Last Time | Lecture 19

Central Potentials

Energy ES

$\phi(\vec{r}) = R(r) Y_{\ell m}(\theta,\phi)$

$\Leftrightarrow \quad \hat{E}_r R(r) = \left(\frac{-\hbar^2}{2m} \frac{1}{r} \partial_r^2 r + \underbrace{\frac{\hbar^2}{2mr^2} \ell(\ell+1) + V(r)}_{V_{effective}(r)} \right) R(r)$

radial function trick!

use $u(r) = r\, R(r)$

$\Leftrightarrow \quad \hat{E}_0 u(r) = \left(-\frac{\hbar^2}{2m} \partial_r^2 + V_{eff}(r) \right) u(r)$

just like in 1D!!

and we saw how some of our old friends (ISW, QHO) become complicated by the addition of the $\frac{1}{r^2}$ term in the effective potential.

Today (following Gr. 4.2.1)

The Coulomb potential!

Useful for attraction between charged particles (e.g. proton + electron):

$$V(r) = \frac{-e^2}{4\pi\epsilon_0} \frac{1}{r} = -\frac{g_e}{r}$$

Dimensional Analysis!

$[g_e] = E \cdot L = \frac{P^2 L}{M}$, $[\hbar] = P \cdot L$, $[m] = M$

$\Leftrightarrow r_0 = \frac{\hbar^2}{2m\, g_e}$, $E_0 = \frac{g_e}{r_0} = \frac{2m g_e^2}{\hbar^2}$

Start w/

$$-\frac{\hbar^2}{2m} \partial_r^2 U(r) = \left(E + g_e \frac{1}{r} - \frac{\hbar^2}{2mr^2} l(l+1)\right) U(r)$$

change $r \to \rho = \frac{r}{r_0}$, $E \to \epsilon = \frac{-E}{E_0}$ negative to make bound states have $\epsilon > 0$

$$\underbrace{-\frac{\hbar^2}{2m}\frac{1}{r_0^2}}_{=E_0} \partial_\rho^2 U(\rho) = \left(-E_0 \epsilon + \underbrace{\frac{g_e}{r_0}}_{=E_0} \frac{1}{\rho} - \underbrace{\frac{\hbar^2}{2m r_0^2}}_{=E_0} \frac{1}{\rho^2} l(l+1)\right) U(\rho)$$

$$\Leftrightarrow \partial_\rho^2 U(\rho) = \left(\epsilon - \frac{1}{\rho} + \frac{l(l+1)}{\rho^2}\right) U(\rho)$$

Dimensionless! Ready to solve!

Like QHO, start w/ asymptotic behavior, then use polynomial expansion.

Asymptotic

for $\rho \to \infty$ $\partial_\rho^2 U(\rho) \simeq \epsilon\, U(\rho)$

$\Leftrightarrow U(\rho) \simeq A e^{-\sqrt{\epsilon}\rho} + \underbrace{B e^{\sqrt{\epsilon}\rho}}_{\text{not normalizable}} \Rightarrow B = 0$

for $\rho \to 0$ $\partial_\rho^2 U(\rho) \simeq \frac{l(l+1)}{\rho^2} U(\rho)$

$\Rightarrow U(\rho) \simeq C\rho^{l+1} + \underbrace{D\rho^{-l}}_{\text{singular}} \Rightarrow D = 0$

$$\partial_\rho^2 U(\rho) = \partial_\rho^2\left(C\rho^{l+1} + D\rho^{-l}\right)$$

$$\partial_\rho\left(C(l+1)\rho^{l} + D(-l)\rho^{-(l+1)}\right)$$

$$C\,l(l+1)\rho^{l-1} + D\,l(l+1)\rho^{-l-2}$$

$$\frac{l(l+1)}{\rho^2}\left(C\rho^{l+1} + D\rho^{-l}\right)$$

Asym' cont'

$\Leftrightarrow$ look for $U(\rho) = e^{-\sqrt{\epsilon}\rho}\rho^{l+1}\cdot V(\rho)$

such that $V(\rho) \to$ nothing exciting @ $\rho = 0$ + $\rho = \infty$

plugging into our dimensionless ODE

$$\rho V'' + 2(l+1-\sqrt{\epsilon}\rho)V' + (1 - 2\sqrt{\epsilon}(l+1))V = 0$$

(no mystery here, just the product rule!)

$\Rightarrow$ use Mathematica $\Leftarrow$

polynomial $V(r) = \sum_{j=0}^{\infty} a_j \rho^j$

$$\Leftrightarrow \rho V'' = \rho \sum_{j=2}^{\infty} a_j j(j-1)\rho^{j-2} = \sum_{j=1}^{\infty} a_{j+1}(j+1)j\rho^j$$

$$V' = \sum_{j=1}^{\infty} a_j j \rho^{j-1} = \sum_{j=0}^{\infty} a_{j+1}(j+1)\rho^j$$

can start sum @ $j=0$

$$\rho V' = \sum_{j=1} a_j j \rho^j$$

plug + chug!

$$\sum_{j=0}^{\infty}\underbrace{\left(a_{j+1}(j+1)j + 2(l+1)a_{j+1}(j+1) - 2\sqrt{\epsilon}a_j j + (1-2\sqrt{\epsilon}(l+1))a_j\right)}_{\text{must be zero for all } j}\rho^j = 0$$

$$\Leftrightarrow a_{j+1}\cdot(j+1)(2(l+1)+j) = a_j\left(2\sqrt{\epsilon}(l+j+1) - 1\right)$$

recursion relation!

$$a_{j+1} = \frac{2\sqrt{\epsilon}(l+j+1) - 1}{(j+1)(2(l+1)+j)}a_j$$

$$\partial_\rho^2 \left(e^{-\sqrt{E}\rho} \rho^{l+1} v(\rho) \right) =$$

$$\left(E - \frac{1}{\rho} + \frac{l(l+1)}{\rho^2}\right)\left(e^{-\sqrt{E}\rho} \rho^{l+1} v(\rho)\right)$$

$$\partial_\rho \left(-\sqrt{E}\, U(\rho) + \frac{l+1}{\rho} U(\rho) + e^{-\sqrt{E}\rho} \rho^{l+1} \underbrace{\partial_\rho V}_{V'} \right) =$$

do it again, with feeling!

As w/ the QHO we need this recursion relation to terminate so that $v(\rho)$ does not dominate $e^{-\sqrt{\epsilon}\rho}$ as $\rho \to \infty$

This constrains the allowable values of ϵ such that

$$2\sqrt{\epsilon}\,(\ell + n_r + 1) - 1 = 0$$

"principal quantum number"

$$\Leftrightarrow \quad \epsilon = \frac{1}{4\,(\ell + n_r + 1)^2} = \frac{1}{4n^2}, \quad n = \ell + n_r + 1$$

total angular momentum

highest power of ρ in $v(\rho) = j_{max}$

$\Leftrightarrow u(\rho)$ has $\rho^{\ell + n_r + 1} = \rho^n$

$\Rightarrow R(r)$ has $r^{\ell + n_r} = \rho^{n-1}$

Since the bound state energy only depends on $n = \ell + n_r + 1$

$$E_n = -E_0\epsilon = \frac{-2mg_e^2}{\hbar^2} \cdot \frac{1}{n^2} = -13.6\,eV\,\frac{1}{n^2}$$

Bohr!!

$\Rightarrow$ Rydberg

note that since $n_r \geq 0$ & $\ell \geq 0$

$$\Leftrightarrow n \geq \ell + 1 \quad \Rightarrow \quad n \geq 1$$

note also that

$$e^{-\sqrt{\epsilon}\,\rho} = e^{-\frac{r}{2nr_0}}$$

$\Leftrightarrow$ wave function "size" $\sim 2nr_0$ grows linearly w/ n

(lucky Bohr!!)

All Together

$$\phi_{n\ell m}(\vec{r}) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\phi)$$

$$\equiv N_{n\ell}\, e^{-\frac{r}{2n r_0}} \frac{r^\ell}{r_0^{\ell+1}} V_{n\ell}\left(\frac{r}{r_0}\right) Y_{\ell m}$$

$N_{n\ell}$ = normalization factor

$V_{n\ell}\left(\frac{r}{r_0}\right)$ = polnomial of order $n-(\ell+1) = n_r$
"Laguerre Polynomial"

$E_{n\ell} = -E_{Ry}\frac{1}{n^2}$ does not depend on m, but be careful because n depends on ℓ.

Our definition of r_0 is a factor of 2 different from the Bohr radius, a_0

$$2r_0 = a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \simeq 53\,\text{pm}$$

Using a_0

$$R_{10}(r) = \left(\frac{1}{a_0}\right)^{3/2} 2\, e^{-r/a_0}$$

$$R_{20}(r) = \left(\frac{1}{2a_0}\right)^{3/2} 2\left(1 - \frac{r}{2a_0}\right) e^{-\frac{r}{2a_0}}$$

$$R_{21}(r) = \left(\frac{1}{2a_0}\right)^{3/2} \frac{1}{\sqrt{3}}\left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$$

$\vdots$

Degeneracy

We have a lot of degeneracy here!

The ground state is unique w/

$n=1,\ \ell=0,\ m=0 \qquad E_1 = -E_{Ry} \qquad \times 1$

$\Rightarrow n_r = 0$

for principal Quantum number 2

$n=2 \qquad n_r = 1,\ \ell=0,\ m=0$

$E_2 = \frac{1}{4}E_1 \qquad n_r = 0,\ \ell = 1,\ m = \pm 1, 0 \qquad \times 4$

for $n=3$

$n_r = 2,\ \ell=0,\ m=0$

$E_3 = \frac{1}{9}E_1 \qquad n_r = 1,\ \ell = 1,\ m = \pm 1, 0 \qquad \times 9$

$n_r = 0,\ \ell = 2,\ m = \pm 2, \pm 1, 0$

degeneracy goes as n^2

Aside

Symmetry? Constant of motion?

Yes! in $\frac{1}{r}$ potential elliptical orbits don't precess. Mathematically, one can define an operator based on the classical Lenz vector $\vec{A}$ which commutes with $\hat{E}$ (i.e. $[E, \hat{A}] = 0$).

Is This Hydrogen?

not quite, for lots of little reasons

Using the Coulomb potential would mean that the proton is fixed in space @ $r=0$.
Instead both e^- and p^+ move around the CM, which is fixed. As in Classical Mechanics we can account for this by replacing the mass of the "orbiting" particle by its reduced mass.

Reduced Mass

$$m \to \mu = \frac{m_e m_p}{m_e + m_p} = 0.9995\, m_e$$

not reduced by much!!

Relativistic Corrections

$$\hat{E}_{RC} = \hat{E} - \frac{\hat{p}^4}{4 m_e^3 c^2}$$

but c^2 is big, so ΔE is small

leads to "Fine Structure"

Spin-Spin Interaction

both e^- and p^+ have an intrinsic angular momentum called "spin" which we will talk about next time. A charged particle w/ spin has a B-field... these interact!

Myths of Hydrogen

Q: Does the electron orbit?

A: No! (well, maybe...)

Does X move (classically)? Is best interpreted in QM as is $\partial_t \langle \vec{r} \rangle = 0$?

For any energy eigenstate, $\partial_t \langle \vec{r} \rangle = 0$, so an e^- in a state $\phi_{n\ell m}$ does NOT move (classically).

On the other hand, the probability current $\vec{J}(\vec{r})$ may not be zero... so QMally speaking, something moves.

No motion $\Rightarrow$ no radiation $\Rightarrow$ classical death avoided!

Q: How do we get the emmission spectrum?

$$h\nu_{rad} = \Delta E = E_{n_2} - E_{n_1} = E_{Ry}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

and a superposition of states w/ E_{n_2} & E_{n_1} will have

$$\psi = \underbrace{\phi_{n_2\ell_2 m_2}}_{\phi_2} e^{-i\overbrace{\frac{E_{n_2}}{\hbar}}^{\omega_2} t} + \underbrace{\phi_{n_1\ell_1 m_1}}_{\phi_1} e^{-i\overbrace{\frac{E_{n_1}}{\hbar}}^{\omega_1} t}$$

$$\langle \vec{r} \rangle = \langle \psi | \hat{\vec{r}} | \psi \rangle = \langle \phi_2 e^{-i\omega_2 t} + \phi_1 e^{-i\omega_1 t} | \hat{\vec{r}} | \ldots \rangle$$

$$= \langle \phi_2 | \hat{\vec{r}} | \phi_2 \rangle + \langle \phi_1 | \hat{\vec{r}} | \phi_1 \rangle + \langle \phi_2 | \hat{\vec{r}} | \phi_1 \rangle e^{i(\omega_2 - \omega_1)t} + \langle \phi_1 | \hat{\vec{r}} | \phi_2 \rangle e^{-i(\omega_2 - \omega_1)t}$$

$$\langle \phi_2 | \hat{\vec{r}} | \phi_1 \rangle = \left(\langle \phi_1 | \hat{\vec{r}} | \phi_2 \rangle \right)^*$$

$$= \langle \phi_1 | \hat{\vec{r}} | \phi_2 \rangle \quad \text{since } \phi_1 + \phi_2 \in \mathbb{R}$$

$$\equiv \langle r \rangle_{12}$$

also

$$\langle \phi_1 | \hat{\vec{r}} | \phi_1 \rangle = 0 \quad \text{for all } \phi_{nlm} \text{ by symmetry of } Y_{lm}$$

$$\Rightarrow \langle \vec{r} \rangle = \langle r \rangle_{12} \left(e^{i\overbrace{(\omega_2 - \omega_1)}^{\Delta\omega} t} + e^{-i(\omega_2 - \omega_1)t} \right)$$

$$= 2 \langle r \rangle_{12} \cos(\Delta\omega\, t)$$

so we get motion w/ frequency

$$\Delta\omega = \frac{E_{n_2} - E_{n_1}}{\hbar} = \frac{E_{Ry}}{\hbar} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 2\pi \nu_{rad}$$

which sounds right, but there are no photons, and nothing like Maxwell's eqns in our model !!

Need QFT for that.

Next time

how to deal with small corrections and finally, spin and other strange features of QM