(C1)

Time Dependent Perturbation Theory

We now want to study the time evolution of systems $H(t)$ under the influence of a time-dependent perturbation $W(t)$:

$$H(t) = H_0 + \lambda W(t) \qquad \lambda << 1 \qquad W(t) = 0 \text{ for } t < 0$$

$$H_0 |n\rangle = E_n |n\rangle$$

From the Schrodinger Equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \left[H_0 + \lambda W(t) \right] |\psi(t)\rangle$$

We are interested in systems where

$$|\psi(t=0)\rangle = |i\rangle \qquad \text{some initial state } i$$

We wish to calculate the probability that at time t after $t=0$ the system has evolved into some final state f:

$$P_{if}(t) = \left| \langle f | \psi(t) \rangle \right|^2$$

The eigenvector $|\psi(t)\rangle$ can be expressed in terms of the orthonormal basis vectors $|n\rangle$:

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle$$

where $c_n(t) = \langle n | \psi(t) \rangle$

Note that c_n <u>varies</u> with time.

(C2)

If we multiply the Schrodinger Eqn above by $\langle n|$:

$$i\hbar \frac{d}{dt} c_n(t) = E_n c_n(t) + \lambda \langle n|W(t)|\psi(t)\rangle$$

$$= E_n c_n(t) + \lambda \sum_k \underbrace{\langle n|W(t)|k\rangle}_{\equiv W_{nk}(t)} c_k(t)$$

Zeroth Order Solutions:

If $\lambda = 0$, then the Schrodinger is a simple, uncoupled differential equation:

$$i\hbar \frac{d}{dt} c_n(t) = E_n c_n(t)$$

$$c_n(t) = b_n e^{-iE_n t/\hbar}$$

b_n is a constant that depends upon the initial conditions

If λ is small then we can write the solution to the Schrodinger equation as

$$c_n(t) = b_n(t) e^{-iE_n t/\hbar}$$

where we hope that $b_n(t)$ is just a slowly varying function of time. Plugging back in:

$$i\hbar \left[e^{-iE_n t/\hbar} \frac{db_n}{dt} + \frac{-iE_n}{\hbar} e^{-iE_n t/\hbar} b_n \right] = E_n b_n e^{-iE_n t/\hbar} + \lambda \sum_k W_{nk} e^{-iE_k t/\hbar}$$

C3

If we define $\omega_{nk} \equiv \frac{1}{\hbar}(E_n - E_k)$, then

$$i\hbar \frac{d\, b_n(t)}{dt} = \lambda \sum_k e^{i\omega_{nk}t} W_{nk}(t)\, b_k(t)$$

We now expand b_n in powers of λ, and collect terms:

$$b_n(t) = b_n^{(0)}(t) + \lambda\, b_n^{(1)}(t) + \lambda^2\, b_n^{(2)}(t) + \cdots$$

<u>0th order</u>:

$$i\hbar \frac{d\, b_n^{(0)}(t)}{dt} = 0 \qquad \therefore\ b_n^{(0)}(t) = b_n^{(0)} = \text{constant}$$

<u>1st order</u>:

$$i\hbar \frac{d\, b_n^{(1)}(t)}{dt} = \sum_k e^{i\omega_{nk}t} W_{nk}(t)\, b_k^{(0)}(t)$$

To solve this equations, we choose our particular problem of a system where $|\psi(t)\rangle = |i\rangle$ for $t<0$. In that case, since the Schrodinger equations must be continuous at $t=0$:

$$b_n(t=0) = \delta_{ni}$$

and $$b_n^{(0)}(t=0) = \delta_{ni}$$

$$b_n^{(1)}(t=0) = 0$$

Since $b_n^{(0)}(t)$ is constant in time, we require that

$$b_n^{(0)}(t) = \delta_{ni} \qquad t>0$$

Plugging back into our 1st order differential equation yields:

$$i\hbar \frac{d b_n^{(1)}(t)}{dt} = \sum_k e^{i\omega_{nk}t} W_{nk}(t) \delta_{ki}$$

$$= e^{i\omega_{ni}t} W_{ni}(t)$$

And formally:

$$b_n^{(1)}(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{ni}t'} W_{ni}(t') dt'$$

The transition probability $P_{if}(t)$ for $|f\rangle \neq |i\rangle$ is

$$P_{if}(t) = \left| b_f(t) \right|^2$$

$$= \left| b_f^{(0)}(t) + b_f^{(1)}(t) \right|^2$$

$b_f^{(0)} \to 0$

$$= \left| b_f^{(1)}(t) \right|^2$$

$$\boxed{P_{if}(t) = \frac{1}{\hbar^2} \left| \int_0^t e^{i\omega_{fi}t'} W_{fi}(t') dt' \right|^2}$$

We will use these transition probabilities to determine the intensities and selection rules for our spectroscopic transitions.

(C5)

Case of a Sinusoidal Perturbation:

For the interaction of a quantum system with an electromagnetic wave, we will find that $W(t)$ can be written to a first approximation as

$$W(t) = W \cos \omega t$$

where ω is the frequency of the light wave, and W is an operator that is proportional to the dipole moment of the quantum system. You can think of this interaction as the energy of the dipole $\underline{D}$ in the electric field $\underline{E} = E_0 \hat{z} \cos \omega t$

$$W(t) = -\underline{D} \cdot \underline{E} = -D_z E_0 \cos \omega t$$

Let's leave it as $W \cos \omega t$ for now. To find $P_{if}(t)$:

$$W_{fi}(t) = W_{fi} \cos \omega t = \frac{W_{fi}}{2} \left(e^{i\omega t} - e^{-i\omega t} \right)$$

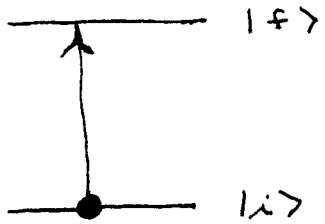
Plugging in and integrating yields:

$$b_n^{(1)}(t) = \frac{W_{ni}}{2\hbar} \left[\frac{1 - e^{i(\omega_{ni} + \omega)t}}{\omega_{ni} + \omega} + \frac{1 - e^{i(\omega_{ni} - \omega)t'}}{\omega_{ni} - \omega} \right]$$

$$P_{if}(t) = \frac{|W_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi} + \omega)t}}{\omega_{fi} + \omega} + \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2$$

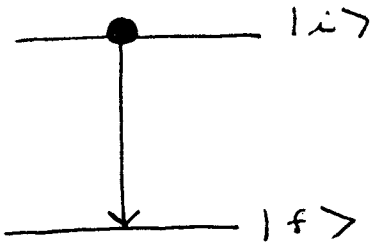
C6

$P_{if}(t)$ has two resonant maxima: one at $\omega = \omega_{fi}$ & one at $\omega = -\omega_{fi}$. If we restrict $\omega \geq 0$, then one of two possibilities can occur:



i) $\omega_{fi} > 0$

Absorption



ii) $\omega_{fi} < 0$

Emission

Thus the first term in P_{if} corresponds to the emission of radiation, & the second term in P_{if} corresponds to the Absorption of radiation.

C7

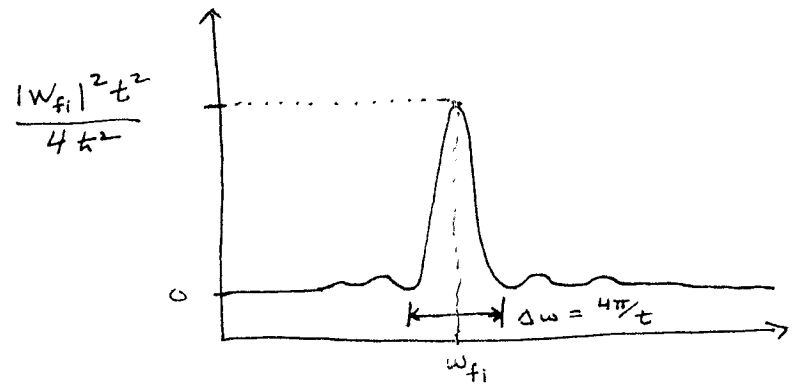
Time Dependent Perturbations, continued

If we examine the case when $E_f > E_i$, then only the absorption term in $P_{if}(t)$ need be considered near resonance:

$$P_{if}(t) \simeq \frac{|W_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2$$

$$= \frac{|W_{fi}|^2}{4\hbar^2} \left(\frac{\sin(\omega_{fi} - \omega)t/2}{(\omega_{fi} - \omega)/2} \right)^2$$

This expression has a maximum at $\omega = \omega_{fi}$



The width of this resonance $\Delta\omega$ decreases as $1/t$

Continuous Spectra: Fermi's Golden Rule

If instead of a single final state $|f\rangle$, there is a continuous band of final states which in the energy range dE around E_f have a density $\rho(E_f)$, then the transition probability summed over all final states can be expressed as:

$$P_{if}(t) \simeq \frac{2\pi}{\hbar} t \, |W_{fi}|^2 \rho(E_f)$$

The transition rate from state i into the final states is given by the derivative of P_{if}:

$$R_{if} = \frac{dP_{if}}{dt} = \frac{2\pi}{\hbar} |W_{fi}|^2 \rho(E_f)$$

This is called Fermi's Golden Rule, and states that the transition rate is proportional to the square of the perturbation matrix element W_{if}. See C-T or Athins for a more complete derivation of this formula.

Selection Rules

Transitions which occur under this sinusoidal perturbation from an electromagnetic field are called "electric dipole transitions" because of the form of interaction:

$$W = -\underline{d} \cdot \underline{E}$$

$$\underline{E} = E_0 \hat{k} \cos\omega t$$

$$\underline{d} = \text{dipole moment} = \sum_\alpha q_\alpha r_\alpha$$

α = all charged particles in the system

$\underline{d}$ is therefore a vector operator that looks like $\hat{x}$. The matrix element $W_{if} \propto d_{if}$ is called the transition dipole moment, because it is not a real dipole moment (e.g. d_{ii} or d_{ff}) but instead connects states $i \neq f$ in the unperturbed basis.

We can use our knowledge of matrix elements of x to predict which transitions have non-zero W_{if}'s. These predictions are called selection rules.

Examples of Selection Rules for Dipole-Dipole transitions:

1) A Charged Harmonic oscillator in an oscillating E field:

$$\underline{E}(t) = \hat{x} E_0 \cos\omega t$$

$$W(t) = -\underline{d}\cdot\underline{E} = -qxE_0\cos\omega t$$

$$|W_{if}|^2 = |\langle i | qE_0 x | f\rangle|^2$$

$$= q^2 E_0^2 |\langle i|x|f\rangle|^2$$

Since $x \propto a^+ + a$, $|f\rangle$ must be $|i+1\rangle$ or $|i-1\rangle$ to be non-zero. If we start in the ground state $|0\rangle$, then only transitions to $|1\rangle$ are allowed. Selection Rule: $n' = n \pm 1$

2) Rigid Rotor w/ a permanent dipole moment d_0:

$$\langle j' m' | d_0 | j m \rangle$$

If we apply an oscillating electromagnetic field in the Z direction, then we need matrix elements of the form

$$\langle j' m' | z | j m \rangle = r_e \delta_{mm'} \left[\delta_{l',l-1} \sqrt{\frac{l^2-m^2}{4l^2-1}} + \delta_{l',l+1} \sqrt{\frac{(l+1)^2-m^2}{4(l+1)^2-m^2}} \right]$$

This leads to selection rules of $\boxed{\Delta l = \pm 1 \;,\; \Delta m = 0}$.

For X & Y polarized $\underline{E}$ fields, $\boxed{\Delta l = \pm 1 \quad \Delta m = \pm 1}$

We will return to the harmonic oscillator & rigid rotor when we discuss vibrational - rotational spectroscopy.

3) Atom in an Electromagnetic Wave field.

$$W_{dipole}(t) = -q E_0 z \cos \omega t$$

Selection rules are determined by $\langle i | z | f \rangle$, as in the rigid rotor case.

z-polarized transitions: $\Delta l = \pm 1 \;,\; \Delta m = 0$

X or Y-polarized transitions: $\Delta l = \pm 1 \;,\; \Delta m = \pm 1$

If there is spin-orbit coupling between $\underline{L}$ & $\underline{S}$ where $\underline{S}$ is the e⁻ spin, then we must recalculate the states & matrix elements.

(C11)

The Zeeman Effect & Spin-Orbit Coupling in Hydrogen

I. Zeeman Effect on the $1s \to 2p$ Transition w/o Spin-Orbit Coupling

$$H_0 |n,\ell,m\rangle = -\frac{E_I}{n^2} |n,\ell,m\rangle$$

$1s \to |1,0,0\rangle$; $2p \to |2,1,m\rangle$ $\quad m = -1,0,1$

with no magnetic field,

$$E_{1s} = -E_I \quad , \quad E_{2p} = -E_I/4$$

$$\Delta E = E_{2p} - E_{1s} = \tfrac{3}{4} E_I \equiv \hbar\Omega$$

in a magnetic field, $H = H_0 + W_z$ where

$$W_z = -\frac{\mu_B}{\hbar} \underline{L} \cdot \underline{B} \qquad \mu_B = \frac{-e\hbar}{2m_e} \quad \text{"Bohr Magneton"}$$

If $\underline{B} = B\hat{z}$

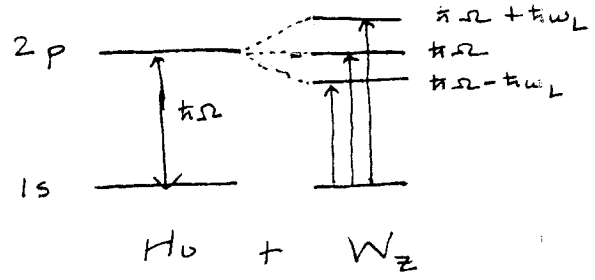
$$W_z |n,\ell,m\rangle = -\frac{\mu_B}{\hbar} B L_z |n,\ell,m\rangle$$

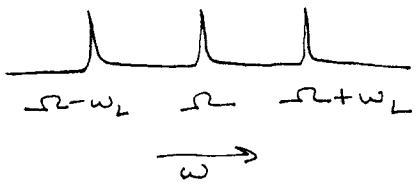
$$= -m\mu_B B |n,\ell,m\rangle \equiv m\hbar\omega_L |n,\ell,m\rangle$$

H is diagonal in $|n,\ell,m\rangle$:

$$H|1,0,0\rangle = -E_I |1,0,0\rangle$$
$$H|2,1,m\rangle = (-E_I + \hbar\Omega + m\hbar\omega_L)|2,1,m\rangle \qquad m = -1,0,1$$

(C12)





To understand the transition probabilities & polarizations, we will examine the electric dipole $\underline{D} = e\underline{r}$ in detail. First, since $\underline{D}$ is an odd function, we can say immediately that:

$$\langle \underline{D} \rangle_{1s} = \langle 1,0,0 | \underline{D} | 1,0,0 \rangle = 0$$
$$\langle \underline{D} \rangle_{2p} = \langle 2,1,m' | \underline{D} | 2,1,m \rangle = 0 \qquad \text{for } \underline{\text{all}}\ m \& m'.$$

Thus, only transition dipole matrix elements of the form $\langle 2,1,m | \underline{D} | 1,0,0 \rangle$ are non-zero:

$$\langle 2,1,1 | D_x | 1,0,0 \rangle = -\langle 2,1,-1 | D_x | 1,0,0 \rangle = -\frac{q\chi}{\sqrt{6}}$$
$$\langle 2,1,0 | D_x | 1,0,0 \rangle = 0$$

$$\langle 2,1,1 | D_y | 1,0,0 \rangle = \langle 2,1,-1 | D_y | 1,0,0 \rangle = \frac{iq\chi}{\sqrt{6}}$$
$$\langle 2,1,0 | D_y | 1,0,0 \rangle = 0$$

$$\langle 2,1,1 | D_z | 1,0,0 \rangle = \langle 2,1,-1 | D_z | 1,0,0 \rangle = 0$$
$$\langle 2,1,0 | D_z | 1,0,0 \rangle = q\chi/\sqrt{3}$$

where $\chi = \int_0^\infty R_{2,1}(r)\, R_{1,0}(r)\, r^3\, dr$

see C-T Complement D_{XII} for details.

C13

If we assume that $|\psi\rangle$ is some linear combination of 1s & 2p at time $t=0$:

$$|\psi_m(t=0)\rangle = \cos\alpha\,|1,0,0\rangle + \sin\alpha\,|2,1,m\rangle$$

where α is real & $m=-1, 0$ or 1, then at time t

$$|\psi_m(t)\rangle = \cos\alpha\,|1,0,0\rangle + \sin\alpha\, e^{-i(\Omega+m\omega_L)t}\,|2,1,m\rangle$$

where I have neglected a global phase factor of $e^{iE_I t/\hbar}$ which would drop out. We now calculate $\langle \underline{D}\rangle_m(t)$, the expectation value of $\underline{D}$ in $\psi_m(t)$; $\langle\psi_m(t)|\,\underline{D}\,|\psi_m(t)\rangle$:

$m=1$
$$\langle D_x\rangle_1 = -\frac{q\chi}{\sqrt{6}}\sin 2\alpha\cos(\Omega+\omega_L)t$$
$$\langle D_y\rangle_1 = -\frac{q\chi}{\sqrt{6}}\sin 2\alpha\sin(\Omega+\omega_L)t$$
$$\langle D_z\rangle_1 = 0$$

$m=0$
$$\langle D_x\rangle_0 = \langle D_y\rangle_0 = 0$$
$$\langle D_z\rangle_0 = \frac{q\chi}{\sqrt{3}}\sin 2\alpha\cos\Omega t$$

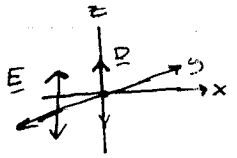
$m=-1$
$$\langle D_x\rangle_{-1} = \frac{q\chi}{\sqrt{6}}\sin 2\alpha\cos(\Omega-\omega_L)t$$
$$\langle D_y\rangle_{-1} = -\frac{q\chi}{\sqrt{6}}\sin 2\alpha\sin(\Omega-\omega_L)t$$

These equations show that for $m=\pm 1$, $\langle \underline{D}(t)\rangle$ rotates in the x-y plane either clockwise w/ frequency $\Omega-\omega_L$ ($m=-1$), or counterclockwise with frequency $\Omega+\omega_L$ ($m=+1$). For $m=0$, $\langle \underline{D}(t)\rangle$ oscillates linearly along the z axis.

(C14)

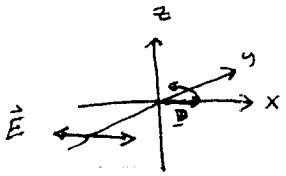
The 3 frequencies $\Omega - \omega_L$, Ω & $\Omega + \omega_L$ are the frequencies that we calculated earlier. We can show that the oscillating dipole $\langle \underline{D} \rangle_m(t)$ will lead to radiation of light at these three frequencies. One additional piece of information that we can obtain from this calculation is the polarization of the radiation from the three states:

$m = 0$ the dipole oscillating linearly along the z axis will emit linearly polarized light parallel to the z axis in a direction in the x-y plane, & no light in the z direction:

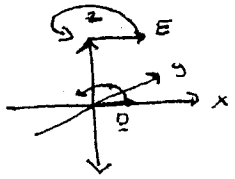


// polarization in the x-y plane

$m = +1$ the rotating dipole will emit circularly polarized radiation (σ_+) in the z-direction, and linearly polarized radiation ~~perpendicular~~ parallel to the x-y plane:



⊥ polarization in the x-y plane



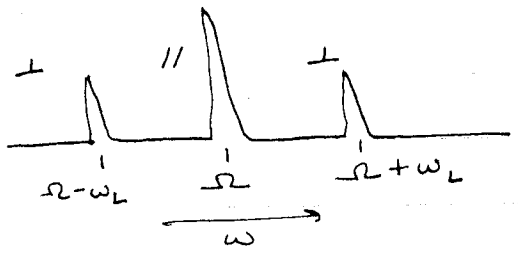
σ_+ polarization in the z-direction

$m = -1$ the rotating dipole will emit circularly polarized radiation (σ_-) in the z-direction (w/ the opposite sense of σ_+), and linearly polarized radiation parallel to the x-y plane (& ⊥ to the z-axis).

C15

Thus the light emitted from a sampling containing H atoms in the 2p state w/ equal populations of $m = +1, 0$ & -1 levels will look like:

perpendicular to $\underline{B}$:



parallel to $\underline{B}$:

II. Spin-Orbit Coupling in the H atom

We have neglected the effect of the e^- spin S on the Hamiltonian in our calculations. We can treat this additional energy term as a perturbation on H_0: $H = H_0 + W_{SO}$ where

$$W_{SO} = \frac{e^2}{2 m_e^2 c^2} \cdot \frac{1}{R^3} \underline{L} \cdot \underline{S} = \xi(R)\, \underline{L} \cdot \underline{S}$$

The key to W_{SO} is that it is diagonal in the J, m_J basis. Recall that we can describe the eigenvectors of H_0 (including spin) with the states:

$$H_0 \,|n, \ell, s, m_L, m_s\rangle = \frac{-E_I}{n^2} |n, \ell, s, m_L, m_s\rangle$$

C16

The term $\underline{L} \cdot \underline{S}$ can be rewritten in terms of J^2, L^2 & S^2:

$$\underline{L} \cdot \underline{S} = \frac{1}{2}\left(J^2 - L^2 - S^2 \right)$$

and the kets are given as: $|n, l, s, j, m_j\rangle$

1s level: $n=1$, $l=0$, $s=\frac{1}{2}$, $j=\frac{1}{2}$, $m_j = \pm\frac{1}{2}$ $\quad$ $^2S_{1/2}$ state

$$\langle 1s | W_{so} | 1s \rangle = \langle n=1 | \xi(R) | n=1 \rangle \cdot \frac{\hbar^2}{2}\left(\frac{1}{2}\left(\frac{3}{2}\right) - 0 - \frac{1}{2}\left(\frac{3}{2}\right)\right) = 0$$

$\therefore$ Spin orbit coupling does not shift the 1s level.

2p level: $n=2$, $l=1$, $s=\frac{1}{2}$, $j=3/2$ $\quad m_j = 3/2, 1/2, -1/2, -3/2$

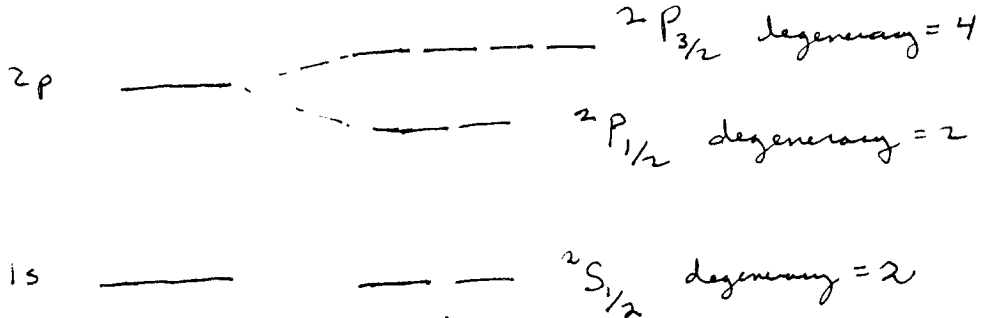
$j=1/2$ $\quad m_j = 1/2, -1/2$ $\quad$ $^2P_{3/2} \neq {}^2P_{1/2}$

$$\langle 2p | W_{so} | 2p \rangle = \frac{1}{2}\xi_{2p}\hbar^2\left(j(j+1) - 2 - \frac{3}{4}\right)$$

where $\xi_{2p} = \langle n=2 | \xi(R) | n=2 \rangle$

for $j = 3/2$, $\langle W_{so} \rangle = +\frac{1}{2}\xi_{2p}\hbar^2$

for $j = 1/2$, $\langle W_{so} \rangle = -\xi_{2p}\hbar^2$



(C17)

III. Zeeman Effect on the $1s \to 2p$ transition with W_{so}.

If we now include both the Zeeman Effect & spin-orbit coupling, we get:

$$H = H_0 + W_{so} + W_z$$

W_z now includes interactions with the orbital angular momentum and the e^- spin:

$$W_z = \omega_L (L_z + 2 S_z)$$

Note that states $|n, \ell, \overset{S}{m_z}, m_L, m_S\rangle$ are eigenstates of H_0 & W_z, whereas states $|n, \ell, s, j, m_j\rangle$ are eigenstates of $H_0 + W_{so}$. We therefore will examine two cases: (i) $W_z \gg W_{so}$, and the m_L, m_S states are valid (strong field or Paschen-Back limit) and (ii) $W_{so} \gg W_z$ where the j, m_j states are valid (weak-field limit).

Weak field Limit: $W_{so} \gg W_z$

$$E_{n,\ell,s,j,m_j} = E_n^\circ + \langle W_{so} \rangle + m_J g_J \hbar \omega_L$$

$$g_J = 1 \frac{\hbar}{\hbar} + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \text{"Landé g-factor}$$

$g_J = 4/3$ for $^2P_{3/2}$

$= 2/3$ for $^2P_{1/2}$

$= 2$ for $^2S_{1/2}$

C18

In the 1s level:

$$E_{1s} = -E_I + 2 m_s \hbar\omega_L \qquad m_s = \pm \tfrac{1}{2}$$

In the 2p level:

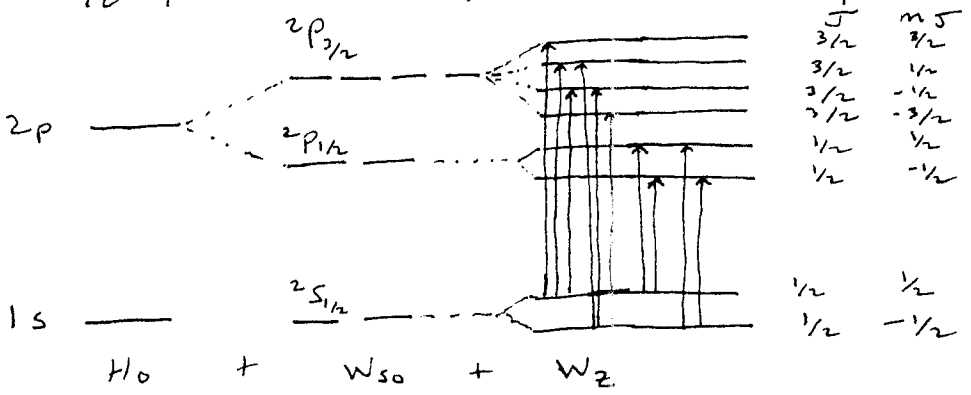
$$E(^2P_{3/2}) = -E_I + \hbar\Omega + \tfrac{1}{2}\zeta_{2p}\hbar^2 + \tfrac{4}{3} m_J \hbar\omega_L$$

$m_J = \pm 1/2, \pm 3/2$

$$E(^2P_{1/2}) = -E_I + \hbar\Omega - \zeta_{2p}\hbar^2 + \tfrac{2}{3} m_J \hbar\omega_L$$

$m_J = \pm \tfrac{1}{2}$

$^2P_{3/2}$ splits into 4 states, & $^2P_{1/2}$ and $^2S_{1/2}$ split into two states:



Selection rules:

$\Delta J = 0, \pm 1$

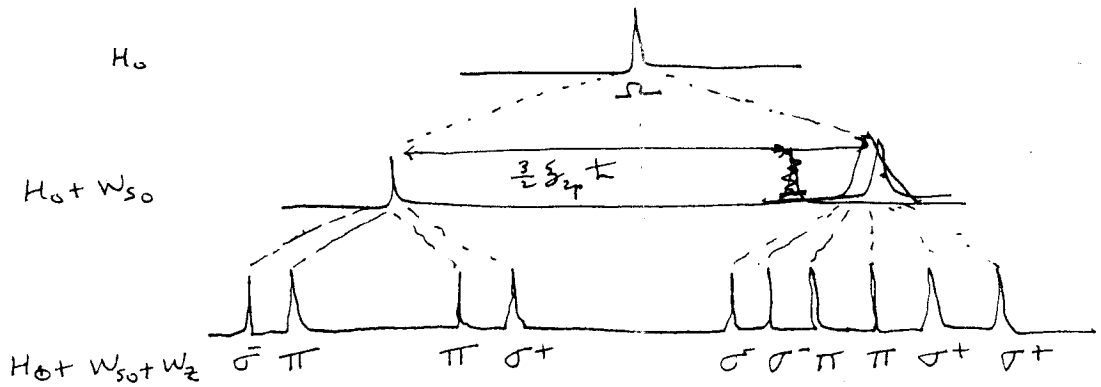
$\Delta m_J = 0^*, \pm 1$

$\Delta L = 0, \pm 1$

$\Delta S = 0$

* $M_J = 0$ to $M_J = 0$, $\Delta J = 0$ combination forbidden

The spectra proceed from one, to two, to ten transitions:



C19

Strong Field Limit: $W_z \gg W_{so}$

Use $|n, \ell, s, m_\ell, m_s\rangle$ basis:

$$E_{n,\ell,s,m_\ell,m_s} = E_n^\circ + \hbar\omega_L(m_L + 2m_s) + \hbar^2 m_L m_s \xi_{2p}$$

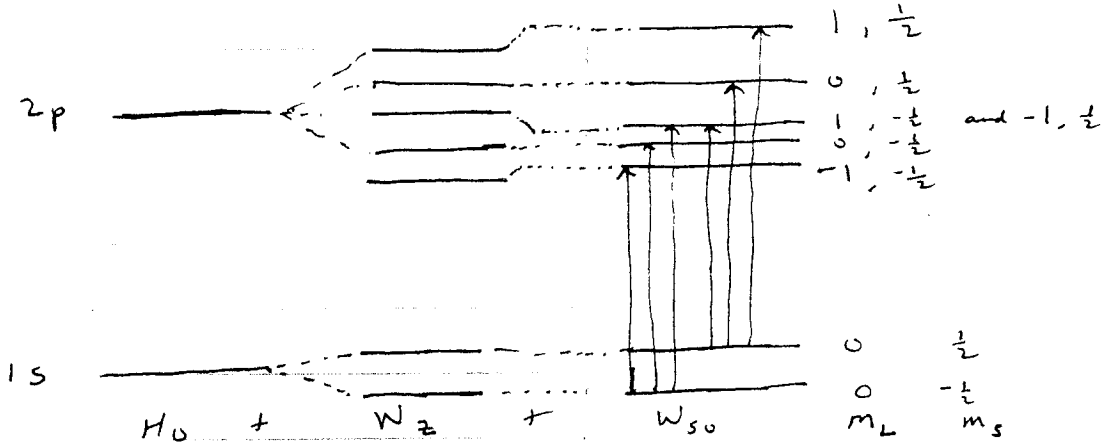
(only $L_z S_z$ of $\underline{L}\cdot\underline{S}$ is kept out of W_{so}).

$$E_{1s} = -E_I + 2m_s\hbar\omega_L \qquad m_s = \pm\tfrac{1}{2} \quad \text{(same as weak field limit)}$$

$$E_{2p}(m_L, m_s) = -E_I + \hbar\Omega + \hbar\omega_L(m_L + 2m_s) + m_L m_s \hbar^2 \xi_{2p}$$

$m_L = -1, 0, 1$

$m_s = \pm\frac{1}{2}$



Selection Rule: $\Delta m_s = 0$