Quantum Physics

(UCSD Physics 130b)

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15 Hydrogen

The Hydrogen atom consists of an electron bound to a proton by the Coulomb potential.

\[ V(r) = -\frac{e^2}{r} \]

We can generalize the potential to a nucleus of charge Ze without complication of the problem.

\[ V(r) = -\frac{Ze^2}{r} \]

Since the potential is spherically symmetric, the problem separates and the solutions will be a product of a radial wavefunction and one of the spherical harmonics.

\[ \psi_{n\ell m}(\vec{r}) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi) \]

We have already studied the spherical harmonics.

The radial wavefunction satisfies the differential equation that depends on the angular momentum quantum number \( \ell \),

\[ \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) R_{E\ell}(r) + \frac{2\mu}{\hbar^2} \left( E + \frac{Ze^2}{r} - \frac{\ell(\ell + 1)\hbar^2}{2\mu r^2} \right) R_{E\ell}(r) = 0 \]

where \( \mu \) is the reduced mass of the nucleus and electron.

\[ \mu = \frac{m_e m_N}{m_e + m_N} \]

The differential equation can be solved (See section 15.3.1) using techniques similar to those used to solve the 1D harmonic oscillator equation. We find the eigen-energies

\[ E = -\frac{1}{2\hbar^2} Z^2 \alpha^2 \mu e^2, \]

and the radial wavefunctions

\[ R_{n\ell}(\rho) = \rho^\ell \sum_{k=0}^\infty a_k \rho^k e^{-\rho/2} \]

where the coefficients of the polynomials can be found from the recursion relation

\[ a_{k+1} = \frac{k + \ell + 1 - n}{(k + 1)(k + 2\ell + 2)} a_k \]

and

\[ \rho = \sqrt{-8\mu E \hbar^2 r}. \]

The principle quantum number \( n \) is an integer from 1 to infinity.

\[ n = 1, 2, 3, \ldots \]
This principle quantum number is actually the sum of the radial quantum number plus $\ell$ plus 1.

$$n = n_r + \ell + 1$$

and therefore, the total angular momentum quantum number $\ell$ must be less than $n$.

$$\ell = 0, 1, 2, ..., n - 1$$

This unusual way of labeling the states comes about because a radial excitation has the same energy as an angular excitation for Hydrogen. This is often referred to as an accidental degeneracy.

### 15.1 The Radial Wavefunction Solutions

Defining the **Bohr radius**

$$a_0 = \frac{\hbar^2}{\kappa mc},$$

we can compute the radial wave functions (See section 15.3.2) Here is a list of the first several radial wave functions $R_{n\ell}(r)$.

$$R_{10} = 2 \left( \frac{Z}{a_0} \right)^{\frac{1}{2}} e^{-Zr/a_0}$$

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

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

$$R_{02} = \frac{2\sqrt{2}}{27\pi} \left( \frac{Z}{3a_0} \right)^{\frac{2}{3}} \left( \frac{Zr}{a_0} \right)^{\frac{2}{3}} e^{-Zr/3a_0}$$

$$R_{31} = \frac{4\sqrt{2}}{3} \left( \frac{Z}{3a_0} \right)^{\frac{1}{3}} \left( \frac{Zr}{a_0} \right) \left( 1 - \frac{Zr}{6a_0} \right) e^{-Zr/3a_0}$$

$$R_{30} = 2 \left( \frac{Z}{3a_0} \right)^{\frac{1}{3}} \left( 1 - \frac{Zr}{3a_0} + \frac{2(Zr)^2}{27a_0} \right) e^{-Zr/3a_0}$$

For a given principle quantum number $n$, the largest $\ell$ radial wavefunction is given by

$$R_{n,n-1} \propto r^{n-1} e^{-Zr/na_0}$$

The radial wavefunctions should be normalized as below.

$$\int_0^\infty r^2 R_{n\ell}^* R_{n\ell} \, dr = 1$$

* See Example 15.4.2: Compute the expected values of $E$, $L^2$, $L_z$, and $L_y$ in the Hydrogen state $\frac{1}{\sqrt{6}}(\psi_{100} + 3\psi_{211} - i\psi_{210} + \sqrt{10}\psi_{211-1}).$*

The pictures below depict the probability distributions in space for the Hydrogen wavefunctions.
The graphs below show the radial wave functions. Again, for a given $n$ the maximum $\ell$ state has no radial excitation, and hence no nodes in the radial wavefunction. As $\ell$ gets smaller for a fixed $n$, we see more radial excitation.
A useful integral for Hydrogen atom calculations is:

\[
\int_{0}^{\infty} dx \, x^n \, e^{-ax} = \frac{n!}{a^{n+1}}
\]

* See Example 15.4.2: What is the expectation value of \(\frac{1}{r}\) in the state \(\psi_{100}\)?

* See Example 15.4.3: What is the expectation value of \(r\) in the state \(\psi_{100}\)?

* See Example 15.4.4: What is the expectation value of the radial component of velocity in the state
15.2 The Hydrogen Spectrum

The figure shows the transitions between Hydrogen atom states.

The ground state of Hydrogen has \( n = 1 \) and \( \ell = 0 \). This is conventionally called the 1s state. The convention is to name \( \ell = 0 \) states 's', \( \ell = 1 \) states 'p', \( \ell = 2 \) states 'd', and \( \ell = 4 \) states 'f'. From there on follow the alphabet with g, h, i, ...

The first excited state of Hydrogen has \( n = 2 \). There are actually four degenerate states (not counting different spin states) for \( n = 2 \). In terms of \( \psi_{n\ell m} \), these are \( \psi_{200} \), \( \psi_{211} \), \( \psi_{210} \), and \( \psi_{21-1} \). These would be called the 2s and 2p states. Remember, all values of \( \ell < n \) are allowed.

The second excited state has \( n = 3 \) with the 3s, 3p and 3d states being degenerate. This totals 9 states with the different allowed \( m \) values.

In general there are \( n^2 \) degenerate states, again not counting different spin states.

The Hydrogen spectrum was primarily investigated by measuring the energy of photons emitted in transitions between the states, as depicted in the figures above and below.
Transitions which change $\ell$ by one unit are strongly preferred, as we will later learn.

### 15.3 Derivations and Calculations

#### 15.3.1 Solution of Hydrogen Radial Equation

The differential equation we wish to solve is:

$$
\left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) R_{E\ell}(r) + \frac{2\mu}{\hbar^2} \left( E + \frac{Ze^2}{r} - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \right) R_{E\ell}(r) = 0
$$

First we change to a **dimensionless variable** $\rho$,

$$\rho = \sqrt{-\frac{8\mu E}{\hbar^2}} r,$$

giving the differential equation

$$
\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} - \frac{\ell(\ell+1)}{\rho^2} R + \left( \frac{\lambda}{\rho} - \frac{1}{4} \right) R = 0,
$$

where the constant

$$\lambda = \frac{Ze^2}{\hbar} \sqrt{\frac{-\mu}{2E}} = Z\alpha \sqrt{\frac{-\mu c^2}{2E}}.$$
Next we look at the equation for large $r$.
\[
\frac{d^2 R}{d\rho^2} - \frac{1}{4} R = 0
\]
This can be solved by $R = e^{\frac{-\rho}{2}}$, so we explicitly include this.
\[
R(\rho) = G(\rho)e^{\frac{-\rho}{2}}
\]
We should also pick of the small $r$ behavior.
\[
\frac{d^2 R}{d\rho^2} + \frac{2dR}{\rho\,d\rho} - \ell(\ell+1)R = 0
\]
Assuming $R = \rho^s$, we get
\[
s(s-1)\frac{R}{\rho^2} + 2s\frac{R}{\rho^2} - \ell(\ell+1)\frac{R}{\rho^2} = 0
\]
\[
s^2 - s + 2s = \ell(\ell+1)
\]
\[
s(s+1) = \ell(\ell+1)
\]
So either $s = \ell$ or $s = -\ell - 1$. The second is not well normalizable. We write $G$ as a sum.
\[
G(\rho) = \rho^\ell \sum_{k=0}^{\infty} a_k \rho^k = \sum_{k=0}^{\infty} a_k \rho^{k+\ell}
\]
The differential equation for $G(\rho)$ is
\[
\frac{d^2 G}{d\rho^2} - \left(1 - \frac{2}{\rho}\right) \frac{dG}{d\rho} + \left(\frac{\lambda-1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right)G(\rho) = 0.
\]
We plug the sum into the differential equation.
\[
\sum_{k=0}^{\infty} a_k ((k + \ell)(k + \ell - 1)\rho^{k+\ell-2} - (k + \ell)\rho^{k+\ell-1} + 2(k + \ell)\rho^{k+\ell-2} + (\lambda - 1)\rho^{k+\ell-1} - \ell(\ell+1)\rho^{k+\ell-2}) = 0
\]
\[
\sum_{k=0}^{\infty} a_k ((k + \ell)(k + \ell - 1) + 2(k + \ell) - \ell(\ell+1))\rho^{k+\ell-2} = \sum_{k=0}^{\infty} a_k ((k + \ell) - (\lambda - 1))\rho^{k+\ell-1}
\]
Now we shift the sum so that each term contains $\rho^{k+\ell-1}$.
\[
\sum_{k=1}^{\infty} a_{k+1} ((k + \ell + 1)(k + \ell) + 2(k + \ell + 1) - \ell(\ell+1))\rho^{k+\ell-1} = \sum_{k=0}^{\infty} a_k ((k + \ell) - (\lambda - 1))\rho^{k+\ell-1}
\]
The coefficient of each power of $\rho$ must be zero, so we can derive the recursion relation for the constants $a_k$.
\[
\frac{a_{k+1}}{a_k} = \frac{k + \ell + 1 - \lambda}{(k + \ell + 1)(k + \ell) + 2(k + \ell + 1) - \ell(\ell+1)} = \frac{k + \ell + 1 - \lambda}{k(k + 2\ell + 1) + 2(k + \ell + 1) - \ell(\ell+1)}
\]
\[
\frac{k + \ell + 1 - \lambda}{(k + 1)(k + 2\ell + 2)} \to \frac{1}{k}
\]

This is then the power series for
\[G(\rho) \to \rho^\ell e^{\rho}\]
unless it somehow terminates. We can terminate the series if for some value of \( k = n_r \),
\[\lambda = n_r + \ell + 1 \equiv n.\]

The number of nodes in \( G \) will be \( n_r \). We will call \( n \) the principal quantum number, since the energy will depend only on \( n \).

Plugging in for \( \lambda \) we get the energy eigenvalues.
\[Z\alpha \sqrt{-\frac{\mu c^2}{2E}} = n.
\]
\[E = -\frac{1}{2n^2} Z^2 \alpha^2 \mu c^2\]

The solutions are
\[R_{n\ell}(\rho) = \rho^\ell \sum_{k=0}^{\infty} a_k \rho^k e^{-\rho/2}.
\]

The recursion relation is
\[a_{k+1} = \frac{k + \ell + 1 - n}{(k + 1)(k + 2\ell + 2)} a_k.
\]

We can rewrite \( \rho \), substituting the energy eigenvalue.
\[\rho = \sqrt{\frac{-8\mu E}{\hbar^2} r} = \sqrt{\frac{4\mu^2 c^2 Z^2 \alpha^2}{\hbar^2 n^2} r} = \frac{2\mu Z \alpha}{\hbar n} r = \frac{2Z}{na_0} r \]

15.3.2 Computing the Radial Wavefunctions

The radial wavefunctions are given by
\[R(\rho) = \rho^\ell \sum_{k=0}^{n-\ell-1} a_k \rho^k e^{-\rho/2}
\]

where
\[\rho = \frac{2Z}{na_0} r \]

and the coefficients come from the recursion relation
\[a_{k+1} = \frac{k + \ell + 1 - n}{(k + 1)(k + 2\ell + 2)} a_k.
\]

The series terminates for \( k = n - \ell - 1 \).
Let's start with $R_{10}$.

\[ R_{10}(r) = \rho^0 \sum_{k=0}^{0} a_k \rho^k e^{-\rho/2} \]

\[ R_{10}(r) = C e^{-Zr/a_0} \]

We determine $C$ from the normalization condition.

\[ \int_0^\infty r^2 R_{nt}^* R_{nt} \, dr = 1 \]

\[ |C|^2 \int_0^\infty r^2 e^{-2Zr/a_0} \, dr = 1 \]

This can be integrated by parts twice.

\[ 2 \left( \frac{a_0}{2Z} \right)^2 |C|^2 \int_0^\infty e^{-2Zr/a_0} \, dr = 1 \]

\[ 2 \left( \frac{a_0}{2Z} \right)^3 |C|^2 = 1 \]

\[ C^2 = \frac{1}{2} \left( \frac{2Z}{a_0} \right)^3 \]

\[ C = \frac{1}{\sqrt{2}} \left( \frac{2Z}{a_0} \right)^{3/2} \]

\[ R_{10}(r) = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \]

$R_{21}$ can be computed in a similar way. No recursion is needed.

Let's try $R_{20}$.

\[ R_{20}(r) = \rho^0 \sum_{k=0}^{1} a_k \rho^k e^{-\rho/2} \]

\[ R_{20}(r) = (a_0 + a_1 \rho) e^{-\rho/2} \]

\[ a_{k+1} = \frac{k + \ell + 1 - n}{(k + 1)(k + 2\ell + 2)} a_k. \]

\[ a_1 = \frac{0 + 0 + 1 - 2}{(0 + 1)(0 + 2(0) + 2)} a_0 = \frac{-1}{2} a_0 \]

\[ R_{20}(r) = C \left( 1 - \frac{Zr}{2a_0} \right) e^{-Zr/2a_0} \]

We again normalize to determine the constant.
15.4 Examples

15.4.1 Expectation Values in Hydrogen States

An electron in the Coulomb field of a proton is in the state described by the wave function
\( \frac{1}{2}(4\psi_{100} + 3\psi_{211} - i\psi_{210} + \sqrt{10}\psi_{21-1}) \). Find the expected value of the Energy, \( L^2 \), \( L_z \), and \( L_y \).

First check the normalization.
\[
\frac{|4|^2 + |3|^2 + (-i)^2 + |\sqrt{10}|^2}{36} = \frac{36}{36} = 1
\]

The terms are eigenstates of \( E \), \( L^2 \), and \( L_z \), so we can easily compute expectation values of those operators.
\[
E_n = -\frac{1}{2} \alpha^2 \mu e^2 \frac{1}{n^2}
\]
\[
\langle E \rangle = -\frac{1}{2} \alpha^2 \mu e^2 \frac{16 \frac{1}{12} + 9 \frac{1}{12} + 1 \frac{1}{12} + 10 \frac{1}{12}}{36} = -\frac{1}{2} \alpha^2 \mu e^2 \frac{21}{36} = -\frac{1}{2} \alpha^2 \mu e^2 \frac{7}{12}
\]

Similarly, we can just square probability amplitudes to compute the expectation value of \( L^2 \). The eigenvalues are \( \ell(\ell + 1)\hbar^2 \).
\[
\langle L^2 \rangle = \hbar^2 \frac{16(0) + 9(2) + 1(2) + 10(2)}{36} = \frac{10 \hbar^2}{9}
\]

The Eigenvalues of \( L^z \) are \( m\hbar \).
\[
\langle L_z \rangle = \hbar \frac{16(0) + 9(1) + 10(0) + 10(-1)}{36} = \frac{-1}{36}\hbar
\]

Computing the expectation value of \( L_y \) is harder because the states are not eigenstates of \( L_y \). We must write \( L_y = (L_+ - L_-)/2i \) and compute.
\[
\langle L_y \rangle = \frac{1}{72i} \left( 4\psi_{100} + 3\psi_{211} - i\psi_{210} + \sqrt{10}\psi_{21-1} \right) L_+ + \left(-4\psi_{100} + 3\psi_{211} - i\psi_{210} + \sqrt{10}\psi_{21-1} \right) L_-
\]
\[
= \frac{1}{72i} \left( 4\psi_{100} + 3\psi_{211} - i\psi_{210} + \sqrt{10}\psi_{21-1} - 3L_- \psi_{211} + i(L_+ - L_-)\psi_{210} + \sqrt{10}L_+ \psi_{21-1} \right)
\]
\[
= \frac{\hbar}{72i} \left( 4\psi_{100} + 3\psi_{211} - i\psi_{210} + \sqrt{10}\psi_{21-1} - 3\sqrt{2}\psi_{210} - i\sqrt{2}\psi_{211} + i\sqrt{2}\psi_{21-1} + \sqrt{10}\sqrt{2}\psi_{210} \right)
\]
\[
= \frac{\sqrt{2}\hbar}{72i} \left( -3i - 3i + \sqrt{10}i + \sqrt{10}i \right) = \frac{(-6 + 2\sqrt{10})i\sqrt{2}\hbar}{72i} = \frac{(2\sqrt{5} - 3\sqrt{2})\hbar}{36}
\]
15.4.2 The Expectation of $\frac{1}{r}$ in the Ground State

\[
\langle \psi_{100} | \frac{1}{r} | \psi_{100} \rangle = \int Y^*_\ell m Y_m d\Omega \int_0^\infty r^2 \frac{1}{r} R_{10}^* R_{10} dr \\
= \int_0^\infty r R_{10}^* R_{10} dr = \int_0^\infty r^4 \left( \frac{Z}{a_0} \right)^3 e^{-2Zr/a_0} dr = 4 \left( \frac{Z}{a_0} \right)^3 \frac{a_0^2}{2Z} \int_0^\infty xe^{-x} dx \\
= \frac{Z}{a_0} \int_0^\infty xe^{-x} dx = \frac{Z}{a_0}
\]

We can compute the expectation value of the potential energy.

\[
\langle \psi_{100} \rangle - \frac{Ze^2}{r} | \psi_{100} \rangle = -\frac{Z^2e^2}{a_0} = \frac{Z^2e^2\alpha m c}{\hbar} = -Z^2\alpha^2 mc^2 = 2E_{100}
\]

15.4.3 The Expectation Value of $r$ in the Ground State

\[
\langle \psi_{100} | r | \psi_{100} \rangle = \int_0^\infty r^2 R_{10}^* R_{10} dr = 4 \left( \frac{Z}{a_0} \right)^3 \int_0^\infty r^3 e^{-2Zr/a_0} dr = 3! \frac{a_0}{4Z} = \frac{3}{2a_0}
\]

15.4.4 The Expectation Value of $v_r$ in the Ground State

For $\ell = 0$, there is no angular dependence to the wavefunction so no velocity except in the radial direction. So it makes sense to compute the radial component of the velocity which is the full velocity.

We can find the term for $\frac{p_r^2}{2m}$ in the radial equation.

\[
\langle \psi_{100} | (v_r)^2 | \psi_{100} \rangle = \int_0^\infty r^2 R_{10}^* \frac{-\hbar^2}{m^2} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) R_{10} dr \\
= \frac{-\hbar^2}{m^2} 4 \left( \frac{Z}{a_0} \right)^3 \int_0^\infty r^2 e^{-2Zr/a_0} \left( \frac{Z^2}{a_0^4} - \frac{2Z}{a_0^3} \right) e^{2Zr/a_0} dr \\
= \frac{-\hbar^2}{m^2} 4 \left( \frac{Z}{a_0} \right)^3 \left( \frac{Z^2}{a_0^4} \frac{a_0^2}{2Z} - \frac{2Z}{a_0^3} \left( \frac{a_0}{2Z} \right)^2 \right) \\
= \frac{\hbar^2}{m^2} \left( \frac{Z}{a_0} \right)^2
\]

Since $a_0 = \frac{\alpha}{mc}$, we get

\[
\langle \psi_{100} | (v_r)^2 | \psi_{100} \rangle = Z\alpha^2 c^2
\]
For $Z = 1$, the RMS velocity is $\alpha c$ or
$$\beta = \alpha = \frac{1}{137}$$

We can compute the expected value of the kinetic energy.
$$K.E. = \frac{1}{2}mv^2 = \frac{h^2}{2m} \frac{Z^2}{a_0^2} = \frac{1}{2}Z^2\alpha^2mc^2 = -E_{100}$$

This is what we expect from the Virial theorem.

### 15.5 Sample Test Problems

1. A Hydrogen atom is in its 4D state $(n = 4, \ell = 2)$. The atom decays to a lower state by emitting a photon. Find the possible photon energies that may be observed. Give your answers in eV.

   **Answer**

   The $n = 4$ state can decay into states with $n = 1, 2, 3$. (Really the $n = 1$ state will be suppressed due to selection rules but this is supposed to be a simple question.) The energies of the states are

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

   The photon energy is given by the energy difference between the states.

   $$E_{\gamma} = 13.6\left(\frac{1}{n^2} - \frac{1}{4^2}\right)$$

   For the $n = 1$ final state, $E = \frac{13.6}{1} = 13.6$ eV.
   For the $n = 2$ final state, $E = \frac{13.6}{4} = 3.4$ eV.
   For the $n = 3$ final state, $E = \frac{13.6}{9} = 1.5$ eV.

2. Using the $\psi_{nlm}$ notation, list all the $n = 1, 2, 3$ hydrogen states. (Neglect the existence of spin.)

   **Answer**

   The states are, $\psi_{100}$, $\psi_{200}$, $\psi_{211}$, $\psi_{210}$, $\psi_{21-1}$, $\psi_{300}$, $\psi_{311}$, $\psi_{310}$, $\psi_{31-1}$, $\psi_{322}$, $\psi_{321}$, $\psi_{320}$, $\psi_{32-1}$, $\psi_{32-2}$.

3. Find the difference in wavelength between light emitted from the $3P \rightarrow 2S$ transition in Hydrogen and light from the same transition in Deuterium. (Deuterium is an isotope of Hydrogen with a proton and a neutron in the nucleus.) Get a numerical answer.

4. An electron in the Coulomb field of a proton is in the state described by the wave function $\frac{1}{6}(4\psi_{100} + 3\psi_{211} - \psi_{210} + \sqrt{10}\psi_{21-1})$. Find the expected value of the Energy, $L^2$ and $L_z$. Now find the expected value of $L_y$.

5. Write out the (normalized) hydrogen energy eigenstate $\psi_{311}(r, \theta, \phi)$.

6. Calculate the expected value of $r$ in the Hydrogen state $\psi_{200}$.

7. Write down the wave function of the hydrogen atom state $\psi_{321}(r)$.

8. A Hydrogen atom is in its $4D$ state $(n = 4, \ell = 2)$. The atom decays to a lower state by emitting a photon. Find the possible photon energies that may be observed. Give your answers in eV.
9. A Hydrogen atom is in the state:

\[ \psi(r) = \frac{1}{\sqrt{30}} (\psi_{100} + 2\psi_{211} - \psi_{322} - 2i\psi_{310} + 2i\psi_{300} - 4\psi_{433}) \]

For the Hydrogen eigenstates, \(\langle \psi_{nm} | \hat{H} | \psi_{nm} \rangle = \frac{Z}{a_0} m^2\). Find the expected value of the potential energy for this state. Find the expected value of \(L_x\).

10. A Hydrogen atom is in its 3D state \((n = 3, l = 2)\). The atom decays to a lower state by emitting a photon. Find the possible photon energies that may be observed. Give your answers in eV.

11. The hydrogen atom is made up of a proton and an electron bound together by the Coulomb force.

The electron has a mass of 0.51 MeV/c^2. It is possible to make a hydrogen-like atom from a proton and a muon. The force binding the muon to the proton is identical to that for the electron but the muon has a mass of 106 MeV/c^2.

   a) What is the ground state energy of muonic hydrogen (in eV).

   b) What is the“Bohr Radius” of the ground state of muonic hydrogen.

12. A hydrogen atom is in the state: \(\psi(r) = \frac{1}{\sqrt{10}} (\psi_{322} + 2i\psi_{221} + 2i\psi_{220} + \psi_{11-1})\) Find the possible measured energies and the probabilities of each. Find the expected value of \(L_z\).

13. Find the difference in frequency between light emitted from the \(2P \rightarrow 1S\) transition in Hydrogen and light from the same transition in Deuterium. (Deuterium is an isotope of Hydrogen with a proton and a neutron in the nucleus.)

14. Tritium is an isotope of hydrogen having 1 proton and 2 neutrons in the nucleus. The nucleus is unstable and decays by changing one of the neutrons into a proton with the emission of a positron and a neutrino. The atomic electron is undisturbed by this decay process and therefore finds itself in exactly the same state immediately after the decay as before it. If the electron started off in the \(\psi_{200}\) \((n = 2, l = 0)\) state of tritium, compute the probability to find the electron in the ground state of the new atom with \(Z=2\).

15. At \(t = 0\) a hydrogen atom is in the state \(\psi(t = 0) = \frac{1}{\sqrt{2}} (\psi_{100} - \psi_{200})\). Calculate the expected value of \(r\) as a function of time.

Answer

\[ \psi(t) = \frac{1}{\sqrt{2}} (\psi_{100}e^{-i(E_1t)/\hbar} - \psi_{200}e^{-i(E_2t)/\hbar}) = e^{-i(E_1t)/\hbar} \frac{1}{\sqrt{2}} (\psi_{100} - \psi_{200}e^{i(E_2-E_1)t/\hbar}) \]

\[ \langle \psi r | \psi \rangle = \frac{1}{2} \langle \psi_{100} - \psi_{200}e^{i(E_2-E_1)t/\hbar} \rangle r|\psi_{100} - \psi_{200}e^{i(E_2-E_1)t/\hbar}\rangle \]

The angular part of the integral can be done. All the terms of the wavefunction contain a \(Y_{00}\) and \(r\) does not depend on angles, so the angular integral just gives 1.

\[ \langle \psi r | \psi \rangle = \frac{1}{2} \int_0^\infty (R_{10} - R_{20}e^{-i(E_2-E_1)t/\hbar})^* r(R_{10} - R_{20}e^{-i(E_2-E_1)t/\hbar}) r^2 dr \]

The cross terms are not zero because of the \(r\).

\[ \langle \psi r | \psi \rangle = \frac{1}{2} \int_0^\infty \left( R_{10}^2 + R_{20}^2 - R_{10}R_{20} (e^{i(E_2-E_1)t/\hbar} + e^{-i(E_2-E_1)t/\hbar}) \right) r^3 dr \]
\[ \langle \psi | r | \psi \rangle = \frac{1}{2} \int_0^\infty \left( R_{10}^2 + R_{20}^2 - 2R_{10}R_{20}\cos\left(\frac{E_2 - E_1}{\hbar} t\right) \right) r^3 dr \]

Now we will need to put in the actual radial wavefunctions.

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

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

\[ \langle \psi | r | \psi \rangle = \frac{1}{2a_0^3} \int_0^\infty \left( 4e^{-2r/a_0} + \frac{1}{2} \left( 1 - \frac{r}{a_0} + \frac{r^2}{4a_0^2} \right) e^{-r/a_0} - 2\sqrt{2} \left( 1 - \frac{r}{2a_0} \right) e^{-3r/2a_0} \cos\left( \frac{E_2 - E_1}{\hbar} t \right) \right) r^3 dr \]

\[ = \frac{1}{2a_0^3} \left[ 24 \left( \frac{a_0}{2} \right)^4 + 3a_0^4 - \frac{1}{2a_0^2} - 24a_0^5 + \frac{1}{8a_0^3} - 120a_0^5 + \left( -2\sqrt{2} + \frac{2a_0^4}{3} + \frac{\sqrt{2}}{a_0} \frac{24}{243} \right) \cos\left( \frac{E_2 - E_1}{\hbar} t \right) \right] \]

\[ = \frac{a_0}{2} \left[ \frac{3}{2} + 3 - 12 + 15 + \left( -12\sqrt{2} + \frac{256}{81} + \frac{256a_0}{81} \right) \cos\left( \frac{E_2 - E_1}{\hbar} t \right) \right] \]

\[ = \frac{a_0}{2} \left[ \frac{15}{4} + \frac{32\sqrt{2}}{81} \cos\left( \frac{E_2 - E_1}{\hbar} t \right) \right] \]

16 3D Symmetric HO in Spherical Coordinates

We have already solved the problem of a 3D harmonic oscillator by separation of variables in Cartesian coordinates (See section 12.2). It is instructive to solve the same problem in spherical coordinates to and compare the results. The potential is

\[ V(r) = \frac{1}{2} \mu \omega^2 r^2. \]

Our radial equation is

\[ \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) R_{\ell}(r) + \frac{2\mu}{\hbar^2} \left( E - V(r) - \frac{\ell(\ell + 1)\hbar^2}{2\mu r^2} \right) R_{\ell}(r) = 0 \]

\[ \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{\mu^2 \omega^2}{\hbar^2} r^2 R - \frac{\ell(\ell + 1)}{r^2} R + \frac{2\mu E}{\hbar^2} R = 0 \]
Write the equation in terms of the dimensionless variable

\[ y = \frac{r}{\rho}, \]

\[ \rho = \sqrt{\frac{h}{\mu \omega}} \]

\[ \frac{d}{dr} \left( \frac{y}{\rho y} \right) = \frac{d}{dy} \frac{dy}{d\rho} = \frac{1}{\rho} \frac{d}{dy} \]

\[ \frac{d^2}{dr^2} = \frac{1}{\rho^2} \frac{d^2}{dy^2} \]

Plugging these into the radial equation, we get

\[ \frac{1}{\rho^2} \frac{d^2 R}{dy^2} + \frac{1}{\rho^2} \frac{2 dR}{y dy} - \frac{1}{\rho^2} \rho^2 y^2 R - \frac{1}{\rho^2} \frac{\ell(\ell + 1)}{y^2} R + \frac{2 \mu E}{h^2} R = 0 \]

\[ \frac{d^2 R}{dy^2} + \frac{2 dR}{y dy} - \frac{\ell(\ell + 1)}{y^2} R + \frac{2 E}{h \omega} R = 0. \]

Now find the behavior for large \( y \).

\[ \frac{d^2 R}{dy^2} - y^2 R = 0 \]

\[ R \approx e^{-y^2/2} \]

Also, find the behavior for small \( y \).

\[ \frac{d^2 R}{dy^2} + \frac{2 dR}{y dy} - \frac{\ell(\ell + 1)}{y^2} R = 0 \]

\[ R \approx y^\ell \]

\[ s(s - 1)y^{s-2} + 2sy^{s-2} = \ell(\ell + 1)y^{s-2} \]

\[ s(s + 1) = \ell(\ell + 1) \]

\[ R \approx y^\ell \]

Explicitly put in this behavior and use a power series expansion to solve the full equation.

\[ R = y^\ell \sum_{k=0}^{\infty} a_k y^k e^{-y^2/2} = \sum_{k=0}^{\infty} a_k y^{\ell+k} e^{-y^2/2} \]

We'll need to compute the derivatives.

\[ \frac{dR}{dy} = \sum_{k=0}^{\infty} a_k [(\ell + k)y^{\ell+k-1} - y^{\ell+k+1}] e^{-y^2/2} \]

\[ \frac{d^2 R}{dy^2} = \sum_{k=0}^{\infty} a_k [(\ell + k)(\ell + k - 1)y^{\ell+k-2} - (\ell + k)y^{\ell+k} - (\ell + k + 1)y^{\ell+k+1} + y^{\ell+k+2}] e^{-y^2/2} \]

\[ \frac{d^2 R}{dy^2} = \sum_{k=0}^{\infty} a_k [(\ell + k)(\ell + k - 1)y^{\ell+k-2} - (2\ell + 2k + 1)y^{\ell+k} + y^{\ell+k+2}] e^{-y^2/2} \]
We can now plug these into the radial equation.

\[ \frac{d^2 R}{dy^2} + \frac{2}{y} \frac{dR}{dy} - \frac{\ell(\ell+1)}{y^2} R + \frac{2E}{\hbar \omega} R = 0 \]

Each term will contain the exponential \( e^{-y^2/2} \), so we can factor that out. We can also run a single sum over all the terms.

\[ \sum_{k=0}^{\infty} a_k \left[ (\ell + k)(\ell + k - 1) y^{\ell+k-2} - (2\ell + 2k + 1) y^{\ell+k} + y^{\ell+k+2} + 2(\ell + k) y^{\ell+k-2} - 2y^{\ell+k} - y^{\ell+k+2} \right] - \ell(\ell+1) y^{\ell+k-2} + \frac{2E}{\hbar \omega} y^{\ell+k} = 0 \]

The terms for large \( y \) which go like \( y^{\ell+k+2} \) and some of the terms for small \( y \) which go like \( y^{\ell+k-2} \) should cancel if we did our job right.

\[ \sum_{k=0}^{\infty} a_k \left[ (\ell + k)(\ell + k - 1) - \ell(\ell+1) + 2(\ell + k) y_{\ell+k-2} + \left[ \frac{2E}{\hbar \omega} - 2 + (2\ell + 2k + 1) \right] y_{\ell+k} \right] = 0 \]

\[ \sum_{k=0}^{\infty} a_k \left[ (\ell + k)(\ell + k - 1) - \ell(\ell+1) + 2\ell y_{\ell+k-2} + \left[ \frac{2E}{\hbar \omega} + 2 - (2\ell + 2k + 1) \right] y_{\ell+k} \right] = 0 \]

\[ \sum_{k=0}^{\infty} a_k \left[ k(2\ell + k + 1) y_{\ell+k-2} + \left[ \frac{2E}{\hbar \omega} - \frac{1}{2} (2\ell + 2k + 3) \right] y_{\ell+k} \right] = 0 \]

Now as usual, the coefficient for each power of \( y \) must be zero for this sum to be zero for all \( y \). Before shifting terms, we must examine the first few terms of this sum to learn about conditions on \( a_0 \) and \( a_1 \). The first term in the sum runs the risk of giving us a power of \( y \) which cannot be cancel by the second term if \( k < 2 \). For \( k = 0 \), there is no problem because the term is zero. For \( k = 1 \) the term is \( (2\ell + 2) y^{\ell-1} \) which cannot be made zero unless \( a_1 = 0 \).

This indicates that all the odd terms in the sum will be zero, as we will see from the recursion relation.

Now we will do the usual shift of the first term of the sum so that everything has a \( y^{\ell+k} \) in it.

\[ k \rightarrow k + 2 \]

\[ \sum_{k=0}^{\infty} \left[ a_{k+2} (k+2)(2\ell + k + 3) y^{\ell+k} + a_k \left[ \frac{2E}{\hbar \omega} - \frac{1}{2} (2\ell + 2k + 3) \right] y^{\ell+k} \right] = 0 \]

\[ a_{k+2} (k+2)(2\ell + k + 3) + a_k \left[ \frac{2E}{\hbar \omega} - \frac{1}{2} (2\ell + 2k + 3) \right] = 0 \]

\[ a_{k+2} (k+2)(2\ell + k + 3) - a_k \left[ \frac{2E}{\hbar \omega} - \frac{1}{2} (2\ell + 2k + 3) \right] = 0 \]

\[ a_{k+2} = \frac{2E}{(k+2)(2\ell + k + 3)} a_k \]
For large $k$,

$$a_{k+2} \approx \frac{2}{k} a_k,$$

which will cause the wave function to diverge. We must terminate the series for some $k = n_r = 0, 2, 4...$, by requiring

$$\frac{2E}{\hbar \omega} - (2\ell + 2n_r + 3) = 0$$

$$E = \left( n_r + \ell + \frac{3}{2} \right) \frac{\hbar \omega}{2}$$

These are the same energies as we found in Cartesian coordinates. Let’s plug this back into the recursion relation.

$$a_{k+2} = \left( \frac{2(\ell + 2n_r + 3) - (2\ell + 2k + 3)}{(k + 2)(2\ell + k + 3)} \right) a_k$$

$$a_{k+2} = \frac{2(k - n_r)}{(k + 2)(2\ell + k + 3)} a_k$$

If we rewrite the series in $y^2$, we get

$$a_{k+1} = \left( \frac{k - n_r}{(k + 1)\ell + k + 3/2} \right) a_k$$

$$R_{n_r \ell} = \sum_{k=0}^{\infty} a_k y^{\ell + 2k} e^{-y^2/2}$$

$$E = \left( 2n_r + \ell + \frac{3}{2} \right) \frac{\hbar \omega}{2}$$

The table shows the quantum numbers for the states of each energy for our separation in spherical coordinates, and for separation in Cartesian coordinates. Remember that there are $2\ell + 1$ states with different $z$ components of angular momentum for the spherical coordinate states.

<table>
<thead>
<tr>
<th>$E$</th>
<th>$n_r \ell$</th>
<th>$n_x n_y n_z$</th>
<th>$N_{\text{spherical}}$</th>
<th>$N_{\text{Cartesian}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\hbar \omega}{2}$</td>
<td>00</td>
<td>000</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\frac{\hbar \omega}{4}$</td>
<td>01</td>
<td>001 (3 perm)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>$\frac{\hbar \omega}{8}$</td>
<td>10, 02</td>
<td>002 (3 perm), 011 (3 perm)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>$\frac{\hbar \omega}{16}$</td>
<td>11, 03</td>
<td>003 (3 perm), 210 (6 perm), 111</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>$\frac{\hbar \omega}{32}$</td>
<td>20, 12, 04</td>
<td>004 (3 perm), 310 (6 perm), 220 (3 perm), 211 (3 perm)</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

The number of states at each energy matches exactly. The parities of the states also match. Remember that the parity is $(-1)^{\ell}$ for the angular momentum states and that it is $(-1)^{n_x + N_y + N_z}$ for the Cartesian states. If we were more industrious, we could verify that the wave functions in spherical coordinates are just linear combinations of the solutions in Cartesian coordinates.
17 Operators Matrices and Spin

We have already solved many problems in Quantum Mechanics using wavefunctions and differential operators. Since the eigenfunctions of Hermitian operators are orthogonal (and we normalize them) we can now use the standard linear algebra to solve quantum problems with vectors and matrices. To include the spin of electrons and nuclei in our discussion of atomic energy levels, we will need the matrix representation.

These topics are covered at very different levels in Gasiorowicz Chapter 14, Griffiths Chapter 3, and, more rigorously, in Cohen-Tannoudji et al. Chapters II, IV and IX.

17.1 The Matrix Representation of Operators and Wavefunctions

We will define our vectors and matrices using a complete set of, orthonormal basis states (See Section 7.1) $u_i$, usually the set of eigenfunctions of a Hermitian operator. These basis states are analogous to the orthonormal unit vectors in Euclidean space $\hat{x}_i$.

$$\langle u_i|u_j \rangle = \delta_{ij}$$

Define the components of a state vector $\psi$ (analogous to $x_i$).

$$\psi_i \equiv \langle u_i|\psi \rangle \quad |\psi\rangle = \sum_i \psi_i|u_i\rangle$$

The wavefunctions are therefore represented as vectors. Define the matrix element

$$O_{ij} \equiv \langle u_i|O|u_j \rangle.$$ 

We know that an operator acting on a wavefunction gives a wavefunction.

$$|O\psi\rangle = O|\psi\rangle = \sum_j O\psi_j|u_j\rangle$$

If we dot $\langle u_i|$ into this equation from the left, we get

$$\langle u_i|O\psi\rangle = \sum_j \psi_j\langle u_i|O|u_j \rangle = \sum_j O_{ij}\psi_j$$

This is exactly the formula for a state vector equals a matrix operator times a state vector.

$$\begin{pmatrix} (O\psi)_1 \\ (O\psi)_2 \\ \vdots \\ (O\psi)_i \\ \vdots \end{pmatrix} = \begin{pmatrix} O_{11} & O_{12} & \cdots & O_{1j} & \cdots \\ O_{21} & O_{22} & \cdots & O_{2j} & \cdots \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ O_{i1} & O_{i2} & \cdots & O_{ij} & \cdots \\ \vdots & \vdots & \ddots & \vdots & \vdots \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_j \\ \vdots \end{pmatrix}$$

Similarly, we can look at the product of two operators (using the identity $\sum_k |u_k\rangle\langle u_k| = 1$).

$$(OP)_{ij} = \langle u_i|OP|u_j \rangle = \sum_k \langle u_i|O|u_k \rangle\langle u_k|P|u_j \rangle = \sum_k O_{ik}P_{kj}$$
This is exactly the formula for the product of two matrices.

\[
\begin{pmatrix}
  (OP)_{11} & (OP)_{12} & \ldots & (OP)_{1j} & \ldots \\
  (OP)_{21} & (OP)_{22} & \ldots & (OP)_{2j} & \ldots \\
  \vdots & \vdots & \ddots & \vdots & \ddots \\
  (OP)_{i1} & (OP)_{i2} & \ldots & (OP)_{ij} & \ldots \\
  \vdots & \vdots & \ddots & \vdots & \ddots \\
\end{pmatrix} =
\begin{pmatrix}
  O_{11} & O_{12} & \ldots & O_{1j} & \ldots \\
  O_{21} & O_{22} & \ldots & O_{2j} & \ldots \\
  \vdots & \vdots & \ddots & \vdots & \ddots \\
  O_{i1} & O_{i2} & \ldots & O_{ij} & \ldots \\
  \vdots & \vdots & \ddots & \vdots & \ddots \\
\end{pmatrix}
\begin{pmatrix}
  P_{11} & P_{12} & \ldots & P_{1j} & \ldots \\
  P_{21} & P_{22} & \ldots & P_{2j} & \ldots \\
  \vdots & \vdots & \ddots & \vdots & \ddots \\
  P_{i1} & P_{i2} & \ldots & P_{ij} & \ldots \\
  \vdots & \vdots & \ddots & \vdots & \ddots \\
\end{pmatrix}
\]

So, wave functions are represented by vectors and operators by matrices, all in the space of orthonormal functions.

* See Example 17.10.1: The Harmonic Oscillator Hamiltonian Matrix.*
* See Example 17.10.2: The harmonic oscillator raising operator.*
* See Example 17.10.3: The harmonic oscillator lowering operator.*

Now compute the matrix for the Hermitian Conjugate (See Section 7.2) of an operator.

\[
(O^\dagger)_{ij} = \langle u_i | O^\dagger | u_j \rangle = \langle Ou_i | u_j \rangle = \langle u_j | Ou_i \rangle^* = O_{ji}^*
\]

The Hermitian Conjugate matrix is the (complex) conjugate transpose.

Check that this is true for \( A \) and \( A^\dagger \).

We know that there is a difference between a **bra vector** and a ket vector. This becomes explicit in the matrix representation. If \( \psi = \sum_j \psi_j u_j \) and \( \phi = \sum_k \phi_k u_k \) then, the dot product is

\[
\langle \psi | \phi \rangle = \sum_{j,k} \psi_j^* \phi_k \langle u_j | u_k \rangle = \sum_{j,k} \psi_j^* \phi_k \delta_{jk} = \sum_k \psi_k^* \phi_k.
\]

We can write this in **dot product in matrix notation** as

\[
\langle \psi | \phi \rangle = \begin{pmatrix} \psi_1^* & \psi_2^* & \psi_3^* & \ldots \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \ldots \end{pmatrix}
\]

The bra vector is the conjugate transpose of the ket vector. The both represent the same state but are different mathematical objects.

### 17.2 The Angular Momentum Matrices

An important case of the use of the matrix form of operators is that of Angular Momentum (See Section 13.1) Assume we have an atomic state with \( \ell = 1 \) (fixed) but \( m \) free. We may use the eigenstates
of $L_z$ as a basis for our states and operators. Ignoring the (fixed) radial part of the wavefunction, our state vectors for $\ell = 1$ must be a linear combination of the $Y_{1m}$

$$\psi = \psi_Y Y_{10} + \psi_0 Y_{10} + \psi_Y Y_{11}$$

where $\psi_Y$, for example, is just the numerical coefficient of the eigenstate.

We will write our 3 component vectors like

$$\psi = \begin{pmatrix} \psi_Y \\ \psi_0 \\ \psi_Y \end{pmatrix}.$$ 

The angular momentum operators are therefore 3X3 matrices. We can easily derive (see section 17.11.1) the matrices representing the angular momentum operators for $\ell = 1$.

$$L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad L_y = \frac{\hbar}{\sqrt{2}i} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \quad L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The matrices must satisfy the same commutation relations as the differential operators.

$$[L_x, L_y] = i\hbar L_z$$

We verify this with an explicit computation of the commutator. (see section 17.11.2)

Since these matrices represent physical variables, we expect them to be Hermitian. That is, they are equal to their conjugate transpose. Note that they are also traceless.

As an example of the use of these matrices, let’s compute an expectation value of $L_x$ in the matrix representation for the general state $\psi$.

$$\langle \psi | L_x | \psi \rangle = \begin{pmatrix} \psi_1^* & \psi_2^* & \psi_3^* \end{pmatrix} \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix}$$

$$= \frac{\hbar}{\sqrt{2}} (\psi_1^* \psi_2 + \psi_2^* \psi_3)$$

$$= \frac{\hbar}{\sqrt{2}} (\psi_1^* \psi_2 + \psi_2^* (\psi_1 + \psi_3) + \psi_3^* \psi_2)$$

17.3 Eigenvalue Problems with Matrices

It is often convenient to solve eigenvalue problems like $A\psi = \alpha\psi$ using matrices. Many problems in Quantum Mechanics are solved by limiting the calculation to a finite, manageable, number of states, then finding the linear combinations which are the energy eigenstates. The calculation is simple in principle but large dimension matrices are difficult to work with by hand. Standard computer utilities are readily
available to help solve this problem.

\[
\begin{pmatrix}
A_{11} & A_{12} & A_{13} & \cdots \\
A_{21} & A_{22} & A_{23} & \cdots \\
A_{31} & A_{32} & A_{33} & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{pmatrix} \begin{pmatrix}
\psi_1 \\
\psi_2 \\
\psi_3 \\
\vdots
\end{pmatrix} = a \begin{pmatrix}
\psi_1 \\
\psi_2 \\
\psi_3 \\
\vdots
\end{pmatrix}
\]

Subtracting the right hand side of the equation, we have

\[
\begin{pmatrix}
A_{11} - a & A_{12} & A_{13} & \cdots \\
A_{21} & A_{22} - a & A_{23} & \cdots \\
A_{31} & A_{32} & A_{33} - a & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{pmatrix} \begin{pmatrix}
\psi_1 \\
\psi_2 \\
\psi_3 \\
\vdots
\end{pmatrix} = 0.
\]

For the product to be zero, the determinant of the matrix must be zero. We solve this equation to get the eigenvalues.

\[
\begin{vmatrix}
A_{11} - a & A_{12} & A_{13} & \cdots \\
A_{21} & A_{22} - a & A_{23} & \cdots \\
A_{31} & A_{32} & A_{33} - a & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{vmatrix} = 0
\]

* See Example 17.10.4: Eigenvectors of \( L_x \).*

The eigenvectors computed in the above example show that the x axis is not really any different than the z axis. The eigenvalues are \( \pm \hbar \), 0, and \(-\hbar\), the same as for z. The normalized eigenvectors of \( L_x \) are

\[
\psi^{(x)}_{+\hbar} = \left( \begin{array}{c} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{1}{\sqrt{2}} \end{array} \right) \quad \psi^{(x)}_{0\hbar} = \left( \begin{array}{c} \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{array} \right) \quad \psi^{(x)}_{-\hbar} = \left( \begin{array}{c} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{1}{\sqrt{2}} \end{array} \right)
\]

These vectors, and any \( \ell = 1 \) vectors, can be written in terms of the eigenvectors of \( S_z \).

We can check whether the eigenvectors are orthogonal, as they must be.

\[
\langle \psi_{0\hbar} | \psi_{+\hbar} \rangle = \left( \frac{1}{\sqrt{2}} \quad 0 \quad -\frac{1}{\sqrt{2}} \right) \left( \begin{array}{c} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{1}{\sqrt{2}} \end{array} \right) = 0
\]

The others will also prove orthogonal.

Should \( \psi^{(x)}_{+\hbar} \) and \( \psi^{(x)}_{-\hbar} \) be orthogonal?

NO. They are eigenvectors of different hermitian operators.

The eigenvectors may be used to compute the probability or amplitude of a particular measurement. For example, if a particle is in a angular momentum state \( \chi \) and the angular momentum in the x direction is measured, the probability to measure \( +\hbar \) is

\[
P_{+\hbar} = \left| \langle \psi^{(x)}_{+\hbar} | \chi \rangle \right|^2
\]
17.4 An \( \ell = 1 \) System in a Magnetic Field

We will derive the Hamiltonian terms added when an atom is put in a magnetic field in section 18. For now, we can be satisfied with the classical explanation that the circulating current associated with nonzero angular momentum generates a \textit{magnetic moment}, as does a classical current loop. This magnetic moment has the same interaction as in classical EM,

\[
H = -\vec{\mu} \cdot \vec{B}.
\]

For the \textit{orbital angular momentum} in a normal atom, the magnetic moment is

\[
\vec{\mu} = -\frac{e}{2mc} \vec{L}.
\]

For the electron mass, in normal atoms, the magnitude of \( \vec{\mu} \) is one \textit{Bohr magneton},

\[
\mu_B = \frac{e\hbar}{2mc}.
\]

If we choose the direction of \( \vec{B} \) to be the \( z \) direction, then the \textit{magnetic moment term in the Hamiltonian} becomes

\[
H = \frac{\mu_B B}{\hbar} L_z = \mu_B B \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.
\]

So the eigenstates of this magnetic interaction are the eigenstates of \( L_z \) and the \textit{energy eigenvalues} are \( +\mu_B B \), \( 0 \), and \( -\mu_B B \).

* See Example 17.10.6: The energy eigenstates of an \( \ell = 1 \) system in a B-field.*

* See Example 17.10.8: Time development of a state in a B field.*

17.5 Splitting the Eigenstates with Stern-Gerlach

A beam of atoms can be split into the eigenstates of \( L_z \) with a \textit{Stern-Gerlach apparatus}. A magnetic moment is associated with angular momentum.

\[
\vec{\mu} = -\frac{e}{2mc} \vec{L} = \mu_B \frac{\vec{L}}{\hbar}
\]

This magnetic moment interacts with an external field, adding a term to the Hamiltonian.

\[
H = -\vec{\mu} \cdot \vec{B}
\]

If the magnetic field has a gradient in the \( z \) direction, there is a force exerted (classically).

\[
\vec{F} = -\frac{\partial U}{\partial z} = \mu_z \frac{\partial B}{\partial z}
\]

A magnet with a \textit{strong gradient to the field} is shown below.
Gradient in B-field

Let's assume the field gradient is in the z direction.

In the Stern-Gerlach experiment, a beam of atoms (assume $\ell = 1$) is sent into a magnet with a strong field gradient. The atoms come from an oven through some colimator to form a beam. The beam is said to be unpolarized since the three $m$ states are equally likely no particular state has been prepared. An unpolarized, $\ell = 1$ beam of atoms will be split into the three beams (of equal intensity) corresponding to the different eigenvalues of $L_z$.

The atoms in the top beam are in the $m = 1$ state. If we put them through another Stern-Gerlach apparatus, they will all go into the top beam again. Similarly for the middle beam in the $m = 0$ state and the lower beam in the $m = -1$ state.

We can make a fancy Stern-Gerlach apparatus which puts the beam back together as shown below.
We can represent the apparatus by the symbol to the right.

We can use this apparatus to **prepare an eigenstate**. The apparatus below picks out the \( m = 1 \) state

\[
\begin{pmatrix}
  S \\
  N \\
  S \\
\end{pmatrix} 
\begin{pmatrix}
  + \\
  0 \\
  - \\
\end{pmatrix}_z \rightarrow
\begin{pmatrix}
  + \\
  0 \\
  - \\
\end{pmatrix}_z
\]

again representing the apparatus by the symbol at the right. We could also represent our apparatus plus blocking by an operator

\[
O = |+\rangle \langle +|
\]

where we are writing the states according to the \( m \) value, either +, -, or 0. This is a projection operator onto the + state.

An apparatus which block both the + and - beams

\[
\begin{pmatrix}
  S \\
  N \\
  S \\
\end{pmatrix} 
\begin{pmatrix}
  + \\
  0 \\
  - \\
\end{pmatrix}_z \rightarrow
\begin{pmatrix}
  + \\
  0 \\
  - \\
\end{pmatrix}_z
\]

would be represented by the projection operator

\[
O = |0\rangle \langle 0|
\]

Similarly, an apparatus with no blocking could be written as the sum of the three projection operators.

\[
\begin{pmatrix}
  + \\
  0 \\
  - \\
\end{pmatrix}_z \rightarrow |+\rangle \langle +| + |0\rangle \langle 0| + |\rangle \langle -| = \sum_{m=-1}^{+1} |z_m\rangle \langle z_m| = 1
\]
If we block only the $m = 1$ beam, the apparatus would be represented by

$$
\begin{pmatrix}
+1 \\
0 \\
-1
\end{pmatrix}_z \rightarrow |0\rangle \langle 0| + |\rangle \langle |.
$$

* See Example 17.10.7: A series of Stern-Gerlachs *

### 17.6 Rotation operators for $\ell = 1$

We have chosen the $z$ axis arbitrarily. We could choose any other direction to define our basis states. We wish to know how to transform from one coordinate system to another. Experience has shown that knowing how an object transforms under rotations is important in classifying the object: scalars, vectors, tensors...

We can derive (see section 17.11.3) the operator for rotations about the $z$-axis. This operator transforms an angular momentum state vector into an angular momentum state vector in the rotated system.

$$
R_z(\theta_z) = e^{i\theta_z L_z / \hbar}
$$

$$
\psi' = R_z(\theta_z)\psi
$$

Since there is nothing special about the $z$-axis, rotations about the other axes follow the same form.

$$
R_x(\theta_x) = e^{i\theta_x L_x / \hbar}
$$

$$
R_y(\theta_y) = e^{i\theta_y L_y / \hbar}
$$

The above formulas for the rotation operators must apply in both the matrix representation and in the differential operator representation.

Redefining the coordinate axes cannot change any scalars, like dot products of state vectors. Operators which preserve dot products are called unitary. We proved that operators of the above form, (with hermitian matrices in the exponent) are unitary.

A computation (see section 17.11.4) of the operator for rotations about the $z$-axis gives

$$
R_z(\theta_z) = \begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & e^{-i\theta_z}
\end{pmatrix}.
$$

A computation (see section 17.11.5) of the operator for rotations about the $y$-axis yields

$$
R_y(\theta_y) = \begin{pmatrix}
\frac{1}{2}(1 + \cos(\theta_y)) & \frac{1}{\sqrt{2}}\sin(\theta_y) & \frac{1}{2}(1 - \cos(\theta_y)) \\
-\frac{1}{\sqrt{2}}\sin(\theta_y) & \cos(\theta_y) & \frac{1}{\sqrt{2}}\sin(\theta_y) \\
\frac{1}{2}(1 - \cos(\theta_y)) & -\frac{1}{\sqrt{2}}\sin(\theta_y) & \frac{1}{2}(1 + \cos(\theta_y))
\end{pmatrix}.
$$

Try calculating the rotation operator for the $x$-axis yourself.
Note that both of the above rotation matrices reduce to the identity matrix for rotations of 2\pi radians. For a rotation of \pi radians, \( R_y \) interchanges the plus and minus components (and changes the sign of the zero component), which is consistent with what we expect. Note also that the above rotation matrices are quite different than the ones used to transform vectors and tensors in normal Euclidean space. Hence, the states here are of a new type and are referred to as **spinors**.

* See Example 17.10.5: A 90 degree rotation about the z axis. *

### 17.7 A Rotated Stern-Gerlach Apparatus

Imagine a Stern-Gerlach apparatus that first separates an \( \ell = 1 \) atomic beam with a strong B-field gradient in the z-direction. Let’s assume the beam has atoms moving in the y-direction. The apparatus blocks two separated beams, leaving only the eigenstate of \( L_z \) with eigenvalue +\( \hbar \). We follow this with an apparatus which separates in the u-direction, which is at an angle \( \theta \) from the z-direction, but still perpendicular to the direction of travel of the beam, y. **What fraction of the (remaining) beam will go into each of the three beams which are split in the u-direction?**

We could represent this problem with the following **diagram**.

\[
\text{Oven} \rightarrow \begin{pmatrix} + \\ 0 \\ -1 \end{pmatrix}_z \rightarrow \begin{pmatrix} + D_+ \\ 0 \\ -D_- \end{pmatrix}_u
\]

We put a detector in each of the beams split in u to determine the intensity.

To solve this with the rotation matrices, we first determine the **state after the first apparatus**. It is just \( \psi^{(z)}_+ = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \) with the usual basis. Now we **rotate to a new (primed) set of basis states** with the \( z' \) along the u direction. This means a rotation through an angle \( \theta \) about the y direction. The problem didn’t clearly define whether it is +\( \theta \) or -\( \theta \), but, if we only need to know the intensities, it doesn’t matter. So the **state coming out of the second apparatus** is

\[
R_y(\theta)\psi^{(z)}_+ = \begin{pmatrix}
\frac{1}{\sqrt{2}}(1 + \cos(\theta_y)) & \frac{1}{\sqrt{2}}\sin(\theta_y) & \frac{1}{2}(1 - \cos(\theta_y)) \\
-\frac{1}{\sqrt{2}}\sin(\theta_y) & \cos(\theta_y) & \frac{1}{\sqrt{2}}\sin(\theta_y) \\
\frac{1}{2}(1 - \cos(\theta_y)) & -\frac{1}{\sqrt{2}}\sin(\theta_y) & \frac{1}{2}(1 + \cos(\theta_y))
\end{pmatrix}
\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}
\]

\[
= \begin{pmatrix}
\frac{1}{2}(1 + \cos(\theta_y)) \\
-\frac{1}{2}\sin(\theta_y) \\
\frac{1}{2}(1 - \cos(\theta_y))
\end{pmatrix}
\]

The 3 amplitudes in this vector just need to be (absolute) **squared to get the 3 intensities**.

\[
I_+ = \frac{1}{4}(1 + \cos(\theta_y))^2 \\
I_0 = \frac{1}{2}\sin^2(\theta_y) \\
I_- = \frac{1}{4}(1 - \cos(\theta_y))^2
\]

These add up to 1.

An alternate solution would be to use the \( L_u = \hat{u} \cdot \vec{L} = \cos \theta L_z + \sin \theta L_x \) operator. Find the eigenvectors of this operator, like \( \psi^{(u)}_+ \). The intensity in the + beam is then \( I_+ = |\langle \psi^{(u)}_+ | \psi^{(u)}_+ \rangle|^2 \).
17.8 Spin \( \frac{1}{2} \)

Earlier, we showed that both integer and half integer angular momentum could satisfy (See section 13.4.5) the commutation relations but that there is no functional representation for the half integer type.

Some particles have half integer internal angular momentum, also called spin. We will now develop a spinor representation for spin \( \frac{1}{2} \). There are no coordinates \( \theta \) and \( \phi \) associated with internal angular momentum so the only thing we have is our spinor representation.

The usual basis states are the eigenstates of \( S_z \). We know the eigenvalues are \( +\frac{1}{2} \hbar \) and \( -\frac{1}{2} \hbar \). It is easy to derive (see section 17.11.6) the matrix operators for spin.

\[
S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\
S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]

These satisfy the usual commutation relations from which we derived the properties of angular momentum operators.

The Pauli Spin Matrices, \( \sigma_i \), are simply defined and have the following properties.

\[
S_i = \frac{\hbar}{2} \sigma_i \\
S = \frac{\hbar}{2} \sigma \\
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\
\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]

\[
[\sigma_i, \sigma_j] = 2i \epsilon_{ijk} \sigma_k \\
\sigma^2 = 1
\]

They also anti-commute.

\[
\sigma_x \sigma_y = -\sigma_y \sigma_x \quad \sigma_x \sigma_z = -\sigma_z \sigma_x \quad \sigma_z \sigma_y = -\sigma_y \sigma_z
\]

\[
\{\sigma_i, \sigma_j\} = 2 \delta_{ij}
\]

The \( \sigma \) matrices are the Hermitian, Traceless matrices of dimension 2. Any 2 by 2 matrix can be written as a linear combination of the \( \sigma \) matrices and the identity.

* See Example 17.10.9: The expectation value of \( S_x \).
* See Example 17.10.10: The eigenvectors of \( S_x \).
* See Example 17.10.11: The eigenvectors of \( S_y \).

The rotation operators, for rotations of the coordinate axes can be computed (see section 17.11.7) from the formula \( R_i(\theta_i) = e^{i S_i \theta_i / \hbar} \).

\[
R_x(\theta) = \begin{pmatrix} e^{i \theta / 2} & 0 \\ 0 & e^{-i \theta / 2} \end{pmatrix} \\
R_y(\theta) = \begin{pmatrix} \cos \frac{\theta}{2} & i \sin \frac{\theta}{2} \\ i \sin \frac{\theta}{2} & \cos \frac{\theta}{2} \end{pmatrix} \\
R_y(\theta) = \begin{pmatrix} \cos \frac{\theta}{2} & \sin \frac{\theta}{2} \\ -\sin \frac{\theta}{2} & \cos \frac{\theta}{2} \end{pmatrix}
\]

Note that the operator for a rotation through \( 2\pi \) radians is minus the identity matrix for any of the axes (because \( \hat{z} \) appears everywhere). The surprising result is that the sign of the wave function of all fermions is changed if we rotate through 360 degrees.
As for orbital angular momentum ($\hat{L}$), there is also a magnetic moment associated with internal angular momentum ($\hat{S}$).

$$\vec{\mu}_{\text{spin}} = -\frac{e\hbar}{2mc} \vec{\hat{S}}$$

This formula has an additional factor of $g$, the gyromagnetic ratio, compared to the formula for orbital angular momenta. For point-like particles, like the electron, $g$ has been computed in Quantum Electrodynamics to be a bit over 2, $g = 2 + \frac{a}{s} + \ldots$. For particles with structure, like the proton or neutron, $g$ is hard to compute, but has been measured. Because the factor of 2 from $g$ cancels the factor of 2 from $s = \frac{1}{2}$, the magnetic moment due to the spin of an electron is almost exactly equal to the magnetic moment due to the orbital angular momentum in an $\ell = 1$ state. Both are 1 Bohr Magneton, $\mu_B = \frac{e\hbar}{2mc}$.

$$H = -\vec{\mu} \cdot \vec{B} = \frac{e\hbar}{2mc} \vec{\hat{\sigma}} \cdot \vec{B} = \mu_B \vec{\hat{\sigma}} \cdot \vec{B}$$

If we choose the $z$ axis to be in the direction of $B$, then this reduces to

$$H = \mu_B B\sigma_z.$$

* See Example 17.10.12: The time development of an arbitrary electron state in a magnetic field.*

* See Example 17.10.13: Nuclear Magnetic Resonance (NMR and MRI).*

### 17.9 Other Two State Systems

#### 17.9.1 The Ammonia Molecule (Maser)

The Feynman Lectures (Volume III, chapters 8 and 9) makes a complete study of the two ground states of the Ammonia Molecule. Feynman's discussion is very instructive. Feynman starts with two states, one with the Nitrogen atom above the plane defined by the three Hydrogen atoms, and the other with the Nitrogen below the plane. There is clearly symmetry between these two states. They have identical properties. This is an example of an SU(2) symmetry like that in angular momentum (and the weak interactions). We just have two states which are different but completely symmetric.

Since the Nitrogen atom can tunnel from one side of the molecule to the other, there are cross terms in the Hamiltonian (limiting ourselves to the two symmetric ground states).

$$\langle \psi_{\text{above}} | H | \psi_{\text{above}} \rangle = \langle \psi_{\text{below}} | H | \psi_{\text{below}} \rangle = E_0$$

$$\langle \psi_{\text{above}} | H | \psi_{\text{below}} \rangle = -A$$

$$H = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}$$

We can adjust the phases of the above and below states to make $A$ real.

The energy eigenvalues can be found from the usual equation.

$$\begin{vmatrix} E_0 - E & -A \\ -A & E_0 - E \end{vmatrix} = 0$$

$$(E_0 - E)^2 = A^2$$

$$E - E_0 = \pm A$$

$$E = E_0 \pm A$$
Now find the eigenvectors.

\[ H\psi = E\psi \]

\[
\begin{pmatrix}
E_0 & -A \\
-A & E_0
\end{pmatrix}
\begin{pmatrix}
a \\
b
\end{pmatrix} = (E_0 \pm A)
\begin{pmatrix}
a \\
b
\end{pmatrix}
\]

\[
\begin{pmatrix}
E_0a - Ab \\
E_0b - Aa
\end{pmatrix} = \begin{pmatrix}
(E_0 \pm A)a \\
(E_0 \pm A)b
\end{pmatrix}
\]

These are solved if \( b = \mp a \). Substituting auspiciously, we get.

\[
\begin{pmatrix}
E_0a \pm Aa \\
E_0b \pm Ab
\end{pmatrix} = \begin{pmatrix}
(E_0 \pm A)a \\
(E_0 \pm A)b
\end{pmatrix}
\]

So the eigenstates are

\[ E = E_0 - A \]
\[ \begin{pmatrix}
\frac{1}{\sqrt{2}} \\
-\frac{1}{\sqrt{2}}
\end{pmatrix} \]

\[ E = E_0 + A \]
\[ \begin{pmatrix}
\frac{1}{\sqrt{2}} \\
\frac{1}{\sqrt{2}}
\end{pmatrix} \]

The states are split by the interaction term.

Feynman goes on to further split the states by putting the molecules in an electric field. This makes the diagonal terms of the Hamiltonian slightly different, like a magnetic field does in the case of spin.

Finally, Feynman studies the effect of Ammonia in an oscillating Electric field, the Ammonia Maser.

17.9.2 The Neutral Kaon System

The neutral Kaons, \( K^0 \) and \( \bar{K}^0 \) form a very interesting two state system. As in the Ammonia molecule, there is a small amplitude to make a transition from one to the other. The Energy (mass) eigenstates are similar to those in the example above, but the CP (Charge conjugation times Parity) eigenstates are important because they determine how the particles can decay. A violation of CP symmetry is seen in the decays of these particles.

17.10 Examples

17.10.1 Harmonic Oscillator Hamiltonian Matrix

We wish to find the matrix form of the Hamiltonian for a 1D harmonic oscillator.

The basis states are the harmonic oscillator energy eigenstates. We know the eigenvalues of \( H \).

\[ H u_j = E_j u_j \]

\[ \langle i | H | j \rangle = E_j \delta_{ij} = \left( j + \frac{1}{2} \right) \hbar \omega \delta_{ij} \]
The Kronecker delta gives us a diagonal matrix:

\[ H = \hbar \omega \begin{pmatrix}
\frac{1}{\hbar} & 0 & 0 & 0 & \cdots \\
0 & \frac{1}{\hbar} & 0 & 0 & \cdots \\
0 & 0 & \frac{1}{\hbar} & 0 & \cdots \\
0 & 0 & 0 & \frac{1}{\hbar} & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{pmatrix} \]

17.10.2 Harmonic Oscillator Raising Operator

We wish to find the matrix representing the 1D harmonic oscillator raising operator.

We use the raising operator (See section 9) equation for an energy eigenstate.

\[ A^\dagger u_n = \sqrt{n + 1} u_{n+1} \]

Now simply compute the matrix element.

\[ A^\dagger_{ij} = \langle i | A^\dagger | j \rangle = \sqrt{j + 1}\delta_{i,j+1} \]

Now this Kronecker delta puts us one off the diagonal. As we have it set up, i gives the row and j gives the column. Remember that in the Harmonic Oscillator we start counting at 0. For \( i = 0 \), there is no allowed value of \( j \) so the first row is all 0. For \( i = 1 \), \( j = 0 \), so we have an entry for \( A^\dagger_{10} \) in the second row and first column. All other entries will be on a diagonal from that one.

\[ A^\dagger = \begin{pmatrix}
0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & \cdots \\
0 & \sqrt{2} & 0 & 0 & \cdots \\
0 & 0 & \sqrt{3} & 0 & \cdots \\
0 & 0 & 0 & \sqrt{4} & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{pmatrix} \]

17.10.3 Harmonic Oscillator Lowering Operator

We wish to find the matrix representing the 1D harmonic oscillator lowering operator. This is similar to the last section.

The lowering operator (See section 9) equation is.

\[ Au_n = \sqrt{n} u_{n-1} \]

Now we compute the matrix element from the definition.

\[ A_{ij} = \langle i | A | j \rangle = \sqrt{j}\delta_{i,j-1} \]

\[ A = \begin{pmatrix}
0 & \sqrt{1} & 0 & 0 & \cdots \\
0 & 0 & \sqrt{2} & 0 & \cdots \\
0 & 0 & 0 & \sqrt{3} & \cdots \\
0 & 0 & 0 & 0 & \sqrt{4} & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{pmatrix} \]

This should be the Hermitian conjugate of \( A^\dagger \).
17.10.4 Eigenvectors of $L_x$

We will do it as if we don’t already know that the eigenvalues are $m\hbar$.

$$L_x \psi = a \psi$$

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} = \frac{\sqrt{2}a}{2} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} \equiv b \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix}$$

$$\begin{vmatrix} -b & 1 & 0 \\ 1 & -b & 1 \\ 0 & 1 & -b \end{vmatrix} = 0$$

where $a = \frac{\hbar}{\sqrt{2}}b$. 

$$-b(b^2 - 1) - 1(-b - 0) = 0$$

$$b(b^2 - 2) = 0$$

There are three solutions to this equation: $b = 0$, $b = +\sqrt{2}$, and $b = -\sqrt{2}$ or $a = 0$, $a = +\hbar$, and $a = -\hbar$. These are the eigenvalues we expected for $\ell = 1$. For each of these three eigenvalues, we should go back and find the corresponding eigenvector by using the matrix equation.

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} = b \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix}$$

$$\begin{pmatrix} \psi_2 \\ \psi_1 + \psi_3 \\ \psi_2 \end{pmatrix} = b \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix}$$

Up to a normalization constant, the solutions are:

$$\psi_{+\hbar} = c \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$$

$$\psi_{0\hbar} = c \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

$$\psi_{-\hbar} = c \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$$

We should normalize these eigenvectors to represent one particle. For example:

$$\langle \psi_{+\hbar} | \psi_{+\hbar} \rangle = 1$$

$$|c|^2 \begin{pmatrix} \frac{1}{\sqrt{2}} & 1 \\ \frac{1}{\sqrt{2}} & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix} = 2|c|^2 = 1$$

$$c = \frac{1}{\sqrt{2}}$$

Try calculating the eigenvectors of $L_y$.

You already know what the eigenvalues are.

17.10.5 A 90 degree rotation about the z axis.

If we rotate our coordinate system by 90 degrees about the z axis, the old x axis becomes the new y axis. So we would expect that the state with angular momentum $+\hbar$ in the x direction, $\psi_{+\hbar}^{(x)}$, will rotate
into $\psi_{\downarrow}^{(y)}$ within a phase factor. Let's do the rotation.

$$R_z(\theta_z) = \begin{pmatrix} e^{i\theta_z} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\theta_z} \end{pmatrix}.$$  

$$R_z(\theta_z = 90) = \begin{pmatrix} i & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -i \end{pmatrix}.$$  

Before rotation the state is

$$\psi_{\downarrow}^{(x)} = \begin{pmatrix} \frac{i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}.$$  

The rotated state is.

$$\psi' = \begin{pmatrix} i & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -i \end{pmatrix} \begin{pmatrix} \frac{i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \frac{i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}.$$  

Now, what remains is to check whether this state is the one we expect. What is $\psi_{\downarrow}^{(y)}$? We find that state by solving the eigenvalue problem.

$$L_y \psi_{\downarrow}^{(y)} = -\hbar \psi_{\downarrow}^{(y)}$$

$$\frac{\hbar}{\sqrt{2i}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = -\hbar \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

$$\begin{pmatrix} \frac{i\hbar}{\sqrt{2}} \\ \frac{i(\sqrt{2}-a)}{\sqrt{2}} \\ \frac{-ib}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

Setting $b = 1$, we get the unnormalized result.

$$\psi_{\downarrow}^{(y)} = C \begin{pmatrix} \frac{i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$$

Normalizing, we get.

$$\psi_{\downarrow}^{(y)} = \begin{pmatrix} \frac{i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$$

This is exactly the same as the rotated state. A 90 degree rotation about the z axis changes $\psi_{\downarrow}^{(x)}$ into $\psi_{\downarrow}^{(y)}$. 
17.10.6 Energy Eigenstates of an $\ell = 1$ System in a B-field

Recall that the Hamiltonian for a magnetic moment in an external B-field is

$$H = \frac{\mu_B B}{\hbar} L_z.$$ 

As usual, we find the eigenstates (eigenvectors) and eigenvalues of a system by solving the time-independent Schrödinger equation $H\psi = E\psi$. We see that everything in the Hamiltonian above is a (scalar) constant except the operator $L_z$, so that

$$H\psi = \frac{\mu_B B}{\hbar} L_z\psi = \text{constant} \ast (L_z\psi).$$

Now if $\psi_m$ is an eigenstate of $L_z$, then $L_z\psi_m = m\hbar\psi_m$, thus

$$H\psi_m = \frac{\mu_B B}{\hbar} \ast (m\hbar\psi_m) = (m\mu_B B)\psi_m$$

Hence the normalized eigenstates must be just those of the operator $L_z$ itself, i.e., for the three values of $m$ (eigenvalues of $L_z$), we have

$$\psi_{m=+1} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \psi_{m=0} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \psi_{m=-1} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$ 

and the energy eigenvalues are just the values that $E = m\mu_B B$ takes on for the three values of $m$ i.e.,

$$E_{m=+1} = +\mu_B B \quad E_{m=0} = 0 \quad E_{m=-1} = -\mu_B B.$$ 

17.10.7 A series of Stern-Gerlachs

Now that we have the shorthand notation for a Stern-Gerlach apparatus, we can put some together and think about what happens. The following is a simple example in which three successive apparatus separate the atomic beam using a field gradient along the $z$ direction.

Oven($I_0$) → \{ \begin{pmatrix} + \\ 0 \\ z \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix} \} \rightarrow \{ \begin{pmatrix} + \\ 0 \\ z \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix} \} \rightarrow \{ \begin{pmatrix} + \\ 0 \\ z \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix}, \begin{pmatrix} + \\ 0 \end{pmatrix} \} \rightarrow$$

If the intensity coming out of the oven is $I_0$, what are the intensities at positions 1, 2, and 3? We assume an unpolarized beam coming out of the oven so that 1/3 of the atoms will go into each initial beam in apparatus 1. This is essentially a classical calculation since we don’t know the exact state of the particles coming from the oven. Now apparatus 1 removes the $m = 1$ component of the beam, leaving a state with a mixture of $m = 0$ and $m = -1$.

$$I_1 = \frac{2}{3} I_0$$
We still don’t know the relative phase of those two components and, in fact, different atoms in the beam will have different phases.

The beam will split into only two parts in the second apparatus since there is no \( m = 1 \) component left. Apparatus 2 blocks the \( m = 0 \) part, now leaving us with a state that we can write.

\[
I_2 = \frac{1}{3} I_0
\]

All the particles in the beam are in the same state.

\[
\psi = \psi_{\pm}^{(z)}
\]

The beam in apparatus 3 all goes along the same path, the lower one. Apparatus 3 blocks that path.

\[
I_3 = 0
\]

The following is a more complex example using a field gradients in the \( z \) and \( x \) directions (assuming the beam is moving in \( y \)).

\[
\text{Oven}(I_0) \rightarrow \begin{cases} + \\ 0 \end{cases} \bigg| I_1 \bigg| \begin{cases} + \\ 0 \end{cases} \bigg| I_2 \bigg| \begin{cases} + \\ 0 \end{cases} \bigg| I_3 \bigg|
\]

If the intensity coming out of the oven is \( I_0 \), what are the intensities at positions 1, 2, and 3?

Now we have a Quantum Mechanics problem. After the first apparatus, we have an intensity as before

\[
I_1 = \frac{2}{3} I_0
\]

and all the particles are in the state

\[
\psi_{\pm}^{(z)} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.
\]

The second apparatus is oriented to separate the beam in the \( x \) direction. The beam separates into 3 parts. We can compute the intensity of each but lets concentrate on the bottom one because we block the other two.

\[
I_2 = \langle \psi_{\pm}^{(x)} | \psi_{\pm}^{(z)} \rangle^2 I_1
\]

We have written the probability that one particle, initially in the the state \( \psi_{\pm}^{(z)} \), goes into the state \( \psi_{\pm}^{(x)} \) when measured in the \( x \) direction (times the intensity coming into the apparatus). Lets compute that probability.

\[
\langle \psi_{\pm}^{(x)} | \psi_{\pm}^{(z)} \rangle = \begin{pmatrix} -\frac{1}{2} \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{2} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = -\frac{1}{2}
\]

So the probability is \( \frac{1}{4} \).

\[
I_2 = \frac{1}{4} I_1 = \frac{1}{12} I_0
\]
The third apparatus goes back to a separation in $z$ and blocks the $m = 1$ component. The incoming state is

$$
\psi_{-}^{(x)} = \begin{pmatrix}
-\frac{i}{\sqrt{2}} \\
\frac{1}{\sqrt{2}} \\
\end{pmatrix}
$$

Remember that the components of this vector are just the amplitudes to be in the different $m$ states (using the $z$ axis). The probability to get through this apparatus is just the probability to be in the $m = 0$ beam plus the probability to be in the $m = -1$ beam.

$$
P = \left| -\frac{1}{\sqrt{2}} \right|^2 + \left| \frac{1}{2} \right|^2 = \frac{3}{4}
$$

$$
I_3 = \frac{3}{4} I_2 = \frac{1}{16} I_0
$$

Now let's see what happens if we remove the blocking in apparatus 2.

$$
\text{Oven}(I_0) \rightarrow \begin{cases} 
+ & \\
0 & \\
- & 
\end{cases} z 
\rightarrow \begin{cases} 
+ & \\
0 & \\
- & 
\end{cases} x 
\rightarrow \begin{cases} 
+ & \\
0 & \\
- & 
\end{cases} z 
$$

Assuming there are no bright lights in apparatus 2, the beam splits into 3 parts then recombines yielding the same state as was coming in, $\psi_{-}^{(z)}$. The intensity coming out of apparatus 2 is $I_2 = I_1$. Now with the pure state $\psi_{-}^{(z)}$ going into apparatus 3 and the top beam being blocked there, no particles come out of apparatus 3.

$$
I_3 = 0
$$

By removing the blocking in apparatus 2, the intensity dropped from $\frac{1}{16} I_0$ to zero. How could this happen?

What would happen if there were bright lights in apparatus 2?

17.10.8 Time Development of an $\ell = 1$ System in a B-field: Version I

We wish to determine how an angular momentum 1 state develops with time (See Section 6.4), develops with time, in an applied B field. In particular, if an atom is in the state with $x$ component of angular momentum equal to $+\hbar$, $\psi_{+}^{(x)}$, what is the state at a later time $t$? What is the expected value of $L_x$ as a function of time?

We will choose the $z$ axis so that the B field is in the $z$ direction. Then we know the energy eigenstates are the eigenstates of $L_z$ and are the basis states for our vector representation of the wave function. Assume that we start with a general state which is known at $t = 0$.

$$
\psi(t = 0) = \begin{pmatrix} 
\psi_+ \\
\psi_0 \\
\psi_- 
\end{pmatrix}
$$

But we know how each of the energy eigenfunctions develops with time so its easy to write

$$
\psi(t) = \begin{pmatrix} 
\psi_+ e^{-\frac{iE_+ t}{\hbar}} \\
\psi_0 e^{-\frac{iE_0 t}{\hbar}} \\
\psi_- e^{-\frac{iE_- t}{\hbar}} 
\end{pmatrix} = \begin{pmatrix} 
\psi_+ e^{-i\mu B t / \hbar} \\
\psi_0 \\
\psi_- e^{i\mu B t / \hbar} 
\end{pmatrix}.
$$
As a concrete example, let’s assume we start out in the eigenstate of $L_x$ with eigenvalue $+\hbar$.

$$\psi(t = 0) = \psi_{x+} = \left( \frac{1}{\sqrt{2}} \right)$$

$$\psi(t) = \psi_{x+} = \left( \frac{e^{-i \frac{\mu_B B t}{\hbar} \tau/2}}{\sqrt{2}} \right)$$

$$\langle \psi(t)|L_x|\psi(t) \rangle = \left( \frac{\hbar}{\sqrt{2}} \right) \left( \frac{e^{i \frac{\mu_B B t}{\hbar} \tau/2}}{\sqrt{2}} \right) \left( \frac{1}{2} \right) \left( \frac{1}{2} \right) \left( \frac{1}{2} \right) = \frac{\hbar}{4} \cos \left( \frac{\mu_B B t}{\hbar} \right) = \hbar \cos \left( \frac{\mu_B B t}{\hbar} \right)$$

Note that this agrees with what we expect at $t = 0$ and is consistent with the angular momentum precessing about the z axis. If we checked $\langle \psi|L_y|\psi \rangle$, we would see a sine instead of a cosine, confirming the precession.

17.10.9 Expectation of $S_x$ in General Spin $\frac{1}{2}$ State

Let $\chi = \left( \begin{array}{c} \alpha_+ \\ \alpha_- \end{array} \right)$, be some arbitrary spin $\frac{1}{2}$ state. Then the expectation value of the operator

$$\langle S_x \rangle = \langle \chi | S_x | \chi \rangle$$

$$= (\alpha_+^* \alpha_-^* \frac{\hbar}{2}) \left( \begin{array}{c} 0 \\ 1 \end{array} \right) \left( \begin{array}{c} \alpha_+ \\ \alpha_- \end{array} \right)$$

$$= \frac{\hbar}{2} (\alpha_+^* \alpha_-^* \alpha_+ + \alpha_-^* \alpha_-)$$

17.10.10 Eigenvectors of $S_x$ for Spin $\frac{1}{2}$

First the quick solution. Since there is no difference between x and z, we know the eigenvalues of $S_x$ must be $\pm \hbar$. So, factoring out the constant, we have

$$\left( \begin{array}{c} 0 \\ 1 \end{array} \right) \left( \begin{array}{c} a \\ b \end{array} \right) = \pm \left( \begin{array}{c} a \\ b \end{array} \right)$$

$$\left( \begin{array}{c} b \\ a \end{array} \right) = \pm \left( \begin{array}{c} a \\ b \end{array} \right)$$

$$a = \pm b$$

$$\chi^{(x)}_{\pm} = \left( \frac{a}{\sqrt{2}} \right)$$
\[ \chi^{(x)}_{-} = \left( \frac{1}{\sqrt{2}} \right) \]

These are the eigenvectors of \( S_x \). We see that if we are in an eigenstate of \( S_x \) the spin measured in the \( z \) direction is equally likely to be up and down since the absolute square of either amplitude is \( \frac{1}{2} \).

The remainder of this section goes into more detail on this calculation but is currently notationally challenged.

Recall the standard method of finding eigenvectors and eigenvalues:

\[ A\psi = \alpha \psi \]
\[ (A - \alpha) \psi = 0 \]

For spin \( \frac{1}{2} \) system we have, in matrix notation,

\[
\begin{pmatrix}
  a_1 & a_2 \\
  a_3 & a_4
\end{pmatrix}
\begin{pmatrix}
  \chi_1 \\
  \chi_2
\end{pmatrix}
= \alpha
\begin{pmatrix}
  1 & 0 \\
  0 & 1
\end{pmatrix}
\begin{pmatrix}
  \chi_1 \\
  \chi_2
\end{pmatrix}
\]

\[
\Rightarrow
\begin{pmatrix}
  a_1 - \alpha & a_2 \\
  a_3 & a_4 - \alpha
\end{pmatrix}
\begin{pmatrix}
  \chi_1 \\
  \chi_2
\end{pmatrix}
= 0
\]

For a matrix times a nonzero vector to give zero, the determinant of the matrix must be zero. This gives the “characteristic equation” which for spin \( \frac{1}{2} \) systems will be a quadratic equation in the eigenvalue \( \alpha \):

\[
\begin{vmatrix}
  a_1 - \alpha & a_2 \\
  a_3 & a_4 - \alpha
\end{vmatrix}
= (a_1 - \alpha)(a_4 - \alpha) - a_2a_3 = 0
\]

\[
\alpha^2 - (a_1 + a_4)\alpha + (a_1a_4 - a_2a_3) = 0
\]

whose solution is

\[
\alpha_{\pm} = \frac{(a_1 + a_4)}{4} \pm \sqrt{\frac{(a_1 + a_4)^2}{4} - (a_1a_4 - a_2a_3)}
\]

To find the eigenvectors, we simply replace (one at a time) each of the eigenvalues above into the equation

\[
\begin{pmatrix}
  a_1 - \alpha & a_2 \\
  a_3 & a_4 - \alpha
\end{pmatrix}
\begin{pmatrix}
  \chi_1 \\
  \chi_2
\end{pmatrix}
= 0
\]

and solve for \( \chi_1 \) and \( \chi_2 \).

Now specifically, for the operator \( A = S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \), the eigenvalue equation \((S_x - \alpha)\chi = 0\) becomes, in matrix notation,

\[
\frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}
\begin{pmatrix}
  \chi_1 \\
  \chi_2
\end{pmatrix}
= \begin{pmatrix}
  \alpha & 0 \\
  0 & \alpha
\end{pmatrix}
\begin{pmatrix}
  \chi_1 \\
  \chi_2
\end{pmatrix}
= 0
\]

\[
\Rightarrow
\begin{pmatrix}
  -\alpha & \frac{\hbar}{2} \\
  \frac{\hbar}{2} & -\alpha
\end{pmatrix}
\begin{pmatrix}
  \chi_1 \\
  \chi_2
\end{pmatrix}
= 0
\]
The characteristic equation is \( \det[S_x - \alpha] = 0 \), or
\[
\alpha^2 - \frac{\hbar^2}{4} = 0 \quad \Rightarrow \quad \alpha = \pm \frac{\hbar}{2}
\]
These are the two eigenvalues (we knew this, of course). Now, substituting \( \alpha_+ \) back into the eigenvalue equation, we obtain
\[
\begin{pmatrix}
-\alpha_+ & \frac{\hbar}{2} \\
\frac{\hbar}{2} & -\alpha_+
\end{pmatrix}
\begin{pmatrix}
\chi_1 \\
\chi_2
\end{pmatrix}
= \begin{pmatrix}
-\frac{\hbar}{2} & \frac{\hbar}{2} \\
\frac{\hbar}{2} & -\frac{\hbar}{2}
\end{pmatrix}
\begin{pmatrix}
\chi_1 \\
\chi_2
\end{pmatrix}
= \frac{\hbar}{2}\begin{pmatrix}
-1 & 1 \\
i & -1
\end{pmatrix}
\begin{pmatrix}
\chi_1 \\
\chi_2
\end{pmatrix}
= 0
\]
The last equality is satisfied only if \( \chi_1 = \chi_2 \) (just write out the two component equations to see this). Hence the normalized eigenvector corresponding to the eigenvalue \( \alpha_+ = +\frac{\hbar}{2} \) is
\[
\chi_+^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix}1 \\
1
\end{pmatrix}
\]
Similarly, we find for the eigenvalue \( \alpha = -\frac{\hbar}{2} \).
\[
\chi_-^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix}1 \\
-1
\end{pmatrix}
\]

17.10.11 Eigenvectors of \( S_y \) for Spin \( \frac{1}{2} \)

To find the eigenvectors of the operator \( S_y \) we follow precisely the same procedure as we did for \( S_x \) (see previous example for details). The steps are:

1. Write the eigenvalue equation \( (S_y - \alpha)\chi = 0 \)
2. Solve the characteristic equation for the eigenvalues \( \alpha \)
3. Substitute the eigenvalues back into the original equation
4. Solve this equation for the eigenvectors

Here we go! The operator \( S_y = \frac{\hbar}{2}\begin{pmatrix}0 & -i \\
i & 0
\end{pmatrix} \), so that, in matrix notation the eigenvalue equation becomes
\[
\begin{pmatrix}
-\alpha & -i\hbar/2 \\
i\hbar/2 & -\alpha
\end{pmatrix}
\begin{pmatrix}
\chi_1 \\
\chi_2
\end{pmatrix}
= 0
\]
The characteristic equation is \( \det[S_y - \alpha] = 0 \), or
\[
\alpha^2 - \frac{\hbar^2}{4} = 0 \quad \Rightarrow \quad \alpha = \pm \frac{\hbar}{2}
\]
These are the same eigenvalues we found for \( S_x \) (no surprise!) Plugging \( \alpha_+ \) back into the equation, we obtain
\[
\begin{pmatrix}
-\alpha_+ & -i\hbar/2 \\
i\hbar/2 & -\alpha_+
\end{pmatrix}
\begin{pmatrix}
\chi_1 \\
\chi_2
\end{pmatrix}
= \frac{\hbar}{2}\begin{pmatrix}
-1 & -i \\
i & -1
\end{pmatrix}
\begin{pmatrix}
\chi_1 \\
\chi_2
\end{pmatrix}
= 0
\]
Writing this out in components gives the pair of equations

\[-\chi_1 - i\chi_2 = 0 \quad \text{and} \quad i\chi_1 - \chi_2 = 0\]

which are both equivalent to \(\chi_2 = i\chi_1\). Repeating the process for \(\alpha_-\), we find that \(\chi_2 = -i\chi_1\). Hence the two eigenvalues and their corresponding normalized eigenvectors are

\[\alpha_+ = \frac{\hbar}{2} \quad \chi_+^{(y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \]

\[\alpha_- = -\frac{\hbar}{2} \quad \chi_-^{(y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \]

17.10.12 Time Development of a Spin \(\frac{1}{2}\) State in a B field

Assume that we are in an arbitrary spin state \(\chi(t = 0) = \begin{pmatrix} a \\ b \end{pmatrix}\) and we have chosen the z axis to be in the field direction. The upper component of the vector (a) is the amplitude to have spin up along the z direction, and the lower component (b) is the amplitude to have spin down. Because of our choice of axes, the spin up and spin down states are also the energy eigenstates with energy eigenvalues of \(\mu_B B\) and \(-\mu_B B\) respectively. We know that the energy eigenstates evolve with time quite simply (recall the separation of the Schrödinger equation where \(T(t) = e^{-i\mu_B Bt/\hbar}\)). So its simple to write down the time evolved state vector.

\[\chi(t) = \begin{pmatrix} ae^{-i\mu_B Bt/\hbar} \\ be^{i\mu_B Bt/\hbar} \end{pmatrix} = \begin{pmatrix} e^{-i\omega t} \\ e^{i\omega t} \end{pmatrix}\]

where \(\omega = \frac{\mu_B B}{\hbar}\).

So let’s say we start out in the state with spin up along the x axis, \(\chi(0) = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}\). We then have

\[\chi(t) = \begin{pmatrix} \frac{1}{\sqrt{2}} e^{-i\omega t} \\ \frac{1}{\sqrt{2}} e^{i\omega t} \end{pmatrix}\]

\[\langle \chi(t) | S_x | \chi(t) \rangle = \frac{\hbar}{2} \begin{pmatrix} 1 & e^{+2i\omega t} \\ e^{-2i\omega t} & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} e^{-i\omega t} \\ 0 \end{pmatrix}
\]

\[= \frac{\hbar}{2} \begin{pmatrix} 1 & e^{+2i\omega t} \\ e^{-2i\omega t} & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} e^{+i\omega t} \\ \frac{1}{\sqrt{2}} e^{-i\omega t} \end{pmatrix}
\]

\[= \frac{\hbar}{2} \left( e^{+2i\omega t} + e^{-2i\omega t} \right) = \frac{\hbar}{2} \cos(2\mu_B Bt/\hbar)\]

So again the spin precesses around the magnetic field. Because \(g = 2\) the rate is twice as high as for \(\ell = 1\).
17.10.13 Nuclear Magnetic Resonance (NMR and MRI)

Nuclear Magnetic Resonance is an important tool in chemical analysis. As the name implies, it uses the spin magnetic moments of nuclei (particularly hydrogen) and resonant excitation. Magnetic Resonance Imaging uses the same principle to get an image (of the inside of the body for example). In basic NMR, a strong static B field is applied. A spin \( \frac{1}{2} \) proton in a hydrogen nucleus then has two energy eigenstates. After some time, most of the protons fall into the lower of the two states. We now use an electromagnetic wave (RF pulse) to excite some of the protons back into the higher energy state. Surprisingly, we can calculate this process already. The proton’s magnetic moment interacts with the oscillating B field of the EM wave.

\[
\begin{align*}
&\text{As excited state} \\
&\text{decays back to} \\
&\text{ground state,} \\
&\text{EM radiation is} \\
&\text{emitted}
\end{align*}
\]

As we derived, the Hamiltonian is

\[
H = -\mu \cdot \vec{B} = \frac{g_p e}{2m_p c} \vec{\sigma} \cdot \vec{B} = \frac{g_p e \hbar}{4m_p c} \vec{\sigma} \cdot \vec{B} = \frac{g_p}{2} \mu_N \vec{\sigma} \cdot \vec{B}
\]

Note that the gyromagnetic ratio of the proton is about +5.6. The magnetic moment is 2.79 \( \mu_N \) (Nuclear Magnetons). Different nuclei will have different gyromagnetic ratios, giving us more tools to work with. Let’s choose our strong static B field to be in the z direction and the polarization on our oscillating EM wave so that the B field points in the x direction. The EM wave has (angular) frequency \( \omega \).

\[
H = \frac{g_p}{2} \mu_N B_z \sigma_z + B_x \cos(\omega t) \sigma_x = \frac{g_p}{2} \mu_N \begin{pmatrix}
B_z & B_x \cos \omega t \\
B_x \cos \omega t & -B_z
\end{pmatrix}
\]

Now we apply the time dependent Schrödinger equation.

\[
\begin{align*}
&\frac{i\hbar}{\hbar} \frac{d\chi}{dt} = H\chi \\
\hbar \chi \begin{pmatrix}
a \\
b
\end{pmatrix} &= \frac{g_p}{2} \mu_N \begin{pmatrix}
B_z & B_x \cos \omega t \\
B_x \cos \omega t & -B_z
\end{pmatrix} \begin{pmatrix}
a \\
b
\end{pmatrix} \\
\begin{pmatrix}
a \\
b
\end{pmatrix} &= -i \frac{g_p \mu_N}{2\hbar} \begin{pmatrix}
B_z & B_x \cos \omega t \\
B_x \cos \omega t & -B_z
\end{pmatrix} \begin{pmatrix}
a \\
b
\end{pmatrix} \\
&= -i \begin{pmatrix}
\omega_0 & \omega_1 \cos \omega t \\
\omega_1 \cos \omega t & -\omega_0
\end{pmatrix} \begin{pmatrix}
a \\
b
\end{pmatrix}
\end{align*}
\]
The solution (see section 17.11.8) of these equations represents an early example of time dependent perturbation theory:

\[
\frac{d}{dt}(e^{-i\omega t}) = \frac{-i\omega}{2}(e^{i(\omega-2\omega_0)t} + e^{-i(\omega+2\omega_0)t})
\]

Terms that oscillate rapidly will average to zero. The second term oscillates very rapidly. The first term will only cause significant transitions if \(\omega \approx 2\omega_0\). Note that this is exactly the condition that requires the energy of the photons in the EM field \(E = \hbar \omega\) to be equal to the energy difference between the two spin states \(\Delta E = 2\hbar \omega_0\). The conservation of energy condition must be satisfied well enough to get a significant transition rate. Actually we will find later that for rapid transitions, energy conservation does not have to be exact.

So we have proven our person-hood and can calculate that we should set the frequency \(\omega\) of our EM wave according to the energy difference between the two spin states. This allows us to cause transitions to the higher energy state. In NMR, we observe the transitions back to the lower energy state. These emit EM radiation at the same frequency and we can detect it after the stronger input pulse ends (or by more complex methods). We don’t yet know why the higher energy state will spontaneously decay to the lower energy state. To calculate this, we will have to quantize the field. But we already see that the energy terms \(e^{-i\omega t/\hbar}\) of standard wave mechanics will require energy conservation with photon energies of \(E = \hbar \omega\).

NMR is a powerful tool in chemical analysis because the molecular field adds to the external B field so that the resonant frequency depends on the molecule as well as the nucleus. We can learn about molecular fields or just use NMR to see what molecules are present in a sample.

In MRI, we typically concentrate on one nucleus like hydrogen. We can put a gradient in \(B_z\) so that only a thin slice of the material has \(\omega\) tuned to the resonant frequency. Therefore we can excite transitions to the higher energy state in only a slice of the sample. If we vary (in the orthogonal direction!) the B field during the decay of the excited state, we can get a two dimensional picture. If we vary B as a function of time during the decay, we can get to 3D. While there are more complex methods used in MRI, we now understand the basis of the technique. MRIs are a very safe way to examine the inside of the body. All the field variation takes some time though. Ultimately, a very powerful tool for scanning materials (a la Star Trek) is possible.

### 17.11 Derivations and Computations

#### 17.11.1 The \(\ell = 1\) Angular Momentum Operators

We will use states of definite \(L_z\), the \(Y_{1m}\).

\[
\langle \ell m' | L_z | \ell m \rangle = m \hbar \delta_{m'm}
\]

\[
L_z = \hbar \begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]

\[
\langle \ell m' | L_z | \ell m \rangle = \sqrt{\ell(\ell + 1) - m(m \pm 1)} \hbar \delta_{m'm}(m \pm 1)
\]
\[ L_+ = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} \]

\[ L_- = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix} \]

\[ L_x = \frac{1}{2}(L_+ + L_-) = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \]

\[ L_y = \frac{1}{2i}(L_+ - L_-) = \frac{\hbar}{\sqrt{2i}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \]

What is the dimension of the matrices for \( \ell = 2 \)?

Dimension 5. Derive the matrix operators for \( \ell = 2 \).

Just do it.

17.11.2 Compute \([L_x, L_y]\) Using Matrices.

\[
[L_x, L_y] = \frac{\hbar^2}{2i} \left( \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} - \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 1 & 0 \end{pmatrix} \right)
\]

\[
\frac{\hbar^2}{2i} \left( \begin{pmatrix} -1 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{pmatrix} - \begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & -1 \end{pmatrix} \right) = \frac{\hbar^2}{2i} \begin{pmatrix} -2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} = i\hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} = i\hbar L_z
\]

The other relations will prove to be correct too, as they must. Its a reassuring check and a calculational example.

17.11.3 Derive the Expression for Rotation Operator \( R_z \)

The laws of physics do not depend on what axes we choose for our coordinate system. There is rotational symmetry. If we make an infinitesimal rotation (through and angle \( d\phi \)) about the z-axis, we get the transformed coordinates

\[
x' = x - d\phi y \\
y' = y + d\phi x.
\]

We can Taylor expand any function \( f \),

\[
f(x', y') = f(x, y) - \frac{\partial f}{\partial x} d\phi y + \frac{\partial f}{\partial y} d\phi x = (1 + i \frac{\hbar}{\hbar} d\phi L_z) f(x, y).
\]

So the rotation operator for the function is

\[ R_z(d\phi) = (1 + i \frac{\hbar}{\hbar} d\phi L_z) \]
A finite rotation can be made by applying the operator for an infinitesimal rotation over and over. Let \( \theta_z = n \delta \phi \). Then

\[
R_z(\theta_z) = \lim_{n \to \infty} \left( 1 + \frac{i \theta_z}{\hbar} L_z \right)^n = e^{i \theta_z L_z / \hbar}.
\]

The last step, converting the limit to an exponential is a known identity. We can verify it by using the log of the quantity. First we expand \( \ln(x) \) about \( x = 1 \): \( \ln(x) = \ln(1) + \frac{1}{x-1} = (x-1) \).

\[
\lim_{n \to \infty} \ln(1 + \frac{i \theta_z}{\hbar} L_z) = n \left( \frac{i \theta_z}{\hbar} L_z \right) = \frac{i \theta_z L_z}{\hbar}
\]

So exponentiating, we get the identity.

17.11.4 Compute the \( \ell = 1 \) Rotation Operator \( R_z(\theta_z) \)

\[
e^{i \theta L_z / \hbar} = \sum_{n=0}^{\infty} \frac{(i \theta L_z / \hbar)^n}{n!}
\]

\[
\left( \frac{L_z}{\hbar} \right)^0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\]

\[
\left( \frac{L_z}{\hbar} \right)^1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}
\]

\[
\left( \frac{L_z}{\hbar} \right)^2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\]

\[
\left( \frac{L_z}{\hbar} \right)^3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} = L_z / \hbar
\]

All the odd powers are the same. All the nonzero even powers are the same. The \( \hbar s \) all cancel out. We now must look at the sums for each term in the matrix and identify the function it represents. If we look at the sum for the upper left term of the matrix, we get a 1 times \( \frac{(i \theta)^n}{n!} \). This is just \( e^{i \theta} \). There is only one contribution to the middle term, that is a one from \( n = 0 \). The lower right term is like the upper left except the odd terms have a minus sign. We get \( \frac{(-i \theta)^n}{n!} \) term \( n \). This is just \( e^{-i \theta} \). The rest of the terms are zero.

\[
R_z(\theta_z) = \begin{pmatrix} e^{i \theta_z} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i \theta_z} \end{pmatrix}
\]
17.11.5 Compute the $\ell = 1$ Rotation Operator $R_y(\theta_y)$

$$e^{i\theta_y \hbar / \hbar} = \sum_{n=0}^{\infty} \left( \frac{i \theta_y \hbar}{\hbar} \right)^n / n!$$

$$\left( \frac{L_y}{\hbar} \right)^0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\left( \frac{L_y}{\hbar} \right)^1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$$

$$\left( \frac{L_y}{\hbar} \right)^2 = \frac{1}{2} \begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix}$$

$$\left( \frac{L_y}{\hbar} \right)^3 = \frac{1}{\sqrt{2} \cdot 2} \begin{pmatrix} 0 & 2 & 0 \\ -2 & 0 & 2 \\ 0 & -2 & 0 \end{pmatrix} = \left( \frac{L_y}{\hbar} \right)$$

All the odd powers are the same. All the nonzero even powers are the same. The $\hbar$s all cancel out. We now must look at the sums for each term in the matrix and identify the function it represents.

- The $n = 0$ term contributes 1 on the diagonals.
- The $n = 1, 3, 5, \ldots$ terms sum to $\sin(\theta) \left( \frac{i \theta_y}{\hbar} \right)$.
- The $n = 2, 4, 6, \ldots$ terms (with a -1 in the matrix) are nearly the series for $\frac{1}{2} \cos(\theta)$. The $n = 0$ term is missing so subtract 1. The middle matrix element is twice the other even terms.

$$e^{i\theta_y \hbar / \hbar} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \sin(\theta) \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} + \frac{1}{2} \cos(\theta) - 1 \begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix}$$

Putting this all together, we get

$$R_y(\theta_y) = \begin{pmatrix} \frac{1}{\sqrt{2}}(1 + \cos(\theta_y)) & \frac{1}{\sqrt{2}} \sin(\theta_y) & \frac{1}{\sqrt{2}}(1 - \cos(\theta_y)) \\ -\frac{1}{\sqrt{2}} \sin(\theta_y) & \cos(\theta_y) & \frac{1}{\sqrt{2}} \sin(\theta_y) \\ \frac{1}{\sqrt{2}}(1 - \cos(\theta_y)) & -\frac{1}{\sqrt{2}} \sin(\theta_y) & \frac{1}{\sqrt{2}}(1 + \cos(\theta_y)) \end{pmatrix}.$$
17.11.6 Derive Spin $\frac{1}{2}$ Operators

We will again use eigenstates of $S_z$, as the basis states.

\[
\chi^+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi^- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad S_z \chi^\pm = \pm \frac{\hbar}{2} \chi^\pm
\]

It's easy to see that this is the only matrix that works. It must be diagonal since the basis states are eigenvectors of the matrix. The correct eigenvalues appear on the diagonal.

Now we do the raising and lowering operators.

\[
S_+ \chi^+ = 0, \quad S_+ \chi^- = \sqrt{s(s+1) - m(m+1)}\hbar \chi^+ = \hbar \chi^+, \\
S_+ \chi^- = \sqrt{s(s+1) - m(m+1)}\hbar \chi^- = \hbar \chi^-
\]

We can now calculate $S_x$ and $S_y$.

\[
S_x = \frac{1}{2} (S_+ + S_-) = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \\
S_y = \frac{1}{2i} (S_+ - S_-) = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}
\]

These are again Hermitian, Traceless matrices.

17.11.7 Derive Spin $\frac{1}{2}$ Rotation Matrices

In section 17.11.3, we derived the expression for the rotation operator for orbital angular momentum vectors. The rotation operators for internal angular momentum will follow the same formula.

\[
R_z(\theta) = e^{i\frac{\pi \sigma_z}{\hbar}} = e^{\frac{i}{\hbar} \sigma_z}, \\
R_y(\theta) = e^{i\frac{\pi \sigma_y}{\hbar}} = e^{\frac{i}{\hbar} \sigma_y}, \\
R_y(\theta) = e^{i\frac{\pi \sigma_y}{\hbar}}, \\
e^{i\frac{\pi \sigma_z}{\hbar}} = \sum_{n=0}^{\infty} \frac{(i \hbar)^n}{n!} \sigma_z^n
\]
We now can compute the series by looking at the behavior of $\sigma_j^n$.

\[
\begin{align*}
\sigma_z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} & \sigma_z^2 &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
\sigma_y &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} & \sigma_y^2 &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
\sigma_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} & \sigma_x^2 &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\end{align*}
\]

Doing the sums

\[
R_z(\theta) = e^{i\theta\sigma_z} = \begin{pmatrix} \sum_{n=0}^{\infty} \frac{1}{n!} (\frac{i\theta}{n})^n & 0 \\ 0 & \sum_{n=0}^{\infty} \frac{1}{n!} (\frac{-i\theta}{n})^n \end{pmatrix} = \begin{pmatrix} e^{\frac{i\theta}{2}} & 0 \\ 0 & e^{-i\frac{\theta}{2}} \end{pmatrix}
\]

\[
R_y(\theta) = \begin{pmatrix} \sum_{n=0,2,4,...} \frac{1}{n!} (\frac{i\theta}{n})^n & -i \sum_{n=1,3,5,...} \frac{1}{n!} (\frac{-i\theta}{n})^n \\ i \sum_{n=1,3,5,...} \frac{1}{n!} (\frac{i\theta}{n})^n & \sum_{n=0,2,4,...} \frac{1}{n!} (\frac{-i\theta}{n})^n \end{pmatrix} = \begin{pmatrix} \cos \frac{\theta}{2} & \sin \frac{\theta}{2} \\ -\sin \frac{\theta}{2} & \cos \frac{\theta}{2} \end{pmatrix}
\]

\[
R_x(\theta) = \begin{pmatrix} \sum_{n=0,2,4,...} \frac{1}{n!} (\frac{i\theta}{n})^n & \sum_{n=1,3,5,...} \frac{1}{n!} (\frac{-i\theta}{n})^n \\ \sum_{n=0,2,4,...} \frac{1}{n!} (\frac{i\theta}{n})^n & \sum_{n=1,3,5,...} \frac{1}{n!} (\frac{-i\theta}{n})^n \end{pmatrix} = \begin{pmatrix} \cos \frac{\theta}{2} & i \sin \frac{\theta}{2} \\ i \sin \frac{\theta}{2} & \cos \frac{\theta}{2} \end{pmatrix}
\]

Note that all of these rotation matrices become the identity matrix for rotations through 720 degrees and are minus the identity for rotations through 360 degrees.

17.11.8 NMR Transition Rate in an Oscillating B Field

We have the time dependent Schrödinger equation for a proton in a static field in the z direction plus an oscillating field in the x direction.

\[
\begin{align*}
\frac{i\hbar}{\mu} \frac{d\chi}{dt} &= H \chi \\
i\hbar \begin{pmatrix} a \\ b \end{pmatrix} &= \frac{g_p}{2} \mu_N \begin{pmatrix} B_z & B_x \cos \omega t \\ B_x \cos \omega t & -B_z \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} \\
\begin{pmatrix} a \\ b \end{pmatrix} &= -i g_p \mu_N \begin{pmatrix} B_z & B_x \cos \omega t \\ B_x \cos \omega t & -B_z \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = -i \begin{pmatrix} \omega_0 & \omega_1 \cos \omega t \\ \omega_1 \cos \omega t & -\omega_0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}
\end{align*}
\]

So far all we have done is plugged things into the Schrödinger equation. Now we have to solve this system of two equations. This could be hard but we will do it only near $t = 0$, when the EM wave starts. Assume that at $t = 0$, $a = 1$ and $b = 0$, that is, the nucleus is in the lower energy state. Then we have

\[
\begin{align*}
\dot{a} &= -i \omega_1 a \\
a &= 1 e^{-i\omega_1 t} \\
\dot{b} &= -i \omega_1 \cos \omega t a + i \omega_0 b = -i \omega_1 \cos \omega t e^{-i\omega_1 t} + i \omega_0 b \\
b &= \frac{-i \omega_1}{2} (e^{i(\omega_1 - \omega_0) t} + e^{-i(\omega_1 + \omega_0) t}) + i \omega_0 b
\end{align*}
\]
Now comes the one tricky part of the calculation. The diagonal terms in the Hamiltonian cause a very rapid time dependence to the amplitudes. To get \( b \) to grow, we need to keep adding \( \dot{b} \) in phase with \( b \). To see that clearly, let's compute the time derivative of \( be^{-i\omega t} \).

\[
\frac{d}{dt}(be^{-i\omega t}) = \left(\frac{-i\omega_1}{2} e^{i(\omega_2-2\omega_3)t} + e^{-i(\omega_2+2\omega_3)t} + i\omega_0 be^{-i\omega t} - i\omega_0 be^{-i\omega t}\right)
\]

Terms that oscillate rapidly will average to zero. To get a net change in \( be^{-i\omega t} \), we need to have \( \omega \approx 2\omega_0 \). Then the first term is important and we can neglect the second which oscillates with a frequency of the order of \( 10^{11} \). Note that this is exactly the condition that requires the energy of the photons in the EM field \( E = \hbar \omega \) to be equal to the energy difference between the two spin states \( \Delta E = 2\hbar \omega_0 \).

\[
\frac{d}{dt}(be^{-i\omega t}) = \frac{-i\omega_1}{2} \\
be^{-i\omega t} = \frac{-i\omega_1}{2}
\]

It appears that the amplitude grows linearly with time and hence the probability would grow like \( t^2 \). Actually, once we do the calculation (only a bit) more carefully, we will see that the probability increases linearly with time and there is a delta function of energy conservation. We will do this more generally in the section on time dependent perturbation theory.

In any case, we can only cause transitions if the EM field is tuned so that \( \omega \approx 2\omega_0 \) which means the photons in the EM wave have an energy equal to the difference in energy between the spin down state and the spin up state. The transition rate increases as we increase the strength of the oscillating B field.

17.12 Homewor Problems

1. An angular momentum 1 system is in the state \( \chi = \frac{1}{\sqrt{2\pi}} \begin{pmatrix} 1 \\ 3 \\ 4 \end{pmatrix} \). What is the probability that a measurement of \( L_x \) yields a value of 0?

2. A spin \( \frac{1}{2} \) particle is in an eigenstate of \( S_y \) with eigenvalue \( +\frac{1}{2} \) at time \( t = 0 \). At that time it is placed in a constant magnetic field \( B \) in the \( z \) direction. The spin is allowed to precess for a time \( T \). At that instant, the magnetic field is very quickly switched to the \( x \) direction. After another time interval \( T \), a measurement of the \( y \) component of the spin is made. What is the probability that the value \( -\frac{1}{2} \) will be found?

3. Consider a system of spin \( \frac{1}{2} \). What are the eigenstates and eigenvalues of the operator \( S_x + S_y \)? Suppose a measurement of this quantity is made, and the system is found to be in the eigenstate with the larger eigenvalue. What is the probability that a subsequent measurement of \( S_y \) yields \( \frac{1}{2} \)?

4. The Hamiltonian matrix is given to be

\[
H = \hbar \omega \begin{pmatrix} 8 & 4 & 6 \\ 4 & 10 & 4 \\ 6 & 4 & 8 \end{pmatrix}
\]
What are the eigen-energies and corresponding eigenstates of the system? (This isn't too messy.)

5. What are the eigenfunctions and eigenvalues of the operator $L_x L_y + L_y L_x$ for a spin 1 system?

6. Calculate the $\ell = 1$ operator for arbitrary rotations about the $x$-axis. Use the usual $L_z$ eigenstates as a basis.

7. An electron is in an eigenstate of $S_z$ with eigenvalue $\frac{5}{2}$. What are the amplitudes to find the electron with a) $S_z = \frac{5}{2}$, b) $S_z = -\frac{5}{2}$, $S_y = +\frac{5}{2}$, $S_u = +\frac{5}{2}$, where the $u$-axis is assumed to be in the $x - y$ plane rotated by and angle $\theta$ from the $z$-axis.

8. Particles with angular momentum 1 are passed through a Stern-Gerlach apparatus which separates them according to the $z$-component of their angular momentum. Only the $m = -1$ component is allowed to pass through the apparatus. A second apparatus separates the beam according to its angular momentum component along the $u$-axis. The $u$-axis and the $z$-axis are both perpendicular to the beam direction but have an angle $\theta$ between them. Find the relative intensities of the three beams separated in the second apparatus.

9. Find the eigenstates of the harmonic oscillator lowering operator $A$. They should satisfy the equation $A|\alpha\rangle = \alpha|\alpha\rangle$. Do this by finding the coefficients $(n|\alpha\rangle$ where $|n\rangle$ is the $n^{th}$ energy eigenstate. Make sure that the states $|\alpha\rangle$ are normalized so that $\langle \alpha|\alpha\rangle = 1$. Suppose $|\alpha'\rangle$ is another such state with a different eigenvalue. Compute $\langle \alpha'|\alpha\rangle$. Would you expect these states to be orthogonal?

10. Find the matrix which represents the $p^2$ operator for a 1D harmonic oscillator. Write out the upper left $5 \times 5$ part of the matrix.

11. Let's define the $u$ axis to be in the $x$-$z$ plane, between the positive $x$ and $z$ axes and at an angle of 30 degrees to the $x$ axis. Given an unpolarized spin $\frac{1}{2}$ beam of intensity $I$ going into the following Stern-Gerlach apparatus, what intensity comes out?

\[
I \rightarrow \begin{cases} + & \rightarrow \begin{array}{c} + \\ - \end{array} \\ - & \rightarrow \begin{array}{c} - \\ - \end{array} \end{cases}_{x} \]

\[
I \rightarrow \begin{cases} + & \rightarrow \begin{array}{c} + \\ - \end{array} \\ - & \rightarrow \begin{array}{c} + \\ - \end{array} \end{cases}_{u} \]

\[
I \rightarrow \begin{cases} + & \rightarrow \begin{array}{c} + \\ - \end{array} \\ - & \rightarrow \begin{array}{c} + \\ - \end{array} \end{cases}_{z} \]

17.13 Sample Test Problems

1. We have shown that the Hermitian conjugate of a rotation operator $R(\theta)$ is $R(-\theta)$. Use this to prove that if the $\phi_i$ form an orthonormal complete set, then the set $\phi'_i = R(\theta)\phi_i$ are also orthonormal and complete.

2. Given that $u_n$ is the $n^{th}$ one dimensional harmonic oscillator energy eigenstate: a) Evaluate the matrix element $\langle u_m|p^2|u_n\rangle$. b) Write the upper left 5 by 5 part of the $p^2$ matrix.
3. A spin 1 system is in the following state in the usual $L_z$ basis: \( \chi = \frac{1}{\sqrt{3}} \begin{pmatrix} \sqrt{2} \\ 1 + i \\ -i \end{pmatrix} \). What is the probability that a measurement of the $x$ component of spin yields zero? What is the probability that a measurement of the $y$ component of spin yields $+\hbar$?

4. In a three state system, the matrix elements are given as \( \langle \psi_1 | H | \psi_1 \rangle = E_1, \langle \psi_2 | H | \psi_2 \rangle = \langle \psi_3 | H | \psi_3 \rangle = E_2, \langle \psi_1 | H | \psi_2 \rangle = 0, \langle \psi_1 | H | \psi_3 \rangle = 0 \), and \( \langle \psi_2 | H | \psi_3 \rangle = \alpha \). Assume all of the matrix elements are real. What are the energy eigenvalues and eigenstates of the system? At \( t = 0 \) the system is in the state \( \psi_2 \). What is \( \psi(t) \)?

5. Find the (normalized) eigenvectors and eigenvalues of the \( S_x \) (matrix) operator for \( s = 1 \) in the usual \( (S_z) \) basis.

6. A spin \( \frac{1}{2} \) particle is in a magnetic field in the \( x \) direction giving a Hamiltonian \( H = \mu_B B \sigma_x \). Find the time development (matrix) operator \( e^{-iHt/\hbar} \) in the usual basis. If \( \chi(t = 0) = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \), find \( \chi(t) \).

7. A spin \( \frac{1}{2} \) system is in the following state in the usual \( S_z \) basis: \( \chi = \frac{1}{\sqrt{3}} \begin{pmatrix} \sqrt{2} \\ 1 + i \\ -i \end{pmatrix} \). What is the probability that a measurement of the \( x \) component of spin yields \( +\frac{\hbar}{2} \)?

8. A spin \( \frac{1}{2} \) system is in the state \( \chi = \frac{1}{\sqrt{2}} \begin{pmatrix} i \\ 1 \end{pmatrix} \) (in the usual \( S_z \) eigenstate basis). What is the probability that a measurement of \( S_x \) yields \( \pm \frac{\hbar}{2} \)? What is the probability that a measurement of \( S_y \) yields \( \mp \frac{\hbar}{2} \)?

9. A spin \( \frac{1}{2} \) object is in an eigenstate of \( S_y \) with eigenvalue \( \frac{\hbar}{2} \) at \( t = 0 \). The particle is in a magnetic field \( B = (0, 0, B) \) which makes the Hamiltonian for the system \( H = \mu_B B \sigma_z \). Find the probability to measure \( S_y = \frac{\hbar}{2} \) as a function of time.

10. Two degenerate eigenfunctions of the Hamiltonian are properly normalized and have the following properties.

\[
H \psi_1 = E_0 \psi_1 \quad H \psi_2 = E_0 \psi_2 \\
P \psi_1 = -\psi_2 \quad P \psi_2 = -\psi_1
\]

What are the properly normalized states that are eigenfunctions of \( H \) and \( P \)? What are their energies?

11. What are the eigenvectors and eigenvalues for the spin \( \frac{1}{2} \) operator \( S_x + S_z \)?

12. A spin \( \frac{1}{2} \) object is in an eigenstate of \( S_y \) with eigenvalue \( \frac{\hbar}{2} \) at \( t = 0 \). The particle is in a magnetic field \( B = (0, 0, B) \) which makes the Hamiltonian for the system \( H = \mu_B B \sigma_z \). Find the probability to measure \( S_y = \frac{\hbar}{2} \) as a function of time.

13. A spin 1 system is in the following state, (in the usual \( L_z \) eigenstate basis):

\[
\chi = \frac{1}{\sqrt{3}} \begin{pmatrix} \sqrt{2} \\ 1 + i \\ -i \end{pmatrix}.
\]

What is the probability that a measurement of \( L_x \) yields 0? What is the probability that a measurement of \( L_y \) yields \( -\hbar \)?
14. A spin \( \frac{1}{2} \) object is in an eigenstate of \( S_z \) with eigenvalue \( \frac{\hbar}{2} \) at \( t=0 \). The particle is in a magnetic field \( \mathbf{B} = (0, B, 0) \) which makes the Hamiltonian for the system \( H = \mu_B \mathbf{B} \sigma_y \). Find the probability to measure \( S_z = \frac{\hbar}{2} \) as a function of time.

15. A spin 1 particle is placed in an external field in the \( u \) direction such that the Hamiltonian is given by

\[
H = \alpha \left( \frac{\sqrt{3}}{2} S_x + \frac{1}{2} S_y \right)
\]

Find the energy eigenstates and eigenvalues.

16. A (spin \( \frac{1}{2} \)) electron is in an eigenstate of \( S_y \) with eigenvalue \( -\frac{\hbar}{2} \) at \( t = 0 \). The particle is in a magnetic field \( \mathbf{B} = (0, 0, B) \) which makes the Hamiltonian for the system \( H = \mu_B \mathbf{B} \sigma_z \). Find the spin state of the particle as a function of time. Find the probability to measure \( S_y = +\frac{\hbar}{2} \) as a function of time.
18 Electrons in an Electromagnetic Field

In this section, we will study the interactions of electrons in an electromagnetic field. We will compute the additions to the Hamiltonian for magnetic fields. The gauge symmetry exhibited in electromagnetism will be examined in quantum mechanics. We will show that a symmetry allowing us to change the phase of the electron wave function requires the existence of EM interactions (with the gauge symmetry).

These topics are covered in Gasiorowicz Chapter 13, and in Cohen-Tannoudji et al. Complements $E_{VI}$, $D_{VII}$ and $H_{III}$.

18.1 Review of the Classical Equations of Electricity and Magnetism in CGS Units

Maxwell’s Equations in CGS units are

\[ \nabla \cdot \vec{B} = 0 \]
\[ \nabla \times \vec{E} + \frac{1}{c} \frac{\partial \vec{B}}{\partial t} = 0 \]
\[ \nabla \cdot \vec{E} = 4\pi \rho \]
\[ \nabla \times \vec{B} + \frac{1}{c} \frac{\partial \vec{E}}{\partial t} = \frac{4\pi}{c} \vec{j} \]

The Lorentz Force is

\[ \vec{F} = -e(\vec{E} + \frac{1}{c} \vec{\partial} \times \vec{B}) \]

If we derive the fields from potentials,

\[ \vec{B} = \nabla \times \vec{A} \]
\[ \vec{E} = -\nabla \phi - \frac{1}{c} \frac{\partial \vec{A}}{\partial t} \]

then the first two Maxwell equations are automatically satisfied. Applying the second two equations we get wave equations in the potentials.

\[ -\nabla^2 \phi - \frac{1}{c} \frac{\partial}{\partial t}(\nabla \cdot \vec{A}) = 4\pi \rho \]
\[ -\nabla^2 \vec{A} + \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} + \nabla \left( \nabla \cdot \vec{A} + \frac{1}{c} \frac{\partial \phi}{\partial t} \right) = \frac{4\pi}{c} \vec{j} \]

The two results we want are

- the classical gauge symmetry and
- the classical Hamiltonian.

The Maxwell equations are invariant under a gauge transformation of the potentials.

\[ \vec{A} \rightarrow \vec{A} - \nabla f(\vec{r}, t) \]
\[ \phi \rightarrow \phi + \frac{1}{c} \frac{\partial f(\vec{r}, t)}{\partial t} \]
Note that when we quantize the field, the potentials will play the role that wave functions do for the electron, so this gauge symmetry will be important in quantum mechanics. We can use the gauge symmetry to simplify our equations. For time independent charge and current distributions, the **coulomb gauge**, $\nabla \cdot A = 0$, is often used. For time dependent conditions, the **Lorentz gauge**, $\nabla \cdot A + \frac{1}{c^2} \frac{\partial \phi}{\partial t} = 0$, is often convenient. These greatly simplify the above wave equations in an obvious way.

Finally, the classical **Hamiltonian for electrons in an electromagnetic field** becomes

$$H = \frac{p^2}{2m} - \frac{1}{2m} \left( \vec{p} + \frac{e}{c} \vec{A} \right)^2 - e\phi$$

The magnetic force is not a conservative one so we cannot just add a scalar potential. We know that there is momentum contained in the field so the additional momentum term, as well as the usual force due to an electric field, makes sense. The electron generates an E-field and if there is a B-field present, $\vec{E} \times \vec{B}$ gives rise to momentum density in the field. The evidence that this is the correct classical Hamiltonian is that we can derive (see section 18.5.1) the Lorentz Force from it.

### 18.2 The Quantum Hamiltonian Including a B-field

We will quantize the Hamiltonian

$$H = \frac{1}{2m} \left( \vec{p} + \frac{e}{c} \vec{A} \right)^2 - e\phi$$

in the usual way, by replacing the momentum by the momentum operator, for the case of a constant magnetic field.

Note that the momentum operator will now include momentum in the field, not just the particle’s momentum. As this Hamiltonian is written, $\vec{p}$ is the variable conjugate to $\vec{r}$ and is related to the velocity by

$$\vec{p} = m\vec{v} - \frac{e}{c} \vec{A}$$

as seen in our derivation of the Lorentz force (See Section 18.5.1).

The computation (see section 18.5.2) yields

$$-\hbar^2 \frac{\nabla^2}{2m} \psi + \frac{e}{2mc} \vec{B} \cdot \vec{\hat{L}} \psi + \frac{e^2}{8mc^2} \left( e^2 \vec{B}^2 - (\vec{r} \cdot \vec{B})^2 \right) \psi = (E + e\phi)\psi.$$  

The usual kinetic energy term, the first term on the left side, has been recovered. The standard potential energy of an electron in an Electric field is visible on the right side. We see two additional terms due to the magnetic field. An estimate (see section 18.5.3) of the size of the two B field terms for atoms shows that, for realizable magnetic fields, the first term is fairly small (down by a factor of $\frac{B}{10^4}$ gauss compared to hydrogen binding energy), and the second can be neglected. The second term may be important in very high magnetic fields like those produced near neutron stars or if distance scales are larger than in atoms like in a plasma (see example below).

So, for atoms, the dominant additional term is the one we anticipated classically in section 17.4,

$$H_B = \frac{e}{2mc} \vec{B} \cdot \vec{L} = -\vec{\mu} \cdot \vec{B},$$

where $\vec{\mu} = -\frac{e}{2mc} \vec{L}$. This is, effectively, the **magnetic moment** due to the electron’s orbital angular momentum. In atoms, this term gives rise to the **Zeeman effect**; otherwise degenerate atomic states
split in energy when a magnetic field is applied. Note that the electron spin which is not included here also contributes to the splitting and will be studied later.

The *Zeeman effect*, neglecting electron spin, is particularly simple to calculate because the hydrogen energy eigenstates are also eigenstates of the additional term in the Hamiltonian. Hence, the correction can be calculated exactly and easily.

* See Example 18.4.1: Splitting of orbital angular momentum states in a B field.*

The result is that the shifts in the eigen-energies are

$$\Delta E = \mu_B B m_e$$

where $m_e$ is the usual quantum number for the z component of orbital angular momentum. The Zeeman splitting of Hydrogen states, with spin included, was a powerful tool in understanding Quantum Physics and we will discuss it in detail in 21.

The additional magnetic field terms are important in a plasma because the typical radii can be much bigger than in an atom. A plasma is composed of ions and electrons, together to make a (usually) electrically neutral mix. The charged particles are essentially free to move in the plasma. If we apply an external magnetic field, we have a quantum mechanics problem to solve. On earth, we use plasmas in magnetic fields for many things, including nuclear fusion reactors. Most regions of space contain plasmas and magnetic fields.

In the example below, we will solve the Quantum Mechanics problem two ways: one using our new Hamiltonian with B field terms, and the other writing the Hamiltonian in terms of A. The first one will exploit both rotational symmetry about the B field direction and translational symmetry along the B field direction. We will turn the radial equation into the equation we solved for Hydrogen. In the second solution, we will use translational symmetry along the B field direction as well as translational symmetry transverse to the B field. We will now turn the remaining 1D part of the Schrödinger equation into the 1D harmonic oscillator equation, showing that the two problems we have solved analytically are actually related to each other!

* See Example 18.4.2: A neutral plasma in a constant magnetic field.*

The result in either solution for the eigen-energies can be written as

$$E_n = \frac{eB\hbar}{m_e c} \left( n + \frac{1}{2} \right) + \frac{\hbar^2 k^2}{2m_e},$$

which depends on 2 quantum numbers. $\hbar k$ is the conserved momentum along the field direction which can take on any value. $n$ is an integer dealing with the state in x and y. In the first solution we understand $n$ in terms of the radial wavefunction in cylindrical coordinates and the angular momentum about the field direction. In the second solution, the physical meaning is less clear.

### 18.3 Gauge Symmetry in Quantum Mechanics

Gauge symmetry in Electromagnetism was recognized before the advent of quantum mechanics. We have seen that symmetries play a very important role in the quantum theory. Indeed, in quantum mechanics, gauge symmetry can be seen as the basis for electromagnetism and conservation of charge.
We know that the all observables are unchanged if we make a global change of the phase of the wavefunction, \( \psi \rightarrow e^{i\lambda} \psi \). We could call this **global phase symmetry**. All relative phases (say for amplitudes to go through different slits in a diffraction experiment) remain the same and no physical observable changes. This is a symmetry in the theory which we already know about. Let’s postulate that there is a bigger symmetry and see what the consequences are.

\[ \psi(\vec{r}, t) \rightarrow e^{i\lambda(\vec{r}, t)} \psi(\vec{r}, t) \]

That is, we can change the phase by a different amount at each point in spacetime and the physics will remain unchanged. This **local phase symmetry** is bigger than the global one.

It’s clear that this transformation leaves the **absolute square of the wavefunction** the same, but what about the Schrödinger equation? It must also be unchanged. The **derivatives in the Schrödinger equation** will act on \( \lambda(\vec{r}, t) \) changing the equation unless we do something else to cancel the changes.

\[ \frac{1}{2m} \left( \vec{p} + \frac{e}{c} \vec{A} \right)^2 \psi = (E + e\phi)\psi \]

A little **calculation** (see section 18.5.6) shows that the equation remains unchanged if we also transform the potentials

\[
\begin{align*}
\vec{A} & \rightarrow \vec{A} - \vec{\nabla} f(\vec{r}, t) \\
\phi & \rightarrow \phi + \frac{1}{c} \frac{\partial f(\vec{r}, t)}{\partial t} \\
f(\vec{r}, t) & = \frac{\hbar c}{e} \lambda(\vec{r}, t).
\end{align*}
\]

This is just the **standard gauge transformation of electromagnetism**, but, we now see that local phase symmetry of the wavefunction requires gauge symmetry for the fields and indeed even requires the existence of the EM fields to cancel terms in the Schrödinger equation. Electromagnetism is called a **gauge theory** because the gauge symmetry actually defines the theory. It turns out that the **weak and the strong interactions are also gauge theories** and, in some sense, have the next simplest possible gauge symmetries after the one in Electromagnetism.

We will write our **standard gauge transformation** in the traditional way to conform a bit better to the textbooks.

\[
\begin{align*}
\vec{A} & \rightarrow \vec{A} - \vec{\nabla} f(\vec{r}, t) \\
\phi & \rightarrow \phi + \frac{1}{c} \frac{\partial f(\vec{r}, t)}{\partial t} \\
\psi(\vec{r}, t) & \rightarrow e^{-i\frac{\hbar}{\epsilon} f(\vec{r}, t)} \psi(\vec{r}, t)
\end{align*}
\]

There are measurable **quantum physics consequences** of this symmetry. We can understand a number of them by looking at the **vector potential in a field free regions**. If \( B = 0 \) then \( \vec{A} \) can be written as the gradient of a function \( f(\vec{r}) \). To be specific, take our gauge transformation of the vector potential. Make a gauge transformation such that \( \vec{A}' = 0 \). This of course is still consistent with \( \vec{B} = 0 \).

\[
\vec{A}' = \vec{A} - \vec{\nabla} f(\vec{r}) = 0
\]

Then the old vector potential is then given by

\[
\vec{A} = \vec{\nabla} f(\vec{r}).
\]
Integrating this equation, we can write the function $f(\vec{r})$ in terms of $\vec{A}(\vec{r})$.

$$\int_{\vec{r}_0}^{\vec{r}} d\vec{r} \cdot \vec{A} = \int_{\vec{r}_0}^{\vec{r}} d\vec{r} \cdot \vec{\nabla} f = f(\vec{r}) - f(\vec{r}_0)$$

If we choose $f$ so that $f(\vec{r}_0) = 0$, then we have a very useful relation between the gauge function and the vector potential in a field free region.

$$f(\vec{r}) = \int_{\vec{r}_0}^{\vec{r}} d\vec{r} \cdot \vec{A}.$$

We can derive (see section 18.5.7) the quantization of magnetic flux by calculating the line integral of $\vec{A}$ around a closed loop in a field free region.

$$\Phi = \frac{2\pi \hbar c}{e}$$

A good example of a $B = 0$ region is a superconductor. Magnetic flux is excluded from the superconducting region. If we have a superconducting ring, we have a $B=0$ region surrounding some flux. We have shown then, that the flux going through a ring of superconductor is quantized.

Flux is observed to be quantized but the charge of the particle seen is $2e$.

$$\Phi = \frac{2\pi \hbar c}{2e}$$

This is due to the pairing of electrons inside a superconductor.

The Aharanov Böhm Effect brings us back to the two slit diffraction experiment but adds magnetic fields.
The electron beams travel through two slits in field free regions but we have the ability to vary a magnetic field enclosed by the path of the electrons. At the screen, the amplitudes from the two slits interfere $\psi = \psi_1 + \psi_2$. Let’s start with $B = 0$ and $A = 0$ everywhere. When we change the $B$ field, the wavefunctions must change.

$$
\psi_1 \rightarrow \psi_1 e^{-i \frac{e}{\hbar} \int \vec{A} \cdot d\vec{x}}
$$

$$
\psi_2 \rightarrow \psi_2 e^{-i \frac{e}{\hbar} \int \vec{A} \cdot d\vec{x}}
$$

$$
\psi = \left( \psi_1 e^{-i \frac{e}{\hbar} \int \vec{A} \cdot d\vec{x}} + \psi_2 \right) e^{-i \frac{e}{\hbar} \int \vec{A} \cdot d\vec{x}}
$$

The relative phase from the two slits depends on the flux between the slits. By varying the $B$ field, we will shift the diffraction pattern even though $B = 0$ along the whole path of the electrons. While this may at first seem amazing, we have seen similar effects in classical E&M with an EMF induced in a loop by a changing $B$ field which does not touch the actual loop.

18.4 Examples

18.4.1 The Naive Zeeman Splitting

The additional term we wish to consider in the Hamiltonian is $\frac{e}{2\mu c} \vec{B} \cdot \vec{L}$. Choosing the $z$ axis so that the constant field points in the $z$ direction, we have

$$
H_{\text{Zeeman}} = \frac{eB_z}{2\mu c} L_z.
$$
In general, the addition of a new term to the Hamiltonian will require us to use an approximation to solve the problem. In this case, however, the energy eigenstates we derived in the Hydrogen problem are still eigenstates of the full Hamiltonian $H = H_{\text{hydrogen}} + H_{\text{Zeeman}}$. Remember, our hydrogen states are eigenstates of $H$, $L^2$ and $L_z$.

\[ (H_{\text{hydrogen}} + H_{\text{Zeeman}})\psi_{nm} = (E_n + m\mu BB)\psi_{nm} \]

This would be a really nice tool to study the number of degenerate states in each hydrogen level. When the experiment was done, things did not work our according to plan at all. The magnetic moment of the electron's spin greatly complicates the problem. We will solve this later.

18.4.2 A Plasma in a Magnetic Field

An important place where both magnetic terms come into play is in a plasma. There, many electrons are not bound to atoms and external Electric fields are screened out. Let’s assume there is a constant (enough) B field in the z direction. We then have cylindrical symmetry and will work in the coordinates, $\rho$, $\phi$, and $z$.

\[-\frac{\hbar^2}{2m_e}\nabla^2\psi + \frac{eB}{2m_e}\rho \psi + \frac{e^2B^2}{8m_e^2c^2}(x^2 + y^2)\psi = (E + e\phi)\psi\]

The problem clearly has translational symmetry along the z direction and rotational symmetry around the z axis. Given the symmetry, we know that $L_z$ and $p_z$ commute with the Hamiltonian and will give constants of the motion. We therefore will be able to separate variables in the usual way.

\[\psi(r) = u_{nmk}(\rho)e^{im\phi}e^{ikz}\]

In solving (see section 18.5.4) the equation in $\rho$ we may reuse the Hydrogen solution ultimately get the energies

\[E = \frac{eB\hbar}{m_e c} \left( n + \frac{1 + m + |m|}{2} \right) + \frac{\hbar^2 k^2}{2m}\]

and associated Laguerre polynomials (as in Hydrogen) in $\rho^2$ (instead of $r$).

The solution turns out to be simpler using the Hamiltonian written in terms of $A$ if we choose the right gauge by setting $A = Bx\hat{y}$.

\[H = \frac{1}{2m_e} \left( \vec{p} + \frac{e}{c} \vec{A} \right)^2 = \frac{1}{2m_e} \left( p_x^2 + \left( p_y + \frac{eB}{c} x \right)^2 + p_z^2 \right) = \frac{1}{2m_e} \left( p_x^2 + p_y^2 + \frac{2eB}{c} xp_y + \left( \frac{eB}{c} \right)^2 x^2 + p_z^2 \right)\]

This Hamiltonian does not depend on $y$ or $z$ and therefore has translational symmetry in both $x$ and $y$ so their conjugate momenta are conserved. We can use this symmetry to write the solution and reduce to a 1D equation in $v(x)$.

\[\psi = v(x)e^{ib_0 y}e^{ikz}\]

Then we actually can use our harmonic oscillator solution instead of hydrogen! The energies come out to be

\[E_n = \frac{eB\hbar}{m_e c} \left( n + \frac{1}{2} \right) + \frac{\hbar^2 k^2}{2m_e}\]

Neglecting the free particle behavior in $z$, these are called the Landau Levels. This is an example of the equivalence of the two real problems we know how to solve.
18.5 Derivations and Computations

18.5.1 The Lorentz Force from the Classical Hamiltonian

In this section, we wish to verify that the Hamiltonian

$$H = \frac{1}{2m} \left( \dot{\vec{p}} + \frac{e}{c} \vec{A} \right)^2 - e\phi$$

gives the correct Lorentz Force law in classical physics. We will then proceed to use this Hamiltonian in Quantum Mechanics.

**Hamilton’s equations** are

$$\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q}$$

where $\dot{\vec{q}} \equiv \vec{v}$ and the conjugate momentum is already identified correctly $\dot{\vec{p}} \equiv \vec{p}$. Remember that these are applied assuming $q$ and $p$ are independent variables.

Beginning with $\dot{q} = \partial H / \partial p$, we have

$$\frac{d\vec{v}}{dt} = \frac{1}{m} \left( \vec{p} + \frac{e}{c} \vec{A} \right)$$

$$m\vec{v} = \vec{p} + \frac{e}{c} \vec{A}$$

$$\vec{p} = m\vec{v} - \frac{e}{c} \vec{A}$$

Note that $\vec{p} \neq m\vec{v}$. The momentum conjugate to $\vec{r}$ includes momentum in the field. We now time differentiate this equation and write it in terms of the components of a vector.

$$\frac{dp_i}{dt} = m \frac{dv_i}{dt} - \frac{e}{c} \frac{dA_i}{dt}.$$ 

Similarly for the other Hamilton equation (in each vector component) $\dot{p}_i = -\frac{\partial H}{\partial q_i}$, we have

$$\frac{dp_i}{dt} = \dot{p}_i = -\frac{e}{mc} \left( \vec{p} + \frac{e}{c} \vec{A} \right) \cdot \frac{\partial \vec{A}}{\partial x_i} + \frac{e}{c} \frac{\partial \phi}{\partial x_i}.$$ 

We now have two equations for $\frac{dp_i}{dt}$ derived from the two Hamilton equations. We equate the two right hand sides yielding

$$ma_i = m \frac{dv_i}{dt} = -\frac{e}{mc} \left( \vec{p} + \frac{e}{c} \vec{A} \right) \cdot \frac{\partial \vec{A}}{\partial x_i} + \frac{e}{c} \frac{\partial \phi}{\partial x_i} + \frac{e}{c} \frac{dA_i}{dt}.$$ 

$$ma_i = -\frac{e}{mc} (m\vec{v}) \cdot \frac{\partial \vec{A}}{\partial x_i} + \frac{e}{c} \frac{\partial \phi}{\partial x_i} + \frac{e}{c} \frac{dA_i}{dt}.$$ 

The **total time derivative** of $A$ has one part from $A$ changing with time and another from the particle moving and $A$ changing in space.

$$\frac{d\vec{A}}{dt} = \frac{\partial \vec{A}}{\partial t} + \left( \vec{v} \cdot \nabla \right) \vec{A}$$
so that
\[ F_i = m a_i = -\frac{e}{c} \vec{v} \cdot \frac{\partial \vec{A}}{\partial x_i} + e \frac{\partial \phi}{\partial x_i} + e \frac{\partial A_i}{\partial t} + \frac{e}{c} \left( \vec{v} \cdot \vec{\nabla} \right) A_i. \]

We notice the electric field term in this equation.
\[ e \frac{\partial \phi}{\partial x_i} + e \frac{\partial A_i}{\partial t} = -e E_i \]
\[ F_i = m a_i = -e E_i + \frac{e}{c} \left[ -\vec{v} \cdot \frac{\partial \vec{A}}{\partial x_i} + \left( \vec{v} \cdot \vec{\nabla} \right) A_i \right]. \]

Let’s work with the other two terms to see if they give us the rest of the Lorentz Force.
\[ \frac{e}{c} \left( \vec{v} \cdot \vec{\nabla} \right) A_i - \vec{v} \cdot \frac{\partial \vec{A}}{\partial x_i} = \frac{e}{c} \left[ v_j \frac{\partial}{\partial x_j} A_i - v_j \frac{\partial A_j}{\partial x_i} \right] = \frac{e}{c} v_j \frac{\partial A_i}{\partial x_j} - \frac{\partial A_i}{\partial x_i} \]

We need only prove that
\[ \left( \vec{v} \times \vec{B} \right)_i = v_j \left( \frac{\partial A_j}{\partial x_i} - \frac{\partial A_i}{\partial x_j} \right). \]

To prove this, we will expand the expression using the totally antisymmetric tensor.
\[ \left( \vec{v} \times \vec{B} \right)_i = \left( \vec{v} \times \left( \vec{\nabla} \times \vec{A} \right) \right)_i = v_j \left( \frac{\partial A_n}{\partial x_m} \varepsilon_{mnk} \right) \varepsilon_{jki} = v_j \frac{\partial A_n}{\partial x_m} \left( \varepsilon_{mnk} \varepsilon_{jki} \right) \]
\[ = -v_j \frac{\partial A_n}{\partial x_m} \left( \varepsilon_{mnk} \varepsilon_{jik} \right) = -v_j \frac{\partial A_n}{\partial x_m} \left( \delta_{nj} \delta_{mi} - \delta_{ni} \delta_{mj} \right) = +v_j \left( \frac{\partial A_j}{\partial x_i} - \frac{\partial A_i}{\partial x_j} \right). \]

Q.E.D.

So we have
\[ F_i = -e E_i - \frac{e}{c} \left( \vec{v} \times \vec{B} \right)_i \]

which is the Lorentz force law. So this is the right Hamiltonian for an electron in an electromagnetic field. We now need to quantize it.

18.5.2 The Hamiltonian in terms of B

Start with the Hamiltonian
\[ H = \frac{1}{2\mu} \left( \frac{\hbar}{i} \vec{v} \right)^2 - e \phi \]

Now write the Schrödinger equations.
\[ \frac{1}{2\mu} \left( \frac{\hbar}{i} \vec{\nabla} + \frac{e}{c} \vec{A} \right)^2 \psi = \left( E + e \phi \right) \psi \]
\[ -\hbar^2 \nabla^2 \psi - \frac{i e \hbar}{2\mu c} \vec{\nabla} \cdot \left( \vec{A} \psi \right) - \frac{i e \hbar}{2\mu c} \vec{\nabla} \cdot \vec{\nabla} \psi + \frac{e^2}{2mc^2} \vec{A}^2 \psi = \left( E + e \phi \right) \psi \]
\[ -\hbar^2 \nabla^2 \psi - \frac{i e \hbar}{2\mu c} \left( \vec{\nabla} \cdot \vec{A} \right) \psi - \frac{i e \hbar}{\mu c} \vec{\nabla} \cdot \vec{\nabla} \psi + \frac{e^2}{2mc^2} \vec{A}^2 \psi = \left( E + e \phi \right) \psi \]
The second term vanishes in the Coulomb gauge i.e., \( \vec{\nabla} \cdot \vec{A} = 0 \), so

\[
-\frac{\hbar^2}{2\mu} \nabla^2 \psi - \frac{ie\hbar}{2\mu c} \vec{A} \cdot \vec{\nabla} \psi + \frac{e^2}{2mc^2} \vec{A}^2 \psi = (E + e\phi) \psi
\]

Now for constant \( B_z \), we choose the vector potential

\[
\vec{A} = -\frac{1}{2} \vec{r} \times \vec{B}
\]

since

\[
\left( \vec{\nabla} \times \vec{A} \right)_k = \frac{\partial}{\partial x_i} A_j \varepsilon_{ijk} = -\frac{1}{2} \frac{\partial}{\partial x_i} (x_m B_n \varepsilon_{mnj}) \varepsilon_{ijk} = -\frac{1}{2} \delta_{im} B_n \varepsilon_{mnj} \varepsilon_{ijk} = \frac{1}{2} \frac{\partial}{\partial x_i} \left( \sum_j \varepsilon_{ijn} \varepsilon_{ijk} \right) = \frac{1}{2} \frac{\partial}{\partial x_i} \left( \sum_j \varepsilon_{ij}^2 \right) = B_k
\]

it gives the right field and satisfies the Coulomb gauge condition.

Substituting back, we obtain

\[
-\frac{\hbar^2}{2\mu} \nabla^2 \psi + \frac{ie\hbar}{2\mu c} \vec{r} \times \vec{B} \cdot \vec{\nabla} \psi + \frac{e^2}{8mc^2} \left( \vec{r} \times \vec{B} \right)^2 \psi = (E + e\phi) \psi
\]

Now let’s work on the vector arithmetic.

\[
\left( \vec{r} \times \vec{B} \cdot \vec{\nabla} \psi \right) = r_i B_j \varepsilon_{ijk} \frac{\partial \psi}{\partial x_k} = B_j \left( \vec{r} \cdot \nabla \varepsilon_{ijk} \right) = -B_j \cdot \vec{r} \times \vec{\nabla} \psi = -\frac{i}{\hbar} \vec{B} \cdot \vec{\nabla} \psi
\]

\[
\left( \vec{r} \times \vec{B} \right)^2 = r_i B_j \varepsilon_{ijk} r_m B_n \varepsilon_{mnk} = (r_i B_j r_i B_j - r_i B_j r_j B_k) (1 - \delta_{ij}) = r^2 B^2 - \left( \vec{r} \cdot \vec{B} \right)^2 - 0
\]

So, plugging these two equations in, we get

\[
-\frac{\hbar^2}{2\mu} \nabla^2 \psi + \frac{e}{2\mu c} \vec{B} \cdot \vec{\nabla} \psi + \frac{e^2}{8mc^2} \left( r^2 B^2 - \left( \vec{r} \cdot \vec{B} \right)^2 \right) \psi = (E + e\phi) \psi.
\]

We see that there are two new terms due to the magnetic field. The first one is the magnetic moment term we have already used and the second will be negligible in atoms.

18.5.3 The Size of the B field Terms in Atoms

In the equation

\[
-\frac{\hbar^2}{2\mu} \nabla^2 \psi + \frac{e}{2\mu c} \vec{B} \cdot \vec{\nabla} \psi + \frac{e^2}{8mc^2} \left[ r^2 B^2 - \left( \vec{r} \cdot \vec{B} \right)^2 \right] \psi = (E + e\phi) \psi.
\]
the second term divided by \((e^2/a_0)\)

\[
\frac{e}{2\mu_c} \cdot \hat{B} \cdot \hat{L} / (e^2/a_0) = \frac{e}{2\mu_c} B(m\hbar) / (e^2/a_0) = m\frac{\alpha e B a_0}{2} / (e^2/a_0) = m\frac{\alpha a_0^2 B}{2e} = mB \frac{(0.5 \times 10^{-8} \text{ cm})^2}{(2)(137)(4.8 \times 10^{-10})} = mB \frac{5 \times 10^9}{10^{10}} \text{ gauss}
\]

\[
\left( \alpha = \frac{e^2}{\hbar c} \quad a_0 = \frac{\hbar}{\alpha mc} \right)
\]

Divide the second term by the third:

\[
\frac{B^2 a_0^2 \frac{\hbar^2}{2m_e c^2}}{2\mu_c B\hbar} = \alpha \frac{a_0^2}{4e} B = \frac{(0.5 \times 10^{-8})^2}{(4)(137)(4.8 \times 10^{-10})} = \frac{B}{10^{10}} \text{ gauss}
\]

18.5.4 **Energy States of Electrons in a Plasma I**

\[
- \frac{\hbar^2}{2m_e} \nabla^2 \psi + \frac{eB}{2m_e c^2} L_z \psi + \frac{e^2 B^2}{8m_e c^2} (x^2 + y^2) \psi = E \psi
\]

For uniform \(\vec{B}\) field, cylindrical symmetry \(\Rightarrow\) apply **cylindrical coordinates** \(\rho, \phi, z\). Then

\[
\nabla^2 = \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2}
\]

From the symmetry of the problem, we can guess (and verify) that \([H, p_z] = [H, L_z] = 0\). These variables will be constants of the motion and we therefore choose

\[
\psi(\vec{r}) = u_{mk}(\rho) e^{im\phi} e^{ikz}. \\
L_z \psi = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \psi = m\hbar \psi \\
p_z \psi = \frac{\hbar}{i} \frac{\partial}{\partial z} \psi = \hbar k \psi \\
\nabla^2 \psi = -k^2 \psi - \frac{m^2}{\rho^2} \psi + \frac{\partial^2 u}{\partial \rho^2} e^{im\phi} e^{ikz} + \frac{1}{\rho} \frac{\partial u}{\partial \rho} e^{im\phi} e^{ikz}
\]

\[
\frac{d^2 u}{d\rho^2} + \frac{1}{\rho} \frac{du}{d\rho} - \frac{m^2}{\rho^2} u - \frac{e^2 B^2}{4\hbar^2 c^2} \rho^2 u + \left( \frac{2m_e E}{\hbar^2} - \frac{eBm}{\hbar c} - k^2 \right) u = 0
\]

Let \(x = \sqrt{\frac{eB}{2\hbar c}} \rho\) (dummy variable, not the coordinate) and \(\lambda = \frac{4m_e c^2}{eB^2} \left( E - \frac{e^2 B^2}{2m_e c^2} \right) - 2m\). Then

\[
\frac{d^2 u}{dx^2} + \frac{1}{x} \frac{du}{dx} - \frac{m^2}{x^2} u - x^2 u + \lambda = 0
\]

In the limit \(x \to \infty\),

\[
\frac{d^2 u}{dx^2} - x^2 u = 0 \quad \Rightarrow \quad u \sim e^{-x^2/2}
while in the other limit \( x \to 0 \),
\[
\frac{d^2 u}{dx^2} + \frac{1}{x} \frac{du}{dx} - \frac{m^2}{x^2} u = 0
\]

Try a solution of the form \( x^s \). Then
\[
s(s - 1) x^{s-2} + sx^{s-2} - m^2 x^{s-2} = 0 \quad \Rightarrow \quad s^2 = m^2
\]

A well behaved function \( \Rightarrow s \geq 0 \Rightarrow s = |m| \)

Plugging this in, we have
\[
u(x) = xe^{-x^2/2} G(x)
\]

We can turn this into the hydrogen equation for
\[
y = x^2
\]

and hence
\[
dy = 2x \, dx \\
\frac{d}{dy} = \frac{1}{2x} \frac{d}{dx}
\]

Transforming the equation we get
\[
\frac{d^2 G}{dy^2} + \left( \frac{|m| + 1}{y} - 1 \right) \frac{dG}{dy} + \frac{\lambda - 2 - 2|m|}{4y} G = 0
\]

Compare this to the equation we had for hydrogen
\[
\frac{d^2 H}{dp^2} + \left( \frac{2\ell + 2}{\rho} - 1 \right) \frac{dH}{dp} + \frac{\lambda - 1 - \ell}{\rho} H = 0
\]

with \( \lambda = n_r + \ell + 1 \). The equations are the same if we set our \( \frac{\lambda}{4} = n_r + \frac{1+|m|}{2} \) where \( n_r = 0, 1, 2, \ldots \)

Recall that our \( \lambda = \frac{4mc^2}{\epsilon B h} \left( E - \frac{\hbar^2 \ell^2}{2m} \right) = 2m \). This gives us the energy eigenvalues
\[
\Rightarrow \quad E - \frac{\hbar^2 \ell^2}{2m_c} = \frac{\epsilon B h}{m_c} \left( n_r + \frac{1 + |m| + m}{2} \right).
\]

As in Hydrogen, the eigenfunctions are
\[
G(y) = L_n^{|m|}(y).
\]

We can localize electrons in classical orbits for large \( E \) and \( n_r \approx 0 \). This is the classical limit.
\[
n_r = 0 \quad \Rightarrow \quad L_0 = \text{const} \quad \Rightarrow \quad |\psi|^2 \sim e^{-x^2 / 2|m|}
\]

Max when
\[
\frac{d|\psi|^2}{dx} = 0 = \left( -2xe^{-x^2 / 2|m|} + 2|m|e^{-x^2 / 2|m|} - 1 \right)
\]
\[
|m| = x^2 \quad \Rightarrow \quad \rho = \left( \frac{2e}{\epsilon B \hbar m} \right)^{1/2}
\]
Now let’s put in some numbers: Let \( B \approx 20 \text{ kGauss} = 2 \times 10^4 \text{ Gauss}. \) Then

\[
\rho = \sqrt{\frac{2 \left( 3 \times 10^{10} \text{ cm} \right) \left( 1.05 \times 10^{-27} \text{ erg sec} \right)}{(4.8 \times 10^{-10} \text{ esu}) (2 \times 10^4 \text{ g})} m \approx 2.5 \times 10^{-6} \sqrt{m \text{ cm}}
\]

This can be compared to the purely classical calculation for an electron with angular momentum \( m\hbar \) which gives \( \rho = \sqrt{\frac{m^2 \hbar^2}{B r}} \). This simple calculation neglects to count the angular momentum stored in the field.

18.5.5 Energy States of Electrons in a Plasma II

We are going to solve the same plasma in a constant \( B \) field in a different gauge. If \( \vec{A} = (0, Bx, 0) \), then

\[
\vec{B} = \vec{\nabla} \times \vec{A} = \frac{\partial A_y \hat{z}}{\partial x} = B\hat{z}.
\]

This \( \vec{A} \) gives us the same \( B \) field. We can then compute \( H \) for a constant \( B \) field in the \( z \) direction.

\[
H = \frac{1}{2m_e} \left( \vec{p} + \frac{eA}{c} \right)^2 = \frac{1}{2m_e} \left( p_x^2 + \left( p_y + \frac{eB}{c} x \right)^2 + p_z^2 \right)
\]

\[
= \frac{1}{2m_e} \left( p_x^2 + p_y^2 + \frac{2eB}{c} x p_y + \left( \frac{eB}{c} \right)^2 x^2 + p_z^2 \right)
\]

With this version of the same problem, we have

\[
[H, p_y] = [H, p_z] = 0.
\]

We can treat \( p_z \) and \( p_y \) as constants of the motion and solve the problem in Cartesian coordinates! The terms in \( x \) and \( p_x \) are actually a perfect square.

\[
\psi = v(x) e^{ik_y y} e^{ik_z z}
\]

\[
\frac{1}{2m_e} \left( -\hbar^2 \frac{d^2}{dx^2} + \left( \frac{eB}{c} \right)^2 \left( x + \frac{\hbar k_y}{eB} \right)^2 \right) v(x) = \left( E - \frac{\hbar^2 k_z^2}{2m_e} \right) v(x)
\]

\[
-\hbar^2 \frac{d^2}{dx^2} + \left( \frac{1}{2m_e} \left( \frac{eB}{m_e c} \right)^2 \left( x + \frac{\hbar k_y}{eB} \right)^2 \right) v(x) = \left( E - \frac{\hbar^2 k_z^2}{2m_e} \right) v(x)
\]

This is the same as the 1D harmonic oscillator equation with \( \omega = \frac{eB}{m_e c} \) and \( x_0 = -\frac{\hbar k_y}{eB} \).

\[
E = \left( n + \frac{1}{2} \right) \hbar \omega = \frac{\hbar eB}{m_e c} \left( n + \frac{1}{2} \right) + \frac{\hbar^2 k_z^2}{2m_e}
\]

So we get the same energies with a much simpler calculation. The resulting states are somewhat strange and are not analogous to the classical solutions. (Note that an electron could be circulating about any field line so there are many possible states, just in case you are worrying about the choice of \( k_y \) and \( x_0 \) and counting states.)
18.5.6 A Hamiltonian Invariant Under Wavefunction Phase (or Gauge) Transformations

We want to investigate what it takes for the Hamiltonian to be invariant under a local phase transformation of the wave function.

$$\psi(\vec{r}, t) \rightarrow e^{i\lambda(\vec{r}, t)} \psi(\vec{r}, t)$$

That is, we can change the phase by a different amount at each point in spacetime and the physics will remain unchanged. We know that the absolute square of the wavefunction is the same. The Schrödinger must also be unchanged.

$$\left( \frac{\hbar}{i} \nabla + \frac{e}{c} \vec{A} + \frac{e}{c} \Delta \vec{A} \right)^2 \psi = (E + e\phi)\psi$$

So let’s postulate the following transformation then see what we need to keep the equation invariant.

$$\psi(\vec{r}, t) \rightarrow e^{i\lambda(\vec{r}, t)} \psi(\vec{r}, t)$$

$$\vec{A} \rightarrow \vec{A} + \Delta \vec{A}$$

$$\phi \rightarrow \phi + \Delta \phi$$

We now need to apply this transformation to the Schrödinger equation.

$$\left( \frac{\hbar}{i} \nabla + \frac{e}{c} \vec{A} + \frac{e}{c} \Delta \vec{A} \right)^2 e^{i\lambda(\vec{r}, t)} \psi = \left( i\hbar \frac{\partial}{\partial t} + e\phi + e\Delta \phi - \hbar \frac{\partial \lambda(\vec{r}, t)}{\partial t} \right) e^{i\lambda(\vec{r}, t)} \psi$$

Now we will apply the differential operator to the exponential to identify the new terms. Note that \( \nabla e^{i\lambda(\vec{r}, t)} = e^{i\lambda(\vec{r}, t)} \nabla \lambda(\vec{r}, t) \).

$$e^{i\lambda(\vec{r}, t)} \left( \frac{\hbar}{i} \nabla + \frac{e}{c} \vec{A} + \frac{e}{c} \Delta \vec{A} + \hbar \nabla \lambda(\vec{r}, t) \right)^2 \psi = e^{i\lambda(\vec{r}, t)} \left( i\hbar \frac{\partial}{\partial t} + e\phi + e\Delta \phi - \hbar \frac{\partial \lambda(\vec{r}, t)}{\partial t} \right) \psi$$

It’s easy to see that we can leave this equation invariant with the following choices.

$$\Delta \vec{A} = -\frac{\hbar c}{e} \nabla \lambda(\vec{r}, t)$$

$$\Delta \phi = \frac{\hbar}{c} \frac{\partial \lambda(\vec{r}, t)}{\partial t}$$

We can argue that we need Electromagnetism to give us the local phase transformation symmetry for electrons. We now rewrite the gauge transformation in the more conventional way, the convention being set before quantum mechanics.

$$\psi(\vec{r}, t) \rightarrow e^{i\lambda(\vec{r}, t)} \psi(\vec{r}, t)$$

$$\vec{A} \rightarrow \vec{A} - \nabla f(\vec{r}, t)$$

$$\phi \rightarrow \phi + \frac{1}{c} \frac{\partial f(\vec{r}, t)}{\partial t}$$

$$f(\vec{r}, t) = \frac{\hbar c}{\lambda(\vec{r}, t)}.$$
18.5.7 Magnetic Flux Quantization from Gauge Symmetry

We’ve shown that we can compute the function $f(\vec{r})$ from the vector potential.

$$ f(\vec{r}) = \oint_{\vec{n}_0} d\vec{r} \cdot \vec{A} $$

A superconductor excludes the magnetic field so we have our field free region. If we take a ring of superconductor, as shown, we get a condition on the magnetic flux through the center.

Consider two different paths from $\vec{n}_0$ to $\vec{r}$.

$$ f_1(\vec{r}) - f_2(\vec{r}) = \oint_{\vec{r}_1} d\vec{r} \cdot \vec{A} = \int d\vec{S} \cdot \nabla \times \vec{A} = \int d\vec{S} \cdot \vec{B} = \Phi $$

The difference between the two calculations of $f$ is the flux.

Now $\phi$ is not a physical observable so the $f_1 - f_2$ does not have to be zero, but, $\psi$ does have to be single valued.

$$ \psi_1 = \psi_2 \Rightarrow e^{-i\phi_1} = e^{-i\phi_2} \Rightarrow e^{\phi_1} = e^{\phi_2} \Rightarrow \frac{\mathcal{E}}{\hbar c}(f_1 - f_2) = 2n\pi \Rightarrow \Phi = f_1 - f_2 = \frac{2n\pi \hbar c}{e} $$

The flux is quantized.

Magnetic flux is observed to be quantized in a region enclosed by a superconductor. However, the fundamental charge seen is $2e$. 

18.6 Homework Problems

1. Show that the Hamiltonian \( H = \frac{1}{2\mu}[\mathbf{p} + \frac{e}{c}\mathbf{A}(\mathbf{r}, t)]^2 - e\phi(\mathbf{r}, t) \) yields the Lorentz force law for an electron. Note that the fields must be evaluated at the position of the electron. This means that the total time derivative of \( \mathbf{A} \) must also account for the motion of the electron.

2. Calculate the wavelengths of the three Zeeman lines in the \( 3d \rightarrow 2p \) transition in Hydrogen atoms in a \( 10^4 \) gauss field.

3. Show that the probability flux for system described by the Hamiltonian

\[
H = \frac{1}{2\mu} \left| \mathbf{p} + \frac{e}{c} \mathbf{A} \right|^2
\]

is given by

\[
\mathbf{j} = \frac{\hbar}{2\mu} [\psi^* \nabla \psi - (\nabla \psi^*) \psi + \frac{2ie}{\hbar c} \mathbf{A} \psi^* \psi].
\]

Remember the flux satisfies the equations \( \frac{\partial \psi^* \psi}{\partial t} + \nabla \cdot \mathbf{j} = 0 \).

4. Consider the problem of a charged particle in an external magnetic field \( \mathbf{B} = (0, 0, B) \) with the gauge chosen so that \( \mathbf{A} = (-yB, 0, 0) \). What are the constants of the motion? Go as far as you can in solving the equations of motion and obtain the energy spectrum. Can you explain why the same problem in the gauges \( \mathbf{A} = (-yB/2, xB/2, 0) \) and \( \mathbf{A} = (0, xB, 0) \) can represent the same physical situation? Why do the solutions look so different?

5. Calculate the top left \( 4 \times 4 \) corner of the matrix representation of \( x^4 \) for the harmonic oscillator. Use the energy eigenstates as the basis states.

6. The Hamiltonian for an electron in a electromagnetic field can be written as \( H = \frac{1}{2m}[\mathbf{p} + \frac{e}{c}\mathbf{A}(\mathbf{r}, t)]^2 - e\phi(\mathbf{r}, t) + \frac{e^2}{2m} \mathbf{\sigma} \cdot \mathbf{B}(\mathbf{r}, t) \). Show that this can be written as the Pauli Hamiltonian

\[
H = \frac{1}{2m} \left( \mathbf{\sigma} \cdot [\mathbf{p} + \frac{e}{c}\mathbf{A}(\mathbf{r}, t)] \right)^2 - e\phi(\mathbf{r}, t).
\]

18.7 Sample Test Problems

1. A charged particle is in an external magnetic field. The vector potential is given by \( \mathbf{A} = (-yB, 0, 0) \). What are the constants of the motion? Prove that these are constants by evaluating their commutator with the Hamiltonian.

2. A charged particle is in an external magnetic field. The vector potential is given by \( \mathbf{A} = (0, xB, 0) \). What are the constants of the motion? Prove that these are constants by evaluating their commutator with the Hamiltonian.

3. Gauge symmetry was noticed in electromagnetism before the advent of Quantum Mechanics. What is the symmetry transformation for the wave function of an electron from which the gauge symmetry for EM can be derived?
19 Addition of Angular Momentum

Since total angular momentum is conserved in nature, we will find that eigenstates of the total angular momentum operator are usually energy eigenstates. The exceptions will be when we apply external Fields which break the rotational symmetry. We must therefore learn how to add different components of angular momentum together. One of our first uses of this will be to add the orbital angular momentum in Hydrogen to the spin angular momentum of the electron.

\[ \mathbf{\bar{J}} = \mathbf{\bar{L}} + \mathbf{\bar{S}} \]

Our results can be applied to the addition of all types of angular momentum.

This material is covered in Gasiorowicz Chapter 15, in Cohen-Tannoudji et al. Chapter X and very briefly in Griffiths Chapter 6.

19.1 Adding the Spins of Two Electrons

The coordinates of two particles commute with each other: \([p_{(1)} r, x_{(2)} j]\) = 0. They are independent variables except that the overall wave functions for identical particles must satisfy the (anti)symmetrization requirements. This will also be the case for the spin coordinates.

\[ [S_{(1)} r, S_{(2)} j] = 0 \]

We define the total spin operators

\[ \mathbf{\bar{S}} = \mathbf{\bar{S}}_{(1)} + \mathbf{\bar{S}}_{(2)} \].

It's easy to show (see section 19.8.1) the total spin operators obey the same commutation relations as individual spin operators

\[ [S_i, S_j] = i\hbar \epsilon_{ijk} S_k \]

This is a very important result since we derived everything about angular momentum from the commutators. The sum of angular momentum will be quantized in the same way as orbital angular momentum.

As with the combination of independent spatial coordinates, we can make product states to describe the spins of two particles. These products just mean, for example, the spin of particle 1 is up and the spin of particle 2 is down. There are four possible (product) spin states when we combine two spin 1/2 particles. These product states are eigenstates of total \( S_z \) but not necessarily of total \( S^2 \). The states and their \( S_z \) eigenvalues are given below.

<table>
<thead>
<tr>
<th>Product State</th>
<th>Total ( S_z ) eigenvalue</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi^+<em>{(1)} \chi^+</em>{(2)} )</td>
<td>( \hbar )</td>
</tr>
<tr>
<td>( \chi^-<em>{(1)} \chi^-</em>{(2)} )</td>
<td>0</td>
</tr>
<tr>
<td>( \chi^+<em>{(1)} \chi^-</em>{(2)} )</td>
<td>0</td>
</tr>
<tr>
<td>( \chi^-<em>{(1)} \chi^+</em>{(2)} )</td>
<td>( -\hbar )</td>
</tr>
<tr>
<td>( \chi^-<em>{(1)} \chi^-</em>{(2)} )</td>
<td>0</td>
</tr>
</tbody>
</table>
Verify the quoted eigenvalues by calculation using the operator $S_z = S^{(1)}_z + S^{(2)}_z$.

We expect to be able to form eigenstates of $S^2$ from linear combinations of these four states. From pure counting of the number of states for each $S_z$ eigenvalue, we can guess that we can make one $s = 1$ multiplet plus one $s = 0$ multiplet. The $s = 1$ multiplet has three component states, two of which are obvious from the list above. We can use the lowering operator to derive (see section 19.8.2) the other eigenstates of $S^2$.

$$\chi_{s=1,m=1} = \chi^{(1)}_+ \chi^{(2)}_+$$
$$\chi_{s=1,m=0} = \frac{1}{\sqrt{2}} (\chi^{(1)}_+ \chi^{(2)}_- + \chi^{(1)}_- \chi^{(2)}_+)$$
$$\chi_{s=1,m=-1} = \chi^{(1)}_- \chi^{(2)}_-$$
$$\chi_{s=0,m=0} = \frac{1}{\sqrt{2}} (\chi^{(1)}_+ \chi^{(2)}_- - \chi^{(1)}_- \chi^{(2)}_+)$$

As a necessary check, we operate on these states with $S^2$ and verify (see section 19.8.3) that they are indeed the correct eigenstates.

Note that by deciding to add the spins together, we could not change the nature of the electrons. They are still spin $\frac{1}{2}$ and hence, these are all still eigenstates of $S^{(1)}_z$ and $S^{(2)}_z$. However, some of the above states are not eigenstates of $S^{(1)}_z$ and $S^{(2)}_z$. This will prove to be a general feature of adding angular momenta. Our states of definite total angular momentum and $z$ component of total angular momentum will still also be eigenstates of the individual angular momenta squared.

### 19.2 Total Angular Momentum and The Spin Orbit Interaction

The spin-orbit interaction (between magnetic dipoles) will play a role in the fine structure of Hydrogen as well as in other problems. It is a good example of the need for states of total angular momentum. The additional term in the Hamiltonian is

$$H_{SO} = \frac{Ze^2}{2\mu^2 c^2} \frac{\vec{L} \cdot \vec{S}}{r^3}$$

If we define the total angular momentum $\vec{J}$ in the obvious way we can write $\vec{L} \cdot \vec{S}$ in terms of quantum numbers.

audio

$$\vec{J} = \vec{L} + \vec{S}$$
$$J^2 = L^2 + 2 \vec{L} \cdot \vec{S} + S^2$$
$$\vec{L} \cdot \vec{S} = \frac{1}{2} (J^2 - L^2 - S^2) \rightarrow \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1))$$
Since our eigenstates of $J^2$ and $J_z$ are also eigenstates of $L^2$ and $S^2$ (but not $L_z$ or $S_z$), these are ideal for computing the spin orbit interaction. In fact, they are going to be the true energy eigenstates, as rotational symmetry tells us they must.

19.3 Adding Spin $\frac{1}{2}$ to Integer Orbital Angular Momentum

Our goal is to add orbital angular momentum with quantum number $\ell$ to spin $\frac{1}{2}$. We can show in several ways that, for $\ell \neq 0$, that the total angular momentum quantum number has two possible values $j = \ell + \frac{1}{2}$ or $j = \ell - \frac{1}{2}$. For $\ell = 0$, only $j = \frac{1}{2}$ is allowed. First lets argue that this makes sense when we are adding two vectors. For example if we add a vector of length 3 to a vector of length 0.5, the resulting vector could take on a length between 2.5 and 3.5 For quantized angular momentum, we will only have the half integers allowed, rather than a continuous range. Also we know that the quantum numbers like $\ell$ are not exactly the length of the vector but are close. So these two values make sense physically.

We can also count states for each eigenvalue of $J_z$ as in the following examples.

* See Example 19.7.1: Counting states for $\ell = 3$ plus spin $\frac{1}{2}$. *
* See Example 19.7.2: Counting states for any $\ell$ plus spin $\frac{1}{2}$. *

As in the last section, we could start with the highest $J_z$ state, $Y_{\ell+}\chi_+$, and apply the lowering operator to find the rest of the multiplet with $j = \ell + \frac{1}{2}$. This works well for some specific $\ell$ but is hard to generalize.

We can work the problem in general. We know that each eigenstate of $J^2$ and $J_z$ will be a linear combination of the two product states with the right $m$.

$$\psi_{j\ell m \pm \frac{1}{2}} = a Y_{\ell m \chi_+} + b Y_{\ell(m+1)\chi_-}$$

The coefficients $a$ and $b$ must be determined (see section 19.8.4) by operating with $J^2$.

$$\psi_{(\ell+\frac{1}{2})m \pm \frac{1}{2}} = \sqrt{\frac{\ell + m + 1}{2\ell + 1}} Y_{\ell m \chi_+} + \sqrt{\frac{\ell - m}{2\ell + 1}} Y_{\ell(m+1)\chi_-}$$

$$\psi_{(\ell-\frac{1}{2})m \pm \frac{1}{2}} = \sqrt{\frac{\ell - m}{2\ell + 1}} Y_{\ell m \chi_+} - \sqrt{\frac{\ell + m + 1}{2\ell + 1}} Y_{\ell(m+1)\chi_-}$$

We have made a choice in how to write these equations: $m$ must be the same throughout. The negative $m$ states are symmetric with the positive ones. These equations will be applied when we calculate the fine structure of Hydrogen and when we study the anomalous Zeeman effect.

19.4 Spectroscopic Notation

A common way to name states in atomic physics is to use spectroscopic notation. It is essentially a standard way to write down the angular momentum quantum numbers of a state. The general form is $N^{2s+1}L_j$, where $N$ is the principal quantum number and will often be omitted, $s$ is the total spin quantum number ($(2s + 1)$ is the number of spin states), $L$ refers to the orbital angular momentum...
quantum number $\ell$ but is written as $S$, $P$, $D$, $F$, … for $\ell = 0, 1, 2, 3, \ldots$, and $j$ is the total angular momentum quantum number.

A quick example is the single electron states, as we find in Hydrogen. These are:

\[
1^2S_{\frac{1}{2}}, 2^2S_{\frac{1}{2}}, 2^2P_{\frac{1}{2}}, 3^2S_{\frac{1}{2}}, 3^2P_{\frac{1}{2}}, 3^2P_{\frac{3}{2}}, 3^2D_{\frac{5}{2}}, 3^2D_{\frac{3}{2}}, 4^2S_{\frac{1}{2}}, 4^2P_{\frac{1}{2}}, 4^2P_{\frac{3}{2}}, 4^2P_{\frac{5}{2}}, 4^2D_{\frac{5}{2}}, 4^2D_{\frac{3}{2}}, 4^2F_{\frac{7}{2}}, 4^2F_{\frac{5}{2}}, \ldots
\]

All of these have the pre-superscript 2 because they are all spin one-half. There are two $j$ values for each $\ell$.

For atoms with more than one electron, the total spin state has more possibilities and perhaps several ways to make a state with the same quantum numbers.

19.5 General Addition of Angular Momentum: The Clebsch-Gordan Series

We have already worked several examples of addition of angular momentum. Let’s work one more.

* See Example 19.7.3: Adding $\ell = 4$ to $\ell = 2$.*

The result, in agreement with our classical vector model, is multiplets with $j = 2, 3, 4, 5, 6$.

The vector model qualitatively explains the limits.

audio

In general, $j$ takes on every value between the maximum and minimum in integer steps.

\[
|\ell_1 - \ell_2| \leq j \leq \ell_1 + \ell_2
\]

The maximum and minimum lengths of the sum of the vectors makes sense physically. Quantum Mechanics tells up that the result is quantized and that, because of the uncertainty principle, the two vectors can never quite achieve the maximum allowed classically. Just like the z component of one vector can never be as great as the full vector length in QM.
We can check (see section 19.8.5) that the number of states agrees with the number of product states.

We have been expanding the states of definite total angular momentum $j$ in terms of the product states for several cases. The general expansion is called the Clebsch-Gordan series:

$$\psi_{jm} = \sum_{m_1, m_2} \langle \ell_1 m_1 \ell_2 m_2 | jm | \ell_1 \ell_2 \rangle Y_{\ell_1 m_1} Y_{\ell_2 m_2}$$

or in terms of the ket vectors

$$|jm\ell_1 \ell_2\rangle = \sum_{m_1, m_2} \langle \ell_1 m_1 \ell_2 m_2 | jm \ell_1 \ell_2 \rangle |\ell_1 m_1 \ell_2 m_2\rangle$$

The Clebsch-Gordan coefficients are tabulated. We have computed some of them here by using the lowering operator and some by making eigenstates of $\hat{J}^2$.

### 19.6 Interchange Symmetry for States with Identical Particles

If we are combining the angular momentum from two identical particles, like two electrons in an atom, we will be looking for the interchange symmetry of the angular momentum state. Let’s use the combination of two spin $\frac{1}{2}$ particles as an example. We know that we get total spin states of $s = 1$ and $s = 0$. The $s = 1$ state is called a triplet because there are three states with different $m$ values. The $s = 0$ state is called a singlet. The triplet state is symmetric under interchange. The **highest total angular momentum state**, $s = s_1 + s_2$, **will always be symmetric under interchange**. We can see this by looking at the highest $m$ state, $m = s$. To get the maximum $m$, both spins have to have the maximum $z$ component. So the product state has just one term and it is symmetric under interchange, in this case,

$$\chi_{11} = \chi^{(1)}_+ \chi^{(2)}_+ .$$

When we lower this state with the (symmetric) lowering operator $S_- = S^{(1)}_- + S^{(2)}_-$, the result remains symmetric under interchange. To make the **next highest state**, with two terms, we must choose a state orthogonal to the symmetric state and this will always be **antisymmetric**.

In fact, for identical particles, the **symmetry of the angular momentum wave function will alternate**, beginning with a symmetric state for the maximum total angular momentum. For example, if we add two spin 2 states together, the resulting states are: $4_s$, $3_A$, $2_s$, $1_A$ and $0_s$. In the language of group theory, when we take the **direct product of two representations of the the SU(2) group** we get:

$$5 \otimes 5 = 9_s \oplus 7_A \oplus 5_s \oplus 3_A \oplus 1_s$$

where the numbers are the number of states in the multiplet.

* See Example 19.7.4: Two electrons in a P state. *

* See Example 19.7.5: The parity of the pion from $\pi d \to nn$. *

### 19.7 Examples

#### 19.7.1 Counting states for $\ell = 3$ Plus spin $\frac{1}{2}$

For $\ell = 3$ there are $2\ell + 1 = 7$ different eigenstates of $L_z$. There are two different eigenstates of $S_z$ for spin $\frac{1}{2}$. We can have any combination of these states, implying $2 \times 7 = 14$ possible product states like
We will argue based on adding vectors... that there will be two total angular momentum states that can be made up from the 14 product states, \( j = \ell \pm \frac{1}{2} \), in this case \( j = \frac{5}{2} \) and \( j = \frac{7}{2} \). Each of these has \( 2j + 1 \) states, that is 6 and 8 states respectively. Since \( 6 + 8 = 14 \) this gives us the right number of states.

19.7.2 Counting states for Arbitrary \( \ell \) Plus spin \( \frac{1}{2} \)

For angular momentum quantum number \( \ell \), there are \( (2\ell + 1) \) different \( m \) states, while for spin we have 2 states \( \chi_{\pm} \). Hence the composite system has \( 2(2\ell + 1) \) states total.

Max \( j_z = \ell + \frac{1}{2} \) so we have a state with \( j = \ell + \frac{1}{2} \). This makes up \( (2j + 1) = (2\ell + 2) \) states, leaving

\[
(4\ell + 2) - (2\ell + 2) = 2\ell = 2 \left( \ell - \frac{1}{2} \right) + 1
\]

Thus we have a state with \( j = \ell - \frac{1}{2} \) and that's all.

19.7.3 Adding \( \ell = 4 \) to \( \ell = 2 \)

As an example, we count the states for each value of total \( m \) (z component quantum number) if we add \( \ell_1 = 4 \) to \( \ell_2 = 2 \).

<table>
<thead>
<tr>
<th>Total ( m )</th>
<th>((m_1, m_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>((4,2))</td>
</tr>
<tr>
<td>5</td>
<td>((3,2)) , ((4,1))</td>
</tr>
<tr>
<td>4</td>
<td>((2,2)) , ((3,1)) , ((4,0))</td>
</tr>
<tr>
<td>3</td>
<td>((1,2)) , ((2,1)) , ((3,0)) , ((4, -1))</td>
</tr>
<tr>
<td>2</td>
<td>((0,2)) , ((1,1)) , ((2,0)) , ((3, -1)) , ((4, -2))</td>
</tr>
<tr>
<td>1</td>
<td>((-1,2)) , ((0,1)) , ((1,0)) , ((2, -1)) , ((3, -2))</td>
</tr>
<tr>
<td>0</td>
<td>((-2,2)) , ((-1,1)) , ((0,0)) , ((1, -1)) , ((2, -2))</td>
</tr>
<tr>
<td>-1</td>
<td>((-1,-2)) , ((-0,-1)) , ((-1,0)) , ((-2,1)) , ((-3,2))</td>
</tr>
<tr>
<td>-2</td>
<td>((-0,-2)) , ((-1,-1)) , ((-2,0)) , ((-3,1)) , ((-4,2))</td>
</tr>
<tr>
<td>-3</td>
<td>((-1,-3)) , ((-2,-1)) , ((-3,0)) , ((-4,1))</td>
</tr>
<tr>
<td>-4</td>
<td>((-2,-4)) , ((-3,-1)) , ((-4,0))</td>
</tr>
<tr>
<td>-5</td>
<td>((-3,-5)) , ((-4,-1))</td>
</tr>
<tr>
<td>-6</td>
<td>((-4,-6))</td>
</tr>
</tbody>
</table>

Since the highest \( m \) value is 6, we expect to have a \( j = 6 \) state which uses up one state for each \( m \) value from -6 to +6. Now the highest \( m \) value left is 5, so a \( j = 5 \) states uses up a state at each \( m \) value between -5 and +5. Similarly we find a \( j = 4 \), \( j = 3 \), and \( j = 2 \) state. This uses up all the states, and uses up the states at each value of \( m \). So we find in this case,

\[
|\ell_1 - \ell_2| \leq j \leq |\ell_1 + \ell_2|
\]

and that \( j \) takes on every integer value between the limits. This makes sense in the vector model.
19.7.4 Two electrons in an atomic P state

If we have two atomic electrons in a P state with no external fields applied, states of definite total angular momentum will be the energy eigenstates. We will learn later that closed shells in atoms (or nuclei) have a total angular momentum of zero, allowing us to treat only the valence electrons. Examples of atoms like this would be Carbon, Silicon, and Germanium.

Our two electrons each have $ell = 1$ (P state) and $s = \frac{1}{2}$ (electrons). We need to add four angular momenta together to get the total:

$$\vec{J} = \vec{L}_1 + \vec{L}_2 + \vec{S}_1 + \vec{S}_2$$

We will find it useful to do this addition in two steps. For low $Z$ atoms, it is most useful to add $\vec{L}_1 + \vec{L}_2 = \vec{L}$ and $\vec{S}_1 + \vec{S}_2 = \vec{S}$ then to add these results $\vec{L} + \vec{S} = \vec{J}$.

Since the electrons are identical particles and they are in the same radial state, the angular momentum part of the wavefunction must be antisymmetric under interchange. This will limit the allowed states. So let’s do the spinor arithmetic:

$$|\ell_1 - \ell_2| \leq \ell \leq \ell_1 + \ell_2$$

$$\ell = 0, 1, 2$$

$$s = 0, 1$$

These states have a definite symmetry under interchange. Before going on to make the total angular momentum states, let’s note the symmetry of each of the above states. The maximum allowed state will always need to be symmetric in order to achieve the maximum. The symmetry will alternate as we go down in the quantum number. So, for example, the $\ell = 2$ and $\ell = 0$ states are symmetric, while the $\ell = 1$ state is antisymmetric. The $s = 1$ state is symmetric and the $s = 0$ state is antisymmetric. The overall symmetry of a state will be a product of these two symmetries (since when we add $\ell$ and $s$ to give $j$ we are not adding identical things anymore). The overall state must be antisymmetric so we can use:

$$\ell = 1 \quad s = 1 \quad j = 0, 1, 2 \quad 3P_0, 3P_1, 3P_2$$

$$\ell = 2 \quad s = 0 \quad j = 2 \quad 1D_2$$

$$\ell = 0 \quad s = 0 \quad j = 0 \quad 1S_0$$

Each atomic state will have the angular momentum quantum numbers

$$\ell_1, \ell_2, s_1, s_2, \ell, s, j, m.$$ 

Normally we will not bother to include that the spins are one half since that’s always true for electrons. We will (and must) keep track of the intermediate $\ell$ and $s$ quantum numbers. As can be seen above, we need them to identify the states.

In the atomic physics section, we will even deal with more than two electrons outside a closed shell.

19.7.5 The parity of the pion from $\pi d \rightarrow mn$.
We can determine the internal parity of the pion by studying pion capture by a deuteron, \( \pi + d \rightarrow n + n \). The pion is known to have spin 0, the deuteron spin 1, and the neutron spin \( \frac{1}{2} \). The internal parity of the deuteron is +1. The pion is captured by the deuteron from a 15 states, implying \( \ell = 0 \) in the initial state. So the total angular momentum quantum number of the initial state is \( j = 1 \).

So the parity of the initial state is

\[ (-1)^\ell \sigma_i \sigma_d = (-1)^0 \sigma_i \sigma_d = \sigma_i \]

The parity of the final state is

\[ \sigma_i \sigma_n (-1)^\ell = (-1)^\ell \]

Therefore,

\[ \sigma_i = (-1)^\ell. \]

Because the neutrons are identical fermions, the allowed states of two neutrons are \( ^1S_0, \ ^3P_{0,1,2}, \ ^1D_2, \ ^3F_{2,3,4,5} \). The only state with \( j = 1 \) is the \( ^3P_1 \) state, so \( \ell = 1 \)

\[ \Rightarrow \sigma_i = -1. \]

### 19.8 Derivations and Computations

#### 19.8.1 Commutators of Total Spin Operators

\[
\hat{S} = \hat{S}_1 + \hat{S}_2
\]

\[
[S_i, S_j] = [S_i^{(1)}, S_j^{(1)}, S_i^{(2)}, S_j^{(2)}]
\]

\[
= [S_i^{(1)}, S_j^{(1)}] + [S_i^{(2)}, S_j^{(2)}] + [S_i^{(1)}, S_j^{(1)}] + [S_i^{(2)}, S_j^{(2)}]
\]

\[
= i\hbar \varepsilon_{ijk} S_k^{(1)} + 0 + 0 + i\hbar \varepsilon_{ijk} S_k^{(2)} = i\hbar \varepsilon_{ijk} S_k
\]

Q.E.D.

#### 19.8.2 Using the Lowering Operator to Find Total Spin States

The total spin lowering operator is

\[ S^- = S_1^- + S_2^- \]

First let's remind ourselves of what the individual lowering operators do.

\[ S_1^{(1)} \chi_+^{(1)} = \hbar \sqrt{\frac{1}{2} \left( \frac{3}{2} \right) - \left( \frac{1}{2} \right) \left( \frac{-1}{2} \right)} \chi_-^{(1)} = \hbar \chi_-^{(1)} \]

Now we want to identify \( \chi_{11} = \chi_+^{(1)} \chi_+^{(2)} \). Let's operate on this equation with \( S_- \). First the RHS gives

\[ S_- \chi_+^{(1)} \chi_+^{(2)} = \left( S_- \chi_+^{(1)} \right) \chi_+^{(2)} + \chi_+^{(1)} \left( S_- \chi_+^{(2)} \right) = \hbar \left( \chi_-^{(1)} \chi_+^{(2)} + \chi_+^{(1)} \chi_-^{(2)} \right). \]
Operating on the LHS gives
\[ S_- \chi_{11} = \hbar \sqrt{(1)(2) - (0)(0)} \chi_{10} = \sqrt{2} \hbar \chi_{10} \]
So equating the two we have
\[ \sqrt{2} \hbar \chi_{10} = \hbar \left( \chi_-^{(1)} \chi_+^{(2)} + \chi_+^{(1)} \chi_-^{(2)} \right) \]
\[ \chi_{10} = \frac{1}{\sqrt{2}} \left( \chi_-^{(1)} \chi_+^{(2)} + \chi_+^{(1)} \chi_-^{(2)} \right) \]
Now we can lower this state. Lowering the LHS, we get
\[ S_- \chi_{10} = \hbar \sqrt{(1)(2) - (0)(-1)} \chi_{10} = \sqrt{2} \hbar \chi_{11} \]
Lowering the RHS, gives
\[ S_- \frac{1}{\sqrt{2}} \left( \chi_-^{(1)} \chi_+^{(2)} + \chi_+^{(1)} \chi_-^{(2)} \right) = \hbar \frac{1}{\sqrt{2}} \left( \chi_-^{(1)} \chi_-^{(2)} + \chi_-^{(1)} \chi_-^{(2)} \right) = \sqrt{2} \hbar \chi_-^{(1)} \chi_-^{(2)} \]
\[ \Rightarrow \chi_{11} = \chi_-^{(1)} \chi_-^{(2)} \]
Therefore we have found 3 s=1 states that work together. They are all symmetric under interchange of the two particles.

There is one state left over which is orthogonal to the three states we identified. Orthogonal state:
\[ \chi_{00} = \frac{1}{\sqrt{2}} \left( \chi_+^{(1)} \chi_-^{(2)} - \chi_-^{(1)} \chi_+^{(2)} \right) \]
We have guessed that this is an s = 0 state since there is only one state and it has m=0. We could verify this by using the \( S^2 \) operator.

### 19.8.3 Applying the \( S^2 \) Operator to \( \chi_{1m} \) and \( \chi_{00} \).  

We wish to verify that the states we have d We will really compute this in the most brute force.

\[ S^2 = \left( \vec{S}_1 + \vec{S}_2 \right)^2 = S_1^2 + S_2^2 + 2 \vec{S}_1 \cdot \vec{S}_2 \]
\[ S^2 \chi_+^{(1)} \chi_+^{(2)} = s_1(s_1+1)\hbar^2 \chi_+^{(1)} \chi_+^{(2)} + s_2(s_2+1)\hbar^2 \chi_+^{(1)} \chi_+^{(2)} + 2 \vec{S}_1 \cdot \vec{S}_2 \chi_+^{(1)} \chi_+^{(2)} \]
\[ = \frac{3}{2} \hbar^2 \chi_+^{(1)} \chi_+^{(2)} + 2 \left( S_x^{(1)} S_x^{(2)} + S_y^{(1)} S_y^{(2)} + S_z^{(1)} S_z^{(2)} \right) \chi_+^{(1)} \chi_+^{(2)} \]

\[ S_x \chi_+ = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \chi_- \]
\[ S_y \chi_+ = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ i \end{pmatrix} = \frac{\hbar}{2} \chi_- \]
\[ S_x \chi_- = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \chi_+ \]
\[ S_y \chi_- = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} -i \\ 0 \end{pmatrix} = -i \frac{\hbar}{2} \chi_+ \]
\[ S^2 \chi_{+}^{(1)} \chi_{+}^{(2)} = \frac{3}{2} \hbar^2 \chi_{+}^{(1)} \chi_{+}^{(2)} + \frac{\hbar^2}{2} \left[ \begin{pmatrix} 0 \\ 1 \\ i \end{pmatrix} \begin{pmatrix} 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ i \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ i \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \right] \]
\[ = \frac{3}{2} \hbar^2 \chi_{+}^{(1)} \chi_{+}^{(2)} + \frac{\hbar^2}{2} \left[ \begin{pmatrix} 0 \\ 1 \\ i \end{pmatrix} \begin{pmatrix} 0 \\ 0 \end{pmatrix} - \begin{pmatrix} 0 \\ i \end{pmatrix} \begin{pmatrix} 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right] \]
\[ = \frac{3}{2} \hbar^2 \chi_{+}^{(1)} \chi_{+}^{(2)} + \frac{\hbar^2}{2} \chi_{+}^{(1)} \chi_{+}^{(2)} = 2 \hbar^2 \chi_{+}^{(1)} \chi_{+}^{(2)} \]

Note that \( s(s + 1) = 2 \), so that the \( 2\hbar \) is what we expected to get. This confirms that we have an \( s=1 \) state.

Now let us do the \( \chi_{00} \) state.

\[ S^2 \chi_{00} = \left( S_1^2 + S_2^2 + 2S_1 \cdot S_2 \right) \chi_{00} \]
\[ = \left( S_1^2 + S_2^2 + 2 \left( S_x^{(1)} S_x^{(2)} + S_y^{(1)} S_y^{(2)} + S_z^{(1)} S_z^{(2)} \right) \right) \chi_{00} \]
\[ = \left( S_1^2 + S_2^2 + 2S_z^{(2)} + 2 \left( S_x^{(1)} S_x^{(2)} + S_y^{(1)} S_y^{(2)} \right) \right) \chi_{00} \]
\[ = \left( \frac{3}{4} + 3 - \frac{1}{4} \right) \hbar^2 \chi_{00} + 2 \left( S_x^{(1)} S_x^{(2)} + S_y^{(1)} S_y^{(2)} \right) \chi_{00} \]
\[ = \hbar^2 \chi_{00} + 2 \left( S_x^{(1)} S_x^{(2)} + S_y^{(1)} S_y^{(2)} \right) \frac{1}{\sqrt{2}} \left( \chi_{+}^{(1)} \chi_{+}^{(2)} - \chi_{-}^{(1)} \chi_{-}^{(2)} \right) \]
\[ = \hbar^2 \chi_{00} + \frac{1}{2} \sqrt{2} \left( \chi_{-}^{(1)} \chi_{+}^{(2)} - \chi_{+}^{(1)} \chi_{-}^{(2)} + i(-i) \chi_{-}^{(1)} \chi_{+}^{(2)} - (-i)i \chi_{+}^{(1)} \chi_{-}^{(2)} \right) \]
\[ = \hbar^2 \left( \chi_{00} - \frac{1}{2\sqrt{2}} \left( \chi_{+}^{(1)} \chi_{+}^{(2)} - \chi_{-}^{(1)} \chi_{-}^{(2)} + \chi_{+}^{(1)} \chi_{-}^{(2)} - \chi_{-}^{(1)} \chi_{+}^{(2)} \right) \right) \]
\[ = \hbar^2 \left( 1 - 1 \right) \chi_{00} = 0 \hbar^2 \chi_{00} \]

19.8.4 Adding any \( \ell \) plus spin \( \frac{1}{2} \).

We wish to write the states of total angular momentum \( j \) in terms of the product states \( Y_{\ell m} \chi_{\pm} \). We will do this by operating with the \( J^2 \) operator and setting the coefficients so that we have eigenstates.

\[ J^2 \psi_{jmj} = j(j + 1) \hbar^2 \psi_{jmj} \]

We choose to write the the quantum number \( m_j \) as \( m + \frac{1}{2} \). This is really just the definition of the dummy variable \( m \). (Other choices would have been possible.)

The \( z \) component of the total angular momentum is just the sum of the \( z \) components from the orbital and the spin.

\[ m_j = m_l + m_s \]

There are only two product states which have the right \( m_j = m + \frac{1}{2} \). If the spin is up we need \( Y_{\ell m} \) and if the spin is down, \( Y_{\ell(m+1)} \):

\[ \psi_{j(m+\frac{1}{2})} = \alpha Y_{\ell m} \chi_{+} + \beta Y_{\ell(m+1)} \chi_{-} \]

audio
We will find the coefficients $\alpha$ and $\beta$ so that $\psi$ will be an eigenstate of

$$J^2 = (\vec{L} + \vec{S})^2 = L^2 + S^2 + 2LzS_z + L_+S_- + L_-S_+.$$

So operate on the right hand side with $J^2$.

$$J^2\psi_{j,m+\frac{1}{2}} = \alpha \hbar^2 \left[ \ell(\ell + 1)Y_{\ell m\chi_+} + \frac{3}{4}Y_{\ell m\chi_+} + 2m\frac{1}{2}Y_{\ell m\chi_+} \right. \\
+ \sqrt{\ell(\ell + 1) - m(m + 1)}\sqrt{Y_{\ell(m+1)\chi_-}} \\
+ \beta \hbar^2 \left[ \ell(\ell + 1)Y_{\ell,m+1\chi_-} + \frac{3}{4}Y_{\ell,m+1\chi_-} + 2(m + 1) \left( \frac{-1}{2} \right) Y_{\ell,m+1\chi_-} \right. \\
+ \sqrt{\ell(\ell + 1) - (m + 1)m}\sqrt{Y_{\ell m\chi_+}} \right]$$

And operate on the left hand side.

$$J^2\psi_{j,m+\frac{1}{2}} = j(j + 1)\hbar^2 \psi_{j,m+\frac{1}{2}} = j(j + 1)\hbar^2 \left( \alpha Y_{\ell m\chi_+} + \beta Y_{\ell(m+1)\chi_-} \right)$$

Since the two terms are orthogonal, we can equate the coefficients for each term, giving us two equations.

The $Y_{\ell m\chi_+}$ term gives

$$\alpha j(j + 1) = \alpha \left( \ell(\ell + 1) + \frac{3}{4} + m \right) + \beta \sqrt{\ell(\ell + 1) - m(m + 1)}.$$

The $Y_{\ell(m+1)\chi_-}$ term gives

$$\beta j(j + 1) = \beta \left( \ell(\ell + 1) + \frac{3}{4} - (m + 1) \right) + \alpha \sqrt{\ell(\ell + 1) - m(m + 1)}.$$

Collecting $\alpha$ terms on the LHS and $\beta$ terms on the RHS, we get two equations.

$$j(j + 1) - \ell(\ell + 1) - \frac{3}{4} - m = \sqrt{(\ell - m)(\ell + m + 1)}$$

$$\sqrt{(\ell - m)(\ell + m + 1)}\alpha = \left[ j(j + 1) - \ell(\ell + 1) - \frac{3}{4} + (m + 1) \right] \beta$$

Now we just cross multiply so we have one equation with a common factor of $\alpha\beta$.

$$(\ell - m)(\ell + m + 1) = \left[ j(j + 1) - \ell(\ell + 1) - \frac{3}{4} - m \right] \left[ j(j + 1) - \ell(\ell + 1) - \frac{3}{4} + (m + 1) \right]$$

While this equation looks like a mess to solve, if we notice the similarity between the LHS and RHS, we can solve it if

$$\ell = j(j + 1) - \ell(\ell + 1) - \frac{3}{4}.$$

If we look a little more carefully at the LHS, we can see that another solution (which just interchanges the two terms in parentheses) is to replace $\ell$ by $-\ell - 1$.

$$-\ell - 1 = j(j + 1) - \ell(\ell + 1) - \frac{3}{4}$$

These are now simple to solve

$$j(j + 1) = \ell(\ell + 1) + \frac{3}{4} \Rightarrow j = \ell + \frac{1}{2}.$$
\[ j(j+1) = \ell(\ell + 1) - \ell - 1 + \frac{3}{4} \Rightarrow j = \ell - \frac{1}{2} \]

So these are (again) the two possible values for \( j \). We now need to go ahead and find \( \alpha \) and \( \beta \).

Plugging \( j = \ell + \frac{1}{2} \) into our first equation,

\[
(\ell - m)\alpha = \sqrt{(\ell - m)(\ell + m + 1)}\beta
\]

we get the ratio between \( \beta \) and \( \alpha \). We will normalize the wave function by setting \( \alpha^2 + \beta^2 = 1 \). So let's get the squares.

\[
\beta^2 = \frac{(\ell - m)^2}{(\ell - m)(\ell + m + 1)} \alpha^2 = \frac{(\ell - m)}{(\ell + m + 1)} \alpha^2
\]

\[ \alpha^2 + \beta^2 = 1 \Rightarrow \frac{\ell + m + 1 + \ell - m}{\ell + m + 1} \alpha^2 = 1 \]

\[ \alpha = \sqrt{\frac{\ell + m + 1}{2\ell + 1}} \]

\[ \beta = \sqrt{\frac{\ell - m}{\ell + m + 1}} \sqrt{\frac{\ell + m + 1}{2\ell + 1}} = \sqrt{\frac{\ell - m}{2\ell + 1}} \]

So we have completed the calculation of the coefficients. We will make use of these in the hydrogen atom, particularly for the anomalous Zeeman effect.

Writing this in the notation of matrix elements or Clebsch-Gordan coefficients of the form,

\[ \langle jm_\ell \ell s|\ell m_\ell sm_s \rangle \]

we get,

\[
\langle (\ell + \frac{1}{2}) (m + \frac{1}{2}) \ell \frac{1}{2} \mid (m \frac{1}{2} 1 \frac{1}{2}) \rangle = \alpha = \sqrt{\frac{\ell + m + 1}{2\ell + 1}}
\]

\[
\langle (\ell + \frac{1}{2}) (m + \frac{1}{2}) \ell \frac{1}{2} \mid (m + 1 \frac{1}{2} 1 \frac{1}{2}) \rangle = \beta = \sqrt{\frac{\ell - m}{2\ell + 1}}
\]

\[
\langle (\ell + \frac{1}{2}) (m + \frac{1}{2}) \ell \frac{1}{2} \mid (m \frac{1}{2} 1 \frac{1}{2}) \rangle = 0
\]

\[
\langle (\ell + \frac{1}{2}) (m + \frac{1}{2}) \ell \frac{1}{2} \mid (m + 1 \frac{1}{2} 1 \frac{1}{2}) \rangle = 0
\]

Similarly

\[
\langle (\ell - \frac{1}{2}) (m + \frac{1}{2}) \ell \frac{1}{2} \mid (m \frac{1}{2} 1 \frac{1}{2}) \rangle = \sqrt{\frac{\ell - m}{2\ell + 1}}
\]

\[
\langle (\ell - \frac{1}{2}) (m + \frac{1}{2}) \ell \frac{1}{2} \mid (m + 1 \frac{1}{2} 1 \frac{1}{2}) \rangle = -\sqrt{\frac{\ell + m + 1}{2\ell + 1}}
\]
19.8.5 Counting the States for $|\ell_1 - \ell_2| \leq j \leq \ell_1 + \ell_2$.

If we add $\ell_1$ to $\ell_2$ there are $(2\ell_1 + 1)(2\ell_2 + 1)$ product states. Let's add up the number of states of total $\ell$. To keep things simple we assume we ordered things so $\ell_1 \geq \ell_2$.

$$
\sum_{\ell=\ell_1-\ell_2}^{\ell_1+\ell_2} (2\ell + 1) = \sum_{n=0}^{\ell_2} (2(\ell_1 - \ell_2 + n) + 1) = (2\ell_2 + 1)(2\ell_1 - 2\ell_2 + 1) + 2 \sum_{n=0}^{\ell_2} n
$$

$$
= (2\ell_2 + 1)(2\ell_1 - 2\ell_2 + 1) + (2\ell_2 + 1)(2\ell_2) = (2\ell_2 + 1)(2\ell_1 + 1)
$$

This is what we expect.

19.9 Homework Problems

1. Find the allowed total spin states of two spin 1 particles. Explicitly write out the 9 states which are eigenfunctions of $S^2$ and $S_z$.

2. The Hamiltonian of a spin system is given by $H = A + \frac{BS_1^2}{k^2} + \frac{C(S_1 + S_2)}{\hbar}$. Find the eigenvalues and eigenfunctions of the system of two particles (a) when both particles have spin $\frac{1}{2}$, (b) when one particle has spin $\frac{1}{2}$ and the other spin 1. What happens in (a) when the two particles are identical?

3. Consider a system of two spinless identical particles. Show that the orbital angular momentum of their relative motion can only be even. ($l = 0, 2, 4, ...$) Show by direct calculation that, for the triplet spin states of two spin $\frac{1}{2}$ particles, $\sigma_1 \cdot \sigma_2 \chi_{lm} = \chi_{lm}$ for all allowed $m$. Show that for the singlet state $\sigma_1 \cdot \sigma_2 \chi_{00} = -3\chi_{00}$.

4. A deuteron has spin 1. What are the possible spin and total angular momentum states of two deuterons. Include orbital angular momentum and assume the two particles are identical.

5. The state of an electron is given by $\psi = R(r)[\sqrt{\frac{1}{2}}Y_{10}(\theta, \phi)\chi_+ + \sqrt{\frac{2}{3}}Y_{11}(\theta, \phi)\chi_-]$. Find the possible values and the probabilities of the $z$ component of the electron's total angular momentum. Do the same for the total angular momentum squared. What is the probability density for finding an electron with spin up at $r, \theta, \phi$? What is it for spin down? What is the probability density independent of spin? (Do not leave your answer in terms of spherical harmonics.)

6. The $n = 2$ states of hydrogen have an 8-fold degeneracy due to the various $l$ and $m$ states allowed and the two spin states of the electron. The spin orbit interaction partially breaks the degeneracy by adding a term to the Hamiltonian $H_1 = \frac{A}{m_e^2}\mathbf{L}\cdot\mathbf{S}$. Use first order perturbation theory to find how the degeneracy is broken under the full Hamiltonian and write the approximate energy eigenstates in terms of $R_n$, $Y_{lm}$, and $\chi_{\pm}$.

7. The nucleus of a deuterium ($A=2$ isotope of H) atom is found to have spin 1. With a neutral atom, we have three angular momenta to add, the nuclear spin, the electron spin, and the orbital angular momentum. Define $\vec{J} = \vec{L} + \vec{S}$ in the usual way and $\vec{F} = \vec{J} + \vec{I}$ where $I$ denotes the nuclear spin operator. What are the possible quantum numbers $j$ and $I$ for an atom in the ground state? What are the possible quantum numbers for an atom in the 2p state?
19.10 Sample Test Problems

1. Two identical spin \( \frac{3}{2} \) particles are bound together into a state with total angular momentum \( l \). a) What are the allowed states of total spin for \( l = 0 \) and for \( l = 1 \)? b) List the allowed states using spectroscopic notation for \( l = 0 \) and 1. \((2l+1)J_j\)

2. A hydrogen atom is in the state \( \psi = R_{43}Y_{30} \chi_+ \). A combined measurement of of \( J^2 \) and of \( J_z \) is made. What are the possible outcomes of this combined measurement and what are the probabilities of each? You may ignore nuclear spin in this problem. We want to find the eigenstates of total \( S^2 \) and \( S_z \) for two spin 1 particles which have an \( S_1 \cdot S_2 \) interaction. \((S = S_1 + S_2)\)
   a) What are the allowed values of \( s \), the total spin quantum number.
   b) Write down the states of maximum \( m_s \) for the maximum \( s \) state. Use \(|sm_s\rangle\) notation and \(|s_1m_1\rangle s_2m_2\rangle\) for the product states.
   c) Now apply the lowering operator to get the other \( m_s \) states. You only need to go down to \( m_s = 0 \) because of the obvious symmetry.
   d) Now find the states with the other values of \( s \) in a similar way.

3. Two (identical) electrons are bound in a Helium atom. What are the allowed states \(|jll_1l_2\rangle\) if both electrons have principal quantum number \( n = 1 \)? What are the states if one has \( n = 1 \) and the other \( n = 2 \)?

4. A hydrogen atom is in an eigenstate \((\psi)\) of \( J^2 \), \( L^2 \), and of \( J_z \) such that \( J^2 \psi = \frac{15}{4} \hbar^2 \psi \), \( L^2 \psi = 6 \hbar^2 \psi \), \( J_z \psi = -\frac{1}{2} \hbar \psi \), and of course the electron's spin is \( \frac{1}{2} \). Determine the quantum numbers of this state as well as you can. If a measurement of \( L_z \) is made, what are the possible outcomes and what are the probabilities of each.

5. A hydrogen atom is in the state \( \psi = R_{02}Y_{21} \chi_- \). If a measurement of \( J^2 \) and of \( J_z \) is made, what are the possible outcomes of this measurement and what are the probabilities for each outcome? If a measurement of the energy of the state is made, what are the possible energies and the probabilities of each? You may ignore the nuclear spin in this problem.

6. Two identical spin 1 particles are bound together into a state with orbital angular momentum \( l \). What are the allowed states of total spin \( (s) \) for \( l = 2 \), for \( l = 1 \), and for \( l = 0 \)? List all the allowed states giving, for each state, the values of the quantum numbers for total angular momentum \((j)\), orbital angular momentum \((l)\) and spin angular momentum \((s)\) if \( l \) is 2 or less. You need not list all the different \( m_j \) values.

7. List all the allowed states of total spin and total z-component of spin for 2 identical spin 1 particles. What \( \ell \) values are allowed for each of these states? Explicitly write down the \((2s + 1)\) states for the highest \( s \) in terms of \( \chi_i^{(1)} \), \( \chi_i^{(2)} \), \( \chi_0 \), \( \chi_0 \), \( \chi_1 \), and \( \chi_1 \).

8. Two different spin \( \frac{1}{2} \) particles have a Hamiltonian given by \( H = E_0 + \frac{1}{2} \hbar \vec{S}_1 \cdot \vec{S}_2 + \frac{1}{2} B(S_{1z} + S_{2z}) \). Find the allowed energies and the energy eigenstates in terms of the four basis states \(|++\rangle\), \(|+-\rangle\), \(|-+\rangle\), and \(|- -\rangle\).

9. A spin 1 particle is in an \( \ell = 2 \) state. Find the allowed values of the total angular momentum quantum number, \( j \). Write out the \(|j,m_j\rangle\) states for the largest allowed \( j \) value, in terms of the \(|m_i,m_s\rangle\) basis. (That is give one state for every \( m_j \) value.) If the particle is prepared in the state \(|m_i = 0, m_s = 0\rangle\), what is the probability to measure \( J^2 = 2 \hbar^2 \)?

10. Two different spin \( \frac{1}{2} \) particles have a Hamiltonian given by \( H = E_0 + A S_1 \cdot S_2 + B(S_{1z} + S_{2z}) \). Find the allowed energies and the energy eigenstates in terms of the four product states \( \chi_+^{(1)} \chi_+^{(2)} \), \( \chi_-^{(1)} \chi_-^{(2)} \), \( \chi_+^{(1)} \chi_-^{(2)} \), and \( \chi_-^{(1)} \chi_+^{(2)} \).
Time Independent Perturbation Theory

Perturbation Theory is developed to deal with small corrections to problems which we have solved exactly, like the harmonic oscillator and the hydrogen atom. We will make a series expansion of the energies and eigenstates for cases where there is only a small correction to the exactly soluble problem.

First order perturbation theory will give quite accurate answers if the energy shifts calculated are (nonzero and) much smaller than the zeroth order energy differences between eigenstates. If the first order correction is zero, we will go to second order. If the eigenstates are (nearly) degenerate to zeroth order, we will diagonalize the full Hamiltonian using only the (nearly) degenerate states.

Cases in which the Hamiltonian is time dependent will be handled later.

This material is covered in Gasiorowicz Chapter 16, in Cohen-Tannoudji et al. Chapter XI, and in Griffiths Chapters 6 and 7.

20.1 The Perturbation Series

Assume that the energy eigenvalue problem for the Hamiltonian $H_0$ can be solved exactly

$$H_0 \psi_n = E_n^{(0)} \phi_n$$

but that the true Hamiltonian has a small additional term or perturbation $H_1$.

$$H = H_0 + H_1$$

The Schrödinger equation for the full problem is

$$(H_0 + H_1) \psi_n = E_n \psi_n$$

Presumably this full problem, like most problems, cannot be solved exactly. To solve it using a perturbation series, we will expand both our energy eigenvalues and eigenstates in powers of the small perturbation.

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + ...$$

$$\psi_n = N \left( \phi_n + \sum_{k \neq n} c_{nk} \phi_k \right)$$

$$c_{nk} = c_{nk}^{(1)} + c_{nk}^{(2)} + ...$$

where the superscript (0), (1), (2) are the zeroth, first, and second order terms in the series. $N$ is there to keep the wave function normalized but will not play an important role in our results.

By solving the Schrödinger equation at each order of the perturbation series, we compute the corrections to the energies and eigenfunctions. (see section 20.4.1)

$$E_n^{(1)} = \langle \phi_n | H_1 | \phi_n \rangle$$
\[ c_{nk}^{(1)} = \frac{\langle \phi_k | H_1 | \phi_n \rangle}{E_n^{(0)} - E_k^{(0)}} \]
\[ E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \phi_k | H_1 | \phi_n \rangle|^2}{E_n^{(0)} - E_k^{(0)}} \]

So the first order correction to the energy of the \( n^{th} \) eigenstate, \( E_n^{(1)} \), is just the expectation value of the perturbation in the unperturbed state. The first order admixture of \( \phi_k \) in \( \psi_n \), \( c_{nk}^{(1)} \), depends on a matrix element and the energy difference between states. The second order correction to the energy, \( E_n^{(2)} \), has a similar dependence. Note that the higher order corrections may not be small if states are nearby in energy.

The application of the first order perturbation equations is quite simple in principal. The actual calculation of the matrix elements depends greatly on the problem being solved.

* See Example 20.3.1: H.O. with anharmonic perturbation \((ax^2)\).*

Sometimes the first order correction to the energy is zero. Then we will need to use the second order term \( E_n^{(2)} \) to estimate the correction. This is true when we apply an electric field to a hydrogen atom.

* See Example 20.3.2: Hydrogen Atom in a E-field, the Stark Effect.*

We will exercise the use of perturbation theory in section 21 when we compute the fine structure, and other effects in Hydrogen.

### 20.2 Degenerate State Perturbation Theory

The perturbation expansion has a problem for states very close in energy. The energy difference in the denominators goes to zero and the corrections are no longer small. The series does not converge. We can very effectively solve this problem by treating all the (nearly) degenerate states like we did \( \phi_n \) in the regular perturbation expansion. That is, the zeroth order state will be allowed to be an arbitrary linear combination of the degenerate states and the eigenvalue problem will be solved.

Assume that two or more states are (nearly) degenerate. Define \( \mathcal{N} \) to be the set of those nearly degenerate states. Choose a set of basis state in \( \mathcal{N} \) which are orthonormal

\[ \langle \phi^{(j)} | \phi^{(i)} \rangle = \delta_{ji} \]

where \( i \) and \( j \) are in the set \( \mathcal{N} \). We will use the indices \( i \) and \( j \) to label the states in \( \mathcal{N} \).

By looking at the zeroth and first order terms in the Schrödinger equation and dotting it into one of the degenerate states \( \phi^{(j)} \), we derive (see section 20.4.2) the energy equation for first order (nearly) degenerate state perturbation theory

\[ \sum_{i \in \mathcal{N}} \langle \phi^{(j)} | H_0 + H_1 | \phi^{(i)} \rangle \alpha_i = E \alpha_j, \]
This is an eigenvalue equation with as many solutions as there are degenerate states in our set. We recognize this as simply the (matrix) energy eigenvalue equation limited the list of degenerate states. We solve the equation to get the energy eigenvalues and energy eigenstates, correct to first order.

Written as a matrix, the equation is

\[
\begin{pmatrix}
H_{11} & H_{12} & \cdots & H_{1n} \\
H_{21} & H_{22} & \cdots & H_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
H_{n1} & H_{n2} & \cdots & H_{nn}
\end{pmatrix}
\begin{pmatrix}
\alpha_1 \\
\alpha_2 \\
\vdots \\
\alpha_n
\end{pmatrix}
= E
\begin{pmatrix}
\alpha_1 \\
\alpha_2 \\
\vdots \\
\alpha_n
\end{pmatrix}
\]

where \( H_{ij} = \langle \phi^j | H_0 + H_1 | \phi^i \rangle \) is the matrix element of the full Hamiltonian. If there are \( n \) nearly degenerate states, there are \( n \) solutions to this equation.

The Stark effect for the (principle quantum number) \( n=2 \) states of hydrogen requires the use of degenerate state perturbation theory since there are four states with (nearly) the same energies. For our first calculation, we will ignore the hydrogen fine structure and assume that the four states are exactly degenerate, each with unperturbed energy of \( E_0 \). That is \( H_0 | \phi_{2m} \rangle = E_0 | \phi_{2m} \rangle \). The degenerate states \( \phi_{200}, \phi_{211}, \phi_{210}, \text{ and } \phi_{21(-1)} \).

* See Example 20.3.3: The Stark Effect for \( n=2 \) States.*

The perturbation due to an electric field in the \( z \) direction is \( H_1 = +eEz \). The linear combinations that are found to diagonalize the full Hamiltonian in the subspace of degenerate states are: \( \phi_{211}, \phi_{21(-1)} \) and \( \frac{1}{\sqrt{2}} (\phi_{200} \pm \phi_{210}) \) with energies of \( E_2, E_2, \text{ and } E_2 \pm 3eEa_0 \).

### 20.3 Examples

#### 20.3.1 H.O. with anharmonic perturbation \((ax^4)\).

Anharmonic Oscillator

\[
H_1 = ax^4
\]

We will just write \( x \) in terms of \( A \) and \( A^\dagger \) and compute the expectation value as we have done before.

\[
\Delta E_n^{(1)} = a\langle \phi_n | x^4 | \phi_n \rangle = a \frac{3\hbar^2}{4m^2 \omega^2}
\]

#### 20.3.2 Hydrogen Atom Ground State in a E-field, the Stark Effect.

We have solved the Hydrogen problem with the following Hamiltonian.

\[
H_0 = \frac{p^2}{2\mu} - \frac{Ze^2}{r}
\]
Now we want to find the correction to that solution if an Electric field is applied to the atom. We choose the axes so that the Electric field is in the z direction. The perturbation is then

$$H_1 = eEZ$$

It is typically a small perturbation. For non-degenerate states, the first order correction to the energy is zero because the expectation value of $Z$ is an odd function.

$$E_{nlm}^{(1)} = eE \langle \phi_{nlm} | Z | \phi_{nlm} \rangle = 0$$

We therefore need to calculate the second order correction. This involves a sum over all the other states.

$$E_{100}^{(2)} = e^2E^2 \sum_{nlm \neq 100} \left| \frac{\langle \phi_{nlm} | Z | \phi_{100} \rangle}{E_{nlm}^{(0)} - E_{100}^{(0)}} \right|^2$$

We need to compute all the matrix elements of $Z$ between the ground state and the other Hydrogen states.

$$\langle \phi_{nlm} | Z | \phi_{100} \rangle = \int d^3r R_{nl}^* (r \cos \theta) R_{10} Y_{lm}^* Y_{10}$$

We can do the angular integral by converting the $\cos \theta$ term into a spherical harmonic.

$$Y_{10} \cos \theta = \frac{1}{\sqrt{4\pi}} \sqrt{\frac{4\pi}{3}} Y_{10}$$

The we can just use the orthonormality of the spherical harmonics to do the angular integral, leaving us with a radial integral to do.

$$\langle \phi_{nlm} | Z | \phi_{100} \rangle = \frac{1}{\sqrt{3}} \int r^3 dr R_{nl}^* R_{10} \int d\Omega Y_{lm}^* Y_{10}$$

$$= \frac{\delta_{l0} \delta_{m0}}{\sqrt{3}} \int r^3 R_{nl}^* R_{10} dr$$

The radial part of the integral can be done with some work, yielding

$$|\langle \phi_{nlm} | Z | \phi_{100} \rangle|^2 = \frac{1}{3} \frac{2\pi^2 (n - 1)^{2n-5}}{(n + 1)^{2n+5}} a_0^2 \delta_{n0} \delta_{m0} \equiv f(n) a_0^2 \delta_{n0} \delta_{m0}$$

We put this back into the sum. The Kronecker deltas eliminate the sums over $\ell$ and $m$. We write the energy denominators in terms of the Bohr radius.

$$E_{100}^{(2)} = e^2E^2 \sum_{n=2}^{\infty} \frac{f(n) a_0^2}{2n^2 + \frac{2}{2m^2}}$$

$$= a_0^2 e^2 \sum_{n=2}^{\infty} \frac{2 f(n)}{n^2 - 1 + \frac{1}{n^2}}$$

$$= -2a_0^2 e^2 \sum_{n=2}^{\infty} \frac{n^2 f(n)}{n^2 - 1}$$
This is all a little dissatisfying because we had to insert the general formula for the radial integral and it just goes into a nasty sum. In fact, we could just start with the first few states to get a good idea of the size of the effect. The result comes out to be.

\[ E^{(2)}_{100} = -2a_0^3 e^2 (0.74 + 0.10 + \ldots) = -2.25 a_0^3 e^2 \]

The first two terms of the sum get us pretty close to the right answer. We could have just done those radial integrals.

Now we compute \( d \), the electric dipole moment of the atom which is induced by the electric field.

\[ d = -\frac{\partial \Delta E}{\partial E} = 4(1.125) a_0^3 e \]

The dipole moment is proportional to the electric field, indicating that it is induced. The E field induces the dipole moment, then the dipole moment interacts with the E field causing a energy shift. This indicates why the energy shift is second order.

### 20.3.3 The Stark Effect for \( n=2 \) Hydrogen.

The Stark effect for the \( n=2 \) states of hydrogen requires the use of degenerate state perturbation theory since there are four states with (nearly) the same energies. For our first calculation, we will ignore the hydrogen fine structure and assume that the four states are exactly degenerate, each with unperturbed energy of \( E_0 \). That is \( H_0 \phi_{2\ell m} = E_0 \phi_{2\ell m} \). The degenerate states \( \phi_{200} \), \( \phi_{211} \), \( \phi_{210} \), and \( \phi_{21(-1)} \).

The perturbation due to an electric field in the z direction is \( H_1 = +eEz \). So our first order degenerate state perturbation theory equation is

\[ \sum_i a_i \langle \phi^{(j)}|H_0 + eEZ|\phi^{(i)} \rangle = (E_0 + E^{(1)}) \alpha_j. \]

This is essentially a 4X4 matrix eigenvalue equation. There are 4 eigenvalues \( (E_0 + E^{(1)}) \), distinguished by the index \( n \).

Because of the exact degeneracy \( (H_0 \phi^{(j)} = E_0 \phi^{(j)}) \), \( H_0 \) and \( E_0 \) can be eliminated from the equation.

\[ \sum_i a_i (E_0 \delta_{ij} + \langle \phi^{(j)}|eEZ|\phi^{(i)} \rangle) = (E_0 + E^{(1)}) \alpha_j \]

\[ E_0 \alpha_j + \sum_i a_i \langle \phi^{(j)}|eEZ|\phi^{(i)} \rangle = E_0 \alpha_j + E^{(1)} \alpha_j \]

\[ \sum_i a_i \langle \phi^{(j)}|eEZ|\phi^{(i)} \rangle = E^{(1)} \alpha_j \]

This is just the eigenvalue equation for \( H_1 \) which we can write out in (pseudo)matrix form

\[ \begin{pmatrix} H_1 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} \]

Now, in fact, most of the matrix elements of \( H_1 \) are zero. We will show that because \([L_z, z] = 0\), that all the matrix elements between states of unequal \( m \) are zero. Another way of saying this is that the operator \( z \) doesn’t “change” \( m \). Here is a little proof.

\[ \langle Y_{lm} [L_z, z] Y_{l'm'} | = 0 = (m - m') \langle Y_{lm} | z | Y_{l'm'} \rangle \]
This implies that \( \langle Y_m | z | Y_{m'} \rangle = 0 \) unless \( m = m' \).

Let's define the one remaining nonzero (real) matrix element to be \( \gamma \).

\[
\gamma = eE \langle \phi_{200} | z | \phi_{210} \rangle
\]

The equation (labeled with the basis states to define the order) is:

\[
\begin{pmatrix}
\phi_{200} \\
\phi_{211} \\
\phi_{210} \\
\phi_{21-1}
\end{pmatrix}
\begin{pmatrix}
0 & 0 & \gamma & 0 \\
0 & 0 & 0 & 0 \\
\alpha_1 & \alpha_2 & \alpha_3 & \alpha_4 \\
0 & 0 & 0 & 0
\end{pmatrix}
= E^{(1)}
\begin{pmatrix}
\alpha_1 \\
\alpha_2 \\
\alpha_3 \\
\alpha_4
\end{pmatrix}
\]

We can see by inspection that the eigenfunctions of this operator are \( \phi_{211}, \phi_{21-1}, \) and \( \pm \frac{1}{\sqrt{2}} (\phi_{200} \pm \phi_{210}) \) with eigenvalues (of \( H_1 \)) of 0, 0, and \( \pm \gamma \).

What remains is to compute \( \gamma \). Recall \( Y_{00} = \frac{1}{\sqrt{4\pi}} \) and \( Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta \).

\[
\gamma = eE \int (2a_0)^{-3/2} \frac{1}{\sqrt{3}} \int r^3 d^3r \left( 1 - \frac{r}{2a_0} \right) e^{-r/a_0} \frac{1}{\sqrt{3}} \int \frac{r}{a_0} e^{-r/2a_0} Y_{10} d\Omega
\]

\[
= 2eE \int (2a_0)^{-3} \frac{1}{\sqrt{3}} \int r^3 d^3r \left( 1 - \frac{r}{2a_0} \right) \left( \frac{r}{a_0} \right) e^{-r/a_0} \int 1 \frac{1}{\sqrt{4\pi}} \cos \theta Y_{10} d\Omega
\]

\[
= 2eE(2)^{-3} \frac{1}{\sqrt{3}} \int \int (\frac{r^4}{a_0^4} - \frac{r^5}{2a_0^5}) e^{-r/a_0} dr
\]

\[
= a_0 eE \int_0^\infty x^4 e^{-x} dx - \frac{1}{2} \int_0^\infty x^3 e^{-x} dx
\]

\[
= a_0 eE \left[ 4 \cdot 3 \cdot 2 \cdot 1 - \frac{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{2} \right]
\]

\[
= a_0 eE \left[ -36 \right]
\]

\[
= -3eEa_0 \quad \Rightarrow \quad E^{(1)} = \mp 3eEa_0
\]

This is first order in the electric field, as we would expect in first order (degenerate) perturbation theory.

If the states are not exactly degenerate, we have to leave in the diagonal terms of \( H_0 \). Assume that the energies of the two (mixed) states are \( E_0 \pm \Delta \), where \( \Delta \) comes from some other perturbation, like the hydrogen fine structure. (The \( \phi_{211} \) and \( \phi_{21(-1)} \) are still not mixed by the electric field.)

\[
\begin{pmatrix}
E_0 - \Delta \\
\gamma \\
E_0 + \Delta
\end{pmatrix}
\begin{pmatrix}
\alpha_1 \\
\alpha_2
\end{pmatrix}
= E
\begin{pmatrix}
\alpha_1 \\
\alpha_2
\end{pmatrix}
\]

\[
E = E_0 \pm \sqrt{\gamma^2 + \Delta^2}
\]

This is OK in both limits, \( \Delta \gg \gamma \), and \( \gamma \gg \Delta \). It is also correct when the two corrections are of the same order.

### 20.4 Derivations and Computations

#### 20.4.1 Derivation of 1st and 2nd Order Perturbation Equations

To keep track of powers of the perturbation in this derivation we will make the substitution \( H_1 \rightarrow \lambda H_1 \) where \( \lambda \) is assumed to be a small parameter in which we are making the series expansion of our energy
eigenvalues and eigenstates. It is there to do the book-keeping correctly and can go away at the end of the derivations.

To solve the problem using a perturbation series, we will expand both our energy eigenvalues and eigenstates in powers of $\lambda$.

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$

$$\psi_n = N(\lambda) \left( \phi_n + \sum_{k \neq n} c_{nk}(\lambda) \phi_k \right)$$

$$c_{nk}(\lambda) = \lambda c_{nk}^{(1)} + \lambda^2 c_{nk}^{(2)} + \ldots$$

The full Schrödinger equation is

$$(H_0 + \lambda H_1) \left( \phi_n + \sum_{k \neq n} c_{nk}(\lambda) \phi_k \right) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots) \left( \phi_n + \sum_{k \neq n} c_{nk}(\lambda) \phi_k \right)$$

where the $N(\lambda)$ has been factored out on both sides. For this equation to hold as we vary $\lambda$, it must hold for each power of $\lambda$. We will investigate the first three terms.

$$
\begin{array}{c|c}
\lambda^0 & H_0 \phi_n = E_n^{(0)} \phi_n \\
\lambda^1 & \lambda H_1 \phi_n + H_0 \lambda \sum_{k \neq n} c_{nk}^{(1)} \phi_k = \lambda E_n^{(1)} \phi_n + \lambda E_n^{(0)} \sum_{k \neq n} c_{nk}^{(1)} \phi_k \\
\lambda^2 & H_0 \sum_{k \neq n} \lambda^2 c_{nk}^{(2)} \phi_k + \lambda H_1 \sum_{k \neq n} \lambda c_{nk}^{(1)} \phi_k = E_n^{(0)} \sum_{k \neq n} \lambda^2 c_{nk}^{(2)} \phi_k + \lambda E_n^{(1)} \sum_{k \neq n} \lambda c_{nk}^{(1)} \phi_k + \lambda^2 E_n^{(2)} \phi_n
\end{array}
$$

The zero order term is just the solution to the unperturbed problem so there is no new information there. The other two terms contain linear combinations of the orthonormal functions $\phi_i$. This means we can dot the equations into each of the $\phi_i$ to get information, much like getting the components of a vector individually. Since $\phi_n$ is treated separately in this analysis, we will dot the equation into $\phi_n$ and separately into all the other functions $\phi_k$.

The first order equation dotted into $\phi_n$ yields

$$\langle \phi_n | \lambda H_1 | \phi_n \rangle = \lambda E_n^{(1)}$$

and dotted into $\phi_k$ yields

$$\langle \phi_k | \lambda H_1 | \phi_n \rangle = E_k^{(0)} \lambda c_{nk}^{(1)} = E_n^{(0)} \lambda c_{nk}^{(1)}.$$

From these it is simple to derive the first order corrections

$$\lambda E_n^{(1)} = \langle \phi_n | \lambda H_1 | \phi_n \rangle$$

$$\lambda c_{nk}^{(1)} = \langle \phi_k | \lambda H_1 | \phi_n \rangle / E_n^{(0)} - E_k^{(0)}$$

The second order equation projected on $\phi_n$ yields

$$\sum_{k \neq n} \lambda c_{nk}^{(1)} \langle \phi_n | \lambda H_1 | \phi_k \rangle = \lambda^2 E_n^{(2)}.$$
We will not need the projection on \( \phi_k \) but could proceed with it to get the second order correction to the wave function, if that were needed. Solving for the second order correction to the energy and substituting for \( c_{nk}^{(1)} \), we have

\[
\lambda^2 E_n^{(2)} = \sum_{k \neq n} \frac{\langle \phi_k | \lambda H_1 | \phi_n \rangle^2}{E_n^{(0)} - E_k^{(0)}}.
\]

The normalization factor \( N(\lambda) \) played no role in the solutions to the Schrödinger equation since that equation is independent of normalization. We do need to go back and check whether the first order corrected wavefunction needs normalization.

\[
\frac{1}{N(\lambda)^2} = \left| \langle \phi_n + \sum_{k \neq n} \lambda c_{nk}^{(1)} \phi_k | \phi_n \rangle + \sum_{k \neq n} \lambda c_{nk}^{(1)} \phi_k \right|^2 = 1 + \sum_{k \neq n} \lambda^2 |c_{nk}^{(1)}|^2
\]

\[
N(\lambda) \approx 1 - \frac{1}{2} \sum_{k \neq n} \lambda^2 |c_{nk}^{(1)}|^2
\]

The correction is of order \( \lambda^2 \) and can be neglected at this level of approximation.

These results are rewritten with all the \( \lambda \) removed in section 20.1.

### 20.4.2 Derivation of 1st Order Degenerate Perturbation Equations

To deal with the problem of degenerate states, we will allow an arbitrary linear combination of those states at zeroth order. In the following equation, the sum over \( i \) is the sum over all the states degenerate with \( \phi_n \) and the sum over \( k \) runs over all the other states.

\[
\psi_n = N(\lambda) \left( \sum_{i \in N} \alpha_i \phi_i^{(i)} + \sum_{k \not\in N} \lambda c_{nk}^{(1)} \phi_k + \ldots \right)
\]

where \( N \) is the set of zeroth order states which are (nearly) degenerate with \( \phi_n \). We will only go to first order in this derivation and we will use \( \lambda \) as in the previous derivation to keep track of the order in the perturbation.

The full Schrödinger equation is.

\[
(H_0 + \lambda H_1) \left( \sum_{i \in N} \alpha_i \phi_i^{(i)} + \sum_{k \not\in N} \lambda c_{nk}^{(1)} \phi_k \right) = (E_n^{(0)} + \lambda E^{(1)}) \left( \sum_{i \in N} \alpha_i \phi_i^{(i)} + \sum_{k \not\in N} \lambda c_{nk}^{(1)} \phi_k \right)
\]

If we keep the zeroth and first order terms, we have

\[
(H_0 + \lambda H_1) \sum_{i \in N} \alpha_i \phi_i^{(i)} + H_0 \sum_{k \not\in N} \lambda c_{nk}^{(1)} \phi_k = (E_n^{(0)} + \lambda E^{(1)}) \sum_{i \in N} \alpha_i \phi_i^{(i)} + E_n^{(0)} \sum_{k \not\in N} \lambda c_{nk}^{(1)} \phi_k.
\]

Projecting this onto one of the degenerate states \( \phi^{(j)} \), we get

\[
\sum_{i \in N} \langle \phi^{(j)} | H_0 + \lambda H_1 | \phi_i^{(i)} \rangle \alpha_i = (E_n^{(0)} + \lambda E^{(1)}) \alpha_j.
\]
By putting both terms together, our calculation gives us the full energy to first order, not just the correction. It is useful both for degenerate states and for nearly degenerate states. The result may be simplified to
\[ \sum_{i \in \mathcal{N}} \langle \phi^{(j)} | H | \phi^{(i)} \rangle \alpha_i = E \alpha_j. \]

This is just the standard eigenvalue problem for the full Hamiltonian in the subspace of (nearly) degenerate states.

### 20.5 Homework Problems

1. An electron is bound in a harmonic oscillator potential \( V_0 = \frac{1}{2} m \omega^2 x^2 \). Small electric fields in the \( x \) direction are applied to the system. Find the lowest order nonzero shifts in the energies of the ground state and the first excited state if a constant field \( E_1 \) is applied. Find the same shifts if a field \( E_1 x^3 \) is applied.

2. A particle is in a box from \(-a\) to \(a\) in one dimension. A small additional potential \( V_1 = \lambda \cos(\frac{2\pi x}{a}) \) is applied. Calculate the energies of the first and second excited states in this new potential.

3. The proton in the hydrogen nucleus is not really a point particle like the electron is. It has a complicated structure, but a good approximation to its charge distribution is a uniform charge density over a sphere of radius 0.5 fermis. Calculate the effect of this potential change for the energy of the ground state of hydrogen. Calculate the effect for the \( n = 2 \) states.

4. Consider a two dimensional harmonic oscillator problem described by the Hamiltonian \( H_0 = \frac{p_x^2 + p_y^2}{2m} + \frac{1}{2} m \omega^2 (x^2 + y^2) \). Calculate the energy shifts of the ground state and the degenerate first excited states, to first order, if the additional potential \( V = 2 \lambda xy \) is applied. Now solve the problem exactly. Compare the exact result for the ground state to that from second order perturbation theory.

5. Prove that \( \sum_n (E_n - E_0) \langle n|x|a \rangle \|^2 = \frac{\alpha^2}{2m} \) by starting from the expectation value of the commutator \([p,x]\) in the state \(a\) and summing over all energy eigenstates. Assume \( p = m \frac{df}{dx} \) and write \( \frac{df}{dx} \) in terms of the commutator \([H,x]\) to get the result.

6. If the general form of the spin-orbit coupling for a particle of mass \( m \) and spin \( \vec{S} \) moving in a potential \( V(r) \) is \( H_{SO} = \frac{1}{2m^2 c^2} \vec{L} \cdot \vec{S} \frac{dV(r)}{dr} \), what is the effect of this coupling on the spectrum of a three dimensional harmonic oscillator? Compute the relativistic correction for the ground state of the three dimensional harmonic oscillator.

### 20.6 Sample Test Problems

1. Assume an electron is bound to a heavy positive particle with a harmonic potential \( V(x) = \frac{1}{2} m \omega^2 x^2 \). Calculate the energy shifts to all the energy eigenstates in an electric field \( E \) (in the \( x \) direction).

2. Find the energies of the \( n = 2 \) hydrogen states in a strong uniform electric field in the \( z \)-direction. (Note, since spin plays no role here there are just 4 degenerate states. Ignore the fine structure corrections to the energy since the E-field is strong. Remember to use the fact that \([L_z, z] = 0\). If you are pressed for time, don’t bother to evaluate the radial integrals.)
3. An electron is in a three dimensional harmonic oscillator potential $V(r) = \frac{1}{2}m\omega^2r^2$. A small electric field, of strength $E_z$, is applied in the $z$ direction. Calculate the lowest order nonzero correction to the ground state energy.

4. Hydrogen atoms in the $n = 2$ state are put in a strong electric field. Assume that the 2s and 2p states of Hydrogen are degenerate and spin is not important. Under these assumptions, there are 4 states: the 2s and three 2p states. Calculate the shifts in energy due to the E-field and give the states that have those energies. Please work out the problem in principle before attempting any integrals.
21 Fine Structure in Hydrogen

In this section, we will calculate the fine structure corrections to the Hydrogen spectrum. Some of the degeneracy will be broken. Since the Hydrogen problem still has spherical symmetry, states of definite total angular momentum will be the energy eigenstates.

We will break the spherical symmetry by applying a weak magnetic field, further breaking the degeneracy of the energy eigenstates. The effect of a weak magnetic field is known as the anomalous Zeeman effect, because it was hard to understand at the time it was first measured. It will not be anomalous for us.

We will use many of the tools of the last three sections to make our calculations. Nevertheless, a few of the correction terms we use will not be fully derived here.

This material is covered in Gasiorowicz Chapter 17, in Cohen-Tannoudji et al. Chapter XII, and in Griffiths Chapter 6.

21.1 Hydrogen Fine Structure

The basic hydrogen problem we have solved has the following Hamiltonian.

\[ H_0 = \frac{p^2}{2\mu} - \frac{Ze^2}{r} \]

To this simple Coulomb problem, we will add several corrections:

1. The relativistic correction to the electron's kinetic energy.
2. The Spin-Orbit correction.
3. The “Darwin Term” correction to s states from Dirac eq.
4. The ((anomalous) Zeeman) effect of an external magnetic field.

Correction (1) comes from relativity. The electron's velocity in hydrogen is of order $\alpha c$. It is not very relativistic but a small correction is in order. By calculating (see section 21.1.1) the next order relativistic correction to the kinetic energy we find the additional term in the Hamiltonian

\[ H_1 = -\frac{1}{8} \frac{p_e^4}{m^3c^2} \]

Our energy eigenstates are not eigenfunctions of this operator so we will have to treat it as a perturbation.

We can estimate the size of this correction compared to the Hydrogen binding energy by taking the ratio to the Hydrogen kinetic energy. (Remember that, in the hydrogen ground state, \( \langle \frac{p^2}{2m} \rangle = -E = \frac{1}{2} \alpha^2 mc^2 \).)

\[ \frac{p^4}{8m^3c^2} : \frac{p^2}{2m} = \frac{p^2}{4m^3c^2} = \frac{(p^2 / 2m)}{2mc^2} = \frac{1}{4} \alpha^2 \]
Like all the fine structure corrections, this is down by a factor of order $\alpha^2$ from the Hydrogen binding energy.

The second term, due to Spin-Orbit interactions, is harder to derive correctly. We understand the basis for this term. The magnetic moment from the electron’s spin interacts with the B field produced by the current seen in the electron’s rest frame from the circulating proton.

$$H_2 = -\vec{\mu}_e \cdot \vec{B}$$

We can derive (see section 21.4.2) B from a Lorentz transformation of the E field of a static proton (We must also add in the Thomas Precession which we will not try to understand here).

$$H_2 = \frac{g}{2} \frac{ec^2}{2m^2 c^2} \overline{L} \cdot \overline{S}$$

This will be of the same order as the relativistic correction.

Now we compute (see section 21.4.3) the relativity correction in first order perturbation theory.

$$\langle \psi_{n\ell \ell m} | H_1 | \psi_{n\ell \ell m} \rangle = \frac{E_{n\ell m}^{(0)^2}}{2mc} \left[ 3 - \frac{4n}{\ell + \frac{1}{2}} \right]$$

The result depends on $\ell$ and $n$, but not on $m$. This means that we could use either the $\psi_{n\ell m j \ell s}$ or the $\psi_{n\ell m j \ell}$ to calculate the effect of $H_1$. We will need to use the $\psi_{n\ell m j \ell s}$ to add in the spin-orbit.

The first order perturbation energy shift from the spin orbit correction is calculated (see section 21.4.4) for the states of definite $j$.

$$\langle \psi_{n\ell \ell m} | H_2 | \psi_{n\ell \ell m} \rangle = \frac{g}{2} \frac{ec^2}{2mc^2} \left[ \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{r^{3/2}} \right]$$

$$= \left( \frac{g}{2} \right) \frac{E_{n\ell m}^{(0)^2}}{2mc^2} \left[ \frac{n}{(\ell+\frac{1}{2})(\ell+\frac{3}{2})} \right]$$

$$\begin{cases} j = \ell + \frac{1}{2} \\ j = \ell - \frac{1}{2} \end{cases}$$

Actually, the $\overline{L} \cdot \overline{S}$ term should give 0 for $\ell = 0$! In the above calculation there is an $\frac{1}{r}$ factor which makes the result for $\ell = 0$ undefined. There is an additional Dirac Equation contribution called the “Darwin term” (see section 21.4.5) which is important for $\ell = 0$ and surprisingly makes the above calculation right, even for $\ell = 0$!

We will now add these three fine structure corrections together for states of definite $j$. We start with a formula which has slightly different forms for $j = \ell \pm \frac{1}{2}$.

$$E_{n\ell m j \ell s} = E_{n\ell m}^{(0)} + \frac{E_{n\ell m}^{(0)^2}}{2mc^2} \left[ 3 - \frac{4n}{\ell + \frac{1}{2}} + \left\{ \frac{2n}{(\ell+\frac{3}{2})(\ell+\frac{5}{2})} \right\}_{(+)} \right]$$

$$E_{n\ell m j \ell s} = E_{n\ell m}^{(0)} + \frac{E_{n\ell m}^{(0)^2}}{2mc^2} \left[ 3 - \frac{n}{(\ell + \frac{1}{2})} \left\{ \frac{4 - \frac{2}{\ell+\frac{1}{2}}}{4 + \frac{2}{\ell+\frac{1}{2}}} \right\}_{(-)} \right]$$
\[ E_{n \ell m} = E_n^{(0)} + \frac{E_n^{(0)^2}}{2mc^2} \left[ 3 - n - \frac{4 + \frac{2}{j + \frac{1}{2}}}{\ell + \frac{1}{2}} \right] \]

We can write \((\ell + \frac{1}{2})\) as \((j + \frac{1}{2} + \frac{1}{2})\), so that

\[ \frac{4 + \frac{2}{j + \frac{1}{2}}}{\ell + \frac{1}{2}} = \frac{4j + 2}{(j + \frac{1}{2})(j + \frac{1}{2} + \frac{1}{2})} = 4 \frac{(j + \frac{1}{2} + \frac{1}{2})}{(j + \frac{1}{2})(j + \frac{1}{2} + \frac{1}{2})} \]

and we get a nice cancellation giving us a simple formula.

\[ E_{n \ell m} = E_n^{(0)} + \frac{E_n^{(0)^2}}{2mc^2} \left[ 3 - \frac{4n}{j + \frac{1}{2}} \right] \]

This is independent of \(\ell\) so the states of different total angular momentum split in energy but there is still a good deal of degeneracy.

We have calculated the fine structure effects in Hydrogen. There are, of course, other, smaller corrections to the energies. A correction from field theory, the Lamb Shift, causes states of different \(\ell\) to shift apart slightly. Nevertheless, the states of definite total angular momentum are the energy eigenstates until we somehow break spherical symmetry.
21.2 Hydrogen Atom in a Weak Magnetic Field

One way to break the spherical symmetry is to apply an external B field. Let’s assume that the field is weak enough that the energy shifts due to it are smaller than the fine structure corrections. Our Hamiltonian can now be written as $H = H_0 + (H_1 + H_2) + H_3$, where $H_0 = \frac{e B}{2mc} \cdot (\vec{L} + 2\vec{S}) = \frac{eB}{2mc}(L_z + 2S_z)$ is the normal Hydrogen problem, $H_1 + H_2$ is the fine structure correction, and

$$H_3 = \frac{e \vec{B} \cdot (\vec{L} + 2\vec{S})}{2mc} = \frac{e B}{2mc}(L_z + 2S_z)$$

is the term due to the weak magnetic field.

We now run into a problem because $H_1 + H_2$ picks eigenstates of $J^2$ and $J_z$ while $H_3$ picks eigenstates of $L_z$ and $S_z$. In the weak field limit, we can do perturbation theory using the states of definite $j$. A direct calculation (see section 21.4.6) of the Anomalous Zeeman Effect gives the energy shifts in a weak B field.

$$\Delta E = \langle \psi_{n\ell j m_j} | \frac{e \vec{B} \cdot (\vec{L} + 2\vec{S})}{2mc} | \psi_{n\ell j m_j} \rangle = \frac{e B}{2mc} m_j \left( 1 \pm \frac{1}{2\ell + 1} \right)$$

This is the correction, due to a weak magnetic field, which we should add to the fine structure energies.

$$E_{nj\ell m_\ell} = -\frac{1}{2} \alpha^2 mc^2 \left( \frac{1}{n^2} + \frac{\alpha^2}{n^3} \left[ \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right] \right)$$

Thus, in a weak field, the degeneracy is completely broken for the states $\psi_{nj\ell m_\ell}$. All the states can be detected spectroscopically.
The factor \( \left( 1 \pm \frac{1}{2n+1} \right) \) is known as the Lande \textit{g} Factor because the state splits as if it had this gyromagnetic ratio. We know that it is in fact a combination of the orbital and spin \( g \) factors in a state of definite \( j \).

In the strong field limit we could use states of definite \( m_\ell \) and \( m_s \) and calculate the effects of the fine structure, \( H_1 + H_2 \), as a correction. We will not calculate this here. If the field is very strong, we can neglect the fine structure entirely. Then the calculation is easy.

\[
E = E_n^0 + \frac{\epsilon B \hbar}{2mc} (m_\ell + 2m_s)
\]

In this limit, the field has partially removed the degeneracy in \( m_\ell \) and \( m_s \), but not \( \ell \). For example, the energies of all these \( n = 3 \) states are the same.

\[
\begin{align*}
\ell = 2 & \quad m_\ell = 0 \quad m_s = \frac{1}{2} \\
\ell = 1 & \quad m_\ell = 0 \quad m_s = \frac{1}{2} \\
\ell = 2 & \quad m_\ell = 2 \quad m_s = -\frac{1}{2}
\end{align*}
\]
21.3 Examples

21.4 Derivations and Computations

21.4.1 The Relativistic Correction

Moving from the non-relativistic formula for the energy of an electron to the relativistic formula we make the change
\[ mc^2 + \frac{p^2}{2m} \rightarrow (p^2 c^2 + m^2 c^4)^{1/2} = mc^2 \left(1 + \frac{p^2 c^2}{m^2 c^4}\right)^{1/2}. \]

Taylor expanding the square root around \( p^2 = 0 \), we find
\[ (p^2 c^2 + m^2 c^4)^{1/2} = mc^2 + \frac{1}{2} \frac{p^2 c^2}{mc^2} - \frac{1}{8} \frac{p^4 c^4}{m^3 c^6} + \cdots \approx mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2}. \]

So we have our next order correction term. Notice that \( \frac{p^2}{2m} \) was just the lowest order correction to \( mc^2 \).

What about the “reduced mass problem”? The proton is very non-relativistic so only the electron term is important and the reduced mass is very close to the electron mass. We can therefore neglect the small correction to the small correction and use
\[ H_1 = -\frac{1}{2} \frac{p^4}{8m^3 c^2}. \]

21.4.2 The Spin-Orbit Correction

We calculate the classical Hamiltonian for the spin-orbit interaction which we will later apply as a perturbation. The B field from the proton in the electron’s rest frame is
\[ \vec{B} = \frac{-\vec{v} \times \vec{E}}{c}. \]

Therefore the correction is
\[ H_2 = \frac{ge}{2mc} \vec{S} \cdot \vec{B} = -\frac{ge}{2mc^2} \vec{S} \cdot \vec{v} \times \vec{E} = \frac{ge}{2m^2 c^2} \vec{S} \cdot \vec{p} \times \vec{v} \phi. \]

\( \phi \) only depends on \( r \) \( \Rightarrow \nabla \phi = \hat{r} \frac{d\phi}{dr} = \frac{\vec{r} \cdot \vec{p} \phi}{r} \)
\[ \Rightarrow H_2 = \frac{ge}{2m^2 c^2} \vec{S} \cdot \vec{p} \times \frac{1}{r} \frac{d\phi}{dr} = \frac{-ge}{2m^2 c^2} \vec{S} \cdot \hat{L} \frac{1}{r} \frac{d\phi}{dr}. \]

\[ \phi = \frac{e}{r} \Rightarrow \frac{d\phi}{dr} = -\frac{e}{r^2} \]
\[ H_2 = \frac{1}{2} \frac{ge^2}{2m^2 c^2 r^3} \hat{L} \cdot \vec{S} \]
Note that this was just a classical calculation which we will apply to quantum states later. It is correct for the EM forces, but, the electron is actually in a rotating system which gives an additional \( \vec{L} \cdot \vec{S} \) term (not from the B field!). This term is 1/2 the size and of opposite sign. We have already included this factor of 2 in the answer given above.

Recall that

\[
H_2 \propto \vec{L} \cdot \vec{S} = \frac{1}{2} \left[ J^2 - L^2 - S^2 \right]
\]

and we will therefore want to work with states of definite \( j, \ell, \) and \( s. \)

### 21.4.3 Perturbation Calculation for Relativistic Energy Shift

Rewriting \( H_1 = -\frac{1}{2} \frac{\hbar^2}{m^2 c^2} \) as \( H_1 = -\frac{1}{2m^2 c^2} \left( \frac{\hbar^2}{2m} \right)^2 \) we calculate the energy shift for a state \( \psi_{n j m j \ell s}. \)

While there is no spin involved here, we will need to use these states for the spin-orbit interaction

\[
\langle \psi_{n j m j \ell s} | H_1 | \psi_{n j m j \ell s} \rangle = -\frac{1}{2mc^2} \left\langle \psi_{n j m j \ell s} \right| \left( \frac{\hbar^2}{2m} \right)^2 \left| \psi_{n j m j \ell s} \right\rangle
\]

\[
= -\frac{1}{2mc^2} \left\langle \psi_{n j m j \ell s} \right| \left( \frac{\hbar^2}{2m} \right)^2 \left| \psi_{n j m j \ell s} \right\rangle
\]

\[
= -\frac{1}{2mc^2} \left\langle \psi_{n j m j \ell s} \right| \left( \frac{\hbar^2}{2m} \right)^2 \left| \psi_{n j m j \ell s} \right\rangle
\]

\[
= -\frac{1}{2mc^2} \left[ E_n^2 + \left\langle \psi_{n j m j \ell s} \right| \frac{\hbar^2}{4m} \left| \psi_{n j m j \ell s} \right\rangle + \left\langle \psi_{n j m j \ell s} \right| \frac{\hbar^2}{4m} \left| \psi_{n j m j \ell s} \right\rangle + \left\langle \psi_{n j m j \ell s} \right| \frac{\hbar^2}{4m} \left| \psi_{n j m j \ell s} \right\rangle \right]
\]

where we can use some of our previous results.

\[
E_n = -\frac{1}{2} \frac{\alpha^2 mc^2}{n^2} = \frac{-\frac{e^2}{2\alpha n^2}}
\]

\[
\left\langle \frac{1}{r} \right\rangle_n = \left( \frac{1}{a_0 n^2} \right)
\]

\[
\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{a_0^2 n^2 (\ell + \frac{3}{2})}
\]

\[
\langle \psi_{n j m j \ell s} | H_1 | \psi_{n j m j \ell s} \rangle = -\frac{1}{2mc^2} \left[ \left( -\frac{\hbar^2}{2m} \right)^2 \left( \frac{-\frac{\alpha^2 mc^2}{n^2}}{n^2} \right)^2 \right] + 2 \left( \frac{-\frac{\alpha^2 mc^2}{n^2}}{a_0 n^2} \right) \frac{e^2}{2m c^2} \left( \frac{e^4}{a_0^2 n^2 (\ell + \frac{3}{2})} \right)
\]

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

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

Since this does not depend on either \( m_\ell \) or \( j, \) total \( j \) states and the product states give the same answer. We will choose to use the total \( j \) states, \( \psi_{n j m j \ell s}, \) so that we can combine this correction with the spin-orbit correction.
21.4.4 Perturbation Calculation for \( H_2 \) Energy Shift

We now calculate the expectation value of \( H_2 \). We will immediately use the fact that \( j = \ell \pm \frac{1}{2} \).

\[
\langle \psi_{n\ell m} | H_2 | \psi_{n\ell m} \rangle = \frac{ge^2 \hbar^2}{4\hbar^2} \left[ \frac{1}{2} [j(j + 1) - \ell(\ell + 1) - s(s + 1)] \right] \left\langle \frac{1}{r^3} \right\rangle
\]

\[
= \frac{ge^2 \hbar^2}{8m^2 c^2} \left[ \ell + \frac{1}{2} \right] \left[ \ell + \frac{1}{2} \right] \left( \frac{1}{n^3 \ell(\ell + \frac{1}{2})(\ell + 1)} \right) - \frac{3}{4} \frac{1}{a_0^3} \left( \frac{1}{n^3 \ell(\ell + \frac{1}{2})(\ell + 1)} \right)
\]

\[
= -E_n \left( \frac{g}{2} \right) \frac{eh \hbar^2}{m \alpha^2 n^2} \left[ \frac{n}{\ell + 1} \right] \left( \frac{\ell}{\ell + \frac{1}{2}} \right) \left( \frac{n}{\ell(\ell + \frac{1}{2})} \right).
\]

\[
= \left( \frac{g}{2} \right) \left( \frac{-E_n}{2mc^2} \right) \frac{\hbar^2}{m^2 c^2} \left[ \frac{n}{\ell + 1} \right] \left( \frac{\ell}{\ell + \frac{1}{2}} \right) \left( \frac{n}{\ell + \frac{1}{2}} \right).
\]

\[
= \left( \frac{g}{2} \right) \left( \frac{E_n}{2mc^2} \right) \frac{\hbar^2}{m^2 c^2} \left[ \frac{n}{\ell + 1} \right] \left( \frac{\ell}{\ell + \frac{1}{2}} \right) \left( \frac{n}{\ell + \frac{1}{2}} \right).
\]

Note that in the above equation, we have canceled a term \( \frac{1}{\ell} \) which is not defined for \( \ell = 0 \). We will return to this later.

21.4.5 The Darwin Term

We get a correction at the origin from the Dirac equation.

\[
H_D = \frac{\pi e^2 \hbar^2}{2m^2 c^2} \delta^3 (\mathbf{r})
\]

When we take the expectation value of this, we get the probability for the electron and proton to be at the same point.

\[
\langle \psi | H_D | \psi \rangle = \frac{\pi e^2 \hbar^2}{2m^2 c^2} |\psi(0)|^2
\]

Now, \( \psi(0) = 0 \) for \( \ell > 0 \) and \( \psi(0) = \frac{1}{\sqrt{4\pi}} \left( \frac{e^2}{\pi m n} \right)^{3/2} \) for \( \ell = 0 \), so

\[
\langle H_D \rangle_{n \ell 0} = \frac{4e^2 \hbar^2}{8m^3 a_0^3 m^2 c^2} \frac{e^2 \hbar^2}{2m^3 a_0 c^2 m^2 c^2} = \frac{2nE^2}{mc^2}
\]

This is the same as \( \ell = 0 \) term that we got for the spin orbit correction. This actually replaces the \( \ell = 0 \) term in the spin-orbit correction (which should be zero) making the formula correct!

21.4.6 The Anomalous Zeeman Effect

We compute the energy change due to a weak magnetic field using first order Perturbation Theory.
\[
\left\langle \psi_{n\ell m_j} \left| \frac{eB}{2mc} (L_z + 2S_z) \right| \psi_{n\ell m_j} \right\rangle \\
= (L_z + 2S_z) = J_z + S_z
\]

The \( J_z \) part is easy since we are in eigenstates of that operator.

\[
\left\langle \psi_{n\ell m_j} \left| \frac{eB}{2mc} J_z \right| \psi_{n\ell m_j} \right\rangle = \frac{eB}{2mc} \hbar m_j
\]

The \( S_z \) is harder since we are not in eigenstates of that one. We need \( \left\langle \psi_{n\ell m_j} \left| \frac{eB}{2mc} S_z \right| \psi_{n\ell m_j} \right\rangle \), but we don’t know how \( S_z \) acts on these. So, we must write \( \left| \psi_{n\ell m_j, s_z} \right\rangle \) in terms of \( \left| \psi_{n\ell m, s_z} \right\rangle \).

\[
E_n^{(1)} = \left\langle \psi_{n\ell m_j} \left| \frac{eB}{2mc} (J_z + S_z) \right| \psi_{n\ell m_j} \right\rangle \\
= \frac{eB}{2mc} (m_j \hbar + \left\langle \psi_{n\ell m_j} \left| S_z \right| \psi_{n\ell m_j} \right\rangle)
\]

We already know how to write in terms of these states of definite \( m_\ell \) and \( m_s \).

\[
\psi_{n(\ell + \frac{1}{2}) m_\ell m_s} = \alpha Y_{\ell m} \chi_+ + \beta Y_{\ell (m+1)} \chi_-
\]

\[
\psi_{n(\ell - \frac{1}{2}) m_\ell m_s} = \beta Y_{\ell m} \chi_+ - \alpha Y_{\ell (m+1)} \chi_-
\]

\[
\alpha = \sqrt{\frac{\ell + m + 1}{2\ell + 1}}
\]

\[
\beta = \sqrt{\frac{\ell - m}{2\ell + 1}}
\]

Let’s do the \( j = \ell + \frac{1}{2} \) state first.

\[
\left\langle \psi_{n\ell m_j} \left| S_z \right| \psi_{n\ell m_j} \right\rangle = \left\langle \alpha Y_{\ell m_j} \chi_+ + \beta Y_{\ell (m_j + \frac{1}{2})} \chi_- \left| S_z \right| \alpha Y_{\ell m_j} \chi_+ + \beta Y_{\ell (m_j + \frac{1}{2})} \chi_- \right\rangle
\]

\[
= \frac{1}{2} \hbar \left( \alpha^2 - \beta^2 \right)_{m=m_j} - \frac{1}{2}
\]

For \( j = \ell - \frac{1}{2} \),

\[
\left\langle \psi_{n\ell m_j} \left| S_z \right| \psi_{n\ell m_j} \right\rangle = \frac{1}{2} \hbar \left( \beta^2 - \alpha^2 \right)_{m=m_j} - \frac{1}{2}
\]

We can combine the two formulas for \( j = \ell \pm \frac{1}{2} \).

\[
\left\langle \psi_{n\ell m_j} \left| S_z \right| \psi_{n\ell m_j} \right\rangle = \pm \frac{\hbar}{2} \left( \alpha^2 - \beta^2 \right) = \pm \frac{\hbar}{2} \left( m_j \hbar + \frac{1}{2\ell + 1} \right)
\]

So adding this to the (easier) part above, we have

\[
E_n^{(1)} = \frac{eB}{2mc} \left( m_j \hbar \pm \frac{m_j \hbar}{2\ell + 1} \right) = \frac{eB}{2mc} m_j \left( 1 \pm \frac{1}{2\ell + 1} \right)
\]
for $j = \ell \pm \frac{1}{2}$.

In summary then, we rewrite the fine structure shift.

$$\Delta E = -\frac{1}{2}mc^2 (Z \alpha)^4 \frac{1}{n^3} \left[ \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right].$$

To this we add the anomalous Zeeman effect

$$\Delta E = \frac{eBm}{2mc} m_j \left( 1 \pm \frac{1}{2\ell + 1} \right).$$

### 21.5 Homework Problems

1. Consider the fine structure of the $n = 2$ states of the hydrogen atom. What is the spectrum in the absence of a magnetic field? How is the spectrum changed when the atom is placed in a magnetic field of 25,000 gauss? Give numerical values for the energy shifts in each of the above cases. Now, try to estimate the binding energy for the lowest energy $n = 2$ state including the relativistic, spin-orbit, and magnetic field.

2. Verify the relations used for $\frac{1}{r}$, $\frac{1}{r^2}$, and $\frac{1}{r^3}$ for hydrogen atom states up to $n = 3$ and for any $n$ if $\ell = n - 1$.

3. Calculate the fine structure of hydrogen atoms for spin 1 electrons for $n = 1$ and $n = 2$. Compute the energy shifts in eV.

### 21.6 Sample Test Problems

1. The relativistic correction to the Hydrogen Hamiltonian is $H_1 = -\frac{p^4}{8m_c^2c^4}$. Assume that electrons have spin zero and that there is therefore no spin-orbit correction. Calculate the energy shifts and draw an energy diagram for the $n=3$ states of Hydrogen. You may use $\langle \psi_{nlm} | \frac{1}{r} | \psi_{nlm} \rangle = \frac{1}{n^2a_0^2(\ell + \frac{1}{2})}$.

2. Calculate the fine structure energy shifts (in eV) for the $n = 1$, $n = 2$, and $n = 3$ states of Hydrogen. Include the effects of relativistic corrections, the spin-orbit interaction, and the so-called Darwin term (due to Dirac equation). Do not include hyperfine splitting or the effects of an external magnetic field. (Note: I am not asking you to derive the equations.) Clearly list the states in spectroscopic notation and make a diagram showing the allowed electric dipole decays of these states.

3. Calculate and show the splitting of the $n = 3$ states (as in the previous problem) in a weak magnetic field $B$. Draw a diagram showing the states before and after the field is applied.

4. If the general form of the spin-orbit coupling for a particle of mass $m$ and spin $\frac{3}{2}$ moving in a potential $V(r)$ is $H_{SO} = \frac{1}{2mr^2} \mathbf{L} \cdot \text{S} \frac{1}{2} \frac{dV}{dr}$, what is the effect of that coupling on the spectrum of an electron bound in a 3D harmonic oscillator? Give the energy shifts and draw a diagram for the $0s$ and $1p$ states.

$$V = \frac{1}{2}m\omega^2r^2$$

$$\frac{dV}{dr} = m\omega^2 r$$
\[
\langle H_{SO} \rangle = \frac{e^2}{2 \hbar c^2} \left[ j(j + 1) - l(l + 1) - s(s + 1) \right] m \omega^2
\]
\[
\langle H_{SO} \rangle = \frac{e^2}{4 \hbar c^2} \left[ j(j + 1) - l(l + 1) - s(s + 1) \right]
\]

for the \(0S_{1/2}\), \(\Delta E = 0\),
for the \(1P_{1/2}\), \(\Delta E = -2\frac{e^2}{4 \hbar c^2}\),
for the \(1P_{1/2}\), \(\Delta E = +1\frac{e^2}{4 \hbar c^2}\).

5. We computed that the energies after the fine structure corrections to the hydrogen spectrum are 
\(E_{nij} = -\frac{\alpha^2 \hbar c^2}{8n^3} + \frac{\alpha^2 \hbar c^2}{8n^3} (3 - \frac{4n}{j + \frac{1}{2}})\). Now a weak magnetic field \(B\) is applied to hydrogen atoms in the \(3d\) state. Calculate the energies of all the \(3d\) states (ignoring hyperfine effects). Draw an energy level diagram, showing the quantum numbers of the states and the energy splittings.

6. In Hydrogen, the \(n = 3\) state is split by fine structure corrections into states of definite \(j, m_j, \ell\), and \(s\). According to our calculations of the fine structure, the energy only depends on \(j\). We label these states in spectroscopic notation: \(N^{2s+1}L_j\). Draw an energy diagram for the \(n = 3\) states, labeling each state in spectroscopic notation. Give the energy shift due to the fine structure corrections in units of \(\alpha^4 \hbar c^2\).

7. The energies of photons emitted in the Hydrogen atom transition between the \(3S\) and the \(2P\) states are measured, first with no external field, then, with the atoms in a uniform magnetic field \(B\). Explain in detail the spectrum of photons before and after the field is applied. Be sure to give an expression for any relevant energy differences.
22 Hyperfine Structure

The interaction between the magnetic moment, due to the spin of the nucleus, and the larger magnetic moment, due to the electron’s spin, results in energy shifts which are much smaller than those of the fine structure. They are of order $\frac{m_e}{m} \alpha^2 E_n$ and are hence called hyperfine.

The hyperfine corrections may be difficult to measure in transitions between states of different $n$, however, they are quite measurable and important because they split the ground state. The different hyperfine levels of the ground state are populated thermally. Hyperfine transitions, which emit radio frequency waves, can be used to detect interstellar gas.

This material is covered in Gasiorowicz Chapter 17, in Cohen-Tannoudji et al. Chapter XII, and briefly in Griffiths Chapter 6.

22.1 Hyperfine Splitting

We can think of the nucleus as a single particle with spin $\vec{I}$. This particle is actually made up of protons and neutrons which are both spin $\frac{1}{2}$ particles. The protons and neutrons in turn are made of spin $\frac{1}{2}$ quarks. The magnetic dipole moment due to the nuclear spin is much smaller than that of the electron because the mass appears in the denominator. The magnetic moment of the nucleus is

$$\vec{\mu}_N = \frac{Ze g_N}{2m_N} \vec{I}$$

where $\vec{I}$ is the nuclear spin vector. Because the nucleus has internal structure, the nuclear gyromagnetic ratio is not just 2. For the proton, it is $g_p \approx 5.56$. This is the nucleus of hydrogen upon which we will concentrate. Even though the neutron is neutral, the gyromagnetic ratio is about -3.83. (The quarks have gyromagnetic ratios of 2 (plus corrections) like the electron but the problem is complicated by the strong interactions which make it hard to define a quark’s mass.) We can compute (to some accuracy) the gyromagnetic ratio of nuclei from that of protons and neutrons as we can compute the proton’s gyromagnetic ratio from its quark constituents.

In any case, the nuclear dipole moment is about 1000 times smaller than that for e-spin or $\vec{I}$. We will calculate $\Delta E$ for $\ell = 0$ states (see Condon and Shortley for more details). This is particularly important because it will break the degeneracy of the Hydrogen ground state.

To get the perturbation, we should find $\vec{B}$ from $\vec{\mu}$ (see Gasiorowicz page 287) then calculate the energy change in first order perturbation theory $\Delta E = \langle -\vec{\mu}_e \cdot \vec{B} \rangle$. Calculating (see section 22.4.1) the energy shift for $\ell = 0$ states.

$$\Delta E = \frac{e}{m_c} \langle \vec{S} \cdot \vec{B} \rangle = \frac{4}{3} (Z \alpha)^4 \left( \frac{m}{M_N} \right) \left( \frac{m c^2}{n^3} \right) g_N \frac{1}{n^3} \frac{\vec{S} \cdot \vec{I}}{\hbar^2}$$

Now, just as in the case of the $\vec{L} \cdot \vec{S}$, spin-orbit interaction, we will define the total angular momentum

$$\vec{F} = \vec{S} + \vec{I}.$$
It is in the states of definite \( f \) and \( m_f \) that the hyperfine perturbation will be diagonal. In essence, we are doing degenerate state perturbation theory. We could diagonalize the 4 by 4 matrix for the perturbation to solve the problem or we can use what we know to pick the right states to start with. Again like the spin orbit interaction, the **total angular momentum states** will be the right states because we can write the perturbation in terms of quantum numbers of those states.

\[
\hat{S} \cdot \hat{I} = \frac{1}{2} \left( E^2 - S^2 - I^2 \right) = \frac{1}{2} \hbar^2 \left( f(f + 1) - \frac{3}{4} \right)
\]

\[
\Delta E = \frac{2}{3} (Z \alpha)^4 \left( \frac{m_e}{M_N} \right) (mc^2) g_N \frac{1}{\hbar^2} \left( f(f + 1) - \frac{3}{2} \right) \equiv \frac{A}{\Delta} \left( f(f + 1) - \frac{3}{2} \right)
\]

For the hydrogen ground state we are just adding two spin \( \frac{1}{2} \) particles so the possible values are \( f = 0, 1 \).

* See Example 22.3.1: The Hyperfine Splitting of the Hydrogen Ground State.*

The transition between the two states gives rise to EM waves with \( \lambda = 21 \) cm.

### 22.2 Hyperfine Splitting in a B Field

If we apply a B-field the states will split further. As usual, we choose our coordinates so that the field is in \( \hat{z} \) direction. The perturbation then is

\[
W_z = -\hat{B} \cdot (\hat{\mu}_L + \hat{\mu}_S + \hat{\mu}_I) = \frac{\mu_B B}{\hbar} (L_z + 2S_z) + \frac{g\mu_N}{\hbar} BI_z
\]

where the magnetic moments from orbital motion, electron spin, and nuclear spin are considered for now. Since we have already specialized to \( s \) states, we can drop the orbital term. For fields achievable in the laboratory, we can **neglect the nuclear magnetic moment** in the perturbation. Then we have

\[
W_z = 2\mu_B B \frac{S_z}{\hbar}.
\]

As an examples of perturbation theory, we will work this problem for weak fields, for strong fields, and also work the general case for intermediate fields. Just as in the Zeeman effect, **if one perturbation is much bigger than another**, we choose the set of states in which the larger perturbation is diagonal. In this case, the hyperfine splitting is diagonal in states of definite \( f \) while the above perturbation due to the B field is diagonal in states of definite \( m_s \). For a weak field, the hyperfine dominates and we use the states of definite \( f \). For a strong field, we use the \( m_s, m_f \) states. If the two perturbations are of the same order, we must diagonalize the full perturbation matrix. This calculation will always be correct but more time consuming.

We can estimate the field at which the perturbations are the same size by comparing \( \mu_B B \) to \( \frac{2}{3} \alpha^4 \frac{m_s m_f c^2 g_N}{\hbar} = 2.9 \times 10^{-6} \). The weak field limit is achieved if \( B \ll 500 \) gauss.
* See Example 22.3.2: The Hyperfine Splitting in a Weak B Field.*

The result of this example is quite simple \( E = E_{n00} + \frac{A}{2} (f(f + 1) - \frac{3}{2}) + \mu_B B m_f \). It has the hyperfine term we computed before and adds a term proportional to \( B \) which depends on \( m_f \).

In the strong field limit we use states \( |m_s, m_i \rangle \) and treat the hyperfine interaction as a perturbation. The unperturbed energies of these states are \( E = E_{n00} + 2\mu_B B m_s + g \mu_N B m_f \). We kept the small term due to the nuclear moment in the B field without extra effort.

* See Example 22.3.3: The Hyperfine Splitting in a Strong B Field.*

The result in this case is

\[
E = E_{n00} + 2\mu_B B m_s + g \mu_N B m_f + A m_s m_f.
\]

Finally, we do the full calculation.

* See Example 22.3.4: The Hyperfine Splitting in an Intermediate B Field.*

The general result consists of four energies which depend on the strength of the B field. Two of the energy eigenstates mix in a way that also depends on B. The four energies are

\[
E = E_{n00} + \frac{A \hbar^2}{4} \pm \mu_B B
\]

and

\[
E = E_{n00} - \frac{A \hbar^2}{4} \pm \sqrt{\left(\frac{A \hbar^2}{2}\right)^2 + (\mu_B B)^2}.
\]

These should agree with the previous calculations in the two limits: B small, or B large. The figure shows how the eigenenergies depend on B.
We can make a more general calculation, in which the interaction of the nuclear magnetic moment is of the same order as the electron. This occurs in muonic hydrogen or positronium. * See Example 22.3.6: The Hyperfine Splitting in an Intermediate B Field.*

### 22.3 Examples

#### 22.3.1 Splitting of the Hydrogen Ground State

The ground state of Hydrogen has a spin \( \frac{1}{2} \) electron coupled to a spin \( \frac{1}{2} \) proton, giving total angular momentum state of \( f = 0, 1 \). We have computed in first order perturbation theory that

\[
\Delta E = \frac{2}{3} (Z \alpha)^4 \left( \frac{m}{M_N} \right) (mc^2) g_N \frac{1}{n^3} \left( f(f + 1) - \frac{3}{2} \right).
\]

The energy difference between the two hyperfine levels determines the wave length of the radiation emitted in hyperfine transitions.

\[
\Delta E_f=1 - \Delta E_f=0 = \frac{4}{3} (Z \alpha)^4 \left( \frac{m}{M_N} \right) (mc^2) g_N \frac{1}{n^3}
\]

For \( n = 1 \) Hydrogen, this gives
\[ \Delta E_{f=1} - \Delta E_{f=0} = \frac{4}{3} \left( \frac{1}{137} \right)^4 \left( \frac{.51 \times 10^6}{938} \right) = 5.84 \times 10^{-6} \text{ eV} \]

Recall that at room temperature, \( k_B T \) is about \( \frac{1}{40} \text{ eV} \), so the states have about equal population at room temperature. Even at a few degrees Kelvin, the upper state is populated so that transitions are possible. The wavelength is well known.

\[ \lambda = 2\pi \frac{\hbar c}{E} = \frac{2\pi \frac{1973}{5.84 \times 10^{-6}}}{2} \text{\AA} = 2 \times 10^9 \text{\AA} = 21.2 \text{ cm} \]

This transition is seen in interstellar gas. The \( f = 1 \) state is excited by collisions. Electromagnetic transitions are slow because of the selection rule \( \Delta \ell = \pm 1 \) we will learn later, and because of the small energy difference. The \( f = 1 \) state does emit a photon to de-excite and those photons have a long mean free path in the gas.

### 22.3.2 Hyperfine Splitting in a Weak B Field

Since the field is weak we work in the states \( | f m_f \rangle \) in which the hyperfine perturbation is diagonal and compute the matrix elements for \( W_z = \mu_B B \sigma_z \). But to do the computation, we will have to write those states in terms of \( | m_s, m_i \rangle \) which we will abbreviate like \( | + - \rangle \), which means the electron’s spin is up and the proton’s spin is down.

\[
\begin{align*}
\sigma_z |11 \rangle &= \sigma_z |++ \rangle = |11 \rangle \\
\sigma_z |1 -1 \rangle &= \sigma_z |-- \rangle = -|1 -1 \rangle \\
\sigma_z |10 \rangle &= \sigma_z \frac{1}{\sqrt{2}} (|+ - \rangle + | - + \rangle) = \frac{1}{\sqrt{2}} (|+ - \rangle - | - + \rangle) = |00 \rangle \\
\sigma_z |00 \rangle &= \sigma_z \frac{1}{\sqrt{2}} (|+ - \rangle - | - + \rangle) = \frac{1}{\sqrt{2}} (|+ - \rangle + | - + \rangle) = |10 \rangle
\end{align*}
\]

Now since the three \( (f = 1) \) states are degenerate, we have to make sure all the matrix elements between those states are zero, otherwise we should bite the bullet and do the full problem as in the intermediate field case. The \( f = 1 \) matrix is diagonal, as we could have guessed.

\[
\mu_B B \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}
\]

The only nonzero connection between states is between \( f = 1 \) and \( f = 0 \) and we are assuming the hyperfine splitting between these states is large compared to the matrix element.

So the full answer is

\[ E_z^{(1)} = \mu_B B m_f \]

which is correct for both \( f \) states.
### 22.3.3 Hydrogen in a Strong B Field

We need to compute the matrix elements of the hyperfine perturbation using $|m_s m_i\rangle$ as a basis with energies $E = E_{n\infty} + 2\mu_B B m_s$. The perturbation is

$$H_{hf} = A \vec{S} \cdot \vec{I}$$

where $A = \frac{4}{3}(Z\alpha)^4 \left( \frac{m_e}{m_N} \right) m_e c^2 g_N \frac{1}{\hbar^2} \frac{1}{r^3}$.

Recalling that we can write

$$\vec{S} \cdot \vec{I} = I_z S_z + \frac{1}{2} I_+ S_+ + \frac{1}{2} I_- S_-,$$

the matrix elements can be easily computed. Note that the terms like $I_- S_+$ which change the state will give zero.

$$A \langle + - | \vec{I} \cdot \vec{S} | + - \rangle = A \langle + - | I_z S_z + \frac{1}{2} I_+ S_+ + \frac{1}{2} I_- S_- | + - \rangle = -A \frac{\hbar^2}{4}$$

$$\langle - + | H_{hf} | - + \rangle = -A \frac{\hbar^2}{4}$$

$$\langle + + | H_{hf} | + + \rangle = A \frac{\hbar^2}{4}$$

$$\langle - - | H_{hf} | - - \rangle = A \frac{\hbar^2}{4}$$

We can write all of these in one simple formula that only depends on relative sign of $m_s$ and $m_i$.

$$E = E_{n\infty} + 2\mu_B B m_s = E_{n\infty} + 2\mu_B B m_s + A \frac{\hbar^2}{4} (m_s m_i)$$

### 22.3.4 Intermediate Field

Now we will work the full problem with no assumptions about which perturbation is stronger. This is really not that hard so if we were just doing this problem on the homework, this assumption free method would be the one to use. The reason we work the problem all three ways is as an example of how to apply degenerate state perturbation theory to other problems.

We continue on as in the last section but work in the states of $|f m_f\rangle$. The matrix for $\langle f m_f | H_{hf} + H_B | f' m'_f \rangle$ is

$$
\begin{pmatrix}
1 & 1 & 1 & 1 & 1 & 1 \\
1 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
$$

$$
\left( \frac{\Delta \hbar^2}{4} + \mu_B B \right) \\
0 \\
0 \\
0 \\
0 \\
0 \\
\mu_B B \\
\mu_B B \\
\mu_B B \\
\frac{3\Delta \hbar^2}{4} \\
\frac{3\Delta \hbar^2}{4} \\
\frac{3\Delta \hbar^2}{4}
\right)
$$
The top part is already diagonal so we only need to work in bottom right 2 by 2 matrix, solving the eigenvalue problem.

\[
\begin{pmatrix}
  A & B \\
  B & -3A
\end{pmatrix}
\begin{pmatrix}
a \\
b
\end{pmatrix}
= E
\begin{pmatrix}
a \\
b
\end{pmatrix}
\quad \text{where} \quad A \equiv \frac{4\alpha^2}{4} \\
B \equiv \mu_B B
\]

Setting the determinant equal to zero, we get

\[(A - E)(-3A - E) - B^2 = 0.\]

\[E^2 + 2AE - 3A^2 - B^2 = 0\]

\[E = \frac{-2A \pm \sqrt{4A^2 + 4(3A^2 + B^2)}}{2} = -A \pm \sqrt{A^2 + (3A^2 + B^2)}
\]

\[= -A \pm \sqrt{4A^2 + B^2}\]

The eigenvalues for the \(m_f = 0\) states, which mix differently as a function of the field strength, are

\[E = -\frac{\mathcal{A} \hbar^2}{4} \pm \sqrt{\left(\frac{\mathcal{A} \hbar^2}{2}\right)^2 \left(\mu_B B\right)^2}\]

The eigenvalues for the other two states which remain eigenstates independent of the field strength are

\[\frac{\mathcal{A} \hbar^2}{4} + \mu_B B\]
and

\[\frac{\mathcal{A} \hbar^2}{4} - \mu_B B.\]

### 22.3.5 Positronium

Positronium, the Hydrogen-like bound state of an electron and a positron, has a "hyperfine" correction which is as large as the fine structure corrections since the magnetic moment of the positron is the same size as that of the electron. It is also an interesting laboratory for the study of Quantum Physics. The two particles bound together are symmetric in mass and all other properties. Positronium can decay by annihilation into two or more photons.

In analyzing positronium, we must take some care to correctly handle the relativistic correction in the case of a reduced mass much different from the electron mass and to correctly handle the large magnetic moment of the positron.

The zero order energy of positronium states is

\[E_n = \frac{1}{2} \mathcal{A} \mu e^2 \frac{1}{\mathcal{r}^2}\]

where the reduced mass is given by \(\mu = \frac{m_e m_p}{m_e + m_p}\).

The relativistic correction must take account of both the motion of the electron and the positron. We use \(\mathcal{r} \equiv \mathcal{r}_1 - \mathcal{r}_2\) and \(\mathcal{p} = \mu \mathcal{\dot{r}} = \frac{\mathcal{p}_1 - \mathcal{p}_2}{2}\). Since the electron and positron are of equal mass, they are
always exactly oposite each other in the center of mass and so the momentum vector we use is easily related to an individual momentum.

\[ \vec{p} = \frac{\vec{p}_1 - \vec{p}_2}{2} = \vec{p}_1 \]

We will add the relativistic correction for both the electron and the positron.

\[ H_{rel} = -\frac{1}{8}\frac{p_1^4 + p_2^4}{m^3c^2} - \frac{1}{4}\frac{p^4}{m^3c^2} = -\frac{1}{32}\frac{p^4}{\mu^2c^2} \left( \frac{p}{2\mu} \right)^2 \]

This is just half the correction we had in Hydrogen (with \( m_e \) essentially replaced by \( \mu \)).

The spin-orbit correction should be checked also. We had \( H_{SO} = \frac{ge}{2m\mu c^2} \vec{S} \cdot \vec{\nabla} \phi \) as the interaction between the spin and the B field produced by the orbital motion. Since \( \vec{p} = \mu \vec{v} \), we have \( H_{SO} = \frac{ge^2}{2m\mu c^2} \vec{S} \cdot \vec{\nabla} \phi \)

for the electron. We just need to add the positron. A little thinking about signs shows that we just at the positron spin. Lets assume the Thomas precession is also the same. We have the same formula as in the fine structure section except that we have \( m\mu \) in the denominator. The final formula then is

\[ H_{SO} = \frac{1}{2}\frac{ge^2}{2m\mu c^2} \vec{L} \cdot \left( \vec{S}_1 + \vec{S}_2 \right) = \frac{e^2}{2}\frac{\vec{L} \cdot \left( \vec{S}_1 + \vec{S}_2 \right)}{\mu c^2} \]

again just one-half of the Hydrogen result if we write everything in terms of \( \mu \) for the electron spin, but, we add the interaction with the positron spin.

The calculation of the spin-spin (or hyperfine) term also needs some attention. We had

\[ \Delta E_{SS} = \frac{2}{3}\frac{Z^2 \alpha g_N}{m_e M_N c^2} \vec{S}_1 \cdot \vec{S}_2 \left( \frac{\alpha m_e c^3}{\hbar} \right)^3 \]

where the masses in the deominator of the first term come from the magnetic moments and thus are correctly the mass of the particle and the mass in the last term comes from the wavefunction and should be replaced by \( \mu \). For positronium, the result is

\[ \Delta E_{SS} = \frac{2}{3}\frac{e^2}{2m^2c^2} \vec{S}_1 \cdot \vec{S}_2 \left( \frac{\alpha m_e c^3}{\hbar} \right)^3 = \frac{2}{3}\frac{e^2}{2m^2c^2} \vec{S}_1 \cdot \vec{S}_2 \left( \frac{\alpha m_e c^3}{\hbar} \right)^3 = \frac{32}{3}\frac{1}{\alpha^4 \mu c^2} \frac{1}{\hbar^2} \left[ \vec{S}_1 \cdot \vec{S}_2 \right] \]

22.3.6 Hyperfine and Zeeman for H, muonium, positronium

We are able to set up the full hyperfine (plus B field) problem in a general way so that different hydrogen-like systems can be handled. We know that as the masses become more equal, the hyperfine interaction becomes more important.

Let’s define our perturbation \( W \) as

\[ W = \mathcal{A} \vec{S}_1 \cdot \vec{S}_2 + w_1 S_{1z} + w_2 S_{2z} \]
Here, we have three constants that are determined by the strength of the interactions. We include the interaction of the “nuclear” magnetic moment with the field, which we have so far neglected. This is required because the positron, for example, has a magnetic moment equal to the electron so that it could not be neglected.

\[
\begin{pmatrix}
  1 & 1 \\
  1 & -1 \\
  1 & 0 \\
  0 & 0
\end{pmatrix}
\begin{pmatrix}
  \frac{A^2}{4} + \frac{\hbar}{2}(w_1 + w_2) \\
  0 \\
  \frac{A^2}{4} - \frac{\hbar}{2}(w_1 + w_2) \\
  \frac{\hbar}{2}(w_1 - w_2)
\end{pmatrix}
\begin{pmatrix}
  0 \\
  0 \\
  \frac{A^2}{4} + \frac{\hbar^2}{2}(w_1 - w_2) \\
  -\frac{3A^2}{4}
\end{pmatrix}
\]

\[
E_3 = -\frac{A^2}{4} + \sqrt{\left(\frac{A^2}{2}\right)^2 + \left(\frac{\hbar^2}{2}(w_1 - w_2)\right)^2}
\]

\[
E_4 = -\frac{A^2}{4} - \sqrt{\left(\frac{A^2}{2}\right)^2 + \left(\frac{\hbar^2}{2}(w_1 - w_2)\right)^2}
\]

Like previous hf except now we take (proton) other \( \vec{B} \cdot \vec{S} \) term into account.

### 22.4 Derivations and Computations

#### 22.4.1 Hyperfine Correction in Hydrogen

We start from the magnetic moment of the nucleus

\[
\vec{\mu} = \frac{Ze g_N \vec{r}}{2M_N c I}.
\]

Now we use the classical vector potential from a point dipole (see (green) Jackson page 147)

\[
\vec{A}(\vec{r}) = -(\vec{\mu} \times \vec{\nabla}) \frac{1}{r}.
\]

We compute the field from this.

\[
\vec{B} = \vec{\nabla} \times \vec{A}
\]

\[
B_k = \frac{\partial A_j}{\partial x_i} \epsilon_{ijk} = -\frac{\partial}{\partial x_i} \mu_m \epsilon_{mnj} \frac{1}{r} \epsilon_{ijk} = -\mu_m \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_n} (-\epsilon_{mnj} \epsilon_{ijk}) \frac{1}{r} \\
= -\mu_m \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_n} (\delta_{km} \delta_{ln} - \delta_{kn} \delta_{lm}) \frac{1}{r} = -\left( \mu_k \frac{\partial}{\partial x_i} - \mu_l \frac{\partial}{\partial x_i} \right) \frac{1}{r} \\
\vec{B} = -\left( \vec{\mu} \nabla^2 \frac{1}{r} - \vec{\nabla}(\vec{\mu} \cdot \vec{\nabla}) \frac{1}{r} \right)
\]

Then we compute the energy shift in first order perturbation theory for s states.

\[
\Delta E = \left( \frac{e}{m_e c} \frac{\vec{S} \cdot \vec{\nabla}}{r} \right) = -\frac{Ze g_N}{2m_e M_N c^2} \left( \vec{S} \cdot \vec{I} \left( \nabla^2 \frac{1}{r} \right) + \left( S_i I_j \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} \frac{1}{r} \right) \right)
\]
The second term can be simplified because of the spherical symmetry of s states. (Basically the derivative with respect to \( x \) is odd in \( x \) so when the integral is done, only the terms where \( i = j \) are nonzero).

\[
\int d^3r \ |\phi_{n\ell_{\text{odd}}}(\vec{r})|^2 \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} \frac{1}{r} = \frac{\delta_{ij}}{3} \int d^3r \ |\phi_{n\ell_{\text{odd}}}(\vec{r})|^2 \nabla^2 \frac{1}{r}.
\]

So we have
\[
\Delta E = -\frac{2}{3} \frac{Z e^2 g_{\text{N}}}{2 m_e M_{\text{N}} c^2} \vec{s} \cdot \vec{I} \left\langle \nabla^2 \frac{1}{r} \right\rangle.
\]

Now working out the \( \nabla^2 \) term in spherical coordinates,
\[
\left( \frac{\partial^2}{\partial r^2} + \frac{2 \partial}{r \partial r} \right) \frac{1}{r} = \frac{2}{r^3} + 2 \left( -\frac{1}{r^2} \right) = 0
\]
we find that it is zero everywhere but we must be careful at \( r = 0 \).

To find the effect at \( r = 0 \) we will integrate.
\[
\int_{r=0}^{\varepsilon} \frac{\nabla^2 \frac{1}{r}}{r} d^3r = \int_{r=0}^{\varepsilon} \vec{\nabla} \cdot \left( \nabla \frac{1}{r} \right) d^3r = \int \left( \nabla \frac{1}{r} \right) \cdot \vec{dS} = \int \frac{\partial}{\partial r} \frac{1}{r} dS
\]
\[
= \int_{r=0}^{\varepsilon} \frac{-1}{r^2} dS = (4\pi \varepsilon^2) \left( -\frac{1}{\varepsilon^2} \right) = -4\pi
\]
So the integral is nonzero for any region including the origin, which implies
\[
\left( \nabla^2 \frac{1}{r} \right) = -4\pi \delta^3(\vec{r}).
\]

We can now evaluate the expectation value.
\[
\Delta E = -\frac{2}{3} \frac{Z e^2 g_{\text{N}}}{2 m_e M_{\text{N}} c^2} \vec{s} \cdot \vec{I} \left( -4\pi |\phi_{n\ell_{\text{odd}}}(0)|^2 \right)
\]
\[
4\pi |\phi_{n\ell_{\text{odd}}}(0)|^2 = |R_{n\ell_{\text{odd}}}(0)|^2 = \frac{4}{n^3} \left( \frac{Z m_e c}{\hbar} \right)^3
\]
\[
\Delta E = \frac{2}{3} \frac{Z e^2 g_{\text{N}}}{2 m_e M_{\text{N}} c^2} \vec{s} \cdot \vec{I} \frac{4}{n^3} \left( \frac{Z m_e c}{\hbar} \right)^3
\]
Simply writing the \( e^2 \) in terms of \( \alpha \) and regrouping, we get
\[
\Delta E = \frac{4}{3} (Z\alpha)^4 \left( \frac{m_e}{M_N} \right) (m_e c^2) g_{\text{N}} \frac{1}{n^3} \frac{\vec{s} \cdot \vec{I}}{\hbar^2}.
\]
We will sometimes group the constants such that
\[
\Delta E \equiv \mathcal{A} \vec{s} \cdot \vec{I}.
\]
(The textbook has numerous mistakes in this section.)
22.5 Homework Problems

1. Calculate the shifts in the hydrogen ground states due to a 1 kilogauss magnetic field.

2. Consider positronium, a hydrogen-like atom consisting of an electron and a positron (anti-electron). Calculate the fine structure of positronium for \( n = 1 \) and \( n = 2 \). Determine the hyperfine structure for the ground state. Compute the energy shifts in eV.

3. List the spectroscopic states allowed that arise from combining \( (s = \frac{1}{2}, \ l = 1) \), \( (s = 2, \ l = 2) \), \( (s_1 = \frac{1}{2}, \ s_2 = 1 \) and \( l = 4 \).

22.6 Sample Test Problems

1. Calculate the energy shifts to the four hyperfine ground states of hydrogen in a weak magnetic field. (The field is weak enough so that the perturbation is smaller than the hyperfine splitting.)

2. Calculate the splitting for the ground state of positronium due to the spin-spin interaction between the electron and the positron. Try to correctly use the reduced mass where required but don’t let this detail keep you from working the problem.

3. A muonic hydrogen atom (proton plus muon) is in a relative 1\( s \) state in an external magnetic field. Assume that the perturbation due to the hyperfine interaction and the magnetic field is given by \( W = \mu S_1 \cdot S_2 + \omega_{1z} S_{1z} + \omega_{2z} S_{2z} \). Calculate the energies of the four nearly degenerate ground states. Do not assume that any terms in the Hamiltonian are small.

4. A hydrogen atom in the ground state is put in a magnetic field. Assume that the energy shift due to the B field is of the same order as the hyperfine splitting of the ground state. Find the eigenenergies of the (four) ground states as a function of the B field strength. Make sure you define any constants (like \( A \)) you use in terms of fundamental constants.
23 The Helium Atom

Hydrogen has been a great laboratory for Quantum Mechanics. After Hydrogen, Helium is the simplest atom we can use to begin to study atomic physics. Helium has two protons in the nucleus ($Z = 2$), usually two neutrons ($A = 4$), and two electrons bound to the nucleus.

This material is covered in Gasiorowicz Chapters 18, in Cohen-Tannoudji et al. Complement $B_{XIV}$, and briefly in Griffiths Chapter 7.

23.1 General Features of Helium States

We can use the hydrogenic states to begin to understand Helium. The Hamiltonian has the same terms as Hydrogen but has a large perturbation due to the repulsion between the two electrons.

\[ H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|} \]

We can write this in terms of the ($Z = 2$) Hydrogen Hamiltonian for each electron plus a perturbation,

\[ H = H_1 + H_2 + V \]

where $V(r_1, r_2) = \frac{e^2}{|r_1 - r_2|}$. Note that $V$ is about the same size as the rest of the Hamiltonian so first order perturbation theory is unlikely to be accurate.

For our zeroth order energy eigenstates, we will use product states of Hydrogen wavefunctions.

\[ u(r_1, r_2) = \phi_{n_1, l_1, m_1}(r_1) \phi_{n_2, l_2, m_2}(r_2) \]

These are not eigenfunctions of $H$ because of $V$, the electron coulomb repulsion term. Ignoring $V$, the problem separates into the energy for electron 1 and the energy for electron 2 and we can solve the problem exactly.

\[ (H_1 + H_2)u = Eu \]

We can write these zeroth order energies in terms of the principal quantum numbers of the two electrons, $n_1$ and $n_2$. Recalling that there is a factor of $Z^2 = 4$ in these energies compared to hydrogen, we get

\[ E = E_{n_1} + E_{n_2} = \frac{1}{2} Z^2 \alpha^2 m_e c^2 \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) = -54.4 \text{ eV} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right). \]

\[ E_{11} = E_{2s} = -108.8 \text{ eV} \]

\[ E_{12} = E_{1st} = -68.0 \text{ eV} \]

\[ E_{1\infty} = E_{ionization} = -54.4 \text{ eV} \]

\[ E_{22} = -27.2 \text{ eV} \]

Note that $E_{22}$ is above ionization energy, so the state can decay rapidly by ejecting an electron.
Now let's look at the (anti) symmetry of the states of two identical electrons. For the ground state, the spatial state is symmetric, so the spin state must be antisymmetric \( \Rightarrow s = 0 \).

\[
\begin{align*}
 u_0 &= \phi_{100}\phi_{100} \frac{1}{\sqrt{2}} (\chi^+ \chi^- - \chi^- \chi^+)
\end{align*}
\]

For excited states, we can make either symmetric or antisymmetric space states.

\[
\begin{align*}
 u_1^{(s)} &= \frac{1}{\sqrt{2}} (\phi_{100}\phi_{2\ell m} + \phi_{2\ell m}\phi_{100}) \frac{1}{\sqrt{2}} (\chi^+ \chi^- - \chi^- \chi^+)
\end{align*}
\]

\[
\begin{align*}
 u_1^{(t)} &= \frac{1}{\sqrt{2}} (\phi_{100}\phi_{2\ell m} - \phi_{2\ell m}\phi_{100}) \chi^+ \chi^+
\end{align*}
\]

The first state is \( s = 0 \) or spin singlet. The second state is \( s = 1 \) or spin triplet and has three \( m_s \) states. Only the +1 state is shown. Because the large correction due to electron repulsion is much larger for symmetric space states, the spin of the state determines the energy.

We label the states according to the spin quantum numbers, singlet or triplet. We will treat \( V \) as a perturbation. It is very large, so first order perturbation theory will be quite inaccurate.
23.2 The Helium Ground State

Calculating the first order correction to the ground state is simple in principle.

\[
\Delta E_{gs} = \langle \Phi_0 | V | \Phi_0 \rangle = \int d^3 r_1 d^3 r_2 \phi_{100}(\mathbf{r}_1) \phi_{100}(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = 5 \frac{Z e^2}{8 a_0} = 5 \frac{Z}{4} \left(\frac{1}{2} \alpha^2 mc^2\right) = 5 \frac{Z}{4} (13.6) = 34 \text{ eV}
\]

The calculation (see section 23.7.1) of the energy shift in first order involves an integral over the coordinates of both electrons.

So the ground state energy to first order is

\[
E_{gs} = -108.8 + 34 = -74.8 \text{ eV}
\]

compared to -78.975 eV from experiment. A 10% error is not bad considering the size of the perturbation. First order perturbation theory neglects the change in the electron’s wave function due to screening of the nuclear charge by the other electron. Higher order perturbation theory would correct this, however, it is hard work doing that infinite sum. We will find a better way to improve the calculation a bit.

23.3 The First Excited State(s)

Now we will look at the energies of the excited states. The Pauli principle will cause big energy differences between the different spin states, even though we neglect all spin contribution in \( H_1 \). This effect is called the exchange interaction. In the equation below, the \( s \) stands for singlet corresponding to the plus sign.

\[
E_{1st}^{(s,t)} = \frac{e^2}{2} \left\langle \phi_{100} \phi_{2t} \pm \phi_{t} \phi_{100} \right| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \left| \phi_{100} \phi_{2t} \pm \phi_{t} \phi_{100} \right\rangle = \frac{e^2}{2} \left\{ 2 \left| \phi_{100} \phi_{2t} \pm \phi_{t} \phi_{100} \right| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\} = J_{2t} \pm K_{2t}
\]

It’s easy to show that \( K_{2t} > 0 \). Therefore, the spin triplet energy is lower. We can write the energy in terms of the Pauli matrices:

\[
\begin{align*}
\vec{S}_1 \cdot \vec{S}_2 &= \frac{1}{2}(S^2 - S_1^2 - S_2^2) = \frac{1}{2} \left[ s(s + 1) - \frac{3}{2} \right] \hbar^2 \\
\vec{\sigma}_1 \cdot \vec{\sigma}_2 &= 4 \vec{S}_1 \cdot \vec{S}_2 / \hbar^2 = 2 \left[ s(s + 1) - \frac{3}{2} \right] = \begin{cases} 1 \text{ triplet} \\ -3 \text{ singlet} \end{cases} \\
\frac{1}{2} \left( 1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2 \right) &= \begin{cases} 1 \text{ triplet} \\ -1 \text{ singlet} \end{cases} \\
E_{1st}^{(s,t)} &= J_{nt} - \frac{1}{2} \left( 1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2 \right) K_{nt}
\end{align*}
\]

Thus we have a large effective spin-spin interaction entirely due to electron repulsion. There is a large difference in energy between the singlet and triplet states. This is due to the exchange antisymmetry and the effect of the spin state on the spatial state (as in ferromagnetism).
The first diagram below shows the result of our calculation. All states increase in energy due to the Coulomb repulsion of the electrons. Before the perturbation, the first excited state is degenerate. After the perturbation, the singlet and triplet spin states split significantly due to the symmetry of the spatial part of the wavefunction. We designate the states with the usual spectroscopic notation.

\[ \Delta \ell = \pm 1 \]
\[ \Delta s = 0 \]

In addition to the large energy shift between the singlet and triplet states, \textit{Electric Dipole} decay selection rules cause decays from triplet to singlet states (or vice-versa) to be suppressed by a large factor (compared to decays from singlet to singlet or from triplet to triplet). This caused early researchers to think that there were two separate kinds of Helium. The diagrams below shows the levels for ParaHelium (singlet) and for OthroHelium (triplet). The second diagrams shows the dominant decay modes.
<table>
<thead>
<tr>
<th>eV</th>
<th>Paraheium</th>
<th>Orthoheium</th>
</tr>
</thead>
<tbody>
<tr>
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<td>4s 4p 4d 4f</td>
<td>4s 4p 4d 4f</td>
</tr>
<tr>
<td>3s</td>
<td>3p 3d 3f</td>
<td>3p 3d 3f</td>
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<td>2p</td>
<td></td>
<td>2p</td>
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<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(h)
23.4 The Variational Principle (Rayleigh-Ritz Approximation)

Because the ground state has the lowest possible energy, we can vary a test wavefunction, minimizing the energy, to get a good estimate of the ground state energy.

\[ H\psi_E = E\psi_E \]

for the ground state \( \psi_E \).

\[ E = \frac{\int \psi_E^*H\psi_E dx}{\int \psi_E^*\psi_E dx} \]

For any trial wavefunction \( \psi \),

\[ E' = \frac{\int \psi^*H\psi dx}{\int \psi^*\psi dx} = \frac{\langle \psi^*|H|\psi \rangle}{\langle \psi|\psi \rangle} \]
We wish to show that $E'$ errors are second order in $\delta \psi$

$$
\Rightarrow \quad \frac{\partial E}{\partial \psi} = 0
$$
at eigenenergies.

To do this, we will add a variable amount of an arbitrary function $\phi$ to the energy eigenstate.

$$
E' = \frac{\langle \psi_E + \alpha \phi | H | \psi_E + \alpha \phi \rangle}{\langle \psi_E + \alpha \phi | \psi_E + \alpha \phi \rangle}
$$

Assume $\alpha$ is real since we do this for any arbitrary function $\phi$. Now we differentiate with respect to $\alpha$ and evaluate at zero.

$$
\left. \frac{dE'}{d\alpha} \right|_{\alpha=0} = \frac{\langle \psi_E | \psi_E \rangle (\langle \phi | H | \psi_E \rangle + \langle \psi_E | H | \phi \rangle) - \langle \psi_E | H | \psi_E \rangle (\langle \phi | \psi_E \rangle + \langle \psi_E | \phi \rangle)}{\langle \psi_E | \psi_E \rangle^2}
$$

$$
= E \langle \phi | \psi_E \rangle + E \langle \psi_E | \phi \rangle - E \langle \phi | \psi_E \rangle - E \langle \psi_E | \phi \rangle = 0
$$

We find that the derivative is zero around any eigenfunction, proving that variations of the energy are second order in variations of the wavefunction.

That is, $E'$ is stationary (2nd order changes only) with respect to variation in $\psi$. Conversely, it can be shown that $E'$ is only stationary for eigenfunctions $\psi_E$. We can use the variational principle to approximately find $\psi_E$ and to find an upper bound on $E_0$.

$$
\psi = \sum_E c_E \psi_E
$$

$$
E' = \sum_E |c_E|^2 E \geq E_0
$$

For higher states this also works if trial $\psi$ is automatically orthogonal to all lower states due to some symmetry (Parity, $\ell$ ...)

* See Example 23.6.1: Energy of 1D Harmonic Oscillator using a polynomial trial wave function.*
* See Example 23.6.2: 1D H.O. using Gaussian.*

### 23.5 Variational Helium Ground State Energy

We will now add one parameter to the hydrogenic ground state wave function and optimize that parameter to minimize the energy. We could add more parameters but let’s keep it simple. We will start with the hydrogen wavefunctions but allow for the fact that one electron “screens” the nuclear charge from the other. We will assume that the wave function changes simply by the replacement

$$
Z \to Z^* < Z.
$$

Of course the $Z$ in the Hamiltonian doesn’t change.

So our ground state trial function is

$$
\psi \to \phi_{100}^{Z^*}(r_1) \phi_{100}^{Z^*}(r_2).
$$
Minimize the energy.

\[
\langle \psi | H | \psi \rangle = \int d^3 r_1 d^3 r_2 \phi_{100}^*(\mathbf{r}_1) \phi_{100} (\mathbf{r}_2) \left[ \frac{p_1^2}{2m} - \frac{Ze^2}{r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|} \right] \phi_{100} (\mathbf{r}_1) \phi_{100} (\mathbf{r}_2)
\]

We can recycle our previous work to do these integrals. First, replace the \( Z \) in \( H_1 \) with a \( Z^* \) and put in a correction term. This makes the \( H_1 \) part just a hydrogen energy. The correction term is just a constant over \( r \) so we can also write that in terms of the hydrogen ground state energy.

\[
x = \int d^3 r_1 \phi^*_{100} \left( \frac{p_1^2}{2m} - \frac{Z e^2}{r_1} \right) \phi_{100}
= \int d^3 r_1 \phi^*_{100} \left( \frac{p_1^2}{2m} - \frac{Z^* e^2}{r_1} + \frac{(Z^* - Z) e^2}{r_1} \right) \phi_{100}
= Z^*^2 (-13.6 \text{ eV}) + (Z^* - Z) e^2 \int d^3 r_1 |\phi_{100}|^2 \frac{1}{r_1}
= Z^*^2 (-13.6 \text{ eV}) + (Z^* - Z) e^2 \frac{Z^*}{a_0}
= -Z^*^2 \frac{1}{2} \alpha^2 mc^2 + Z^* (Z^* - Z) \alpha^2 mc^2
= \alpha^2 mc^2 \left( Z^* (Z^* - Z) - \frac{1}{2} Z^*^2 \right)
\]

Then we reuse the perturbation theory calculation to get the \( \mathcal{V} \) term.

\[
\langle \psi | H | \psi \rangle = 2[x] + \frac{5}{4} Z^* \left( \frac{1}{2} \alpha^2 mc^2 \right)
= -\frac{1}{2} \alpha^2 mc^2 \left[ 2Z^*^2 - 4Z^* (Z^* - Z) - \frac{5}{4} Z^* \right]
= -\frac{1}{2} \alpha^2 mc^2 \left[ -2Z^*^2 + 4ZZ^* - \frac{5}{4} Z^* \right]
\]

Use the variational principle to determine the best \( Z^* \).

\[
\frac{\partial \langle \psi | H | \psi \rangle}{\partial Z^*} = 0 \quad \Rightarrow \quad -4Z^* + 4Z - \frac{5}{4} = 0
\]

\[
Z^* = Z - \frac{5}{16}
\]

Putting these together we get our estimate of the ground state energy.

\[
E_0 = -\frac{1}{2} \alpha^2 mc^2 \left[ 2 \left( Z - \frac{5}{16} \right)^2 \right] = -77.38 \text{ eV}
\]

(really -78.975 eV).

Now we are within a few percent. We could use more parameters for better results.
23.6 Examples

23.6.1 1D Harmonic Oscillator

Use
\[ \psi = (a^2 - x^2)^2 \quad |x| \leq a \]

and \( \psi = 0 \) otherwise. Recall the actual wave function is \( e^{-m\omega x^2/\hbar^2} \) as a trial wave function. The energy estimate is
\[
E' = \frac{\left\langle (a^2 - x^2)^2 \mid 1 \right\rangle}{\left\langle (a^2 - x^2)^2 \mid (a^2 - x^2)^2 \right\rangle}
\]

We need to do some integrals of polynomials to compute
\[
E' = \frac{3}{2} \frac{\hbar^2}{ma^2} + \frac{1}{22} m\omega^2 a^2.
\]

Now we optimize the parameter.

\[
dE' = \frac{d}{da^2} = -\frac{3}{2} \frac{\hbar^2}{ma^4} + \frac{1}{22} m\omega^2 \Rightarrow a^2 = \sqrt{\frac{33 \hbar^2}{m \omega^2}} = \sqrt{33} \frac{\hbar}{m \omega}
\]

\[
E' = \frac{3}{2} \frac{\hbar \omega}{\sqrt{33}} + \frac{1}{22} m\omega^2 \sqrt{33} \frac{\hbar}{m \omega} = \left( \frac{3}{2\sqrt{33}} + \frac{\sqrt{33}}{22} \right) \hbar \omega = \frac{1}{2} \hbar \omega \left( \frac{\sqrt{33} + \sqrt{33}}{11} \right)
\]

\[
= \frac{1}{2} \hbar \omega \sqrt{\frac{4 \cdot 3}{11}} = \frac{1}{2} \hbar \omega \sqrt{\frac{12}{11}}
\]

This is close to the right answer. As always, it is treated as an upper limit on the ground state energy.

23.6.2 1-D H.O. with exponential wavefunction

As a check of the procedure, take trial function \( e^{-ax^2/2} \). This should give us the actual ground state energy
\[
E' = \frac{\int_{-\infty}^{\infty} \psi^* \left[ \frac{x^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{\hbar m \omega^2 x^2}{2} \psi \right] dx}{\int_{-\infty}^{\infty} \psi^* \psi dx}
\]

\[
= \left\{ \frac{\int_{-\infty}^{\infty} e^{-ax^2} \left[ a^2 x^2 e^{-ax^2} - ae^{-ax^2} \right] dx + \frac{1}{2} \hbar m \omega^2 \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx}{\int_{-\infty}^{\infty} e^{-ax^2} dx} \right\}
\]
\[
E' = \left[ -\frac{a \hbar^2}{4m} + \frac{1}{4a^4} \frac{3}{4} m \omega^2 \right] + \frac{\hbar^2 a}{2m} = \frac{1}{4a^4} \frac{3}{4} m \omega^2 + \frac{\hbar^2}{4m} \\
\frac{\partial E'}{\partial a} = -\frac{m \omega^2}{4a^2} + \frac{\hbar^2}{4m} = 0 \\
4a^2 \hbar^2 = 4m^2 \omega^2 \\
a = \frac{m \omega}{\hbar} \\
\psi = e^{-\frac{m \omega}{\hbar} x^2} \\
E' = \frac{m \omega}{4} \frac{\hbar}{m^2 \omega^2} + \frac{\hbar^2 m \omega}{4m} = \frac{1}{4} \hbar \omega + \frac{1}{4} \hbar \omega
\]

OK.

23.7 Derivations and Computations

23.7.1 Calculation of the ground state energy shift

To calculate the first order correction to the He ground state energy, we need to do this integral.

\[
\Delta E_{gs} = \langle u_0 | V | u_0 \rangle = \int d^3 r_1 d^3 r_2 [\phi_{100}(r_1)]^2 [\phi_{100}(r_2)]^2 \frac{e^2}{|r_1 - r_2|}
\]

First, plug in the Hydrogen ground state wave function (twice).

\[
\Delta E_{gs} = \left[ \frac{1}{4\pi} \left( \frac{Z}{a_0} \right)^3 \right]^2 e^2 \int_0^\infty r_1^2 dr_1 e^{-2Zr_1/a_0} \int_0^\infty r_2^2 dr_2 e^{-2Zr_2/a_0} \int d\Omega_1 \int d\Omega_2 \frac{1}{|r_1 - r_2|}
\]
\[
\frac{1}{|r_1 - r_2|} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta}}
\]

Do the \(d\Omega_1\) integral and prepare the other.

\[
\Delta E_{gs} = \frac{4\pi}{\alpha^2} e^2 \left( \frac{Z}{a_0} \right)^6 \int_0^\infty r_1^2 dr_1 e^{-2Zr_1/a_0} \int_0^\infty r_2^2 dr_2 e^{-2Zr_2/a_0} \int d\phi_2 d\cos \theta_2 \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}}
\]

The angular integrals are not hard to do.

\[
\Delta E_{gs} = \frac{4\pi}{\alpha^2} e^2 \left( \frac{Z}{a_0} \right)^6 \int_0^\infty r_1^2 dr_1 e^{-2Zr_1/a_0} \int_0^\infty r_2^2 dr_2 e^{-2Zr_2/a_0} 2\pi \frac{-2}{2r_1r_2} \sqrt{\frac{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}{r_1^2 + r_2^2 + 2r_1r_2}}
\]

\[
\Delta E_{gs} = \frac{4\pi}{\alpha^2} e^2 \left( \frac{Z}{a_0} \right)^6 \int_0^\infty r_1^2 dr_1 e^{-2Zr_1/a_0} \int_0^\infty r_2^2 dr_2 e^{-2Zr_2/a_0} \left[ -\sqrt{\frac{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}{r_1^2 + r_2^2 + 2r_1r_2}} \right]^{-1}
\]

\[
\Delta E_{gs} = \frac{4\pi}{\alpha^2} e^2 \left( \frac{Z}{a_0} \right)^6 \int_0^\infty r_1^2 dr_1 e^{-2Zr_1/a_0} \int_0^\infty r_2^2 dr_2 e^{-2Zr_2/a_0} \frac{2\pi}{r_1r_2} [-|r_1 - r_2| + (r_1 + r_2)]
\]

\[
\Delta E_{gs} = 8e^2 \left( \frac{Z}{a_0} \right)^6 \int_0^\infty r_1 dr_1 e^{-2Zr_1/a_0} \int_0^\infty r_2 dr_2 e^{-2Zr_2/a_0} (r_1 + r_2 - |r_1 - r_2|)
\]

We can do the integral for \(r_2 < r_1\) and simplify the expression. Because of the symmetry between \(r_1\) and \(r_2\) the rest of the integral just doubles the result.

\[
\Delta E_{gs} = 16e^2 \left( \frac{Z}{a_0} \right)^6 \int_0^\infty r_1 dr_1 e^{-2Zr_1/a_0} \int_0^{r_1} r_2 dr_2 e^{-2Zr_2/a_0} (2r_2)
\]

\[
\Delta E_{gs} = e^2 \left( \frac{Z}{a_0} \right)^6 \int_0^\infty x_1 dx_1 e^{-x_1} \int_0^{x_1} x_2 dx_2 e^{-x_2}
\]

\[
= \frac{Ze^2}{a_0} \int_0^\infty x_1 dx_1 e^{-x_1} \left[ -x_1^2 e^{-x_1} + \int_0^{x_1} 2x_2 dx_2 e^{-x_2} \right]
\]

\[
= \frac{Ze^2}{a_0} \int_0^\infty x_1 dx_1 e^{-x_1} \left[ -x_1^2 e^{-x_1} + 2x_1 e^{-x_1} + 2 \int_0^{x_1} e^{-x_2} dx_2 \right]
\]

\[
= \frac{Ze^2}{a_0} \int_0^\infty x_1 dx_1 e^{-x_1} \left[ -x_1^2 e^{-x_1} + 2x_1 e^{-x_1} + 2 \right]
\]
\[ = \frac{Ze^2}{a_0} \int_0^\infty x_1 dx_1 e^{-x_1} \left\{ -x_1^2 e^{-x_1} - 2x_1 e^{-x_1} - 2(e^{-x_1} - 1) \right\} \]

\[ = -\frac{Ze^2}{a_0} \int_0^\infty \left[ (x_1^3 + 2x_1^2 + 2x_1) e^{-2x_1} - 2x_1 e^{-x_1} \right] dx_1 \]

\[ = -\frac{Ze^2}{a_0} \left[ 3 \frac{3}{8} - \frac{21}{2} \frac{1}{22} + 2 \frac{11}{2} \frac{1}{22} - 2 \frac{11}{1} \right] \]

\[ = -\frac{Ze^2}{a_0} \left[ \frac{3}{8} + \frac{4}{8} + \frac{4}{8} - \frac{16}{8} \right] = + \frac{5 Ze^2}{8 a_0} \]

\[ = \frac{5}{4} Z(13.6 \text{ eV}) \to 34 \text{ eV for } Z=2 \]

### 23.8 Homework Problems

1. Calculate the lowest order energy shift for Helium \( \Delta E_{2J}^{(1)} \) where \( \ell = 0, 1 \).

2. Consider the lowest state of ortho-helium. What is the magnetic moment? That is what is the interaction with an external magnetic field?

3. A proton and neutron are bound together into a deuteron, the nucleus of an isotope of hydrogen. The binding energy is found to be -2.23 MeV for the nuclear ground state, an \( \ell = 0 \) state. Assuming a potential of the form \( V(r) = V_0 e^{-r/r_0} \), with \( r_0 = 2.8 \) Fermis, use the variational principle to estimate the strength of the potential.

4. Use the variational principle with a gaussian trial wave function to prove that a one dimensional attractive potential will always have a bound state.

5. Use the variational principle to estimate the ground state energy of the anharmonic oscillator, \( H = \frac{p^2}{2m} + \lambda x^4 \).

### 23.9 Sample Test Problems

1. We wish to get a good upper limit on the Helium ground state energy. Use as a trial wave function the 1s hydrogen state with the parameter a screened nuclear charge \( Z^* \) to get this limit. Determine the value of \( Z^* \) which gives the best limit. The integral \( \langle (1s)^2 \rangle = \frac{e^2}{[r_i - r_j]} \langle (1s)^2 \rangle = \frac{5}{8} Z^* \alpha^2 mc^2 \) for a nucleus of charge \( Z^* e \).

2. A Helium atom has two electrons bound to a \( Z = 2 \) nucleus. We have to add the coulomb repulsion term (between the two electrons) to the zeroth order Hamiltonian.

\[ H = \frac{p_1^2}{2m} - \frac{Ze^2}{r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|} = H_1 + H_2 + V \]
The first excited state of Helium has one electron in the 1S state and the other in the 2S state. Calculate the energy of this state to zeroth order in the perturbation $V$. Give the answer in eV. The spins of the two electrons can be added to give states of total spin $S$. The possible total spin states are $s = 0$ and $s = 1$. Write out the full first excited Helium state which has $s = 1$ and $m_s = -1$. Include the spatial wave function and don't forget the Pauli principle. Use bra-ket notation to calculate the energy shift to this state in first order perturbation theory. Don't do any integrals.
24 Atomic Physics

This material is covered in Gasiorowicz Chapter 19, and in Cohen-Tannoudji et al. Complement \textit{AIV}.

24.1 Atomic Shell Model

The Hamiltonian for an atom with \( Z \) electrons and protons is

\[
\sum_{i=1}^{Z} \left( \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i>j} \frac{e^2}{|r_i - r_j|} \psi = E\psi.
\]

We have seen that the coulomb repulsion between electrons is a very large correction in Helium and that the three body problem in quantum mechanics is only solved by approximation. The states we have from hydrogen are modified significantly. What hope do we have to understand even more complicated atoms?

The physics of \textit{closed shells} and angular momentum enable us to make sense of even the most complex atoms. Because of the Pauli principle, we can put only one electron into each state. When we have enough electrons to fill a shell, say the 1s or 2p, The resulting electron distribution is spherically symmetric because

\[
\sum_{m=-\ell}^{\ell} |Y_{\ell m}(\theta, \phi)|^2 = \frac{2\ell + 1}{4\pi}.
\]

With all the states filled and the relative phases determined by the antisymmetry required by Pauli, the quantum numbers of the closed shell are determined. There is only one possible state representing a closed shell.

As in Helium, the two electrons in the same spatial state, \( \phi_{n\ell m} \), must by symmetric in space and hence antisymmetric in spin. This implies each pair of electrons has a total spin of 0. Adding these together gives a total spin state with \( s = 0 \), which is antisymmetric under interchange. The spatial state must be totally symmetric under interchange and, since all the states in the shell have the same \( n \) and \( \ell \), it is the different \( m \) states which are symmetrized. This can be shown to give us a total \( \ell = 0 \) state.

So the \textit{closed shell contributes a spherically symmetric charge and spin distribution} with the quantum numbers

\[
s = 0 \\
\ell = 0 \\
j = 0
\]

The closed shell screens the nuclear charge. Because of the \textit{screening}, the potential no longer has a pure \( \frac{1}{r} \) behavior. Electrons which are far away from the nucleus see less of the nuclear charge and shift up in energy. This is a large effect and single electron states with larger \( \ell \) have larger energy. The 4s and 3d states have about the same energy in atoms because of screening.
24.2 The Hartree Equations

The Hartree method allows us to change the 3Z dimensional Schrödinger equation (Z electrons in 3 dimensions) into a 3 dimensional equation for each electron. This equation depends on the wavefunctions of the other electrons but can be solved in a self-consistent way using the variational principle and iterating:

$$\psi = \phi_1(r_1) \phi_2(r_2) \cdots \phi_Z(r_Z)$$

$$\left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + e^2 \sum_{j \neq i} \int d^3r_j \frac{|\phi_j(r_j)|^2}{|r_i - r_j|} \right] \phi_i(r_i) = \varepsilon_i \phi_i(r_i)$$

In the Hartree equation above, $\varepsilon_i$ represents the energy contribution of electron $i$. The term $e^2 \sum_{j \neq i} \int d^3r_j \frac{|\phi_j(r_j)|^2}{|r_i - r_j|}$ represents the potential due to the other electrons in which electron $i$ moves. In this equation we can formally see the effect of screening by the other electrons. The equation is derived (see Gasiorowicz pp 309-311) from the Schrödinger equation using $\psi = \phi_1 \phi_2 \cdots \phi_Z$. Since we will not apply these equations to solve problems, we will not go into the derivation, however, it is useful to know how one might proceed to solve more difficult problems.

An improved formalism known as the Hartree-Fock equations, accounts for the required antisymmetry and gives slightly different results.

24.3 Hund’s Rules

A set of guidelines, known as Hund’s rules, help us determine the quantum numbers for the ground states of atoms. The hydrogenic shells fill up giving well defined $j = 0$ states for the closed shells. As we add valence electrons we follow Hund’s rules to determine the ground state. We get a great simplification by treating nearly closed shells as a closed shell plus positively charged, spin $\frac{1}{2}$ holes. For example, if an atom is two electrons short of a closed shell, we treat it as a closed shell plus two positive holes.)

1. Couple the valence electrons (or holes) to give maximum total spin.

2. Now choose the state of maximum $\ell$ (subject to the Pauli principle. The Pauli principle rather than the rule, often determines everything here.)

3. If the shell is more than half full, pick the highest total angular momentum state $j = \ell + s$ otherwise pick the lowest $j = |\ell - s|$.

This method of adding up all the spins and all the $L$s, is called LS or Russel-Saunders coupling. This method and these rules are quite good until the electrons become relativistic in heavy atoms and spin-orbit effects becomes comparable to the electron repulsion (around $Z=40$). We choose the states in which the total $s$ and the total $\ell$ are good quantum numbers are best for minimizing the overlap of electrons, and hence the positive contribution to the energy.

For very heavy atoms, we add the total angular momentum from each electron first then add up the $J$s. This is called $j$-$j$ coupling. For heavy atoms, electrons are relativistic and the spin-orbit interaction becomes more important than the effect of electron repulsion. Thus we need to use states in which the total angular momentum of each electron is a good quantum number.
We can understand Hund’s rules to some extent. The maximum spin state is symmetric under interchange, requiring an antisymmetric spatial wavefunction which has a lower energy as we showed for Helium. We have not demonstrated it, but, the larger the total \( \ell \) the more lobes there are in the overall electron wavefunction and the lower the effect of electron repulsion. Now the spin orbit interaction comes into play. For electrons with their negative charge, larger \( j \) increases the energy. The reverse is true for holes which have an effective positive charge.

A simpler set of rules has been developed for chemists, who can’t understand addition of angular momentum. It is based on the same principles. The only way to have a totally antisymmetric state is to have no two electrons in the same state. We use the same kind of trick we used to get a feel for addition of angular momentum; that is, we look at the maximum \( z \) component we can get consistent with the Pauli principle. Make a table with space for each of the different \( m_\ell \) states in the outer shell. We can put two electrons into each space, one with spin up and one with spin down. Fill the table with the number of valence electrons according to the following rules.

1. Make as many spins as possible parallel, then compute \( m_s \) and call that \( s \).

2. Now set the orbital states to make maximum \( m_\ell \), and call this \( \ell \), but don’t allow any two electrons to be in the same state (of \( m_s \) and \( m_\ell \)).

3. Couple to get \( j \) as before.

This method is rather easy to use compared to the other where addition of more than two angular momenta can make the symmetry hard to determine.

* See Example 24.6.1: The Boron ground State.
* See Example 24.6.2: The Carbon ground State.
* See Example 24.6.3: The Nitrogen ground State.
* See Example 24.6.4: The Oxygen ground State.

### 24.4 The Periodic Table

The following table gives the electron configurations for the ground states of light atoms.
<table>
<thead>
<tr>
<th>Z</th>
<th>El.</th>
<th>Electron Configuration</th>
<th>$^2S_{1/2}$$^\ast L_j$</th>
<th>Ioniz. Pot.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>(1s)</td>
<td>$^2S_{1/2}$</td>
<td>13.6</td>
</tr>
<tr>
<td>2</td>
<td>He</td>
<td>(1s)$^2$</td>
<td>$^1S_0$</td>
<td>24.6</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>He(2s)</td>
<td>$^2S_{1/2}$</td>
<td>5.4</td>
</tr>
<tr>
<td>4</td>
<td>Be</td>
<td>He (2s)$^2$</td>
<td>$^1S_0$</td>
<td>9.3</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>He (2s)$^2$(2p)</td>
<td>$^2P_{1/2}$</td>
<td>8.3</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>He (2s)$^2$(2p)$^2$</td>
<td>$^3P_0$</td>
<td>11.3</td>
</tr>
<tr>
<td>7</td>
<td>N</td>
<td>He (2s)$^2$(2p)$^3$</td>
<td>$^4S_{1/2}$</td>
<td>14.5</td>
</tr>
<tr>
<td>8</td>
<td>O</td>
<td>He (2s)$^2$(2p)$^4$</td>
<td>$^3P_2$</td>
<td>13.6</td>
</tr>
<tr>
<td>9</td>
<td>F</td>
<td>He (2s)$^2$(2p)$^5$</td>
<td>$^2P_{3/2}$</td>
<td>17.4</td>
</tr>
<tr>
<td>10</td>
<td>Ne</td>
<td>He (2s)$^2$(2p)$^6$</td>
<td>$^1S_0$</td>
<td>21.6</td>
</tr>
<tr>
<td>11</td>
<td>Na</td>
<td>Ne (3s)</td>
<td>$^2S_{1/2}$</td>
<td>5.1</td>
</tr>
<tr>
<td>12</td>
<td>Mg</td>
<td>Ne (3s)$^2$</td>
<td>$^1S_0$</td>
<td>7.6</td>
</tr>
<tr>
<td>13</td>
<td>Al</td>
<td>Ne (3s)$^2$(3p)</td>
<td>$^2P_{1/2}$</td>
<td>6.0</td>
</tr>
<tr>
<td>14</td>
<td>Si</td>
<td>Ne (3s)$^2$(3p)$^2$</td>
<td>$^3P_0$</td>
<td>8.1</td>
</tr>
<tr>
<td>15</td>
<td>P</td>
<td>Ne (3s)$^2$(3p)$^3$</td>
<td>$^4S_{3/2}$</td>
<td>11.0</td>
</tr>
<tr>
<td>16</td>
<td>S</td>
<td>Ne (3s)$^2$(3p)$^4$</td>
<td>$^3P_2$</td>
<td>10.4</td>
</tr>
<tr>
<td>17</td>
<td>Cl</td>
<td>Ne (3s)$^2$(3p)$^5$</td>
<td>$^2P_{3/2}$</td>
<td>13.0</td>
</tr>
<tr>
<td>18</td>
<td>Ar</td>
<td>Ne (3s)$^2$(3p)$^6$</td>
<td>$^1S_0$</td>
<td>15.8</td>
</tr>
<tr>
<td>19</td>
<td>K</td>
<td>Ar (4s)</td>
<td>$^2S_{1/2}$</td>
<td>4.3</td>
</tr>
<tr>
<td>20</td>
<td>Ca</td>
<td>Ar (4s)$^2$</td>
<td>$^1S_0$</td>
<td>6.1</td>
</tr>
<tr>
<td>21</td>
<td>Sc</td>
<td>Ar (4s)$^2$(3d)</td>
<td>$^2D_{3/2}$</td>
<td>6.5</td>
</tr>
<tr>
<td>22</td>
<td>Ti</td>
<td>Ar (4s)$^2$(3d)$^2$</td>
<td>$^3P_2$</td>
<td>6.8</td>
</tr>
<tr>
<td>23</td>
<td>V</td>
<td>Ar (4s)$^2$(3d)$^3$</td>
<td>$^4F_{3/2}$</td>
<td>6.7</td>
</tr>
<tr>
<td>24</td>
<td>Cr</td>
<td>Ar (4s)(3d)$^5$</td>
<td>$^7S_3$</td>
<td>6.7</td>
</tr>
<tr>
<td>25</td>
<td>Mn</td>
<td>Ar (4s)$^2$(3d)$^5$</td>
<td>$^6S_{3/2}$</td>
<td>7.4</td>
</tr>
<tr>
<td>26</td>
<td>Fe</td>
<td>Ar (4s)$^2$(3d)$^6$</td>
<td>$^5D_4$</td>
<td>7.9</td>
</tr>
<tr>
<td>36</td>
<td>Kr</td>
<td>(Ar) (4s)$^2$(3d)$^{10}$(4p)$^6$</td>
<td>$^1S_0$</td>
<td>14.0</td>
</tr>
<tr>
<td>54</td>
<td>Xe</td>
<td>(Kr) (5s)$^2$(4d)$^{10}$(5p)$^6$</td>
<td>$^1S_0$</td>
<td>12.1</td>
</tr>
<tr>
<td>86</td>
<td>Rn</td>
<td>(Xe) (6s)$^2$(4f)$^{14}$(5d)$^{10}$(6p)$^6$</td>
<td>$^1S_0$</td>
<td>10.7</td>
</tr>
</tbody>
</table>

We see that the atomic shells fill up in the order 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p. The effect of screening increasing the energy of higher ℓ states is clear. Its no wonder that the periodic table is not completely periodic.

The **Ionization Potential** column gives the energy in eV needed to remove one electron from the atom, essentially the Binding energy of the last electron. The Ionization Potential peaks for atoms with closed shells, as the electron gains binding energy from more positive charge in the the nucleus without much penalty from repulsion of the other electrons in the shell. As charge is added to the nucleus, the atom shrinks in size and becomes more tightly bound. A single electron outside a closed shell often has the lowest Ionization Potential because it is well screened by the inner electrons. The figure below shows a plot of ionization potential versus Z.
FIG. 7.3. Dependence of the ionization potential of the neutral atom on atomic number [taken from Herzberg (44)].
The periodic table of elements is based on the fact that atoms with the same number of electrons outside a closed shell have similar properties. The rows of the periodic table contain the following states.

1. 1s
2. 2s, 2p
3. 3s, 3p
4. 4s, 3d, 4p
5. 5s, 4d, 5p

Soon after, the periodicity is broken and special “series” are inserted to contain the 4f and 5f shells.

24.5 The Nuclear Shell Model

We see that the atomic shell model works even though the hydrogen states are not very good approximations due to the coulomb repulsion between electrons. It works because of the tight binding and simplicity of closed shells. This is based on angular momentum and the Pauli principle.

Even with the strong nuclear force, a shell model describes important features of nuclei. Nuclei have tightly bound closed shells for both protons and neutrons. Tightly bound nuclei correspond to the most
abundant elements. What elements exist is governed by nuclear physics and we can get a good idea from a simple shell model. Nuclear magic numbers occur for neutron or proton number of 2, 8, 20, 28, 50, 82, and 126, as indicated in the figure below. Nuclei where the number of protons or neutrons is magic are more tightly bound and often more abundant. Heavier nuclei tend to have more neutrons than protons because of the coulomb repulsion of the protons (and the otherwise symmetric strong interactions). Nuclei which are doubly magic are very tightly bound compared to neighboring nuclei. $^{208}_{\text{Pb}}$ is a good example of a doubly magic nucleus with many more protons than neutrons.

Remember, its only hydrogen states which are labeled with a principle quantum number $n = n_r + \ell + 1$. In the nuclear shell model, $n$ refers only to the radial excitation so states like the $1h_{\frac{1}{2}}$ show up in real nuclei and on the following chart. The other feature of note in the nuclear shell model is that the nuclear spin orbit interaction is strong and of the opposite sign to that in atoms. The splitting between states of different $j$ is smaller than that but of the same order as splitting between radial or angular excitations. It is this effect and the shell model for which Maria Mayer got her Nobel prize.

Another feature of nuclei not shown in the table is that the spin-spin force very much favors nucleons
which are paired. So nuclear isotopes with odd numbers of protons or odd numbers of neutrons have less binding energy and nuclei with odd numbers of both protons and neutrons are unstable (with one exception).

24.6 Examples

24.6.1 Boron Ground State

Boron, with \( Z = 5 \) has the 1S and 2S levels filled. They add up to \( j = 0 \) as do all closed shells. The valence electron is in the 2P state and hence has \( \ell = 1 \) and \( s = \frac{1}{2} \). Since the shell is not half full we couple to the the lowest \( j = |\ell - s| = \frac{1}{2} \). So the ground state is \( ^2P_{\frac{1}{2}} \).

\[
\begin{array}{c|c}
 m_\ell & \mathbf{e} \\
 \hline
 1 & \uparrow \\
 0 & \\
 -1 & \\
 \end{array}
\]

\[
s = \sum m_s = \frac{1}{2} \\
\ell = \sum m_\ell = 1
\]

24.6.2 Carbon Ground State

Carbon, with \( Z = 6 \) has the 1S and 2S levels filled giving \( j = 0 \) as a base. It has two valence 2P electrons. Hund’s first rule, maximum total \( s \), tells us to couple the two electron spins to \( s = 1 \). This is the symmetric spin state so we’ll need to make the space state antisymmetric. Hund’s second rule, maximum \( \ell \), doesn’t play a role because only the \( \ell = 1 \) state is antisymmetric. Remember, adding two P states together, we get total \( \ell = 0, 1, 2 \). The maximum state is symmetric, the next antisymmetric, and the \( \ell = 0 \) state is again symmetric under interchange. This means \( \ell = 1 \) is the only option. Since the shell is not half full we couple to the the lowest \( j = |\ell - s| = 0 \). So the ground state is \( ^3P_0 \). The simpler way works with a table.

\[
\begin{array}{c|c}
 m_\ell & \mathbf{e} \\
 \hline
 1 & \uparrow \\
 0 & \uparrow \\
 -1 & \\
 \end{array}
\]

\[
s = \sum m_s = 1 \\
\ell = \sum m_\ell = 1
\]

We can take a look at the excited states of carbon to get an appreciation of Hund’s rules. The following chart shows the states of a carbon atom. For most states, a basis of \((1s)^2(2s)^2(2p)^1\) is assumed and the state of the sixth electron is given. Some states have other excited electrons and are indicated by a superscript. Different \( j \) states are not shown since the splitting is small. Electric dipole transitions are shown changing \( \ell \) by one unit.
The ground state has \( s = 1 \) and \( \ell = 1 \) as we predicted. Other states labeled \( 2p \) are the ones that Hund’s first two rules determined to be of higher energy. They are both spin singlets so its the symmetry of the space wavefunction that is making the difference here.

### 24.6.3 Nitrogen Ground State

Now, with \( Z = 7 \) we have three valence 2P electrons and the shell is half full. Hund’s first rule, maximum total \( s \), tells us to couple the three electron spins to \( s = \frac{3}{2} \). This is again the symmetric spin state so we’ll need to make the space state antisymmetric. We now have the truly nasty problem of figuring out which total \( \ell \) states are totally antisymmetric. All I have to say is \( 3 \otimes 3 \otimes 3 = 7_s \oplus 5_{MS} \oplus 3_{MS} \oplus 5_{MA} \oplus 3_{MA} \oplus 1_A \oplus 3_{MS} \). Here MS means mixed symmetric. That is; it is symmetric under the interchange of two of the electrons but not with the third. Remember, adding two P states together, we get total \( \ell_{12} = 0, 1, 2 \). Adding another P state to each of these gives total \( \ell = 1 \) for \( \ell_{12} = 0, \ell = 0, 1, 2 \) for \( \ell_{12} = 1 \). and \( \ell = 1, 2, 3 \) for \( \ell_{12} = 2 \). Hund’s second rule, maximum \( \ell \), doesn’t play a role, again, because
only the $\ell = 0$ state is totally antisymmetric. Since the shell is just half full we couple to the the lowest $j = |\ell - s| = \frac{3}{2}$. So the ground state is $^4S_{\frac{5}{2}}$.

<table>
<thead>
<tr>
<th>$m_{\ell}$</th>
<th>$e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>↑</td>
</tr>
<tr>
<td>0</td>
<td>↑</td>
</tr>
<tr>
<td>-1</td>
<td>↑</td>
</tr>
</tbody>
</table>

$s = \sum m_s = \frac{3}{2}$

$\ell = \sum m_{\ell} = 0$

The chart of nitrogen states is similar to the chart in the last section. Note that the chart method is clearly easier to use in this case. Our prediction of the ground state is again correct and a few space symmetric states end up a few eV higher than the ground state.
24.6.4 Oxygen Ground State

Oxygen, with \( Z = 8 \) has the 1S and 2S levels filled giving \( j = 0 \) as a base. It has four valence 2P electrons which we will treat as two valence 2P holes. Hund's first rule, maximum total \( s \), tells us to couple the two hole spins to \( s = 1 \). This is the symmetric spin state so we'll need to make the space state antisymmetric. Hund's second rule, maximum \( \ell \), doesn't play a role because only the \( \ell = 1 \) state is antisymmetric. Since the shell is more than half full we couple to the the highest \( j = \ell + s = 2 \). So the ground state is \( ^3P_2 \).

<table>
<thead>
<tr>
<th>( m_\ell )</th>
<th>( e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>↑↓</td>
</tr>
<tr>
<td>0</td>
<td>↑</td>
</tr>
<tr>
<td>-1</td>
<td>↑</td>
</tr>
</tbody>
</table>

\[ s = \sum m_s = 1 \]

\[ \ell = \sum m_\ell = 1 \]

24.7 Homework Problems

1. List the possible spectroscopic states that can arise in the following electronic configurations: \((1s)^2, (2p)^2, (2p)^3, (2p)^4\), and \((3d)^4\). Take the exclusion principle into account. Which should be the ground state?

2. Use Hund's rules to find the spectroscopic description of the ground states of the following atoms: N(\( Z = 7 \)), K(\( Z = 19 \)), Sc(\( Z = 21 \)), Co(\( Z = 27 \)). Also determine the electronic configuration.

3. Use Hund's rules to check the \((S, L, J)\) quantum numbers of the elements with \( Z = 14, 15, 24, 30, 34 \).

24.8 Sample Test Problems

1. Write down the electron configuration and ground state for the elements from \( Z = 1 \) to \( Z = 10 \). Use the standard \( ^{2s+1}L_j \) notation.

2. Write down the ground state (in spectroscopic notation) for the element Oxygen (\( Z = 8 \)).
25 Molecular Physics

In this section, we will study the binding and excitation of simple molecules. Atoms bind into molecules by sharing electrons, thus reducing the kinetic energy. Molecules can be excited in three ways.

- Excitation of electrons to higher states. $E \sim 4 \text{ eV}$
- Vibrational modes (Harmonic Oscillator). Nuclei move slowly in background of electrons. $E \sim 0.1 \text{ eV}$
- Rotational modes ($L = n\hbar$). Entire molecule rotates. $E \sim 0.001 \text{ eV}$

Why don’t atoms have rotational states?
The atomic state already accounts for electrons angular momentum around the nucleus.

About which axes can a molecule rotate?

Do you think identical atoms will make a difference?

This material is covered in Gasiorowicz Chapter 20, and in Cohen-Tannoudji et al. Complements $C_{VI}$, $E_{VII}$, $C_{XI}$.

25.1 The $H_2^+$ Ion

The simplest molecule we can work with is the $H_2^+$ ion. It has two nuclei (A and B) sharing one electron (1).

$$H_0 = \frac{\mu^2}{2m} \frac{1}{r_1A} - \frac{e^2}{r_1B} + \frac{e^2}{R_{AB}}$$

$R_{AB}$ is the distance between the two nuclei.

The lowest energy wavefunction can be thought of as a (anti)symmetric linear combination of an electron in the ground state near nucleus A and the ground state near nucleus B

$$\psi_{\pm} = C_{\pm}(R)[\psi_A \pm \psi_B]$$

where $\psi_A = \sqrt{\frac{1}{\pi a_0^3}} e^{-r_1A/a_0}$ is g.s. around nucleus A. $\psi_A$ and $\psi_B$ are not orthogonal; there is overlap.

We must compute the normalization constant to estimate the energy

$$\frac{1}{C^2_{\pm}} = \langle \psi_A \pm \psi_B | \psi_A \pm \psi_B \rangle = 2 \mp 2\langle \psi_A | \psi_B \rangle = 2 \mp 2S(R)$$

where

$$S(R) \equiv \langle \psi_A | \psi_B \rangle = \left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^3}\right) e^{-R/a_0}$$

These calculations are “straightforward but tedious” (Gasiorowicz).
We can now compute the energy of these states.

\[
\langle H_0 \rangle_\pm = \frac{1}{2[1 \pm S(R)]} \langle \psi_A \pm \psi_B | H_0 | \psi_A \pm \psi_B \rangle \\
= \frac{1}{2[1 \pm S(R)]} \left[ \langle \psi_A | H_0 | \psi_A \rangle + \langle \psi_B | H_0 | \psi_B \rangle \pm \langle \psi_A | H_0 | \psi_B \rangle \pm \langle \psi_B | H_0 | \psi_A \rangle \right] \\
= \frac{\langle \psi_A | H_0 | \psi_A \rangle \pm \langle \psi_A | H_0 | \psi_B \rangle}{1 \pm S(R)}
\]

We can compute the integrals needed.

\[
\langle \psi_A | H_0 | \psi_A \rangle = E_1 + \frac{e^2}{R} \left( 1 + \frac{R}{a_0} \right) e^{-2R/a_0}
\]

\[
\langle \psi_A | H_0 | \psi_B \rangle = \left( E_1 + \frac{e^2}{R} \right) S(R) - \frac{e^2}{a_0} \left( 1 + \frac{R}{a_0} \right) e^{-R/a_0}
\]

We have reused the calculation of \( S(R) \) in the above. Now, we plug these in and rewrite things in terms of \( y = R/a_0 \), the distance between the atoms in units of the Bohr radius.

\[
\langle H_0 \rangle_\pm = \frac{E_1 + \frac{e^2}{R} (1 + R/a_0) e^{-2R/a_0} \pm \left( E_1 + \frac{e^2}{R} \right) S(R) - \frac{e^2}{a_0} (1 + R/a_0) e^{-R/a_0}}{1 \pm S(R)}
\]

\[
\langle H_0 \rangle_\pm = E_1 \frac{1 - (2/y)(1 + y)e^{-2y} \pm [(1 - 2/y)(1 + y + y^2/3)e^{-y} - 2(1 + y)e^{-y}]}{1 \pm (1 + y + y^2/3)e^{-y}}
\]

The symmetric (bonding) state has a large probability for the electron to be found between nuclei. The antisymmetric (antibonding) state has a small probability there, and hence, a much larger energy.

The graph below shows the energies from our calculation for the space symmetric \( (E_g) \) and antisymmetric \( (E_u) \) states as well as the result of a more complete calculation (Exact \( E_g \)) as a function of the distance between the protons \( R \). Our calculation for the symmetric state shows a minimum around 1.3 Angstroms between the nuclei and a Binding Energy of 1.76 eV. We could get a better estimate by introducing some parameters in our trial wave function and using the variational method.

The antisymmetric state shows no minimum and never goes below -13.6 eV so there is no binding in this state.
By setting \( \frac{d(H)}{dy} = 0 \), we can get the distance between atoms and the energy.

<table>
<thead>
<tr>
<th>Distance</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>1.3 Å</td>
</tr>
<tr>
<td>Actual</td>
<td>1.06 Å</td>
</tr>
</tbody>
</table>

It's clear we would need to introduce some wfn. parameters to get good precision.

### 25.2 The H\(_2\) Molecule

The H\(_2\) molecule consists of four particles bound together: \( e_1 \), \( e_2 \), proton\(_A\), and proton\(_B\). The Hamiltonian can be written in terms of the H\(_2^+\) Hamiltonian, the repulsion between electrons, plus a correction term for double counting the repulsion between protons.

\[
H = H_1 + H_2 + \frac{e^2}{r_{12}} - \frac{e^2}{R_{AB}}
\]

\[
H_1 = \frac{\mu_1^2}{2m} - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{B1}} + \frac{e^2}{R_{AB}}
\]

We wish to compute variational upper bound on \( R_{AB} \) and the energy.

We will again use symmetric electron wavefunctions,

\[
\psi(r_1, r_2) = \frac{1}{\sqrt{1 + S(R_{AB})}} [\psi_A(r_1) + \psi_B(r_1)] [\psi_A(r_2) + \psi_B(r_2)] \chi_s
\]
where the spin singlet is required because the spatial wfn is symmetric under interchange.

The space symmetric state will be the ground state as before.

$$\langle \psi | H | \psi \rangle = 2E_{H_2^+} (R_{AB}) - \frac{e^2}{R_{AB}} + \langle \psi | \frac{e^2}{r_{12}} | \psi \rangle$$

From this point, we can do the calculation to obtain

<table>
<thead>
<tr>
<th>Distance</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>0.85 Å</td>
</tr>
<tr>
<td>Actual</td>
<td>0.74 Å</td>
</tr>
</tbody>
</table>

with a multiterm wavefunction, we could get good agreement.

### 25.3 Importance of Unpaired Valence Electrons

Inner (closed shell) electrons stick close to nucleus so they do not get near to other atoms. The outer (valence) electrons may participate in bonding either by sharing or migrating to the other atom. **Electrons which are paired into spin singlets don’t bond.** If we try to share one of the paired electrons, in a bonding state, with another atom, the electron from the other atom is not antisymmetric with the (other) paired electron. Therefore only the antibonding (or some excited state) will work and binding is unlikely. Unpaired electrons don’t have this problem.

\[ \uparrow \downarrow \uparrow \downarrow \ldots \text{first four don’t bond!} \]

The strongest bonds come from s and p orbitals (not d,f).

### 25.4 Molecular Orbitals

Even with additional parameters, parity symmetry in diatomic molecules implies we will have symmetric and antisymmetric wavefunctions for single electrons. The symmetric or bonding state has a larger probability to be between the two nuclei, sees more positive charge, and is therefore lower energy. As in our simple model of a molecule, the kinetic energy can be lowered by sharing an electron.

There is an axis of symmetry for diatomic molecules. This means \( L_z \) commutes with \( H \) and \( m_l \) is a good quantum number. The different \( m_l \) states, we have seen, have quite different shapes therefore bond differently. Imagine that a valence electron is in a \( d \) state. The \( m_l = 0, \pm 1, \pm 2 \) are called molecular orbitals \( \sigma, \pi, \delta \) respectively. Each has a bonding and an antibonding state.

Pictures of molecular orbitals are shown for \( s \) and \( p \) states in the following figure. Both bonding and antibonding orbitals are shown first as atomic states then as molecular. The antibonding states are denoted by a *.
Figure 33.4 Molecular orbital interactions in H₂.
25.5 Vibrational States

We have seen that the energy of a molecule has a minimum for some particular separation between atoms. This looks just like a harmonic oscillator potential for small variations from the minimum. The molecule can "vibrate" in this potential giving rise to a harmonic oscillator energy spectrum.

We can estimate the energy of the vibrational levels. If \( E_c \sim \hbar \omega = \hbar \sqrt{\frac{k}{m}} \), then crudely the proton has the same spring constant \( \sqrt{k} \approx \frac{E_c \sqrt{m}}{\hbar} \).

\[
E_{\text{vib}} \sim \hbar \sqrt{\frac{k}{M}} = \sqrt{\frac{m}{M}} E_c \sim \frac{1}{10} \text{ eV}
\]

Recalling that room temperature is about \( \frac{1}{10} \) eV, this is approximately thermal energy, infrared. The energy levels are simply

\[
E = (n + \frac{1}{2}) \hbar \omega_{\text{vib}}
\]

Complex molecules can have many different modes of vibration. Diatomic molecules have just one.

The graph below shows the energy spectrum of electrons knocked out of molecular hydrogen by UV photons (photoelectric effect). The different peaks correspond to the vibrational state of the final H\(^+\) ion.

Can you calculate the number of vibrational modes for a molecule compose of \( N > 3 \) atoms.
25.6 Rotational States

Molecules can rotate like classical rigid bodies subject to the constraint that angular momentum is quantized in units of \( \hbar \). We can estimate the energy of these rotations to be

\[
E_{\text{rot}} = \frac{1}{2} I \left( \ell (\ell + 1) \hbar^2 \right) = \frac{\hbar^2}{2M a_0^2} = \frac{m \alpha^2 mc^2}{2M} \approx \frac{mE}{M} \approx \frac{1}{1000} eV
\]

where we have used \( a_0 = \frac{\hbar}{amc} \). These states are strongly excited at room temperature.

Let's look at the energy changes between states as we might get in a radiative transition with \( \Delta \ell = 1 \).

\[
E = \frac{\ell (\ell + 1) \hbar^2}{2I}
\]

\[
\Delta E = \frac{\hbar^2}{2I} \left[ \ell (\ell + 1) - (\ell - 1) \ell \right] = \frac{\hbar^2}{2I} (2\ell) = \frac{\hbar^2 \ell}{I}
\]

These also have equal energy steps in emitted photon energy.

With identical nuclei, \( \ell \) is required to be even for (nuclear) spin singlet and odd for triplet. This means steps will be larger.

A complex molecule will have three principle axes, and hence, three moments of inertia to use in our quantized formula.

Counting degrees of freedom, which should be equal to the number of quantum numbers needed to describe the state, we have 3 coordinates to give the position of the center of mass, 3 for the rotational state, and 3N-6 for vibrational. This formula should be modified if the molecule is too simple to have three principle axes.

The graph below shows the absorption coefficient of water for light of various energies. For low energies, rotational and vibrational states cause the absorption of light. At higher energies, electronic excitation and photoelectric effect take over. It is only in the region around the visible spectrum that water transmits light well. Can you think of a reason for that?
25.7 Examples

25.8 Derivations and Computations

25.9 Homework Problems

1. In HCl, absorption lines with wave numbers in inverse centimeters of 83.03, 103.73, 124.30, 145.05, 165.51 and 185.86 have been observed. Are these rotational or vibrational transitions? Estimate some physical parameters of the molecule from these data.

2. What is the ratio of the number of HCl molecules in the $j = 10$ rotational state to that in the $j = 0$ state if the gas is at room temperature?

25.10 Sample Test Problems
26 Time Dependent Perturbation Theory

We have used time independent perturbation theory to find the energy shifts of states and to find the change in energy eigenstates in the presence of a small perturbation. We will not consider the case of a perturbation that is time dependent. Such a perturbation can cause transitions between energy eigenstates. We will calculate the rate of those transitions.

This material is covered in Gasiorowicz Chapter 21, in Cohen-Tannoudji et al. Chapter XIII, and briefly in Griffiths Chapter 9.

26.1 General Time Dependent Perturbations

Assume that we solve the unperturbed energy eigenvalue problem exactly: $H_0 \phi_n = E_n \phi_n$. Now we add a perturbation that depends on time, $V(t)$. Our problem is now inherently time dependent so we go back to the time dependent Schrödinger equation.

$$i\hbar \frac{\partial \psi(t)}{\partial t} = (H_0 + V(t)) \psi(t)$$

We will expand $\psi$ in terms of the eigenfunctions: $\psi(t) = \sum_k c_k(t) e^{-iE_k t / \hbar}$ with $\sum_k c_k(t) e^{-iE_k t / \hbar} = \langle \phi_k | \psi(t) \rangle$. The time dependent Schrödinger equations is

$$\sum_k (H_0 + V(t)) c_k(t) e^{-iE_k t / \hbar} \phi_k = \sum_k \left( i \hbar \frac{\partial c_k(t)}{\partial t} e^{-iE_k t / \hbar} + E_k c_k(t) \right) e^{-iE_k t / \hbar} \phi_k$$

Now dot $\langle \phi_n |$ into this equation to get the time dependence of one coefficient.

$$\sum_k V_{nk}(t) c_k(t) e^{-iE_k t / \hbar} = \sum_k \left( i \hbar \frac{\partial c_n(t)}{\partial t} e^{-iE_n t / \hbar} \right) e^{-iE_k t / \hbar}$$

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i \hbar} \sum_k V_{nk}(t) c_k(t) e^{i(E_n - E_k) t / \hbar}$$

Assume that at $t = 0$, we are in an initial state $\psi(t = 0) = \phi_i$ and hence all the other $c_k$ are equal to zero: $c_k = \delta_{ki}$.

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i \hbar} \left( V_{ni}(t) e^{i\omega_{ni} t} + \sum_{k \neq i} V_{nk}(t) c_k(t) e^{i\omega_k t} \right)$$
Now we want to calculate transition rates. To first order, all the \( c_k(t) \) are small compared to \( c_i(t) \approx 1 \), so the sum can be neglected.

\[
\frac{\partial c_n^{(1)}(t)}{\partial t} = \frac{1}{i\hbar} V_{ni}(t) e^{i\omega_{ni} t}
\]

\[
c_n^{(1)}(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{ni} t'} V_{ni}(t') dt'
\]

This is the equation to use to compute transition probabilities for a general time dependent perturbation. We will also use it as a basis to compute transition rates for the specific problem of harmonic potentials. Again we are assuming \( t \) is small enough that \( c_i \) has not changed much. This is not a limitation. We can deal with the decrease of the population of the initial state later.

Note that, if there is a large energy difference between the initial and final states, a slowly varying perturbation can average to zero. We will find that the perturbation will need frequency components compatible with \( \omega_{ni} \) to cause transitions.

If the first order term is zero or higher accuracy is required, the second order term can be computed. In second order, a transition can be made to an intermediate state \( \phi_k \), then a transition to \( \phi_i \). We just put the first order \( c_n^{(1)}(t) \) into the sum.

\[
\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar} \left( V_{ni}(t) e^{i\omega_{ni} t} + \sum_{k \neq i} V_{nk}(t) c_k^{(1)}(t) e^{i\omega_{nk} t} \right)
\]

\[
\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar} \left( V_{ni}(t) e^{i\omega_{ni} t} + \sum_{k \neq i} V_{nk}(t) \frac{1}{i\hbar} \int_0^t e^{i\omega_{nk} t'} V_{ki}(t') dt' \right)
\]

\[
c_n^{(2)}(t) = -\frac{1}{\hbar^2} \sum_{k \neq i} \int_0^t dt'' V_{nk}(t'') e^{i\omega_{nk} t''} \int_0^t dt' e^{i\omega_{nk} t'} V_{ki}(t')
\]

\[
c_n^{(2)}(t) = -\frac{1}{\hbar^2} \sum_{k \neq i} \int_0^t dt'' V_{nk}(t'') e^{i\omega_{nk} t''} \int_0^t dt' e^{i\omega_{nk} t'} V_{ki}(t')
\]

* See Example 26.3.1: Transitions of a 1D harmonic oscillator in a transient E field.*
26.2 Sinusoidal Perturbations

An important case is a pure sinusoidal oscillating (harmonic) perturbation. We can make up any time dependence from a linear combination of sine and cosine waves. We define our perturbation carefully.

\[ V(\mathbf{r}, t) = 2V(\mathbf{r}) \cos(\omega t) \rightarrow 2V(\cos(\omega t) = V \left( e^{i\omega t} + e^{-i\omega t} \right) \]

We have introduced the factor of 2 for later convenience. With that factor, we have \( V \) times a positive exponential plus a negative exponential. As before, \( V \) depends on position but we don't bother to write that for most of our calculations.

Putting this perturbation into the expression for \( c_n(t) \), we get

\[ c_n(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_n t'} V_n(t') dt' \]

\[ = \frac{1}{i\hbar} V_n \int_0^t dt' e^{i\omega_n t'} \left( e^{i\omega t} + e^{-i\omega t} \right) \]

\[ = \frac{1}{i\hbar} V_n \int_0^t dt' \left( e^{i(\omega_n + \omega) t'} + e^{i(\omega_n - \omega) t'} \right) \]

Note that the terms in the time integral will average to zero unless one of the exponents is nearly zero. If one of the exponents is zero, the amplitude to be in the state \( \phi_n \) will increase with time. To make an exponent zero we must have one of two conditions satisfied.

\[ \omega = \omega_n \]

\[ \omega = -\frac{E_n - E_i}{\hbar} \]

\[ \hbar \omega = E_i - E_n \]

\[ E_i = E_n + \hbar \omega \]

This is energy conservation for the emission of a quantum of energy \( \hbar \omega \).

\[ \omega = \omega_n \]

\[ \omega = \frac{E_n - E_i}{\hbar} \]

\[ \hbar \omega = E_n - E_i \]

\[ E_i = E_n - \hbar \omega \]

This is energy conservation for the absorption of a quantum of energy \( \hbar \omega \). We can see the possibility of absorption of radiation or of stimulated emission.

For \( t \rightarrow \infty \), the time integral of the exponential gives (some kind of) delta function of energy conservation. We will expend some effort to determine exactly what delta function it is.

Let's take the case of radiation of an energy quantum \( \hbar \omega \). If the initial and final states have energies such that this transition goes, the absorption term is completely negligible. (We can just use one of the exponentials at a time to make our formulas simpler.)
The amplitude to be in state $\phi_n$ as a function of time is

$$c_n(t) = \frac{1}{\hbar} V_{ni} \int_0^t dt' e^{i(\omega_{ni} + \omega)t'}$$

$$= \frac{V_{ni}}{\hbar} \left[ \frac{e^{i(\omega_{ni} + \omega)t'}}{i(\omega_{ni} + \omega)} \right]_{t'=0}^{t'=t}$$

$$= \frac{V_{ni}}{\hbar} \left[ e^{i(\omega_{ni} + \omega)t} - 1 \right]$$

$$= \frac{V_{ni}}{\hbar} e^{i(\omega_{ni} + \omega)t/2} \left[ \frac{e^{i(\omega_{ni} + \omega)t/2} - e^{-i(\omega_{ni} + \omega)t/2}}{i(\omega_{ni} + \omega)} \right]$$

$$= \frac{V_{ni}}{\hbar} e^{i(\omega_{ni} + \omega)t/2} \frac{2 \sin((\omega_{ni} + \omega)t/2)}{i(\omega_{ni} + \omega)}$$

$$P_n(t) = \frac{V_{ni}^2}{\hbar^2} \left[ \frac{4 \sin^2 ((\omega_{ni} + \omega)t/2)}{(\omega_{ni} + \omega)^2} \right]$$

In the last line above we have squared the amplitude to get the probability to be in the final state. The last formula is appropriate to use, as is, for short times. For long times (compared to $\hbar/\omega_{ni}$ which can be a VERY short time), the term in square brackets looks like some kind of delta function.

We will show (See section 26.4.1), that the quantity in square brackets in the last equation is $2\pi t \delta(\omega_{ni} + \omega)$. The probability to be in state $\phi_n$ then is

$$P_n(t) = \frac{V_{ni}^2}{\hbar^2} 2\pi t \delta(\omega_{ni} + \omega) = \frac{2\pi V_{ni}^2}{\hbar^2} \delta(\omega_{ni} + \omega)t = \frac{2\pi V_{ni}^2}{\hbar} \delta(E_n - E_i + \hbar\omega)t$$

The probability to be in the final state $\phi_n$ increases linearly with time. There is a delta function expressing energy conservation. The frequency of the harmonic perturbation must be set so that $\hbar\omega$ is the energy difference between initial and final states. This is true both for the (stimulated) emission of a quantum of energy and for the absorption of a quantum.

Since the probability to be in the final state increases linearly with time, it is reasonable to describe this in terms of a transition rate. The transition rate is then given by

$$\Gamma_{i\rightarrow n} \equiv \frac{dP_n}{dt} = \frac{2\pi V_{ni}^2}{\hbar} \delta(E_n - E_i + \hbar\omega)$$

We would get a similar result for increasing $E$ (absorbing energy) from the other exponential.

$$\Gamma_{i\rightarrow n} = \frac{2\pi V_{ni}^2}{\hbar} \delta(E_n - E_i - \hbar\omega)$$

It does not make a lot of sense to use this equation with a delta function to calculate the transition rate from a discrete state to a discrete state. If we tune the frequency just right we get infinity otherwise we get zero. This formula is what we need if either the initial or final state is a continuum state. If there is a free particle in the initial state or the final state, we have a continuum state. So, the absorption or emission of a particle, satisfies this condition.
The above results are very close to a transition rate formula known as Fermi’s Golden Rule. Imagine that instead of one final state $\phi_n$, there are a continuum of final states. The total rate to that continuum would be obtained by integrating over final state energy, an integral done simply with the delta function. We then have

$$\Gamma_{i \rightarrow f} = \frac{2\pi V_m^2}{\hbar} \rho_f(E)$$

where $\rho_f(E)$ is the density of final states. When particles (like photons or electrons) are emitted, the final state will be a continuum due to the continuum of states available to a free particle. We will need to carefully compute the density of those states, often known as phase space.

### 26.3 Examples

#### 26.3.1 Harmonic Oscillator in a Transient E Field

Assume we have an electron in a standard one dimensional harmonic oscillator of frequency $\omega$ in its ground state. A weak electric field is applied for a time interval $T$. Calculate the probability to make a transition to the first (and second) excited state.

The perturbation is $eE$ for $0 < t < T$ and zero for other times. We can write this in terms of the raising an lowering operators.

$$\mathcal{V} = eE \sqrt{\frac{\hbar}{2m\omega}} (A + A^\dagger)$$

We now use our time dependent perturbation result to compute the transition probability to the first excited state.

$$c_n(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_n t'} V_{n1}(t')dt'$$

$$c_1 = \frac{1}{i\hbar} eE \sqrt{\frac{\hbar}{2m\omega}} \int_0^T e^{i\omega t'} (1|A + A^\dagger|0)dt'$$

$$= eE \sqrt{\frac{\hbar}{2m\omega}} \int_0^T e^{i\omega t'} dt'$$

$$= eE \sqrt{\frac{\hbar}{2m\omega}} \left[ e^{i\omega T} \right]^T$$

$$= eE \sqrt{\frac{\hbar}{2m\omega}} \frac{e^{i\omega T} - 1}{i\omega}$$

$$= eE \sqrt{\frac{\hbar}{2m\omega}} e^{i\omega T/2} \left[ e^{i\omega T/2} - e^{-i\omega T/2} \right]$$

$$= eE \sqrt{\frac{\hbar}{2m\omega}} e^{i\omega T/2} 2i \sin(\omega T/2)$$
\[ P_1 = \frac{e^2 E^2}{\hbar^2 \omega^2} \frac{\hbar}{2m\omega} \sin^2(\omega T/2) \]
\[ P_1 = \frac{2e^2 E^2}{m\hbar \omega^3} \sin^2(\omega T/2) \]

As long as the E field is weak, the initial state will not be significantly depleted and the assumption we have made concerning that is valid. We do see that the transition probability oscillates with the time during which the E field is applied. We would get a (much) larger transition probability if we applied an oscillating E field tuned to have the right frequency to drive the transition.

Clearly the probability to make a transition to the second excited state is zero in first order. If we really want to compute this, we can use our first order result for \( c_1 \) and calculate the transition probability to the \( n = 2 \) state from that. This is a second order calculation. Its not too bad to do since there is only one intermediate state.

### 26.4 Derivations and Computations

#### 26.4.1 The Delta Function of Energy Conservation

For harmonic perturbations, we have derived a probability to be in the final state \( \phi_n \) proportional to the following.

\[ P_n \propto \left[ \frac{4\sin^2(\omega n_1 + \omega)t/2}{(\omega_1 + \omega)^2} \right] \]

For simplicity of analysis lets consider the characteristics of the function

\[ g(\Delta \equiv \omega n_1 + \omega) = \left[ \frac{4\sin^2(\omega n_1 + \omega)t/2}{(\omega_1 + \omega)^2 t^2} \right] = \frac{4\sin^2((\Delta t)/2)}{\Delta^2 t^2} \]

for values of \( t >> \frac{1}{\Delta} \). (Note that we have divided our function to be investigated by \( t^2 \). For \( \Delta = 0 \), \( g(\Delta) = 1 \) while for all other values for \( \Delta \), \( g(\Delta) \) approaches zero for large \( t \). This is clearly some form of a delta function.

To find out exactly what delta function it is, we need to integrate over \( \Delta \).

\[
\int_{-\infty}^{\infty} d\Delta \ f(\Delta)g(\Delta) = f(\Delta = 0) \int_{-\infty}^{\infty} d\Delta \ g(\Delta)
\]
\[
= f(\Delta = 0) \int_{-\infty}^{\infty} d\Delta \ \frac{4\sin^2(\Delta t/2)}{\Delta^2 t^2}
\]
\[
= f(\Delta = 0) \int_{-\infty}^{\infty} d\Delta \ \frac{4\sin^2(y)}{4y^2}
\]
\[
= f(\Delta = 0) \frac{2}{t} \int_{-\infty}^{\infty} dy \ \frac{\sin^2(y)}{y^2}
\]
\[ f(\Delta = 0) \frac{2}{t} \int_{-\infty}^{\infty} dy \sin^2(y) \frac{\sin(y)}{y^2} \]

We have made the substitution that \( y = \frac{\Delta}{t} \). The definite integral over \( y \) just gives \( \pi \) (consult your table of integrals), so the result is simple.

\[
\int_{-\infty}^{\infty} d\Delta \ f(\Delta) g(\Delta) = f(\Delta = 0) \frac{2\pi}{t}
\]

\[
g(\Delta) = \frac{2\pi}{t} \delta(\Delta)
\]

\[
\left[ \frac{4 \sin^2((\omega_{ni} + \omega)t/2)}{(\omega_{ni} + \omega)^2} \right] = 2\pi t \delta(\omega_{ni} + \omega)
\]

Q.E.D.

26.5 Homework Problems

1. A hydrogen atom is placed in an electric field which is uniform in space and turns on at \( t = 0 \) then decays exponentially. That is, \( \vec{E}(t) = 0 \) for \( t < 0 \) and \( \vec{E}(t) = E_0 e^{-\gamma t} \) for \( t > 0 \). What is the probability that, as \( t \to \infty \), the hydrogen atom has made a transition to the \( 2p \) state?

2. A one dimensional harmonic oscillator is in its ground state. It is subjected to the additional potential \( W = -e \xi x \) for a time interval \( \tau \). Calculate the probability to make a transition to the first excited state (in first order). Now calculate the probability to make a transition to the second excited state. You will need to calculate to second order.

26.6 Sample Test Problems

1. A hydrogen atom is in a uniform electric field in the \( z \) direction which turns on abruptly at \( t = 0 \) and decays exponentially as a function of time, \( E(t) = E_0 e^{-t/\tau} \). The atom is initially in its ground state. Find the probability for the atom to have made a transition to the \( 2P \) state as \( t \to \infty \). You need not evaluate the radial part of the integral. What \( z \) components of orbital angular momentum are allowed in the \( 2P \) states generated by this transition?
27 Radiation in Atoms

Now we will go all the way back to Plank who proposed that the emission of radiation be in quanta with \( E = h\omega \) to solve the problem of Black Body Radiation. So far, in our treatment of atoms, we have not included the possibility to emit or absorb real photons nor have we worried about the fact that Electric and Magnetic fields are made up of virtual photons. This is really the realm of Quantum Electrodynamics, but we do have the tools to understand what happens as we quantize the EM field.

We now have the solution of the Harmonic Oscillator problem using operator methods. Notice that the emission of a quantum of radiation with energy of \( h\omega \) is like the raising of a Harmonic Oscillator state. Similarly the absorption of a quantum of radiation is like the lowering of a HO state. Plank was already integrating over an infinite number of photon (like HO) states, the same integral we would do if we had an infinite number of Harmonic Oscillator states. Plank was also correctly counting this infinite number of states to get the correct Black Body formula. He did it by considering a cavity with some volume, setting the boundary conditions, then letting the volume go to infinity.

This material is covered in Gasiorowicz Chapter 22, in Cohen-Tannoudji et al. Chapter XIII, and briefly in Griffiths Chapter 9.

27.1 The Photon Field in the Quantum Hamiltonian

The Hamiltonian for a charged particle in an ElectroMagnetic field (See Section 18.1) is given by

\[
H = \frac{1}{2m}(\vec{p} + \frac{e}{c}\vec{A})^2 + V(r).
\]

Let's assume that there is some ElectroMagnetic field around the atom. The field is not extremely strong so that the \( A^2 \) term can be neglected (for our purposes) and we will work in the Coulomb gauge for which \( \vec{p} \cdot \vec{A} = \frac{e}{c}\vec{\nabla} \cdot \vec{A} = 0 \). The Hamiltonian then becomes

\[
H \approx \frac{\vec{p}^2}{2m} + \frac{e}{mc}\vec{A} \cdot \vec{p} + V(r).
\]

Now we have a potentially time dependent perturbation that may drive transitions between the atomic states.

\[
\mathcal{V} = \frac{e}{mc}\vec{A} \cdot \vec{p}
\]

Let's also assume that the field has some frequency \( \omega \) and corresponding wave vector \( \vec{k} \). (In fact, and arbitrary field would be a linear combination of many frequencies, directions of propagation, and polarizations.)

\[
\vec{A}(\vec{r},t) \equiv 2\vec{A}_0 \cos(\vec{k} \cdot \vec{r} - \omega t)
\]

where \( \vec{A}_0 \) is a real vector and we have again introduced the factor of 2 for convenience of splitting the cosine into two exponentials.

We need to quantize the EM field into photons satisfying Plank's original hypothesis, \( E = h\omega \). Lets start by writing \( A \) in terms of the number of photons in the field (at frequency \( \omega \) and wave vector
Using classical E&M to compute the energy in a field (See Section 27.14.1) represented by a vector potential \( \tilde{A}(\vec{r}, t) = 2A_0 \cos(\tilde{k} \cdot \vec{r} - \omega t) \), we find that the energy inside a volume \( V \) is

\[
\text{Energy} = \frac{\omega^2}{2\pi c^2} V |A_0|^2.
\]

We may then turn this around and write \( \tilde{A} \) in terms of the number of photons \( N \).

\[
\tilde{A}(\vec{r}, t) = \left[ \frac{2\pi \hbar c^2 N^*}{\omega V} \right]^{\frac{1}{2}} \hat{\epsilon} 2 \cos(\tilde{k} \cdot \vec{r} - \omega t)
\]

\[
\tilde{A}(\vec{r}, t) = \left[ \frac{2\pi \hbar c^2 N^*}{\omega V} \right]^{\frac{1}{2}} \hat{\epsilon} \left( e^{i(\tilde{k} \cdot \vec{r} - \omega t)} + e^{-i(\tilde{k} \cdot \vec{r} - \omega t)} \right)
\]

We have introduced the unit vector \( \hat{\epsilon} \) to give the direction (or polarization) of the vector potential. We now have a perturbation that may induce radiative transitions. There are terms with both negative and positive \( \omega \) so that we expect to see both stimulated emission of quanta and absorption of quanta in the the presence of a time dependent E&M field.

But what about decays of atoms with no applied field? Here we need to go beyond our classical E&M calculation and quantize the field. Since the terms in the perturbation above emit or absorb a photon, and the photon has energy \( \hbar \omega \), let's assume the number of photons in the field is the \( n \) of a harmonic oscillator. It has the right steps in energy. Essentially, we are postulating that the vacuum contains an infinite number of harmonic oscillators, one for each wave vector (or frequency...) of light.

We now want to go from a classical harmonic oscillator to a quantum oscillator, in which the ground state energy is not zero, and the hence the perturbing field is never really zero. We do this by changing \( N \) to \( N + 1 \) in the term that creates a photon in analogy to the raising operator \( A^\dagger \) in the harmonic oscillator.

With this change, our perturbation becomes

\[
\tilde{A}(\vec{r}, t) = \left[ \frac{2\pi \hbar c^2}{\omega V} \right]^{\frac{1}{2}} \hat{\epsilon} \left( \sqrt{N} e^{i(\tilde{k} \cdot \vec{r} - \omega t)} + \sqrt{N + 1} e^{-i(\tilde{k} \cdot \vec{r} - \omega t)} \right)
\]

Remember that one exponential corresponds to the emission of a photon and the other corresponds to the the absorption of a photon. We view \( \tilde{A} \) as an operator which either creates or absorbs a photon, raising or lowering the harmonic oscillator in the vacuum.

Now there is a perturbation even with no applied field (\( N = 0 \)).

\[
\mathcal{V}_{N=0} = V_{N=0} e^{i \omega t} = \frac{e}{mc} \tilde{A} \cdot \vec{p} = \frac{e}{mc} \left[ \frac{2\pi \hbar c^2}{\omega V} \right]^{\frac{1}{2}} \hat{\epsilon} \cdot \vec{p} e^{-i(\tilde{k} \cdot \vec{r} - \omega t)}
\]

We can plug this right into our expression for the decay rate (removing the \( e^{i\omega t} \) into the delta function as was done when we considered a general sinusoidal time dependent perturbation). Of course we have this for all frequencies, not just the one we have been assuming without justification. Also note that our perturbation still depends on the volume we assume. This factor will be canceled when we correctly compute the density of final states.

We have taken a step toward quantization of the EM field, at least when we emit or absorb a photon. With this step, we can correctly compute the EM transition rates in atoms. Note that we have postulated
that the vacuum has an infinite number of oscillators corresponding to the different possible modes of EM waves. When we quantize these oscillators, the vacuum has a ground state energy density in the EM field (equivalent to half a photon of each type). That vacuum EM field is then responsible for the spontaneous decay of excited states of atoms through the emission of a photon. We have not yet written the quantum equations that the EM field must satisfy, although they are closely related to Maxwell’s equations.

27.2 Decay Rates for the Emission of Photons

Our expression for the decay rate of an initial state $\phi_i$ into some particular final state $\phi_n$ is

$$\Gamma_{i\rightarrow n} = \frac{2\pi V^2}{\hbar} \delta(E_n - E_i + \hbar \omega).$$

The delta function reminds us that we will have to integrate over final states to get a sensible answer. Nevertheless, we proceed to include the matrix element of the perturbing potential.

Taking out the harmonic time dependence (to the delta function) as before, we have the matrix element of the perturbing potential.

$$V_{ni} = \langle \phi_n | e - \frac{e^2}{mc} \mathbf{\tilde{A}} \cdot \mathbf{\tilde{p}} | \phi_i \rangle = \frac{e}{mc} \left[ \frac{2\pi \hbar}{\omega V} \right]^2 \langle \phi_n | e^{-i\mathbf{k} \cdot \mathbf{\tilde{p}}} \mathbf{\tilde{p}} | \phi_i \rangle$$

We just put these together to get

$$\Gamma_{i\rightarrow n} = \frac{2\pi}{\hbar} \frac{e^2}{m c^2} \left[ \frac{2\pi \hbar}{\omega V} \right] \langle \phi_n | e^{-i\mathbf{k} \cdot \mathbf{\tilde{p}}} \mathbf{\tilde{p}} | \phi_i \rangle^2 \delta(E_n - E_i + \hbar \omega)$$

$$\Gamma_{i\rightarrow n} = \frac{(2\pi)^2 e^2}{m^2 \omega V} \langle \phi_n | e^{-i\mathbf{k} \cdot \mathbf{\tilde{p}}} \mathbf{\tilde{p}} | \phi_i \rangle^2 \delta(E_n - E_i + \hbar \omega)$$

We must sum (or integrate) over final states. The states are distinguishable so we add the decay rates, not the amplitudes. We will integrate over photon energies and directions, with the aid of the delta function. We will sum over photon polarizations. We will sum over the final atomic states when that is applicable. All of this is quite doable. Our first step is to understand the number of states of photons as Plank (and even Rayleigh) did to get the Black Body formulas.

27.3 Phase Space: The Density of Final States

We have some experience with calculating the number of states for fermions in a 3D box (See Section 12.1.1). For the box we had boundary conditions that the wavefunction go to zero at the wall of the box. Now we wish to know how many photon states are in a region of phase space centered on the wave vector $k$ with (small) volume in $k$-space of $\Delta^3 k$. (Remember $\omega = |k| c$ for light.) We will assume for the sake of calculation that the photons are confined to a cubic volume in position space of $V = L^3$ and impose periodic boundary conditions on our fields. (Really we could require the fields to be zero on the boundaries of the box by choosing a sine wave. The PBC are equivalent to this but allow...
us to deal with single exponentials instead of real functions.) Our final result, the decay rate, will be independent of volume so we can let the volume go to infinity.

\[ k_x L = 2\pi n_x \quad d n_x = \frac{k_x}{2\pi} d k_x \]

\[ k_y L = 2\pi n_y \quad d n_y = \frac{k_y}{2\pi} d k_y \]

\[ k_z L = 2\pi n_z \quad d n_z = \frac{k_z}{2\pi} d k_z \]

\[ d^3 n = \frac{1}{(2\pi)^3} d^3 k = \frac{V}{(2\pi)^3} d^3 k \]

That was easy. We will use this phase space formula for decays of atoms emitting a photon. A more general phase space formula (See Section 27.14.2) based on our calculation can be used with more than one free particle in the final state. (In fact, even our simple case, the atom recoils in the final state, however, its momentum is fixed due to momentum conservation.)

### 27.4 Total Decay Rate Using Phase Space

Now we are ready to sum over final (photon) states to get the total transition rate. Since both the momentum of the photon and the electron show up in this equation, we will label the electron’s momentum to avoid confusion.

\[
\Gamma_{tot} = \sum_{k, pol} \Gamma_{i \rightarrow n} \rightarrow \sum_{pol} \int \frac{V d^3 p}{(2\pi)^3} \Gamma_{i \rightarrow n} = \sum_{pol} \int \frac{V d^3 p}{(2\pi)^3} \Gamma_{i \rightarrow n}
\]

\[
= \sum_{\lambda} \int \frac{V d^3 p}{(2\pi)^3} \left[ \frac{e^2}{\hbar^2 m^2} \right] \left[ \langle \phi_n | e^{-i\vec{k} \cdot \vec{p}} | \phi_i \rangle \right]^2 \delta(E_n - E_i + \hbar \omega)
\]

\[
= \frac{e^2}{2\pi \hbar^2 m^2} \sum_{\lambda} \int \frac{d^3 p}{\omega} \left[ \langle \phi_n | e^{-i\vec{k} \cdot \vec{p}} | \phi_i \rangle \right]^2 \delta(E_n - E_i + \hbar \omega)
\]

\[
= \frac{e^2}{2\pi \hbar^2 m^2} \sum_{\lambda} \int \frac{d(\hbar \omega) d\Omega_{\lambda}}{\hbar \omega} \left[ \langle \phi_n | e^{-i\vec{k} \cdot \vec{p}} | \phi_i \rangle \right]^2 \delta(E_n - E_i + \hbar \omega)
\]

\[
= \frac{e^2}{2\pi \hbar^2 m^2} \sum_{\lambda} \int \frac{E_n - E_i}{c} d\Omega_{\lambda} \left[ \langle \phi_n | e^{-i\vec{k} \cdot \vec{p}} | \phi_i \rangle \right]^2
\]

\[
\Gamma_{tot} = \frac{e^2 (E_i - E_n)}{2\pi \hbar^2 m^2 c^3} \sum_{\lambda} \int d\Omega_{\lambda} \left[ \langle \phi_n | e^{-i\vec{k} \cdot \vec{p}} | \phi_i \rangle \right]^2
\]

This is the general formula for the decay rate emitting one photon. Depending on the problem, we may also need to sum over final states of the atom. The two polarizations are transverse to the photon direction, so they must vary inside the integral.

A quick estimate of the decay rate of an atom (See Section 27.14.3) gives

\[ \tau \approx 50 \text{ psec}. \]
27.5 Electric Dipole Approximation and Selection Rules

We can now expand the $e^{-i\vec{k} \cdot \vec{r}} \approx 1 - \frac{i}{\hbar} \vec{k} \cdot \vec{r} + \ldots$ term to allow us to compute matrix elements more easily. Since $\vec{k} \cdot \vec{r} \approx \frac{\phi}{\hbar}$ and the matrix element is squared, our expansion will be in powers of $\phi^2$ which is a small number. The dominant decays will be those from the zeroth order approximation which is

$$e^{-i\vec{k} \cdot \vec{r}} \approx 1.$$

This is called the **Electric dipole approximation**.

In this Electric Dipole approximation, we can make general progress on computation of the matrix element. If the Hamiltonian is of the form $H = \frac{p^2}{2m} + V$ and $[V, \vec{r}] = 0$, then

$$[H, \vec{r}] = \frac{\hbar}{i} \frac{p}{m}$$

and we can write $\vec{p} = \frac{i\hbar}{\epsilon} [H, \vec{r}]$ in terms of the commutator.

$$\langle \phi_n | e^{-i\vec{p} \cdot \vec{r}} \vec{p} \cdot \phi_i \rangle \approx \langle \phi_n | \vec{p} \cdot \phi_i \rangle = \frac{i m}{\hbar} \langle \phi_n | [H, \vec{r}] | \phi_i \rangle$$

$$= \frac{i m}{\hbar} (E_n - E_i) \langle \phi_n | \vec{r} | \phi_i \rangle$$

$$= \frac{i m (E_n - E_i)}{\hbar} \langle \phi_n | \vec{p} \cdot \vec{r} | \phi_i \rangle$$

This equation indicates the origin of the name Electric Dipole: the matrix element is of the vector $\vec{r}$ which is a dipole.

We can proceed further, with the angular part of the (matrix element) integral.

$$\langle \phi_n | \vec{p} \cdot \vec{r} | \phi_i \rangle = \int_0^\infty r^2 dr R_{n \ell}^* R_{n \ell} \int \Omega_e \vec{y} \cdot \vec{r} \Omega_{e \ell} d\Omega_e$$

$$= \int_0^\infty r^3 dr R_{n \ell}^* R_{n \ell} \int \Omega_e \vec{y} \cdot \vec{r} \Omega_{e \ell} d\Omega_e$$

$$\vec{y} \cdot \vec{r} = \epsilon_x \sin \theta \cos \phi + \epsilon_y \sin \theta \sin \phi + \epsilon_z \cos \theta = \sqrt{\frac{4\pi}{3}} \left( \epsilon_x Y_{10} + \frac{-\epsilon_x + i \epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i \epsilon_y}{\sqrt{2}} Y_{1-1} \right)$$

$$\langle \phi_n | \vec{p} \cdot \vec{r} | \phi_i \rangle = \sqrt{\frac{4\pi}{3}} \int_0^\infty r^3 dr R_{n \ell}^* R_{n \ell} \int \Omega_e \left( \epsilon_x Y_{10} + \frac{-\epsilon_x + i \epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i \epsilon_y}{\sqrt{2}} Y_{1-1} \right) Y_{e \ell} d\Omega_e$$

At this point, let's bring all the terms in the formula back together so we know what we are doing.

$$\Gamma_{tot} = \frac{\epsilon^2 (E_i - E_n)}{2\pi \hbar m^2 c^3} \sum \lambda \int d\Omega_e \left| \langle \phi_n | e^{-i\vec{p} \cdot \vec{r}(\lambda)} \vec{p} \cdot \phi_i \rangle \right|^2$$

$$= \frac{\epsilon^2 (E_i - E_n)}{2\pi \hbar m^2 c^3} \sum \lambda \int d\Omega_e \left| \frac{i m (E_n - E_i)}{\hbar} \langle \phi_n | \vec{p} \cdot \vec{r} | \phi_i \rangle \right|^2$$
\[ \Gamma_{\text{tot}} = \frac{\alpha r_m^3}{2\pi c^2} \sum_{\lambda} \int d\Omega_\lambda \left| \langle \phi_n | \hat{r} | \phi_i \rangle \right|^2 \]

This is a useful version of the total decay rate formula to remember.

We proceed with the calculation to find the E1 selection rules.

\[ = \frac{\alpha r_m^3}{2\pi c^2} \sum_{\lambda} \int d\Omega_\lambda \left[ \phi_n \left( \frac{1}{3} \right) \left( \epsilon_x Y_{10} + \frac{-\epsilon_x + ie_y Y_{11} + \epsilon_x + ie_y Y_{1-1}}{\sqrt{2}} \right) \phi_i \right]^2 \]

We will attempt to clearly separate the terms due to \( \langle \phi_n | \hat{r} | \phi_i \rangle \) for the sake of modularity of the calculation.

The integral with three spherical harmonics in each term looks a bit difficult, but, we can use a Clebsch-Gordan series like the one in addition of angular momentum to help us solve the problem. We will write the product of two spherical harmonics in terms of a sum of spherical harmonics. Its very similar to adding the angular momentum from the two \( Y \)s. Its the same series as we had for addition of angular momentum (up to a constant). (Note that things will be very simple if either the initial or the final state have \( \ell = 0 \), a case we will work out below for transitions to s states.) The general formula for rewriting the product of two spherical harmonics (which are functions of the same coordinates) is

\[ Y_{\ell_1, m_1}(\theta, \phi)Y_{\ell_2, m_2}(\theta, \phi) = \sum_{\ell = |\ell_1 - \ell_2|}^{\ell_1 + \ell_2} \sqrt{\frac{(2\ell_1 + 1)(2\ell_2 + 1)}{4\pi(2\ell + 1)}} \langle 0|\ell_1\ell_200\rangle \langle \ell(m_1+m_2)|\ell_1\ell_2m_1m_2 \rangle Y_{\ell(m_1+m_2)}(\theta, \phi) \]

The square root and \( \left( \langle 0|\ell_1\ell_200\rangle \right) \) can be thought of as a normalization constant in an otherwise normal Clebsch-Gordan series. (Note that the normal addition of the orbital angular momenta of two particles would have product states of two spherical harmonics in different coordinates, the coordinates of particle one and of particle two.) (The derivation of the above equation involves a somewhat detailed study of the properties of rotation matrices and would take us pretty far off the current track (See Merzacher page 396).)

First add the angular momentum from the initial state \( (Y_{\ell_1, m_1}) \) and the photon \( (Y_{1m}) \) using the Clebsch-Gordan series, with the usual notation for the Clebsch-Gordan coefficients \( \langle \ell, m | \ell_1, m_1 \rangle \).

\[ Y_{1m}(\theta, \phi)Y_{\ell_1, m_1}(\theta, \phi) = \sum_{\ell = |\ell_1 - 1|}^{\ell_1 + 1} \sqrt{\frac{3(2\ell_1 + 1)}{4\pi(2\ell + 1)}} \langle 0|\ell_1100\rangle \langle \ell(m + m_1)|\ell_1m_1m \rangle Y_{\ell_1m}(\theta, \phi) \]

\[ \int d\Omega Y_{\ell_1, m_1}^* Y_{1m} Y_{\ell_1, m_1} = \sqrt{\frac{3(2\ell_1 + 1)}{4\pi(2\ell + 1)}} \langle 0|\ell_1100\rangle \langle \ell_1m_1|\ell_1m \rangle \]
\[
\int d\Omega_{\ell_i m_i} \left( \epsilon_z Y_{\ell_0} + \frac{-e_x + i e_y}{\sqrt{2}} Y_{\ell_0-1}+ \frac{e_x + i e_y}{\sqrt{2}} Y_{\ell_0+1} \right) Y_{\ell_i m_i}
\]

\[
= \sqrt{\frac{3(2\ell_i + 1)}{4\pi(2\ell_n + 1)}} \langle \ell_i 0 | \ell_i 1 100 \rangle \left( \epsilon_z \langle \ell_n m_n | \ell_1 m_10 \rangle + \frac{-e_x + i e_y}{\sqrt{2}} \langle \ell_n m_n | \ell_1 m_11 \rangle + \frac{e_x + i e_y}{\sqrt{2}} \langle \ell_n m_n | \ell_1 m_1 - 1 \rangle \right)
\]

I remind you that the Clebsch-Gordan coefficients in these equations are just numbers which are less than one. They can often be shown to be zero if the angular momentum doesn’t add up. The equation we derive can be used to give us a great deal of information.

\[
\langle \phi_n | \hat{\mathbf{r}} \cdot \hat{\mathbf{r}} | \phi_i \rangle = \frac{(2\ell_i + 1)}{(2\ell_n + 1)} \langle \ell_i 0 | \ell_i 100 \rangle \int_0^\infty r^3 dr R^*_{\ell_n \ell_i} R_{\ell_n \ell_i} \left( \epsilon_z \langle \ell_n m_n | \ell_1 m_10 \rangle + \frac{-e_x + i e_y}{\sqrt{2}} \langle \ell_n m_n | \ell_1 m_11 \rangle + \frac{e_x + i e_y}{\sqrt{2}} \langle \ell_n m_n | \ell_1 m_1 - 1 \rangle \right)
\]

We know, from the addition of angular momentum, that adding angular momentum 1 to \( \ell_1 \) can only give answers in the range \( |\ell_1 - 1| < \ell_n < \ell_1 + 1 \) so the change in in \( \ell \) between the initial and final state can only be \( \Delta \ell = 0, \pm 1 \). For other values, all the Clebsch-Gordan coefficients above will be zero.

We also know that the \( Y_{\ell m} \) are odd under parity so the other two spherical harmonics must have opposite parity to each other implying that \( \ell_n \neq \ell_i \), therefore

\[
\Delta \ell = \pm 1.
\]

We also know from the addition of angular momentum that the z components just add like integers, so the three Clebsch-Gordan coefficients allow

\[
\Delta m = 0, \pm 1.
\]

We can also easily note that we have no operators which can change the spin here. So certainly

\[
\Delta s = 0.
\]

We actually haven’t yet included the interaction between the spin and the field in our calculation, but, it is a small effect compared to the Electric Dipole term.

The above selection rules apply only for the Electric Dipole (E1) approximation. Higher order terms in the expansion, like the Electric Quadrupole (E2) or the Magnetic Dipole (M1), allow other decays but the rates are down by a factor of \( \alpha^2 \) or more. There is one absolute selection rule coming from angular momentum conservation, since the photon is spin 1. **No \( j = 0 \) to \( j = 0 \) transitions in any order of approximation.**

As a summary of our calculations in the Electric Dipole approximation, let’s write out the decay rate formula.
27.6 Explicit 2p to 1s Decay Rate

Starting from the summary equation for electric dipole transitions, above,

\[ \Gamma_{1,d} = \frac{\alpha \omega_{1d}^3}{2\pi c^2} \sum \int d\Omega \left( \frac{4\pi}{3} \int_0^\infty r^3 dr R_{n_1 n_{1e} n}^* R_{n_1 \ell i} \int d\Omega Y_{n_{1m}, n}^* \left( \epsilon_x Y_{10} + \frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} \right) Y_{\ell i m} \right)^2 \]

we specialize to the 2p to 1s decay,

\[ \Gamma_{1,d} = \frac{\alpha \omega_{1d}^3}{2\pi c^2} \sum \int d\Omega \left( \frac{4\pi}{3} \int_0^\infty r^3 dr R_{10 R_{21}}^* \int d\Omega Y_{00}^* \left( \epsilon_x Y_{10} + \frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} \right) Y_{1 m_i} \right)^2 \]

perform the radial integration,

\[
\int_0^\infty r^3 dr R_{10 R_{21}}^* = \int_0^\infty r^3 dr \int_0^{\infty} r^4 dr e^{-3r/2a_0} = \frac{1}{\sqrt{6}} \left( \frac{1}{a_0} \right)^4 \frac{2a_0}{3} \int_0^\infty r^4 dr e^{-r/2a_0} = 4\sqrt{6} \left( \frac{2}{3} \right)^5 a_0(4!) \]

and perform the angular integration.

\[
\int d\Omega Y_{00}^* \left( \epsilon_x Y_{10} + \frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} \right) Y_{1 m_i} = \int d\Omega \left( \epsilon_x Y_{10} + \frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} \right) Y_{1 m_i} + \frac{1}{4\pi} \left( \epsilon_x \delta_{m_i 0} + \frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} \delta_{m_i (-1)} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} \delta_{m_i 1} \right) \left( \delta_{m_i 0} + \delta_{m_i 1} \right) \left( \delta_{m_i 0} + \delta_{m_i 1} \right) \]

Lets assume the initial state is unpolarized, so we will sum over \( m_i \) and divide by 3, the number of different \( m_i \) allowed.

\[
\frac{1}{3} \sum_{m_i} \left( \epsilon_x Y_{10} + \frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} \right) Y_{\ell i m_i} \]
\[
\begin{align*}
&= \frac{1}{4\pi} \frac{1}{3} \sum_{m_i} \left( e_2^2 \delta_{m,0} + \frac{1}{2} (e_x^2 + e_y^2) (\delta_{m,(-1)} + \delta_{m,1}) \right) \\
&= \frac{1}{12\pi} \left( e_z^2 + \frac{1}{2} (e_x^2 + e_y^2) (1 + 1) \right) \\
&= \frac{1}{12\pi} (e_z^2 + e_x^2 + e_y^2) \\
&= \frac{1}{12\pi}
\end{align*}
\]

Our result is independent of photon polarization since we assumed the initial state was unpolarized, but, we must still sum over photon polarization. Let's assume that we are not interested in measuring the photon's polarization. The polarization vector is constrained to be perpendicular to the photon's direction

\[ \hat{e} \cdot \hat{k}_p = 0 \]

so there are two linearly independent polarizations to sum over. This just introduces a factor of two as we sum over final polarization states.

The integral over photon direction clearly just gives a factor of \(4\pi\) since there is no direction dependence left in the integrand (due to our assumption of an unpolarized initial state).

\[
\Gamma_{t,\ell} = \frac{2\kappa\omega_m^3}{3\varepsilon_0^2} \left( \frac{2}{3} \right)^5 a_0 \left| \frac{1}{12\pi} = \frac{4\kappa\omega_m^3}{9\varepsilon_0^2} \left| \frac{4\sqrt{6}}{3} \right. \cdot \left| a_0 \right. \right| \]

27.7 General Unpolarized Initial State

If we are just interested in the total decay rate, we can go further. The decay rate should not depend on the polarization of the initial state, based on the rotational symmetry of our theory. Usually we only want the total decay rate to some final state so we sum over polarizations of the photon, integrate over photon directions, and (eventually) sum over the different \(m_n\) of the final state atoms. We begin with a simple version of the total decay rate formula in the E1 approximation.

\[
\begin{align*}
\Gamma_{t,\ell} &= \frac{\alpha\omega_m^3}{2\pi\varepsilon_0^2} \sum_{\lambda \lambda'} \int d\Omega_{\gamma} \left| \langle \phi_{n_i} | \hat{e} \cdot \hat{r} | \phi_{i} \rangle \right|^2 \\
\Gamma_{t,\ell} &= \frac{\alpha\omega_m^3}{2\pi\varepsilon_0^2} \sum_{\lambda \lambda'} \int d\Omega_{\gamma} \left| \langle \phi_{n_i} | \hat{r} | \phi_{i} \rangle \cdot \hat{e} \right|^2 \\
\Gamma_{t,\ell} &= \frac{\alpha\omega_m^3}{2\pi\varepsilon_0^2} \sum_{\lambda \lambda'} \int d\Omega_{\gamma} \left| \hat{r}_{ni} \cdot \hat{e} \right|^2 \\
\Gamma_{t,\ell} &= \frac{\alpha\omega_m^3}{2\pi\varepsilon_0^2} \sum_{\lambda \lambda'} \int d\Omega_{\gamma} \left| \hat{r}_{ni} \right|^2 \cos^2 \Theta
\end{align*}
\]

Where \( \Theta \) is the angle between the matrix element of the position vector \( \hat{r}_{ni} \) and the polarization vector \( \hat{e} \). It is far easier to understand the sum over polarizations in terms of familiar vectors in 3-space than by using sums of Clebsch-Gordan coefficients.
Let's pick two transverse polarization vectors (to sum over) that form a right handed system with the direction of photon propagation. 

\[ \mathbf{e}^{(1)} \times \mathbf{e}^{(2)} = \mathbf{k} \]

The figure below shows the angles, basically picking the photon direction as the polar axis, and the \( \mathbf{e}^{(1)} \) direction as what is usually called the x-axis.

The projection of the vector \( \mathbf{r}_{ni} \) into the transverse plan gives a factor of \( \sin \theta \). It is then easy to see that

\[
\cos \Theta_1 = \sin \theta \cos \phi \\
\cos \Theta_2 = \sin \theta \sin \phi
\]

The sum of \( \cos^2 \Theta \) over the two polarizations then just gives \( \sin^2 \theta \). Therefore the decay rate becomes

\[
\Gamma_{tot} = \frac{\alpha \omega_{in}^3}{2\pi c^2} \sum \lambda \int d\Omega \, |\mathbf{r}_{ni}|^2 \cos^2 \Theta \\
\Gamma_{tot} = \frac{\alpha \omega_{in}^3}{2\pi c^2} |\mathbf{r}_{ni}|^2 \int d\Omega \, \sin^2 \theta \\
\Gamma_{tot} = \frac{\alpha \omega_{in}^3}{2\pi c^2} |\mathbf{r}_{ni}|^2 \frac{2\pi}{(\cos \theta)(1 - \cos^2 \theta)}
\]

\[
\Gamma_{tot} = \frac{\alpha \omega_{in}^3}{2\pi c^2} |\mathbf{r}_{ni}|^2 \frac{2\pi}{(\cos \theta)(1 - \cos^2 \theta)}
\]
This is the same result we got in the explicit calculation.

As a simple check, let’s recompute the $2p$ to $1s$ decay rate for hydrogen. We must choose the $l = l - 1$ case and $l = 1$.

The result is independent of $m$ as we would expect from rotational symmetry.

We still need to sum over the final atomic states as necessary. For the case of a transition in a single electron atom $(\nu_{in} \rightarrow \nu_{in}, \nu_{out} \rightarrow \nu_{out})$, summed over $m$, the properties of the Clebsch-Gordan coefficients can be used to show (see Merzbacher, second edition, page 467)

$$\Gamma_{ld} = \frac{4\alpha^2}{3\pi} \int_{0}^{\infty} \frac{R_l^2 R_0^2}{R_l R_0} dr$$

for $l = \ell + 1$.

This is now a very nice and simple result for the total decay rate of a state, summed over photon polarizations and integrated over photon direction.

$$\Gamma_{ld} = \frac{4\alpha^2}{3\pi} \int_{0}^{\infty} \frac{R_l^2 R_0^2}{R_l R_0} dr$$
27.8 Angular Distributions

We may also deduce the angular distribution of photons from our calculation. Let’s take the 2p to 1s calculation as an example. We had the equation for the decay rate.

\[
\Gamma_{1d} = \frac{\alpha e^3}{2\pi c^2} \sum_i \int d\Omega_i \int_0^\infty \frac{4\pi}{3} dr_r R^{*}_{10} R_{21} \int d\Omega^{*}_{10} \left( \epsilon_z Y_{10} + \frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} \right) Y_{1m_l^*}^2
\]

We have performed that radial integration which will be unchanged. Assume that we start in a polarized state with \( m_i = 1 \). We then look at our result for the angular integration in the matrix element

\[
\left( \epsilon_z Y_{10} + \frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} \right) Y_{1m_i}^2
\]

where we have set \( m_i = 1 \) eliminating two terms.

Let’s study the rate as a function of the angle of the photon from the z axis, \( \theta_1 \). The rate will be independent of the azimuthal angle. We see that the rate is proportional to \( \epsilon_x^2 + \epsilon_y^2 \). We still must sum over the two independent transverse polarizations. For clarity, assume that \( \phi = 0 \) and the photon is therefore emitted in the x-z plane. One transverse polarization can be in the y direction. The other is in the x-z plane perpendicular to the direction of the photon. The x component is proportional to \( \cos \theta_1 \). So the rate is proportional to \( \epsilon_x^2 + \epsilon_y^2 = 1 + \cos^2 \theta_1 \).

If we assume that \( m_i = 0 \) then only the \( \epsilon_z \) term remains and the rate is proportional to \( \epsilon_z^2 \). The angular distribution then goes like \( \sin^2 \theta_1 \).

27.9 Vector Operators and the Wigner Eckart Theorem

There are some general features that we can derive about operators which are vectors, that is, operators that transform like a vector under rotations. We have seen in the sections on the Electric Dipole approximation and subsequent calculations that the vector operator \( \vec{r} \) could be written as its magnitude \( r \) and the spherical harmonics \( Y_{1m} \). We found that the \( Y_{1m} \) could change the orbital angular momentum (from initial to final state) by zero or one unit. This will be true for any vector operator.

In fact, because the vector operator is very much like adding an additional \( \ell = 1 \) to the initial state angular momentum, Wigner and Eckart proved that all matrix elements of vector operators can be written as a reduced matrix element which does not depend on any of the \( m \), and Clebsch-Gordan coefficients. The basic reason for this is that all vectors transform the same way under rotations, so all have the same angular properties, being written in terms of the \( Y_{1m} \).

Note that it makes sense to write a vector \( \vec{V} \) in terms of the spherical harmonics using

\[
V_\pm = \frac{V_x \pm iV_y}{\sqrt{2}}
\]
and

\[ V_0 = V_z. \]

We have already done this for angular momentum operators.

Let's consider our vector \( V^q \) where the integer \( q \) runs from 0 to 1. The Wigner-Eckart theorem says

\[ \langle \alpha' j' m' \mid V^q \mid \alpha j m \rangle = \langle j' m' | j 1 m q \rangle \langle \alpha' j' || V || \alpha j \rangle \]

Here \( \alpha \) represents all the (other) quantum numbers of the state, not the angular momentum quantum numbers. \( j m \) represent the usual angular momentum quantum numbers of the states. \( \langle \alpha' j' || V || \alpha j \rangle \) is a reduced matrix element. Its the same for all values of \( m \) and \( q \). Its easy to understand that if we take a matrix element of \( 10r \) it will be 10 times the matrix element of \( r \). Nevertheless, all the angular part is the same. This theorem states that all vectors have essentially the same angular behavior. This theorem again allows us to deduce that \( \Delta \ell = -1, 0, +1 \).

The theorem can be generalized for spherical tensors of higher (or even lower) rank than a vector.

### 27.10 Exponential Decay

We have computed transition rates using our theory of radiation. In doing this, we have assumed that our calculations need only be valid near \( t = 0 \). More specifically, we have assumed that we start out in some initial state \( i \) and that the amplitude to be in that initial state is one. The probability to be in the initial state will become depleted for times on the order of the lifetime of the state. We can account for this in terms of the probability to remain in the initial state.

Assume we have computed the total transition rate.

\[ \Gamma_{t,\text{tot}} = \sum_n \Gamma_{i \rightarrow n} \]

This transition rate is the probability per unit time to make a transition away from the initial state evaluated at \( t = 0 \). Writing this as an equation we have.

\[ \left. \frac{dP_i}{dt} \right|_{t=0} = -\Gamma_{t,\text{tot}} \]

For larger times we can assume that the probability to make a transition away from the initial state is proportional to the probability to be in the initial state.

\[ \frac{dP_i(t)}{dt} = -\Gamma_{t,\text{tot}} P_i(t) \]

The solution to this simple first order differential equation is

\[ P_i(t) = P_i(t = 0)e^{-\Gamma_{t,\text{tot}}t} \]

If you are having any trouble buying this calculation, think of a large ensemble of hydrogen atoms prepared to be in the 2p state at \( t = 0 \). Clearly the number of atoms remaining in the 2p state will obey the equation

\[ \frac{dN_{2p}(t)}{dt} = -\Gamma_{t,\text{tot}} N_{2p}(t) \]

and we will have our exponential time distribution.
We may define the lifetime of a state to the the time after which only $\frac{1}{e}$ of the decaying state remains.

$$\tau = \frac{1}{\Gamma_{1}\text{ord}}$$

### 27.11 Lifetime and Line Width

Now we have computed the lifetime of a state. For some atomic, nuclear, or particle states, this lifetime can be very short. We know that energy conservation can be violated for short times according to the uncertainty principle

$$\Delta E \Delta t \leq \frac{\hbar}{2}$$

This means that an unstable state can have an energy width on the order of

$$\Delta E \approx \frac{\hbar \Gamma_{1}\text{ord}}{2}$$

We may be more quantitative. If the probability to be in the initial state is proportional to $e^{-\Gamma t}$, then we have

$$|\psi_{i}(t)|^{2} = e^{-\Gamma t}$$

$$\psi_{i}(t) \propto e^{-\Gamma t/2}$$

$$\psi_{i}(t) \propto e^{-i E_{1}/\hbar} e^{-\Gamma t/2}$$

We may take the Fourier transform of this time function to the the amplitude as a function of frequency.

$$\phi_{i}(\omega) \propto \int_{0}^{\infty} \psi_{i}(t)e^{i\omega t} dt$$

$$\propto \int_{0}^{\infty} e^{-i E_{1}/\hbar} e^{-\Gamma t/2} e^{i\omega t} dt$$

$$= \int_{0}^{\infty} e^{-i\omega t} e^{-\Gamma t/2} e^{i\omega t} dt$$

$$= \int_{0}^{\infty} e^{i(\omega - \omega_{0} + i\frac{\Gamma}{2}) t} dt$$

$$= \left[ \frac{1}{i(\omega - \omega_{0} + i\frac{\Gamma}{2})} e^{i(\omega - \omega_{0} + i\frac{\Gamma}{2}) t} \right]_{0}^{\infty}$$

$$= \frac{i}{(\omega - \omega_{0} + i\frac{\Gamma}{2})}$$

We may square this to get the probability or intensity as a function of $\omega$ (and hence $E = \hbar \omega$).

$$I_{i}(\omega) = |\phi_{i}(\omega)|^{2} = \frac{1}{(\omega - \omega_{0})^{2} + \frac{\Gamma^{2}}{4}}$$

This gives the energy distribution of an unstable state. It is called the Breit-Wigner line shape. It can be characterized by its Full Width at Half Maximum (FWHM) of $\Gamma$. 

The Breit-Wigner will be the observed line shape as long as the density of final states is nearly constant over the width of the line.

As $\Gamma \to 0$ this line shape approaches a delta function, $\delta (\omega - \omega_0)$.

For the 2p to 1s transition in hydrogen, we’ve calculated a decay rate of $0.6 \times 10^9$ per second. We can compute the FWHM of the width of the photon line.

$$\Delta E = h\Gamma = \frac{(1.05 \times 10^{-27} \text{erg s}) (0.6 \times 10^9 \text{ s}^{-1})}{1.602 \times 10^{-12} \text{erg eV}^{-1}} \approx 0.4 \times 10^{-6} \text{ eV}$$

Since the energy of the photon is about 10 eV, the width is about $10^{-7}$ of the photon energy. It’s narrow but not enough for example make an atomic clock. Weaker transitions, like those from E2 or M1 will be relatively narrower, allowing use in precision systems.

### 27.11.1 Other Phenomena Influencing Line Width

We have calculated the line shape due to the finite lifetime of a state. If we attempt to measure line widths, other phenomena, both of a quantum and non-quantum nature, can play a role in the observed line width. These are:

- Collision broadening,
- Doppler broadening, and
- Recoil.

Collision broadening occurs when excited atoms or molecules have a large probability to change state when they collide with other atoms or molecules. If this is true, and it usually is, the mean time to collision is an important consideration when we are assessing the lifetime of a state. If the mean time between collisions is less than the lifetime, then the line-width will be dominated by collision broadening.

An atom or molecule moving through a gas sweeps through a volume per second proportional to its cross section $\sigma$ and velocity. The number of collisions it will have per second is then

$$\Gamma_c = N_{\text{collision/sec}} = nv\sigma$$

where $n$ is the number density of molecules to collide with per unit volume. We can estimate the velocity from the temperature.

$$\frac{1}{2}mv^2 = \frac{3}{2}kT$$

$$v_{RMS} = \sqrt{\frac{3kT}{m}}$$

$$\Gamma_c = n\sqrt{\frac{3kT}{m}\sigma}$$

The width due to collision broadening increases with the pressure of the gas. It also depends on temperature. This is basically a quantum mechanical effect broadening a state because the state only exists for a short period of time.
Doppler broadening is a simple non-quantum effect. We know that the frequency of photons is shifted if
the source is moving — shifted higher if the source is moving toward the detector, and shifted lower if it
is moving away.

\[
\Delta \omega = \frac{v}{c} \omega
\]

\[
\frac{\Delta \omega}{\omega} = \frac{\sqrt{kT/m}}{c} = \frac{\sqrt{kT}}{mc^2}
\]

This becomes important when the temperature is high.

Finally, we should be aware of the effect of recoil. When an atom emits a photon, the atom must recoil
to conserve momentum. Because the atom is heavy, it can carry a great deal of momentum while taking
little energy, still the energy shift due to recoil can be bigger than the natural line width of a state. The
photon energy is shifted downward compared to the energy difference between initial and final atomic
states. This has the consequence that a photon emitted by an atom will not have the right energy to be
absorbed by another atom, raising it up to the same excited state that decayed. The same recoil effect
shifts the energy need to excite a state upward. Let's do the calculation for Hydrogen.

\[
\vec{p}_H = \vec{p}_\gamma
\]

\[
p_\gamma \approx \frac{E}{c}
\]

\[
E_H = \frac{\gamma^2}{2m_p} = \frac{E^2}{2m_pc^2}
\]

\[
\frac{\Delta E}{E} = \frac{E}{2m_pc^2}
\]

For our 2p to 1s decay in Hydrogen, this is about 10 eV over 1860 MeV, or less than one part in \(10^8\).
One can see that the effect of recoil becomes more important as the energy radiated increases. The
energy shift due to recoil is more significant for nuclear decays.

\section*{27.12 Phenomena of Radiation Theory}

\subsection*{27.12.1 The Mössbauer Effect}

In the case of the emission of x-rays from atoms, the recoil of the atom will shift the energy of the x-ray
so that it is not reabsorbed. For some experiments it is useful to be able to measure the energy of the
x-ray by reabsorbing it. One could move the detector at different velocities to find out when re-absorption
was maximum and thus make a very accurate measurement of energy shifts. One example of this would
be to measure the gravitational red (blue) shift of x-rays.

Mössbauer discovered that atoms in a crystal need not recoil significantly. In fact, the whole crystal, or
at least a large part of it may recoil, making the energy shift very small. Basically, the atom emitting
an x-ray is in a harmonic oscillator (ground) state bound to the rest of the crystal. When the x-ray is
emitted, there is a good chance the HO remains in the ground state. An analysis shows that the
probability is approximately

\[
P_0 = e^{-E_{recoil}/\hbar\omega_{HO}}
\]

Thus a large fraction of the radiation is emitted (and reabsorbed) without a large energy shift. (Remember
that the crystal may have \(10^{23}\) atoms in it and that is a large number.
The Mössbauer effect has been used to measure the gravitational red shift on earth. The red shift was compensated by moving a detector, made from the same material as the emitter, at a velocity (should be equal to the free fall velocity). The blue shift was measured to be

\[ \frac{\Delta \omega}{\omega} = (5.13 \pm 0.51) \times 10^{-15} \]

when \( 4.92 \times 10^{-15} \) was expected based upon the general principle of equivalence.

### 27.12.2 LASERs

Light Amplification through Stimulated Emission of Radiation is the phenomenon with the acronym LASER. As the name would indicate, the LASER uses stimulated emission to generate an intense pulse of light. Our equations show that the decay rate of a state by emission of a photon is proportional to the number (plus one) of photons in the field (with the same wave-number as the photon to be emitted).

\[ \tilde{A}(\vec{r}, t) = \left[ \frac{2\pi \hbar c^2}{\omega V} \right]^{\frac{1}{2}} \hat{e} \left( \sqrt{N} e^{i(\vec{k} \cdot \vec{r} - \omega t)} + \sqrt{N + 1} e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right) \]

Here “plus one” is not really important since the number of photons is very large.

Let's assume the material we wish to use is in a cavity. Assume this material has an excited state that can decay by the emission of a photon to the ground state. In normal equilibrium, there will be many more atoms in the ground state and transitions from one state to the other will be in equilibrium and black body radiation will exist in the cavity. We need to circumvent equilibrium to make the LASER work. To cause many more photons to be emitted than are reabsorbed a LASER is designed to produce a population inversion. That is, we find a way to put many more atoms in the excited state than would be the case in equilibrium.

If this population inversion is achieved, the emission from one atom will increase the emission rate from the other atoms and that emission will stimulate more. In a pulsed laser, the population of the excited state will become depleted and the light pulse will end until the inversion can be achieved again. If the population of the excited state can be continuously pumped up, then the LASER can run continuously.

This optical pumping to achieve a population inversion can be done in a number of ways. For example, a Helium-Neon LASER has a mixture of the two gases. If a high voltage is applied and an electric current flows through the gases, both atoms can be excited. It turns out that the first and second excited states of Helium have almost the same excitation energy as the 4s and 5s excitations of Neon. The Helium states can't make an E1 transition so they are likely to excite a Neon atom instead. An excited Helium atom can de-excite in a collision with a Neon atom, putting the Neon in a highly excited state. Now there is a population inversion in the Neon. The Neon decays more quickly so its de-excitation is dominated by photon emission.
Another way to get the population inversion is just the use of a metastable state as in a ruby laser. A normal light source can excite a higher excited state which decays to a metastable excited state. The metastable state will have a much larger population than in equilibrium.

A laser with a beam coming out if it would be made in a cavity with a half silvered mirror so that the radiation can build up inside the cavity, but some of the radiation leaks out to make the beam.
27.13 Examples

27.13.1 The 2P to 1S Decay Rate in Hydrogen

27.14 Derivations and Computations

27.14.1 Energy in Field for a Given Vector Potential

We have the vector potential

\[ \vec{A}(\vec{r}, t) \equiv 2 \tilde{A}_0 \cos(\vec{k} \cdot \vec{r} - \omega t). \]

First find the fields.

\[
\vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} = \frac{2\omega}{c} \tilde{A}_0 \sin(\vec{k} \cdot \vec{r} - \omega t)
\]

\[
\vec{B} = 2\vec{v} \times \vec{A} = 2\vec{k} \times \tilde{A}_0 \sin(\vec{k} \cdot \vec{r} - \omega t)
\]

Note that, for an EM wave, the vector potential is transverse to the wave vector. The energy density in the field is

\[ U = \frac{1}{8\pi} \left( E^2 + B^2 \right) = \frac{1}{8\pi} 4 \left( \frac{\omega^2}{c^2} + k^2 \right) \tilde{A}_0^2 \sin^2(\vec{k} \cdot \vec{r} - \omega t) = \frac{2\omega^2}{2\pi c^2} \tilde{A}_0^2 \sin^2(\vec{k} \cdot \vec{r} - \omega t) \]

Averaging the sine square gives one half, so, the energy in a volume \( V \) is

\[ E \text{nergy} = \frac{\omega^2 \tilde{A}_0^2 V}{2\pi c^2} \]

27.14.2 General Phase Space Formula

If there are \( N \) particles in the final state, we must consider the number of states available for each one. Our phase space calculation for photons was correct even for particles with masses.

\[ d^3 n = \frac{VD^p}{(2\pi \hbar)^3} \]

Using Fermi’s Golden Rule as a basis, we include the general phase space formula into our formula for transition rates.

\[
\Gamma_{i \rightarrow f} = \int \prod_{k=1}^{N} \left( \frac{Vd^3p_k}{(2\pi \hbar)^3} \right) |M_{fi}|^2 \delta \left( E_i - E_f - \sum_k E_k \right) \delta^3 \left( \vec{p}_i - \vec{p}_f - \sum_k \vec{p}_k \right)
\]

In our case, for example, of an atom decaying by the emission of one photon, we have two particles in the final state and the delta function of momentum conservation will do one of the 3D integrals getting us back to the same result. We have not bothered to deal with the free particle wave function of the recoiling atom, which will give the factor of \( \frac{1}{V} \) to cancel the \( V \) in the phase space for the atom.
27.14.3 Estimate of Atomic Decay Rate

We have the formula

\[ \Gamma_{tot} = \frac{e^2(E_i - E_f)}{2\pi \hbar^2 m^2 c^3} \int d\Omega_\nu |\langle \phi_n | e^{-i\hat{\mathbf{p}} \cdot \mathbf{r} \hat{\mathbf{r}} \cdot \mathbf{p}_i \rangle \phi_i \rangle|^2 \]

Let's make some approximations.

\[ \hat{\mathbf{p}} \cdot \mathbf{r} \approx |\mathbf{p}| = m|\nu| \approx m\nu c = \alpha \nu c \]

\[ \hat{k} \cdot \mathbf{r} \approx \frac{\hbar}{\nu} a_0 \approx \frac{\alpha^2 m c^2}{\hbar} a_0 = \frac{\alpha^2 m c^2}{2\hbar c} \approx \alpha \frac{\hbar}{\nu} \approx 1 + \frac{i\alpha}{2} \approx 1 \]

\[ e^{-i\hat{k} \cdot \mathbf{r}} \approx e^{i\varphi} \approx 1 + \frac{i\alpha}{2} \approx 1 \]

\[ \Gamma_{tot} = \frac{e^2(E_i - E_f)}{2\pi \hbar^2 m^2 c^3} (4\pi) |\alpha \nu c|^2 = \frac{\alpha(E_i - E_f)}{2\pi \hbar^2 m^2 c^3} (4\pi) |\alpha \nu c|^2 = \frac{\alpha^2 m c^2}{\hbar} \]

\[ \approx \frac{\alpha^2 m c^2}{\hbar} \]

\[ = \frac{0.51 \text{ MeV} \times 10^{10} \text{ cm/sec}}{137^2(197 \text{ MeV}^2)} \approx 2 \times 10^{10} \text{ sec}^{-1} \]

This gives a life time of about 50 psec.

27.15 Homework Problems

1. The interaction term for Electric Quadrupole transitions correspond to a linear combination of spherical harmonics, \( Y_{2m} \), and are parity even. Find the selection rules for E2 transitions.

2. Magnetic dipole transitions are due to an axial vector operator and hence are proportional to the \( Y_{1m} \) but do not change parity (unlike a vector operator). What are the M1 selection rules?

3. Draw the energy level diagram for hydrogen up to \( n = 3 \). Show the allowed E1 transitions. Use another color to show the allowed E2 and M1 transitions.

4. Calculate the decay rate for the \( 3p \rightarrow 1s \) transition.

5. Calculate the decay rate for the \( 3d \rightarrow 2p \) transition in hydrogen.

6. Assume that we prepare Hydrogen atoms in the \( \psi_{211} = \psi_{211} \) state. We set up an experiment with the atoms at the origin and detectors sensitive to the polarization along each of the 3 coordinate axes. What is the probability that a photon with its wave vector pointing along the axis will be Left Circularly Polarized?

7. Photons from the \( 3p \rightarrow 1s \) transition are observed coming from the sun. Quantitatively compare the natural line width to the widths from Doppler broadening and collision broadening expected for radiation from the sun's surface.
27.16 Sample Test Problems

1. A hydrogen atom is in the $n = 5$, $^3D_{\frac{3}{2}}$ state. To which states is it allowed to decay via electric dipole transitions? What will be the polarization for a photon emitted along the $z$-axis if $m_l$ decreases by one unit in the decay?

2. Derive the selection rules for radiative transitions between hydrogen atom states in the electric dipole approximation. These are rules for the change in $l$, $m$, and $s$.

3. State the selection rules for radiative transitions between hydrogen atom states in the electric dipole approximation. These are rules for the allowed changes in $l$, $m$, $s$, and parity. They can be easily derived from the matrix element given on the front of the test. Draw an energy level diagram (up to $n = 3$) for hydrogen atoms in a weak $B$ field. Show the allowed E1 transitions from $n = 3$ to $n = 1$ on that diagram.

4. Calculate the differential cross section, $\frac{d\sigma}{d\Omega}$, for high energy scattering of particles of momentum $p$, from a spherical shell delta function

$$V(r) = \lambda \delta(r - r_0)$$

Assume that the potential is weak so that perturbation theory can be used. Be sure to write your answer in terms of the scattering angles.

5. Assume that a heavy nucleus attracts $K_0$ mesons with a weak Yukawa potential $V(r) = \frac{\lambda e^{-\alpha r}}{r}$. Calculate the differential cross section, $\frac{d\sigma}{d\Omega}$, for scattering high energy $K_0$ mesons (mass $m_{K^0}$) from that nucleus. Give your answer in terms of the scattering angle $\theta$. 