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Nuclear Hyperfine Structure in One-Electron Atoms

We shall use the magnetic nuclear hyperfine structure calculation in one-electron atoms to illustrate how the Wigner–Eckart theorem can be exploited in actual calculations. So far, we have calculated the perturbed one-electron spectrum (in hydrogen or in alkali atoms) only under the assumption the nucleus (the proton in hydrogen or the alkali atomic nucleus) have a charge but no magnetic properties. Because the proton has a spin (with spin quantum number $\frac{1}{2}$), it also has a magnetic moment, similarly for alkali atoms. The spin of the stable isotope of Na, e.g., is $\frac{3}{2}$, and hence, it also has a nuclear magnetic moment. These nuclear magnetic moments will have a magnetic interaction with the spin magnetic moment of the electron. In addition, the motion of the electron relative to the nucleus will set up an effective magnetic field at the nucleus (proportional to the orbital angular momentum of the electron). The magnetic moment of the nucleus will also lead to a $-(\vec{\mu}^{\text{magn.}} \cdot \vec{B})$ magnetic interaction caused by this field. These magnetic interactions of nuclear origin will give rise to the so-called hyperfine structure splitting of the $nlsj$ states of the one-electron atoms. If we call the electron magnetic moment $\vec{\mu}_s$ and the nuclear magnetic moment $\vec{\mu}_I$,

$$\vec{\mu}_s = \frac{e\hbar}{2mc} 2\vec{s} = -\frac{|e|\hbar}{2mc} 2\vec{s}, \qquad \vec{\mu}_I = \frac{|e|\hbar}{2Mc} g_I \vec{I}, \tag{1}$$

where we use the vector, $\vec{I}$, for the nuclear spin operator, with quantum number, I, e.g., $I = \frac{1}{2}$ for the proton, $I = \frac{3}{2}$ for ^{23}Na. Also, m is the electron mass, whereas M is the proton mass. (Even in the Na nucleus, the magnetic moment is caused by the last odd valence proton in the nucleus, so it is the proton mass in the so-called nuclear magneton, $\frac{|e|\hbar}{2Mc}$, which gives a natural measure for nuclear magnetic moments.) The g factor for the nuclear magnetic moment is not simply equal to

2.0, as for the point electron (as follows from Dirac theory), but is "anomalous," e.g., $g_I = 2 \times 2.793$ for the proton. This "anomalous" factor is now rather well understood in terms of the quark structure of the nucleon.

The magnet–magnet interaction between the magnetic moments of the electron and the nucleus is given by [see, e.g., J. D. Jackson, 2^{nd} ed., eq. (5.73)]

$$H_{\text{magn.-magn.}} = \left(\left[(\vec{\mu}_s \cdot \vec{\mu}_I) - 3(\frac{\vec{r}}{r} \cdot \vec{\mu}_s)(\frac{\vec{r}}{r} \cdot \vec{\mu}_I)\right]\frac{1}{r^3} - \frac{8\pi}{3}(\vec{\mu}_s \cdot \vec{\mu}_I)\delta(\vec{r})\right)$$
$$= \frac{e^2\hbar^2}{2mMc^2}g_I\left(\left[-(\vec{s} \cdot \vec{I}) + 3(\frac{\vec{r}}{r} \cdot \vec{s})(\frac{\vec{r}}{r} \cdot \vec{I})\right]\frac{1}{r^3} + \frac{8\pi}{3}(\vec{s} \cdot \vec{I})\delta(\vec{r})\right), \quad (2)$$

including the delta-function term that comes into play only if the two magnets can be on top of each other. This so-called contact term, (part of *classical* electrodynamics according to J. D. Jackson, *Classical Electrodynamics*, New York: John Wiley, 1967), comes into play only in atomic s-states, $l = 0$ states, where the electron has a finite probability of sitting "on" the nucleus. The additional $-(\vec{\mu}_I \cdot \vec{B}_{\text{eff.}})$ term, with

$$\vec{B}_{\text{eff.}} = \frac{e}{cr^3}[\vec{r} \times \frac{\vec{p}}{m}] = -\frac{|e|\hbar}{mcr^3}\vec{l}, \quad (3)$$

caused by the effective magnetic field of the moving electron at the nucleus, leads to an additional interaction term

$$H_{\text{orb.-nucl. magn.}} = \frac{e^2\hbar^2}{2mMc^2}g_I(\vec{l} \cdot \vec{I})\frac{1}{r^3}. \quad (4)$$

In these relations, the quantity r is $r_{\text{phys.}} = a_0 r$, where the last r is our usual dimensionless r. In terms of this dimensionless r, the combined magnetic interactions give

$$H_{\text{int.}} = \frac{mc^2\alpha^4}{2}\frac{m}{M}g_I\left(\left[-(\vec{s}\cdot\vec{I})+3(\frac{\vec{r}}{r}\cdot\vec{s})(\frac{\vec{r}}{r}\cdot\vec{I})\right]\frac{1}{r^3}+\frac{8\pi}{3}(\vec{s}\cdot\vec{I})\delta(\vec{r})+(\vec{l}\cdot\vec{I})\frac{1}{r^3}\right), \quad (5)$$

where we have also used

$$\delta(a_0\vec{r}) = \frac{1}{a_0^3}\delta(\vec{r}), \quad (6)$$

and $\alpha = (1/137)$ is the fine structure constant. This hyperfine structure term is $\frac{m}{M}g_I$ times the fine structure term. Now, express the magnetic moment–magnetic moment interaction in terms of spherical tensor operators. In terms of the coupled spherical tensors, defined by

$$[V^{k_1} \times U^{k_2}]^k_q \equiv \sum_{q_1, q_2} V^{k_1}_{q_1} U^{k_2}_{q_2} \langle k_1 q_1 k_2 q_2 | kq \rangle, \quad (7)$$

we need the spherical tensors $[r^1 \times r^1]^2_q \equiv r^2_q$, and $[s^1 \times I^1]^2_q$. These have spherical components

$$r^2_{\pm 2} = \tfrac{1}{2}(x \pm iy)^2, \qquad r^2_{\pm 1} = \mp z(x \pm iy), \qquad r^2_0 = \frac{1}{\sqrt{6}}(2z^2 - x^2 - y^2), \quad (8)$$

and

$$[s^1 \times I^1]^2_{\pm 2} = \tfrac{1}{2} s_\pm I_\pm; \qquad [s^1 \times I^1]^2_{\pm 1} = \mp\tfrac{1}{2}(s_\pm I_0 + s_0 I_\pm),$$
$$[s^1 \times I^1]^2_0 = -\frac{1}{\sqrt{6}}\Big(\tfrac{1}{2}(s_+ I_- + s_- I_+) - 2 s_0 I_0\Big). \tag{9}$$

Also, r^2_q can be expressed in terms of standard spherical harmonics by

$$r^2_q = r^2 \sqrt{\frac{8\pi}{15}} Y_{2.q}(\theta, \phi). \tag{10}$$

In terms of these spherical tensors of rank, $k = 2$, the magnetic dipole–magnetic dipole interaction term can be expressed through

$$\Big(-(\vec{s}\cdot\vec{I}) + 3(\vec{s}\cdot\frac{\vec{r}}{r})(\vec{I}\cdot\frac{\vec{r}}{r})\Big) = 3\sqrt{\frac{8\pi}{15}}\sum_q (-1)^q Y_{2,q}[s^1 \times I^1]^2_{-q}$$

$$= 3\sqrt{\frac{8\pi}{15}}\big(Y^2 \cdot [s^1 \times I^1]^2\big), \tag{11}$$

where the dot in the last form stands for the generalized scalar product of two spherical tensors each of spherical rank 2. This type of interaction is therefore sometimes called a "tensor" interaction, but the term is somewhat of a misnomer. The full interaction is a scalar, a rotationally invariant $k = 0$ spherical tensor, but the term "tensor" is used because it involves the scalar product of two spherical tensors each of spherical rank 2. Because we want to calculate matrix elements of this interaction in an $|n[[l \times s]j \times I]FM_F\rangle$ basis, corresponding to the vector coupling

$$(\vec{l} + \vec{s}) + \vec{I} = \vec{j} + \vec{I} = \vec{F} \tag{12}$$

basis, rather than a

$$\vec{l} + (\vec{s} + \vec{I}) = \vec{l} + \vec{S} = \vec{F} \tag{13}$$

basis, we need to tailor the magnet–magnet interaction to the coupling scheme of eq. (12), where $\vec{l}$ and $\vec{s}$ are coupled to resultant $\vec{j}$, which is then coupled to the nuclear spin $\vec{I}$ to resultant total angular momentum $\vec{F}$. The form of eq. (11) is tailored more to the coupling scheme of eq. (13), where the electron spin, $\vec{s}$, and the nuclear spin, $\vec{I}$, are coupled to total spin $\vec{S}$, which is then coupled with $\vec{l}$ to resultant total angular momentum $\vec{F}$. By rearranging the order of the couplings, we can also express the magnet–magnet interaction through

$$\Big(-(\vec{s}\cdot\vec{I}) + 3(\vec{s}\cdot\frac{\vec{r}}{r})(\vec{I}\cdot\frac{\vec{r}}{r})\Big)$$

$$= -\sqrt{8\pi}\big([Y^2 \times s^1]^1 \cdot I^1\big) = -\sqrt{8\pi}\sum_q (-1)^q [Y^2 \times s^1]^1_q I^1_{-q}. \tag{14}$$

As a specific example, we shall now calculate the hyperfine splitting of the $2p_{\frac{3}{2}}$, i.e., the $n = 2, l = 1, j = \frac{3}{2}$, fine structure level of hydrogen. Because the proton has a spin $I = \frac{1}{2}$, this level will be split into two hyperfine components, with quantum numbers $F = 2$ and $F = 1$. Because the contact term, with the delta function, can contribute only in s states, with $l = 0$, for which the electron has a nonzero probability of being on the proton, this term cannot contribute to the p-state hyperfine splitting. Thus, both the nonzero terms have a $\frac{1}{r^3}$ radial dependence and lead to the radial integral

$$\beta_{\text{h.f.s.}} = \frac{mc^2}{2}\alpha^4 \frac{m}{M} g_I \int_0^\infty dr r^2 |R_{nl}(r)|^2 \frac{1}{r^3}. \tag{15}$$

This hyperfine structure integral, $\beta_{\text{h.f.s.}} = \frac{m}{M} g_I \beta_{nl}$, where $\beta_{nl} = \beta_{\text{f.s.}}$ gives the stength of the fine structure splitting.

We shall now exploit the Wigner–Eckart theorem in two ways: (1) Because $H_{\text{int.}}$ is a $k = 0$ scalar operator, it will be sufficient to calculate the diagonal matrix element of this interaction for states with $M_F = F$. (2) In addition, the calculation can be reduced to a calculation of the reduced or double-barred matrix elements of the two operators, $[Y^2 \times s^1]^1_q$ and l^1_q, in the $|n[l \times s]jm_j\rangle$ basis. The needed matrix elements of I^1_q are very simple and can then be combined with these after application of the Wigner–Eckart theorem. To calculate the double-barred matrix elements of $[Y^2 \times s^1]^1$ and l^1, let us use the state with $m_j = +j = +\frac{3}{2}$,

$$|[l = 1 \times s = \tfrac{1}{2}]j = \tfrac{3}{2} m_j = +\tfrac{3}{2}\rangle = |l = 1 \;\; m_l = +1 \;\; s = \tfrac{1}{2} \;\; m_s = +\tfrac{1}{2}\rangle, \tag{16}$$

for the calculation, so

$$\begin{aligned}
&\langle j = m_j = \tfrac{3}{2}|[Y^2 \times s^1]^1_0|j = m_j = \tfrac{3}{2}\rangle = \langle \tfrac{3}{2}\tfrac{3}{2}10|\tfrac{3}{2}\tfrac{3}{2}\rangle \frac{\langle \frac{3}{2}\|[Y^2 \times s^1]^1\|\frac{3}{2}\rangle}{\sqrt{4}} \\
&= \langle l = m_l = 1, s = m_s = \tfrac{1}{2}|[Y^2 \times s^1]^1_0|l = 1 m_l = 1, s = m_s = \tfrac{1}{2}\rangle \\
&= \langle 1 + 1\tfrac{1}{2} + \tfrac{1}{2}|Y_{20} \;\; s_0|1 + 1\tfrac{1}{2} + \tfrac{1}{2}\rangle\langle 2010|10\rangle \\
&= \langle 1 \;\; m_l = +1|Y_{20}|1 \;\; m_l = +1\rangle(+\tfrac{1}{2})\langle 2010|10\rangle \\
&= \sqrt{\frac{3 \cdot 5}{3 \cdot 4\pi}}\langle 1120|11\rangle\langle 1020|10\rangle\langle 2010|10\rangle(+\tfrac{1}{2}) \\
&= \frac{1}{5}\sqrt{\frac{1}{8\pi}},
\end{aligned} \tag{17}$$

where only the $Y_{20}s_0$ component of $[Y^2 \times s^1]^1_0$ contributes to our matrix element because it is diagonal in *both* m_l and m_s. This simplification is related to our "clever" choice of $m_j = +\frac{3}{2}$ in the full matrix element. In the above, we have used eq. (32) of Chapter 30 for the matrix element of Y_{20} and the values of the Clebsch–Gordan coefficients

$$\begin{aligned}
\langle 2010|10\rangle &= \langle 1020|10\rangle = -\sqrt{\frac{2}{5}}, \\
\langle 1120|11\rangle &= +\sqrt{\frac{1}{10}}.
\end{aligned} \tag{18}$$

Finally, using

$$\langle \tfrac{3}{2}\tfrac{3}{2}10|\tfrac{3}{2}\tfrac{3}{2}\rangle = \sqrt{\frac{3}{5}} \tag{19}$$

for the first step in eq. (17), we get the desired reduced matrix element

$$\langle \tfrac{3}{2}\|[Y^2 \times s^1]^1\|\tfrac{3}{2}\rangle = \frac{1}{\sqrt{30\pi}}. \tag{20}$$

Similarly, we can get the reduced matrix element of l^1_q from

$$\begin{aligned}\langle j = \tfrac{3}{2} \;\; m_j = +\tfrac{3}{2}|l^1_0|j = \tfrac{3}{2} \;\; m_j = +\tfrac{3}{2}\rangle &= \langle \tfrac{3}{2}\tfrac{3}{2}10|\tfrac{3}{2}\tfrac{3}{2}\rangle \frac{\langle \tfrac{3}{2}\|l^1\|\tfrac{3}{2}\rangle}{\sqrt{4}} \\ = \langle l = 1 \;\; m_l = +1 \;\; s = m_s = \tfrac{1}{2}|l_0|l = 1 \;\; m_l = +1 \;\; s = m_s = \tfrac{1}{2}\rangle \\ = +1,\end{aligned} \tag{21}$$

so

$$\langle \tfrac{3}{2}\|l^1\|\tfrac{3}{2}\rangle = 2\sqrt{\frac{5}{3}}. \tag{22}$$

Although the calculation of this reduced matrix element in the state with $j = (l+\frac{1}{2})$ was extremely trivial, we note an alternative method that might be useful for states with $j = (l - \frac{1}{2})$ or for states with $s > \frac{1}{2}$ and several possible j values. From eq. (9) of Chapter 32, we could also have written

$$\begin{aligned}\langle [l \times s]j\|\vec{l}\|[l \times s]j\rangle &= \frac{\langle [l \times s]j\|(\vec{l}\cdot\vec{j})\vec{j}\|[l \times s]j\rangle}{j(j+1)} \\ &= \frac{[j(j+1) + l(l+1) - s(s+1)]}{2j(j+1)}\langle j\|\vec{j}\|j\rangle \\ &= \tfrac{1}{2}[j(j+1) + l(l+1) - s(s+1)]\sqrt{\frac{(2j+1)}{j(j+1)}},\end{aligned} \tag{23}$$

where we have used eq. (7) of Chapter 32 for the reduced matrix element of $\vec{j} \equiv j^1$, and have also used

$$(\vec{l}\cdot\vec{j}) = (\vec{l}\cdot(\vec{l}+\vec{s})) = (\vec{l}\cdot\vec{l}) + (\vec{l}\cdot\vec{s}), \tag{24}$$

with

$$(\vec{l}\cdot\vec{s}) = \tfrac{1}{2}[(\vec{j}\cdot\vec{j}) - (\vec{l}\cdot\vec{l}) - (\vec{s}\cdot\vec{s})]. \tag{25}$$

With $l = 1$, $s = \frac{1}{2}$, and $j = \frac{3}{2}$, this relation immediately gives the result of eq. (22). Now that we have the reduced matrix elements of $[Y^2 \times s^1]^1$ and $l^1 \equiv \vec{l}$, we can calculate the matrix elements of $H_{\text{int.}}$ in the needed states with $M_F = F$. First, for $F = 2$, with

$$|[j \times I]F \;\; M_F\rangle = |[\tfrac{3}{2} \times \tfrac{1}{2}]F = 2 \;\; M_F = +2\rangle = |j = m_j = \tfrac{3}{2} \quad I = M_I = \tfrac{1}{2}\rangle, \tag{26}$$

we get

$$\begin{aligned}
&\langle F = M_F = 2|H_{\text{int.}}|F = M_F = 2\rangle = \beta_{\text{h.f.s.}}(-\sqrt{8\pi}) \\
&\times \langle F = M_F = 2|([Y_2 \times s^1]^1 \cdot I^1) + (\vec{l} \cdot \vec{I})|F = M_F = 2\rangle \\
&= \beta_{\text{h.f.s.}}\Big(-\sqrt{8\pi}\langle j = m_j = \tfrac{3}{2}|[Y^2 \times s^1]^1_0|j = m_j = \tfrac{3}{2}\rangle \\
&+ \ \langle j = m_j = \tfrac{3}{2}|l_0|j = m_j = \tfrac{3}{2}\rangle\Big)\langle I = M_I = \tfrac{1}{2}|I_0|I = M_I = \tfrac{1}{2}\rangle \\
&= \beta_{\text{h.f.s.}}\Big(-\sqrt{8\pi}\frac{\langle \frac{3}{2}\|[Y^2 \times s^1]^1\|\frac{3}{2}\rangle}{\sqrt{4}} + \frac{\langle \frac{3}{2}\|l^1\|\frac{3}{2}\rangle}{\sqrt{4}}\Big)\langle \tfrac{3}{2}\tfrac{3}{2}10|\tfrac{3}{2}\tfrac{3}{2}\rangle(+\tfrac{1}{2}) \\
&= \beta_{\text{h.f.s.}}\Big(-\sqrt{8\pi}\frac{1}{2\sqrt{30\pi}} + 2\sqrt{\frac{5}{3}} \cdot \tfrac{1}{2}\Big)\sqrt{\frac{3}{5}}(+\tfrac{1}{2}) \\
&= \beta_{\text{h.f.s.}}\Big(-\frac{1}{5} + 1\Big)(+\tfrac{1}{2}) = \frac{2}{5}\beta_{\text{h.f.s.}}.
\end{aligned} \tag{27}$$

For the state with $F = 1$, the calculation is somewhat more complicated. We shall again choose the state with $M_F = F$ to do the calculation, where now

$$\begin{aligned}
&|[j = \tfrac{3}{2} \times I = \tfrac{1}{2}]F = M_F = 1\rangle = \sum_{m_j M_I} |\tfrac{3}{2}m_j\tfrac{1}{2}M_I\rangle\langle \tfrac{3}{2}m_j\tfrac{1}{2}M_I|11\rangle \\
&= |\tfrac{3}{2} + \tfrac{3}{2}\tfrac{1}{2} - \tfrac{1}{2}\rangle\langle \tfrac{3}{2} + \tfrac{3}{2}\tfrac{1}{2} - \tfrac{1}{2}|1 + 1\rangle + |\tfrac{3}{2} + \tfrac{1}{2}\tfrac{1}{2} + \tfrac{1}{2}\rangle\langle \tfrac{3}{2} + \tfrac{1}{2}\tfrac{1}{2} + \tfrac{1}{2}|1 + 1\rangle \\
&= |\tfrac{3}{2} + \tfrac{3}{2}\tfrac{1}{2} - \tfrac{1}{2}\rangle\frac{\sqrt{3}}{2} + |\tfrac{3}{2} + \tfrac{1}{2}\tfrac{1}{2} + \tfrac{1}{2}\rangle(-\tfrac{1}{2}).
\end{aligned} \tag{28}$$

Calculating first the matrix element for the $([Y^2 \times s^1]^1 \cdot I^1)$ term, we get

$$\begin{aligned}
&\langle [\tfrac{3}{2} \times \tfrac{1}{2}]F = 1 \ \ M_F = 1|([Y^2 \times s^1]^1 \cdot I^1)|[\tfrac{3}{2} \times \tfrac{1}{2}]F = 1 \ \ M_F = 1\rangle \\
&= \frac{3}{4}\langle \tfrac{3}{2} + \tfrac{3}{2}\tfrac{1}{2} - \tfrac{1}{2}|[Y^2 \times s^1]^1_0 \ \ I_0|\tfrac{3}{2} + \tfrac{3}{2}\tfrac{1}{2} - \tfrac{1}{2}\rangle \\
&+ \frac{1}{4}\langle \tfrac{3}{2} + \tfrac{1}{2}\tfrac{1}{2} + \tfrac{1}{2}|[Y^2 \times s^1]^1_0 \ \ I_0|\tfrac{3}{2} + \tfrac{1}{2}\tfrac{1}{2} + \tfrac{1}{2}\rangle \\
&- \frac{\sqrt{3}}{4}\langle \tfrac{3}{2} + \tfrac{3}{2}\tfrac{1}{2} - \tfrac{1}{2}|\Big(-[Y^2 \times s^1]^1_{+1} \ \ I_{-1}\Big)|\tfrac{3}{2} + \tfrac{1}{2}\tfrac{1}{2} + \tfrac{1}{2}\rangle \\
&- \frac{\sqrt{3}}{4}\langle \tfrac{3}{2} + \tfrac{1}{2}\tfrac{1}{2} + \tfrac{1}{2}|\Big(-[Y^2 \times s^1]^1_{-1} \ \ I_{+1}\Big)|\tfrac{3}{2} + \tfrac{3}{2}\tfrac{1}{2} - \tfrac{1}{2}\rangle,
\end{aligned} \tag{29}$$

where the state vectors in the four terms are given in the $|j \ \ m_j \ \ I \ \ M_I\rangle$ basis. Noting the matrix elements of the spherical components of $\vec{I}$ are given by

$$\langle \tfrac{1}{2}M_I|I_0|\tfrac{1}{2}M_I\rangle = M_I \qquad \text{and} \qquad \langle \tfrac{1}{2} \pm \tfrac{1}{2}|I_{\pm 1}|\tfrac{1}{2} \mp \tfrac{1}{2}\rangle = \mp\frac{1}{\sqrt{2}}, \tag{30}$$

and using the Wigner–Eckart theorem for the matrix elements of the operators $[Y^2 \times s^1]^1_q$ in the $|j \ \ m_j\rangle$ basis, we get

$$\begin{aligned}
&-\sqrt{8\pi}\langle [\tfrac{3}{2} \times \tfrac{1}{2}]F = M_F = 1|([Y^2 \times s^1]^1 \cdot I^1)|[\tfrac{3}{2} \times \tfrac{1}{2}]F = M_F = 1\rangle \\
&= -\sqrt{8\pi}\Big[\frac{3}{4}\langle \tfrac{3}{2}\tfrac{3}{2}10|\tfrac{3}{2}\tfrac{3}{2}\rangle(-\tfrac{1}{2}) + \frac{1}{4}\langle \tfrac{3}{2}\tfrac{1}{2}10|\tfrac{3}{2}\tfrac{1}{2}\rangle(+\tfrac{1}{2}) \\
&+ \frac{\sqrt{3}}{4}\langle \tfrac{3}{2}\tfrac{1}{2}1 + 1|\tfrac{3}{2}\tfrac{3}{2}\rangle(\frac{1}{\sqrt{2}}) + \frac{\sqrt{3}}{4}\langle \tfrac{3}{2}\tfrac{3}{2}1 - 1|\tfrac{3}{2}\tfrac{1}{2}\rangle(-\frac{1}{\sqrt{2}})\Big]\frac{1}{\sqrt{4}}\langle \tfrac{3}{2}\|[Y^2 \times s^1]^1\|\tfrac{3}{2}\rangle
\end{aligned}$$

$$= -\sqrt{8\pi}\left[\frac{3}{4}\sqrt{\frac{3}{5}}(-\tfrac{1}{2}) + \frac{1}{4}\frac{1}{\sqrt{15}}(+\tfrac{1}{2}) + \frac{\sqrt{3}}{4}(-\sqrt{\frac{2}{5}})(\frac{1}{\sqrt{2}}) + \frac{\sqrt{3}}{4}(+\sqrt{\frac{2}{5}})(-\frac{1}{\sqrt{2}})\right]\frac{1}{\sqrt{4}}\frac{1}{\sqrt{30\pi}}$$
$$= +\frac{1}{6}. \tag{31}$$

The matrix element of the $(\vec{l}\cdot\vec{I})$ term differs from this matrix element only by the ratio of the reduced matrix elements, which is a factor of -5. Thus,

$$\langle F = M_F = 1|H_{\text{int.}}|F = M_F = 1\rangle = \beta_{\text{h.f.s.}}(\frac{1}{6} - \frac{5}{6}) = -\frac{2}{3}\beta_{\text{h.f.s.}}. \tag{32}$$

Thus, the hyperfine levels of the hydrogen $2p_{\frac{3}{2}}$ fine structure level, with $F = 2$ and $F = 1$ are shifted by $+\frac{2}{5}\beta_{\text{h.f.s.}}$ and $-\frac{2}{3}\beta_{\text{h.f.s.}}$, leading to a splitting of $\frac{16}{15}\beta_{\text{h.f.s.}}$. We leave as an exercise the splitting for the $2p_{\frac{1}{2}}$ fine structure level with a shift of $+\frac{2}{3}\beta_{\text{h.f.s.}}$ for the $F = 1$ hyperfine level and a shift of $-2\beta_{\text{h.f.s.}}$ for the $F = 0$ hyperfine level.

Problems

43. In a one-electron atom, such as sodium, find the relative intensities for the transitions, $n[l\frac{1}{2}]j \rightarrow n'[(l-1)\frac{1}{2}]j'$ for the four possibilities: $j = (l \pm \frac{1}{2})$; $j' = (l-1) \pm \frac{1}{2}$. Express your answers in terms of general functions of l. Show first that

$$\sum_{\alpha=x,y,z} |\langle n'l'\tfrac{1}{2}j'm'|\mu_\alpha^{(\text{el.})}|nl\tfrac{1}{2}jm\rangle|^2 = \sum_{q=\pm 1,0} |\langle n'l'\tfrac{1}{2}j'm'|\mu_q^{(\text{el.})}|nl\tfrac{1}{2}jm\rangle|^2,$$

where $\mu_q^{(\text{el.})}$ are spherical components of the electric dipole moment operator. Also, show that

$$\sum_{m,q,m'} |\langle n'l'\tfrac{1}{2}j'm'|\mu_q^{(\text{el.})}|nl\tfrac{1}{2}jm\rangle|^2 = |\langle n'l'\tfrac{1}{2}j'\|\vec{\mu}^{(\text{el.})}\|nl\tfrac{1}{2}j\rangle|^2,$$

so only the reduced (or double-barred) matrix elements of $\vec{\mu}^{(\text{el.})}$, a spherical tensor of rank 1, need to be calculated. Also, use the fact that the m sublevels of the initial state are all populated with an equal probability of $1/(2j+1)$.

44. In an atom with an atomic nucleus, with a nuclear spin, $I \geq 1$, a hyperfine interaction exists, caused by the electrostatic interaction between the nuclear electric quadrupole moment and the atomic electrons. In a one-electron atom, such as Na, this interaction gives rise to a hyperfine perturbation

$$H_{\text{int.}} = -e^2\sum_m(-1)^m Q_{2,m}\sqrt{\frac{4\pi}{5}}Y_{2,-m}(\theta,\phi)\frac{1}{r^3},$$

where the $Q_{2,m}$ are the (spherical) laboratory components of the nuclear quadrupole operator, a spherical tensor of rank 2, and r, θ, ϕ give the position of the valence electron. The ${}^{23}_{11}\mathrm{Na}_{12}$ nucleus has a spin $I = \frac{3}{2}$ and a nuclear quadrupole moment, $Q = 0.14$ barns (1 barn $\equiv 10^{-24}\mathrm{cm}^2$). "The" nuclear quadrupole moment, Q, is defined as

$$Q = 2\langle IM_I = I|Q_{2,0}|IM_I = I\rangle = 2\langle II20|II\rangle \frac{\langle I\|Q_2\|I\rangle}{\sqrt{(2I+1)}}$$

$$= 2\sqrt{\frac{I(2I-1)}{(2I+1)(I+1)(2I+3)}}\langle I\|Q_2\|I\rangle.$$

We can evaluate the reduced matrix element of Q_2 in terms of the experimental Q through this relation. Also, Q is related to the nuclear charge density, $\rho_{\mathrm{nucl.}}$, through

$$Q = \frac{1}{|e|}\int d\vec{r}_{\mathrm{nucl.}} r^2_{\mathrm{nucl}}(3\cos^2\theta_{\mathrm{nucl.}} - 1)\rho_{\mathrm{nucl.}},$$

so Q has the dimension cm^2, because the charge $|e|$ is factored out in the definition.

Calculate the hyperfine splitting caused by this perturbation for the $3p_{\frac{3}{2}}$ and $3p_{\frac{1}{2}}$ levels of the Na atom. Show, in particular, the F=1, 2 hyperfine levels for $p_{\frac{1}{2}}$ are not affected by this perturbation, whereas the $p_{\frac{3}{2}}$ state is split into hyperfine sublevels with F = 0, 1, 2, 3. Show, however, the F=1 and F=3 sublevels remain (accidentally) degenerate. Express the hyperfine splitting in terms of Q and the quantity

$$\beta_{nl} = \frac{me^4}{\hbar^2}\alpha^2\int_0^\infty dr r^2 |R_{nl}(r)|^2 \frac{1}{r^3},$$

where r is the dimensionless radial coordinate measured in atomic units.

45. The hyperfine splitting of the $1s_{\frac{1}{2}}$ ground state of the hydrogen atom arises solely through the delta function contact term of

$$H_{\mathrm{h.f.int.}} = \frac{mc^2\alpha^4}{2}\frac{m}{M}g_I\left(\left[-(\vec{s}\cdot\vec{I}) + 3(\frac{\vec{r}}{r}\cdot\vec{s})(\frac{\vec{r}}{r}\cdot\vec{I})\right]\frac{1}{r^3} + \frac{8\pi}{3}(\vec{s}\cdot\vec{I})\delta(\vec{r}) + (\vec{l}\cdot\vec{I})\frac{1}{r^3}\right).$$

Calculate the hyperfine splitting of the hydrogen atom ground state. Find the numerical value of the energy difference between the $F = 1$ and $F = 0$ hyperfine sublevels. (Recall $g_I = 2 \times 2.793$ for the proton.)

46. In a diatomic molecule with one atomic nucleus with a spin, $I \geq 1$, a hyperfine interaction exists through the electrostatic interaction between the nuclear electric quadrupole moment and the electric field at the nucleus caused by the molecular electrons and the second nuclear charge. This interaction gives rise to a quadrupole hyperfine perturbation

$$H_{\mathrm{h.f.int.}} = eq\sum_m (-1)^m Q_{2,m} Y_{2,-m}(\theta,\phi)\sqrt{\frac{4\pi}{5}},$$

where $Q_{2,m}$ are the (spherical) laboratory components of the nuclear quadrupole operator (see problem 44) and the angles θ, ϕ give the orientation in the laboratory of the diatomic molecule symmetry axis. The number, eq, gives the θ, ϕ-independent part of the molecular matrix element of the inhomogeneous electric field at the nucleus, using the molecular electronic wave function. Here, e is the electronic charge, and q is a commonly used notation. Assume the nuclear spin is $I = 1$. Find the hyperfine splitting of the first excited rotational state with $J = 1$ and zeroth-order rotational wave function, $\psi_{JM}^{\text{rot.}} = Y_{J=1,M}(\theta, \phi)$, as a function of eq and Q, where Q is "the" nuclear quadrupole moment, as defined in problem 44. That is, find the splitting of the rotational level with $J = 1$ into hyperfine levels with $F = 0, 1, 2$, where $\vec{F} = \vec{J} + \vec{I}$.

47. A diatomic molecule rigid rotator with zeroth-order rotational energies, $\hbar^2 J(J+1)/(2\mu r_e^2)$, and zeroth-order rotational eigenfunctions, $Y_{JM}(\theta, \phi)$, has atomic nuclei with nuclear spins, $I_1 = \frac{3}{2}$ and $I_2 = \frac{1}{2}$. Assume the nuclei have no electric quadrupole moments, so the hyperfine interaction is caused by a magnet–magnet type interaction leading to an interaction Hamiltonian of the form

$$H_{\text{int.}} = a(\vec{I}_1 \cdot \vec{I}_2) + b\left[3\left(\vec{I}_1 \cdot \frac{\vec{r}}{r}\right)\left(\vec{I}_2 \cdot \frac{\vec{r}}{r}\right) - (\vec{I}_1 \cdot \vec{I}_2)\right],$$

where $\vec{r}$ is the vector pointing from nucleus 2 to nucleus 1, with angular coordinates, θ, ϕ, and a and b are constants. Assume, however, $a \gg b$ [but both $a, b \ll \hbar^2/(2\mu r_e^2)$]. For these values of the constants, the $|[J[I_1 I_2]I]FM_F\rangle$ basis is a good basis for the hyperfine structure calculation. Here, $\vec{I}_1 + \vec{I}_2 = \vec{I}$, where $\vec{I}$ is the total nuclear spin vector, and $\vec{J} + \vec{I} = \vec{F}$, where $\vec{F}$ is the total angular momentum vector. Find the hyperfine energies as functions of a and b for the rotational state with $J = 1$ and hyperfine multiplet with $I = 1$, $F = 0, 1, 2$, and $I = 2$, $F = 1, 2, 3$.