Answers to the Problems in Chapter 7

Problem 7.1.

The function $A_{k\alpha}$ is defined by Equation7.2.5. The only part of the equation which depends on α is the spherical harmonic $\Psi^*_{k\alpha}(\vartheta,\phi)$ and the only part of the spherical harmonic which depends upon ϕ is the term $\exp(\pm i\alpha\phi) = \cos(\alpha\phi) \pm i\sin(\alpha\phi)$. The four values of ϕ which we have to consider are 0, $+\pi/2$, $-\pi/2$ and π and for each of these angles $\cos(4\phi) = 1.0$ and $\sin(4\phi) = 0$. Therefore, $A_{44} = A_{4-4}$ for all four values of ϕ.

Problem 7.2.

In Section 7.3.1 we find that $|3,+2\rangle = |+2^+,0^+\rangle$ and $|3,-2\rangle = |0^+,-2^+\rangle$. Both of the kets on the right-hand side represent Slater determinants so we should write them as:

$|3,+2\rangle = (1/\surd 2)\{|\psi_{+2}(1)\psi_0(2) - \psi_0(1)\psi_{+2}(2)\rangle\}$

and

$|3,-2\rangle = (1/\surd 2)\{|\psi_0(1)\psi_{-2}(2) - \psi_{-2}(1)\psi_0(2)\rangle\}$

In writing these functions the '2' signifying d-orbital and the '+' for $m_s = +½$ have been omitted since all the orbitals involved are d orbitals and both electrons have $m_s = +½$.

We have to evaluate the integral

$½\langle\psi_{+2}(1)\psi_0(2) - \psi_0(1)\psi_{+2}(2)|\hat{H}_{cf}|\psi_0(1)\psi_{-2}(2) - \psi_{-2}(1)\psi_0(2)\rangle$.

There are four terms, and since the operator is a one-electron operator each term consists of a contribution from electron 1 and from electron 2, e.g.

$$½\langle\psi_{+2}(1)\psi_0(2)|\hat{H}_{cf}|\psi_0(1)\psi_{-2}(2)\rangle = ½\langle\psi_{+2}(1)|\hat{H}_{cf}(1)|\psi_0(1)\rangle\langle\psi_0(2)|\psi_{-2}(2)\rangle$$
$$+½\langle\psi_0(2)|\hat{H}_{cf}(2)|\psi_{-2}(2)\rangle\langle\psi_2(1)|\psi_0(1)\rangle$$

The d-orbitals are orthogonal and the integrals $\langle\psi_0(2)|\psi_{-2}(2)\rangle$ and $\langle\psi_2(1)|\psi_0(1)\rangle$ are both zero. Therefore the above term makes no contribution to the total integral. But, in the case of the term

$$-½\langle\psi_0(1)\psi_{+2}(2)|\hat{H}_{cf}|\psi_0(1)\psi_{-2}(2)\rangle = -½\langle\psi_0(1)|\hat{H}_{cf}(1)|\psi_0(1)\rangle\langle\psi_{+2}(2)|\psi_{-2}(2)\rangle$$
$$-½\langle\psi_{+2}(2)|\hat{H}_{cf}(2)|\psi_{-2}(2)\rangle\langle\psi_0(1)|\psi_0(1)\rangle$$

the product $-½\langle\psi_{+2}(2)|\hat{H}_{cf}(2)|\psi_{-2}(2)\rangle\langle\psi_0(1)|\psi_0(1)\rangle$ makes a contribution of $-½\langle\psi_{+2}(2)|\hat{H}_{cf}(2)|\psi_{-2}(2)\rangle$ to the integral because $\langle\psi_0(1)|\psi_0(1)\rangle = 1$.

When the remaining two terms are broken down in the above manner a further contribution of $-½\langle\psi_{+2}(2)|\hat{H}_{cf}(2)|\psi_{-2}(2)\rangle$ is found so that the total integral is:

$-\langle\psi_{+2}(2)|\hat{H}_{cf}(2)|\psi_{-2}(2)\rangle = -5\Omega/6$ or $-\Delta/2$.

[A sign correction to the matrix elements $\langle 3,+2|\hat{H}_{cf}|3,-2\rangle$ and $\langle 3,-2|\hat{H}_{cf}|3,+2\rangle$ is required on p. 189.]

Problem 7.3.

$|1\ 0\rangle = (2/\sqrt{5})|2^+,-2^+\rangle - (1/\sqrt{5})|1^+,-1^+\rangle$

Expanding the Slater determinants and omitting the '+' signs since both electrons have $m_s = +\frac{1}{2}$, we have:

$|1\ 0\rangle =$

$(2/\sqrt{10})\{|\psi_{+2}(1)\psi_{-2}(2) - \psi_{-2}(1)\psi_{+2}(2)\rangle\} - (1/\sqrt{10})\{|\psi_{+1}(1)\psi_{-1}(2) - \psi_{-1}(1)\psi_{+1}(2)\rangle\}$

The integral to be evaluated is $\langle 1\ 0|e^2/r_{12}|1\ 0\rangle$ and all 16 terms contribute. With experience, it is possible to select, *a priori*, the terms which contribute and those that are equal. Here it is best if we write them all out. Using Table B7.3.2 we find:

$(4/10)\langle\psi_{+2}(1)\psi_{-2}(2)|e^2/r_{12}|\psi_{+2}(1)\psi_{-2}(2)\rangle =$

$(4/10)\langle\psi_{-2}(1)\psi_{+2}(2)|e^2/r_{12}|\psi_{-2}(1)\psi_{+2}(2)\rangle = +(4/10)\{F_0 + 4F_2 + F_4\}$

$-(4/10)\langle\psi_{+2}(1)\psi_{-2}(2)|e^2/r_{12}|\psi_{-2}(1)\psi_{+2}(2)\rangle =$

$-(4/10)\langle\psi_{-2}(1)\psi_{+2}(2)|e^2/r_{12}|\psi_{+2}(1)\psi_{-2}(2)\rangle = -(4/10)\{70F_4\}$

$(1/10)\langle\psi_{+1}(1)\psi_{-1}(2)|e^2/r_{12}|\psi_{+1}(1)\psi_{-1}(2)\rangle =$

$(1/10)\langle\psi_{-1}(1)\psi_{+1}(2)|e^2/r_{12}|\psi_{-1}(1)\psi_{+1}(2)\rangle = +(1/10)\{F_0 + F_2 + 16F_4\}$

$-(1/10)\langle\psi_{+1}(1)\psi_{-1}(2)|e^2/r_{12}|\psi_{-1}(1)\psi_{+1}(2)\rangle =$

$-(1/10)\langle\psi_{-1}(1)\psi_{+1}(2)|e^2/r_{12}|\psi_{+1}(1)\psi_{-1}(2)\rangle = -(1/10)\{6F_2 + 40F_4\}$

$-(2/10)\langle\psi_{+2}(1)\psi_{-2}(2)|e^2/r_{12}|\psi_{+1}(1)\psi_{-1}(2)\rangle =$

$-(2/10)\langle\psi_{+1}(1)\psi_{-1}(2)|e^2/r_{12}|\psi_{+2}(1)\psi_{-2}(2)\rangle =$

$-(2/10)\langle\psi_{-2}(1)\psi_{+2}(2)|e^2/r_{12}|\psi_{-1}(1)\psi_{+1}(2)\rangle =$

$-(2/10)\langle\psi_{-1}(1)\psi_{+1}(2)|e^2/r_{12}|\psi_{-2}(1)\psi_{+2}(2)\rangle = -(2/10)\{-6F_2 - 5F_4\}$

$(2/10)\langle\psi_{+2}(1)\psi_{-2}(2)|e^2/r_{12}|\psi_{-1}(1)\psi_{+1}(2)\rangle =$

$(2/10)\langle\psi_{-1}(1)\psi_{+1}(2)|e^2/r_{12}|\psi_{+2}(1)\psi_{-2}(2)\rangle =$

$(2/10)\langle\psi_{-2}(1)\psi_{+2}(2)|e^2/r_{12}|\psi_{+1}(1)\psi_{-1}(2)\rangle =$

$(2/10)\langle\psi_{+1}(1)\psi_{-1}(2)|e^2/r_{12}|\psi_{-2}(1)\psi_{+2}(2)\rangle = +(2/10)\{-35F_4\}$

Total = $F_0 + 7F_2 - 84F_4 = A + 7B$ in terms of Racah parameters.

Problem 7.4.

Configuration a; $(xy)^1\,(xz)^1$

Since this is a singlet state the wavefunction must be:

$\psi_a = ½\{xy(1)xz(2) + xz(1)xy(2)\}\times\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$

$= ½\{xy\alpha(1)xz\beta(2) - xy\beta(1)xz\alpha(2) + xz\alpha(1)xy\beta(2) - xz\beta(1)xy\alpha(2)\}$

If an integral is to be non-zero the spin of an electron must not change between bra and ket. Therefore of the 16 potential terms only eight need be considered. They fall into two groups:

J integrals, e.g. $<xy\alpha(1)xz\beta(2)|e^2/r_{12}|xy\alpha(1)xz\beta(2)> \equiv J(xy,xz)$. There are 4 of these.

K integrals, e.g. $<xy\alpha(1)xz\beta(2)|e^2/r_{12}|xz\alpha(1)xy\beta(2)> \equiv K(xy,xz)$. There are 4 of these.

Therefore, $<\psi_a|e^2/r_{12}|\psi_a> = ¼\{4J(xy,xz) + 4\,K(xy,xz)\} = J(xy,xz) + K(xy,xz)\}$

and using Table B7.3.1

$= F_0 - 2F_2 - 4F_4 + 3F_2 + 20F_4 = F_0 + F_2 + 16F_4$

Configuration b; $(xy)^2$

$\psi_b = (1/\surd 2)\{xy\alpha(1)xy\beta(2) - xy\beta(1)xy\alpha(2)\}$

Therefore, $<\psi_b|e^2/r_{12}|\psi_b> = ½\{2J(xy,xy)\} = F_0 + 4F_2 + 36F_4$

Problem 7.5.

The d^1 spin-orbit coupling matrix is:

$$\begin{array}{lcccccccccc}
 & |+2+\rangle & |+2-\rangle & |+1+\rangle & |+1-\rangle & |0+\rangle & |0-\rangle & |-1+\rangle & |-1-\rangle & |-2+\rangle & |+2-\rangle \\
\langle +2+| & +\zeta & & & & & & & & & \\
\langle +2-| & & -\zeta & +\zeta & & & & & & & \\
\langle +1+| & & +\zeta & +\zeta/2 & & & & & & & \\
\langle +1+| & & & & -\zeta/2 & +\sigma\zeta & & & & & \\
\langle 0+| & & & & +\sigma\zeta & 0 & & & & & \\
\langle 0-| & & & & & & 0 & +\sigma\zeta & & & \\
\langle -1+| & & & & & & +\sigma\zeta & -\zeta/2 & & & \\
\langle -1-| & & & & & & & & +\zeta/2 & +\zeta & \\
\langle -2+| & & & & & & & & +\zeta & -\zeta & \\
\langle -2-| & & & & & & & & & & +\zeta
\end{array}$$

Where $\sigma = \sqrt{(3/2)}$

Two eigenvalues of $+\zeta$ are already clear.

To find further eigenvalues, we take the first 2×2 matrix, subtract λ from each diagonal element, multiply out as a determinant, equate to zero and solve the quadratic equation in λ.

$$(-\zeta - \lambda)(\zeta/2 - \lambda) - \zeta^2 = 0 \quad \Rightarrow \lambda^2 + \zeta\lambda/2 - 3\zeta^2/2 = 0$$
$$\Rightarrow (\lambda - \zeta)(\lambda + 3\zeta/2) = 0 \quad \Rightarrow \quad \lambda = +\zeta \text{ and } -3\zeta/2$$

The last 2×2 matrix along the diagonal gives the same result.

The two matrices in the centre each give:

$$\lambda(\zeta/2 + \lambda) - 3\zeta^2/2 = 0 \quad \Rightarrow \lambda^2 + \zeta\lambda/2 - 3\zeta^2/2 = 0$$
$$\Rightarrow (\lambda - \zeta)(\lambda + 3\zeta/2) = 0 \quad \Rightarrow \quad \lambda = +\zeta \text{ and } -3\zeta/2$$

Therefore, we have in total 6 eigenvalues of $+\zeta$ and 4 of $-3\zeta/2$.

Problem 7.6.

The energy matrix for the $[MH_4]^{4-}$ ion looks like this:

$$
\begin{array}{cccccccccc}
 & z^2 & x^2\text{-}y^2 & xy & xz & yz & \phi 1 & \phi 2 & \phi 3 & \phi 4 \\
z^2 & E\mathrm{d} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
x^2\text{-}y^2 & 0 & E\mathrm{d} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
xy & 0 & 0 & E\mathrm{d} & 0 & 0 & +\beta & -\beta & -\beta & +\beta \\
xz & 0 & 0 & 0 & E\mathrm{d} & 0 & +\beta & +\beta & -\beta & -\beta \\
yz & 0 & 0 & 0 & 0 & E\mathrm{d} & +\beta & -\beta & +\beta & -\beta \\
\phi 1 & 0 & 0 & +\beta & +\beta & +\beta & E\mathrm{s} & 0 & 0 & 0 \\
\phi 2 & 0 & 0 & -\beta & +\beta & -\beta & 0 & E\mathrm{s} & 0 & 0 \\
\phi 3 & 0 & 0 & -\beta & -\beta & +\beta & 0 & 0 & E\mathrm{s} & 0 \\
\phi 4 & 0 & 0 & +\beta & -\beta & -\beta & 0 & 0 & 0 & E\mathrm{s}
\end{array}
$$

When the ϕ's are combined in the manner suggested the result is the following blocked-out matrix:

$$
\begin{array}{cccccccccc}
 & z^2 & x^2\text{-}y^2 & xy & xz & yz & \Psi xy & \Psi xz & \Psi yz & \Psi s \\
z^2 & E\mathrm{d} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
x^2\text{-}y^2 & 0 & E\mathrm{d} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
xy & 0 & 0 & E\mathrm{d} & 0 & 0 & +2\beta & 0 & 0 & 0 \\
xz & 0 & 0 & 0 & E\mathrm{d} & 0 & 0 & +2\beta & 0 & 0 \\
yz & 0 & 0 & 0 & 0 & E\mathrm{d} & 0 & 0 & +2\beta & 0 \\
\Psi xy & 0 & 0 & +2\beta & 0 & 0 & E\mathrm{s} & 0 & 0 & 0 \\
\Psi xz & 0 & 0 & 0 & +2\beta & 0 & 0 & E\mathrm{s} & 0 & 0 \\
\Psi yz & 0 & 0 & 0 & 0 & +2\beta & 0 & 0 & E\mathrm{s} & 0 \\
\Psi s & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & E\mathrm{s}
\end{array}
$$

There are 2 eigenvalues of Ed and 1 of Es. As inspection of the matrix shows, the two values of Ed correspond to the two d-orbitals, z^2 and x^2-y^2, which do not interact with the H1s orbitals. In group theoretical language, these are the E pair. The value of Es is that of a combination of the H1s orbitals which does not interact with the metal orbitals.

The remainder of the matrix consists of 3 identical 2×2 matrices of the form:

$$
\begin{array}{cc}
E\mathrm{d} & +2\beta \\
+2\beta & E\mathrm{s}
\end{array}
$$

the eigenvalues of which are easily found to be:

$$E = \tfrac{1}{2}[E\mathrm{d} + E\mathrm{s} \pm \{(E\mathrm{d} - E\mathrm{s})^2 + 16\beta^2\}^{\frac{1}{2}}]$$

Clearly, these three matrices will give rise to two sets of three degenerate levels. If we assume, as we do in what follows, that the metal d-orbitals initially lie at a considerably higher energy than the H1s orbitals, then the set of three orbitals which have the higher (less negative energy, T_2 in group-theoretical language) will be the set which are primarily composed of metal d. If the matrices are diagonalised with the energy values given it is found that the percentage of metal d-orbital in the higher-energy set of three is ~85%.

Therefore, using the data provided, the energy of the E set of d-orbitals is -50×10^3 cm^{-1} and that of the T_2 set is calculated from the above equation to be -37.5×10^3 cm^{-1}.

Thus we expect to find the d-d transition at $(-37.5 + 50.0)\times10^3 = 12.5\times10^3$ cm^{-1} which corresponds to a wavelength of $(1/12.5)\times10^{-3}$ cm = 800 nm.