Chapter 7

Atomic spectra and atomic structure

Exercises

7.1 The Rydberg constant R_∞ replaces the μ in eqn 7.2 for R_H by m_e:

$$R_\infty = \frac{m_e e^4}{8h^3 c\varepsilon_0^2} = \frac{1}{2}\left(\frac{e^2}{2hc\varepsilon_0}\right)^2 \times \left(\frac{m_e c}{h}\right) = \frac{\alpha^2}{2\lambda_C}$$

7.2 $\tilde{\nu} = R_{He^+} \times \{(1/n_1^2) - (1/n_2^2)\}$ [eqn 7.3]

$R_{He^+} = Z^2(\mu_{He^+}/m_e)R_\infty$ [eqn 7.31b]

$\mu_{He^+} = mm_e/(m + m_e)$, $m = m(He^{2+})$; $R_\infty = 109\,737.31\ \text{cm}^{-1}$

$$\begin{aligned} m(He^{2+}) &= m({}^4_2He) - 2m_e \\ &= 4.0026 \times (1.660\,54 \times 10^{-27}\ \text{kg}) - 2(9.109\,38 \times 10^{-31}\ \text{kg}) \\ &= 6.6447 \times 10^{-27}\ \text{kg} \end{aligned}$$

$R_{He^+} = 4R_\infty/(1.000\,14) = 4.3889 \times 10^5\ \text{cm}^{-1}$

Therefore, the transitions are predicted to lie at

$$\begin{aligned} \tilde{\nu}/\text{cm}^{-1} &= 4.3889 \times 10^5\{\tfrac{1}{4} - (1/n^2)\},\ n = 3, 4, \ldots \\ &= 6.0957 \times 10^4, 8.2292 \times 10^4, 9.2167 \times 10^4, \ldots 1.0972 \times 10^5 \end{aligned}$$

Exercise: Find the positions of the corresponding lines in Li^{2+}.

7.3 The wavenumber of the transition $n_2 \rightarrow n_1$ in atomic hydrogen is given by eqn 7.3; we will replace μ by m_e and use the value of the Rydberg constant given in the inside front cover. The longest possible wavelength (smallest wavenumber) for a series will be the transition from $n_1 + 1 \rightarrow n_1$ where n_1 for each series is given in Section 7.1. The shortest possible wavelength (the series limit) will be given by $n_2 = \infty \rightarrow n_1$; in this case, the transition wavenumber simplifies to $\mathcal{R}_H \times (1/n_1^2)$.

(a) For the Lyman series, $n_1 = 1$. The smallest wavenumber is

$$\tilde{\nu} = \left(\frac{1}{1^2} - \frac{1}{2^2}\right) \times 1.097\,37 \times 10^5 \text{ cm}^{-1} = 82\,303 \text{ cm}^{-1}$$

and the longest possible wavelength is

$$\lambda = 1/\ \tilde{\nu}\ = 1.2150 \times 10^{-5} \text{ cm} = \underline{121.50 \text{ nm}}$$

The series limit is

$$\tilde{\nu} = \frac{\mathcal{R}}{1^2} = 109\,737 \text{ cm}^{-1}$$

and the shortest possible wavelength is

$$\lambda = 1/\tilde{\nu}\ = 9.1127 \times 10^{-6} \text{ cm} = \underline{91.127 \text{ nm}}$$

(b) For the Balmer series, $n_1 = 2$. The smallest wavenumber is

$$\tilde{\nu} = \left(\frac{1}{2^2} - \frac{1}{3^2}\right) \times 1.097\,37 \times 10^5 \text{ cm}^{-1} = 15\,241 \text{ cm}^{-1}$$

and the longest possible wavelength is

$$\lambda = 1/\ \tilde{\nu} = 6.5612 \times 10^{-5}\ \text{cm} = \underline{656.12\ \text{nm}}$$

The series limit is

$$\tilde{\nu}\ = \frac{\mathrm{R}}{2^2} = 27\ 434\ \text{cm}^{-1}$$

and the shortest possible wavelength is

$$\lambda = 1/\ \tilde{\nu} = 3.6451 \times 10^{-5}\ \text{cm} = \underline{364.51\ \text{nm}}$$

(c) For the Paschen series, $n_1 = 3$. The smallest wavenumber is

$$\tilde{\nu}\ = \left(\frac{1}{3^2} - \frac{1}{4^2}\right) \times 1.097\ 37 \times 10^5\ \text{cm}^{-1} = 5334.5\ \text{cm}^{-1}$$

and the longest possible wavelength is

$$\lambda = 1/\ \tilde{\nu} = 1.8746 \times 10^{-4}\ \text{cm} = \underline{1874.6\ \text{nm}}$$

The series limit is

$$\tilde{\nu} = \frac{\mathrm{R}}{3^2} = 12\ 193\ \text{cm}^{-1}$$

and the shortest possible wavelength is

$$\lambda = 1/\tilde{\nu} = 8.2014 \times 10^{-5}\ \text{cm} = \underline{820.14\ \text{nm}}$$

(d) For the Brackett series, $n_1 = 4$. The smallest wavenumber is

$$\tilde{\nu} = \left(\frac{1}{4^2} - \frac{1}{5^2}\right) \times 1.097\ 37 \times 10^5\ \text{cm}^{-1} = 2469.1\ \text{cm}^{-1}$$

and the longest possible wavelength is

$$\lambda = 1/\tilde{\nu} = 4.0501 \times 10^{-4}\ \text{cm} = \underline{4050.1\ \text{nm}}$$

The series limit is

$$\tilde{\nu} = \frac{\mathsf{R}}{4^2} = 6858.6\ \text{cm}^{-1}$$

and the shortest possible wavelength is

$$\lambda = 1/\tilde{\nu} = 1.4580 \times 10^{-4}\ \text{cm} = \underline{1458.0\ \text{nm}}$$

Exercise: Repeat the problem for the spectrum of He^+.

7.4 $\mu/m_e = 1/(1 + m_e/m_\mu) = 1/(1 + 1/207) = 0.995$

$$\tilde{\nu} = \mathsf{R}_\mu\{(1/n_1^2) - (1/n_2^2)\} = 0.995\mathsf{R}_\infty\{(1/n_1^2) - (1/n_2^2)\}$$

$$= \underline{(1.092 \times 10^5\ \text{cm}^{-1}) \times \{(1/n_1^2) - (1/n_2^2)\}}$$

with $n_1 = 1, 2, \ldots$ and $n_2 = n_1 + 1, n_1 + 2, \ldots$. The ionization limit (for $n_1 = 1$) lies at $1.092 \times 10^5\ \text{cm}^{-1}(\lambda = 91.58\ \text{nm})$.

Exercise: Predict the form of the spectrum of positronium (e^+, e^-).

7.5 Draw on $\Delta l = \pm 1$. Then the allowed transitions are

$$\underline{1s \rightarrow 2p,\ 2p \rightarrow 3d,\ \text{and}\ 3s \rightarrow 5p}$$

Exercise: Which of the following are electric-dipole allowed: 5s → 2p, 5s → 3d, 5s → 5f, 5s → 5p?

7.6 $E_n = -\mathsf{R}/n^2$. For convenience, take the energy minimum as $E_1 \equiv 0$;

$$E_n = \mathrm{R}\{1 - 1/n^2\} = 0,\ \tfrac{3}{4}\mathrm{R},\ \tfrac{8}{9}\mathrm{R},\ \tfrac{15}{16}\mathrm{R},\ldots$$

The data fit this sequence with

$$\mathrm{R}/\mathrm{cm}^{-1} = 2\,743\,963,\ 2\,744\,051,\ 2\,744\,067$$

and mean value 2 744 027. Write $\mathrm{R} = Z^2\mathrm{R}_\infty$ [ignore mass correction]; then $Z = 5.00$. The ion is therefore $\underline{\mathrm{B}^{4+}}$.

The ionization energy is given by the series limit ($n = \infty$), which lies at $\mathrm{R} =$ 2 744 027 cm^{-1}. Hence $I = hc\mathrm{R} = 5.450\,87 \times 10^{-17}$ J, corresponding to 3.283×10^4 kJ mol^{-1} and 340.2 eV.

Exercise: Identify the one-electron ion giving rise to a spectrum showing that its *n*p-orbitals were at 0, 6 666 000 cm^{-1}, 7 901 000 cm^{-1}, . . . Predict its ionization energy (in kJ mol^{-1} and eV).

7.7 The electric dipole transition moment is given by $< 3\mathrm{p}_z \mid \mu_z \mid 1\mathrm{s} >$ where

$$\mu_z = -er\cos\theta$$

$$\psi_{1\mathrm{s}} = \left(\frac{1}{\pi}\right)^{1/2}\left(\frac{Z}{a_0}\right)^{3/2} \mathrm{e}^{-Zr/a_0}$$

$$\psi_{3\mathrm{p}_z} = \left(\frac{1}{648\pi}\right)^{1/2}\left(\frac{Z}{a_0}\right)^{3/2}\left(4 - \frac{2Zr}{3a_0}\right)\left(\frac{2Zr}{3a_0}\right)\mathrm{e}^{-Zr/3a_0}\cos\theta$$

Therefore, the transition dipole moment is

$$\begin{aligned}\langle 3\mathrm{p}_z|\mu_z|1\mathrm{s}\rangle \\ &= -e\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\int_{r=0}^{\infty}\left(\frac{1}{648\pi^2}\right)^{1/2}\left(\frac{Z}{a_0}\right)^3 \\ &\times\left(4 - \frac{2Zr}{3a_0}\right)\left(\frac{2Zr}{3a_0}\right)\mathrm{e}^{-4Zr/3a_0}r^3\cos^2\theta\sin\theta\mathrm{d}\theta\mathrm{d}\varphi\mathrm{d}r\end{aligned}$$

The integration over φ yields 2π and that over θ yields 2/3. The integration over r, which can be done using mathematical software or standard integration tables, yields $(1/648\pi^2)^{1/2}(a_0/Z)\times(-2187/16)$. The net result is

$$\langle 3\mathrm{p}_z|\mu_z|1\mathrm{s}\rangle = \frac{729}{4\sqrt{648}}\frac{ea_0}{Z}$$

7.8 The spin-orbit coupling constant ζ for a hydrogenic atom is given by eqn 7.20; here $Z = 3$ (Li^{2+}). Using the values of α and R_∞ given in the inside front cover, we find (a) $n = 2$, $l = 1$, $\zeta = 19.72\ \mathrm{cm}^{-1}$; (b) $n = 3$, $l = 2$, $\zeta = 1.17\ \mathrm{cm}^{-1}$.

7.9 Li : $1\mathrm{s}^2 2\mathrm{s}^1$, ${}^2\mathrm{S}_{1/2}$

Be : $1\mathrm{s}^2 2\mathrm{s}^2$, ${}^1\mathrm{S}_0$

B : $1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^1$, ${}^2\mathrm{P}_{1/2}$, ${}^2\mathrm{P}_{3/2}$ with $E({}^2\mathrm{P}_{1/2}) < E({}^2\mathrm{P}_{3/2})$

C : $1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^2$, ${}^1\mathrm{D}_2$; ${}^3\mathrm{P}_2$, ${}^3\mathrm{P}_1$, ${}^3\mathrm{P}_0$; ${}^1\mathrm{S}_0$

with $E({}^3\mathrm{P}_0) < E({}^3\mathrm{P}_1) < E({}^3\mathrm{P}_2) < E({}^1\mathrm{D}_2) < E({}^1\mathrm{S}_0)$

N : $1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^3$; $(l = 1) \times (l = 1) = (L = 2, 1, 0)$

$(l = 1) \times (L = 2, 1, 0) = (L = 3, 2, 1 \text{ and } 2, 1, 0 \text{ and } 1)$

Hence, $2\mathrm{p}^3$ gives rise to F, 2D, 3P, S terms. Three spin-$\frac{1}{2}$ species can give rise to $S = (\frac{1}{2}\times\frac{1}{2})\times\frac{1}{2} = (1+0)\times\frac{1}{2} = \frac{3}{2}+\frac{1}{2}+\frac{1}{2}$, or to one quartet and two doublets. Three *equivalent* p-electrons are constrained by the Pauli principle, and can give rise only to ${}^4\mathrm{S}$, ${}^2\mathrm{D}$, ${}^2\mathrm{P}$. Therefore, for N we predict ${}^4\mathrm{S} < {}^2\mathrm{D} < {}^2\mathrm{P}$ (as observed).

O : $1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^4 \equiv 1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^6 2\mathrm{p}^{-2}$ [particle-hole formalism]; this configuration gives rise to ${}^1\mathrm{D}_2$; ${}^3\mathrm{P}_2$, ${}^3\mathrm{P}_1$, ${}^3\mathrm{P}_0$; ${}^1\mathrm{S}_0$ with ${}^3\mathrm{P}_2 < {}^3\mathrm{P}_1 < {}^3\mathrm{P}_0 < {}^1\mathrm{D}_2 < {}^1\mathrm{S}_0$

F : $1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^5 \equiv 1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^6 2\mathrm{p}^{-1}$; ${}^2\mathrm{P}_{1/2}$, ${}^2\mathrm{P}_{3/2}$ with ${}^2\mathrm{P}_{3/2} < {}^2\mathrm{P}_{1/2}$.

Ne : $1s^2 2s^2 2p^6$, ${}^1S_0$.

Exercise: Establish the terms for the atoms Na to Cl.

7.10

$$H = -(\hbar^2/2m_e)(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - (3e^2/4\pi\varepsilon_0)\{(1/r_1) + (1/r_2) + (1/r_3)\}$$

$$+ (e^2/4\pi\varepsilon_0)\{(1/r_{12}) + (1/r_{23}) + (1/r_{13})\}$$

$$= H^{(0)} + H^{(1)}; \qquad H^{(0)} = H_1 + H_2 + H_3$$

$$H_i = -(\hbar^2/2m_e)\nabla_i^2 - (3e^2/4\pi\varepsilon_0)(1/r_i) \quad i = 1, 2, 3$$

$$H^{(1)} = (e^2/4\pi\varepsilon_0)\{(1/r_{12}) + (1/r_{23}) + (1/r_{13})\}$$

$$H^{(0)}\psi(1)\psi(2)\psi(3) = (H_1 + H_2 + H_3)\psi(1)\psi(2)\psi(3)$$

$$= \{H_1\psi(1)\}\psi(2)\psi(3) + \psi(1)\{H_2\psi(2)\}\psi(3) + \psi(1)\psi(2)\{H_3\psi(3)\}$$

$$= (E_1 + E_2 + E_3)\psi(1)\psi(2)\psi(3) = E^{(0)}\psi(1)\psi(2)\psi(3)$$

Exercise: Write the general form of the hamiltonian for a Z-electron neutral atom, and show that $H^{(0)}\psi(1, \ldots, Z) = E^{(0)}\psi(1, \ldots, Z)$, with $\psi(1, \ldots, Z)$ a product of one-electron orbitals.

7.11 We use the notation introduced in Section 7.11 for the spinorbital, a joint spin-space state of the electron. The Slater determinant (eqn 7.42a) corresponding to the ground state of atomic lithium, taking the spin state of the 2s electron to be α, is

$$\psi(1, 2, 3) = (1/3!)^{1/2} \begin{vmatrix} \psi_{1s}^{\alpha}(1) & \psi_{1s}^{\beta}(1) & \psi_{2s}^{\alpha}(1) \\ \psi_{1s}^{\alpha}(2) & \psi_{1s}^{\beta}(2) & \psi_{2s}^{\alpha}(2) \\ \psi_{1s}^{\alpha}(3) & \psi_{1s}^{\beta}(3) & \psi_{2s}^{\alpha}(3) \end{vmatrix}$$

We demonstrate here the antisymmetry of $\psi(1, 2, 3)$ upon interchange of the labels of electrons 1 and 2. Explicitly expanding the above determinant, we find

$$\begin{aligned}\psi(1,2,3) = (1/6)^{1/2} \quad & [\psi_{1s}^{\alpha}(1)\psi_{1s}^{\beta}(2)\psi_{2s}^{\alpha}(3) + \psi_{1s}^{\beta}(1)\psi_{2s}^{\alpha}(2)\psi_{1s}^{\alpha}(3) + \\ & \psi_{2s}^{\alpha}(1)\psi_{1s}^{\alpha}(2)\psi_{1s}^{\beta}(3) - \psi_{2s}^{\alpha}(1)\psi_{1s}^{\beta}(2)\psi_{1s}^{\alpha}(3) - \\ & \psi_{1s}^{\alpha}(1)\psi_{2s}^{\alpha}(2)\psi_{1s}^{\beta}(3) - \psi_{1s}^{\beta}(1)\psi_{1s}^{\alpha}(2)\psi_{2s}^{\alpha}(3)]\end{aligned}$$

while interchange of labels 1 and 2 yields

$$\begin{aligned}\psi(1,2,3) = (1/6)^{1/2} \quad & [\psi_{1s}^{\alpha}(2)\psi_{1s}^{\beta}(1)\psi_{2s}^{\alpha}(3) + \psi_{1s}^{\beta}(2)\psi_{2s}^{\alpha}(1)\psi_{1s}^{\alpha}(3) + \\ & \psi_{2s}^{\alpha}(2)\psi_{1s}^{\alpha}(1)\psi_{1s}^{\beta}(3) - \psi_{2s}^{\alpha}(2)\psi_{1s}^{\beta}(1)\psi_{1s}^{\alpha}(3) - \\ & \psi_{1s}^{\alpha}(2)\psi_{2s}^{\alpha}(1)\psi_{1s}^{\beta}(3) - \psi_{1s}^{\beta}(2)\psi_{1s}^{\alpha}(1)\psi_{2s}^{\alpha}(3)] \\ & = -\psi(1,2,3)\end{aligned}$$

as required.

Exercise: Write the Slater determinant for the configuration $1s^2 2s^1$ of a lithium atom in which both of the 1s electrons have the same spin state; show that this determinant is identically zero.

7.12 To confirm the radial integration in Example 7.2, we need to show

$$\int_0^\infty \left\{\int_0^{r_2} \frac{r_1^2 \mathrm{e}^{-2Zr_1/a_0}}{r_2}\,\mathrm{d}r_1 + \int_{r_2}^\infty \frac{r_1^2 \mathrm{e}^{-2Zr_1/a_0}}{r_1}\,\mathrm{d}r_1\right\} r_2^2 \mathrm{e}^{-2Zr_2/a_0}\,\mathrm{d}r_2 = \frac{5}{2^7}\left(\frac{a_0}{Z}\right)^5$$

We use the following results:

$$\int_0^{r_2} \frac{r_1^2\mathrm{e}^{-2Zr_1/a_0}}{r_2}\mathrm{d}r_1$$
$$= \frac{1}{r_2}\int_0^{r_2} r_1^2\mathrm{e}^{-2Zr_1/a_0}\mathrm{d}r_1 = -\mathrm{e}^{-2Zr_2/a_0}\left(\frac{a_0 r_2}{2Z}+\frac{a_0^2}{2Z^2}\right)$$
$$+\left(-\mathrm{e}^{-2Zr_2/a_0}+1\right)\frac{a_0^3}{4Z^3 r_2}$$

$$\int_{r_2}^{\infty} \frac{r_1^2\mathrm{e}^{-2Zr_1/a_0}}{r_1}\mathrm{d}r_1 = \frac{a_0^2\mathrm{e}^{-2Zr_2/a_0}}{4Z^2}\left(\frac{2Zr_2}{a_0}+1\right)$$

Substitution of the above two integrals then produces

$$\int_0^{\infty}\left\{\int_0^{r_2} \frac{r_1^2\mathrm{e}^{-\frac{2Zr_1}{a_0}}}{r_2}\mathrm{d}r_1 + \int_{r_2}^{\infty} \frac{r_1^2\mathrm{e}^{-\frac{2Zr_1}{a_0}}}{r_1}\mathrm{d}r_1\right\} r_2^2\mathrm{e}^{-\frac{2Zr_2}{a_0}}\mathrm{d}r_2$$
$$= \int_0^{\infty}\left\{-\mathrm{e}^{-4Zr_2/a_0}\left(\frac{a_0 r_2^3}{2Z}+\frac{r_2^2 a_0^2}{2Z^2}\right)\right.$$
$$\left. +\left(-\mathrm{e}^{-4Zr_2/a_0}+\mathrm{e}^{-2Zr_2/a_0}\right)\frac{a_0^3 r_2}{4Z^3} + \frac{a_0^2\mathrm{e}^{-4Zr_2/a_0}}{4Z^2}\left(\frac{2Zr_2^3}{a_0}+r_2^2\right)\right\}\mathrm{d}r_2$$
$$= \int_0^{\infty}\left\{-\mathrm{e}^{-4Zr_2/a_0}\left(\frac{r_2^2 a_0^2}{4Z^2}\right) + \left(-\mathrm{e}^{-4Zr_2/a_0}+\mathrm{e}^{-2Zr_2/a_0}\right)\frac{a_0^3 r_2}{4Z^3}\right\}\mathrm{d}r_2$$

Using the standard integral

$$\int_0^{\infty} r^n\mathrm{e}^{-ar}\mathrm{d}r = \frac{n!}{a^{n+1}}$$

we obtain

$$\int_0^\infty \left\{\int_0^{r_2} \frac{r_1^2 \mathrm{e}^{-\frac{2Zr_1}{a_0}}}{r_2}\,\mathrm{d}r_1 + \int_{r_2}^\infty \frac{r_1^2 \mathrm{e}^{-\frac{2Zr_1}{a_0}}}{r_1}\,\mathrm{d}r_1\right\} r_2^2 \mathrm{e}^{-\frac{2Zr_2}{a_0}}\,\mathrm{d}r_2$$

$$= \left\{\frac{-2a_0^2}{4Z^2\left(\frac{4Z}{a_0}\right)^3} + \frac{-a_0^3}{4Z^3\left(\frac{4Z}{a_0}\right)^2} + \frac{a_0^3}{4Z^3\left(\frac{2Z}{a_0}\right)^2}\right\} = \left(\frac{a_0}{Z}\right)^5\left\{\frac{-1}{2^7} + \frac{-2}{2^7} + \frac{2^3}{2^7}\right\}$$

$$= \frac{5}{2^7}\left(\frac{a_0}{Z}\right)^5$$

as in Example 7.2.

7.13 A 3p Slater orbital of effective nuclear charge Z_{eff} is given by (see 7.41, $n_{\text{eff}} = 3$)

$$\psi = Nr^2\mathrm{e}^{-Z_{\text{eff}}r/3a_0}Y_{1,m_l}$$

We first determine the normalization constant N using the standard integral given in the solution above to Exercise 7.12. Since the spherical harmonic Y is normalized, we only need to be concerned with the radial integral.

$$1 = \int_0^\infty N^2 r^4 \mathrm{e}^{-2Z_{\text{eff}}r/3a_0} r^2\,\mathrm{d}r = N^2\frac{6!\,a_0^7}{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}$$

and therefore

$$N = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^{7/2}}{720^{1/2}a_0^{7/2}}$$

To find the expectation values of r^n, we only need be concerned with the radial integral since the spherical harmonic is normalized. We again make use of the standard integral

$$\int_0^\infty r^n\mathrm{e}^{-ar}\,\mathrm{d}r = \frac{n!}{a^{n+1}}$$

(a)

$$\langle r\rangle = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^2\mathrm{e}^{-Z_{\text{eff}}r/3a_0}rr^2\mathrm{e}^{-Z_{\text{eff}}r/3a_0}r^2\mathrm{d}r = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^7\mathrm{e}^{-2Z_{\text{eff}}r/3a_0}\mathrm{d}r$$

$$= \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\times\frac{7!}{\left(\frac{2Z_{\text{eff}}}{3a_0}\right)^8} = \frac{21a_0}{2Z_{\text{eff}}}$$

(b)

$$\langle 1/r\rangle = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^2\mathrm{e}^{-\frac{Z_{\text{eff}}r}{3a_0}}(1/r)r^2\mathrm{e}^{-Z_{\text{eff}}r/3a_0}r^2\mathrm{d}r = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^5\mathrm{e}^{-2Z_{\text{eff}}r/3a_0}\mathrm{d}r$$

$$= \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\times\frac{5!}{\left(\frac{2Z_{\text{eff}}}{3a_0}\right)^6} = \frac{Z_{\text{eff}}}{9a_0}$$

(c)

$$\langle 1/r^3\rangle = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^2\mathrm{e}^{-\frac{Z_{\text{eff}}r}{3a_0}}(1/r^3)r^2\mathrm{e}^{-Z_{\text{eff}}r/3a_0}r^2\mathrm{d}r = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^3\mathrm{e}^{-2Z_{\text{eff}}r/3a_0}\mathrm{d}r$$

$$= \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\times\frac{3!}{\left(\frac{2Z_{\text{eff}}}{3a_0}\right)^4} = \frac{Z_{\text{eff}}^3}{405a_0^3}$$

7.14 Consider the four-electron Be atom with electron configuration $1s^22s^2$. From eqn 7.49,

$$E = 2\varepsilon_{1s} + 2\varepsilon_{2s} - (2J_{1s1s} - K_{1s1s} + 2J_{1s2s} - K_{1s2s} + 2J_{2s1s} - K_{2s1s} + 2J_{2s2s} - K_{2s2s})$$

Since, $J_{1s1s} = K_{1s1s}$, $J_{2s2s} = K_{2s2s}$, $J_{1s2s} = J_{2s1s}$, and $K_{1s2s} = K_{2s1s}$, this simplifies to

$$E = 2\varepsilon_{1s} + 2\varepsilon_{2s} - (J_{1s1s} + 4J_{1s2s} - 2K_{1s2s} + J_{2s2s})$$

From eqn 7.48a,

$$\varepsilon_{1s} = E_{1s} + 2J_{1s1s} + 2J_{2s1s} - K_{1s1s} - K_{2s1s}$$

$$\varepsilon_{2s} = E_{2s} + 2J_{1s2s} + 2J_{2s2s} - K_{1s2s} - K_{2s2s}$$

Therefore, substituting the above expressions for ε into the equation for E and again noting that $J_{1s1s} = K_{1s1s}$, $J_{2s2s} = K_{2s2s}$, $J_{1s2s} = J_{2s1s}$, and $K_{1s2s} = K_{2s1s}$, we obtain

$$E = 2E_{1s} + 2E_{2s} + J_{1s1s} + J_{2s2s} - 2K_{1s2s} + 4J_{1s2s}$$

This is the expression formally found in Problem 7.19.

7.15 ^{1}S : $J = (0 \times 0) = 0$; hence $\underline{^1\text{S}_0}$

^{2}P : $J = (\frac{1}{2} \times 1) = \frac{3}{2} + \frac{1}{2}$; hence $\underline{^2\text{P}_{3/2}, {}^2\text{P}_{1/2}}$

^{3}P : $J = (1 \times 1) = 2 + 1 + 0$; hence $\underline{^3\text{P}_2, {}^3\text{P}_1, {}^3\text{P}_0}$

^{3}D : $J = (1 \times 2) = 3 + 2 + 1$; hence $\underline{^3\text{D}_3, {}^3\text{D}_2, {}^3\text{D}_1}$

^{2}D : $J = (\frac{1}{2} \times 2) = \frac{5}{2} + \frac{3}{2}$; hence $\underline{^2\text{D}_{5/2}, {}^2\text{D}_{3/2}}$

^{1}D : $J = (0 \times 2) = 2$; hence $\underline{^1\text{D}_2}$

^{4}D : $J = (\frac{3}{2} \times 2) = \frac{7}{2} + \frac{5}{2} + \frac{3}{2} + \frac{1}{2}$;

hence $\underline{^4\text{D}_{7/2}, {}^4\text{D}_{5/2}, {}^4\text{D}_{3/2}, {}^4\text{D}_{1/2}}$

Exercise: What levels may arise from the terms ^{4}F, ^{4}D, ^{4}P?

7.16 $1s^12p^1$: $L = 1$; $S = 0, 1$; hence ^{1}P, ^{3}P with levels $^1\text{P}_1$, $^3\text{P}_2$, $^3\text{P}_1$, $^3\text{P}_0$.

Energies: $\underline{^3\text{P}_0 < {}^3\text{P}_1 < {}^3\text{P}_2 < {}^1\text{P}_1}$ [Hund rules]

$2p^13p^1$: $L = 2, 1, 0$; $S = 0,1$; hence ^{3}D, ^{1}D, ^{3}P, ^{1}P, ^{3}S, ^{1}S.

Energies: $\underline{^3\text{D}_1 < {}^3\text{D}_2 < {}^3\text{D}_3 < {}^3\text{P}_0 < {}^3\text{P}_1 < {}^3\text{P}_2}$

$\underline{< {}^3\text{S}_1 < {}^1\text{D}_2 < {}^1\text{P}_1 < {}^1\text{S}_0}$

$3p^13d^1$: $L = 3, 2, 1$; $S = 0,1$; hence ^{3}F, ^{1}F, ^{3}D, ^{1}D, ^{3}P, ^{1}P.

Energies: $\underline{^3\text{F}_2 < {}^3\text{F}_3 < {}^3\text{F}_4 < {}^3\text{D}_1 < {}^3\text{D}_2 < {}^3\text{D}_3}$

$\underline{< {}^3\text{P}_0 < {}^3\text{P}_1 < {}^3\text{P}_2 < {}^1\text{F}_3 < {}^1\text{D}_2 < {}^1\text{P}_1}$

Exercise: Arrange in order of increasing energy the levels and terms arising from $1s^1 3p^1$, $3p^2$, $2s^1 4f^1$, $5g^2$.

7.17 **(a)** d^2 : $L = (2 \times 2) = 4 + 3 + 2 + 1 + 0$; $S = 1, 0$ but the Pauli principle forbids ^3G (and alternate triplets). Hence $\underline{^1G,\ ^3F,\ ^1D,\ ^3P,\ ^1S}$ arise.

(b) f^2 : $L = (3 \times 3) = 6 + 5 + \ldots + 0$; $S = 1, 0$. Pauli forbids ^3I etc.; hence $\underline{^1I,\ ^3H,\ ^1G,\ ^3F,\ ^1D,\ ^3P,\ ^1S}$ arise.

Exercise: What terms may arise from the general $(nl)^2$ configuration?

7.18 Using group theoretical arguments (as in eqn 7.70), we find:

(a) For d^2: $\Gamma^{(2)} \times \Gamma^{(2)} = \Gamma^{(4)} + [\,\Gamma^{(3)}\,] + \Gamma^{(2)} + [\,\Gamma^{(1)}\,] + \Gamma^{(0)}$

$$\Gamma^{(1/2)} \times \Gamma^{(1/2)} = \Gamma^{(1)} + [\,\Gamma^{(0)}\,]$$

Since $[\,\Gamma^{(0)}\,]$ is associated with the antisymmetric singlet spin state and the overall wavefunction must be antisymmetric, we conclude that (symmetric) $\Gamma^{(4)}$ (a G state) must be a singlet state. Similarly, symmetric $\Gamma^{(2)}$ (a D state) and symmetric $\Gamma^{(0)}$ (an S state) must be singlets. The antisymmetric $[\,\Gamma^{(3)}\,]$ (an F state) and antisymmetric $[\,\Gamma^{(1)}]$ (a P state) must be triplets.

(b) For f^2: $\Gamma^{(3)} \times \Gamma^{(3)} = = \Gamma^{(6)} + [\,\Gamma^{(5)}\,] + \Gamma^{(4)} + [\,\Gamma^{(3)}\,] + \Gamma^{(2)} + [\,\Gamma^{(1)}\,] + \Gamma^{(0)}$

$$\Gamma^{(1/2)} \times \Gamma^{(1/2)} = \Gamma^{(1)} + [\,\Gamma^{(0)}\,]$$

By the same arguments an in part **(a)**, $\Gamma^{(6,4,2,0)}$ (I, G, D, S states) must be singlet states and $[\,\Gamma^{(5,3,1)}\,]$ (H, F, P states) must be triplet states.

7.19 $E^{(1)} = \mu_B \mathcal{B} M_L$ [eqn 7.72]

$\Delta E^{(1)} = \mu_B \mathcal{B}$; $\Delta\tilde{\nu} = (\mu_B/hc)\mathcal{B}$

Therefore, $\mathcal{B} = hc\Delta\tilde{\nu}/\mu_B = \underline{2.14\ \text{T}}$ when $\tilde{\nu} = 1\ \text{cm}^{-1}$.

Exercise: Calculate the magnetic field required to produce a splitting of $1\ \text{cm}^{-1}$ between the states of a $^1D_2$ level.

7.20

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \text{[eqn 7.76]}$$

(a) $J_{\max} = L + S$,

$$g_{L+S} = 1 + \frac{(L+S)(L+S+1) + S(S+1) - L(L+1)}{2(L+S)(L+S+1)}$$

$$= \underline{1 + S/(L+S)}$$

(b) $J_{\min} = L - S$ (for $S \leq L$)

$$g_{L-S} = 1 + \frac{(L-S)(L-S+1) + S(S+1) - L(L+1)}{2(L-S)(L-S+1)}$$

$$= \underline{1 - S/(L-S+1)}$$

Exercise: Calculate the g-factor for a level in which J has its minimum value, but for which $L \leq S$. Evaluate $\sum_J J(J+1)g_J$ for a given S, L.

7.21 Since $^1\text{F} \rightarrow {}^1\text{D}$ is a transition between singlets, the normal Zeeman effect will be observed: the transition splits into three lines with separation $\Delta\tilde{\nu} = (\mu_B/hc)\mathcal{B} =$ 1.87 cm^{-1} for $\mathcal{B} = 4.0$ T [use first part of Problem 7.19].

Exercise: How many lines will be observed in a magnetic field of 4.0 T for a $^1\text{F} \rightarrow {}^1\text{P}$ transition?

7.22 For the $^3\text{P} \rightarrow {}^3\text{S}$ transition we must distinguish the levels and calculate their respective g-factors:

$$g_J(L = S) = 1 + \left\{\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right\}_{L=S}$$

$$= 1 + \tfrac{1}{2} = \tfrac{3}{2}$$

Therefore, $g_J(^3\mathrm{P}) = \frac{3}{2}$ for $J = 0, 1, 2$.

$$g_J(^3\mathrm{S}_1) = 1 + \left\{\frac{J(J+1)+S(S+1)}{2J(J+1)}\right\}_{J=S} = 1+1 = 2$$

At $\mathcal{B} = 4$ T,

$$\Delta\tilde{\nu} = g_J\mu_\mathrm{B}\mathcal{B}/hc = g_J \times (1.87\ \mathrm{cm}^{-1}) = \begin{cases} 2.80\ \mathrm{cm}^{-1} & \text{for } g_J = \frac{3}{2} \\ 3.74\ \mathrm{cm}^{-1} & \text{for } g_J = 2 \end{cases}$$

Construct the diagram in Fig. 7.1. The transitions are those for which $\Delta J = 0, \pm 1$ and $\Delta M_J = 0, \pm 1$.

Exercise: Construct the form of the Zeeman effect on a $^4\mathrm{F} \rightarrow {}^4\mathrm{D}$ transition.

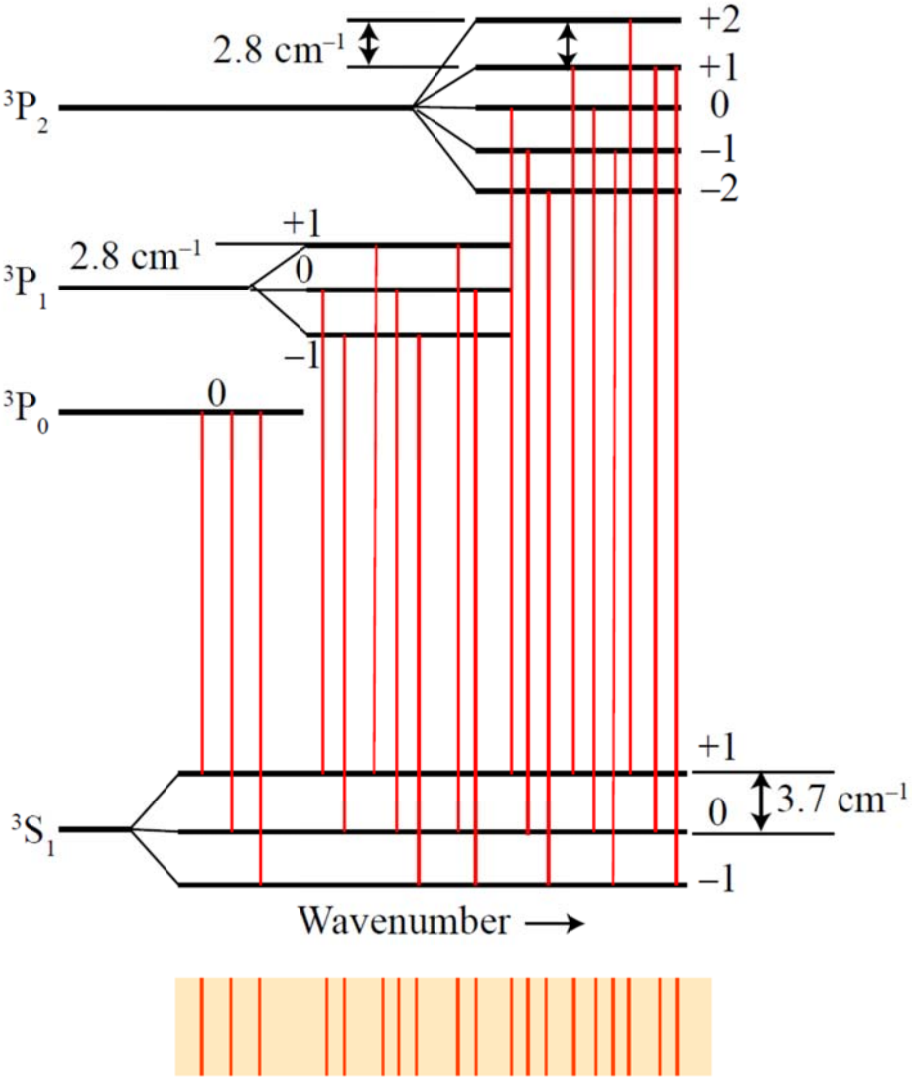

Figure 7.1: The energy levels, transitions, and resulting spectrum of the atom treated in Problem 7.22.

7.23 We seek a solution to eqn 7.98 for the function χ:

$$\frac{\mathrm{d}^2\chi}{\mathrm{d}x^2}=\frac{\chi^{3/2}}{x^{1/2}}$$

where

$$x=\alpha r$$

with

$$\alpha = 2(4)^{2/3}Z^{1/3}/(3\pi)^{2/3}$$

The density ρ is given in terms of the function χ by eqn 7.62. To proceed, assume far from the nucleus that χ is proportional to x^m. Taking,

$$\frac{\mathrm{d}^2\chi}{\mathrm{d}x^2} = am(m-1)x^{m-2}$$

$$\frac{\chi^{3/2}}{x^{1/2}} = a^{3/2}x^{\frac{3m}{2}-\frac{1}{2}}$$

Equating the above two expressions yields:

$$m-2 = \frac{3m}{2} - \frac{1}{2} \quad \text{so} \quad m = -3$$

and

$$am(m-1) = a^{3/2} = 12a \quad \text{so} \quad a = 144$$

Substitution of $\chi = 144x^{-3}$ into eqn 7.62 yields

$$\rho = \frac{32Z^2}{9\pi^3}\left(\frac{\chi}{x}\right)^{3/2} = \frac{32Z^2}{9\pi^3}\left(\frac{1728}{x^6}\right) = \frac{6144Z^2}{\alpha^6\pi^3} \times \frac{1}{r^6}$$

The density is therefore proportional to $1/r^6$ and the constant of proportionality is

$$\frac{6144Z^2}{\alpha^6\pi^3} = \frac{6144Z^2(3\pi)^4}{\pi^3 2^6 4^4 Z^2} = \frac{497664\pi}{16384} = 30.375\pi$$

Problems

7.1 $\langle n'l'm_l'|\mu_m|nlm_l\rangle \propto \int R_{n'l'}Y^*_{l'm_l'}rY_{1m}R_{nl}Y_{lm_l}r^2\mathrm{d}r\sin\theta\mathrm{d}\theta\mathrm{d}\phi$

[The proportionality factor is irrelevant; but because $z = 2(\pi/3)^{1/2}rY_{10}$ and $x \pm \mathrm{i}y = \mp 2(2\pi/3)^{1/2}rY_{1,\pm1}$, with $\mu_0 = \mu_z$ and $\mu_{\pm1} = \mp(\mu_x \pm \mathrm{i}\mu_y)/\sqrt{2}$, it is equal to $-2(\pi/3)^{1/2}e$.] Then

$$\langle n'l'm_l'|\mu_m|nlm_l\rangle \propto \int_0^\infty R_{n'l'}R_{nl}r^3\mathrm{d}r\int Y^*_{l'm_l'}Y_{1m}Y_{lm_l}\sin\theta\mathrm{d}\theta\mathrm{d}\phi$$

Because

$$Y^*_{l'm_l'}Y_{1m}Y_{lm_l} \propto \exp\{\mathrm{i}(m_l+m-m_l')\phi\}$$

the integral vanishes unless $m_l' = m_l + m$; therefore $\Delta m_l = m = 0, \pm1$. Since the spherical harmonics are bases for $\Gamma^{(l')}$, $\Gamma^{(1)}$, and $\Gamma^{(l)}$ in R_3, their product is a basis for the totally symmetric irreducible representation only if $(l', 1, l)$ satisfies the triangle condition. Hence $l' = l, l \pm 1$. The parity of Y_{1m} under inversion is -1. Therefore $Y_{l'm_l'}$ and Y_{lm_l} must be of mutually opposite parity. Consequently $l' = l$ is excluded, and we conclude that $\Delta l = \pm1$. There is no symmetry constraint on the r-integration, and the radial integral is nonzero for all values of $n' - n$. [There are symmetry properties of radial integrals—recall the high, hidden symmetry of the Coulomb potential: see M.J. Englefield, *Group theory and the Coulomb problem*, Wiley-Interscience (1972).]

Exercise: Establish the selection rules for the electric quadrupole transitions of atoms. [The transition operators are proportional to the quadratic forms xx, xy, etc., which themselves are proportional to the Y_{2m}.]

7.4

$$hc\zeta_{nl} = \hbar^2\int_0^\infty \xi(r)R_{nl}^2(r)r^2\mathrm{d}r \quad \text{[eqn 7.15]}$$

$$= (Ze^2\hbar^2/8\pi\varepsilon_0 m_\mathrm{e}^2c^2)\int_0^\infty (1/r)R_{nl}^2(r)\mathrm{d}r \quad \text{[eqn 7.16]}$$

$$= (Ze^2\hbar^2/8\pi\varepsilon_0 m_\mathrm{e}^2c^2)\{Z^3/a_0^3n^3l(l+\tfrac{1}{2})(l+1)\}$$

[Use the values of $\langle 1/r^3\rangle$ quoted in the solution of Exercise 3.19.]

Exercise: Find a relation between $\langle 1/r^3\rangle$ and $1/\langle r\rangle^3$ for an electron in a hydrogenic orbital.

7.7

$$E_{\text{so}}(j) - E_{\text{so}}(j-1) = \tfrac{1}{2}hc\zeta_{nl}\{j(j+1) - (j-1)j\}$$

$$= jhc\zeta_{nl}$$

Exercise: Show that the difference of the squares of neighbouring level energies is proportional to j^3.

7.10 $\langle nlm_l|H^{(1)}|nlm_l\rangle = -(1/2\mu c^2)\langle nlm_l|(E_{nlm_l} - V)^2|nlm_l\rangle$

$$= -(1/2\mu c^2)\langle nlm_l|\, E^2_{nlm_l} + V^2 - 2VE_{nlm_l}|nlm_l\rangle$$

$$= -(1/2\mu c^2)\,\{E^2_{nlm_l} + \langle nlm_l|V^2|nlm_l\rangle - 2\langle nlm_l|V|nlm_l\rangle E_{nlm_l}\}$$

From the virial theorem

$$\langle E\rangle = \langle T\rangle + \langle V\rangle = (\tfrac{1}{2}s + 1)\langle V\rangle = \tfrac{1}{2}\langle V\rangle \quad [s = -1 \text{ for } V \propto 1/r]$$

Consequently

$$\langle nlm_l|H^{(1)}|nlm_l\rangle = -(1/2\mu c^2)\{\langle nlm_l|V^2|nlm_l\rangle - 3E^2_{nlm_l}\}$$

$$V^2 = (e^2/4\pi\varepsilon_0)^2(1/r^2);\ E^2_{nlm_l} = (hc\mathbb{R}_{\text{H}})^2/n^4$$

$$\langle nlm_l|(1/r^2)|nlm_l\rangle = (1/a^2)\{1/(l + \tfrac{1}{2})\,n^3)\}$$

[See L. Pauling and E.B. Wilson, *Introduction to quantum mechanics*, McGraw-Hill (1935), p.145, for values of $\langle 1/r^p \rangle$.]

$$\langle nlm_l|H^{(1)}|nlm_l\rangle = -(1/2\mu c^2)\left\{\frac{(e^2/4\pi\varepsilon_0 a)^2}{(l+\frac{1}{2})n^3} - \frac{3(hc\mathrm{R}_{\mathrm{H}})^2}{n^4}\right\}$$

$$= -\tfrac{1}{2}\,\alpha^4\mu c^2\left\{\frac{1}{(l+\frac{1}{2})n^3} - \frac{3}{4n^4}\right\}$$

For the ground state ($n = 1$, $l = 0$):

$$E^{(1)} = \langle 100|H^{(1)}|100\rangle = -\tfrac{5}{8}\,\alpha^4\mu c^2 = \underline{-1.450 \times 10^{-22}\ \mathrm{J}}\ (-7.299\ \mathrm{cm}^{-1})$$

Exercise: Find the first-order relativistic correction to the energy of a harmonic oscillator.

7.13 Consider a two-electron system involving two orthonormal spinorbitals φ_a and φ_b; for simplicity of notation, these will be denoted a and b. Explicit expansion of the Slater determinant (eqn 7.42a) yields

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\{a(1)b(2) - a(2)b(1)\}$$

Now consider the one- and two-electron operators in eqn 7.43. To confirm the Condon-Slater rules given in eqns 7.44 and 7.45, keep in mind that

$$\langle a(1)|a(1)\rangle = \langle a(2)|a(2)\rangle = \langle b(1)|b(1)\rangle = \langle b(2)|b(2)\rangle = 1$$

$$\langle a(1)|b(1)\rangle = \langle a(2)|b(2)\rangle = \langle b(1)|a(1)\rangle = \langle b(2)|a(2)\rangle = 0$$

First, consider the one-electron operator $\Omega_1 = \Omega(1) + \Omega(2)$.

$$\begin{aligned}\langle\Psi|\Omega_1|\Psi\rangle &= \frac{1}{2}\langle a(1)b(2)-a(2)b(1)|\Omega(1)+\Omega(2)|a(1)b(2)-a(2)b(1)\rangle\\ &= \frac{1}{2}\{\langle a(1)|\Omega(1)|a(1)\rangle+\langle a(2)|\Omega(2)|a(2)\rangle+\langle b(1)|\Omega(1)|b(1)\rangle\\ &+\langle b(2)|\Omega(2)|b(2)\rangle\} = \langle a(1)|\Omega(1)|a(1)\rangle+\langle b(1)|\Omega(1)|b(1)\rangle\end{aligned}$$

which is eqn 7.44a. The last line above follows from the indistinguishability of electrons 1 and 2 so that, for example,

$$\langle a(1)|\Omega(1)|a(1)\rangle = \langle a(2)|\Omega(2)|a(2)\rangle$$

For the two-electron operator $\Omega_2 = \Omega(1,2)$:

$$\begin{aligned}\langle\Psi|\Omega_2|\Psi\rangle &= \frac{1}{2}\langle a(1)b(2)-a(2)b(1)|\Omega(1,2)|a(1)b(2)-a(2)b(1)\rangle\\ &= \frac{1}{2}\{\langle a(1)b(2)|\Omega(1,2)|a(1)b(2)\rangle+\langle a(2)b(1)|\Omega(1,2)|a(2)b(1)\rangle\\ &-\langle a(1)b(2)|\Omega(1,2)|a(2)b(1)\rangle-\langle a(2)b(1)|\Omega(1,2)|a(1)b(2)\rangle\}\end{aligned}$$

which is eqn 7.45a. The other Condon-Slater rules involve one-electron and two-electron-excited state wavefunctions. Consider first the one-electron-excited state wavefunction:

$$\Psi_b^c(1,2) = \frac{1}{\sqrt{2}}\{a(1)c(2)-a(2)c(1)\}$$

The one-electron integral is (recalling the orthonormality of all spinorbitals)

$$\begin{aligned}\langle\Psi|\Omega_1|\Psi_b^c\rangle &= \frac{1}{2}\langle a(1)b(2)-a(2)b(1)|\Omega(1)+\Omega(2)|a(1)c(2)-a(2)c(1)\rangle\\ &= \frac{1}{2}\{\langle b(2)|\Omega(2)|c(2)\rangle+\langle b(1)|\Omega(1)|c(1)\rangle = \langle b(1)|\Omega(1)|c(1)\rangle\end{aligned}$$

which is eqn 7.44b. The two-electron integral is

$$\begin{aligned}\langle\Psi|\Omega_2|\Psi_b^c\rangle &= \frac{1}{2}\langle a(1)b(2)-a(2)b(1)|\Omega(1,2)|a(1)c(2)-a(2)c(1)\rangle\\ &= \frac{1}{2}\{\langle a(1)b(2)|\Omega(1,2)|a(1)c(2)\rangle+\langle a(2)b(1)|\Omega(1,2)|a(2)c(1)\rangle\\ &-\langle a(1)b(2)|\Omega(1,2)|a(2)c(1)\rangle-\langle a(2)b(1)|\Omega(1,2)|a(1)c(2)\rangle\}\\ &= \langle a(2)b(1)|\Omega(1,2)|a(2)c(1)\rangle-\langle a(2)b(1)|\Omega(1,2)|a(1)c(2)\rangle\end{aligned}$$

which is eqn 7.45b, the last line following from the indistinguishability of electrons 1 and 2. The last of the Condon-Slater rules involves the two-electron-excited state wavefunction

$$\Psi_{ab}^{cd}(1,2) = \frac{1}{\sqrt{2}}\{c(1)d(2) - c(2)d(1)\}$$

The two-electron integral is

$$\begin{aligned}\langle\Psi|\Omega_2|\Psi_{ab}^{cd}\rangle &= \frac{1}{2}\langle a(1)b(2) - a(2)b(1)|\Omega(1,2)|c(1)d(2) - c(2)d(1)\rangle \\ &= \frac{1}{2}\{\langle a(1)b(2)|\Omega(1,2)|c(1)d(2)\rangle + \langle a(2)b(1)|\Omega(1,2)|c(2)d(1)\rangle \\ &- \langle a(1)b(2)|\Omega(1,2)|c(2)d(1)\rangle - \langle a(2)b(1)|\Omega(1,2)|c(1)d(2)\rangle\} \\ &= \langle a(1)b(2)|\Omega(1,2)|c(1)d(2)\rangle - \langle a(1)b(2)|\Omega(1,2)|c(2)d(1)\rangle\end{aligned}$$

which is eqn 7.45c.

7.16 $^1E - {}^3E = (E_a + E_b + J + K) - (E_a + E_b + J - K) = 2K$ [eqn 7.37]

$$\{^1E(1s^12s^1) - {}^3E(1s^12s^1)\}/hc = (166\ 272 - 159\ 850)\ \mathrm{cm}^{-1} = 6422\ \mathrm{cm}^{-1}$$

Therefore,

$$K_{1s^12s^1}/hc = \underline{3211\ \mathrm{cm}^{-1}} \quad (0.3981\ \mathrm{eV})$$

$$\{^1E(1s^13s^1) - {}^3E(1s^13s^1)\}/hc = (184\ 859 - 183\ 231)\ \mathrm{cm}^{-1} = 1628\ \mathrm{cm}^{-1}$$

Therefore,

$$K_{1s^13s^1}/hc = \underline{814\ \mathrm{cm}^{-1}}(0.1009\ \mathrm{eV})$$

Exercise: The terms of Li^+ lie at 491 361 cm^{-1}($1s^1\ 2s^1\ {}^1S$), 476 046 cm^{-1} ($1s^12s^1\ {}^3S$), 554 761 cm^{-1}($1s^1\ 3s^1\ {}^3S$), and 558 779 cm^{-1}($1s^13s^1\ {}^1S$). Find $K_{1s^12s^1}$ and $K_{1s^13s^1}$ and suggest reasons why they differ from those for He.

7.19

$$\psi = (1/4!)^{1/2}\begin{vmatrix} 1\mathrm{s}(1) & 1\bar{\mathrm{s}}(1) & 2\mathrm{s}(1) & 2\bar{\mathrm{s}}(1)\\ 1\mathrm{s}(2) & 1\bar{\mathrm{s}}(2) & 2\mathrm{s}(2) & 2\bar{\mathrm{s}}(2)\\ 1\mathrm{s}(3) & 1\bar{\mathrm{s}}(3) & 2\mathrm{s}(3) & 2\bar{\mathrm{s}}(3)\\ 1\mathrm{s}(4) & 1\bar{\mathrm{s}}(4) & 2\mathrm{s}(4) & 2\bar{\mathrm{s}}(4) \end{vmatrix}$$

where 1s and 2s denote α spin-orbitals and $1\bar{\mathrm{s}}$ and $2\bar{\mathrm{s}}$ denote β spin-orbitals.

$$\begin{aligned}
&\langle\|1\mathrm{s}(1)\ldots 2\bar{\mathrm{s}}(4)\||H|\|1s(1)\ldots 2\bar{\mathrm{s}}(4)\|\rangle\\
&= (1/4!)^{1/2}\langle[1\mathrm{s}(1)1\bar{\mathrm{s}}(2)2\mathrm{s}(3)2\bar{\mathrm{s}}(4)] - [1\mathrm{s}(1)1\bar{\mathrm{s}}(2)2\bar{\mathrm{s}}(3)2\mathrm{s}(4)]\\
&\quad - [1\mathrm{s}(1)2\mathrm{s}(2)1\bar{\mathrm{s}}(3)2\bar{\mathrm{s}}(4)] + [1\mathrm{s}(1)2\mathrm{s}(2)2\bar{\mathrm{s}}(3)1\bar{\mathrm{s}}(4)]\\
&\quad + [1\mathrm{s}(1)2\bar{\mathrm{s}}(2)1\bar{\mathrm{s}}(3)2\mathrm{s}(4)] - [1\mathrm{s}(1)2\bar{\mathrm{s}}(2)2\mathrm{s}(3)1\bar{\mathrm{s}}(4)]\\
&\quad - [1\bar{\mathrm{s}}(1)1\mathrm{s}(2)2\mathrm{s}(3)2\bar{\mathrm{s}}(4)] + [1\bar{\mathrm{s}}(1)1\mathrm{s}(2)2\bar{\mathrm{s}}(3)2\mathrm{s}(4)]\\
&\quad + [1\bar{\mathrm{s}}(1)2\mathrm{s}(2)1\mathrm{s}(3)2\bar{\mathrm{s}}(4)] - [1\bar{\mathrm{s}}(1)2\mathrm{s}(2)2\bar{\mathrm{s}}(3)1\mathrm{s}(4)]\\
&\quad - [1\bar{\mathrm{s}}(1)2\bar{\mathrm{s}}(2)1\mathrm{s}(3)2\mathrm{s}(4)] + [1\bar{\mathrm{s}}(1)2\bar{\mathrm{s}}(2)2\mathrm{s}(3)1\mathrm{s}(4)]\\
&\quad + [2\mathrm{s}(1)1\mathrm{s}(2)1\bar{\mathrm{s}}(3)2\bar{\mathrm{s}}(4)] - [2\mathrm{s}(1)1\mathrm{s}(2)2\bar{\mathrm{s}}(3)1\bar{\mathrm{s}}(4)]\\
&\quad - [2\mathrm{s}(1)1\bar{\mathrm{s}}(2)1\mathrm{s}(3)2\bar{\mathrm{s}}(4)] + [2\mathrm{s}(1)1\bar{\mathrm{s}}(2)2\bar{\mathrm{s}}(3)1\mathrm{s}(4)]\\
&\quad + [2\mathrm{s}(1)2\bar{\mathrm{s}}(2)1\mathrm{s}(3)1\bar{\mathrm{s}}(4)] - [2\mathrm{s}(1)2\bar{\mathrm{s}}(2)1\bar{\mathrm{s}}(3)1\mathrm{s}(4)]\\
&\quad - [2\bar{\mathrm{s}}(1)1\mathrm{s}(2)1\bar{\mathrm{s}}(3)2\mathrm{s}(4)] + [2\bar{\mathrm{s}}(1)1\mathrm{s}(2)2\mathrm{s}(3)1\bar{\mathrm{s}}(4)]\\
&\quad + [2\bar{\mathrm{s}}(1)1\bar{\mathrm{s}}(2)1\mathrm{s}(3)2\mathrm{s}(4)] - [2\bar{\mathrm{s}}(1)1\bar{\mathrm{s}}(2)2\mathrm{s}(3)1\mathrm{s}(4)]\\
&\quad - [2\bar{\mathrm{s}}(1)2\mathrm{s}(2)1\mathrm{s}(3)1\bar{\mathrm{s}}(4)] + [2\bar{\mathrm{s}}(1)2\mathrm{s}(2)1\bar{\mathrm{s}}(3)1\mathrm{s}(4)]\\
&\quad \times [T_1 + T_2 + T_3 + T_4 + V_1 + V_2 + V_3 + V_4 + V_{12} + V_{13} + V_{14} + V_{23} + V_{24} + V_{34}]
\end{aligned}$$

$$\times \det|1\text{s}(1)\ldots 2\bar{\text{s}}(4)|\rangle$$

$$= \underline{2E_{1\text{s}} + 2E_{2\text{s}} + \langle 1\text{s}(1)1\text{s}(2)|V_{12}|1\text{s}(1)1\text{s}(2)\rangle}$$

$$\underline{+4\langle 1\text{s}(1)2\text{s}(2)|V_{12}|1\text{s}(1)2\text{s}(2)\rangle}$$

$$\underline{+\langle 2\text{s}(1)2\text{s}(2)|V_{12}|2\text{s}(1)2\text{s}(2)\rangle}$$

$$\underline{-2\langle 1\text{s}(1)2\text{s}(2)|V_{12}|2\text{s}(1)1\text{s}(2)\rangle}$$

[many terms are identical in value], with

$$\langle 1\text{s}(1)1\text{s}(2)|V_{12}|1\text{s}(1)1\text{s}(2)\rangle = j_0\int \psi_{1\text{s}}^2(1)(1/r_{12})\psi_{1\text{s}}^2(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$[j_0 = +e^2/4\pi\varepsilon_0]$$

$$\langle 1\text{s}(1)2\text{s}(2)|V_{12}|1\text{s}(1)2\text{s}(2)\rangle = j_0\int \psi_{1\text{s}}^2(1)(1/r_{12})\psi_{2\text{s}}^2(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$\langle 2\text{s}(1)2\text{s}(2)|V_{12}|2\text{s}(1)2\text{s}(2)\rangle = j_0\int \psi_{2\text{s}}^2(1)(1/r_{12})\psi_{2\text{s}}^2(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$\langle 1\text{s}(1)2\text{s}(2)|V_{12}|2\text{s}(1)1\text{s}(2)\rangle = j_0\int \psi_{1\text{s}}(1)\psi_{2\text{s}}(1)(1/r_{12})\psi_{1\text{s}}(2)\psi_{2\text{s}}(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

In terms of the Hartree–Fock expressions [eqn 7.49]:

$$E = 2E_{1\text{s}} + 2E_{2\text{s}} + \{(2J_{1\text{s}1\text{s}} - K_{1\text{s}1\text{s}}) + (2J_{2\text{s}2\text{s}} - K_{2\text{s}2\text{s}})$$

$$+ (2J_{1\text{s}2\text{s}} - K_{1\text{s}2\text{s}}) + (2J_{2\text{s}1\text{s}} - K_{2\text{s}1\text{s}})\}$$

$$= 2E_{1\text{s}} + 2E_{2\text{s}} + \{J_{1\text{s}1\text{s}} + J_{2\text{s}2\text{s}} + 4J_{1\text{s}2\text{s}} - 2K_{1\text{s}2\text{s}}\}$$

$$= \underline{2E_{1\text{s}} + 2E_{2\text{s}}}$$

$$+ \underline{\langle 1\text{s}(1)1\text{s}(2)|V_{12}|1\text{s}(1)1\text{s}(2)\rangle + \langle 2\text{s}(1)2\text{s}(2)|V_{12}|2\text{s}(1)2\text{s}(2)\rangle}$$

$$+ \underline{4\langle 1\text{s}(1)2\text{s}(2)|V_{12}|1\text{s}(1)2\text{s}(2)\rangle - 2\langle 1\text{s}(1)2\text{s}(2)|V_{12}|2\text{s}(1)1\text{s}(2)\rangle}$$

as before.

Exercise: Find an expression for the (Hartree–Fock) energy of Ne and for its first ionization energy.

7.22 In the Thomas-Fermi method (see eqns 7.58-59),

$$\mu = \frac{5}{3}C\rho(\boldsymbol{r})^{2/3} - j_0\frac{Z}{r} + j_0\int\frac{\rho(\boldsymbol{r}_1)}{|\boldsymbol{r}-\boldsymbol{r}_1|}\mathrm{d}\boldsymbol{r}_1$$

To impose the additional constraint

$$j_0\int \mathrm{e}^{-2kr}\nabla^2\,\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}\ <\ \infty$$

we introduce a Lagrange multiplier λ for the additional constraint, producing

$$\mu = \frac{5}{3}C\rho(\boldsymbol{r})^{2/3} - j_0\frac{Z}{r} + j_0\int\frac{\rho(\boldsymbol{r}_1)}{|\boldsymbol{r}-\boldsymbol{r}_1|}\mathrm{d}\boldsymbol{r}_1 - \lambda j_0\nabla^2\,(\mathrm{e}^{-2kr})$$

Since (see *Further information* 14.1 and the steps leading to eqn 14.112)

$$\nabla^2(\mathrm{e}^{-2kr}) = 4k^2\mathrm{e}^{-2kr} - \frac{4k\mathrm{e}^{-2kr}}{r}$$

we find, by setting $4k\lambda = Z$,

$$\begin{aligned}\mu &= \frac{5}{3}C\rho(\boldsymbol{r})^{2/3} - j_0\frac{Z}{r}\\ &\qquad + j_0\int\frac{\rho(\boldsymbol{r}_1)}{|\boldsymbol{r}-\boldsymbol{r}_1|}\mathrm{d}\boldsymbol{r}_1 - \frac{Zj_0}{4k}\left(4k^2\mathrm{e}^{-2kr} - \frac{4k\mathrm{e}^{-2kr}}{r}\right)\\ &\qquad = \frac{5}{3}C\rho(\boldsymbol{r})^{2/3} - j_0\frac{Z}{r}(1-\mathrm{e}^{-2kr}) + j_0\int\frac{\rho(\boldsymbol{r}_1)}{|\boldsymbol{r}-\boldsymbol{r}_1|}\mathrm{d}\boldsymbol{r}_1 - Zj_0k\,\mathrm{e}^{-2kr}\end{aligned}$$

The presence of the term $(1 - \mathrm{e}^{-2kr})$ removes the singularity at $r = 0$.