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Atomic Spectra - Transition Probabilities and Addendum

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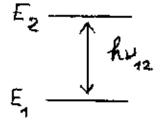
V. TRANSITION PROBABILITIES and ADDENDUM

This chapter is devoted to simple results on the absorption and emission of photons by atomic systems.

1. Emission and absorption.

The Einstein rate equations can first be recalled, for two levels:

$dN_1 = - N_1 B_{12} \rho_\nu(\nu_{12})\, dt$, for absorption;
$dN_2 = - N_2 A_{21}\, dt$, for spontaneous emission;
$dN_2 = - N_2 B_{21} \rho_\nu(\nu_{12})\, dt$, for induced emission.



It is easy to deduce that $\tau_2 = \frac{1}{A_{21}}$ is the natural lifetime of level 2. The comparison with the emission spectrum of the black body (a spectrum interpreted by PLANCK around 1900) gave to EINSTEIN the intuition of the existence of the induced-emission phenomenon, and two formulae :

$\frac{B_{12}}{B_{21}} = \frac{g_2}{g_1}$ and $A_{21} = B_{21} \frac{8\pi h \nu_{12}^3}{c^3}$, where g_1 and g_2 are the degeneracies of levels 1 and 2.

Furthermore, the time-dependent perturbation theory leads to the formula $B_{mn} = \frac{1}{6\varepsilon_0 \hbar^2} |(\Psi_m | \vec{D} | \Psi_n)|^2$ (1)
for electric-dipole transitions (E1), where

$\vec{D} = -e \sum_{i=1} \vec{r}_i$ is the electronic dipolar moment, and m and n are two states of the atom.

Remark: note that the A_{21} coefficient, which is not related with an induced phenomenon in Quantum Mechanics, can be computed directly only in the frame of Quantum Electrodynamics.

Problem. Normally, two different states of the same level, which only differ in their values of M_J, have the same lifetime. Derive the formula $B_{21} = \sum_m B_{nm}$ if the states m belong to the level 1 and the state n is any of the states of the level 2.

2. Computation of the transition probabilities.

The transition probability between the levels 1 and 2 is A_{21}. Through the formulae of p. V.1, it can be easily deduced from results obtained for the relevant B_{mn} coefficients.

A state of a free atom can be written, in general, $|\alpha J M_J)$. The vector $\vec{D}$ can be considered as being a tensor operator of rank 1 (see p. 32 of the Lectures on Angular Momentum). Then

$$|(\alpha J M_J | \vec{D} | \alpha' J' M_J')|^2 = \sum_{q=-1,0,1} |(\alpha J M_J | D_q^{(1)} | \alpha' J' M_J')|^2 .$$

Now, applying the Wigner-Eckart theorem (see p. 36 of the Lectures on Angular Momentum), we write

$$|(\alpha J M_J | D_q^{(1)} | \alpha' J' M_J')|^2 = \begin{pmatrix} J & 1 & J' \\ -M_J & q & M_J' \end{pmatrix}^2 (\alpha J \| D^{(1)} \| \alpha' J')^2 .$$

The remaining reduced matrix element can also be computed by tensor-operator techniques. But, from it and from the 3j symbol we immediately deduce selection rules.

ⓐ Selection rule on J.

For the 3j symbol not to be zero, we must have

$$|J-1| \leq J' \leq J+1$$

ⓑ Selection rule on M_J; polarization.

Only one of the three components ($q = -1, 0$ or 1) may yield a non-zero result, because the 3j is not zero only if $-M_J + q + M_J' = 0$. Moreover, each component can be shown to correspond to a particular polarization of the light emitted or absorbed.

If we define $\Delta M = M_{\text{upper level}} - M_{\text{lower level}}$, then,

- if $\Delta M = 0$, the light is polarized parallel to the Oz axis (that means, in any direction of observation, like the light emitted by a dipole oscillating parallel to Oz);
- if $\Delta M = +1 (-1)$, the light is polarized like that emitted by a circular coil parallel to the xOy plane and where a positive charge runs which creates a magnetic field of the same sense as (opposite sense to) that of $\vec{B}$.

ⓒ Selection rule on parity.

In the previous chapters, the parity quantum number was not introduced because it was not useful. Let us recall now that the parity operator P, acting on a wavefunction, changes all the $\vec{r}_i$ position vectors of the electrons in their opposites.

Now, the hamiltonian $H_0 + H' + \Lambda$ is even, i.e., it is not changed when the P operator is applied to it. Therefore each $|\alpha J M_J)$ state is even (parity +) or odd (parity −) (except in the elementary treatment of hydrogen, where there is an accidental degeneracy between even and odd states)

The $\vec{D}$ operator is odd, because the action of P changes it in $-\vec{D}$. We deduce that the electric-dipole transitions only occur between states of different parities (this is called Laporte's Rule).

ⓓ Selection rules on configuration, and on electronic jump.

Let us now specialize the states $|\alpha J M_J)$ to the case when α is in a given configuration (although this is not said in Lecture III, this is the case if the first-order treatment of H' can be considered a sufficient approximation).

Then, because $\vec{D}$ is a "monoelectronic operator" (i.e., the sum of operators acting only on one electron), one finds that α and α' must not differ by more than one electronic subshell.

Furthermore, in spherical coordinates, the parity operator clearly does not change r, but only θ and φ, i.e., the $Y_{\ell m}$ functions. More precisely, it can be shown that it changes $Y_{\ell m}(\theta,\varphi)$ in $(-1)^{\ell} Y_{\ell m}(\theta,\varphi)$. Therefore the parity of the configuration $(n_1 \ell_1)^{N_1}(n_2 \ell_2)^{N_2}\dots(n_k \ell_k)^{N_k}$ is $(-1)^{\sum_{i=1}^{k} N_i \ell_i}$.

In conclusion, if the configuration scheme is a good

approximation, the E1 transitions only occur between configurations of opposite parities, and this difference in parity must reflect the change in parity of the jumping electron (i.e., of that subshell which is not the same in both configurations).

Moreover, the reduced matrix elements which would remain at the end of the tensor-operator calculation of $(\alpha J \| D^{(1)} \| \alpha' J')$ are of the type $(n\ell \| r^{(1)} \| n'\ell')$, if $n\ell$ jumps to $n'\ell'$ (or the reverse). Because of the triangular rules, we must have $|\ell - 1| \leq \ell' \leq \ell + 1$.

The electronic jumps can only be

$s \rightleftarrows p \quad , \quad p \rightleftarrows d \quad , \quad d \rightleftarrows f \quad$, etc.

ⓔ Selection rules on S and L.

Let us specialize still further the states $|\alpha J M)$ to the case when α represents some Russell-Saunders term of a given configuration (this is a sufficient approximation if Λ has matrix elements much smaller than the differences between the term energy values).

Then, because $\vec{D}$ is spin-independent, we must have $S = S'$.

Moreover, because it is a tensor operator of rank 1, we must also have $|L - 1| \leqslant L' \leqslant L + 1$.

ⓕ Examples.

In carbon ($Z = 6$), if the configuration is considered a good quantum number, transitions may occur between $1s^2 2s^2 2p^2$ (ground configuration) and $1s^2 2s^2 2p\, 3s$, $1s^2 2s^2 2p\, 3d$, $1s^2 2s^2 2p\, 4s$, $1s^2 2s\, 2p^3$, $1s^2 2s\, 2p^2 3p$, $1s\, 2s^2 2p^3$, $1s\, 2s^2 2p^2 4p$, etc.

For what concerns $1s^2 2s^2 2p^2 - 1s^2 2s\, 2p^3$, the transitions occur between the 2 $J = 0$ levels of the first configuration and the 4 $J = 1$ levels of the second configuration; the $J = 1$ level and the $J = 0$, the 4 $J = 1$ and the 4 $J = 2$; the 2 $J = 2$ and the 4 $J = 1$, the 4 $J = 2$ and the $J = 3$ (check all that!).

3. Order of magnitude of the natural lifetimes.

In the B_{mn} quantity (eq. (1)), every dimensioned factor is of the atomic type, i.e., can be expressed as a numerical multiple of m, e, $\hbar$ and ε_0 to various powers. Now, A_{21} is the product of B_{21} by $\frac{8\pi h \nu_{12}^3}{c^3}$, where everything is also atomic except c^3. We conclude that $\tau_2 = \frac{1}{A_{21}}$ is of the atomic type but for a c^3 factor.

τ_2 is, therefore, of the order of magnitude of (atomic unit of time) $\times \left(\frac{e^2}{4\pi\varepsilon_0 \hbar c}\right)^{-3}$. The second factor is equal to $(137)^3$ and

$$\text{atomic unit of time} = \frac{\text{atomic unit of action}}{\text{atomic unit of energy}} = \frac{\hbar}{\frac{me^4}{(4\pi\varepsilon_0)^2\hbar^2}}$$

$\simeq 2.5\ 10^{-17}$ s.

Therefore the order of magnitude of τ_2 is 10^{-10} s.

ADDENDUM

(questions in the exercise sessions)

- He I $1s^2$.

The He I $1s^2$ configuration contains only one state, which is the determinant

$$\Psi(1,2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \frac{R_{1s}(r_1)}{r_1} Y_{00}(\theta_1,\varphi_1)\chi_{s,\frac{1}{2}}(\sigma_1) & \frac{R_{1s}(r_1)}{r_1} Y_{00}(\theta_1,\varphi_1)\chi_{s,-\frac{1}{2}}(\sigma_1) \\ \frac{R_{1s}(r_2)}{r_2} Y_{00}(\theta_2,\varphi_2)\chi_{s,\frac{1}{2}}(\sigma_2) & \frac{R_{1s}(r_2)}{r_2} Y_{00}(\theta_2,\varphi_2)\chi_{s,-\frac{1}{2}}(\sigma_2) \end{vmatrix}$$

which can also be written

$$\underbrace{\frac{R_{1s}(r_1)}{r_1}\,\frac{R_{1s}(r_2)}{r_2}\,\frac{1}{4\pi}}_{\substack{\text{orbital part,}\\ \text{symmetrical vs.}\\ \text{the } 1\leftrightarrow 2 \text{ exchange}}}\ \underbrace{\frac{1}{\sqrt{2}}\left[\chi_{s,\frac{1}{2}}(\sigma_1)\,\chi_{s,-\frac{1}{2}}(\sigma_2) - \chi_{s,-\frac{1}{2}}(\sigma_1)\,\chi_{s,\frac{1}{2}}(\sigma_2)\right]}_{\substack{\text{spin part,}\\ \text{antisymmetrical vs. the } 1\leftrightarrow 2 \text{ exchange}}}$$

For the spin part of two electrons, the $|(s_1 s_2) S M_S\rangle$ function is antisymmetrical if $S=0$ and symmetrical if $S=1$.

- HYDROGENIC IONS

The Schrödinger equation reads

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

. Therefore E is a numerical multiple of $\left(\frac{\hbar^2}{m}\right)^{\alpha}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^{\beta}$. If the latter quantity is an energy, then, $\alpha = -1$ and $\beta = 2$ (this is obtained through identification of the powers of the fundamental dimensions $[M]$, $[L]$, $[T]$ and $[I]$ in the latter quantity and in E).

Conclusion: E is proportional to Z^2.

In the same way, any length, e.g. $\langle r\rangle_{n\ell} \equiv \int_0^\infty [R_{n\ell}(r)]^2 r\,dr$, is a numerical multiple of $\left(\frac{\hbar^2}{m}\right)^{\alpha'}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^{\beta'}$. By identification, one finds $\alpha' = 1$, $\beta' = -1$.

Therefore all lengths are proportional to $\frac{1}{Z}$.

In an analogous way, the expectation value of the spin-orbit operator $\Lambda = \frac{\hbar^2 e^2 Z}{2 m^2 c^2} \frac{1}{r^3} \vec{s}\,\vec{\ell}$

[N.B. The Z factor has not been written in Lecture II, in the computation for hydrogen, but must be introduced for the hydrogenic ion, because the necessary $\vec{B}$ field is due to the orbiting nucleus.]

is proportional to $\underset{\text{coming from the } \Lambda \text{ formula}}{Z} \times \underset{\text{coming from } \langle \frac{1}{r^3}\rangle,\ \text{a } (\text{length})^{-3}}{Z^3} = Z^4$.

- COMPONENTS OF A BALMER LINE

The Balmer line $n = 3 \rightarrow n = 2$ has 7 components:
3d, $J = 5/2 \rightarrow$ 2p, $J = 3/2$; 3d, $J = 3/2 \rightarrow$ 2p, $J = 3/2$ and $1/2$;
3p, $J = 3/2 \rightarrow$ 2s, $J = 1/2$; 3p, $J = 1/2 \rightarrow$ 2s, $J = 1/2$; 3s, $J = 1/2 \rightarrow$ 2p, $J = 3/2$ and $1/2$.

- ORDERS OF MAGNITUDE

A formal result, for any physical problem, contains a limited number of dimensioned constants. These constants, either are properties of the matter (the "hardware" of the problem, in some way) or occur in the fundamental equations relevant to the problem (the "software"). For the problems concerning the structure of matter (Atomic and Molecular Physics, Solid-State Physics, ...) (but we except Nuclear Physics),

the "hardware" is $m, e, \hbar, M$
($\hbar$ is the order of magnitude of the electronic spin, and $M \simeq 10^5 m$ is the mass of a medium-weight nucleus)
and the "software" is
$\hbar$ (Schrödinger eq.)
$4\pi\varepsilon_0$ (Coulomb eq.)
k (Boltzmann eq.)
c (Maxwell eq.)
G (Newton eq. for gravitation)
$\frac{\mu_0}{4\pi}$ (for magnetic problems).

Any quantity built from $m, \hbar, e$ and $4\pi\varepsilon_0$ will be called an atomic quantity, useful for gross atomic structure.

- METHOD OF THE TABLEAU IN M_S, M_L.

Case of p^3 (the results for any p^N, d^N and f^N are on page 208 of the book of Condon and Shortley)

$M_S \backslash M_L$	3	2	1	0	-1	-2	-3
3/2	0	0	0	$\{\overset{+}{1}\,\overset{+}{0}\,\overset{+}{-1}\}$	0	0	0
1/2	0	$\{\overset{+}{1}\,\overset{+}{0}\,\overset{-}{1}\}$	$\{\overset{+}{1}\,\overset{+}{0}\,\overset{-}{0}\}$ $\{\overset{+}{1}\,\overset{+}{-1}\,\overset{-}{1}\}$	$\{\overset{+}{1}\,\overset{+}{-1}\,\overset{-}{0}\}$ $\{\overset{+}{1}\,\overset{+}{0}\,\overset{-}{-1}\}$ $\{\overset{-}{1}\,\overset{+}{0}\,\overset{+}{-1}\}$			0
-1/2	0						0
-3/2	0	0	0		0	0	0

No determinantal state can be found for the boxes with a 0 written in them. As for the states of the other boxes, they can be obtained by changing the signs of all the m_ℓ's and/or of all the m_s's already written in the boxes to which they correspond by symmetry with respect to the heavy horizontal and vertical lines. They are not necessary in the following. The total number of states should, however, be equal to $\binom{6}{3} = \frac{6!}{3!3!} = 20$.

⊗ To use this tableau for finding the αSL Russell–Saunders terms, one goes to the boxes with no state in the box above and no state in the box on the left. There are two such boxes, the one with $M_S = 3/2$, $M_L = 0$ and the one with $M_S = 1/2$, $M_L = 2$. It can now be claimed that there exists, accordingly, an $S = 3/2$, $L = 0$ term and an $S = 1/2, L = 2$ term. (the argument is, for example: the state $\{1^+ 0^+ 1^-\}$ cannot belong to a term with $L < 2$, evidently, but it cannot derive from a term with $S > 1/2$ and for $L > 2$, because the state (of this term) with $M_S = S$ and $M_L = L$ would not exist, an impossible situation). Once the ^4S and ^2D terms are justified in this way, all their "components" must be retained in the relevant boxes: for ^4S, one state (any one if there are several, or a combination of them) in each of the boxes $M_L = 0$, $M_S = 3/2, 1/2, -1/2, -3/2$; for ^2D, one state in each of the boxes $M_S = 1/2, -1/2$, $M_L = 2, 1, 0, -1, -2$. One is then left with $20 - 4 - 10 = 6$ states, to which the same process as that initiated in line ⊗ above can be applied. In this way, a third term (^2P) is found, with 6 states.

- HUND TERMS.

Examples: for the configuration f^5, the highest-M_S highest-M_L state is $\{3^+ 2^+ 1^+ 0^+ -1^+\}$: it is ^6H; for f^{10}, the state of interest is $\{3^+ 3^- 2^+ 2^- 1^+ 1^- 0^+ -1^+ -2^+ -3^+\}$: the Hund term is ^5I.