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

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

S.Eq.: \[ \left\{ \frac{d^2}{dr^2} + \frac{2m}{\hbar^2} \left( E + \frac{e^2}{r^2} - \frac{\ell(\ell+1)}{2mr^2} \right) \right\} \psi_{\ell m}(r) = 0 \]

$$ \psi_{\ell m}(r, \theta, \phi) = \frac{\psi_{\ell m}(r)}{r} \ Y_{\ell m}(\theta, \phi) $$

From the previous chapter we know that asymptotically for large $r$

$$ \psi_{\ell m} \rightarrow r^{-\kappa} \quad \text{(up to a fractional power prefactor)} $$

where $\kappa = \sqrt{\frac{2mE}{\hbar^2}}$

and for small $r$

$$ \psi_{\ell m} \rightarrow r^{\ell+1} $$

Use scaled radial coordinate

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

and write

$$ \psi_{\ell m}(\rho) = \psi_{\ell m}(\rho) \ e^{-\rho} $$

The equation for $\rho$ is then

$$ \frac{d^2\rho}{d\rho^2} - 2\frac{d\rho}{d\rho} + \left( \frac{e^2}{\rho} - \frac{\ell(\ell+1)}{\rho^2} \right) \rho = 0 $$

with $\lambda = \sqrt{\frac{2m|E|}{\hbar^2}}$
We try the power-series ansatz

\[ V_{\text{ee}}(\rho) = \rho^{l+1} \sum_{k=0}^{\infty} C_k \rho^k \]

and plug it into (\ref{eq:recursion}) to obtain the recursion relation

\[
\frac{C_{k+1}}{C_k} = \frac{-e^2\lambda + 2(k+l+1)}{(k+l+2)(k+l+1) - \ell(l+1)} \quad \xrightarrow{k \to \infty} \frac{2}{k}
\]

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, \( V_{\text{ee}} \)
would asymptotically go like \( V_{\text{ee}} \propto \rho^m e^{2\rho} e^{-\rho} \propto \rho^n e^\rho \),
which is not normalizable. To obtain normalizable
state, we must demand that the series terminates at
some \( k \). This will happen for

\[ e^2 \lambda = 2(k+l+1) \Rightarrow \frac{e^4 2m}{\hbar^2 (E)} = 4(k+l+1)^2 \]

\[ E = -\frac{m e^4}{2 \hbar^2} \frac{1}{(k+l+1)^2} \quad k = 0, 1, 2, \ldots; \quad l = 0, 1, 2, \ldots \]

Again, we can introduce a principal quantum number

\[ n = k + l + 1 \]

\[ E_n = -\frac{m e^2}{2 \hbar^2 n^2} \quad (n = 1, 2, 3, \ldots) \] (allowed energy eigenvalues)

For each \( n \), the allowed \( l \) values are

\[ l = n - k - 1 = (n-1, n-2, \ldots, 1, 0) \]
Since each \( l \) value is \( 2l+1 \) times degenerate due to the magnetic quantum number, the total degeneracy of eigenvalue \( E_n \) is

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

\( l = 0, 1, 2, 3, \ldots \) \( \Leftrightarrow \) s, p, d, f, g, h ... states, ("spectroscopic notation")

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

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

2p \( \equiv (n=2, l=1) \) etc

Natural energy unit for the energy levels of hydrogen:

\[
1 \text{Ry} = \frac{m_e^4}{2\hbar^2} \approx 13.6 \text{eV} \quad \text{("Rydberg")}
\]

The wave functions

For given \( n \) and \( l \), the power series terminates at \( k = n - l - 1 \). The function \( \psi(r) \) is then \( p^{l+1} \) times a polynomial of degree \( n-l-1 \)

\[ \rightarrow \text{"associated Laguerre polynomials", } L_{n-l-1}^{2l+1}(2p) \]

\[ \Rightarrow \psi_n^l(r) = \frac{Un^l(r)}{p} e^{-p} p^l L_{n-l-1}^{2l+1}(2p) \]

\[ p = \frac{k_m r \epsilon}{\hbar^2 n} \]
We define the Bohr radius as
\[ a_0 = \frac{\hbar^2}{m e^2} \]
\[ \Rightarrow \frac{r}{n a_0} = \frac{1}{n} \frac{r}{a_0} \]

and
\[ R_{ne}(r) \sim e^{-r/(n a_0)} \left( \frac{r}{n a_0} \right)^l L_{n-l-1} \left( \frac{2r}{na_0} \right) \]

\[ \Rightarrow n \to \infty, \quad r \to \infty, \quad r \to \infty, \quad e^{-r/(n a_0)} = e^{-r/(n a_0)} \]

(independent of l!)

The lowest energy eigenvalues have the normalized eigenfunctions

\[ \Psi_{n\ell m}(r) : \]
\[ \Psi_{100} = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0} \]
\[ \Psi_{200} = \sqrt{\frac{1}{32\pi a_0^3}} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \]
\[ \Psi_{210} = \sqrt{\frac{1}{32\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta \quad (r \cos \theta = z) \]
\[ \Psi_{21\pm 1} = \sqrt{\frac{1}{64\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta \pm i \phi \quad (r \sin \cos \phi = x, \quad r \sin \sin \phi = y) \]

Can show (homework) that
\[ \left< \hat{T} \right> = -\frac{1}{2} \left< \hat{V} \right> \] (virial theorem)

\[ \Rightarrow E = \left< \hat{T} \right> = \left< \hat{H} \right> + \left< \hat{V} \right> = \frac{1}{2} \left< \hat{V} \right> = -\frac{\hbar^2}{2m} \left< \frac{1}{r} \right> \]

\[ \Rightarrow \left< \frac{1}{r} \right>_n = -\frac{2E}{\hbar^2} = \frac{1}{a_0 n^2} \Rightarrow \left< \frac{1}{r} \right>_n \sim n^2 a_0 \]
13.2 The degeneracy of the hydrogen spectrum

Like the 2- and 3-d harmonic oscillator, the hydrogen spectrum feature "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 the among rotationally invariant potentials the \( 1/r \) potential is special because it conserves the range-like vector

\[
\vec{n} = \frac{\vec{p} \times \vec{L}}{m} - \frac{\alpha^2}{r} \vec{r}
\]

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

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

\[
[\hat{H}, \hat{n}] = 0 \quad \Rightarrow \quad \frac{d}{dt} \langle \hat{n} \rangle = 0
\]

where

\[
\hat{n} = \frac{i}{2m} \left( \frac{\vec{P} \times \vec{L} - \vec{L} \times \vec{P}}{\left(\vec{P} \times \vec{L}\right)^2} \right) - \frac{\alpha^2}{\sqrt{\lambda^2 + \tilde{\lambda}^2 + \tilde{\lambda}^2}}
\]

("symmetrization rule")
To explain the degeneracy in \( l \) (\( l=n-1, n-2, \ldots, 1, 0 \)), we must be able to build from the components of \( \hat{\mathbf{L}} \) some operator that commutes with \( \hat{H} \) and raises or lowers \( l \) by one unit. (Just as we were able to build from \( \hat{\mathbf{L}}^2 \) the operators \( \hat{\mathbf{L}}_\pm \) with \( [\hat{\mathbf{L}}^2, \hat{\mathbf{L}}_\pm] = 0 \) 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 \( c_{nl,l+1} = c_{n,l+1} = 0 \).
13.3. Some hydrogen numbers

electron mass \[ m_e c^2 = 0.511 \text{ MeV} \approx 0.5 \text{ MeV} \]
proton mass \[ M_e c^2 = 938.3 \text{ MeV} \approx 1 \text{ GeV} \]
\[ \frac{M}{m} = 1836 \approx 2000 \]

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

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
\[ a_0 = \frac{\hbar^2}{m e^2} \]

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

\[ \alpha = \frac{e^2}{\hbar c} = \frac{1}{137.04} \approx \frac{1}{137} \]

\[ \Rightarrow a_0 = \frac{\hbar^2}{m e^2} \approx \frac{\hbar^2}{m e^2} = \frac{(\hbar c)^2}{(m c^2) e^2} = \frac{\hbar c}{m c^2 \alpha} = \frac{200 \text{ MeV/fm} \cdot 137}{0.5 \text{ MeV}} \]
\[ = 53,000 \text{ fm} = 0.53 \text{ Å} \]

(proton radius \approx 1 \text{ fm})

"point nucleus"

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

Next: 1 Rydberg \[ R_y = \frac{me^4}{2\hbar^2} = \frac{(mc^2)e^4}{2(\hbar c)^2} = \frac{mc^2}{2} \frac{\alpha^2}{\hbar} \]
\[ = \frac{0.511 \text{ MeV}}{2 \cdot 137^2} \approx 18.6 \text{ eV} \]
$\Rightarrow$ hydrogen energy eigenvalues

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

Compton wavelength

\[ \lambda_c = \frac{\hbar c}{mc^2} = \frac{\hbar}{mc} = \lambda_e \]

\[ \lambda_e = \frac{53,000 \text{ fm}}{137} \approx 386 \text{ fm} \]

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

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

\[ \Delta E \leq 2mc^2 \Rightarrow \frac{\hbar c}{\Delta X} \leq 2mc^2 \Rightarrow \Delta X \geq \frac{\hbar c}{2mc^2} \]

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

Classical electron radius

\[ \lambda_e = a \Rightarrow \lambda_e = a^2 a_0 \approx 2.8 \text{ fm} \]

If we imagine the electron as a spherical charge distribution, the energy to assemble this distribution by bringing the charges in from infinity is $O\left(\frac{e^2}{\lambda_e}\right)$
For \( r_e = \alpha^2 a_0 = \alpha^2 \frac{hc}{mc^2} = \frac{\alpha hc}{mc^2} \),
\[
\frac{e^2}{r_e} = \frac{e^2 mc^2}{\alpha \hc} = mc^2, \text{ i.e. this electrostatic potential energy accounts for all of the electron rest mass.}
\]

**Classical Bohr model:**

\[
ma = F \rightarrow m \frac{v^2}{r} = \frac{e^2}{r^2} \rightarrow m v^2 = \frac{e^2}{r}
\]

Any radius satisfying this eq. is allowed.

- any (negative) energy is allowed:

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

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

Since (radially) accelerated charge 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

\[
L = (r \times p) = n \hbar \quad \text{(angular momentum quantization)}
\]

\[
\Rightarrow mv r = n \hbar \quad \Rightarrow v = \frac{n \hbar}{mr}
\]

\[
\Rightarrow \frac{e^2}{r} = mv^2 = m \frac{n^2 \hbar^2}{m^2 r^2} \Rightarrow \boxed{\rho = \frac{n^2 \frac{e^2}{\hbar}}{m c^2} = n^2 a_0}
\]

and
\[
E_n = -\frac{e^2}{2r} = -\frac{e^2}{2a_0} \left( \frac{1}{n^2} \right) = -\frac{e^2 m e^2}{2 \frac{1}{n^2}} = -\frac{Ry}{n^2}
\]
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:

\[ E_i = -\frac{mc^4}{2h^2} = -\frac{1}{2} mv^2 \]

\[ \Rightarrow v = \sqrt{\frac{e^4}{4\hbar^2}} = \sqrt{\alpha^2} = \alpha \Rightarrow \beta = \alpha \text{ easy to remember!} \]

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

Rewriting \( E_i = -\frac{e^2}{2r_i} = -\frac{e^2}{2a_0} \) we also set \( a_0 = \frac{\hbar}{mc} \).

So \( \alpha = \beta \) is really all you need to remember, together with \( E_n = \frac{E_i}{n^2} \).

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

\[ h\omega_{21} = 13.6 \text{eV} \left( 1 - \frac{1}{4} \right) \approx 10 \text{eV} \text{ order of magnitude} \]

\[ \frac{\lambda_{21}}{\hbar \omega_{21}} = \frac{2\pi c}{\omega_{21}} = \frac{2\pi \hbar c}{h \omega_{21}} = \frac{2\pi}{10 \text{eV}} \times 197.33 \times 10^6 \text{eV fm} \]

\[ = \frac{1.216 \times 10^8 \text{eV}}{10^{-15} \text{m}} = 1.216 \times 10^{-7} \text{m} = 1216 \text{Å} \text{ (infrared)} \]

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 \( \frac{v^2}{c^2} \sim \alpha^2 \rightarrow \) "fine structure corrections"
  (Dirac equation)

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

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