order pert. theory, we get:

$$\langle\psi_1^0|\hat{H}'|\psi_1^0\rangle = -\frac{2}{a}\int_0^{a/2}\sin^2\left(\frac{\pi x}{a}\right)U_0\,dx = -\frac{U_0}{2} \checkmark$$

this is also the "lowest order" prediction of WKB.

In each case, then, we'll look at the "residual" energy:

$$r_E \equiv E - \left(\frac{j^2\pi^2\hbar^2}{2ma^2} - \tfrac{1}{2}U_0\right) \qquad (+)$$

result of approx. method

Dimensionless Form

To compare across methods, let's start w/ the dimensionless problem:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x), \quad \psi(0)=\psi(a)=0 \qquad (*)$$

let $x = aX$, then $\frac{d^2}{dx^2} \longrightarrow \frac{1}{a^2}\frac{d^2}{dX^2}$, & $(*)$ becomes:

$$-\frac{d^2\psi(X)}{dX^2} + \underbrace{\frac{2mU(X)a^2}{\hbar^2}}_{\equiv\tilde{U}}\psi(X) = \underbrace{\frac{2mEa^2}{\hbar^2}}_{\equiv\tilde{E}}\psi(X), \quad \psi(0)=\psi(1)=0$$

$$-\frac{d^2\psi(X)}{dX^2} + \tilde{U}(X)\psi(X) = \tilde{E}\psi(X), \quad \psi(0)=\psi(1)=0$$

w/ $\tilde{U}(X) = \begin{cases} \infty & X<0,\ X>1 \\ 0 & 0<X<\frac{1}{2} \\ \tilde{U}_0 & \frac{1}{2}<X<1 \end{cases}$

& the "residual" in (+) becomes $r_{\tilde{E}} = \tilde{E} - \left(j^2\pi^2 - \frac{1}{2}\tilde{U}_0\right)$.