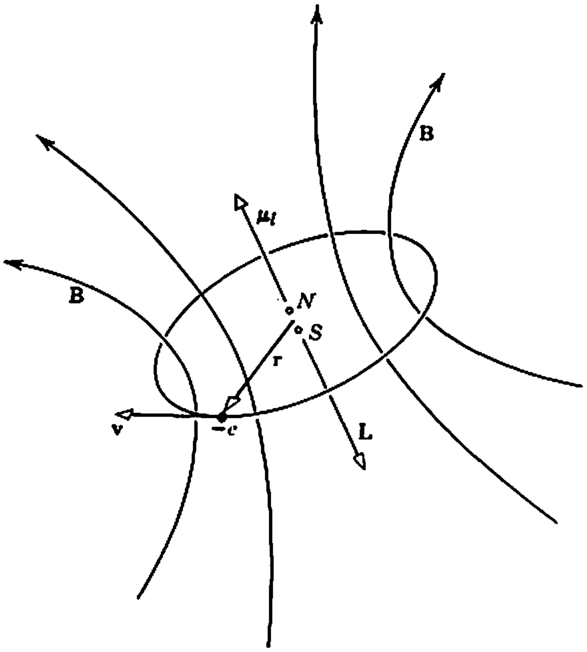
In this Chapter we continue our discussion of one-electron atoms. The energy levels of the states in the atom are shifted when the atom is placed in a magnetic field. The energy shift depends on the dipole moment of the electron.

Let us first examine a classical picture of the electron in a circular orbit of radius r. If the electron is moving with a velocity v, the motion of the electron represents a current I where

$$I = \frac{dq}{dt} = \frac{e}{T} = \frac{e}{\left(\frac{2\pi r}{v}\right)} = \frac{ev}{2\pi r}$$

The classical dipole moment associated with this current is equal to

$$\mu_\ell = IA = \left(\frac{ev}{2\pi r}\right)\left(\pi r^2\right) = \frac{1}{2} evr$$



The circulating current will create a non-uniform magnetic field that is schematically indicated in the Figure.
The angular momentum of the electron is given by

$$L = (mv)r$$

The dipole moment of the electron can thus be rewritten as

$$\mu_\ell = \frac{1}{2} evr = \frac{1}{2}\frac{e}{m} mvr = \frac{1}{2}\frac{e}{m} L$$

We thus conclude that the ratio of the dipole moment of the electron and its angular momentum is constant:

$$\frac{\mu_\ell}{L} = \frac{1}{2}\frac{e}{m} = \text{constant}$$

This ratio is commonly rewritten in terms of the **Bohr magneton**:

$$\frac{\mu_\ell}{L} = \frac{g_\ell \mu_b}{\hbar}$$

where

$$\mu_b = \frac{e\hbar}{2m} \quad \text{(Bohr magneton)}$$

and

$$g_\ell = 1 \quad \text{(orbital } g \text{ factor)}$$

The dipole moment has a direction opposite to the direction of the angular momentum. This is a result of the negative charge of the electron and the fact that the current is thus directed in a direction opposite to the direction of motion of the electron. The expression of the dipole moment in vector notation is

$$\vec{\mu}_\ell = -\frac{g_\ell \mu_b}{\hbar} \vec{L}$$

Applying what we learned from quantum mechanics we obtain the following expressions for the dipole moment of the electron:

$$\left|\vec{\mu}_\ell\right| = \frac{g_\ell \mu_b}{\hbar}\left|\vec{L}\right| = \frac{g_\ell \mu_b}{\hbar}\left(\sqrt{\ell(\ell+1)}\hbar\right) = g_\ell \mu_b \sqrt{\ell(\ell+1)}$$

$$\vec{\mu}_{\ell,z} = -\frac{g_\ell \mu_b}{\hbar} L_z = -\frac{g_\ell \mu_b}{\hbar}\left(m_\ell \hbar\right) = -g_\ell \mu_b m_\ell$$

When the atom is put in an external magnetic field, a torque will be exerted on the electron. The torque depends on the angle between the direction of the dipole moment and the direction of the magnetic field:

$$\vec{\tau} = \vec{\mu}_\ell \times \vec{B}$$

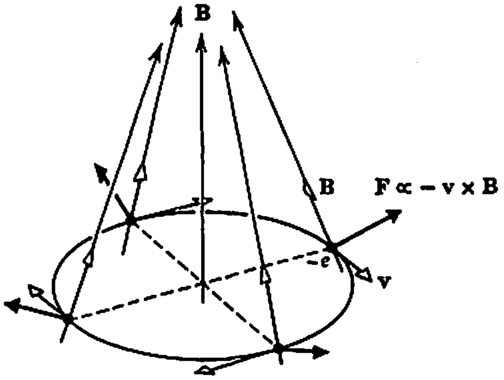
The potential energy of the dipole depends on its orientation with respect to the external magnetic field. The potential energy of the dipole is given by the following expression:

$$U = -\vec{\mu}_\ell \cdot \vec{B}$$

In order to reduce their potential energy, the dipoles will try to align themselves with the external field. In order to change their orientation, the dipoles must be able to dissipate the energy that is released when their orientation changes. If there is no mechanism for the dipoles to dissipate this energy, they will not be able to change their orientation, and instead will start to precess around the direction of the external magnetic field. The precession frequency is equal to

$$\vec{\omega} = \frac{g_\ell \mu_\ell}{\hbar} \vec{B}$$

This equation is obtained from our classical description of the motion of the electron, but the same result is obtained from a proper quantum-mechanical treatment.



If the external magnetic field is not uniform, the effect of the field on the atom/electron is more complicated. Consider the motion of an electron in the field indicated in the Figure on the right. The magnetic force exerted on the electron is directed as indicated in the Figure. The minus sign in front of the cross product between the velocity and the magnetic field is due to the negative charge of the electron. If we assume that the magnitude of the magnetic field is constant around the orbit and only the direction of the magnetic field changes around the orbit, we conclude:

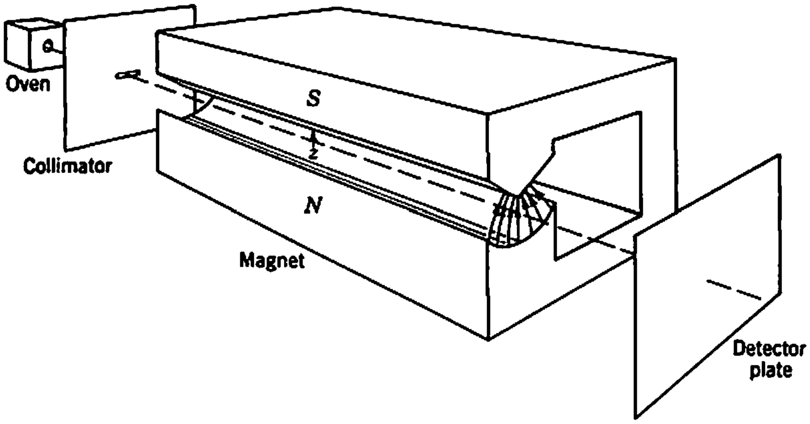
- The components of the force in the plane of the orbit cancel around the orbit. There is thus no net translation in the orbital plane.
- The components of the force in the direction perpendicular to the orbital plane do not cancel around the orbit if the field is non uniform and there will be a net force in the direction of the magnetic field. Note: if the field is uniform, the net force around the orbit in this direction is zero. The vertical component of the average force on the electron is equal to

$$\vec{F}_z = \frac{\partial B_z}{\partial z} \mu_{\ell,z}$$

The electron thus will feel:

- a torque, which leads to precession.
- a force, which leads to a deflection.

Both the torque and the force on the electron are a function of the dipole moment. Since the dipole moment depends on the angular momentum of the electron, we expect that both the torque and the force are quantized.

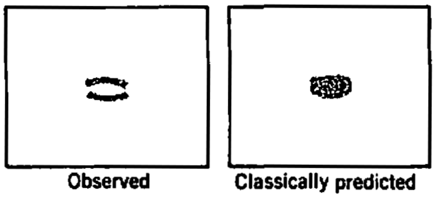


The predictions made by the theory we have discussed so far were studied in the **Stern-Gerlach experiment**, shown schematically in the Figure above. Neutral atoms enter a region with a non-uniform magnetic field, are deflected as a result of the magnetic force, and are detected on a detector plate at the exit of the magnet. Since the net force in the z direction depends on the z component of the dipole moment we expect that the force on an electron in an orbit with an azimuthal quantum number ℓ to have $2\ell+1$ components since the dipole moment will have $2\ell+1$ possible values:

$$\mu_{\ell,z} = -g_\ell \mu_b m_\ell \quad \text{where} \quad m_\ell = -\ell, -\ell+1, ..., 0, ..., \ell-1, \ell$$

Since ℓ is an integer, the number of components is odd, and one component will not be deflected since $m_\ell = 0$.

The first measurements were carried out with neutral Ag atoms. The observations, shown in the Figure on the right, disagreed with the predictions based on the quantum mechanical properties of the angular momentum. The main differences are:



- The number of discrete components observed is 2: even, not odd.
- There is no component that is not deflected.

The experiment was repeated with Hydrogen atoms in their ground state. In this state, the electrons are in an $\ell = 0$ orbit and no deflection of the beam of Hydrogen atoms was expected. However, the observations showed that the beam was separated into two components.

The only way to reconcile these observations was to assume that the electron has a built-in dipole moment, not associated with its orbital motion, but with its spin. The spin state of the electron is specified by a quantum number s which has properties similar to the quantum number ℓ associated with the orbital motion:

- $S = \sqrt{s(s+1)}\hbar$
- $S_z = m_s\hbar$ where $m_s = -s, -s+1, ..., s-1, s$

The dipole moment associated with the spin of the electron has the following properties:

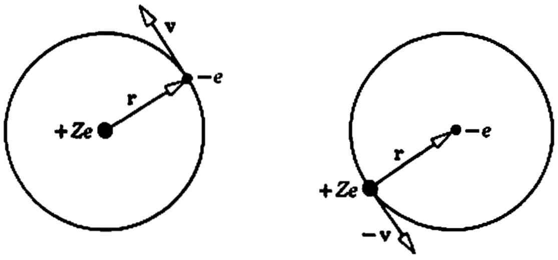
- $\vec{\mu}_s = -\frac{g_s \mu_b}{\hbar}\vec{S}$
- $\mu_{s,z} = -g_s \mu_b m_s$

The factor g_s is called the **spin *g* factor**.

The observation that the Hydrogen beam splits into two components requires that $2s+1 = 2$ or $s = ½$. The amount of deflection can be used to determine that the product $g_s m_s$ must be equal to ±1. This, combined with the possible values of m_s tells us that the spin g factor must be equal to 2.

The fact that the electron carries spin has the following consequences:

- Since the electron has two spin states, the number of electrons that can reside in a state specified by n, ℓ, and m is doubled. Electrons have to satisfy the Pauli exclusion principle for Fermions and two electrons can not occupy a state with the same quantum numbers.
- The electron spin interacts with the magnetic field generated by the nucleus, and this interaction shifts the energy levels. This interaction is called the **spin-orbit interaction**.



To estimate the shift in the energy levels of the states in the atom due to the spin-orbit interaction, we use a classical model to estimate the magnitude of the magnetic field seen by the electron in the Hydrogen atom. From the electrons point of view, the proton is moving in a circular orbit of radius r. The magnetic field generated by the orbiting proton at the location of the electron is equal to

$$\vec{B} = -\frac{Ze\mu_0}{4\pi}\frac{\vec{v}\times\hat{r}}{r^2} = -(\varepsilon_0\mu_0)\vec{v}\times\frac{Ze}{4\pi\varepsilon_0}\frac{\hat{r}}{r^2} = -\frac{1}{c^2}\vec{v}\times\vec{E}$$

The shift in the energy of the electron due to the interaction of its dipole moment with this magnetic field is equal to

$$\Delta E = -\vec{\mu}_s \cdot \vec{B} = \frac{g_s \mu_b}{\hbar}\left(\vec{S} \cdot \vec{B}\right)$$

Note that this energy shift is the energy shift in the rest frame of the electron. When we transform to the reference frame in which the proton is at rest, the energy shift is equal to

$$\Delta E = \frac{1}{2}\frac{g_s \mu_b}{\hbar}\left(\vec{S} \cdot \vec{B}\right) = \frac{\mu_b}{\hbar}\left(\vec{S} \cdot \vec{B}\right)$$

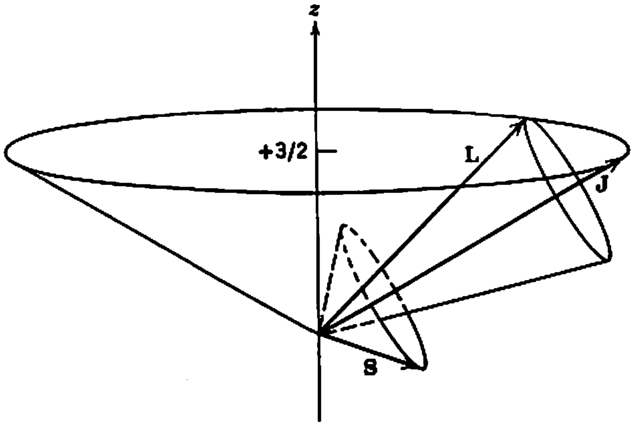
Details on this transformation can be found in Appendix O of the textbook.
The magnetic field seen by the electron can be rewritten in the following way:

$$\vec{B} = \frac{1}{ec^2}\vec{v} \times \left(-e\vec{E}\right) = \frac{1}{emc^2}\left(m\vec{v}\right) \times \vec{F} = \frac{1}{emc^2}\vec{p} \times \left(-\frac{dV}{dr}\frac{\vec{r}}{r}\right) = -\frac{1}{emc^2}\frac{1}{r}\frac{dV}{dr}\vec{p} \times \vec{r} = \frac{1}{emc^2}\frac{1}{r}\frac{dV}{dr}\vec{L}$$

The energy shift of the electron is thus equal to

$$\Delta E = \frac{\mu_b}{\hbar}\left(\vec{S} \cdot \vec{B}\right) = \frac{\mu_b}{\hbar}\frac{1}{emc^2}\frac{1}{r}\frac{dV}{dr}\left(\vec{S} \cdot \vec{L}\right) = \frac{\left(\frac{e\hbar}{2m}\right)}{\hbar}\frac{1}{emc^2}\frac{1}{r}\frac{dV}{dr}\left(\vec{S} \cdot \vec{L}\right) = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\left(\vec{S} \cdot \vec{L}\right)$$

We can express the energy shift in terms of the **total angular momentum** of the electron. The total angular momentum of the electron is the sum of the orbital angular momentum of the electron and the angular momentum associated with the spin:



$$\vec{J} = \vec{L} + \vec{S}$$

The total angular momentum is quantized in the same way as L and S are quantized:

- $J = \sqrt{j(j+1)}\hbar$
- $J_z = m_j \hbar$ where $m_j = -j, -j+1, \ldots, j-1, j$

The component of the projection of the total angular momentum along the z axis is the sum of the projections of the orbital and spin angular momenta along the z axis. The quantum number associated with this projection is equal to

$$m_j = m_\ell + m_s = m_\ell \pm \frac{1}{2}$$

The maximum projection of the total angular momentum along the z axis thus corresponds to a quantum number

$$m_{j,\max} = m_{\ell,\max} + \frac{1}{2} = \ell + \frac{1}{2} \quad \Rightarrow \quad j_{\max} = \ell + \frac{1}{2}$$

If the orbital angular momentum is 0 ($\ell = 0$) the total angular momentum is equal to the spin of the electron and $j = ½$. In all other cases, there are two possible values of j:

$$j = \ell + \frac{1}{2} \quad \text{and} \quad j = \ell - \frac{1}{2}$$

Using basic geometry we can relate the limits of the total angular momentum to the orbital and spin angular momenta (see Figure at the bottom of the page):

$$\left||\vec{L}| - |\vec{S}|\right| \le |\vec{J}| \le |\vec{L}| + |\vec{S}|$$

The relation

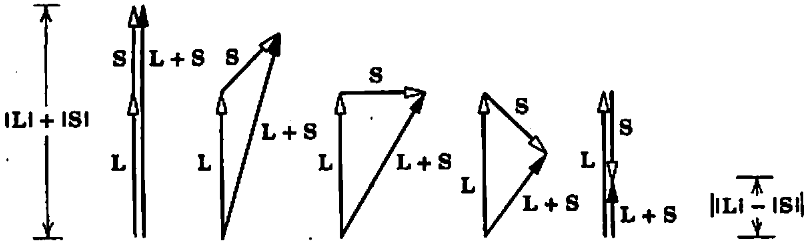
$$|\vec{J}| \le |\vec{L}| + |\vec{S}|$$

was used to determine the maximum quantum number associated with the total angular momentum, $j_{\max}$. The minimum quantum number, $j_{\min}$, is obtained from the relation

$$\left||\vec{L}| - |\vec{S}|\right| \le |\vec{J}|$$

This relation can be rewritten as

$$\left|\sqrt{\ell(\ell+1)} - \sqrt{s(s+1)}\right| \le \sqrt{j(j+1)}$$



Since each side is positive, we can square each side without changing the relative relation:

$$\ell(\ell+1)+s(s+1)-2\sqrt{\ell(\ell+1)}\sqrt{s(s+1)}\leq j(j+1)$$

Since the electron has a spin ½ we can rewrite this relation as

$$\ell(\ell+1)+\frac{3}{4}-\sqrt{3\ell(\ell+1)}=\ell^2+\ell+\frac{3}{4}-\sqrt{3\ell(\ell+1)}\leq j(j+1)$$

Now consider possible values of ℓ:

- Consider $j=\ell-\frac{1}{2}$. Substituting this value of *j* in the inequality we obtain

  $$\ell^2+\ell+\frac{3}{4}-\sqrt{3\ell(\ell+1)}\leq\left(\ell-\frac{1}{2}\right)\left(\ell+\frac{1}{2}\right)=\ell^2-\frac{1}{4}\quad\Rightarrow$$

  $$\ell+1\leq\sqrt{3\ell(\ell+1)}\quad\Rightarrow\quad(\ell+1)^2\leq3\ell(\ell+1)\quad\Rightarrow$$

  $$\ell+1\leq3\ell\quad\Rightarrow\quad1\leq2\ell\quad\Rightarrow\quad\frac{1}{2}\leq\ell$$

  This inequality is satisfied for all ℓ as long as $\ell\neq0$.
- Consider $j=\ell-\frac{3}{2}$. Substituting this value of *j* in the inequality we obtain

  $$\ell^2+\ell+\frac{3}{4}-\sqrt{3\ell(\ell+1)}\leq\left(\ell-\frac{3}{2}\right)\left(\ell-\frac{1}{2}\right)=\ell^2-2\ell+\frac{3}{4}\quad\Rightarrow$$

  $$3\ell\leq\sqrt{3\ell(\ell+1)}\quad\Rightarrow\quad9\ell^2\leq3\ell^2+3\ell\quad\Rightarrow\quad6\ell^2\leq3\ell\quad\Rightarrow$$

  $$6\ell\leq3\quad\Rightarrow\quad\ell\leq\frac{1}{2}$$

  This inequality will never be satisfied if we assume that $\ell\neq0$.
- Any smaller value of *j* will lead to inequalities that are never satisfied and we thus conclude that $j=\ell-\frac{1}{2}$ is the minimum value of *j*.

The energy shift due to the spin orbit interaction

$$\Delta E = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\left(\vec{S}\cdot\vec{L}\right)$$

can be expressed in terms of the quantum parameters specifying the state by observing that

$$\vec{S}\cdot\vec{L} = \frac{1}{2}\left(\left(\vec{L}+\vec{S}\right)\cdot\left(\vec{L}+\vec{S}\right)-\vec{L}\cdot\vec{L}-\vec{S}\cdot\vec{S}\right) = \frac{1}{2}\left(j\left(j+1\right)-\ell\left(\ell+1\right)-s\left(s+1\right)\right)\hbar^2$$

The energy shift is thus equal to

$$\Delta E = \frac{\hbar^2}{4m^2c^2}\left\{\left(j\left(j+1\right)-\ell\left(\ell+1\right)-s\left(s+1\right)\right)\right\}\frac{1}{r}\frac{dV}{dr}$$

Since the potential V for the Hydrogen atom is well known,

$$V\left(r\right) = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r},$$

the expectation value of

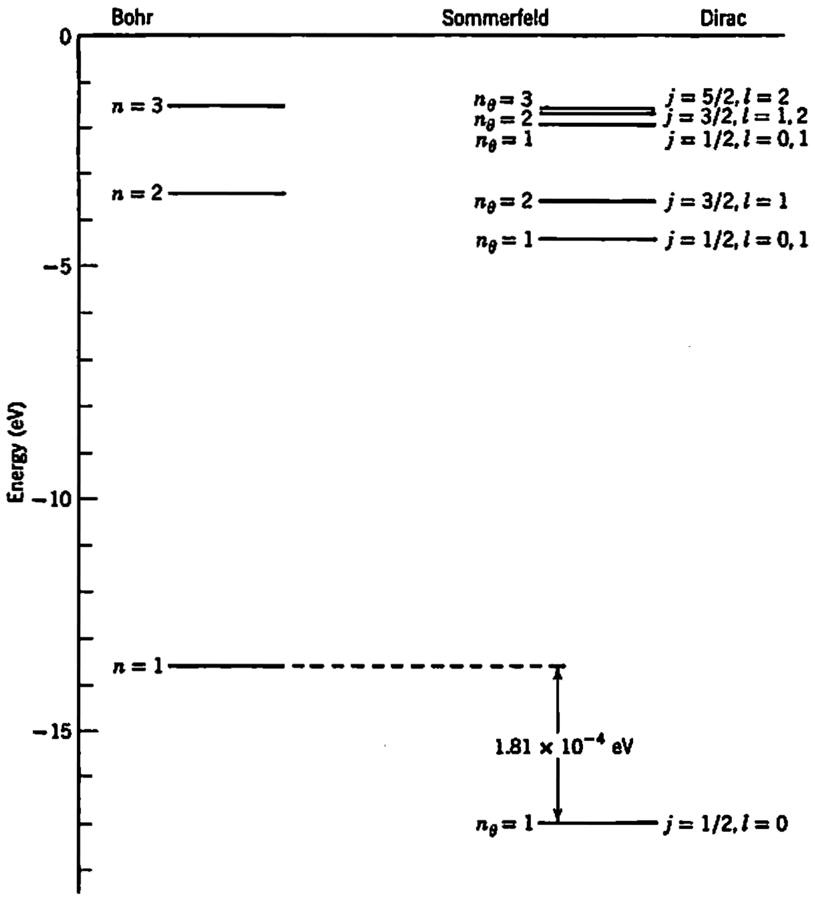
$$\left\langle \frac{1}{r}\frac{dV}{dr}\right\rangle$$

can be determined for the various eigenfunctions of the Hydrogen atom. The energies of the states in the Hydrogen atom, after applying the energy correction, will now not only depend on the principle quantum number n but also on the total angular momentum quantum number j:

$$E = -\frac{\mu e^4}{\left(4\pi\varepsilon_0\right)^2\left(2\hbar^2 n^2\right)}\left\{1+\frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}}-\frac{3}{4n}\right)\right\}$$

The energy levels obtained with this expression are shown in the level scheme on the next page.

Once we have determined the energy levels/states in an atom, we can start looking at the probability to observe transitions between states. Consider an atom that has two states: the initial state with an energy E_i and the final state with an energy E_f. The time dependence of the wavefunction describing these states is governed by the energy of these states:



$$\Psi_i(\vec{r},t) = \psi_i(\vec{r})e^{-iE_it/\hbar}$$

$$\Psi_f(\vec{r},t) = \psi_f(\vec{r})e^{-iE_ft/\hbar}$$

The probability density distribution of the atom in a specific state is independent of time:

$$\Psi_i^*(\vec{r},t)\Psi_i(\vec{r},t) = \left(\psi_i(\vec{r})e^{-iE_it/\hbar}\right)^*\left(\psi_i(\vec{r})e^{-iE_it/\hbar}\right) = \left(\psi_i^*(\vec{r})e^{+iE_it/\hbar}\right)\left(\psi_i(\vec{r})e^{-iE_it/\hbar}\right) = \psi_i^*(\vec{r})\psi_i(\vec{r})$$

We thus conclude that the atom will remain in a given state if it is in a pure eigenstate.

In order to look at transitions between states, we can start to look at the emission of radiation as a result of oscillating charged particles. In classical E&M you should have learned that an oscillating electric dipole, with a dipole moment p and oscillation frequency ν, radiates energy with an average rate of

$$\bar{R} = \frac{4\pi^3\nu^4}{3\varepsilon_0 c^3}p^2$$

The rate of photon emission is thus equal to

$$R = \frac{\overline{R}}{\hbar \nu} = \frac{4\pi^3 \nu^3}{3\varepsilon_0 \hbar c^3} p^2$$

For a single atom, R is the **atomic transition rate**. In order to look at transitions, we must evaluate the expectation value of the dipole moment.
The electric dipole moment associated with the motion of the electron is equal to

$$\vec{p} = -e\vec{r}$$

The expectation value of p is thus proportional to the expectation value of r. Consider the expectation value of p between a given initial state and final state:

$$\left\langle \Psi_f(\vec{r},t) \middle| \vec{r} \middle| \Psi_i(\vec{r},t) \right\rangle = \left\langle \psi_f(\vec{r}) \middle| \vec{r} \middle| \psi_i(\vec{r}) \right\rangle = \left\langle \psi_f(\vec{r}) \middle| \begin{pmatrix} r\sin\theta\cos\varphi \\ r\sin\theta\sin\varphi \\ r\cos\theta \end{pmatrix} \middle| \psi_i(\vec{r}) \right\rangle =$$

$$= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_f^* \begin{pmatrix} r\sin\theta\cos\varphi \\ r\sin\theta\sin\varphi \\ r\cos\theta \end{pmatrix} \psi_i \left(r^2 \sin\theta \, dr d\theta d\varphi \right)$$

Let us first consider the integration over the azimuthal angle. Since the azimuthal angle dependence of the wavefunctions is well established we can carry out this integration:

$$\int_0^{2\pi} e^{-im_f\varphi} \begin{pmatrix} \cos\varphi \\ \sin\varphi \\ 1 \end{pmatrix} e^{im_i\varphi} d\varphi = \int_0^{2\pi} \begin{pmatrix} \frac{1}{2}\left(e^{i\varphi} + e^{-i\varphi}\right) \\ \frac{1}{2i}\left(e^{i\varphi} - e^{-i\varphi}\right) \\ 1 \end{pmatrix} e^{i(m_i - m_f)\varphi} d\varphi =$$

$$= \left[\frac{1}{2} \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix} \int_0^{2\pi} e^{i(m_i - m_f + 1)\varphi} d\varphi \right] + \left[\frac{1}{2} \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix} \int_0^{2\pi} e^{i(m_i - m_f - 1)\varphi} d\varphi \right] +$$

$$+ \left[\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \int_0^{2\pi} e^{i(m_i - m_f)\varphi} d\varphi \right]$$

The first integral is only non-zero when $m_i - m_f + 1 = 0$; the second integral is only non-zero when $m_i - m_f - 1 = 0$; the third integral is only non-zero when $m_i - m_f = 0$. This leads to the first **selection rule** for transitions: $\Delta m = m_f - m_i = 0, \pm 1$.

A second set of selection rules is based on the angular momentum quantum number. The transition probability depends on the expectation value of the dipole moment of the electron. The magnitude of the amplitude of the dipole moment depends on the initial state and the final state and is equal to **the matrix element of the electric dipole moment p_{fi}** between these states where

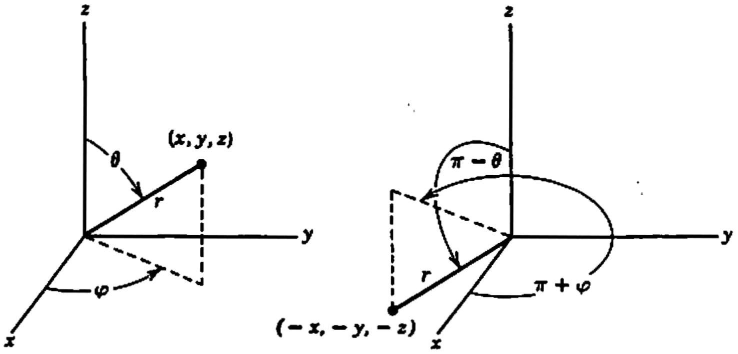
$$p_{fi} \equiv \langle \psi_f | e\vec{r} | \psi_i \rangle = \left| \int \psi_f^* e\vec{r} \psi_i \, d\tau \right|$$

A proper quantum mechanical treatment shows that the transition rate between the initial and final state is equal to

$$R = \frac{16\pi^3 \nu^3}{3\varepsilon_0 \hbar c^3} p_{fi}^2$$

Using the **parity of the wavefunction** we can make very specific production on the conditions under which the matrix element is non-zero. The parity of the wavefunction tells us what happens to the value of the wavefunction when we carry out the following coordinate transformation (shown schematically in the Figure on the right):

$$r \to r$$
$$\theta \to \pi - \theta$$
$$\varphi \to \pi + \varphi$$



A wavefunction has **even parity** when it does not change under this coordinate transformation. A wavefunction has **odd parity** when the wavefunction changes by (-1) under this transformation. The position vector *r* has odd parity. When we examine the solutions of the Schrödinger equation for the one-electron atom we notice that the parity of the wavefunctions depends on ℓ as $(-1)^\ell$. In order for the matrix element to be non-zero, the parity of its argument must be even. This requires that

$$(-1)^{\ell_f}(-1)(-1)^{\ell_i} = +1 \quad \Rightarrow \quad (-1)^{\ell_i+\ell_f} = (-1) \quad \Rightarrow \quad \ell_i + \ell_f = \text{odd}$$

We thus conclude that in order to a transition to have a non-zero transition probability, it must satisfy the following requirement:

$$\Delta\ell = \ell_f - \ell_i = \pm1, \pm3, \pm5, \ldots\ldots$$

The photons involved in the transition carry away angular momentum. The angular momentum carried away by the photon is $1\hbar$. In order to conserve angular momentum the selection rules for ℓ are replaced by the following rule:

$$\Delta j = 0, \pm1$$

It is obvious that when $\Delta j = \pm1$ linear momentum is conserved when a photon carries away one unit of angular momentum. When $\Delta j = 0$ angular momentum is conserved by changing the orientation of the total angular momentum vector.