\[ 0 = \langle \psi_a^0 | \hat{A} H' - H' \hat{A} | \psi_b^0 \rangle = \langle \psi_a^0 | \hat{A} H' | \psi_b^0 \rangle - \langle \psi_a^0 | H' \hat{A} | \psi_b^0 \rangle = A_a \langle \psi_a^0 | H' | \psi_b^0 \rangle - A_b \langle \psi_a^0 | H' | \psi_b^0 \rangle = (A_a - A_b) \langle \psi_a^0 | H' | \psi_b^0 \rangle \]  

(2.281)

If \( A_a \neq A_b \), this equation means that \( \langle \psi_a^0 | H' | \psi_b^0 \rangle = 0 \).

For this situation, although we have a degeneracy, one can just do non-degenerate perturbation for \( | \psi_a^0 \rangle \) and \( | \psi_b^0 \rangle \) (separately) and there will be no singularities at all.

### 2.5. the fine structure of a hydrogen atom

#### 2.5.1. Relativistic correction

In QMI, we solved an ideal model for a hydrogen atom (i.e. a particle in \( 1/r \) potential). In a real hydrogen atom, that model missed some of the physics, and one of them is relativistic effects.

Q: what is the energy of a particle, if the particle is moving at speed \( v \) and the rest mass \( m \).

\[ E = Mc^2 = \frac{m}{\sqrt{1 - \frac{v^2}{c^2}}} \]  

(2.282)

Q: what is the momentum of a particle, if the particle is moving at speed \( v \) and the rest mass \( m \).

\[ p = Mv = \frac{m}{\sqrt{1 - \frac{v^2}{c^2}}} \]  

(2.283)

As a result,

\[ E = \sqrt{p^2 c^2 + m^2 c^4} \]  

(2.284)

To prove this relation, we start from the r.h.s.,

\[ \sqrt{p^2 c^2 + m^2 c^4} = \frac{\sqrt{m^2 v^2 c^2 + m^2 c^4(1 - \frac{v^2}{c^2})}}{\sqrt{1 - \frac{v^2}{c^2}}} = \frac{m^2 v^2 c^2 + m^2 c^4 - m^2 c^2 v^2}{1 - \frac{v^2}{c^2}} = \frac{m^2 c^4}{1 - \frac{v^2}{c^2}} = \sqrt{E} \]  

(2.285)

This relation between \( E \) and \( p \) is an very important relation for relativistic physics!

Q: what is kinetic energy?

A: First, find the energy of a particle when it is not moving \( p = 0 \). Then we measure the energy again when it is moving (with momentum \( p \)). The energy difference between them is the kinetic energy for this particle.

\[ T = E - mc^2 = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 = mc \left( \frac{p}{mc} \right)^2 - 1 \]  

(2.286)

When particle is moving at low velocity (\( v << c \)), \( p << mc \), and thus \( p/mc << 1 \). As a result, we can use the following expansion

\[ \sqrt{1 + x} = 1 + \frac{x}{2} - \frac{x^2}{8} + \ldots \]  

(2.287)

i.e.,

\[ \sqrt{1 + x} - 1 = \frac{x}{2} - \frac{x^2}{8} + \ldots \]  

(2.288)
So,

\[ T = m c^2 \left( \frac{1}{2} \left( \frac{p}{m c} \right)^2 - \frac{1}{8} \left( \frac{p}{m c} \right)^4 + \ldots \right) = \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \ldots \] (2.289)

The first term here is the kinetic energy in classical mechanics. In relativistic physics, the kinetic energy is NOT just \( \frac{p^2}{2m} \). Instead, we have a lot of corrections. These corrections are small if a particle is moving at low speed. There, we can treat them as perturbation

\[ H' = -\frac{p^4}{8m^3 c^2} \] (2.290)

**NOTE:** this treatment is NOT the rigorous way to combine special relativity with quantum mechanics, because this treatment has one major flaw. At larger \( p \) or small \( m \) (e.g. consider a very light particle), the series will diverge. This problem comes from the fact that we used square root in the definite of the Hamiltonian. Square root is NOT an analytic function near small \( x \), and thus will cause trouble (to see this, think about \( f(x) = \sqrt{x} \), one can easily show that for the first order derivative, \( x=0 \) is infinite \( \lim_{x \to 0} f'(x) \to \infty \)).

The correct way to do it is to use a matrix. Notice that for a matrix, square root arises naturally (e.g., the eigenvalue of

\[
\begin{pmatrix}
  m c^2 & p c \\
p c & -m c^2
\end{pmatrix}
\]

are \( \pm \sqrt{p^2 c^2 + m^2 c^4} \). We get square root without having any square root in the matrix). The person who figured this out is Dirac and this is Dirac’s theory for relativistic fermions.

If we ignore higher order terms, our hydrogen atom should follow this Hamiltonian

\[ H = H_0 + H' \] (2.291)

where \( H_0 = \frac{p^2}{2m} + V(r) \). With the perturbation \( H' \), the energy of a hydrogen atom will be different from what we computed early on. How large is the difference? This question can be answered by the perturbation theory.

We have already known the energy spectrum of \( H_0 \),

\[ E_n^0 = -\frac{13.6 \text{ eV}}{n^2} \text{ with } n = 1, 2, 3, \ldots \] (2.292)

More precisely,

\[ E_n^0 = -\frac{1}{n^2} \frac{m}{2 \hbar^2} \left( \frac{e^2}{4 \pi \varepsilon_0} \right)^{\frac{1}{2}} \] (2.293)

We often define Bohr radius \( a \) as

\[ a = \frac{\hbar^2}{4 \pi \varepsilon_0} \] (2.294)

And then,

\[ E_n^0 = -\frac{1}{n^2} \frac{1}{2 \hbar^2} \left( \frac{e^2}{4 \pi \varepsilon_0 a} \right) \] (2.295)

For \( E_n \), there are \( n^2 \) degenerate quantum states (ignore spin at this moment) \( \psi_{nlm} \) where \( l \) is the angular momentum quantum number \( l = 0, 1, 2 \ldots n-1 \) and \( m \) is the quantum number for \( L_z \) and \( m = -l, -l+1, \ldots 0, \ldots, l-1, l \)

\[ L_z \psi_{nlm} = \hbar m \psi_{nlm} \] (2.297)

For, \( n = 1 \) there is no degeneracy, and we can do non-degenerate perturbation theory. For any \( n > 1 \), there are \( n \) degenerate states, and thus we should do degenerate perturbation theory. However, we are very lucky here. We don’t need to worry about degenerate perturbation theory, because \( \psi_{nlm} \) is already a good set of basis:

\[ \langle \psi_{nlm} | H' | \psi_{n'l'm'} \rangle = 0 \] (2.298)

if \( l \neq l' \) or \( m \neq m' \).
This is because both \( H_0 \) and \( H' \) commute with \( L^2 \). And we can also show that both \( H_0 \) and \( H' \) commute with \( L_z \). Here, \( L^2 \) and \( L_z \) serve as the \( \hat{A} \) operator that we defined in the previous section. For a fixed \( n \), because the degenerate states all have different eigenvalues for \( L^2 \) and \( L_z \) (different \( l \) and \( m \)), \( \langle \psi_{n l m} | H' | \psi_{n l m} \rangle = 0 \). So we don’t need to choose any other basis and can start with non-degenerate perturbation.

The correction to the energy is (to the first order)

\[
E_{n l m}^{(1)} = \langle \psi_{n l m} | H' | \psi_{n l m} \rangle = -\frac{p^4}{8 m^3 c^2} \langle \psi_{n l m} | p^4 | \psi_{n l m} \rangle = -\frac{1}{8 m^3 c^2} \langle \psi_{n l m} | p^2 | \psi_{n l m} \rangle = -\frac{1}{8 m^3 c^2} \langle \psi_{n l m} | p^2 | \psi_{n l m} \rangle
\]

(2.299)

For \( | \psi_{0 l m} \rangle \), we know that

\[
H_0 | \psi_{n l m} \rangle = E_{n l m} | \psi_{n l m} \rangle
\]

(2.300)

\[
\frac{p^2}{2m} | \psi_{n l m} \rangle = (E_0 - V) | \psi_{n l m} \rangle
\]

(2.301)

\[
p^2 | \psi_{n l m} \rangle = 2m (E_0 - V) | \psi_{n l m} \rangle
\]

(2.302)

\[
p^2 | \psi_{n l m} \rangle = 2m (E_0 - V) | \psi_{n l m} \rangle
\]

(2.303)

\[
E_{n l m}^{(1)} = (E_0 - V) | \psi_{n l m} \rangle
\]

(2.304)

The conjugate of this equation gives

\[
\langle \psi_{n l m} | p^2 = 2 m (E_0 - V)
\]

(2.305)

So,

\[
\langle \psi_{n l m} | p^2 | \psi_{n l m} \rangle = \langle \psi_{n l m} | 2 m (E_0 - V) | \psi_{n l m} \rangle = 4 m^2 \langle \psi_{n l m} | (E_0^0 - V) \rangle | \psi_{n l m} \rangle
\]

(2.306)

Here, \( V = -\frac{e^2}{4 \pi \epsilon_0 r} \) and

\[
\langle \psi_{n l m} | (E_0 - V) \rangle | \psi_{n l m} \rangle = \langle \psi_{n l m} | (E_0 - V) + V \rangle | \psi_{n l m} \rangle = \langle \psi_{n l m} | (E_0 + V) \rangle | \psi_{n l m} \rangle - 2 \langle \psi_{n l m} | \psi_{n l m} \rangle + \langle \psi_{n l m} | V(r^2) | \psi_{n l m} \rangle
\]

(2.307)

Without going into details, we will just show the results here

\[
\langle \psi_{n l m} | \frac{1}{r} | \psi_{n l m} \rangle = \frac{1}{n^2 a}
\]

(2.308)

\[
\langle \psi_{n l m} | \frac{1}{r^2} | \psi_{n l m} \rangle = \frac{1}{n^2 (l + \frac{1}{2}) a^2}
\]

(2.309)

Thus,

\[
E_{n l m}^{(1)} = \frac{1}{8 m^3 c^2} \langle \psi_{n l m} | p^2 | \psi_{n l m} \rangle = \frac{1}{8 m^3 c^2} \left[ E_0^0 + \frac{e^2}{2 \pi \epsilon_0 n^2 a} + \left( \frac{e^2}{4 \pi \epsilon_0 a} \right)^2 \frac{1}{n^2 (l + \frac{1}{2}) a^2} \right]
\]

(2.310)

As we have shown early on

\[
E_0^0 = -\frac{1}{n^2} \frac{1}{2} \left( \frac{e^2}{4 \pi \epsilon_0 a} \right)
\]

(2.311)
\(-2n^2E_n^0 = \frac{e^2}{4\pi \epsilon_0 a}\)

\[E_{nlm}^1 = -\frac{1}{2mc^2}\left[ (E_n^0)^2 + \frac{2E_n^0}{n^2} + \frac{e^2}{4\pi \epsilon_0 a} + \frac{1}{n^2(l + \frac{1}{2})} \left( \frac{e^2}{4\pi \epsilon_0 a} \right)^2 \right] = \]

\[-\frac{1}{2mc^2}(E_n^0)^2 - \frac{2E_n^0}{n^2} - 2n^2E_n^0 \left( \frac{4n}{2mc^2(l + \frac{1}{2}) - 3} \right)\]

So, the eigen-energy in a H atom shall be

\[E_{nlm} = E_n^0 + E_{nlm}^1 + \ldots = E_n^0 \left( \frac{4n}{2mc^2(l + \frac{1}{2}) - 3} \right) + \ldots\]

The zeroth order term

\[E_n^0 = -\frac{1}{2n^2} \frac{m}{\hbar^2} \left( \frac{e^2}{4\pi \epsilon_0} \right)^2\]

it is proportional to

\[E_n^0 \propto \frac{m}{\hbar^2} \left( \frac{e^2}{4\pi \epsilon_0} \right)^2 \left( \frac{\epsilon_0}{hc} \right)^2 \]

The prefactor \(\frac{e^2}{4\pi \epsilon_0 hc}\) is a very important physics constant, known as the fine structure constant.

\[\alpha = \frac{e^2}{4\pi \epsilon_0 hc} \approx \frac{1}{137.036}\]

So,

\[E_n^0 \propto \alpha^2 mc^2\]

The first order term

\[E_{nlm}^1 \propto \left( \frac{E_n^0}{E_n^0} \right)^2 = \alpha^4 mc^2\]

If we compare the first order and zeroth order term,

\[\frac{E_{nlm}^1}{E_n^0} \propto \frac{\alpha^4 mc^2}{\alpha^2 mc^2} = \alpha^2 \approx \left( \frac{1}{137.036} \right)^2 \approx \frac{1}{10000}\]

So indeed, the perturbation theory works, i.e. higher order term is much smaller than the leading order. (remember that Taylor expansions only converge when the small parameter \(\lambda\) is small enough. Here, our small parameter is \(\alpha\), which is smaller than 1%).

**Relativistic correction is indeed a small correction in a H atom**

NOTE: the fine structure constant is one of the most important physics constant. It is dimensionless. It involves special relativity (contains the speed of light). It involves quantum mechanics (having \(\hbar\) in its definition) and it also involves E&M (having \(\epsilon_0\) and \(e^2\)). In this section, we showed that it is so lucky for us that for a H atom, because \(\alpha\) is small, our relativistic correction is indeed small and thus we can do perturbation theory. In QFT (QED), small \(\alpha\) means that interactions between particles (quantum electron-dynamics) is a small perturbation. To the leading order, we can treat a particle as a free particle, and then add E&M interactions as a perturbation. Because the small parameter \(\alpha\) is so small, in QED, our perturbation theory converge very fast. First order perturbation gives us an accuracy of the order \(\alpha^1 \sim 10^{-2}\). Second order perturbation increases the accuracy to \(\alpha^2 \sim 10^{-4}\). By going to 5th order in perturbation, we can get an accuracy of the order \(\alpha^5 \sim 10^{-10}\). This is the reason why QED is such a successful theory.

**2.5.2. Spin-orbit coupling**