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Problem 1: In the periodic table we see that the Pr atom has an electronic structure given by $4f^3 5d^0 6s^2$.

a) Use Hund rules to obtain S , L , and J for the ground state of the Pr atom. Draw the energy levels in the relevant shells and indicate the electronic placement. Provide your final result using spectroscopic notation: $^{2S+1}L_J$. (Hint: remember that the spectroscopic notation for L is S, P, D, F, G, H, I, J, K, etc.) (5 points)

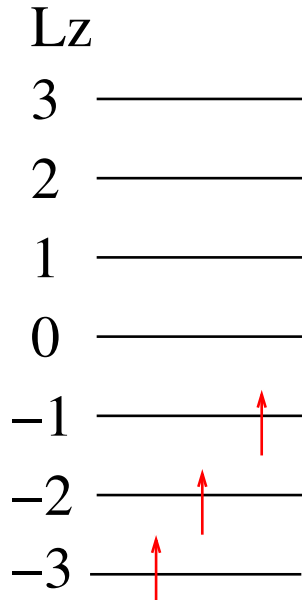


FIG. 1:

Notice that the 6s-shell is filled and the 5d-shell is empty and thus, their electrons do not contribute to the magnetic quantum numbers. Thus, we need to look at the 4f-shell which is less than half-filled (see Fig. 1). We see that the total spin is $S = 3/2$, and $L = 6$, then $J = |L - S| = 9/2$ since the shell is less than half-filled and the spectroscopic notation for the ground state of the atom is: $^4I_{9/2}$.

b) What is the degeneracy of the ground state of Pr? (5 points)

The degeneracy of the ground state is

$$2J + 1 = 9 + 1 = 10. \quad (1)$$

c) Calculate the Landé factor g for the Pr atom. (5 points)

The Landé factor is given by

$$g_{Pr} = \frac{1}{2} \frac{[3J(J+1) - L(L+1) + S(S+1)]}{J(J+1)} = \frac{1}{2} \frac{[\frac{27}{2} \cdot \frac{11}{2} - 42 + \frac{15}{4}]}{\frac{99}{4}} = \frac{2}{99} \left[\frac{3}{4} \cdot 99 + \frac{15}{4} - 42 \right] = \frac{8}{11} = 0.727. \quad (2)$$

d) What is the energy splitting ΔE linear in the magnetic field B for the ground state of a Pr atom placed in a magnetic field B ? Provide the energy of each energy level as a function of B . (5 points)

The energy splitting is given by

$$\Delta E = g\mu_B B = \frac{8}{11}\mu_B B. \quad (3)$$

The degeneracy 10 is now split and each level will have energy

$$E = E_0 + J_z g\mu_B B = E_0 + J_z \frac{8}{11}\mu_B B, \quad (4)$$

where E_0 is the energy of the degenerate level and $J_z = \pm 9/2, \pm 7/2, \pm 5/2, \pm 3/2$, and $\pm 1/2$. Thus, $E_{-9/2} = E_0 - \frac{36}{11}\mu_B B$, $E_{-7/2} = E_0 - \frac{28}{11}\mu_B B$, $E_{-5/2} = E_0 - \frac{20}{11}\mu_B B$, $E_{-3/2} = E_0 - \frac{12}{11}\mu_B B$, $E_{-1/2} = E_0 - \frac{4}{11}\mu_B B$, $E_{1/2} = E_0 + \frac{4}{11}\mu_B B$, $E_{3/2} = E_0 + \frac{12}{11}\mu_B B$, $E_{5/2} = E_0 + \frac{20}{11}\mu_B B$, $E_{7/2} = E_0 + \frac{28}{11}\mu_B B$, and $E_{9/2} = E_0 + \frac{36}{11}\mu_B B$.

e) When the Pr atom is ionized the first electrons being lost are the ones in the 6s shell. Knowing this, provide the electronic structure of the ion Pr^{3+} . (5 points)

The electronic structure of Pr^{3+} is $4f^2 5d^0 6s^0$.

f) Use Hund rules to obtain S, L, and J for the ground state of the Pr^{3+} ion. Draw the energy levels in the relevant shells and indicate the electronic placement. Provide your final result using spectroscopic notation: $^{2S+1}L_J$. (Hint: remember that the spectroscopic notation for L is S, P, D, F, G, H, I, J, K, etc.) (5 points)

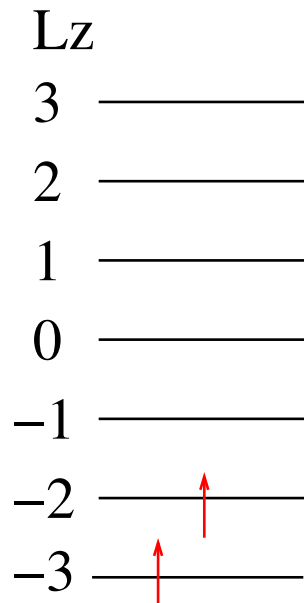


FIG. 2:

Notice that now the 6s-shell and the 5d-shell are empty and thus, their electrons do not contribute to the magnetic quantum numbers. Thus, we need to look at the 4f-shell which is less than half-filled (see Fig. 2). We see that the total spin is $S = 1$, and $L = 5$, then $J = |L - S| = 4$ since the shell is less than half-filled and the spectroscopic notation for the ground state of the atom is: 3H_4 .

g) Calculate the Landé factor g for the Pr^{3+} ion. (5 points)

$$g_{Pr^{3+}} = \frac{1}{2} \frac{[3J(J+1) - L(L+1) + S(S+1)]}{J(J+1)} = \frac{1}{2} \frac{60 - 30 + 2}{20} = \frac{4}{5} = 0.8. \quad (5)$$

h) What is the degeneracy of the ground state of Pr^{3+} ? (5 points)

The degeneracy of the ground state is

$$2J + 1 = 8 + 1 = 9. \quad (6)$$

i) Is the separation between energy levels at a given field B larger in Pr or in Pr^{3+} ? Why? (5 points)

The separation between levels $\Delta E = g\mu_B B$ is proportional to g since $g_{Pr^{3+}} = 0.8 > g_{Pr} = 0.727$ we see that the separation between levels for a fixed magnetic field B will be larger for Pr^{3+} .

j) What is the magnetization \mathbf{M} of a sample of Pr^{3+} that contains N atoms in a volume V ? (5 points)

The magnetization is given by

$$M = n\mu_B g J \mathcal{B}_J(\beta\mu_B g J B) = \frac{N}{V} \mu_B \frac{4}{5} 4 \mathcal{B}_4\left(\frac{16}{5} \beta\mu_B B\right) = \frac{16}{5} \frac{N}{V} \mu_B \mathcal{B}_4\left(\frac{16}{5} \beta\mu_B B\right). \quad (7)$$

Using that

$$\mathcal{B}_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right), \quad (8)$$

we see that

$$\mathcal{B}_4\left(\frac{16}{5} \beta\mu_B B\right) = \frac{9}{8} \coth\left(\frac{18}{5} \beta\mu_B B\right) - \frac{1}{8} \coth\left(\frac{2\beta\mu_B B}{5}\right). \quad (9)$$

Then,

$$M = \frac{N}{V} \frac{2}{5} \mu_B \left[9 \coth\left(\frac{18}{5} \frac{\mu_B B}{kT}\right) - \coth\left(\frac{2}{5} \frac{\mu_B B}{kT}\right) \right]. \quad (10)$$

k) How do you expect the magnetization \mathbf{M} calculated in (j) to evolve from $kT \gg \mu_B B$ to $kT \ll \mu_B B$? Why? (5 points)

I expect at high T , i.e. x very small the magnetization will be zero because the spins will be disordered due to the thermal fluctuations; as the temperature starts to decrease, and x increases, the magnetization will increase linearly with x , Curie's law, and when the temperature becomes very small compared with B , i.e., when x is very large, the magnetization will reach its maximum possible value that corresponds to full polarization of the spins since the magnetic energy now prevails over the thermal energy.

l) Now provide the actual value of the magnetization \mathbf{M} calculated in (j) when $kT \gg \mu_B B$ and when $kT \ll \mu_B B$ and confirm your answer to point (k). (5 points)

For $kT \gg \mu_B B$ we see that x is small and we can use the expansion of $\coth(x)$ in Eq. 10. Then,

$$\lim_{x \rightarrow 0} M = \frac{N}{V} \frac{64}{15} \frac{\mu_B^2 B}{kT}, \quad (11)$$

which vanishes when $x = 0$ and satisfies Curie's law. For $kT \ll \mu_B B$ we see that x is large and we can replace $\coth(x) = \frac{\cosh(x)}{\sinh(x)} \approx \frac{e^x}{e^x} \approx 1$ in Eq. 10. Then,

$$\lim_{x \rightarrow \infty} M = \frac{N}{V} \frac{16}{15} \mu_B, \quad (12)$$

which is the maximum value that the magnetization can have.

Problem 2: A one-dimensional solid made of N atoms with one atom at each point of the Bravais lattice with lattice constant a has a phonon density of states given by

$$D_D(\omega) = \frac{1}{\pi c} \Theta(\omega - \omega_D), \quad (13)$$

in the Debye approximation, with c the speed of sound, $\omega_D = \pi c n$ is the Debye frequency, $n = N/L$ is the atomic density ($L = Na$), and Θ is the Heaviside function.

a) Explain Debye's approximation and why it is important. What progress in our understanding of the heat capacity did it allow? (5 points)

Debye's approximation is important because it provided a model for the density of states of phonon modes according to the low frequency dispersion of the acoustic modes and introducing a cut-off frequency ω_D that is normalized by the total number of modes. The model captures the power law dependence of C with T as $T \rightarrow 0$ and reaches the appropriate classical limit $C = Nk$ at high T .

b) Write an expression for the heat capacity C of the one dimensional material in the Debye's approximation. (5 points)

Using the expression provided for 3D we convert it to 1D:

$$C_L = L \int_0^{\omega_D} d\omega D(\omega) \frac{\partial}{\partial T} \frac{\hbar\omega}{(e^{\beta\hbar\omega} - 1)}. \quad (14)$$

Now we use the Debye approximation for the density of states and we perform the derivative with respect to T remembering that $\beta = 1/(kT)$:

$$C_L = \frac{L}{\pi c} \int_0^{\omega_D} d\omega \frac{(\hbar\omega)^2 e^{\beta\hbar\omega}}{kT^2 (e^{\beta\hbar\omega} - 1)^2} = \frac{L\hbar^2}{kT^2 \pi c} \int_0^{\omega_D} d\omega \frac{\omega^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}. \quad (15)$$

c) What should be the heat capacity of the 1D material at very high temperature? Why? (5 points)

At very high temperature $C = Nk$ according to Dulong and Petit law. We know that $E = NkT$ due to the theorem of equipartition of energy and C is given by the derivative of E with respect to T .

d) Now provide an expression for C when $T \rightarrow \infty$ and verify your answer to part (c). (5 points)

In this case we can use $e^x = 1 + x + \dots$. Then

$$\lim_{T \rightarrow \infty} C_L = \frac{L\hbar^2}{kT^2 \pi c} \int_0^{\omega_D} d\omega \frac{\omega^2}{(\beta\hbar\omega)^2} = \frac{k^2 T^2 L}{kT^2 \pi c} \int_0^{\omega_D} d\omega = \frac{kL}{\pi c} \omega_D = \frac{kL}{\pi c} \pi c \frac{N}{L} = Nk. \quad (16)$$

e) How do you expect the heat capacity to evolve as a function of the temperature from $T = 0$ to $T \rightarrow \infty$? Why? (5 points)

At low temperature I expect the heat capacity to increase from zero following a power law and reach the value Nk at very high temperature.

f) Now provide an expression for C when $T \rightarrow 0$ and verify your answer to part (e). Hint: you can express your results in terms of an integral that does not depend on the temperature. (5 points)

We will define $x = \beta\hbar\omega$, then $dx = \beta\hbar d\omega$, and $x_D = \beta\hbar\omega_D = \frac{\hbar\omega_D}{kT}$. Then we obtain

$$C_L = \frac{Lk^2 T}{\hbar\pi c} \int_0^{x_D} dx \frac{x^2 e^x}{(e^x - 1)^2}. \quad (17)$$

When $T \rightarrow 0$ we see that $x_D \rightarrow \infty$ then we obtain

$$C_L = \frac{Lk^2 T}{\hbar\pi c} \int_0^{\infty} dx \frac{x^2 e^x}{(e^x - 1)^2}. \quad (18)$$

Since the definite integral is now a number independent of T we see that C goes to 0 linearly in T , which is the expected power law behavior.

Useful information:

$$\mathcal{B}_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2L}x\right) - \frac{1}{2J} \coth\left(\frac{c}{2J}\right). \quad (19)$$

$$\coth(x) \approx \frac{1}{x} + \frac{x}{3} + \dots \quad (20)$$

Heat capacity in 3D:

$$C_V = V \int_0^\infty d\omega D(\omega) \frac{\partial}{\partial T} \frac{\hbar\omega}{(e^{\beta\hbar\omega} - 1)}. \quad (21)$$