CH 15 Time-dependent perturbation theory

15-1 Formalism

We want to find the time evolution of the wave function under the action of a time-dependent perturbation $\lambda V(t)$:

$$\boxed{i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = (H_0 + \lambda V(t))|\Psi(t)\rangle} \qquad (1)$$

stationary Hamiltonian, does not depend on time

arbitrary scaling parameter

Stationary states: $H_0 |\varphi_n\rangle = E_n |\varphi_n\rangle$

$$\boxed{|\Psi(t)\rangle = \sum_n c_n(t)\, e^{-iE_n t/\hbar} |\varphi_n\rangle} \qquad (2)$$

We assume that at $t=0$ the system is at state $|\varphi_0\rangle$, $c_n(0) = \delta_{n0}$

Let's substitute (2) into (1):

$$\sum_n \left[i\hbar \frac{dc_n(t)}{dt} + E_n c_n(t)\right] e^{-iE_n t/\hbar} |\varphi_n\rangle =$$

$$= H|\Psi(t)\rangle = \sum_n \left[E_n + \lambda V(t)\right] c_n(t)\, e^{-iE_n t/\hbar} |\varphi_n\rangle$$

$$(3) \quad \boxed{\sum_n \left[i\hbar \frac{dc_n(t)}{dt} - \lambda V(t) c_n(t)\right] e^{-iE_n t/\hbar} |\varphi_n\rangle = 0}$$

We now take the scalar product of (3) with $\langle \varphi_m |$, $\langle \varphi_m | \varphi_n \rangle = \delta_{mn}$:

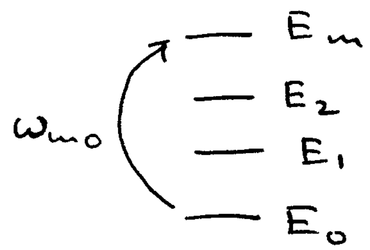
$$i\hbar \frac{d c_m(t)}{dt} = \lambda \sum_n c_n(t) e^{i(E_m - E_n)t/\hbar} \langle \varphi_m | V(t) | \varphi_n \rangle$$

In the lowest order in λ, we put $c_n(t) = c_n(0) = \delta_{n0}$

$$i\hbar \frac{d c_m(t)}{dt} = \lambda\, e^{i\omega_{m0} t} \langle \varphi_m | V(t) | \Phi_0 \rangle ,$$

$$\omega_{m0} = \frac{E_m - E_0}{\hbar}$$

frequency of excitation from level E_0 to E_m



Given that $c_m(0) = 0$ at $m \neq 0$, one gets

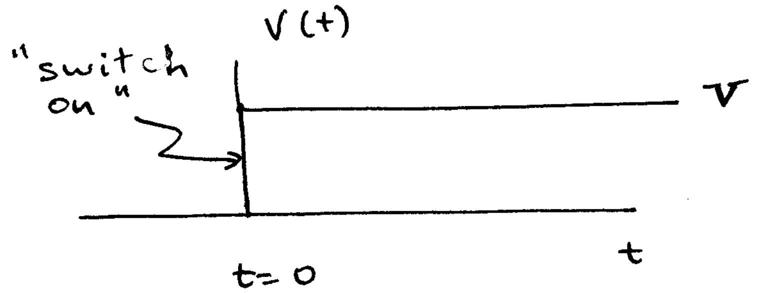
$$\boxed{c_m(t) = \frac{\lambda}{i\hbar} \int_0^t dt'\, e^{i\omega_{m0} t'} \langle \varphi_m | V(t') | \varphi_0 \rangle}$$

The probability that a measurement of $|\Psi(t)\rangle$ at time t will give $|\varphi_m\rangle$ is

$$P_m(t) = |c_m(t)|^2 = \frac{\lambda^2}{\hbar^2} \left| \int_0^t dt'\, V_{m0}(t') e^{i\omega_{m0} t'} \right|^2$$

$$V_{m0}(t) = \langle \varphi_m | V(t) | \varphi_0 \rangle$$

Constant external perturbation:



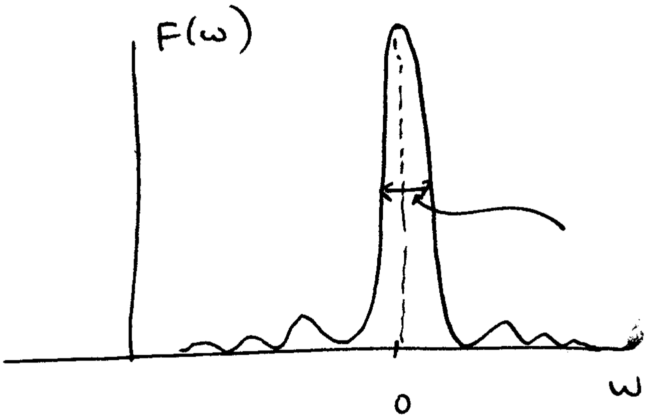
$$P_m(t) = |V_{m0}|^2 \lambda^2 \frac{\sin^2[\omega_{m0} t/2]}{[(E_m - E_0)^2/2]^2}$$

$\lambda = 1$

Fermi's Golden Rule:

Let's consider the function

$$F(\omega) = \left. \frac{P_m(t)}{t\,|V_{m0}|^2} \right|_{\omega_{m0}=\omega} = \frac{\sin^2 \frac{\omega t}{2}}{\hbar^2 t\,(\omega/2)^2}$$



width $\Delta\omega \approx \frac{2\pi}{t}$

Natural width of spectral lines:

If a quantum state has the lifetime τ, the energy of that state is uncertain:

$$\Delta E\, \tau \approx 2\pi\hbar$$

Properties of $F(\omega)$:

$$\int_{-\infty}^{\infty} F(\omega)\, d(\hbar\omega) = \frac{2\pi}{\hbar}$$

$F(\omega)$ becomes increasingly sharp as $t \to \infty$,

$$\Delta\omega \approx \frac{2\pi}{t} \to 0$$

In the limit $t \to \infty$, $F(\omega)$ can be replaced by a δ-function

$$\lim_{t\to\infty} F(\omega) = \frac{2\pi}{\hbar}\,\delta(\hbar\omega)$$

Therefore

$$P_m(t) \xrightarrow[t\to\infty]{} \frac{2\pi t}{\hbar} |V_{om}|^2\, \delta(E_m - E_o)$$

The rate of transition

$$\boxed{w_{mo} = \frac{P_m(t)}{t} = \frac{2\pi}{\hbar} |V_{om}|^2\, \delta(E_m - E_o)}$$

Fermi's Golden Rule

At $t \to \infty$ only transitions that strictly obey the energy conservation, $E_m = E_o$, can be caused by a time-independent perturbation.

15-2 Harmonic time-variation of the potential

Time dependent perturbation

$$V(t) = M e^{\mp i\omega t}$$

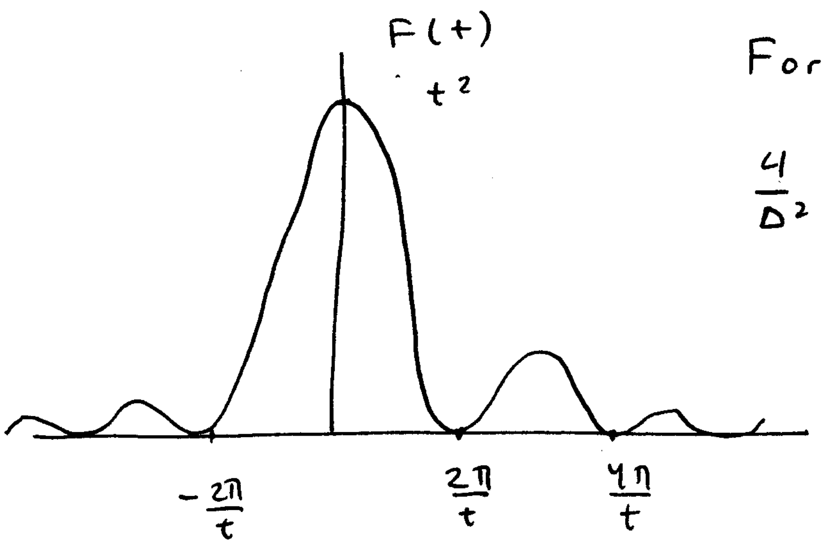
$$c_m(t) = \frac{1}{i\hbar} \langle \varphi_m | M | \varphi_0 \rangle \int_0^t dt' \, e^{i\omega_{mo} t' \mp i\omega t'}$$

$$\int_0^t dt' \, e^{i(\omega_{mo} - \omega)t'} = e^{i(\omega_{mo} \mp \omega)t/2} \frac{\sin[(\omega_{mo} - \omega)t/2]}{(\omega_{mo} - \omega)/2}$$

$$|c_m(t)|^2 = \frac{1}{\hbar^2} |\langle \varphi_m | M | \varphi_0 \rangle|^2 \frac{\sin^2(\omega_{mo} - \omega)t/2}{[(\omega_{mo} - \omega)/2]^2}$$

Let's define

$$F(t) = \frac{4}{\Delta^2} \sin^2 \frac{t\Delta}{2}, \qquad \Delta = \frac{E_m - E_0 \mp \hbar\omega}{\hbar}$$



For large t:

$$\frac{4}{\Delta^2} \sin^2 \frac{t\Delta}{2} \to 2\pi t \, \delta(\Delta) =$$

$$= 2\pi t \hbar \, \delta(E_m - E_0 \mp \hbar\omega)$$

Transition probability:

$$\Gamma_{0\to m} \underset{t\to\infty}{=} \frac{|c_m(t)|^2}{t} = \frac{2\pi}{\hbar} |\langle \Phi_m | M | \Phi_0\rangle|^2 \, \delta(E_m - E_0 \mp \hbar\omega)$$

This is the Fermi Golden Rule which states that transitions occur at resonance of energy

$E_m > E_0$: $\hbar\omega = E_m - E_0$ ← absorption transition

$E_m < E_0$: $\hbar\omega = E_0 - E_m$ ← emission transition

energy conservation

In reality transitions occur to manyfolds of states and one should perform summation over all possible final states which normally eliminates the unphysical discontinuity of the δ-function.

$$\Gamma = \frac{2\pi}{\hbar} \sum_{f} |\langle \Phi_f | M | \Phi_0 \rangle|^2 \, \delta(E_f - E_0 \mp \hbar\omega)$$

all possible final states

15.3 Phase space

Q: If we have a transition to a state of the system characterized by a number of sub-states. How to find the transition probability?

A: One has to use the <u>density of states</u>

If one has a number of independent events, the probabilities will add up:

$$\Gamma = \sum_n \Gamma_{0\to n} \xrightarrow{} \int dn\, \Gamma_{0\to n} =$$

quasicontinuous distribution of states

$$= \int \underbrace{\frac{dn}{dE}}_{\rho(E)} dE\, \frac{2\pi}{\hbar} |\langle \Phi_n | M | \Phi_0 \rangle|^2\, \delta\left(E_n - E_0 \mp E\right)$$

$\rho(E) \longleftarrow$ density of states

Transition $i \to f$ from the initial state "i" to the final state "f":

$$\boxed{\Gamma_{i\to f} = \frac{2\pi}{\hbar}\, |\langle \Phi_f | M | \Phi_i \rangle|^2 \rho(E) \Big|_{E = |E_f - E_i|}}$$

Population of the initial state:

$$P_i(t) = 1 - t \sum_{f\neq i} \Gamma_{i\to f} \approx e^{-\Gamma t}$$

t should not be too large

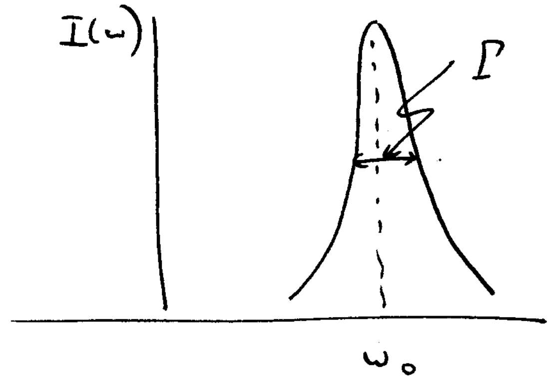
$$\Gamma = \sum_{f\neq i} \Gamma_{i\to f} \quad \leftarrow \text{decay rate}$$

Lifetime for the initial state:

$$\tau = \frac{1}{\Gamma}$$

Because of the uncertainty of energy, $\Delta E \approx \hbar/\tau$, one gets a Lorentzian line shape:

$$I(\omega) = \frac{\Gamma/2}{(\omega - \omega_0) + \Gamma^2/4}$$

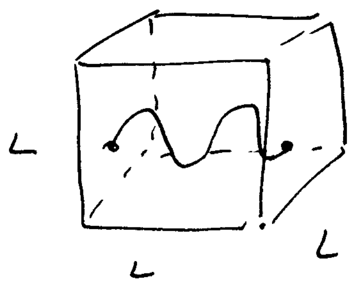


Final state being a photon

$$\rho(E) = \frac{dN}{dE} \leftarrow$$ number of states in the energy interval between E and $E + dE$

Photon is considered to be a free planar wave

$$\psi(\vec{r},t) = \frac{1}{\sqrt{L^3}} e^{i(\vec{p}\cdot\vec{r} - Et)/\hbar}$$



$$\psi(x+L, y, z) = \psi(x,y,z)$$
$$\psi(x, y+L, z) = \psi(x,y,z)$$
$$\psi(x, y, z+L) = \psi(x,y,z)$$

$$e^{ip_x L/\hbar} = e^{ip_y L/\hbar} = e^{ip_z L/\hbar} = 1$$

$$p_x = \frac{2\pi\hbar}{L} n_1, \quad p_y = \frac{2\pi\hbar}{L} n_2, \quad p_z = \frac{2\pi\hbar}{L} n_3$$

$$dN = dn_1\, dn_2\, dn_3 = \left(\frac{L}{2\pi\hbar}\right)^3 d\vec{p}$$

$$\frac{dN}{dE} = \frac{4\pi V}{(2\pi\hbar)^3} \frac{p^2 dp}{dE}, \qquad E = pc = \hbar\omega$$

$$\boxed{\rho(E) = \frac{V}{2\pi\hbar^2} \frac{\hbar^2\omega^2}{c^3}}$$

CH 16. The interaction of charges with the electromagnetic field

Q: How do we write the SE in case when electrons interact with light (electromagnetic field)?

A: We need a Hamiltonian that incorporates both the equations of motions and electric/magnetic field:

$$\boxed{H = \frac{1}{2m_e}\left[\vec{p} + e\vec{A}(\vec{r},t)\right]^2 - e\Phi(r,t)}$$

vector potential defining both the electric and magnetic fields

scalar electrostatic potential

$$\vec{B} = \nabla \times \vec{A}(\vec{r},t)$$

$$\vec{E} = -\frac{\partial \vec{A}(\vec{r},t)}{\partial t} - \nabla\Phi(r,t)$$

See pp. 247-248 on guage transformation

CH 17

17.1 Transition rate

Let's consider electromagnetic field (propagating wave) in the absence of the scalar potential

$$\vec{B} = \nabla \times \vec{A}, \qquad \vec{E} = -\frac{\partial \vec{A}}{\partial t}$$

Propagating wave:

$$A(\vec{r},t) = A_0 \, \underline{\vec{\varepsilon}} \, e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

amplitude polarization

$$\vec{E}(\vec{r},t) = i\omega A_0 \vec{\varepsilon} \, e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

Hamiltonian:

$$H = H_0 + V(t)$$

$$H_0 = \frac{p^2}{2m_e} + V_e, \qquad V(t) = \frac{e}{m_e} \vec{A}\cdot\vec{p} + \frac{e^2 A^2}{2m_e}$$

kinetic energy

potential energy

single-photon process

two-photon process (neglected here)

$$\boxed{V(t) = \frac{eA_0}{m_e} \vec{\varepsilon} \, e^{i(\vec{k}\cdot\vec{r} - \omega t)} \cdot \vec{p}}$$

Transition probability

$$P_{0\to m} = \frac{2\pi}{\hbar} |V_{om}|^2 \, \delta(E_m - E_o \mp \hbar\omega)$$

We need to calculate $|V_{om}|$:

$$|V_{om}| = \frac{eA_o}{m_e} |\langle \phi_m | \vec{\varepsilon} \, e^{i\vec{k}\cdot\vec{r}} \cdot \vec{p} \, | \phi_o \rangle|$$

<u>Dipole approximation</u>:

Assumes that the light intensity is constant on the length of the molecule

$$\underline{\underline{e^{i\vec{k}\cdot\vec{r}} \approx 1}} \longleftarrow \qquad k = \frac{2\pi}{\lambda} \approx \frac{2\pi}{5000\,\text{Å}}$$

wavelength of light

$$|\vec{r}| \approx 10\,\text{Å}$$

typical size of the molecule

$$\bar{k}\cdot\bar{r} \approx \frac{2\pi}{5000\,\text{Å}} \times 10\,\text{Å} \approx \frac{2\pi}{500} << 1$$

$$\boxed{|V_{om}| = \frac{eA_o}{m_e} |\langle \phi_m | \vec{\varepsilon} \cdot \vec{p} \, | \phi_o \rangle|}$$

We can represent $\vec{p}$ as:

$$\vec{p} = \frac{im}{\hbar}\left[H_0, \vec{r}\,\right] = \frac{im}{\hbar}\left[\frac{\vec{p}^{\,2}}{2m}, \vec{r}\,\right]$$

$$\langle \varphi_m | \vec{\varepsilon}\cdot\vec{p}\,|\varphi_0\rangle = \vec{\varepsilon}\cdot\langle\varphi_m|\vec{p}\,|\varphi_0\rangle =$$

$$= \frac{im}{\hbar}\vec{\varepsilon}\cdot\langle\varphi_m|[H_0,\vec{r}\,]|\varphi_0\rangle =$$

$$= \frac{im}{\hbar}\vec{\varepsilon}\cdot\langle\varphi_m|\left(H_0\vec{r} - \vec{r}H_0\right)|\varphi_0\rangle =$$

$$= \frac{im}{\hbar}\vec{\varepsilon}\cdot\underbrace{(E_m - E_0)}_{\hbar\omega}\langle\varphi_m|\vec{r}\,|\varphi_0\rangle$$

Dipole moment operator:

$$\vec{\mu} = e\vec{r}$$

Finally, $\langle\varphi_m|\vec{\varepsilon}\cdot\vec{p}\,|\varphi_0\rangle = \frac{im\omega}{e}\vec{\varepsilon}\cdot\vec{\mu}_{om}$

$$\vec{\mu}_{om} = \langle\varphi_m|\vec{\mu}\,|\varphi_0\rangle$$

is the transition dipole

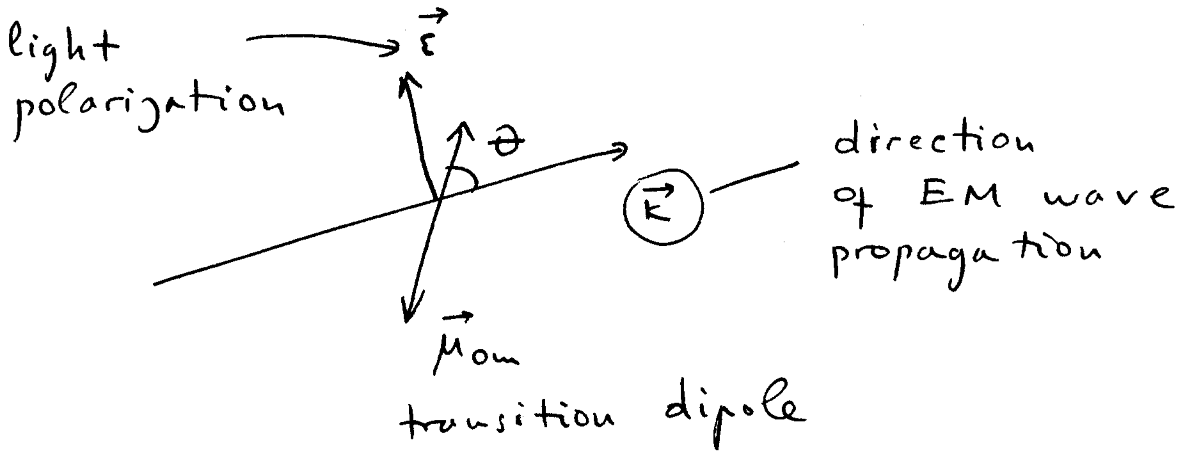
$$\boxed{|V_{om}| = A_0\,\omega\,|\vec{\varepsilon}\cdot\vec{\mu}_{om}|}$$

Transition probability

$$\Gamma_{0\to m} = \frac{2\pi}{\hbar} |V_{om}|^2 \rho(E)$$

$$\rho(E) = \frac{V}{(2\pi c)^3} \frac{\omega^2}{\hbar} d\Omega$$

spherical angle

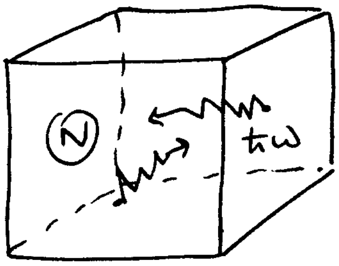


$$d\Gamma_{om} = \frac{2\pi}{\hbar} \underbrace{A_0^2 \omega^2 \mu_{om}^2 \sin^2\theta}_{|V_{om}|^2} \frac{V}{(2\pi c)^3} \frac{\omega^2}{\hbar} d\Omega$$

$$\Gamma_{0\to m} = \int d\Gamma_{om}, \qquad \int \sin^2\theta \, d\Omega = \frac{8\pi}{3}$$

$$\boxed{\Gamma_{0\to m} = \frac{2\omega^4 A_0^2}{3\pi\hbar^2 c^3} |\mu_{om}|^2 V}$$

How to define A_0^2 ?



Let's take a box with N photons, the energy is

$$E = N\hbar\omega$$

On the other hand,

$$E = \int d\vec{r}\, \underbrace{\frac{\vec{E}^2 + \vec{B}^2}{8\pi}}_{\text{energy density of the electromagnetic field}} = \frac{1}{4\pi}\int d\vec{r}\, |\vec{E}|^2 =$$

$$= \frac{1}{4\pi}\int d\vec{r}\, \left| A_0\, \vec{\varepsilon}\, i\omega\, e^{i(\vec{k}\cdot\vec{r} - \omega t)} \right|^2$$

$$= \frac{A_0^2\omega^2}{4\pi} V = N\hbar\omega, \qquad A_0^2 = \frac{4\pi N\hbar}{\omega V}$$

Substituting into equation for $\Gamma_{o\to m}$,

we get

$$\Gamma_{o\to m} = \frac{2\omega^4}{3\pi\hbar^2 c^3} V \times \frac{4\pi N\hbar}{\omega V} |\mu_{om}|^2$$

$$\boxed{\Gamma_{o\to m} = \frac{8}{3}\left(\frac{\omega}{c}\right)^3 N\, |\mu_{om}|^2}$$

Rate of absorption, proportional to the number of photons N

17-3 Angular integration and selection rules

Matrix element for a hydrogen-like atom

$$\langle \Phi_f | \vec{\varepsilon} \cdot \vec{r} | \varphi_i \rangle - ?$$

$$\Phi_f(r,\theta,\varphi) = R_{n_f \ell_f}(r)\, Y_{\ell_f m_f}(\theta,\phi)$$

$$\varphi_i(r,\theta,\phi) = R_{n_i \ell_i}(r)\, Y_{\ell_i m_i}(\theta,\phi)$$

$\vec{\varepsilon} \cdot \vec{r} =$ r x linear combination of $Y_{1m}(\theta,\phi)$

Intergation over ϕ:

$$\int_0^{2\pi} e^{-im_f\varphi + im_i\varphi + im\phi}\, d\varphi = 2\pi\, \delta_{m = m_f - m_i}$$

Since $\vec{e}$ is perpendicular to $\vec{k}$, $m = \pm 1$,

$$\boxed{m_f - m_i = \pm 1}$$

The electronic states must change parity upon the transition,

$$\boxed{\Delta \ell = \pm 1}$$

Conservation of spin:

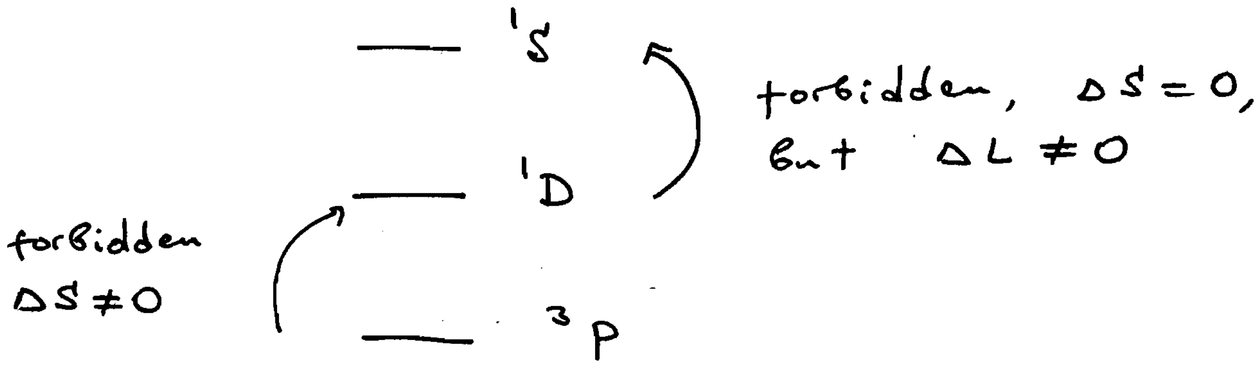
$$\boxed{\Delta S = 0}$$

spin cannot flip in a transition

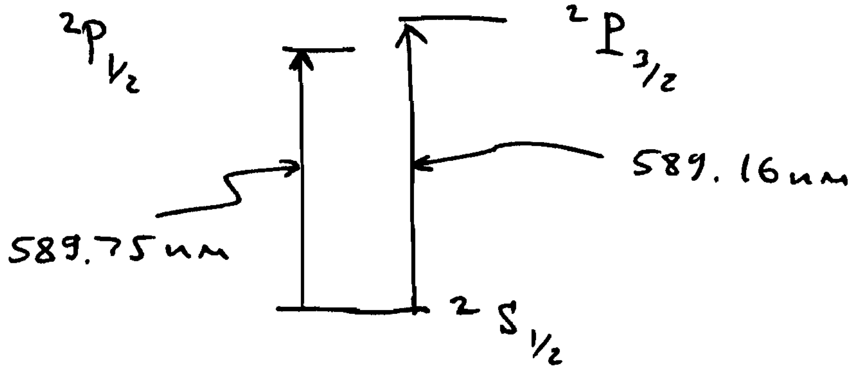
Example of atomic selection rules

Ground state of carbon : $1s^2 2s^2 2p^2$

Electronic levels derived from the electronic configuration:



Sodium doublet :



Both transitions are spin and orbital momentum allowed, $\Delta S = 0$, $\Delta L = 1$.