# Problems Chapter 15

Quantum Mechanics
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## Problem 1

*Write the classical equation of motion for a plane harmonic oscillator and compute the shift in the frequencies due to a magnetic field directed perpendicular to the plane.*

### Solution

The classical equations of motion are

$$m\frac{d^2\mathbf{r}}{dt^2} = -k\,\mathbf{r} + \frac{e}{c}\,\mathbf{v}\wedge\mathbf{B}\,. \tag{1.1}$$

With

$$\omega_0^2 = \frac{k}{m}\,;\ \omega_L = \frac{e\,B}{m\,c}\,;$$

in cartesian coordinates eq(1) become

$$\frac{d^2 x}{d\,t^2} = -\omega_0^2\,x + 2\,\omega_L\frac{dy}{dt}\,;\qquad \frac{d^2 y}{d\,t^2} = -\omega_0^2\,y - 2\,\omega_L\frac{dx}{dt}\,.$$

For $\xi = x + i\,y$ one can obtain, by summing $i$ times the second equation to the first:

$$\frac{d^2\,\xi}{d\,t^2} = -\omega_0^2\,\xi - 2\,i\,\omega_L\frac{d\xi}{dt}. \tag{1.2}$$

The ansatz $\xi = \mathrm{Exp}[i\,\alpha\,t]$ gives for $\alpha$

$$-\alpha^2 = -\omega_0^2 + 2\,\omega_L\,\alpha\,;\quad\Rightarrow\quad \alpha = -\omega_L \pm \sqrt{\omega_0^2+\omega_L^2}\;.$$

We have two independent oscillations with frequencies

$$\omega_+ = \sqrt{\omega_0^2+\omega_L^2} + \omega_L \simeq \omega_0 + \omega_L\,;\qquad \omega_- = \sqrt{\omega_0^2+\omega_L^2} - \omega_L \simeq \omega_0 - \omega_L\,.$$

## Problem 2

*Study the effect of a magnetic field on the n=2 level of Hydrogen atom.*

### Solution

#### General considerations

In a generic case the magnetic interaction can be of the same order of the fine structure splitting. Both Hamiltonian matrix $H_B$ and $H_{FS}$, for magnetic field and fine structure respectively, must be taken and diagonalized. In absence of these interactions it is assumed that the system has a complete set of Hamiltonian eigenstates $|\alpha, L, L_z, S, S_z\rangle$ where $\alpha$ stands for additional quantum numbers needed to specify the state, for instance the principal quantum number for the Hydrogen atom. It is assumed from now on that z is taken along the B field.

This problem is a typical perturbation problem on a degenerate level., the degeneracy being, in the general case, (2L+1)(2S+1). The subspace with fixed quantum numbers $\alpha$ is spanned by the vectors $|\alpha, L, L_z, S, S_z\rangle$. An alternative choice is to use the Clebsch Gordan coefficients to construct eigenstates of J and $J_z$:

$$|\alpha,\ J,\ J_z,\ L,\ S\rangle = \sum_{L_z, S_z} |\alpha,\ L,\ L_z,\ S,\ S_z\rangle\langle L,\ L_z,\ S,\ S_z \mid J,\ J_z,\ L,\ S\rangle \tag{2.1}$$

The Hamiltonian $H_B + H_{FS}$ (and also the unperturbed Hamiltonian) commutes with $J_z$, i.e. states with different $J_z$ do not mix under the perturbation, for this reason base (1) is somewhat preferred.

With $\Omega = \hbar\,\omega_L$, $\omega_L$= e B/2mc = Larmor frequency, the Hamiltonian $H_B$ takes the form

$$H_B = \Omega\,(L_z + 2\,S_z)\,. \tag{2.2}$$

This Hamiltonian acts directly on angular momentum variables, i.e. do not interfere with quantum numbers like $\alpha$, for example radial coordinates. Its matrix elements are simply written as (we omit inessential variables in the following)

$$\langle \alpha\,,\ J',\ J'_z \mid H_B \mid \alpha,\ J,\ J_z\rangle = \Omega\,\langle \alpha \mid \alpha\rangle\,\langle J',\ J'_z \mid (L_z + 2\,S_z) \mid J,\ J_z\rangle\,.$$

We remember ( see text ) that from Wigner Eckart theorem the diagonal matrix elements of $L_z + 2\,S_z$ inside a subspace at fixed J, L, S are given by

$$g_J\,J_z; \qquad g_J = 1 + \frac{J\,(J+1) - L\,(L+1) + S\,(S+1)}{2\,J\,(J+1)} = \text{Landé factor} \tag{2.3}$$

- **The Hydrogen atom**

Let us consider the n = 2 level of the Hydrogen atom. This level has an additional degeneracy 2s-2p, but as the interaction $H_B$ commutes with parity the even and odd subspaces of states (s and p) do not mix with each other.

- **2s-level**

We have L=0, S=1/2 and for the Landè factor we have g = 2. The double degenerate level $2s_{1/2}$ splits in

$$\left\langle E_{2\,s_{1/2}} + 2\,J_z\,\Omega \right\rangle = E_{2\,s_{1/2}} \pm \Omega \tag{2.4}$$

- **2 p - level**

We have two terms, $2p_{1/2}$and $2p_{3/2}$, with energies $E_{1/2}$ and $E_{3/2}$, eigenvalues of the Hamiltonian perturbed by the LS interaction, and other relativistic corrections. The total multiplicity is 6, the sum of the dimension of the two subspace, which would be degenerate without fine structure interaction. This degeneracy is also equal to 6 = (2L+1)(2S+1) as we have L=1 and S=1/2.

To write the matrix elements of $H_B$ we use Clebsch Gordan decomposition:

$$\begin{aligned}
&\left|\tfrac{3}{2},\ \tfrac{3}{2}\right\rangle = |1\rangle\left|\tfrac{1}{2}\right\rangle; && \left|\tfrac{3}{2},\ \tfrac{3}{2}\right\rangle = |1\rangle\left|\tfrac{1}{2}\right\rangle;\\
&\left|\tfrac{3}{2},\ \tfrac{1}{2}\right\rangle = \sqrt{\frac{1}{3}}\,|1\rangle\left|-\tfrac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\,|0\rangle\left|\tfrac{1}{2}\right\rangle; && \left|\tfrac{1}{2},\ \tfrac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\,|1\rangle\left|-\tfrac{1}{2}\right\rangle - \sqrt{\frac{1}{3}}\,|0\rangle\left|\tfrac{1}{2}\right\rangle;\\
&\left|\tfrac{3}{2},\ -\tfrac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\,|0\rangle\left|-\tfrac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}\,|-1\rangle\left|\tfrac{1}{2}\right\rangle; && \left|\tfrac{1}{2},\ -\tfrac{1}{2}\right\rangle = \sqrt{\frac{1}{3}}\,|0\rangle\left|-\tfrac{1}{2}\right\rangle - \sqrt{\frac{2}{3}}\,|-1\rangle\left|\tfrac{1}{2}\right\rangle;
\end{aligned} \tag{2.5}$$

On the lhs we write the states $J$, $J_z$, on the rhs we omitted the indication of L,S, as these numbers are fixed.

As $J_z$is conserved the two states with $J_z$= ± 3/2 do not mix, as they are isolated. As

$$(L_z + 2\,S_z)\left|\frac{3}{2},\ \pm\frac{3}{2}\right\rangle = (L_z + 2\,S_z)\left(|\pm 1\rangle\left|\pm\tfrac{1}{2}\right\rangle\right) = \pm\,2\left|\frac{3}{2},\ \pm\frac{3}{2}\right\rangle.$$

For these two states the energies are

$$E_{3/2} \pm 2\,\Omega\,. \tag{2.6}$$

The Landé factors for the two terms are $g_{3/2}$=4/3; $g_{1/2}$= 2/3. The value (6) correspond to $g_J\,J_z$for g = 4/3, as expected.

For the $2p_{1/2}$states one has easily, from the Clebsch Gordan decomposition:

$$\begin{aligned}
&(L_z + 2\,S_z)\left|\frac{3}{2},\ \frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\,|0\rangle\left|\tfrac{1}{2}\right\rangle; && (L_z + 2\,S_z)\left|\frac{1}{2},\ \frac{1}{2}\right\rangle = -\sqrt{\frac{1}{3}}\,|0\rangle\left|\tfrac{1}{2}\right\rangle;\\
&(L_z + 2\,S_z)\left|\frac{3}{2},\ -\frac{1}{2}\right\rangle = -\sqrt{\frac{2}{3}}\,|0\rangle\left|-\tfrac{1}{2}\right\rangle; && (L_z + 2\,S_z)\left|\frac{1}{2},\ -\frac{1}{2}\right\rangle = -\sqrt{\frac{1}{3}}\,|0\rangle\left|-\tfrac{1}{2}\right\rangle;
\end{aligned}$$

By making the scalar products with kets (5) one has that $J_z$= ± 1/2 blocks do not mix, in agreement with conservation of $J_z$, and the Hamiltonian decompose in two blocks 2×2

$$H_{1/2} = E_{1/2} + \begin{pmatrix} \Delta + \frac{2}{3}\Omega & -\frac{\sqrt{2}}{3}\Omega \\ -\frac{\sqrt{2}}{3}\Omega & \frac{1}{3}\Omega \end{pmatrix}; \quad H_{-1/2} = E_{1/2} + \begin{pmatrix} \Delta - \frac{2}{3}\Omega & -\frac{\sqrt{2}}{3}\Omega \\ -\frac{\sqrt{2}}{3}\Omega & -\frac{1}{3}\Omega \end{pmatrix}. \tag{2.7}$$

The two entries correspond to states with J = 3/2, 1/2 respectively. We used $\Delta = E_{3/2} - E_{1/2}$ for the fine structure splitting.

Introducing the dimensionless parameter x = Ω/Δ the eigenvalues are

$$\begin{aligned} J_z = \frac{1}{2}: \quad & \Delta \cdot \left\{ \begin{array}{l} \frac{1}{6}\left(3 + 3x - \sqrt{9 + 6x + 9x^2}\right) \to \begin{cases} \frac{1}{3}\Omega & \text{as } B \to 0 \\ \frac{1}{3}\Delta & \text{as } B \to \infty \end{cases} \\ \frac{1}{6}\left(3 + 3x + \sqrt{9 - 6x + 9x^2}\right) \to \begin{cases} \Delta + \frac{2}{3}\Omega & \text{as } B \to 0 \\ \Omega & \text{as } B \to \infty \end{cases} \end{array} \right. \\ J_z = -\frac{1}{2}: \quad & \Delta \cdot \left\{ \begin{array}{l} \frac{1}{6}\left(3 - 3x - \sqrt{9 - 6x + 9x^2}\right) \to \begin{cases} -\frac{1}{3}\Omega & \text{as } B \to 0 \\ -\Omega & \text{as } B \to \infty \end{cases} \\ \frac{1}{6}\left(3 - 3x - \sqrt{9 - 6x + 9x^2}\right) \to \begin{cases} \Delta - \frac{2}{3}\Omega & \text{as } B \to 0 \\ \frac{1}{3}\Delta & \text{as } B \to \infty \end{cases} \end{array} \right. \end{aligned} \tag{2.8}$$

From eq (8) one sees that for B→ 0 one recovers the usual small field Zeeman effect.

The splitting 1 and 5 in the preceding equation give ± Ω/3. For states with $J_z = \pm 1/2$ this correspond to the Landé factor for the state J=1/2.

The splitting 3, 7 in (8) give Δ ± 2Ω/3 which, for states with $J_z = \pm 1/2$, corresponds to a Landé factor 4/3, i.e. to a J=3/2 term. These level are the partners of states (6) in the Zeeman splitting of the level J=3/2.

In the large field limit (or Δ → 0 ), from (8) we get the shifts ±2/3 Ω, 0 (double deg.). From (6) the shifts ± 2Ω. These six levels correspond to eigenstates of $J_z$, without LS interaction. This is called the Paschen-Back limit.

### ▫ Level crossing and Lamb shift

As it is apparent form the B→0 limit in (8) the eigenvalues 1 and 3 are those corresponding to the $2p_{1/2}$states in absence of B field. The first of this eigenvalues grows with B. For small x

$$\lambda_1 \simeq \Delta\left(\frac{x}{3} - \frac{2}{9}x^2\right) \simeq \frac{\Omega}{3}; \quad \lambda_3 \simeq \Delta\left(-\frac{x}{3} - \frac{2}{9}x^2\right) \simeq -\frac{\Omega}{3}.$$

These values are in agreement with Landè factors.

We know that in Hydrogen the 2s level is slightly higher than the 2p level, the splitting is named *Lamb shift*, and it is due to radiative corrections. In presence of a magnetic field the $J_z = -1/2$ component of the 2s level has a decreasing energy, while the $J_z = +1/2$ component of the $2p_{1/2}$ level grows: for a certain field there will be a crossing.

We know that the two opposite parity levels 2s, 2p mix in presence of an electric field (Lo Surdo-Stark effect), the amount of mixing being maximal for degenerate states. This means that by tuning the magnetic field one can control the mixing and, for instance, control the decay of the metastable 2s state via mixing with the 2p. This in fact is the principle on which the Lamb experiment has been projected.

To be quantitative the energies we have to compare are

$$E_{2s} - \Omega; \quad E_{1/2} + \Delta \frac{1}{6}\left(3 + 3x - \sqrt{9 + 6x + 9x^2}\right).$$

With $F = E_{2s} - E_{1/2}$for the Lamb shift we have crossing for

$$F = \Omega + \Delta \frac{1}{6}\left(3 + 3x - \sqrt{9 + 6x + 9x^2}\right).$$

Experimentally

$$\frac{F}{\hbar} \simeq 1058\,\text{MHz}; \quad \frac{\Delta}{\hbar} \simeq 10\,969\,\text{MHz}; \quad \Omega \simeq 1.3996\,B\,(\text{gauss})\,\text{MHz}.$$

We have crossing for B ~ 600 gauss.

The discussion has not taken into account the hyperfine structure, which actually cannot be neglected.

## Problem 3

*Let us consider a fine structure doublet, S=1/2 and L > 0. Study the effect of a magnetic field on the system.*

### Solution

This problem is a generalization of the previous one for generic L.

The effective Hamiltonian for LS coupling and an external magnetic field along z is

$$V = \Omega\,(L_z + 2\,S_z) + A\,\mathbf{L}\cdot\mathbf{S} = \Omega\,(L_z + 2\,S_z) + A\left(L_z\,S_z + \frac{1}{2}\,(L_+\,S_- + L_-\,S_+)\right). \qquad (3.1)$$

With $\Omega = \hbar\,\omega_L$, $\omega_L$= e B/2mc = Larmor frequency.

$J_z$ is conserved even in presence of a magnetic field. We call M the eigenvalue of $L_z$ and $M_J$ the eigenvalue of $J_z$.

The multiplicity of the level is (2L+1) 2.

States with $M_J$= ± (L+1/2) are isolated eigenstates of V with eigenvalues

$$\Omega\left(L + 2\times\frac{1}{2}\right) + \frac{A}{2}\,L\,; \quad -\Omega\left(L + 2\times\frac{1}{2}\right) + \frac{A}{2}\,L\,. \qquad (3.2)$$

There are 2L more couples of states with M<L for a fixed $M_J$. A basis for the subspace at fixed $M_J$ is

$$|\,M\rangle\,\left|\,\frac{1}{2}\right\rangle \equiv \left|\,M_J - \frac{1}{2}\right\rangle\,\left|\,\frac{1}{2}\right\rangle\,; \quad \left|\,M+1\,\right\rangle\,\left|\,\frac{1}{2}\right\rangle \equiv \left|\,M_J + \frac{1}{2}\right\rangle\,\left|\,-\frac{1}{2}\right\rangle\,. \qquad (3.3)$$

Hamiltonian matrix elements can be written by using

$$\langle M+1\,|\,L_+\,|\,M\rangle = \sqrt{(L+M+1)\,(L-M)}\,.$$

A similar formula works for the adjoint operator $L_-$. One obtains in the basis (3)

$$\begin{pmatrix} A\,\frac{M}{2} + \Omega\,(M+1) & \frac{A}{2}\,\sqrt{(L+M+1)\,(L-M)} \\ \frac{A}{2}\,\sqrt{(L+M+1)\,(L-M)} & -A\,\frac{M+1}{2} + \Omega\,M \end{pmatrix} \qquad (3.4)$$

with eigenvalues

$$\begin{aligned} \lambda_1 &= -\frac{A}{4} + \frac{\Omega}{2}\,(2\,M+1) - \frac{1}{2}\,\sqrt{\Omega^2 + A^2\left(L + \frac{1}{2}\right)^2 + A\,\Omega\,(2\,M+1)}\,; \\ \lambda_2 &= -\frac{A}{4} + \frac{\Omega}{2}\,(2\,M+1) + \frac{1}{2}\,\sqrt{\Omega^2 + A^2\left(L + \frac{1}{2}\right)^2 + A\,\Omega\,(2\,M+1)}\,. \end{aligned} \qquad (3.5)$$

The reader can verify that for L = 1 these eigenvalues reproduce those found for the 2p level of the Hydrogen atom.

We can write the eigenvalues as a function of $M_J$ by using M = $M_J$-1/2: as M changes $M_J$takes all the values except $|\,M_J\,|$= L+1/2. The result (5) takes the form

$$\begin{aligned} \lambda_1 &= -\frac{A}{4} + \Omega\,M_J - \frac{1}{2}\,\sqrt{\Omega^2 + A^2\left(L + \frac{1}{2}\right)^2 + 2\,A\,\Omega\,M_J}\,; \\ \lambda_2 &= -\frac{A}{4} + \Omega\,M_J + \frac{1}{2}\,\sqrt{\Omega^2 + A^2\left(L + \frac{1}{2}\right)^2 + 2\,A\,\Omega\,M_J}\,. \end{aligned} \qquad (3.6)$$

## Problem 4

*Parametrize the effect of spin-spin and spin-orbit interactions in Russell-Saunders coupling approximation.*

## Solution

The relativistic corrections for spin orbit and spin spin interactions have the form

$$U_{so} = \sum_a \frac{Z e^2}{2 m^2 c^2 r_a^3} \mathbf{L}_a \cdot \mathbf{s}_a ; \tag{4.1}$$

$$U_{soo} = \sum_{a<b} \frac{e^2}{2 m^2 c^2 r_{ab}^3} \left(-(\mathbf{s}_a + 2\,\mathbf{s}_b) \cdot \left(\mathbf{r}_{ab} \wedge \mathbf{p}_a\right) + (\mathbf{s}_b + 2\,\mathbf{s}_a) \cdot \left(\mathbf{r}_{ab} \wedge \mathbf{p}_b\right)\right) \tag{4.2}$$

$$U_{ss} = \sum_{a<b} \frac{e^2}{m^2 c^2 r_{ab}^3} \left(\mathbf{s}_a \cdot s_b - 3\,\frac{(\mathbf{s}_a \cdot \mathbf{r}_{ab})\,(\mathbf{s}_b \cdot \mathbf{r}_{ab})}{r_{ab}^3}\right) \tag{4.3}$$

where $\mathbf{r}_{ab} = \mathbf{r}_b - r_a$ and the indexes a, b run on electrons.

The operators (1) and (2) are products of vectors of orbital variables and vectors in spin variables. The Wigner-Eckart theorem asserts that each of these operators is proportional to **L** or **S** within a multiplet with fixed L and S. In the general case the contribution of (1) and (2) has the form

$$A\,\mathbf{L} \cdot \mathbf{S}\,, \tag{4.4}$$

and gives the known energy spectrum

$$E_J = \frac{A}{2} J\,(J+1) + E_0\,. \tag{4.5}$$

The term (3) is a product of two symmetric tensor operators with vanishing trace. In fact, each term has the form

$$\left(s_{1\,i}\, s_{2\,j} + s_{2\,j}\, s_{1\,i} - \frac{2}{3}\delta_{ij}\,\mathbf{s}_1 \cdot \mathbf{s}_2\right)\left(r_{1\,i}\, r_{2\,j} + r_{2\,j}\, r_{1\,i} - \frac{2}{3}\delta_{ij}\,\mathbf{r}_1 \cdot \mathbf{r}_2\right).$$

Symmetric and traceless tensors of rank two are irreducible tensors of order 2 and to each of them we can apply the Wigner-Eckart theorem, in variable L and S respectively. The the matrix elements of the spin-spin interaction (3) have the form

$$\left(S_i\, S_j + S_j\, S_i - \frac{2}{3}\delta_{ij}\,\mathbf{S}^2\right)\left(L_i\, L_j + L_j\, L_i - \frac{2}{3}\delta_{ij}\,\mathbf{L}^2\right). \tag{4.6}$$

Commutation rule for angular momentum has to be taken into account in expanding the product. As an instance

$$L_i\, L_j\, S_i\, S_j = L_i\, S_i\, L_j\, S_j = (\mathbf{L} \cdot \mathbf{S})^2; \quad L_i\, L_j\, S_j\, S_i = (\mathbf{L} \cdot \mathbf{S})^2 + i\,\varepsilon_{ijk}\, L_k\, S_j\, S_i = (\mathbf{L} \cdot \mathbf{S})^2 + (\mathbf{L} \cdot \mathbf{S})\,.$$

Expanding (6) one obtains

$$(2\,\mathbf{L} \cdot \mathbf{S})^2 + (2\,\mathbf{L} \cdot \mathbf{S}) - \frac{4}{3}\mathbf{L}^2\,\mathbf{S}^2.$$

Using **J** = **L** + **S** this term can be expressed through J. Terms linear in $\mathbf{J}^2$= J(J+1) simply modify the constant A in (4). The additional terms have the J dependence $(J\,(J+1))^2$. The general dependence on J of energy level is then

$$E_J = \frac{A}{2} J\,(J+1) + \frac{B}{4}(J\,(J+1))^2 + C\,. \tag{4.7}$$

The constants A, B, C depend on the term considered, in particular on L and S.

To have an idea of the consistency of the approach we can consider multiplets with at least four terms: from the energies differences one can compute A and B, which must be constant within a multiplet.
With

$$\Delta_J = \frac{E_J - E_{J-1}}{J}$$

one obtains from (7)

$$\Delta_J = A + B\,J^2; \quad B = \frac{\Delta_J - \Delta_{J-1}}{2\,J-1}\,.$$

This is an example of results. Under the row of measured $\Delta_J$ the coefficient A is reported: if the scheme is correct this coefficient must be a constant for each element. Deviations from this feature have to be ascribed to configuration mixing.

```
conf.       El.            <B>        △J        △J-1      △J-2
3d^3 4s^2   V       4F                51.       53.17     54.95
                           -0.284     56.76     56.65     56.73

3d^6 4s^2   Fe      5D                -104.     -96.02    -92.06    -89.94
                           -0.879     -89.92    -88.12    -88.55    -89.06

3d^7 4s^2   Co      4F                -181.3    -168.8    -161.
                           -1.45      -152.3    -151.2    -152.

4d^4 5s     Nb      6D                 78.89    86.65     95.12      102.8
                           -1.433     107.9     104.2     104.1      106.

4d^7 5s     Ru      5F                 -238.    -225.2    -207.2    -196.1
                           -1.433      -186.    -192.     -188.6    -187.8

4f^3 6s^2   Pr      4I                 204.6    226.2     250.3
                           -1.776      304.5    301.2     304.

4f^4 6s^2   Nd      5I                 170.9    187.9     206.4     225.6
                           -1.435      262.7    258.2     258.1     261.5

5d^4 6s^2   W       6D                 318.     441.1     661.5     1013.
                           -46.63      1262.    1012      952.9     1117
```

## Problem 5

*Compute the quadrupole moment for 2p states of Hydrogen atom and show that Q=0 for the 2$p_{1/2}$ state.*

### Solution

#### Definition

The atomic quadrupole operator is defined by

$$Q_{ij} = \sum_a e_a \left(3\, r_{ai}\, r_{aj} - \delta_{ij}\, \mathbf{r}_a^2\right). \tag{5.1}$$

The sum run over electrons. The Wigner-Eckart theorem implies that within an irreducible representation of the angular momentum the matrix elements of the operator (1) are proportional to matrix elements of a rank 2 irreducible tensor built with angular momentum. The proportionality constant is usually defined by

$$\left\langle \psi \middle| Q_{ij} \middle| \psi \right\rangle = \frac{3\, Q_J}{2\, J\, (2\, J - 1)} \left\langle \psi \middle| J_i\, J_j + J_j\, J_i - \frac{2}{3} \mathbf{J}^2\, \delta_{ij} \middle| \psi \right\rangle. \tag{5.2}$$

The constant $Q_J$ coincides with the mean value of $Q_{zz}$ on the state with highest angular momentum projection $J_z = J$, as it is immediate to verify from (2).

A similar formula holds for purely orbital operators with the substitution $J \to L$.

#### Hydrogen

Using these conventions and ignoring for the moment spin variables one can define $Q_L$ on the 2p state of Hydrogen by

$$Q_L = \left\langle 2\, p,\, L_z = +1 \middle| 3\, z^2 - r^2 \middle| 2\, p,\, L_z = +1 \right\rangle. \tag{5.3}$$

The angular dependence in the states is given by the spherical harmonics

$$Y_{1,\pm1}[\theta,\varphi] = \mp\sqrt{\frac{3}{4\pi}}\,\frac{\text{Sin}[\theta]}{\sqrt{2}}\,e^{i\varphi}.$$

Separating the radial integral in (3) one obtains (q = |e| is the absolute value of the electron charge)

$$Q_L = e\left\langle r^2\right\rangle \int d\Omega\,\frac{3}{8\pi}\,\text{Sin}[\theta]^2\left(3\,\text{Cos}[\theta]^2-1\right) = -e\,\frac{2}{5}\left\langle r^2\right\rangle = q\,\frac{2}{5}\left\langle r^2\right\rangle. \tag{5.4}$$

Using the following result for Hydrogen

$$\left\langle r^2\right\rangle_{n,L} = a_B^2\,\frac{n^2}{2}\left(5\,n^2+1-3\,L\,(L+1)\right); \quad a_B = \text{Bohr radius},$$

one gets for the 2p state

$$Q_L = q\,\frac{2}{5}\,30\,a_B^2 = q\,12\,a_B^2. \tag{5.5}$$

Let us consider now $Q_J$.

On the state $2p_{3/2}$ one has

$$\left|\,2p,\frac{3}{2},+\frac{3}{2}\right\rangle = |+1\rangle\left|\frac{1}{2}\right\rangle$$

and it follows, as $Q_{zz}$ depends only on orbital variables that

$$Q_{3/2} = \left\langle 2p,\frac{3}{2},+\frac{3}{2}\right|Q_{zz}\left|2p,\frac{3}{2},+\frac{3}{2}\right\rangle = \left\langle 2p, L_z=+1\right|Q_{zz}\left|2p, L_z=+1\right\rangle = Q_L\;.$$

For the J=1/2 case the highest component of the multiplet is, using the Clebsch-Gordan decomposition,

$$\left|\,2p,\frac{1}{2},+\frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\,|+1\rangle\left|-\frac{1}{2}\right\rangle - \sqrt{\frac{1}{3}}\,|0\rangle\left|+\frac{1}{2}\right\rangle. \tag{5.6}$$

The operator $Q_{zz}$does not depend on spin and it is invariant under rotations around z, then it satisfy the selection rule $\Delta L_z$= 0. The mean value on the state (6) is then

$$Q_{1/2} = e\left\langle r^2\right\rangle\int d\Omega\left(3\,\text{Cos}[\theta]^2-1\right)\left(\frac{2}{3}\,|Y_{1,1}|^2+\frac{1}{3}\,|Y_{10}|^2\right) = 0.$$

The integral is easily done using $Y_{10}=\sqrt{3/4\pi}\,\text{Cos}[\theta]$ . The result is expected as angular momentum composition rule forbid a mean value of quadrupole moment (tensor of rank 2) on a state with angular momentum 1/2; in the decomposition 2⊗1/2 = 3/2 + 5/2 the representation 1/2 do not appear then the scalar product of Q $|\psi\rangle$ with $\langle\psi|$vanishes.

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# Problem 6

*Write the Wigner-Eckart theorem for a vector and a symmetric tensor in subspaces with given orbital momentum L or with given J. Find the relation between the two for a spin independent operator and for an operator depending only on spins.*

## Solution

### General formula

The Wigner-Eckart theorem implies that within an irreducible representation of the angular momentum the matrix elements of an irreducible operator like a vector V or a traceless symmetric tensor T are proportional to the matrix elements of a similar vector or tensor constructed with angular momentum, i.e., in a given representation

$$\langle\alpha\,|\,V_i\,|\,\beta\rangle = g_L\,\langle\alpha\,|\,L_i\,|\,\beta\rangle;\quad \langle\alpha\,|\,T_{ij}\,|\,\beta\rangle = c_L\left\langle\alpha\,\middle|\,L_i\,L_j+L_j\,L_i-\frac{2}{3}\,\delta_{ij}\,\mathbf{L}^2\,\middle|\,\beta\right\rangle. \tag{6.1}$$

The constants depend on the others quantum numbers, usually are given by radial integrals.

If the spin is added to the description then the most general assertion of Wigner - Eckart theorem is

$$\langle\alpha\,|\,V_i\,|\,\beta\rangle = g_J\,\langle\alpha\,|\,J_i\,|\,\beta\rangle;\quad \langle\alpha\,|\,T_{ij}\,|\,\beta\rangle = c_J\left\langle\alpha\,\middle|\,J_i\,J_j+J_j\,J_i-\frac{2}{3}\,\delta_{ij}\,\mathbf{J}^2\,\middle|\,\beta\right\rangle. \tag{6.2}$$

In general, as operators, $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

### Orbital operators

Of particular interest is the case in which the operators act only on orbital variables. We suppose that the system is rotational invariant, then eigenstates of the Hamiltonian admit as good quantum numbers $J$ and $J_z$.

If the orbit spin interaction is small (like in the LS coupling in an atom) the eigenstates of H are constructed by diagonalizing the Hamiltonian within a subspace with L and S fixed. The eigenstates are simply written by the Clebsch-Gordan decomposition

$$|\alpha, J, J_z, L, S\rangle = \sum_{L_z, S_z} |\alpha, L, L_z, S, S_z\rangle \langle L, L_z, S, S_z \mid J, J_z, L, S\rangle . \tag{6.3}$$

For purely orbital operators the spin labels are completely irrelevant then the matrix elements in the L basis is always determined by formulas like (1), this means that it is possible to relate coefficients $g_L, c_L$ to $g_J, c_J$.

We stress this point as can be confusing. In general the angular momentum composition laws imply simply

$$|n, J, J_z\rangle = \sum_{L_z, S_z} \langle L, L_z, S, S_z \mid J, J_z, L, S\rangle \sum_m |m, L, L_z, S, S_z\rangle \tag{6.4}$$

This is a purely group theoretical statement and do not imply any particular simplification. The kets in the rhs of (4) in general are not even energy eigenstate. In particular cases, like the fine structure splitting in an atom, L and S are approximative good quantum numbers and in the rhs of (4) only one term survives, n=m, and in this case, and only in this case, it is meaningful to look for a relation between $g_L$ and $g_J$ etc.

From now on we suppress the indication of states $\alpha, \beta$ and for operators **L, S, J** we will understand their matrices in the given subspace of H.

### Vectors

The representation is $V_i = g_L L_i$, But $L_i$ itself is a vector with respect to $J$, then it must be true that $V_i = g_J J_i$. Multiplication by $J_i$ and summation on the index gives

$$g_L (\mathbf{L} \cdot \mathbf{J}) = g_J (\mathbf{J} \cdot \mathbf{J}) . \tag{6.5}$$

Using the identity

$$2 (\mathbf{L} \cdot \mathbf{J}) = \mathbf{J}^2 + \mathbf{L}^2 - (\mathbf{J} - \mathbf{L})^2 = \mathbf{J}^2 + \mathbf{L}^2 - \mathbf{S}^2;$$

one obtains immediately

$$g_J = g_L \frac{J (J+1) + L (L+1) - S (S+1)}{2 J (J+1)} . \tag{6.6}$$

The reader can easily recognize the procedure used to compute the Landè factor.

Clearly exactly the same procedure works for operators which depend only on spin. With obvious notations if **W** is such a vector operator

$$W_i = g_S S_i; \; W_i = g_J J_i; \;\; g_J = g_S \frac{J (J+1) + S (S+1) - L (L+1)}{2 J (J+1)} \tag{6.7}$$

### Tensors

In this case we mist have, always within an irreducible representation of J

$$\left(L_i L_j + L_j L_i - \frac{2}{3} \delta_{ij} \mathbf{L}^2\right) = d \left(J_i J_j + J_j J_i - \frac{2}{3} \delta_{ij} \mathbf{J}^2\right) . \tag{6.8}$$

Left multiplication by $J_i$ and right multiplication by $J_j$ gives

$$(\mathbf{J} \cdot \mathbf{L})^2 + J_i L_j L_i J_j - \frac{2}{3} \mathbf{L}^2 \mathbf{J}^2 = d \left(\left(\mathbf{J}^2\right)^2 + J_i J_j J_i J_j - \frac{2}{3} \left(\mathbf{J}^2\right)^2\right) . \tag{6.9}$$

Using angular momentum commutation rules it is easy to show

$$J_i J_j J_i J_j = \left(\mathbf{J}^2\right)^2 - \mathbf{J}^2; \quad J_i L_j L_i J_j = (\mathbf{J} \cdot \mathbf{L})^2 - \mathbf{J} \cdot \mathbf{L}. \tag{6.10}$$

By substitution

$$d = \frac{3 (\mathbf{J} \cdot \mathbf{L}) (2 (\mathbf{J} \cdot \mathbf{L}) - 1) - 2 L (L+1) J (J+1)}{J (J+1) (2 J - 1) (2 J + 3)}; \quad c_J = d \, c_L . \tag{6.11}$$

Let us note that, introducing **S = J – L**:

$$\mathbf{J}\cdot\mathbf{L} = \frac{J\,(J+1) + L\,(L+1) - S\,(S+1)}{2}. \tag{6.12}$$

### Special case

Of particular interest is some applications is the tensor built with the direction in space. With **n** = **r**/r let us consider

$$S_{ij} = n_i\, n_j - \frac{1}{3}\,\delta_{ij} \tag{6.13}$$

We used the commutative nature of **n** and that $\mathbf{n}^2 = 1$.

The analogous single particle vector operators have zero matrix elements by parity considerations.

From previous discussion, as a matrix

$$n_i\, n_j - \frac{1}{3}\,\delta_{ij} = c_L \left( L_i\, L_j + L_j\, L_i - \frac{2}{3}\,\delta_{ij}\, \mathbf{L}^2 \right). \tag{6.14}$$

The constant can be easily computed in this case. Let us first note the identity

$$\mathbf{n}\cdot\mathbf{L} = \frac{1}{r}\, x_i\, L_i = \frac{1}{r}\, x_i\, \varepsilon_{ijk}\, x_j\, p_k = 0.$$

This identity together with Wigner - Eckart theorem confirms that $g_L = 0$ for the operator **n** .

With a left and right multiplication by $L_i$and $L_j$ in (14) this identity implies

$$-\mathbf{L}^2 = c_L \left( 3\,\mathbf{L}^2 + 3\, L_i\, L_j\, L_i\, L_j - 2\, \left(\mathbf{L}^2\right)^2 \right).$$

Using the identities (10) with $J \to L$ one obtains

$$c_L = -\frac{1}{(2\,L+3)\,(2\,L-1)}. \tag{6.15}$$

From this relation for a spin 1/2 particle one has

$$c_j = \begin{cases} -\frac{1}{(2\,L+3)\,(2\,L-1)} = -\frac{1}{4}\,\frac{1}{J\,(J+1)}; & J = L + \frac{1}{2} \\ -\frac{1}{(2\,L-1)\,(2\,L+1)} = -\frac{1}{4}\,\frac{1}{J\,(J+1)}; & J = L - \frac{1}{2} \end{cases}. \tag{6.16}$$

## Problem 7

*Sketch the classical theory of magnetism and point out its problems. Define the magnetization for a macroscopic homogenous medium in terms of the microscopic magnetic moment in quantum theory. Give an order of magnitude for the different contributions to the magnetic susceptibility.*

### Solution

### Classical model

In classical statistical physics there is no magnetic effect due to orbital motion of charges, in particular no diamagnetic effect. The coupling to an electromagnetic field is described by the substitution

$$\mathbf{p} \to \mathbf{p} - \frac{e}{c}\,\mathbf{A}. \tag{7.1}$$

For an homogeneous magnetic field we can take

$$\mathbf{A} = \frac{1}{2}\,\mathbf{B} \wedge \mathbf{r}\,. \tag{7.2}$$

The partition function

$$Z = \int d\mathbf{p}\, d\mathbf{q}\, \mathrm{Exp}[-H[p,\, q]\,/\,kT]$$

is invariant for the shift (1) as it can be reabsorbed in a change of variables in the p integration variable.

This is true in classical mechanics because we have a unbounded integral in the phase space, this feature will be absent in quantum theory.

In classical physics the only magnetic effect can be introduced presuming the existence of elementary magnetic dipoles, with magnetic moment $\mu_0$. In this case an interaction

$$H = -\boldsymbol{\mu} \cdot B = -\mu B \operatorname{Cos}[\theta] \tag{7.3}$$

gives rise to a mean magnetic moment along the B axis in the form

$$m = \langle \mu \operatorname{Cos}[\theta] \rangle = \frac{1}{Z} \int d\Omega\, \mu \operatorname{Cos}[\theta] \operatorname{Exp}[\mu B \operatorname{Cos}[\theta] / kT] = \mu \left( \operatorname{Coth}\left[\frac{\mu B}{k T}\right] - \frac{k T}{\mu B} \right). \tag{7.4}$$

For $\mu$B ≪ kT, the usual experimental case,

$$m \sim \frac{1}{3} \mu \frac{\mu B}{k T} \equiv \chi B \tag{7.5}$$

The 1/T dependence is the *Curie law*. The magnetic susceptivity $\chi$ is positive, i.e. only paramagnetism can be described.

## Quantum theory

In quantum statistical mechanics the partition function is defined as

$$Z = \sum_n \operatorname{Exp}[-E_n / k T] \tag{7.6}$$

We will suppose from now on that the system is homogenous and composed of elementary components with negligible interaction (a perfect gas). In this case the partition function for the whole system factorizes and the macroscopic magnetization has the simple expression

$$\mathbf{M} = N \bar{\mathbf{m}}; \qquad \bar{\mathbf{m}} = \sum_n p_n \langle n | \mathbf{m} | n \rangle \tag{7.7}$$

where N is the number of particles in the unit volume, the overlay denotes the statistical average, |n⟩ are energy eigenstates and the probabilities $p_n$ are given by

$$p_n = \frac{1}{Z} \operatorname{Exp}[-E_n / k T]; \quad Z = \sum_n \operatorname{Exp}[-E_n / k T]. \tag{7.8}$$

Let us note that in (8) the index n and the energies $E_n$ refer to states of a single subsystem (atom) and not to the whole macroscopic body, as in (6).

In quantum theory the mean magnetization is defined by (see the Feynman Hellman theorem)

$$\langle n | \mathbf{m} | n \rangle = -\frac{\partial}{\partial \mathbf{B}} E_n[B] \tag{7.9}$$

From (7) , (8) and (9) it is easily shown that

$$\bar{\mathbf{m}} = \sum_n p_n \langle n | \mathbf{m} | n \rangle = kT \frac{\partial}{\partial \mathbf{B}} \operatorname{Log}[Z]. \tag{7.10}$$

### Note

The reader with some knowledge of Statistical Mechanics will recognize in the above formulation the usual definition of magnetization. The magnetization is *defined* by the *isothermal* change of the energy at constant temperature for a small variation of an external magnetic field. The isothermal changes are accounted by variation of the *free energy* of the system, i.e.

$$\delta F = -\mathbf{M}\, \delta \mathbf{B}. \tag{7.11}$$

From usual Thermodynamics

$$Z = \operatorname{Exp}[-F / kT]; \quad F = -kT \operatorname{Log}[Z];$$

and from (11)

$$\mathbf{M} = kT \frac{\partial}{\partial \mathbf{B}} \operatorname{Log}[Z]$$

which coincides with (10) in the factorization limit.

## Quantum average

The magnetic moment has as an order of magnitude the Bohr magneton $\mu_B$. The magnetic energy in then of the order

$$\mu_B B \simeq 6\, 10^{-9} B[\text{gauss}]\ \text{eV}; \quad k T \sim \frac{T[K]}{12\,400} \text{eV}.$$

Up to B ~ 1 Tesla $\left(10^4\right.$gauss ) the magnetic term is small even with respect the fine structure splitting and we can use perturbation theory.

The interaction Hamiltonian, for an atom, is

$$V = -\mu\,\mathbf{B} + \frac{e^2}{8\,m\,c^2}\sum_a (\mathbf{B}\wedge\mathbf{r}_a)^2\,;\quad \mu = \frac{e\,\hbar}{2\,m\,c}\sum_a (\mathbf{L}_a + 2\,\mathbf{S}_a) = -\mu_B\,(\mathbf{L} + 2\,\mathbf{S})\,. \tag{7.12}$$

The sum runs over the electrons. Directing the quantization axis along **B** and using second order perturbation theory one has

$$E_n[B] = E_n - F_n\,B - \frac{1}{2}\,G_n\,B^2; \tag{7.13}$$

where $E_n$ are the unperturbed energies and

$$F_n = \langle n \mid \mu_z \mid n\rangle\,;\quad G_n = 2\sum_n{}' \frac{\mid\langle s \mid \mu_z \mid n\rangle\mid^2}{E_s - E_n} - \frac{e^2}{4\,m\,c^2}\sum_a \left\langle n \,\middle|\, \left(x_a^2 + y_a^2\right) \,\middle|\, n\right\rangle. \tag{7.14}$$

The prime in the sum exclude the subspace s = n,as is known from perturbation theory.

For temperatures not exceedingly small

$$E_n[B] - E_n \sim \mu_B\,B \ll k\,T$$

and we can expand the partition function in powers of B/T :

$$Z \simeq \sum_n e^{-E_0/k\,T}\left(1 + \frac{F_n}{k\,T}\,B + \frac{1}{2}\,B^2\left(\frac{F_n^2}{(k\,T)^2} + \frac{G_n}{k\,T}\right)\right). \tag{7.15}$$

With multiplication and division by the unperturbed partition function $Z_0$

$$Z \simeq \left(1 + \frac{\bar{F}_n}{k\,T}\,B + \frac{1}{2}\,B^2\left(\frac{\overline{F_n^2}}{(k\,T)^2} + \frac{\bar{G}_n}{k\,T}\right)\right) Z_0\,. \tag{7.16}$$

where the bar denotes the statistical average over the initial, *unperturbed*, distribution.

Assuming the unperturbed system invariant under rotations $\bar{F}_n$ = 0. In this case at first order in B, from (10)

$$m = \left(\frac{1}{k\,T}\,\bar{F}_n^2 + \bar{G}_n\right) B \equiv \chi\,B\,. \tag{7.17}$$

$\chi$ is the *magnetic susceptibility*. The Curie law is obeyed by (17). Substances with $\chi$ > 0 are *paramagnetic* materials, while $\chi < 0$ for *diamagnetic* substances.

- **Order of magnitudes**

First of all we note that on the fundamental state the first term in $G_n$is positive. The only diamagnetic contribution comes from the second therm.

Let us give an order of magnitude for the various terms in (17).

1. $F_n^2$/kT ~ $\mu_B^2$/kT
2. The second term in G has order of magnitude

$$G^{(2)} \sim \frac{e^2}{m\,c^2}\,a_B^2 \sim \mu_B^2\,\frac{a_B^2}{e^2} \sim \mu_B^2 \big/ E_0$$

where $E_0$is a typical electronic energy (some eV). This factor is smaller than the first one by $kT / E_0$, a very small quantity, if $F_n$is different from zero.

The first term in $G_n$ requires a special consideration. The magnetic moment act only on angular variables, i.e. do not change the other quantum numbers as principal quantum numbers for Hydrogen-like atoms.

- If the atom *has* a non trivial fine structure the main terms in the sum come from these terms, as the energy denominators are small. The order of magnitude of this contribution is

$$G^{(1)} \sim \frac{\mu_B^2}{\Delta E_{FS}} \sim \frac{\mu_B^2}{\alpha^2\,E_0};$$

  This term is therefore $10^4$ times bigger than the second one in G.
- If the atom *do not have* a fine structure then the energy denominators are of the order $E_0$ *and* the matrix elements of $\mu$ are zero at first order as long as L, S are good quantum numbers ($\mu$ cannot change radial quantum numbers). This means that matrix elements of $\mu$ can be obtained only

through mixing of the base states via LS interaction. The mixing coefficients are of the order $H_{FS} / E_0 \sim \alpha^2$then the contribution of the first term in G in this case is of order

$$G^{(1)} \sim \frac{\mu_B^2}{E_0} \alpha^2$$

negligible with respect to $G^{(2)}$.

In summary : if $F_n \neq 0$ the F term usually dominates and we have a paramagnetic substance. If the ground state has a fine structure splitting in any case we have a paramagnetic substance, while in absence of a fine structure splitting the atom is in general diamagnetic.

## Problem 8

*Compute the magnetic susceptibility for an atom with and without fine structure splitting. Discuss both the limits of low and high temperatures.*

### Solution

#### The results

This problem assumes that the reader is familiar with the content of previous problem. It has been shown that the susceptibility can be written as

$$\chi = \left( \frac{1}{k\,T} \overline{F_n^2} + \bar{G}_n \right); \qquad (8.1)$$

$$F_n = \langle n \mid \mu_z \mid n \rangle ; \quad G_n = 2 \sum_s{}' \frac{\overline{\mid \langle s \mid \mu_z \mid n \rangle \mid^2}}{E_s - E_n} - \frac{e^2}{4\,m\,c^2} \sum_a \langle n \mid (x_a^2 + y_a^2) \mid n \rangle .$$

The overline stands for the statistical average with the unperturbed partition function.

We distinguish different possibilities, assuming always to work with the ground state |0⟩ of an atom.

#### Low temperatures

In this regime only the ground state gives a contribution to $Z_0$. This is true for $k\,T \ll \Delta E$, where ΔE is the energy splitting.

#### L = 0, S = 0

Low temperature in this case means $k\,T \ll E_1 - E_0 \sim$ eV, the separation between ground state and the first excited electronic term. In this case for the F term and the first term in G we have

$$\langle 0 \mid \mu_z \mid 0 \rangle = 0; \qquad G_n^{(1)} \sim \frac{\mu_B^2}{E_0} \alpha^2 \ll G_n^{(2)} \quad (\text{see last point in previous problem})$$

The atom has a diamagnetic structure and

$$\chi \simeq -\frac{e^2}{4\,m\,c^2} \sum_a \langle 0 \mid (x_a^2 + y_a^2) \mid 0 \rangle = -\frac{1}{6} \frac{e^2}{m\,c^2} \sum_a \langle 0 \mid r_a^2 \mid 0 \rangle \qquad (8.2)$$

#### J≠0

In this case if there is no fine structure splitting and the requirement on temperature is satisfied.

If there is fine structure low temperature regime means $k\,T \ll \Delta E_{FS}$.

In both case the ground state has degeneracy 2J+1 and all (unperturbed) states have equal probability. The matrix element of F is the one computed in the study of Zeeman effect:

$$\langle M_J \mid \mu_z \mid M_J \rangle = -g_J\, \mu_B\, M_J ; \qquad g_J = \text{Landè factor.}$$

It follows

$$\overline{F_n^2} = \frac{1}{2\,J+1} \sum_{M_J=-J}^{J} (g_J\, \mu_B\, M_J)^2 = \frac{1}{3} g_J^2\, \mu_B^2\, J\,(J+1) .$$

As we discussed in previous problem this term is the dominant one and we have

$$\chi = \frac{1}{k\,T} \frac{1}{3} g_J^2\, \mu_B^2\, J\,(J+1) . \qquad (8.3)$$

#### J=0, L,S ≠ 0

In this case the F term in the ground state is zero and the main contribution to $\chi$ comes from the second order term (i.e. the first term) in G. The relevant contribution to $\chi$ is

$$\chi \simeq 2\sum_s{}' \frac{\overline{|\langle s|\mu_z|n\rangle|^2}}{E_s-E_n}. \tag{8.4}$$

The system is paramagnetic but do not follow Curie law, as $\chi$ is independent of T, at least in this range of low temperatures (we are neglecting hyperfine structure).

### High temperature

If there is a fine structure splitting the temperature can easily be such that kT $\gg \triangle E_{FS}$, we remember that at room temperature kT~1/40 eV. In this regime all fine structure levels have equal probability. We will discuss in detail this point below.

If we neglect LS interaction the Hamiltonian - $\mu_z$B is completely diagonal in all the subspace with fixed L and S and the contribution to energy is simply

$$\triangle E_n = -\langle n|\mu_z|n\rangle B$$

Inserting this in the partition function one obtain directly

$$\chi = \frac{1}{kT}\overline{|\mu_z|^2}. \tag{8.5}$$

*without* second order contribution like G terms in (1). This point is discussed in the next section.

As all states are degenerate taking the average is equivalent to sum on all states and dividing by the degeneracy, (2L+1)(2S+1). As $\mu_z$is diagonal in the base $L_z$, $S_z$we can write

$$\sum_n |\langle n|\mu_z|n\rangle|^2 = \sum_n \langle n|\mu_z|n\rangle\langle n|\mu_z|n\rangle = \sum_{n,k}\langle n|\mu_z|k\rangle\langle k|\mu_z|n\rangle = \mathrm{Tr}\left[\mu_z^2\right].$$

The trace is invariant under change of base, and it is simpler to compute in the $L_z$, $S_z$ base:

$$\chi = \frac{\mu_B^2}{kT}\overline{\left(L_z^2 + 4S_z^2 + 2L_zS_z + 2S_zL_z\right)}.$$

In this base we have easily

$$\overline{L_z S_z} = 0;\ L_z^2 = \frac{1}{2L+1}\sum_{M_L} M_L^2 = \frac{1}{3}L(L+1);\ \ S_z^2 = \frac{1}{2S+1}\sum_{M_S} M_S^2 = \frac{1}{3}S(S+1);$$

and finally

$$\chi = \frac{\mu_B^2}{kT}\frac{1}{3}\left(L(L+1) + 4S(S+1)\right). \tag{8.6}$$

### Perturbation theory and temperature

The previous solution is based on the effective degeneracy of the fine structure terms if kT$\gg \triangle E_{FS}$. This sounds OK on physical basis but can be a little confusing from the perturbation theory point of view. The G term in $\chi$ has disappeared, but its contribution depends on the ratio $\mu B / \triangle E_{FS}$ in perturbation theory, and this has nothing to do with temperatures. How could it disappear?

Let us write explicitly the G contribution to $\chi$:

$$\chi \simeq 2\sum_s{}' \frac{\overline{|\langle s|\mu_z|n\rangle|^2}}{E_s-E_n}. \tag{8.7}$$

The sum runs on fine structure terms then this contribution seems much bigger than the computed one for kT$\gg \triangle E_{FS}$!

To explain what is going on let us write the exact expression for $\chi$ (neglecting the diamagnetic term in $\chi$ which is irrelevant here)

$$\chi = \frac{1}{Z}\sum_n e^{-E_n/kT}\left(\frac{1}{kT}\langle n|\mu_z|n\rangle^2 + 2\sum_s{}'\frac{|\langle s|\mu_z|n\rangle|^2}{E_s-E_n}\right). \tag{8.8}$$

The zero of the energy is taken as the ground state energy. Here high temperature means $E_n \ll$ kT.

In the denominator at lowest order in 1/T we have simply the degeneracy of the level

$$Z_0 \sim (2L+1)(2S+1).$$

The zeroth order in 1/T in the numerator vanishes,in fact, for equal probability states we have

$$\frac{1}{Z_0} 2 \sum_n {\sum_s}' \frac{1}{E_s - E_n} |\langle s | \mu_z | n\rangle|^2 = \frac{2}{Z_0} \sum_{n \neq s} \frac{|\langle s | \mu_z | n\rangle|^2}{E_s - E_n} = 0$$

as the numerator is even in (s ↔ n) while the denominator is odd. This is way the "big" term (7) is not really there.

At order 1/T the Taylor expansion of (8) is

$$\frac{1}{Z_0} \frac{1}{kT} \sum_n \left( \langle n | \mu_z | n\rangle^2 - 2 \sum_{s \neq n} E_n \frac{|\langle s | \mu_z | n\rangle|^2}{E_s - E_n} \right.$$

Using the antisymmetry in n, s of the denominator the second term can be written as

$$-2 \sum_n \sum_{s \neq n} E_n \frac{|\langle s | \mu_z | n\rangle|^2}{E_s - E_n} = \sum_n \sum_{s \neq n} (E_s - E_n) \frac{|\langle s | \mu_z | n\rangle|^2}{E_s - E_n} = \sum_n \sum_{n \neq s} |\langle s | \mu_z | n\rangle|^2$$

This adds to the first term and reproduces the result (5).

## Problem 9

*Compute the magnetic susceptibility for an atom with S=0 in the ground state, or in general for a single level of fine structure. Neglect diamagnetic contributions.*

### ● Solution

All higher excited states can be neglected and the partition function reads

$$Z = \sum_{M_J} \text{Exp}\left[\frac{1}{kT} (\mu_B g M_J B)\right] \tag{9.1}$$

g is the gyromagnetic factor. The magnetization is

$$m = kT \frac{\partial}{\partial B} \text{Log}[Z]. \tag{9.2}$$

For J = 1/2, the simplest case

$$m = \frac{\mu_B g}{2} \text{Tanh}\left[\frac{\mu_B g B}{kT}\right]. \tag{9.3}$$

The limit

$$m \underset{T\to\infty}{\longrightarrow} \left(\frac{\mu_B g}{2}\right)^2 \frac{1}{kT} B;$$

express the Curie law.

For generic J one can use the identity

$$\sum_{k=-n}^{n} x^k = \frac{x^{n+1/2} - x^{-n-1/2}}{x^{1/2} - x^{-1/2}}$$

to write

$$Z = \text{Sinh}\left[\frac{g \mu_B B}{kT} \left(J + \frac{1}{2}\right)\right] \bigg/ \text{Sinh}\left[\frac{g \mu_B B}{kT} \frac{1}{2}\right];$$

and by taking a derivative with respect to B

$$m = g \mu_B J L_J\left[\frac{g \mu_B B}{kT} J\right]; \tag{9.4}$$

The Langevin functions $L_J$ are given by:

$$L_J[x] = \frac{2J+1}{2J}\mathrm{Coth}\left[\frac{2J+1}{2J}x\right] - \frac{1}{2J}\mathrm{Coth}\left[\frac{x}{2J}\right]. \qquad (9.5)$$

It is interesting how the classical limit is reached. A classical magnetic moment is obtained by J→∞ with $\mu_0 = \mu_B g J$ fixed (this correspond to a finite value of the angular momentum $\hbar$ J). In this limit

$$L_J[x] \to L_\infty[x] = \mathrm{Coth}[x] - \frac{1}{x}$$

and the magnetization tends to the classical result

$$m = \mu_0 \left(\mathrm{Coth}\left[\frac{\mu B}{k T}\right] - \frac{k T}{\mu B}\right).$$