

Phys 438/538 Atomic, Molecular and Optical Physics

First Midterm Examination

8 March 2016

Duration: 110 Minutes, Closed notes/books

1) (25 points) Radial expectations via Hellmann-Feynman theorem

For radial expectations values, a short-cut alternative is to make use of the Hellmann-Feynman theorem, which states that if the Hamiltonian depends on a continuous parameter λ , then

$$\langle \gamma, \lambda | \frac{\partial H(\lambda)}{\partial \lambda} | \gamma, \lambda \rangle = \frac{\partial E_\gamma(\lambda)}{\partial \lambda},$$

where γ designates a group of quantum labels, and $E_\gamma(\lambda)$ satisfies the eigenvalue equation $H(\lambda)|\gamma, \lambda\rangle = E_\gamma(\lambda)|\gamma, \lambda\rangle$. You will apply it to the one-electron H-like ion radial Hamiltonian

$$H_r = -\frac{\hbar^2}{2\mu} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r},$$

having $E_{k\ell}(\lambda) = -\frac{1}{2(k+\ell+1)^2} \frac{Z^2\mu e^4}{(4\pi\epsilon_0\hbar)^2}$, where μ is the reduced mass of the ion, and $n = k + \ell + 1$ is the well-known principal quantum number. Using Hellmann-Feynman theorem, find out the radial expectations $\langle \frac{1}{r} \rangle_{n\ell}$ and $\langle \frac{1}{r^2} \rangle_{n\ell}$. Express your results in terms of Bohr radius, $a_B = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e}$ to clearly show its dimensional correctness.

2) (30 points) Spin-orbit Interaction

In the one-electron case, the spin-orbit interaction term is given as

$$H_{SO} = \frac{1}{2m_e^2 c^2} \frac{Ze^2}{4\pi\epsilon_0 r^3} (\vec{\ell} \cdot \vec{s}).$$

Considering sodium atom with atomic number 11, determine the energy of the splitting due to spin-orbit interaction for the case when the valence electron is *excited* to $5p$ level: Treat it as a hydrogen-like ion and put your final result in the form

$$\Delta E_{SO}(5p) = A \frac{1}{4\pi\epsilon_0} \frac{e^2 \hbar^2}{m_e^2 c^2 a_B^3},$$

and give the numerical value of the coefficient A . Note that $\langle \frac{1}{r^3} \rangle_{n\ell} = \frac{Z^3}{a_B^3 n^3 (\ell+1)(\ell+1/2)\ell}$, which can actually be calculated following the recipe in question 1 (but for the interest of time, use directly this result).

3) (20 points) Angular momentum coupling and Hund's Rules

(a) Scandium has a valence $3d^1$ electron. For the following microstates in orbital and spin angular momentum basis $|m_l = 0, m_s = -1/2\rangle$, $|m_l = 1, m_s = -1/2\rangle$, what are the underlying $|J, m_J\rangle$ microstates states in total angular momentum basis, and their relative probabilities in each case?

(b) Find the ground state spectroscopic term symbols for $\text{Sm}^{15+} [\text{Xe}] 4f$, and $\text{Ir}^{17+} [\text{Xe}] 4f^{13} 5s$.

4) (25 points) Zeeman Splitting

For the ground states of $\text{Pr}^{3+} [\text{Xe}] 4f^2$, and $\text{Eu}^{3+} [\text{Xe}] 4f^6$ work out the and sketch the shifts of all magnetic sublevels as a function of external magnetic field, B . Note that for both cases LS coupling holds, and Landé g -factor, $g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$.

43. CLEBSCH-GORDAN COEFFICIENTS, SPHERICAL HARMONICS, AND d FUNCTIONS

Note: A square-root sign is to be understood over every coefficient, e.g., for $-8/15$ read $-\sqrt{8/15}$.

Notation:

J	J	...
M	M	...
m_1	m_2	
m_1	m_2	Coefficients
\vdots	\vdots	
\vdots	\vdots	

$1/2 \times 1/2$

1		
+1/2	1/2	0
-1/2	1/2	0
-1/2	-1/2	1

$1 \times 1/2$

3/2	1/2	
+1	+1/2	1
+1	-1/2	1/3
0	+1/2	2/3
0	-1/2	1/3
-1	+1/2	2/3
-1	-1/2	1/3

2×1

3	2	
+2	+1	1
+2	0	1/3
+1	+1	2/3
+1	0	1/3
0	+1	2/3
0	0	1
-1	+1	2/3
-1	0	1/3
-2	+1	2/3
-2	0	1/3

1×1

2	1	
+1	+1	1
+1	0	1/2
0	+1	1/2
0	0	1
-1	+1	1/2
-1	0	1/2
-2	+1	1/2
-2	0	1/2

$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$

$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$

$Y_2^0 = \sqrt{\frac{5}{4\pi}} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)$

$Y_2^1 = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$

$Y_2^2 = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{2i\phi}$

$Y_\ell^{-m} = (-1)^m Y_\ell^{m*}$

$d_{m,0}^\ell = \sqrt{\frac{4\pi}{2\ell+1}} Y_\ell^m e^{-im\phi}$

$2 \times 1/2$

5/2	3/2	
+2	+1/2	1
+2	-1/2	1/5
+1	+1/2	4/5
+1	-1/2	2/5
0	+1/2	3/5
0	-1/2	1/5
-1	+1/2	4/5
-1	-1/2	2/5
-2	+1/2	1/5
-2	-1/2	4/5

$3/2 \times 1/2$

2	1	
+3/2	+1/2	1
+3/2	-1/2	1/4
+1/2	+1/2	3/4
+1/2	-1/2	1/4
0	+1/2	3/4
0	-1/2	1/4
-1	+1/2	3/4
-1	-1/2	1/4
-2	+1/2	1/4
-2	-1/2	3/4

$3/2 \times 1$

5/2	3/2	1/2
+3/2	+1	1
+3/2	0	2/5
+1/2	+1	3/5
+1/2	0	1/5
0	+1	3/5
0	0	1
-1	+1	3/5
-1	0	1/5
-2	+1	3/5
-2	0	1/5

$3/2 \times 3/2$

3	2	1
+3/2	+3/2	1
+3/2	+1/2	1/2
+1/2	+3/2	1/2
+1/2	+1/2	3/10
0	+3/2	1/5
0	+1/2	2/5
-1	+3/2	1/5
-1	+1/2	2/5
-2	+3/2	1/5
-2	+1/2	2/5

$\langle j_1 j_2 m_1 m_2 | j_1 j_2 JM \rangle$
 $= (-1)^{J-j_1-j_2} \langle j_2 j_1 m_2 m_1 | j_2 j_1 JM \rangle$

$d_{m',m}^j = (-1)^{m-m'} d_{m,m'}^j = d_{-m,-m'}^j$

$2 \times 3/2$

7/2	5/2	
+2	+3/2	1
+2	+1/2	3/7
+1	+3/2	4/7
+1	+1/2	2/7
0	+3/2	1/7
0	+1/2	6/35
-1	+3/2	4/7
-1	+1/2	2/7
-2	+3/2	3/7
-2	+1/2	6/35

2×2

4	3	
+2	+2	1
+2	+1	1/2
+1	+2	1/2
+1	+1	3/4
0	+2	1/2
0	+1	3/4
-1	+2	1/2
-1	+1	3/4
-2	+2	1/2
-2	+1	3/4

$d_{1,0}^1 = \cos \theta$

$d_{1/2,1/2}^{1/2} = \cos \frac{\theta}{2}$

$d_{1/2,-1/2}^{1/2} = -\sin \frac{\theta}{2}$

$d_{1,1}^1 = \frac{1 + \cos \theta}{2}$

$d_{1,0}^1 = -\frac{\sin \theta}{\sqrt{2}}$

$d_{1,-1}^1 = \frac{1 - \cos \theta}{2}$

$d_{3/2,3/2}^{3/2} = \frac{1 + \cos \theta}{2} \cos \frac{\theta}{2}$

$d_{3/2,1/2}^{3/2} = -\sqrt{3} \frac{1 + \cos \theta}{2} \sin \frac{\theta}{2}$

$d_{3/2,-1/2}^{3/2} = \sqrt{3} \frac{1 - \cos \theta}{2} \cos \frac{\theta}{2}$

$d_{3/2,-3/2}^{3/2} = -\frac{1 - \cos \theta}{2} \sin \frac{\theta}{2}$

$d_{1/2,1/2}^{3/2} = \frac{3 \cos \theta - 1}{2} \cos \frac{\theta}{2}$

$d_{1/2,-1/2}^{3/2} = -\frac{3 \cos \theta + 1}{2} \sin \frac{\theta}{2}$

$d_{2,2}^2 = \left(\frac{1 + \cos \theta}{2} \right)^2$

$d_{2,1}^2 = -\frac{1 + \cos \theta}{2} \sin \theta$

$d_{2,0}^2 = \frac{\sqrt{6}}{4} \sin^2 \theta$

$d_{2,-1}^2 = -\frac{1 - \cos \theta}{2} \sin \theta$

$d_{2,-2}^2 = \left(\frac{1 - \cos \theta}{2} \right)^2$

$d_{1,1}^2 = \frac{1 + \cos \theta}{2} (2 \cos \theta - 1)$

$d_{1,0}^2 = -\sqrt{\frac{3}{2}} \sin \theta \cos \theta$

$d_{1,-1}^2 = \frac{1 - \cos \theta}{2} (2 \cos \theta + 1)$

$d_{0,0}^2 = \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)$

Figure 43.1: The sign convention is that of Wigner (Group Theory, Academic Press, New York, 1959), also used by Condon and Shortley (The Theory of Atomic Spectra, Cambridge Univ. Press, New York, 1953), Rose (Elementary Theory of Angular Momentum, Wiley, New York, 1957), and Cohen (Tables of the Clebsch-Gordan Coefficients, North American Rockwell Science Center, Thousand Oaks, Calif., 1974).

Hellmann-Feynman Theorem

When a parameter λ of the Hamiltonian is (or promoted to being) a continuous variable, then for $H(\lambda)|r, \lambda\rangle = E_r(\lambda)|r, \lambda\rangle$

we have

$$\langle r, \lambda | \frac{\partial H(\lambda)}{\partial \lambda} | r, \lambda \rangle = \frac{\partial E_r(\lambda)}{\partial \lambda}$$

Proof: Based on the normalization of eigenkets: $\langle r, \lambda | r, \lambda \rangle = 1$

So, if we differentiate $\langle r, \lambda | H(\lambda) | r, \lambda \rangle = E_r(\lambda)$ wrt λ

$$\left(\frac{\partial}{\partial \lambda} \langle r, \lambda | \right) \underbrace{H(\lambda) | r, \lambda \rangle}_{E_r(\lambda) | r, \lambda \rangle} + \langle r, \lambda | \underbrace{H(\lambda)}_{E_r(\lambda)} \left(\frac{\partial}{\partial \lambda} | r, \lambda \rangle \right) +$$

$$\hookrightarrow \langle r, \lambda | \frac{\partial H(\lambda)}{\partial \lambda} | r, \lambda \rangle = \frac{\partial E_r(\lambda)}{\partial \lambda}$$

$$\therefore E_r(\lambda) \frac{\partial}{\partial \lambda} \left(\underbrace{\langle r, \lambda | r, \lambda \rangle}_{1 \text{ (indep. of } \lambda)}} \right) + \langle r, \lambda | \frac{\partial H(\lambda)}{\partial \lambda} | r, \lambda \rangle = \frac{\partial E_r(\lambda)}{\partial \lambda}$$

$$\underbrace{\hspace{10em}}_0$$

QED

The Hellmann-Feynman theorem, when applicable greatly simplifies the radial expectations, turning the labor to simple derivatives!

The radial part of the H-like ion is given by

$$H_r = -\frac{\hbar^2}{2\mu} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r}$$

with the corresponding eigenvalue $E_{kl}(\lambda) = -\frac{1}{2(k+l+1)^2} \frac{Z^2 \mu e^4}{(4\pi\epsilon_0 \hbar)^2}$

where $k \in \mathbb{Z}$ that determines when the series obtained in the solution of the radial eqn. terminates (see D.J. Griffiths IQM), and $n = k+l+1$ is the well-known principal quantum number

□

* For $\langle \frac{1}{r} \rangle_{nl}$, we can promote Z to a 'fake' continuous var.

$\Rightarrow \lambda = Z$ so that $-\frac{4\pi\epsilon_0}{e^2} \frac{\partial}{\partial Z} H_r(Z) = \frac{1}{r}$

So, we only need to work out the derivative $-\frac{4\pi\epsilon_0}{e^2} \frac{\partial}{\partial Z} E_{kl}(Z)$

$$\frac{4\pi\epsilon_0}{e^2} \frac{1}{2 \underbrace{(k+l+1)}_n^2} \frac{2Z\mu e^4}{(4\pi\epsilon_0\hbar)^2} = \frac{Z}{n^2} \underbrace{\frac{e^2 m_e}{4\pi\epsilon_0\hbar^2}}_{\frac{1}{a_B}} \frac{\mu}{m_e}$$

$\therefore \langle \frac{1}{r} \rangle_{nl} = \frac{Z}{a_B n^2} \cdot \frac{\mu}{m_e}$

* For $\langle \frac{1}{r^2} \rangle_{nl}$ choose $l \rightarrow \lambda$ the "fake" cont. var.

$\Rightarrow \langle \frac{1}{r^2} \rangle_{nl} = \left\langle -\frac{2\mu}{\hbar^2(2l+1)} \frac{\partial H_r}{\partial l} \right\rangle_{nl} \stackrel{H-F}{=} -\frac{2\mu}{\hbar^2(2l+1)} \frac{\partial}{\partial l} E_{kl}(l)$

$$= \frac{2\mu}{\hbar^2(2l+1)} \frac{1}{2} \cdot \frac{Z^2 \mu e^4}{(4\pi\epsilon_0\hbar)^2} \cdot -2 \cdot (k+l+1)^{-3}$$

$$= \frac{Z^2 \mu e^4}{(4\pi\epsilon_0\hbar^2)^2} \frac{1}{(l+\frac{1}{2})n^3} = \left(\frac{Z\mu}{m_e}\right)^2 \frac{1}{n^3(l+\frac{1}{2})a_B^2}$$

2]

$$H_{so} = \frac{1}{2m_e^2 c^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r^2} \right) \vec{l} \cdot \vec{s}$$

p shell: $l=1$ $s=1/2$ $\frac{1}{r} \frac{dU}{dr}$ term we had in the notes

Using $\vec{j} = \vec{l} + \vec{s}$, $\vec{j} \cdot \vec{j} = j^2 = l^2 + s^2 + 2\vec{l} \cdot \vec{s}$

$$j_1 = \frac{l+s}{3/2} \quad j_2 = \frac{l-s}{1/2} \quad \Rightarrow \vec{l} \cdot \vec{s} = \frac{1}{2} (j^2 - l^2 - s^2)$$

Since $\langle j^2 \rangle = \hbar^2 j(j+1)$, so we can work out the energy splitting due to SOI bet. $j_1 = 3/2$ and $j_2 = 1/2$ states

$$\Delta E_{so} = \frac{Ze^2}{8\pi\epsilon_0 m_e^2 c^2} \frac{\hbar^2}{2} \left[j_1(j_1+1) - j_2(j_2+1) \right] \left\langle \frac{1}{r^3} \right\rangle$$

$\frac{Z^3}{a_B^3 n^3 l(l+\frac{1}{2})(l+1)}$ given in problem

Putting together

$$\Delta E_{soI} = A \frac{1}{4\pi\epsilon_0} \frac{e^2 \hbar^2}{m_e^2 c^2 a_B^3} \quad \text{where} \quad A = \frac{Z^4 [j_1(j_1+1) - j_2(j_2+1)]}{4 n^3 l(l+\frac{1}{2})(l+1)}$$

Sodium 5p

For $Z=11, l=1, n=5$

$$A = 29.28$$

From C-G table for d-shell single e: $l=2, s=1/2$

3]

(a) $|0, -1/2\rangle \rightarrow |5/2, -1/2\rangle$ state with pr. $3/5$ & $|3/2, -1/2\rangle$ with pr. $2/5$

$|1, -1/2\rangle \rightarrow |5/2, 1/2\rangle$ " " " $2/5$, $|3/2, 1/2\rangle$ " " $3/5$

3b]

Sm^{15+}

$4f$

ground
state

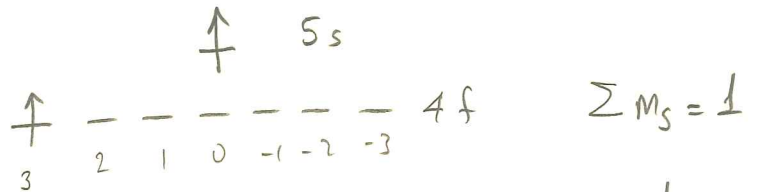


$L = 3, S = 1/2$
 $\rightarrow J_{\text{max}} = 7/2$
 $\rightarrow J_{\text{min}} = 5/2$

Less than half-filled $\Rightarrow J \rightarrow J_{\text{min}}$ $2F_{5/2}$

Ir^{17+}

$4f^{13} 5s$



$\sum m_{li} = 3 \rightarrow L = 3 \rightarrow F, S = 1$

> half filled (f shell dominates)

$J_{\text{min}} = 2, J_{\text{max}} = 4$

$\Rightarrow J \rightarrow J_{\text{max}}$

$3F_4$

4]

Pr^{3+}

$4f^2$



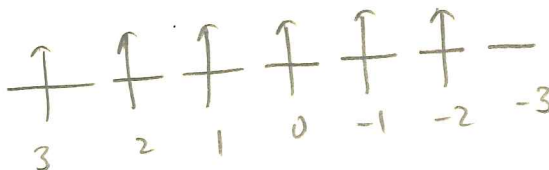
$S = 1, L = 5$
 $J_{\text{max}} = 6$
 $J_{\text{min}} = 4$
 \downarrow
 H

< Half filled

$3H_4$

Eu^{3+}

$4f^6$



$S = 3, L = \sum m_{li} = 3$
 $J_{\text{min}} = 0, J_{\text{max}} = 6$

< Half-filled

$7F_0$

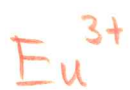
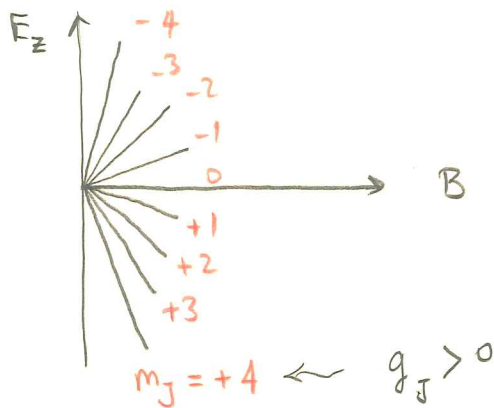
Zeeman Splittings



$$g_J = 1 + \frac{4 \cdot 5 + 1 \cdot 2 - 5 \cdot 6}{2 \cdot 4 \cdot 5} = \frac{4}{5}$$

$$E_z = - \frac{4\mu_B B}{5} m_J \quad ; \quad m_J = 0, \pm 1, \pm 2, \pm 3, \pm 4$$

9 Zeeman sublevels



$$J=0$$

\rightarrow No Zeeman splitting

$$g_J \equiv 0$$