Multi-electron atoms (III)
Optical Excitations

Hartree approximation for an atom with Z electrons

$$\left[\sum_{i=1}^{Z}\left(\frac{\mathbf{p}_i^2}{2m_e}-\frac{Ze^2}{4\pi\varepsilon_0 r_i}\right)+\sum_{i>j}\sum_{j}\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_i-\mathbf{r}_j|}\right]\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_Z)$$

$$V(r) \qquad = E\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_Z)$$

The method makes the following major simplifications in order to deal with this task:

- The Born–Oppenheimer approximation is inherently assumed. The full molecular wave function is actually a function of the coordinates of each of the nuclei, in addition to those of the electrons.
- Typically, relativistic effects are completely neglected. The momentum operator is assumed to be completely non-relativistic.
- The variational solution is assumed to be a linear combination of a finite number of basis functions, which are usually (but not always) chosen to be orthogonal. The finite basis set is assumed to be approximately complete.
- The mean field approximation is implied. Electrons are moving independently in a spherically symmetrical net potential.

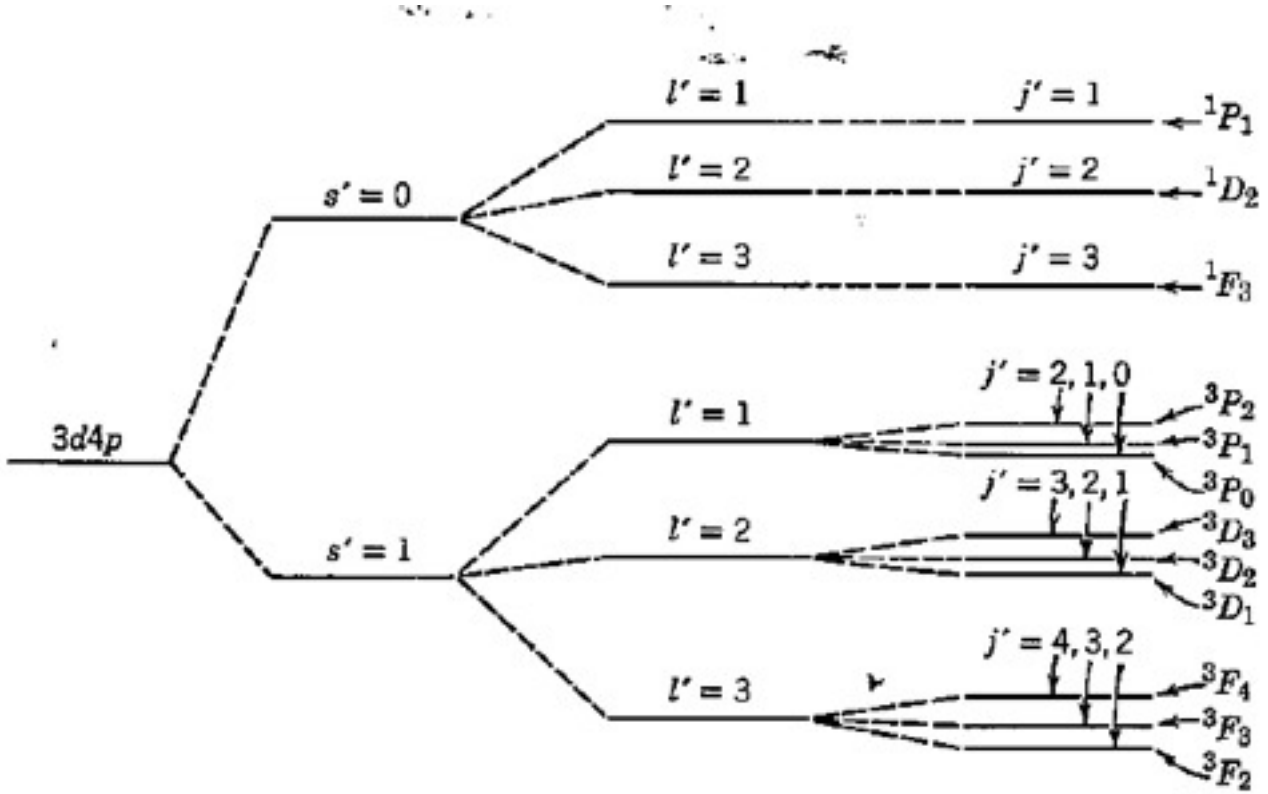

Figure 10-6 The splitting of the energy levels in a typical *LS* coupling configuration.

Time-independent Perturbation Theory

$$\hat{H}\psi_n = E_n\psi_n$$

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

$$\begin{aligned}
\hat{H} &= \hat{H}^{(0)} + \lambda\hat{H}^{(1)} + \lambda^2\hat{H}^{(2)} + \cdots \\
\psi_n &= \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots \\
E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots
\end{aligned}$$

$$\begin{aligned}
& \{\hat{H}^{(0)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(0)}\} \\
+ \; & \lambda\{\hat{H}^{(0)}\psi_n^{(1)} + \hat{H}^{(1)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(1)} - E_n^{(1)}\psi_n^{(0)}\} \\
+ \; & \lambda^2\{\hat{H}^{(0)}\psi_n^{(2)} + \hat{H}^{(1)}\psi_n^{(1)} + \hat{H}^{(2)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(2)} - E_n^{(1)}\psi_n^{(1)} - E_n^{(2)}\psi_n^{(0)}\} \\
+ \; & \cdots = 0
\end{aligned}$$

$$
\begin{aligned}
\hat{H}^{(0)}\psi_n^{(0)} &= E_n^{(0)}\psi_n^{(0)} \\
(\hat{H}^{(0)} - E_n^{(0)})\psi_n^{(1)} &= (E_n^{(1)} - \hat{H}^{(1)})\psi_n^{(0)} \\
(\hat{H}^{(0)} - E_n^{(0)})\psi_n^{(2)} &= (E_n^{(2)} - \hat{H}^{(2)})\psi_n^{(0)} + (E_n^{(1)} - \hat{H}^{(1)})\psi_n^{(1)} \\
&\cdots
\end{aligned}
$$

First order energy correction:

$$E_n^{(1)} = \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle$$

First order wavefunction correction:

$$|n^{(1)}\rangle = \hat{1}|n^{(1)}\rangle = \sum_k |k^{(0)}\rangle\langle k^{(0)}|n^{(1)}\rangle$$

$$|n^{(1)}\rangle = \sum_{k\neq n} |k^{(0)}\rangle \frac{\langle k^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} = \sum_{k\neq n} |k^{(0)}\rangle \frac{H_{kn}^{(1)}}{E_n^{(0)} - E_k^{(0)}}$$

$\cdots$

TIME DEPENDENT SCHROEDINGER EQUATION

THEN SCHROEDINGER EQUATION

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

BY SEPARATION OF VARIABLES,
ASSUME SOLUTION

$$\Psi(x,t)=\psi(x)\Phi(t)$$

Ψ(x,t) : **WAVE FUNCTION**

ψ (x) : **EIGEN FUNCTION**
Φ(t) : **TIME DEPENDENCE OF WAVE FUNCTION**

TIME DEPENDENT SCHROEDINGER EQUATION

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$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

V(x,t)

BY SEPARATION OF VARIABLES,
ASSUME SOLUTION

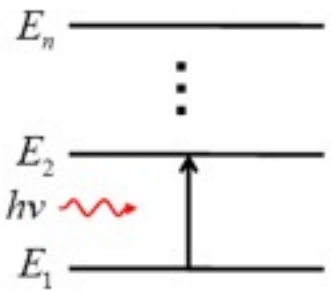
$$\Psi(x,t)=\psi(x)\Phi(t)$$

Ψ(x,t) : **WAVE FUNCTION**

ψ (x) : **EIGEN FUNCTION**
Φ(t) : **TIME DEPENDENCE OF WAVE FUNCTION**

Time-dependent Perturbation Theory

Consider a quantum mechanical system:



$$H_0\phi_n(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\phi_n(\vec{r},t)$$

$$\phi_n(\vec{r},t) = \phi_n(\vec{r})e^{-\frac{iE_nt}{\hbar}}$$

$\phi_n(\vec{r}) = |n\rangle$ an orthonormal set of eigenstates

$$\langle m|n\rangle = \int \phi_m^*(\vec{r})\phi_n(\vec{r})d\vec{r} = \delta_{mn}$$

Consider a single-frequency, time-varying stimulus

$$H'(\vec{r},t) = H'(\vec{r})e^{-i\omega t} + H'^{\dagger}(\vec{r})e^{i\omega t} \quad \text{for } t > 0$$

$$H = H_0 + H'(\vec{r},t)$$

$$H\psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)$$

Assuming $|H'| \ll |H_0|$

The new wavefunction can be expressed as a linear combination of original eigenstates with time-varying coefficients:

$$\psi(\vec{r},t) = \sum_n a_n(t)\phi_n(\vec{r})e^{-iE_nt/\hbar}$$

$|a_n(t)|^2$: probability of electron at state $|n\rangle$ at time t

$$H\psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)$$

$$(H_0 + H')\sum_n a_n(t)\phi_n(\vec{r})e^{-iE_n t/\hbar} = i\hbar\sum_n \frac{da_n(t)}{dt}\phi_n(t)e^{-iE_n t/\hbar} + i\hbar\sum_n a_n(t)\phi_n(\vec{r})\left(\frac{-iE}{\hbar}\right)e^{-iE_n t/\hbar}$$

$$H'\sum_n a_n(t)\left|n\right\rangle e^{-iE_n t/\hbar} = i\hbar\sum_n \frac{da_n(t)}{dt}\left|n\right\rangle e^{-iE_n t/\hbar}$$

Multiply both sides by $\langle m|$ (i.e., multiply by $\phi_m^*(\vec{r})$ and integrate over $\vec{r}$)

$$\sum_n a_n(t)\left\langle m\middle|H'\middle|n\right\rangle e^{-iE_n t/\hbar} = i\hbar\sum_n \frac{da_n(t)}{dt}\left\langle m\middle|n\right\rangle e^{-iE_n t/\hbar} = i\hbar\frac{da_m(t)}{dt}e^{-iE_m t/\hbar}$$

$$\frac{da_m(t)}{dt} = \frac{1}{i\hbar}\sum_n a_n(t)H'_{mn}(t)e^{i\omega_{mn}t}$$

$$\omega_{mn} = \frac{E_m - E_n}{\hbar}$$

First-Order Perturbation

To track the order of perturbation, let

$$H = H_0 + \lambda H'$$

$$a_n(t) = a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \lambda^2 a_n^{(2)}(t) + \ldots$$

Group terms with the same order of λ:

$$\frac{da_m^{(0)}(t)}{dt} = 0 \Rightarrow a_m^{(0)}(t) = \text{constant}$$

$$\frac{da_m^{(1)}(t)}{dt} = \frac{1}{i\hbar}\sum_n a_n^{(0)}(t) H'_{mn}(t) e^{i\omega_{mn}t}$$

$$\frac{da_m^{(2)}(t)}{dt} = \frac{1}{i\hbar}\sum_n a_n^{(1)}(t) H'_{mn}(t) e^{i\omega_{mn}t}$$

Initial state i at t=0 and final state f

$$\begin{cases} a_i^{(0)}(t) = 1 \\ a_m^{(0)}(t) = 0 \ \text{ if } \ m \neq i \end{cases}$$

$$\frac{da_f^{(1)}(t)}{dt} = \frac{1}{i\hbar} H'_{fi}(t) e^{i\omega_{mi}t} = \frac{1}{i\hbar}\left(H'_{fi} e^{-i\omega t} + H'^{\dagger}_{fi} e^{i\omega t} \right) e^{i\omega_{mi}t}$$

$$= \frac{1}{i\hbar}\left(H'_{fi} e^{i(\omega_{mi}-\omega)t} + H'^{\dagger}_{fi} e^{i(\omega_{mi}+\omega)t} \right)$$

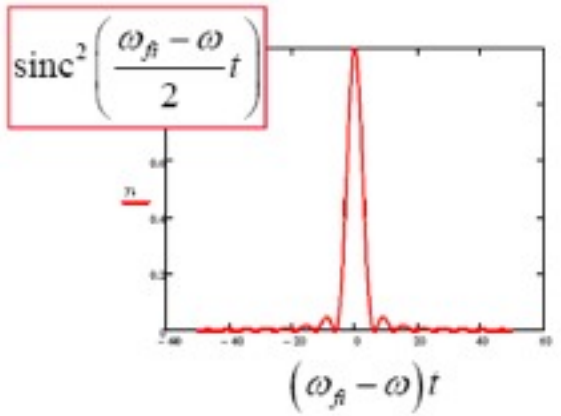
$$a_f^{(1)}(t) = \frac{-1}{\hbar}\left(H'_{fi}\frac{e^{i(\omega_{mi}-\omega)t}-1}{\omega_{mi}-\omega} + H'^{\dagger}_{fi}\frac{e^{i(\omega_{mi}+\omega)t}-1}{\omega_{mi}+\omega} \right)$$

We are only interested at frequencies near resonance:

$$\left|a_f^{(1)}(t)\right|^2 = \frac{4\left|H'_{fi}\right|^2}{\hbar^2}\frac{\sin^2\left(\frac{\omega_{mi}-\omega}{2}t\right)}{(\omega_{mi}-\omega)^2} + \frac{4\left|H'^{\dagger}_{fi}\right|^2}{\hbar^2}\frac{\sin^2\left(\frac{\omega_{mi}+\omega}{2}t\right)}{(\omega_{mi}+\omega)^2}$$

Fermi's Golden Rule

$$\frac{\sin^2\left(\frac{\omega_{fi}-\omega}{2}t\right)}{\left(\omega_{fi}-\omega\right)^2}=\frac{t^2}{4}\operatorname{sinc}^2\left(\frac{\omega_{fi}-\omega}{2}t\right)$$



$$\rightarrow\frac{\pi t}{2}\delta(\omega_{fi}-\omega)\quad\text{as}\quad t\rightarrow\infty$$

$$\left|a_f^{(1)}(t)\right|^2=\frac{2\pi t\left|H'_{fi}\right|^2}{\hbar^2}\delta(\omega_{fi}-\omega)+\frac{2\pi t\left|H'^{\dagger}_{fi}\right|^2}{\hbar^2}\delta(\omega_{fi}+\omega)$$

Transition Rate:

$$W_{i\rightarrow f}=\frac{d}{dt}\left|a_f^{(1)}(t)\right|^2=\frac{2\pi\left|H'_{fi}\right|^2}{\hbar^2}\delta(\omega_{fi}-\omega)+\frac{2\pi\left|H'^{\dagger}_{fi}\right|^2}{\hbar^2}\delta(\omega_{fi}+\omega)$$

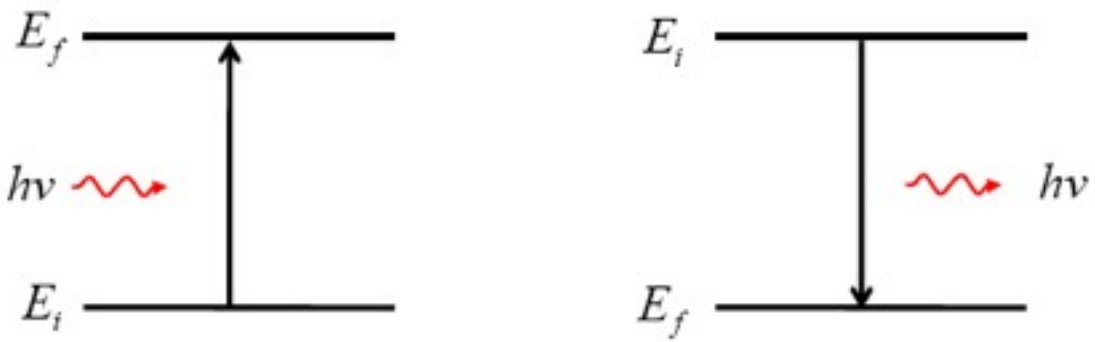
Note: $\delta(E_f-E_i-\hbar\omega)=\frac{1}{\hbar}\delta(\omega_f-\omega_i-\omega)$

$$W_{i\rightarrow f}=\frac{2\pi\left|H'_{fi}\right|^2}{\hbar}\delta(E_f-E_i-\hbar\omega)+\frac{2\pi\left|H'^{\dagger}_{fi}\right|^2}{\hbar}\delta(E_f-E_i+\hbar\omega)$$

Physical Interpretation

$$W_{i\to f} = \frac{2\pi \left| H'_{fi} \right|^2}{\hbar} \delta(E_f - E_i - \hbar\omega) + \frac{2\pi \left| H'^{\dagger}_{fi} \right|^2}{\hbar} \delta(E_f - E_i + \hbar\omega)$$

$E_f = E_i + \hbar\omega$	$E_f = E_i - \hbar\omega$
Absorption of a photon	Emission of a photon



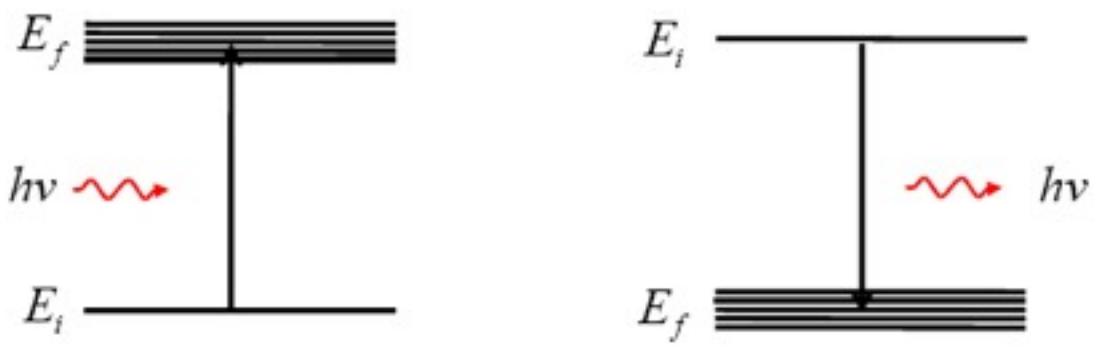
- Conservation of energy
- Transition rate is proportional to the square of the "matrix element"

Distributed Final States

- If the final state is a distribution of states, the transition rate is proportional to the density of states of the final state:

$$W_{i\to f} = \frac{2\pi\left|H'_{fi}\right|^2}{\hbar}\rho_f\delta(E_f - E_i - \hbar\omega) + \frac{2\pi\left|H'^{\dagger}_{fi}\right|^2}{\hbar}\rho_f\delta(E_f - E_i + \hbar\omega)$$

$E_f = E_i + \hbar\omega$	$E_f = E_i - \hbar\omega$
Absorption of a photon	Emission of a photon



Zeeman Effect

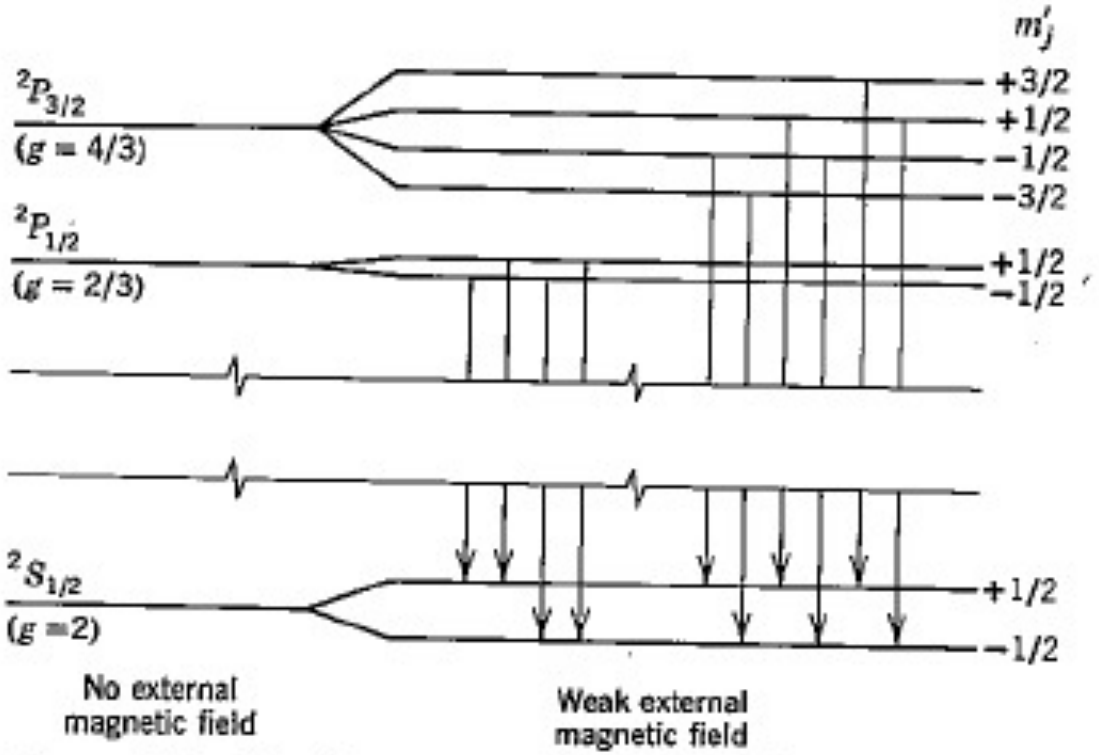


Figure 10-11 The Zeeman splittings of the $^2P_{1/2,3/2}$ first excited state levels of sodium, and of its $^2S_{1/2}$ ground state level. The transitions allowed by the selection rules are shown. Compare the resulting spectral lines with those shown in Figure 10-9.

Homework#8 (Nov. 1, 2010):

Find the possible values of s', l', j' for a configuration with two optically active electrons with quantum numbers $l_1 = 2$, $s_1 = 1/2$; $l_2 = 3$, $s_2 = 1/2$. Specify which j' go with each l' and s' combination.