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WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

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Atomic Spectra

Zeeman Effect

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IV. ZEEMAN EFFECT

The Zeeman effect is the effect of an external magnetic field on the energies of the atomic (or molecular) states.

1. Hamiltonian

The hamiltonian H_Z be found in two ways:

- the electromagnetic interaction of $\vec{B}$ with the magnetic moments present in the system is $W = -\vec{M}\cdot\vec{B}$, where $\vec{M}$ is the sum of the orbital and spin magnetic moments (eqs. (1) and (2) in Lecture II): $H_Z = \frac{e\hbar}{2m}(\vec{L}+2\vec{S})\cdot\vec{B}$ (1) where we consider that $\vec{L}$ and $\vec{S}$ are non-dimensioned, i.e., the ratios of the true orbital and spin momenta to $\hbar$. The quantity $\frac{e\hbar}{2m}$ is denoted μ_B, the Bohr magneton.
- when a charged particle moves in an external electromagnetic field, its kinetic energy in Quantum Mechanics is written not just $\frac{\vec{p}^{\,2}}{2m}$, but $\frac{(\vec{p}-q\vec{A})^2}{2m}$, where $\vec{A}$ is the vector potential of the field. For a uniform magnetic field $\vec{B}$ along Oz, we can take $\vec{A} = \frac{1}{2}\vec{B}\times\vec{r}$, or $A_x = -\frac{1}{2}yB$, $A_y = \frac{1}{2}xB$, $A_z = 0$. Therefore the first order correction to the kinetic energy is equal to $\frac{qB}{2m}(yp_x - xp_y)$ or $\frac{-qB}{2m}\ell_z$. For N electrons, this reproduces the first term in H_Z (eq. (1)).

2. Quantum numbers

The total hamiltonian for a free atom can be written $H_0 + H' + \Lambda$ in a very good approximation (see Lecture III). The quantum numbers for its eigenstates are J and M_J (and the parity quantum number, because the whole hamiltonian is even). In the case where Λ is a very small perturbation compared to H' (this is not frequent), J can be replaced by S, M_S, L, M_L.

Among all these quantum numbers, H_Z only "destroys" J.

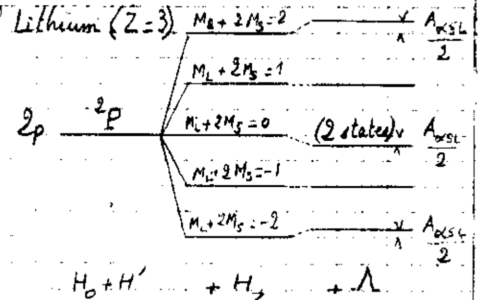
3. Strong-field case: the Paschen Back effect.

We first study a situation where B is large, i.e., where H_Z must be treated by perturbation before Λ is introduced. This is the best case for what concerns the quantum numbers: S, M_S, L, M_L (and M_J) are good quantum numbers.

In the subspace of an αSL Russell-Saunders term, the first order energy is simply $W_Z = \mu_B B(M_L + 2M_S)$ (2). When Λ is introduced, its first-order contribution is $W_\Lambda = A_{\alpha SL} M_S M_L$, if the "effective" form of Λ is used ($A_{\alpha SL}\,\vec{S}\cdot\vec{L}$; see Lecture III, p. III.12).

Problem: prove the latter result, using the formula $\vec{S}\cdot\vec{L} = S_z L_z + \frac{1}{2}[S_+ L_- + S_- L_+]$; the proof is easy when H_Z leaves no degeneracy, and less easy when the quantity $M_L + 2M_S$ has the same value for two different states of the term.

Example: the $2p\ ^2P$ term of Lithium ($Z=3$)



Problem: assign the values of M_S and M_L to each of the sublevels on the right.

4. Weak-field case: the proper Zeeman effect.

If Λ is treated first, its eigenstates are denoted $|\alpha SLJM_J\rangle$, and the levels are αSLJ, with energies $W_\Lambda = A_{\alpha SL}[J(J+1) - S(S+1) - L(L+1)]/2$ (see Lecture III).

Because $|\alpha SLJM_J)$ is an adapted function for the first order of H_Z, we can write directly

$W_Z = (\alpha SLJM_J|H_Z|\alpha SLJM_J)$ (3). The calculation of this matrix element is not simple. Three methods are proposed.

ⓐ Use of Clebsch-Gordan coefficients.

The "coupled" state $|\alpha SLJM_J)$ can be expanded in terms of the "uncoupled" states $|\alpha SM_S LM_L)$, using Clebsch Gordan coefficients (see p. 25 of the Lectures on Angular Momentum in Quantum Mechanics): $|\alpha SLJM_J) = \sum_{M_S M_L} (SM_S LM_L|SLJM_J)|\alpha SM_S LM_L)$.

Then $W_Z = \mu_B B \sum_{M_S M_L} (SM_S LM_L|SLJM_J)^2 (M_L + 2M_S)$, but the general formula for the Clebsch-Gordan coefficient (which can be deduced from that for the 3j coefficient: see p. 28 of the Lectures quoted just above) is too cumbersome to be used here.

ⓑ Vector model.

The vector model is a semi classical method, but it is easily visualized and memorized.

– Let us first consider an orbital angular momentum $\vec{l}$ in a constant magnetic field $\vec{B}$ directed along Oz. It is submitted by the field to a system of forces with moment $\vec{\mathcal{M}}_l \times \vec{B}$, so that its evolution with time is monitored by the equation

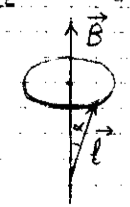
$$\frac{d\vec{l}}{dt} = \vec{\mathcal{M}}_l \times \vec{B} = \frac{-e}{2m}\vec{l} \times \vec{B} \quad (4)$$

From this equation, it can be deduced:

. that $|\vec{l}|$ remains constant (because $\frac{d|\vec{l}|^2}{dt} = 2\vec{l}\cdot\frac{d\vec{l}}{dt} = 0$)

. that the angle α between $\vec{l}$ and $\vec{B}$ is constant (because $\frac{d(\vec{B}\cdot\vec{l})}{dt} = \vec{B}\cdot\frac{d\vec{l}}{dt} = 0$)

. that the angular velocity of the rotation of $\vec{l}$ around $\vec{B}$ is $\omega_l = \frac{eB}{2m}$ (prove it!)

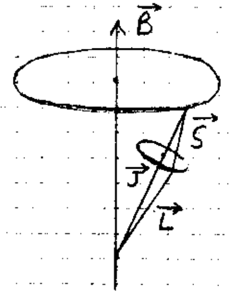


This motion is called the Larmor precession.

– For a spin $\vec{s}$, it is clear that $\omega_s = \frac{eB}{m}$.

– Generalization: any interaction of magnetic origin can be visualized by such a precession, e.g., the spin-orbit interaction, where $\vec{s}$ rotates around $\vec{l}$ (but $\vec{l}$ is not fixed, so that both $\vec{s}$ and $\vec{l}$ rotate around their sum $\vec{j}$, which is fixed in the absence of an external field). Furthermore, the precession velocity ω is proportional to the strength of the interaction.

– Application to the weak-field case.



The triangle defined by $\vec{L}$ and $\vec{S}$ rotates quickly around $\vec{J}$, and $\vec{J}$ rotates slowly around $\vec{B}$.

Problem: show that the average value (in time) of $\mu_B \vec{B}(\vec{L} + 2\vec{S})$ is equal to $W_Z = \mu_B B\, g_{SLJ}\, M_J$

$$\text{with } g_{SLJ} = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (5)$$

($g_{\alpha J}$ is called the Landé factor of the αJ level)

ⓒ Use of the Wigner-Eckart theorem.

L_z and S_z are the $q=0$ components of tensor operators of rank $k=1$ (see p. 32 of the Lectures on Angular Momentum in Quantum Mechanics). We can apply the Wigner-Eckart theorem (pp. 36-37 of the same Lectures), giving

$$W_Z = \mu_B B(\alpha SLJM_J|(L_0^{(1)} + 2S_0^{(1)})|\alpha SLJM_J) = \mu_B B(-1)^{J-M_J}\begin{pmatrix} J & 1 & J \\ -M_J & 0 & M_J \end{pmatrix}(\alpha SLJ\|(L^{(1)} + 2S^{(1)})\|\alpha SLJ) \quad (6)$$

We could look in some Tables to find the formal expression for the 3j symbol of interest, or simply notice that $(\alpha SLJM_J|J_0^{(1)}|\alpha SLJM_J) = (\alpha SLJM_J|J_z|\alpha SLJM_J) = M_J$ can also be computed through the Wigner–Eckart theorem, giving $(-1)^{J-M_J}\begin{pmatrix} J & 1 & J \\ -M_J & 0 & M_J \end{pmatrix}(\alpha SLJ \| J^{(1)} \| \alpha SLJ)$. This expression contains the same phase factor and $3j$ symbol as eq.(6), and accordingly the same dependence on M_J. We conclude that the Zeeman first-order effects on the energies of the states M_J of a J level are proportional to M_J. The proportionality factor, whose J dependence appears in g_{SLJ} (eq.(5)), can be found through the calculation of the reduced matrix element $(\alpha SLJ \| (L^{(1)} + 2S^{(1)}) \| \alpha SLJ)$.

Example: the $6p\ ^2P_{3/2}$ level of Cesium ($Z = 55$).

We compute $g_{SLJ} = \frac{4}{3}$.