

Lectures 11-12

Hydrogen atom in electric field. Quadratic Stark effect. Atomic polarizability. Emission and Absorption of Electromagnetic Radiation by Atoms Transition probabilities and selection rules. Lifetimes of atomic states.

Hydrogen atom in electric field. Quadratic Stark effect.

We consider a hydrogen atom in the ground state in the uniform electric field \vec{E} .


The Hamiltonian of the system is [using CGS units]

$$H = H_0 + H_1$$

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r} \quad H_1 = -\vec{d} \cdot \vec{E} = eEr \cos \theta$$

orienting the quantization axis (z) along the electric field. Since d is odd operator under the parity transformation $\vec{r} \rightarrow -\vec{r}$

$$\Delta E_1^{(1)} = \langle \psi_{100} | d | \psi_{100} \rangle = 0 \quad \psi_{100} \equiv 100$$



even function product

Therefore, need second-order correction to the energy

$$\Delta E_1^{(2)} = \sum_{n \neq 1, m \neq 0} \frac{|\langle n \ell m | H_1 | 100 \rangle|^2}{E_1^{(0)} - E_n^{(0)}} = -\frac{1}{2} \alpha E^2$$

ΔE is written in the form $\Delta E_1 = -\frac{1}{2} \alpha E^2$, where


α is the polarizability.

We will use the approximation $E_1^{(0)} - E_n^{(0)} \approx E_1^{(0)} - E_2^{(0)} \Rightarrow$

$$\frac{1}{2} \alpha E^2 = \frac{1}{E_2^{(0)} - E_1^{(0)}} \sum_{n \ell m} |\langle n \ell m | H_1 | 100 \rangle|^2$$

Note that we included 100 term to make use of the completeness relation since it is zero anyway.

$$\begin{aligned} \sum_{n \ell m} |\langle n \ell m | H_1 | 100 \rangle|^2 &= \langle 100 | H_1 \left(\sum_{n \ell m} |n \ell m\rangle \langle n \ell m| \right) H_1 | 100 \rangle \\ &= \langle 100 | H_1^2 | 100 \rangle \end{aligned}$$



1

$$\frac{1}{2} \alpha \mathcal{E}^2 \approx \frac{\langle 100 | H_1^2 | 100 \rangle}{E_2^{(0)} - E_1^{(0)}}$$

$a \equiv a_0$ (Bohr radius)

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \frac{1}{a^{3/2}} e^{-r/a}$$

$$\begin{aligned} \langle 100 | H_1^2 | 100 \rangle &= \frac{e^2 \mathcal{E}^2}{\pi a^3} \int_0^\infty r^4 e^{-2r/a} \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= e^2 \mathcal{E}^2 a^2 \end{aligned}$$

$$E_2^{(0)} - E_1^{(0)} = -\frac{e^2}{2a} \left(\frac{1}{4} - 1 \right) = \frac{3e^2}{8a}$$

$$\Delta E_1 = \frac{1}{2} \alpha \mathcal{E}^2 = e^2 a^2 \frac{8a}{3e^2} \mathcal{E}^2 = \frac{8}{3} a^3 \mathcal{E}^2 \Rightarrow \alpha = \frac{16}{3} a^3$$

$$\alpha \approx 0.8 \times 10^{-24} \text{ cm}^3$$

Exact value is $0.67 \times 10^{-24} \text{ cm}^3$

Note that polarizability of classical conductive sphere of radius a is a^3 .

Emission and Absorption of Electromagnetic Radiation by Atoms

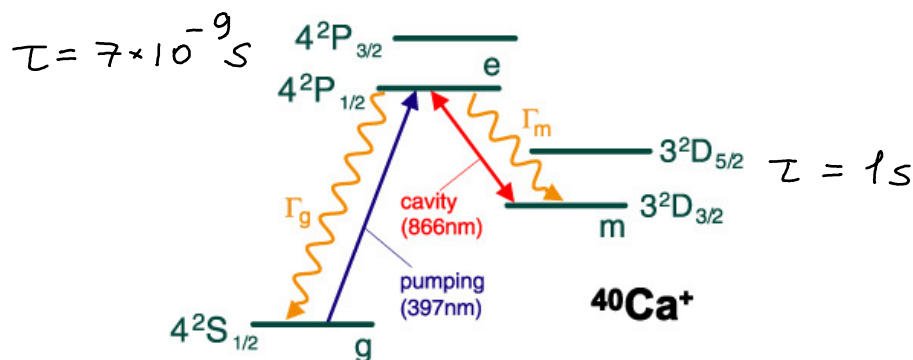
(follows W. Demtröder, chapter 7)

During the past few lectures, we have discussed stationary atomic states that are described by a stationary wave function and by the corresponding quantum numbers.

We also discussed the atoms can undergo transitions between different states with energies E_i and E_k , when a photon with energy

$$\hbar\omega = E_i - E_k \quad (1)$$

is emitted or absorbed. We know from the experiments, however, that the absorption or emission spectrum of an atom does not contain all possible frequencies ω according to the formula above. Therefore, there must be "selection rules" that select the possible radiative transitions from all combinations of E_i and E_k . These selection rules strongly affect the lifetimes of the atomic excited states. For example, we have discussed that the 3d states of Ca^+ have very long lifetimes, on the order of 1 second, while the lifetimes of the 4p states in the same ion are very short, about $7 \text{ ns} = 7 \times 10^{-9}$ seconds:



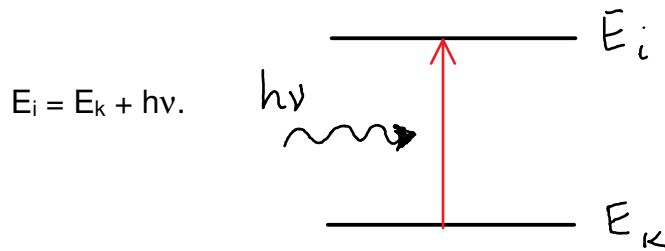
It is experimentally observed that the intensity of the spectral lines can vary by many orders of magnitude, which means that the probability of a transition generally depends strongly on the specific combination of the two atomic states in (1). In turn, the combination of all transition probabilities from the excited state down to the states below determines its lifetime. In addition to the energy conservation expressed by Eq. (1), the total angular momentum of the system (atom + photon) has to be conserved, so the polarization of the emitted or absorbed electromagnetic radiation should also be considered.

The goal of this lecture is to explain vast difference in the lifetimes of the states in the picture above and to provide selection rules and formulas for the calculation of the transition probabilities and the corresponding lifetimes of the excited states.

Transition Probabilities. Induced and Spontaneous Transitions, Einstein Coefficients.

Process 1: Absorption

An atom in the state $|k\rangle$ with energy E_k in the electromagnetic radiation field with spectral energy density $\omega_\nu(\nu)$ can absorb a photon $h\nu$, which brings the atom into a state with higher energy



The spectral energy density $\omega_\nu(\nu)$ is the field energy per unit volume and unit frequency interval $\Delta\nu = 1 \text{ s}^{-1}$.

$$\omega_\nu(\nu) = n(\nu)h\nu$$

where $n(\nu)$ is the number of the photons $h\nu$ per unit volume within the frequency interval $\Delta\nu = 1 \text{ s}^{-1}$.

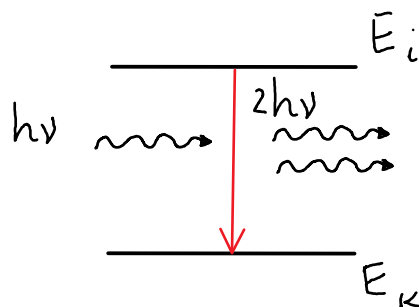
The probability per second for such an absorbing transition is given by

$$\frac{dP_{ki}^{abs}}{dt} = B_{ki} \omega_\nu(\nu)$$

↙ Einstein coefficient for absorption

Process 2: Induced (or simulated) emission

The radiation field can also induce atoms in an excited state with energy E_i to emit a photon with energy $h\nu = E_i - E_k$ and to go into the lower state E_k . This process is called induced (or stimulated) emission.



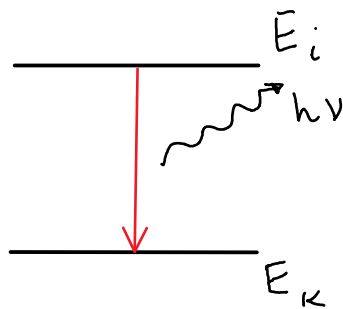
The two photons have identical propagation directions. The energy of the atom is reduced by $\Delta E = h\nu$.

$$\frac{dP_{ki}^{ind}}{dt} = B_{ik} \omega_\nu(\nu)$$

↙ Einstein coefficient for induced emission

Process 3: spontaneous emission

An atom in the excited state can transition to a lower state and give away its excitation energy spontaneously **without an external radiation field**. This process is called spontaneous emission.



Note that unlike the case of the induced emission, the spontaneous emission photon can be emitted into an arbitrary direction. The probability per second for such a spontaneous emission is

$$\frac{dP^{sp}}{dt} = A_{ik}$$

↖ Einstein coefficient for induced emission

The Einstein coefficient for induced emission depends only on the wave functions of the states $|i\rangle$ and $|k\rangle$. This process and the corresponding Einstein coefficients determine the lifetime of the atomic state.

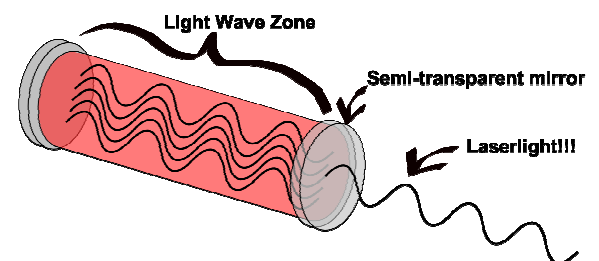
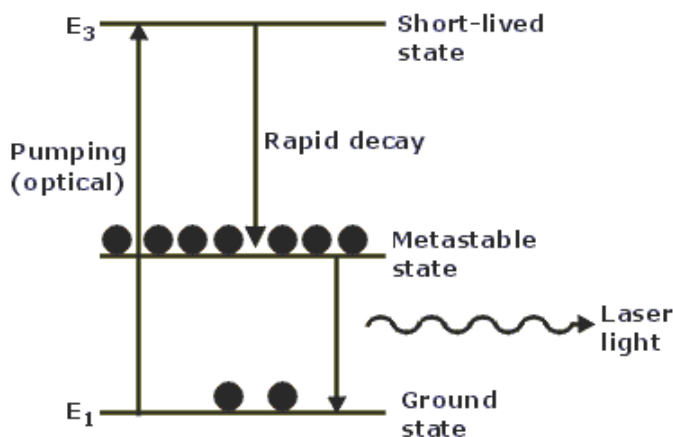
Therefore, we are mostly interested now in the A_{ik} coefficients but will mention important results regarding the other processes:

If both states have equal statistical weights ($g_i = g_k$) the Einstein coefficients for induced absorption and emission are equal.

The statistical weight is number of possible realizations of a state with energy E and total angular momentum quantum number J , i.e. $g=2J+1$.

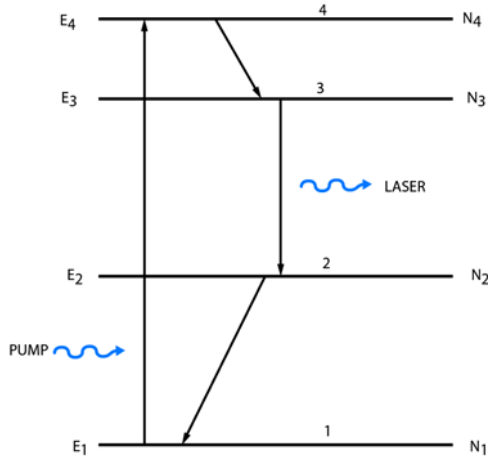
Population inversion (i.e. more atoms in the upper state than in the lower state) is required to make a laser. This can not be achieved in a two level system.

How to make a laser: a 3-level scheme



How to make a laser: a 4-level scheme

4 LEVEL



Question for the class:

What are the requirements for decays
 $4 \rightarrow 3$, $3 \rightarrow 2$, and $2 \rightarrow 1$ to make a laser?
 Which one(s) of the levels 2, 3 and 4 should be metastable?

Answer: Level two should be metastable, i.e.
 $3 \rightarrow 2$ is a slow decay and
 $4 \rightarrow 3$ and $2 \rightarrow 1$ have to be fast decays to
 maintain population inversion between 3 and 2.

Spontaneous emission: transition probability (i.e. Einstein coefficients A_{ik}).

During the absorption or emission of a photon the atom undergoes a transition between two levels $|i\rangle$ and $|k\rangle$, i.e. it changes its eigenstate in time. Therefore it cannot be described by the stationary Schrödinger equation, but we have to use the time-dependent Schrödinger equation. However, the relation between transition probabilities and the quantum mechanical description by matrix elements can be illustrated in a simple way by a comparison with classical oscillators emitting electromagnetic radiation.

A classical oscillating electric dipole (Hertzian dipole) with electric dipole moment

$$\vec{p} = q\vec{r} = \vec{p}_0 \sin \omega t$$

emits the average power, integrated over all directions \mathcal{Q} against the dipole axis

$$\bar{p} = \frac{2}{3} \frac{\bar{p}^2 \omega^4}{4\pi \epsilon_0 c^3} \quad \bar{p}^2 = \frac{1}{2} p_0^2$$

The emitted radiation power is therefore proportional to the average of the squared dipole moment. The quantum mechanical version can be rigorously derived by time-dependent perturbation theory which is relatively lengthy. Therefore, we will just use an analogy with the classical case above.

The time-dependent wave function for the state $|k\rangle$ with energy E_k is

$$\Psi(r,t) = \psi(r) e^{-iE_k t/\hbar}$$

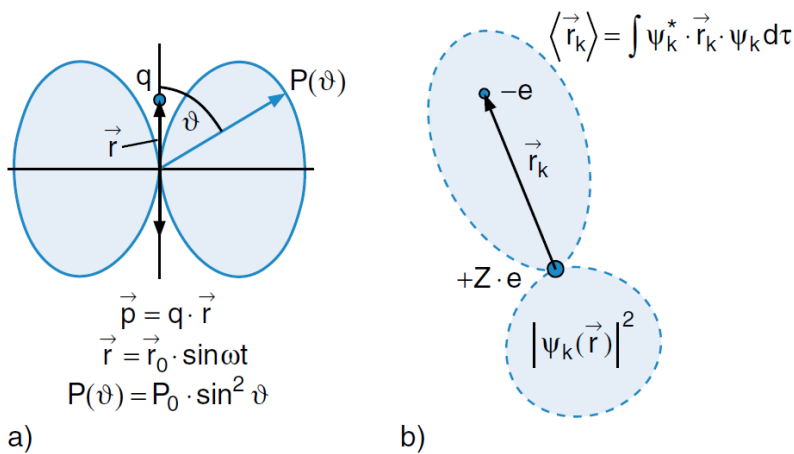


Fig. 7.3. (a) Spatial radiation characteristics of a classical oscillating electric dipole. (b) The expectation value $\langle p_k \rangle = -e \langle r_k \rangle$ of the quantum mechanical dipole moment in level $|k\rangle$, determined by its wave function ψ_k

From W. Demtröder, chapter 7

The linear combination of these solutions is also a solution

$$\psi = \sum c_k |\psi_k\rangle e^{-i E_k t / \hbar}$$

$$-e \int \psi^* \vec{r} \psi d^3r = -e \sum_i \sum_k c_i^* c_k e^{-i \omega_{ik} t} \int \psi_i^* \vec{r} \psi_k d^3r$$

only $i \neq k$ terms are non-zero since r is an odd function

In the classical model, a periodically oscillating dipole moment emits radiation. We define a transition dipole moment for transition between states $|i\rangle$ and $|k\rangle$:

$$D_{ik} = -e \int \psi_i^* \vec{r} \psi_k d^3r$$

We use indices i and k to designate a complete set of quantum numbers. Vector r is from the origin at the atomic nucleus and is shown at the picture above.

Note that many-body problem for transitions in atoms with many electrons will still reduce to the "one-body" dipole matrix elements defined above (in other words $D=er$ is a "one-body" operator).

The correct result for A_{ik} can be obtained by replacing $\langle p^2 \rangle \rightarrow 2 |D_{ik}|^2$

in the classical expression for average radiation power emitted by the atom with the transition $|i\rangle \rightarrow |k\rangle$.

$$\langle P_{ik} \rangle = \frac{4}{3} \frac{\omega_{ik}^4}{4\pi \epsilon_0 c^3} |D_{ik}|^2$$

N_i atoms in level $|i\rangle$ emit the average radiation power

$$\langle P \rangle = N_i \langle P_{ik} \rangle$$

on the transition $|i\rangle \rightarrow |k\rangle$ with frequency ω_{ik} .

The Einstein coefficient A_{ik} for spontaneous emission gives the probability per second that one atom emits a photon on the transition $|i\rangle \rightarrow |k\rangle$ with frequency ω_{ik} . Then, the average power emitted by N_i atoms is given by

$$\langle P \rangle = N_i A_{ik} \hbar \omega_{ik} \equiv N_i \langle P_{ik} \rangle \equiv N_i \frac{4}{3} \frac{\omega_{ik}^4}{4\pi \epsilon_0 c^3} |D_{ik}|^2 \Rightarrow$$

$$A_{ik} = \frac{4}{3} \frac{\omega_{ik}^3}{4\pi \epsilon_0 c^3} \frac{2\pi}{h} |D_{ik}|^2$$

$$A_{ik} = \frac{2}{3} \frac{\omega_{ik}^3}{\epsilon_0 c^3 h} |D_{ik}|^2 \quad \leftarrow \text{Transition probability (or "transition rate")}$$

The expectation values D_{ik} for all possible transitions between arbitrary levels $i, k = 1, 2, \dots, n$ can be arranged in an $n \times n$ matrix. The D_{ik} are therefore called **electric-dipole matrix elements**. If some of the matrix elements are zero, the corresponding transition does not occur. One says that this transition is "not allowed" but "forbidden", or electric-dipole forbidden. Note that the absolute square $|D_{ik}|^2$ of the matrix element is directly proportional to the probability of the transition $|i\rangle \rightarrow |k\rangle$, i.e., of the intensity of the corresponding line in the atomic spectrum. The larger the matrix element, the stronger the transition.

Such electric-dipole transitions associated with the operator $D=er$ are also called E1 transitions. Later, we will also discuss magnetic-dipole M1 and electric-quadrupole E2 transitions which are much weaker than the E1 transitions and have different corresponding expressions for their transition probabilities.

Our next goal is to determine which transitions are electric-dipole allowed, i.e. when does matrix elements D_{ik} are not zero. We already mentioned that the electric-dipole operator is an odd operator since it is $\sim \vec{r}$. Therefore, we first need to discuss the parity of the atomic states.

Parity of the atomic states

Parity (spatial inversion) transformation: $\vec{r} \rightarrow -\vec{r}$, i.e. $x \rightarrow -x, y \rightarrow -y, z \rightarrow -z$.

What are the eigenvalues of the parity operator P ?

Since applying the parity operator twice returns us to the original coordinate system, $P^2=1$, the eigenvalues are 1 and -1.

Wave functions that remain unchanged under the spatial inversion are said to be of even parity. Wave functions that change sign under the spatial inversion are said to be of odd parity.

How do we determine the parity of the atomic state?

Let's assume that electron moves in the central potential of the nucleus and other atomic electrons. Then, the wave function separates into a radial and angular parts.

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi)$$

$$\left. \begin{array}{l} x \rightarrow -x \\ y \rightarrow -y \\ z \rightarrow -z \end{array} \right\} \Rightarrow \text{in spherical coordinates} \quad \begin{array}{l} r \rightarrow r \\ \theta \rightarrow \pi - \theta \\ \varphi \rightarrow \varphi + \pi \end{array}$$

Then, the radial part $R_{nl}(r)$ does not change and the parity of the atomic wave function is determined by the angular part. From the properties of the spherical functions Y_{lm} :

$$Y_{lm}(\pi - \theta, \varphi + \pi) = (-1)^l Y_{lm}(\theta, \varphi).$$

Since a multi-electron wave function is a (antisymmetrized) product of the wave functions of the electrons, the total parity of the many-electron atom is given by the product of the parities for each electron:

$$P = (-1)^{l_1} (-1)^{l_2} \dots (-1)^{l_n} = (-1)^{\sum_{i=1}^n l_i}$$

for atom with n electron. NOTE THAT $\sum_{i=1}^n l_i$ IS NOT EQUAL TO THE TOTAL ORBITAL ANGULAR MOMENTUM L !

One immediate observation from the equation above is that you can exclude all fully closed subshells when determining the parity of the atomic states, since the number of electrons in the subshell is even.

Question to the class:

What is the parity of the $1s^2 2s$ and $1s^2 2p$ states of Li?

What is the parity of $1s^2 2s^2 2p^6 3s 3p$ and $1s^2 2s^2 2p^6 3s 3d$ state of Mg?

$1s^2 \underline{2s}$ $l=0$	$(-1)^l = 1 \Rightarrow \text{even}$	$1s^2 2p$ $l=1$	$(-1)^l = -1 \Rightarrow \text{odd}$
$1s^2 2s^2 2p^6$	$3s 3p$ $\uparrow \quad \uparrow$ $l_1=0 \quad l_2=1$	$(-1)^{l_1+l_2} = -1$	odd
$1s^2 2s^2 2p^6$	$3s 3d$	$(-1)^{l_1+l_2} = (-1)^{0+2} = 1$	even

Selection rules for electric-dipole transitions

1. For the electric dipole transition between the states i and k , the states i and k must be of opposite parity since the dipole operator is odd operator with respect to parity transformation and parity is conserved in electromagnetic interaction.

Next consideration: what differences in the quantum numbers are allowed?
We are going to consider selection rules based on J and M_J quantum numbers.

To answer this question, we need to consider when the electric dipole matrix element between states i and k turns to zero:

$$\text{When } D_{ik} = \langle \psi_i | D | \psi_k \rangle = 0.?$$

The spherical components of the electric dipole moment D_q ($q = 0, \pm 1$) are given by

$$D_1 = -\frac{1}{\sqrt{2}} (D_x + iD_y)$$

$$D_0 = D_z$$

$$D_{-1} = \frac{1}{\sqrt{2}} (D_x - iD_y)$$

The dipole operator is irreducible tensor of rank 1. The general definition of the irreducible tensors is the following: a family of $2k+1$ operators T_q^k satisfying the commutation relations

$$[J_z, T_q^k] = q T_q^k$$
$$[J_{\pm}, T_q^k] = \sqrt{(k \pm q + 1)(k \mp q)} T_{q \pm 1}^k$$

with angular momentum operators J_z and $J_{\pm} = J_x \pm iJ_y$ are called irreducible tensor operators of rank k . For example, the spherical harmonics $Y_{\ell m}(\theta, \varphi)$ are irreducible tensor

operators of rank ℓ . The matrix elements of irreducible tensor operators between angular momentum states are evaluated using the Wigner-Eckart theorem which separates out the part than depends of M_J quantum numbers. We use abbreviated designations

$$|j m \rangle = \psi_{\gamma j m} \quad \gamma \equiv \text{all other quantum numbers except } j, m_j.$$

Wigner-Eckart theorem

$$\langle j_1 m_1 | T^k_q | j_2 m_2 \rangle = (-1)^{j_1 - m_1} \underbrace{\begin{pmatrix} j_1 & k & j_2 \\ -m_1 & q & m_2 \end{pmatrix}}_{\text{only this part depends on } m_1, m_2, \text{ and } q} \langle j_1 || T^k || j_2 \rangle$$

$$\langle j_1 || T^k || j_2 \rangle$$

does not depend on magnetic quantum numbers m_1 , m_2 , and q .

It is called a "reduced matrix element". The quantity in $()$ is called a 3-j coefficient related to the Clebsch-Gordan coefficients as

$$C(j_2 k j_1; m_2 q m_1) = \sqrt{2j_1 + 1} (-1)^{j_1 - m_1} \begin{pmatrix} j_1 & k & j_2 \\ -m_1 & q & m_2 \end{pmatrix}$$

The matrix element of D is zero when the corresponding 3-j coefficient is zero. The 3-j coefficients are non-zero if the following is true:

$$-m_1 + q + m_2 = 0 \quad (\text{sum of the quantities on the bottom is zero})$$

$$|j_1 + k| \leq j_2 \leq |j_1 - k|$$

$$j_1 + j_2 \geq k$$

This leads to the following selection rules for rank 1 irreducible tensor operator $\begin{matrix} k=1 \\ q=0, \pm 1 \end{matrix}$

$$\Delta M_J = 0, \pm 1$$

$$\Delta J = 0, \pm 1 \quad (J_1 = 0 \text{ to } J_2 = 0 \text{ is forbidden})$$

Summary: selection rules for electric-dipole transitions between states i and k

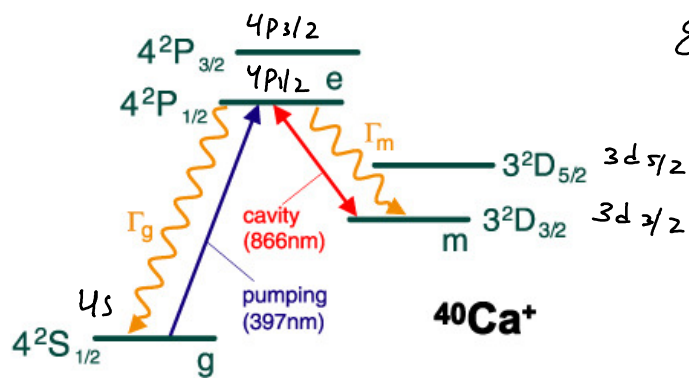
1) States i and k have to be of opposite parity

$$2) \Delta M_J = 0, \pm 1$$

$$\Delta J = 0, \pm 1 \quad (J_i = 0 \text{ to } J_k = 0 \text{ is forbidden})$$

Question for the class:

What electric-dipole transitions are allowed between the Ca⁺ atomic levels on the picture below?



Example: $4p_{1/2} - 4s$

$$4p_{3/2} - 4s$$

$$4p_{3/2} - 3d_{3/2}$$

$$4p_{1/2} - 3d_{3/2}$$

$$4p_{3/2} - 3d_{5/2}$$

Magnetic-dipole and electric-quadrupole transitions

Derivation of the above formulas assumes "dipole approximation"

$$\exp(i\vec{k} \cdot \vec{r}_i) \approx 1$$

Considering the next term in the expansion, $i\vec{k} \cdot \vec{r}_i$ leads to magnetic dipole and electric-quadrupole transitions, which are several orders of magnitude weaker than the electric-dipole transitions. If electric-dipole transition between states i and k is allowed, the contribution of all other transitions to the lifetime is negligible. Magnetic moment operator is

$$\vec{M} = \frac{1}{2m} [\vec{L} + 2\vec{S}]$$

The selection rules for magnetic-dipole (M1) transitions are the following:

1) States i and k have to be of the same parity

$$2) \Delta M_J = 0, \pm 1$$

$$\Delta J = 0, \pm 1 \quad (J_i = 0 \text{ to } J_k = 0 \text{ is forbidden})$$

For non-relativistic single-electron states this would mean $l_i = l_k$, but $n_a l_a \rightarrow n_b l_a$

will vanish because the corresponding wave functions are orthogonal. The relativistic effects will lead to non-zero (but very small) transition amplitudes for such transitions. Therefore, M1 transitions are generally significant for transitions between fine-structure components (for example $3d_{5/2} - 3d_{3/2}$ transition for the figure above) or between Zeeman components.

The **electric-quadrupole operator** in spherical coordinates is given by

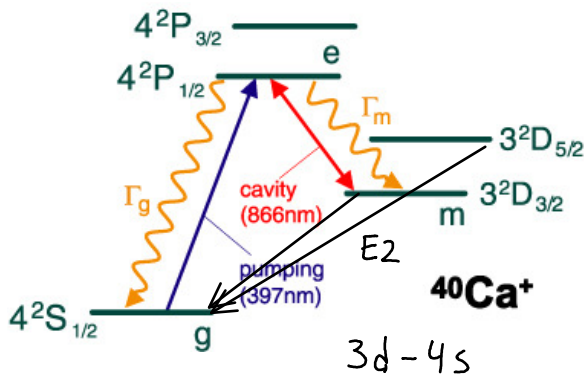
$$Q_{\nu}^2 = r^2 C_{\nu}^{(2)}(\hat{r})$$

$$C_{\nu}^k = \sqrt{\frac{4\pi}{2k+1}} Y_{k\nu}(\theta, \varphi)$$

It is irreducible tensor of rank 2 and parity even (since r^2).

Question for the class: what are the selection rules for electric-quadrupole transitions?

- 1) States i and k have to be of the same parity
- 2) $\Delta M_J = 0, \pm 1, \pm 2$
 $\Delta J = 0, \pm 1, \pm 2 \quad (J_i + J_k \geq 2)$



Transition rates for E1, M1, and E2 transitions

Applying the Wigner-Eckart theorem to sum over possible magnetic quantum numbers, and substituting the relevant constants gives the following expressions for the transition rates for E1, E2, and M1 transitions:

$$A(E1) = \frac{2.02613 \times 10^{18}}{(2J_a + 1)\lambda^3} S(E1),$$

$$A(M1) = \frac{2.69735 \times 10^{13}}{(2J_a + 1)\lambda^3} S(M1),$$

$$A(E2) = \frac{1.11995 \times 10^{18}}{(2J_a + 1)\lambda^5} S(E2),$$

S is reduced matrix element squared in atomic units,

$$S(E1) = |\langle J_a || D || J_b \rangle|^2$$

$$S(E2) = |\langle J_a || Q || J_b \rangle|^2$$

$$S(M1) = |\langle J_a || M || J_b \rangle|^2$$

J_a is total angular momentum of the upper state
 λ is the wavelength of the transition in $\text{\AA} \equiv 10^{-10} \text{m}$

Comparing these formulas illustrates why E1 transition rate is larger than M1 and E2 transition rates by several orders of magnitude even when the reduced matrix elements are similar:

$$\begin{aligned}
 A(E1) &= \frac{2.02613 \times 10^{18}}{(2J_a + 1)\lambda^3} S(E1), \\
 A(M1) &= \frac{2.69735 \times 10^{13}}{(2J_a + 1)\lambda^3} S(M1), \\
 A(E2) &= \frac{1.11995 \times 10^{18}}{(2J_a + 1)\lambda^5} S(E2),
 \end{aligned}$$

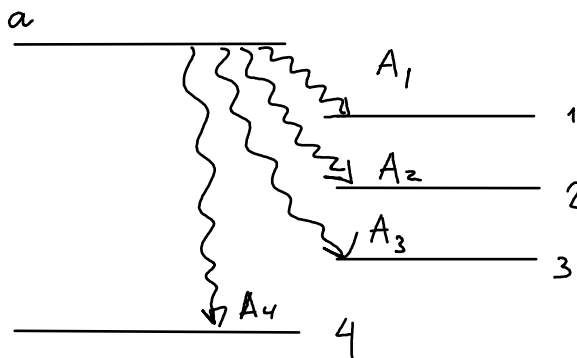
5 orders of magnitude difference

λ^3 vs. λ^5 For example for optical transition, this would be $(6000)^3$ vs. $(6000)^5$

$1 \text{ \AA} = 10 \text{ nm}$

The lifetime of the atomic state a is determined as

$$\tau_a = \frac{1}{\sum_b A_{ab}}$$



$$\tau = \frac{1}{A_1 + A_2 + A_3 + A_4}$$

Therefore, the larger are the transition rates, the smaller is the lifetime. This formula also shows that if E1 is allowed, contributions of all other transitions, M1, E2, etc. are negligible. Note that several E1 transitions may be allowed, these generally should be added (unless λ^3 factor significantly reduce their contributions)