

Chapter 13: The hydrogen atom

3.1 The eigenvalue problem for bound states $E < 0$:

$$V = -\frac{e^2}{r}$$

$$\text{S.Eq.: } \left\{ \frac{d^2}{dr^2} + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{r} - \frac{l(l+1)\hbar^2}{2mr^2} \right) \right\} U_{El}(r) = 0 \quad (E < 0)$$

$$\Psi_{Elm}(r, \theta, \varphi) = \frac{U_{El}(r)}{r} Y_{lm}(\theta, \varphi)$$

From the previous chapter we know that asymptotically for large r

$$U_{El} \xrightarrow{r \rightarrow \infty} \sim e^{-\kappa r} \quad (\text{up to a fractional power prefactor})$$

$$\text{where } \kappa = \sqrt{\frac{2m|E|}{\hbar^2}}$$

and for small r

$$U_{El} \xrightarrow{r \rightarrow 0} \sim r^{l+1}$$

Use scaled radial coordinate

$$\rho = \kappa r = r \sqrt{\frac{2m|E|}{\hbar^2}}$$

and write

$$U_{El}(\rho) = v_{El}(\rho) e^{-\rho}$$

The equation for v is then

$$\boxed{\frac{d^2 v}{d\rho^2} - 2 \frac{dv}{d\rho} + \left(\frac{e^2 \lambda}{\rho} - \frac{l(l+1)}{\rho^2} \right) v = 0}$$

$$\text{with } \lambda = \sqrt{\frac{2m}{\hbar^2 |E|}} \quad (*)$$

We try the power-series ansatz

$$u_{\ell\ell}(\rho) = \rho^{\ell+1} \sum_{k=0}^{\infty} c_k \rho^k$$

and plug it into (*) to obtain the recursion relation

$$\frac{c_{k+1}}{c_k} = \frac{-e^2 \lambda + 2(k+\ell+1)}{(k+\ell+2)(k+\ell+1) - \ell(\ell+1)} \xrightarrow{k \rightarrow \infty} \frac{2}{k}$$

The series $c_{k+1} = \frac{2}{k} c_k$ corresponds to the function $\rho^m e^{2\rho}$,

So if the recursion relation would not truncate, $u_{\ell\ell}$ would asymptotically go like $u_{\ell\ell} \sim \rho e^{-\rho} = \rho^m e^{2\rho} e^{-\rho} \sim \rho^m e^{\rho}$, which is not normalizable. To obtain normalizable states we must demand that the series terminates at some k . This will happen for

$$e^2 \lambda = 2(k+\ell+1) \Rightarrow e^4 \frac{2m}{\hbar^2(-E)} = 4(k+\ell+1)^2$$
$$\Rightarrow \boxed{E = -\frac{me^4}{2\hbar^2} \frac{1}{(k+\ell+1)^2} \quad k=0,1,2,\dots; \ell=0,1,2,\dots}$$

Again, we can introduce a principal quantum number

$$n = k + \ell + 1$$

$$\Rightarrow \boxed{E_n = -\frac{me^2}{2\hbar^2 n^2} \quad (n=1,2,3,\dots)} \quad (\text{allowed energy eigenvalues})$$

For each n , the allowed ℓ values are

$$\ell = n - k - 1 = (n-1, n-2, \dots, 1, 0)$$

Since each l value is $2l+1$ times degenerate due to the magnetic quantum number, the total degeneracy of eigenvalue E_n is

$$\sum_{l=0}^{n-1} (2l+1) = n^2$$

$l = 0, 1, 2, 3, \dots \iff s, p, d, f, g, h \dots$ states
("spectroscopic notation")

$$1s \equiv (n=1, l=0)$$

$$2s \equiv (n=2, l=0)$$

$$2p \equiv (n=2, l=1) \text{ etc}$$

Natural energy unit for the energy levels of hydrogen:

$$|Ry| = \frac{me^4}{2\hbar^2} \approx 13.6 \text{ eV}$$

("Rydberg")

The wave functions

For given n and l , the power series terminates

at $k = n - l - 1$. The function $v(\rho)$ is then

ρ^{l+1} times a polynomial of degree $n - l - 1$

\rightarrow "associated Laguerre polynomials", $L_{n-l-1}^{2l+1}(2\rho)$

$$\Rightarrow R_{nl}(\rho) = \frac{U_{nl}(\rho)}{\rho} \sim e^{-\rho} \rho^l L_{n-l-1}^{2l+1}(2\rho)$$

$$\rho = \kappa_n r = \frac{me^2}{\hbar^2 n} r$$

We define the Bohr radius as

$$a_0 = \frac{\hbar^2}{me^2} \Rightarrow \rho_n = \frac{1}{n} \frac{r}{a_0}$$

and

$$R_{ne}(r) \sim e^{-r/(na_0)} \left(\frac{r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(2\frac{r}{na_0}\right)$$

$$\xrightarrow{r \rightarrow \infty} \sim r^l \cdot r^{n-l-1} \cdot e^{-r/na_0} = \underbrace{r^{n-1}}_{\text{(independent of } l\text{!)}} e^{-r/na_0}$$

The lowest energy eigenvalues have the normalized eigenfunctions

$\Psi_{nlm}(r)$:

$$\Psi_{100} = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0}$$

$$\Psi_{200} = \sqrt{\frac{1}{32\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$\Psi_{210} = \sqrt{\frac{1}{32\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta \quad (r \cos\theta = z)$$

$$\Psi_{21,\pm 1} = \mp \sqrt{\frac{1}{64\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta e^{\pm i\phi} \quad \begin{matrix} (r \sin\theta \cos\phi = x \\ r \sin\theta \sin\phi = y) \end{matrix}$$

Can show (homework) that

$$\langle \hat{T} \rangle = -\frac{1}{2} \langle \hat{V} \rangle \quad (\text{virial theorem})$$

$$\Rightarrow E = \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V} \rangle = \frac{1}{2} \langle \hat{V} \rangle = -\frac{e^2}{2} \left\langle \frac{1}{r} \right\rangle$$

$$\Rightarrow \left\langle \frac{1}{r} \right\rangle_n = -\frac{2E}{e^2} = \frac{1}{a_0 n^2} \Rightarrow \langle r \rangle_n \sim n^2 a_0$$

13.2 The degeneracy of the hydrogen spectrum

Like the 2- and 3-d harmonic oscillator, the hydrogen spectrum features "accidental degeneracy" - i.e. states with different l can have the same energy eigenvalue. This is not explained by rotational symmetry (which explains the $2l+1$ -fold magnetic quantum number degeneracy of states with a given l) - hence the name "accidental". However, we will now see that the degeneracy reflects an additional symmetry of the hydrogen Hamiltonian.

From classical mechanics one knows that among rotationally invariant potentials the $1/r$ potential is special because it conserves the Runge-Lenz vector

$$\vec{n} = \frac{\vec{p} \times \vec{L}}{m} - \frac{e^2}{r} \vec{r}$$

The conservation of \vec{n} ($\frac{d\vec{n}}{dt} = 0$) implies that not only is the orbit confined to a plane $\perp \vec{L}$ ($\frac{d\vec{L}}{dt} = 0$) but it is also closed. (see Exercise 13.2.1).

The conservation of \vec{n} translates quantum mechanically into

$$[\hat{H}, \hat{N}] = 0 \quad \Leftrightarrow \quad \frac{d}{dt} \langle \hat{N} \rangle = 0$$

where

$$\hat{N} = \frac{1}{2m} \left[\hat{\vec{P}} \times \hat{\vec{L}} - \underbrace{\hat{\vec{L}} \times \hat{\vec{P}}}_{=(\hat{\vec{P}} \times \hat{\vec{L}})^\dagger} \right] - \frac{e^2 \hat{\vec{R}}}{\sqrt{\hat{X}^2 + \hat{Y}^2 + \hat{Z}^2}}$$

("Symmetrization rule")

To explain the degeneracy in l ($l=n-1, n-2, \dots, 1, 0$), we must be able to build from the components of \vec{N} some operator that commutes with \hat{H} and raises or lowers l by one unit. (Just as we were able to build from \vec{L} the operators \hat{L}_{\pm} with $[\hat{L}_{\pm}, \hat{H}] = 0$ which raise or lower m by one unit, explaining the degeneracy in m .)

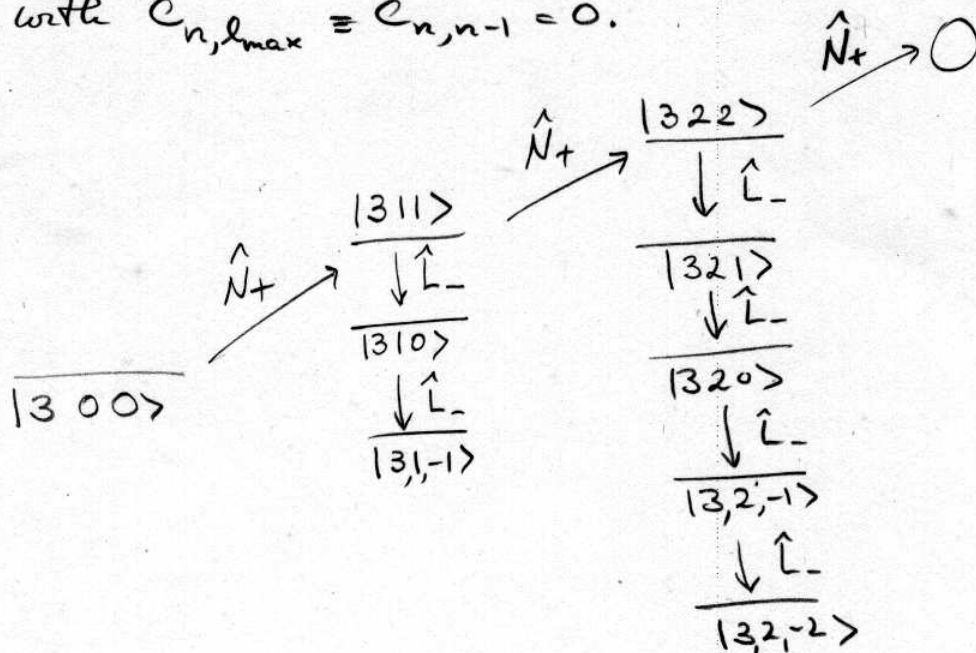
This operator is

$$\hat{N}_{\pm} = \frac{1}{\sqrt{2}} (\hat{N}_x \pm i \hat{N}_y)$$

Since $[\hat{H}, \hat{N}_{\pm}] = 0$, it commutes with \hat{H} . It satisfies

$$\hat{N}_+ |n, l, m=l\rangle = c_{nl} |n, l+1, m=l+1\rangle$$

with $c_{n, l_{\max}} = c_{n, n-1} = 0$.



13.3. Some hydrogen numbers

electron mass	$mc^2 = 0.511 \text{ MeV}$	$\sim 0.5 \text{ MeV}$
proton mass	$Mc^2 = 938.3 \text{ MeV}$	$\sim 1 \text{ GeV}$
	$\frac{M}{m} = 1836$	~ 2000

\Rightarrow reduced mass $\mu = \frac{mM}{m+M} \approx \frac{mM}{M} = m$ within 0.5%

The electron coordinate and the relative coordinate to the proton agree also within 0.5%, and the proton can be considered to stay at rest.

Bohr radius

$$a_0 = \frac{\hbar^2}{me^2}$$

Planck constant $\hbar = 6.6 \times 10^{-34} \text{ Js}$

$\hbar c = 197.33 \text{ MeV fm} \approx 200 \text{ MeV fm}$ (1.5%)

fine structure constant $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.04} \approx \frac{1}{137}$

$$\Rightarrow a_0 = \frac{\hbar^2}{\mu e^2} \approx \frac{\hbar^2}{me^2} = \frac{(\hbar c)^2}{(mc^2)e^2} = \frac{\hbar c}{mc^2 \alpha} = \frac{200 \text{ MeV fm} \cdot 137}{0.5 \text{ MeV}}$$

$$= 53,000 \text{ fm} = 0.53 \text{ \AA}$$

(proton radius $\approx 1 \text{ fm}$)
"point nucleus"

This explains why a typical atomic length scale is 1 Å.

Next: $\underline{1 \text{ Rydberg}} = R_y = \frac{me^4}{2\hbar^2} = \frac{(mc^2)e^4}{2(\hbar c)^2} = \frac{mc^2 \alpha^2}{2}$

$$= \frac{0.511 \text{ MeV}}{2 \cdot 137^2} \approx 13.6 \text{ eV}$$

⇒ hydrogen energy eigenvalues

$$E_n = - \frac{13.6 \text{ eV}}{n^2}$$

Compton wavelength $\alpha a_0 = \frac{e^2}{\hbar c} \frac{\hbar^2}{m e^2} = \frac{\hbar}{m c} = \lambda_e$

$$\lambda_e = \frac{53,000 \text{ fm}}{137} = 386 \text{ fm}$$

The Compton wavelength is the lower limit for how well the particle can be localized. To locate the particle within ΔX , we need a photon with wavenumber $\Delta k \sim \frac{1}{\Delta X} \rightarrow \Delta P \sim \frac{\hbar}{\Delta X}$

$$\xrightarrow{m_y=0} \Delta E \sim \frac{\hbar c}{\Delta X}$$

If $\Delta E > 2m_e c^2$, then the scattering is violent enough that in the measurement process we can create additional e^+e^- pairs. Therefore we demand for a good localization measurement of our targeted electron

$$\Delta E \leq 2m_e c^2 \Rightarrow \frac{\hbar c}{\Delta X} \leq 2m_e c^2 \Rightarrow \Delta X \geq \frac{\hbar}{2m_e c} = \frac{1}{2} \lambda_e$$

Good news: $\lambda_e \ll a_0$, so electron is well localized on the scale of the atom.

Classical electron radius $r_e = \alpha \lambda_e = \alpha^2 a_0 \approx 2.8 \text{ fm}$

If we imagine the electron as a spherical charge distribution of radius r_e , the energy to assemble this distribution by bringing the charges in from infinity is $O\left(\frac{e^2}{r_e}\right)$

$$\text{For } r_e = \alpha^2 a_0 = \alpha^2 \frac{\hbar c}{mc^2 \alpha} = \frac{\alpha \hbar c}{mc^2}$$

$\frac{e^2}{r_e} = \frac{e^2 mc^2}{\alpha \hbar c} = mc^2$, i.e. this electrostatic potential energy accounts for all of the electron rest mass.

Classical Bohr model:

$$ma = F \quad \rightarrow \quad m \frac{v^2}{r} = \frac{e^2}{r^2} \quad \rightarrow \quad mv^2 = \frac{e^2}{r}$$

Any radius satisfying this eq. is allowed.

\Rightarrow any (negative) energy is allowed:

$$E = T + V = \frac{m}{2} v^2 - \frac{e^2}{r} = -\frac{e^2}{2r} = -\frac{1}{2} mv^2$$

\uparrow
virial thm.

As $r \rightarrow 0$, $E \rightarrow -\infty$ and $v \rightarrow \infty$.

Since (radially) accelerated charges radiate, electrons will spiral inward, ending in a singularity at $r=0$, $E=-\infty$, $v=\infty$, and an infinite amount of radiated energy ("radiation catastrophe")

Bohr tried to avoid this by postulating

$$L = |\vec{r} \times \vec{p}| = n\hbar \quad (\text{angular momentum quantization})$$

$$\Rightarrow mvr = n\hbar \quad \Rightarrow v = \frac{n\hbar}{mr}$$

$$\Rightarrow \frac{e^2}{r} = mv^2 = m \frac{n^2 \hbar^2}{m^2 r^2} \Rightarrow \boxed{r = n^2 \frac{\hbar^2}{me^2} = n^2 a_0}$$

$$\text{and } \underline{E_n} = -\frac{e^2}{2r} = -\frac{e^2}{2a_0} \left(\frac{1}{n^2}\right) = -\frac{e^2 me^2}{2\hbar^2} \left(\frac{1}{n^2}\right) = -R_y \frac{1}{n^2}$$

This gives the correct energy eigenvalues
for the hydrogen atom!

So, classical orbits + angular momentum quantization
= successful atomic spectroscopy!
(Nobel prize 1922)

What is the expectation value of the electron's velocity
in the hydrogen ground state? Use Bohr's model:

$$E_1 = -\frac{me^4}{2\hbar^2} = -\frac{1}{2}mv^2$$

$$\Rightarrow v/c = \sqrt{\frac{e^4}{(\hbar c)^2}} = \sqrt{\alpha^2} = \alpha \Rightarrow \boxed{\beta = \alpha} \text{ easy to remember!}$$

So you can reconstruct the ground state energy just
from the virial theorem and the mnemonic " $\alpha = \beta$ " in the
ground state.

Rewriting $E_1 = -\frac{e^2}{2r_1} = -\frac{e^2}{2a_0}$ we also get $a_0 = \frac{\hbar}{me\alpha}$.

So $\alpha = \beta$ is really all you need to remember, together

with $E_n = \frac{E_1}{n^2}$.

Atomic spectra:

$$\hbar\omega_{if} = Ry \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = E_i - E_f \quad \text{transition energy}$$

Lyman series: all transitions to the ground state ($n_f = 1$)

Balmer series: " " " the $n_f = 2$ state

$$\omega_{i1} = \frac{R_y}{\hbar} \left(1 - \frac{1}{n_i^2}\right), \quad \omega_{i2} = \frac{R_y}{\hbar} \left(\frac{1}{4} - \frac{1}{n_i^2}\right) \quad (n_i > 2)$$

$$\hbar\omega_{21} = 13.6 \text{ eV} \left(1 - \frac{1}{4}\right) \approx 10 \text{ eV} \quad \text{order of magnitude}$$

$$\begin{aligned} \lambda_{21} &= \frac{2\pi c}{\omega_{21}} = \frac{2\pi \hbar c}{\hbar\omega_{21}} = \frac{2\pi}{10 \text{ eV}} \cdot 197.33 \times 10^6 \text{ eV fm} \\ &= \frac{1.216 \times 10^8 \text{ eV}}{\text{eV}} \cdot 10^{-15} \text{ m} = 1.216 \times 10^{-7} \text{ m} = \underline{1216 \text{ \AA}} \\ &\quad \text{(infrared)} \end{aligned}$$

works extremely well when compared with experiment!

Required corrections for precise predictions:

- proton recoil
- relativistic energy-momentum relation

$$T = mc^2 \left(\frac{1}{\sqrt{1-v^2/c^2}} - 1 \right)$$

the first correction $\sim \frac{v^2}{c^2} \sim \alpha^2 \rightarrow$ "fine structure corrections"

(Dirac equation)

- quantum field theoretical corrections (Lamb shift)
(QED)

- interactions between spin and magnetic field
and between electron and nuclear spins
"hyperfine interactions"