PHYS 551 Homework 2 Solutions

Problem 1:

Since both operators in the Hamiltonian are scalar, they cannot change the total J of the atomic state or the projection m_J. All m_J states will be degenerate because of the spherical symmetry of H and we can consider just one m_J state for each J, say with $m_J = J$. From the available particles one can construct the wavefunctions which are eigenstates of $j_1 = l_1 + s_1$ as well as total angular momentum J. The wavefunctions can be obtained using Clebsch-Gordon coefficients

$$|l_1 s_1 j_1 s_2 J, m_J = J\rangle = \sum_{m_l, m_{s1}, m_{s2}} C(l_1 m_l, s_1 m_{s1} | l_1 s_1 j_1 m_{j1}) C(j_1 m_{j1}, s_2 m_{s2} | j_1 s_2 J, J) \, |l_1 m_l, s_1 m_{s1}, s_2 m_{s2}\rangle \tag{1}$$

j_1 coupled wavefunctions $\lvert l_1, s_1, j_1, s_2, J, J\rangle$	Uncoupled wavefunctions $\lvert m_l, m_{s1}, m_{s2}\rangle$
$\psi_1 = \left\lvert 1, \frac{1}{2}, \frac{3}{2}, \frac{1}{2}, 2, 2 \right\rangle$	$\left\lvert 1, \frac{1}{2}, \frac{1}{2} \right\rangle$
$\psi_2 = \left\lvert 1, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 1, 1 \right\rangle$	$\sqrt{\frac{2}{3}} \left\lvert 1, -\frac{1}{2}, \frac{1}{2} \right\rangle - \sqrt{\frac{1}{3}} \left\lvert 0, \frac{1}{2}, \frac{1}{2} \right\rangle$
$\psi_3 = \left\lvert 1, \frac{1}{2}, \frac{3}{2}, \frac{1}{2}, 1, 1 \right\rangle$	$\frac{\sqrt{3}}{2} \left\lvert 1, \frac{1}{2}, -\frac{1}{2} \right\rangle - \frac{1}{2\sqrt{3}} \left\lvert 1, -\frac{1}{2}, \frac{1}{2} \right\rangle - \frac{1}{\sqrt{6}} \left\lvert 0, \frac{1}{2}, \frac{1}{2} \right\rangle$
$\psi_4 = \left\lvert 1, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0, 0 \right\rangle$	$\sqrt{\frac{1}{3}} \left\lvert 1, -\frac{1}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{1}{6}} \left\lvert 0, \frac{1}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{1}{6}} \left\lvert 0, -\frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left\lvert -1, \frac{1}{2}, \frac{1}{2} \right\rangle$

With these wavefunctions one can evaluate the terms of the Hamilitonian by writing $\mathbf{l}_1 \cdot \mathbf{s}_1 = [j_1(j_1+1) - l_1(l_1+1) - s_1(s_1+1)]/2$ and $\mathbf{s}_1 \cdot \mathbf{s}_2 = s_{1z} s_{2z} + (\, s_{1+} s_{2-} + s_{1-} s_{2+})/2$

$\mathbf{l}_1 \cdot \mathbf{s}_1 \psi_i$	$\mathbf{s}_1 \cdot \mathbf{s}_2 \psi_i$
$\frac{1}{2}\psi_1$	$\frac{1}{4}\psi_1$
$-\psi_2$	$\frac{1}{2}\sqrt{\frac{2}{3}} \left\lvert 1, \frac{1}{2}, -\frac{1}{2} \right\rangle - \frac{1}{4}\sqrt{\frac{2}{3}} \left\lvert 1, -\frac{1}{2}, \frac{1}{2} \right\rangle - \frac{1}{4}\sqrt{\frac{1}{3}} \left\lvert 0, \frac{1}{2}, \frac{1}{2} \right\rangle = \frac{\sqrt{2}}{3}\psi_3 - \frac{1}{12}\psi_2$
$\frac{1}{2}\psi_3$	$\left(\frac{\sqrt{3}}{4} + \frac{1}{8\sqrt{3}}\right) \left\lvert 1, -\frac{1}{2}, \frac{1}{2} \right\rangle - \left(\frac{\sqrt{3}}{8} + \frac{1}{4\sqrt{3}}\right) \left\lvert 1, \frac{1}{2}, -\frac{1}{2} \right\rangle - \frac{1}{4}\sqrt{\frac{1}{6}} \left\lvert 0, \frac{1}{2}, \frac{1}{2} \right\rangle = -\frac{5}{12}\psi_3 + \frac{\sqrt{2}}{3}\psi_2$
$-\psi_4$	$\frac{1}{4}\sqrt{\frac{1}{3}} \left\lvert 1, -\frac{1}{2}, -\frac{1}{2} \right\rangle - \left(\frac{1}{2} - \frac{1}{4}\right)\sqrt{\frac{1}{6}} \left\lvert 0, \frac{1}{2}, -\frac{1}{2} \right\rangle - \left(\frac{1}{2} - \frac{1}{4}\right)\sqrt{\frac{1}{6}} \left\lvert 0, -\frac{1}{2}, \frac{1}{2} \right\rangle + \frac{1}{4}\sqrt{\frac{1}{3}} \left\lvert -1, \frac{1}{2}, \frac{1}{2} \right\rangle = \frac{1}{4}\psi_4$

Note that we have constructed the wavefunctions to be eigenstates of $j_1 = l_1 + s_1$ and evaluation of $\mathbf{l}_1 \cdot \mathbf{s}_1$ is trivial. One could also constuct the wavefunctions to be eigenstates of $S = s_1 + s_2$, in which case the evaluation of $\mathbf{s}_1 \cdot \mathbf{s}_2$ would be trivial. These two schemes of coupling the angular momenta are related by Racah W coefficients or equivalent 6-j symbols:

$$\begin{aligned} \langle l_1, (s_1, s_2, S), J \, | (l_1, s_1, j_1), s_2, J\rangle &= \sqrt{(2S+1)(2j_1+1)} W(l_1, s_1, J, s_2; S, j_1) && (2) \\ &= \sqrt{(2S+1)(2j_1+1)} (-1)^{l_1+s_1+s_2+J} \begin{Bmatrix} l_1 & s_1 & j_1 \\ s_2 & J & S \end{Bmatrix} && (3) \end{aligned}$$

Using this technique we can express the wavefunctions ψ_i as a sum of the wavefunctions in the $|l_1, (s_1, s_2, S), J, J\rangle$ coupling scheme, where the operator $\mathbf{s}_1 \cdot \mathbf{s}_2$ can be trivially evaluated

$$|(l_1, s_1, j_1), s_2, J\rangle = \sum_{S=0,1} \langle l_1, (s_1, s_2, S), J \, | (l_1, s_1, j_1), s, J\rangle \, |l_1, (s_1, s_2, S), J\rangle \tag{4}$$

S coupling $\lvert l_1,(s_1,s_2,S),J\rangle$	$s_1\cdot s_2\,\lvert l_1,(s_1,s_2,S),J\rangle$
$\psi_1=\left\lvert 1,\frac{1}{2},\frac{1}{2},1,2\right\rangle$	$\frac{1}{4}\left\lvert 1,\frac{1}{2},\frac{1}{2},1,2\right\rangle=\frac{1}{4}\psi_1$
$\psi_2=\sqrt{\frac{2}{3}}\left\lvert 1,\frac{1}{2},\frac{1}{2},1,1\right\rangle-\sqrt{\frac{1}{3}}\left\lvert 1,\frac{1}{2},\frac{1}{2},0,1\right\rangle$	$\frac{1}{4}\sqrt{\frac{2}{3}}\left\lvert 1,\frac{1}{2},\frac{1}{2},1,1\right\rangle+\frac{3}{4}\sqrt{\frac{1}{3}}\left\lvert 1,\frac{1}{2},\frac{1}{2},0,1\right\rangle=\frac{\sqrt{2}}{3}\psi_3-\frac{1}{12}\psi_2$
$\psi_3=\sqrt{\frac{1}{3}}\left\lvert 1,\frac{1}{2},\frac{1}{2},1,1\right\rangle+\sqrt{\frac{2}{3}}\left\lvert 1,\frac{1}{2},\frac{1}{2},0,1\right\rangle$	$\frac{1}{4}\sqrt{\frac{1}{3}}\left\lvert 1,\frac{1}{2},\frac{1}{2},1,1\right\rangle-\frac{3}{4}\sqrt{\frac{2}{3}}\left\lvert 1,\frac{1}{2},\frac{1}{2},0,1\right\rangle=\frac{\sqrt{2}}{3}\psi_2-\frac{5}{12}\psi_3$
$\psi_4=\left\lvert 1,\frac{1}{2},\frac{1}{2},1,0\right\rangle$	$\frac{1}{4}\left\lvert 1,\frac{1}{2},\frac{1}{2},1,0\right\rangle=\frac{1}{4}\psi_4$

This gives the same result but in much fewer steps. Now one can find the eigenstates of the Hamiltonian using its representation in the ψ_i basis:

$$H\left|\begin{array}{c}\psi_1\\ \psi_2\\ \psi_3\\ \psi_4\end{array}\right\rangle=\left(\begin{array}{cccc}-\frac{a}{2}-\frac{b}{4} & & & \\ & a+\frac{b}{12} & -\frac{\sqrt{2}b}{3} & \\ & -\frac{\sqrt{2}b}{3} & -\frac{a}{2}+\frac{5b}{12} & \\ & & & a-\frac{b}{4}\end{array}\right)\left|\begin{array}{c}\psi_1\\ \psi_2\\ \psi_3\\ \psi_4\end{array}\right\rangle \tag{5}$$

Only the two states with $J=1$ mix together. The eigenvalues of the two mixed states are given by the roots of the quadratic $(a+b/12-E)\,(-a/2+5b/12-E)-3b^2/9=0$, $E_\pm=(a+b\pm\sqrt{9a^2-4ab+4b^2})/4$. For $b\to 0$ E_+ corresponds to ψ_2 and E_- corresponds to ψ_3.

The energy levels for the states in the j_1 scheme are given in the NIST atomic energy levels database (http://physics.nist.gov/PhysRefData/ASD/index.html). For Ne I (unionized Ne) the atomic energies corresponding to the four states $(\psi_1,\psi_2,\psi_3,\psi_4)$ = (134041.8400, 135888.7173, 134459.2871, 134818.6405) cm^{-1}. One can solve for a, b and an energy e_0 common to all states using the first three energy levels, for example. There are two possible solutions but only one of them predicts an accurate value for E_4 =134819.98 cm^{-1} with ($e_0=134673, a=518.761, b=1486.18$) cm^{-1}. The error is only 1.3 cm^{-1}, approximately 0.1% of the spin-orbit and spin-exchange interactions. Since a and b are comparable, the states ψ_2 and ψ_3 states are significantly mixed. For Xe I $(\psi_1,\psi_2,\psi_3,\psi_4)$ = (67067.547, 77185.041, 68045.156, 76196.767) cm^{-1}. With similar procedure one finds the solution that gives closer result for E_4 =76607.45 cm^{-1} with ($e_0=70636.3$, $a=6359.94, b=1555.2$) cm^{-1}. Now the error is 410 cm^{-1}, a good fraction of the spin interactions. In a heavy atom like Xe interactions with other electrons are significant, so this is just a rough approximation. Note that a is now much larger, while b is about the same as in Ne atom, indicating that the spin-orbit interaction is increasing with Z while the spin-exchange interaction does not.

Problem 2:

The derivation follows the notes on Tensor Operators, only we start by considering the matrix element $\langle l,s,j,I,F,m_F|\mathbf{E}\cdot\mathbf{r}|l',s,j',I,F',m'_F\rangle$, where $j=l+s$ and $F=j+I$. The reduced matrix element $(l||r||l')$ is replaced by $(l,s,j,I,F||r||l',s,j',I,F')$, but the m_F dependendence is exactly the same as in the notes with l replaced by F. Hence

$$\begin{aligned}|\langle l,s,j,I,F,m_F|\mathbf{E}\cdot\mathbf{r}|l',s,j',I,F',m'_F\rangle|^2 &= E_0^2|(l,s,j,I,F||r||l',s,j',I,F')|^2\times & (6)\\ &\left(\begin{array}{ccc}F & 1 & F'\\ -m_F & m_F-m'_F & m'_F\end{array}\right)^2\varepsilon_{m'_F-m_F}\varepsilon^*_{m_F-m'_F} & (7)\end{aligned}$$

The reduced matrix element can be simplified using 6-j symbols as described at the end of the notes since operator r commutes with all quantum numbers except l.

$$(l,s,j,I,F||r||l',s,j',I,F') = (-1)^{j+I+F'+1}(l,s,j||r||l',s,j')\sqrt{(2F+1)(2F'+1)}\left\{\begin{array}{ccc} j & F & I \\ F' & j' & 1 \end{array}\right\} \tag{8}$$

$$(l,s,j||r||l',s,j') = (-1)^{l+s+j'+1}(l||r||l')\sqrt{(2j+1)(2j'+1)}\left\{\begin{array}{ccc} l & j & s \\ j' & l' & 1 \end{array}\right\} \tag{9}$$

Putting everything together we get for $\left|\left\langle 0,\frac{1}{2},\frac{1}{2},\frac{3}{2},F,m_F|\mathbf{E}\cdot\mathbf{r}|1,\frac{1}{2},\frac{3}{2},\frac{3}{2},F',m'_F\right\rangle\right|^2$ with $j'=3/2$ and with linear polarization ($m_F = m'_F$):

	$F'=0$	$F'=1$			$F'=2$					$F'=3$						
$F\backslash m_{F'}$	0	-1	0	1	-2	-1	0	1	2	-3	-2	-1	0	1	2	3
1	$\frac{1}{9}$	$\frac{5}{36}$	0	$\frac{5}{36}$	0	$\frac{1}{12}$	$\frac{1}{9}$	$\frac{1}{12}$	0	0	0	0	0	0	0	0
2	0	$\frac{1}{60}$	$\frac{1}{45}$	$\frac{1}{60}$	$\frac{1}{9}$	$\frac{1}{36}$	0	$\frac{1}{36}$	$\frac{1}{9}$	0	$\frac{1}{9}$	$\frac{8}{45}$	$\frac{1}{5}$	$\frac{8}{45}$	$\frac{1}{9}$	0

Based on this one gets the following selection rules for allowed transitions: $F' = (F-1, F, F+1)$. For $F' = F$ the transition $m_F = 0 \rightarrow m_F = 0$ is forbidden and transitions get stronger for larger m_F. The strongest transition is $F' = F+1, m_F = 0$; the weakest is $F' = F-1$, $m_F = \pm 1$. There is more than a factor of 10 between the strongest and weakest transitions. Also note that from each $|F, m_F\rangle$ state the sum of transitions to all F' states is the same, equal to 2/9. For completeness, for the $P_{1/2}$ transition with $j' = 1/2$

	$F'=1$			$F'=2$				
$F\backslash m_{F'}$	-1	0	1	-2	-1	0	1	2
1	$\frac{1}{36}$	0	$\frac{1}{36}$	0	$\frac{1}{12}$	$\frac{1}{9}$	$\frac{1}{12}$	0
2	$\frac{1}{12}$	$\frac{1}{9}$	$\frac{1}{12}$	$\frac{1}{9}$	$\frac{1}{36}$	0	$\frac{1}{36}$	$\frac{1}{9}$

Here the sum of transitions from each state to all F' is equal to 1/9. Hence the sum of all possible transitions to levels (j', F') from any given state is 1/3, which is the same as was obtained for a simple $l \rightarrow l'$ transition without any additional structure.