Chapter 7

Atomic spectra and atomic structure

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Exercises

7.1 The Rydberg constant $R_\infty$ replaces the $\mu$ in eqn 7.2 for $R_H$ by $m_e$:

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

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

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

$\mu_{He} = mm_e/(m + m_e)$, $m = m(He^{2+})$, $R_\infty = 109737.31$ cm$^{-1}$

$m(He^{2+}) = m(^4He) - 2m_e$

$$= 4.0026 \times (1.66054 \times 10^{-27} \text{ kg}) - 2(9.10938 \times 10^{-31} \text{ kg})$$

$$= 6.6447 \times 10^{-27} \text{ kg}$$

$R_{He} = 4R_\infty/(1.00014) = 4.3889 \times 10^5$ cm$^{-1}$

Therefore, the transitions are predicted to lie at

$$\tilde{\nu}/\text{cm}^{-1} = 4.3889 \times 10^5 \{(\frac{1}{n_1^2} - (1/n_2^2)), 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$$

**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 $\mu$ 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 $R_H \times (1/n_1^2)$.

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

$$\tilde{\nu} = \left( \frac{1}{1^2} - \frac{1}{2^2} \right) \times 1.09737 \times 10^5 \text{ cm}^{-1} = 82.303 \text{ cm}^{-1}$$

and the longest possible wavelength is

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

The series limit is

$$\tilde{\nu} = \frac{R}{1^2} = 109.737 \text{ cm}^{-1}$$

and the shortest possible wavelength is

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

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

$$\tilde{\nu} = \left( \frac{1}{2^2} - \frac{1}{3^2} \right) \times 1.09737 \times 10^5 \text{ cm}^{-1} = 15.241 \text{ cm}^{-1}$$

and the longest possible wavelength is
\[ \lambda = \frac{1}{\tilde{\nu}} = 6.5612 \times 10^{-5} \text{ cm} = 656.12 \text{ nm} \]

The series limit is
\[ \tilde{\nu} = \frac{R}{2^2} = 27434 \text{ cm}^{-1} \]

and the shortest possible wavelength is
\[ \lambda = \frac{1}{\tilde{\nu}} = 3.6451 \times 10^{-5} \text{ cm} = 364.51 \text{ nm} \]

(c) For the Paschen series, \( n_1 = 3 \). The smallest wavenumber is
\[ \tilde{\nu} = \left( \frac{1}{3^2} - \frac{1}{4^2} \right) \times 1.09737 \times 10^5 \text{ cm}^{-1} = 5334.5 \text{ cm}^{-1} \]

and the longest possible wavelength is
\[ \lambda = \frac{1}{\tilde{\nu}} = 1.8746 \times 10^{-4} \text{ cm} = 1874.6 \text{ nm} \]

The series limit is
\[ \tilde{\nu} = \frac{R}{3^2} = 12193 \text{ cm}^{-1} \]

and the shortest possible wavelength is
\[ \lambda = \frac{1}{\tilde{\nu}} = 8.2014 \times 10^{-5} \text{ cm} = 820.14 \text{ nm} \]

(d) For the Brackett series, \( n_1 = 4 \). The smallest wavenumber is
\[ \tilde{\nu} = \left( \frac{1}{4^2} - \frac{1}{5^2} \right) \times 1.09737 \times 10^5 \text{ cm}^{-1} = 2469.1 \text{ cm}^{-1} \]
and the longest possible wavelength is

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

The series limit is

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

and the shortest possible wavelength is

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

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

7.4  \[ \mu/m_e = 1/(1 + m_e/m_p) = 1/(1 + 1/207) = 0.995 \]

\[ \tilde{\nu} = \frac{R}{4^2} \{1/n_1^2 - (1/n_2^2)\} = 0.995R \{1/n_1^2 - (1/n_2^2)\} \]

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

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

\[ 1s \rightarrow 2p, 2p \rightarrow 3d, \text{ and } 3s \rightarrow 5p \]

**Exercise:** Which of the following are electric-dipole allowed: \( 5s \rightarrow 2p, 5s \rightarrow 3d, 5s \rightarrow 5f, 5s \rightarrow 5p? \)

7.6  \( E_n = -R/n^2 \). For convenience, take the energy minimum as \( E_1 \equiv 0; \)
\[ E_n = R \{1 - 1/n^2\} = 0, \frac{3}{4} R, \frac{5}{9} R, \frac{15}{16} R, \ldots \]

The data fit this sequence with

\[ R/\text{cm}^{-1} = 2 743 963, 2 744 051, 2 744 067 \]

and mean value 2 744 027. Write \( R = Z^2 R_{\infty} \) [ignore mass correction]; then \( Z = 5.00 \). The ion is therefore \( \text{Br}^{4+} \).

The ionization energy is given by the series limit \( (n = \infty) \), which lies at \( R = 2 744 027 \text{ cm}^{-1} \). Hence \( I = \hbar c R = 5.450 87 \times 10^{-17} \text{ J} \), corresponding to \( 3.283 \times 10^4 \text{ kJ mol}^{-1} \) 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 \( < 3p_z | \mu_z | 1s > \) where

\[ \mu_z = -e r \cos \theta \]

\[ \psi_{1s} = \left( \frac{1}{\pi} \right)^{1/2} \left( \frac{Z}{a_0} \right)^{3/2} e^{-2r/a_0} \]

\[ \psi_{3p_z} = \left( \frac{1}{648\pi} \right)^{1/2} \left( \frac{Z}{a_0} \right)^{3/2} \left( 4 - \frac{2Zr}{3a_0} \right) \left( \frac{2Zr}{3a_0} \right) e^{-2r/3a_0 \cos \theta} \]

Therefore, the transition dipole moment is

\[ <3p_z | \mu_z | 1s> \]

\[ = -e \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \int_{r=0}^{\infty} \left( \frac{1}{648\pi^2} \right)^{1/2} \left( \frac{Z}{a_0} \right)^{3} \]

\[ \times \left( 4 - \frac{2Zr}{3a_0} \right) \left( \frac{2Zr}{3a_0} \right) e^{-4Zr/3a_0 \cos \theta} \theta \sin \theta d\theta d\phi dr \]

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The integration over $\phi$ yields $2\pi$ and that over $\theta$ 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

$$\langle 3p_x | \mu_x | 1s \rangle = \frac{729}{4\sqrt{648}} \frac{ea_0}{Z}$$

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

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

Be : 1s$^2$2s$^2$, 1S$^0$

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

C : 1s$^2$2s$^2$2p$^2$, 1D$^2$, 3P$^2$, 3P$^1$, 3P$^0$; 1S$^0$

with $E(3P_0) < E(3P_1) < E(3P_2) < E(1D_2) < E(1S_0)$

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

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

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

Therefore, for N we predict $4S < 2D < 2P$ (as observed).

O : 1s$^2$2s$^2$2p$^4$ $=$ 1s$^2$2s$^2$2p$^6$2p$^{-2}$ [particle-hole formalism]; this configuration gives rise to $1D^2; 3P^2; 3P^1; 3P^0; 1S^0$ with $3P_2 < 3P_1 < 3P_0 < 1D_2 < 1S_0$

F : 1s$^2$2s$^2$2p$^5$ $=$ 1s$^2$2s$^2$2p$^6$2p$^{-1}$; $2P^{1/2}, 2P^{3/2}$ with $2P^{3/2} < 2P^{1/2}$. 
Ne: 1s²2s²2p⁶, ¹S₀.

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

7.10

\[ H = -(\hbar²/2m_e)(\nabla^2_1 + \nabla^2_2 + \nabla^2_3) - (3e^2/4\pi\epsilon_0)(1/r_1) + (1/r_2) + (1/r_3) \]
\[ + (e^2/4\pi\epsilon_0)((1/r_{12}) + (1/r_{23}) + (1/r_{13})) \]
\[ = H^{(0)} + H^{(1)}; \quad H^{(0)} = H_1 + H_2 + H_3 \]

\[ H_i = -(\hbar²/2m_e)\nabla^2_i - (3e^2/4\pi\epsilon_0)(1/r_i) \quad i = 1, 2, 3 \]
\[ H^{(1)} = (e^2/4\pi\epsilon_0)((1/r_{12}) + (1/r_{23}) + (1/r_{13})) \]

\[ H^{(0)}\psi(1)\psi(2)\psi(3) = (H_1 + H_2 + H_3)\psi(1)\psi(2)\psi(3) \]
\[ = \{H_1\psi(1)\} \psi(2)\psi(3) + \psi(1)\{H_2\psi(2)\} \psi(3) + \psi(1)\psi(2)\{H_3\psi(3)\} \]
\[ = (E_1 + E_2 + E_3)\psi(1)\psi(2)\psi(3) = E^{(0)}\psi(1)\psi(2)\psi(3) \]

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 \( \alpha \), is

\[
\psi(1, 2, 3) = (1/3!)^{1/2}\begin{vmatrix}
\psi^\alpha_{1s}(1) & \psi^\beta_{1s}(1) & \psi^\alpha_{2s}(1) \\
\psi^\alpha_{1s}(2) & \psi^\beta_{1s}(2) & \psi^\alpha_{2s}(2) \\
\psi^\alpha_{1s}(3) & \psi^\beta_{1s}(3) & \psi^\alpha_{2s}(3)
\end{vmatrix}
\]
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

\[
\psi(1, 2, 3) = (1/6)^{1/2} \left[ \psi_{1s}^\alpha(1)\psi_{1s}^\beta(2)\psi_{2s}^\alpha(3) + \psi_{1s}^\beta(1)\psi_{2s}^\alpha(2)\psi_{1s}^\alpha(3) + \psi_{2s}^\alpha(1)\psi_{1s}^\alpha(2)\psi_{1s}^\beta(3) - \psi_{2s}^\alpha(1)\psi_{1s}^\beta(2)\psi_{1s}^\alpha(3) - \psi_{1s}^\alpha(1)\psi_{2s}^\alpha(2)\psi_{1s}^\beta(3) - \psi_{1s}^\beta(1)\psi_{1s}^\alpha(2)\psi_{2s}^\alpha(3) \right]
\]

while interchange of labels 1 and 2 yields

\[
\psi(1, 2, 3) = (1/6)^{1/2} \left[ \psi_{1s}^\alpha(2)\psi_{1s}^\beta(1)\psi_{2s}^\alpha(3) + \psi_{1s}^\beta(2)\psi_{2s}^\alpha(1)\psi_{1s}^\alpha(3) + \psi_{2s}^\alpha(2)\psi_{1s}^\alpha(1)\psi_{1s}^\beta(3) - \psi_{2s}^\alpha(2)\psi_{1s}^\beta(1)\psi_{1s}^\alpha(3) - \psi_{1s}^\alpha(2)\psi_{2s}^\alpha(1)\psi_{1s}^\beta(3) - \psi_{1s}^\beta(2)\psi_{1s}^\alpha(1)\psi_{2s}^\alpha(3) \right]
\]

\[
= -\psi(1, 2, 3)
\]

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

\[
\int_0^\infty \left\{ \int_0^{r_2} \frac{r_2^2 e^{-2Zr_1/a_0}}{r_2} \, dr_1 + \int_2^\infty \frac{r_2^2 e^{-2Zr_1/a_0}}{r_2} \, dr_1 \right\} r_2^2 e^{-2Zr_2/a_0} \, dr_2 = \frac{5}{2^7} \left( \frac{a_0}{Z} \right)^5
\]

We use the following results:
\[
\int_0^{r_2} \frac{r_1^2 e^{-2Zr_1/a_0}}{r_2} \, dr_1
\]

\[
= \frac{1}{r_2} \int_0^{r_2} r_1^2 e^{-2Zr_1/a_0} \, dr_1 = -e^{-2Zr_2/a_0} \left( \frac{a_0 r_2}{2Z} + \frac{a_0^2}{2Z^2} \right)
\]
\[
+ (\, e^{-2Zr_2/a_0} + 1) \frac{a_0^3}{4Z^3 r_2}
\]

\[
\int_{r_2}^{\infty} \frac{r_1^2 e^{-2Zr_1/a_0}}{r_1} \, dr_1 = \frac{a_0^2 e^{-2Zr_2/a_0}}{4Z^2} \left( \frac{2Zr_2}{a_0} + 1 \right)
\]

Substitution of the above two integrals then produces

\[
\int_0^{\infty} \left\{ \int_0^{r_2} \frac{r_1^2 e^{\frac{2Zr_1}{a_0}}}{r_2} \, dr_1 + \int_{r_2}^{\infty} \frac{r_1^2 e^{\frac{2Zr_1}{a_0}}}{r_1} \, dr_1 \right\} r_2^2 e^{-\frac{2Zr_2}{a_0}} \, dr_2
\]

\[
= \int_0^{\infty} \left\{ e^{-4Zr_2/a_0} \left( \frac{a_0 r_2^2}{2Z} \right) + \frac{r_2^2 a_0^2}{2Z^2} \right\} \, dr_2
\]
\[
+ (\, -e^{-4Zr_2/a_0} + e^{-2Zr_2/a_0} \frac{a_0^3 r_2^2}{4Z^3} + \frac{a_0^2 e^{-4Zr_2/a_0}}{4Z^2} \left( \frac{2Zr_2^3}{a_0} + r_2^2 \right) \}
\]
\[
= \int_0^{\infty} \left\{ -e^{-4Zr_2/a_0} \left( \frac{r_2^2 a_0^2}{4Z^2} \right) + (\, -e^{-4Zr_2/a_0} + e^{-2Zr_2/a_0} \frac{a_0^3 r_2^2}{4Z^3} \} \, dr_2
\]

Using the standard integral

\[
\int_0^{\infty} r^n e^{-ar} \, dr = \frac{n!}{a^{n+1}}
\]

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

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

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.

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

and therefore

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

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

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

(a)
\[ \langle r \rangle = \left( \frac{2Z_{\text{eff}}}{3} \right)^7 \frac{7!}{720a_0^7} \int_0^\infty r^2 e^{-Z_{\text{eff}}/3a_0} r^2 e^{-Z_{\text{eff}}/3a_0} \, dr = \left( \frac{2Z_{\text{eff}}}{3} \right)^7 \frac{7!}{720a_0^7} \int_0^\infty r^7 e^{-2Z_{\text{eff}}/3a_0} \, dr \]

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

(b)

\[ \langle 1/r \rangle = \left( \frac{2Z_{\text{eff}}}{3} \right)^7 \frac{5!}{720a_0^7} \int_0^\infty r^2 e^{-Z_{\text{eff}}/3a_0} (1/r) r^2 e^{-Z_{\text{eff}}/3a_0} \, dr = \left( \frac{2Z_{\text{eff}}}{3} \right)^7 \frac{5!}{720a_0^7} \int_0^\infty r^5 e^{-2Z_{\text{eff}}/3a_0} \, dr \]

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

(c)

\[ \langle 1/r^3 \rangle = \left( \frac{2Z_{\text{eff}}}{3} \right)^7 \frac{3!}{720a_0^7} \int_0^\infty r^2 e^{-Z_{\text{eff}}/3a_0} (1/r^3) r^2 e^{-Z_{\text{eff}}/3a_0} \, dr = \left( \frac{2Z_{\text{eff}}}{3} \right)^7 \frac{3!}{720a_0^7} \int_0^\infty r^3 e^{-2Z_{\text{eff}}/3a_0} \, dr \]

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

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 \( \varepsilon \) 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

\[ ^1S : J = (0 \times 0) = 0; \text{ hence } ^1S_0 \]

\[ ^2P : J = (1/2 \times 1) = 1/2 + 1/2; \text{ hence } ^2P_{3/2}, ^2P_{1/2} \]

\[ ^3P : J = (1 \times 1) = 2 + 1 + 0; \text{ hence } ^3P_2, ^3P_1, ^3P_0 \]

\[ ^3D : J = (1 \times 2) = 3 + 2 + 1; \text{ hence } ^3D_3, ^3D_2, ^3D_1 \]

\[ ^2D : J = (1/2 \times 2) = 5/2 + 3/2; \text{ hence } ^2D_{5/2}, ^2D_{3/2} \]

\[ ^1D : J = (0 \times 2) = 2; \text{ hence } ^1D_2 \]

\[ ^4D : J = (3/2 \times 2) = 7/2 + 5/2 + 3/2 + 1/2; \text{ hence } ^4D_{7/2}, ^4D_{5/2}, ^4D_{3/2}, ^4D_{1/2} \]

**Exercise:** What levels may arise from the terms \(^4F\), \(^4D\), \(^4P\)?

7.16

\[ ^1s^1^2p^1 : L = 1; S = 0, 1; \text{ hence } ^1P, ^3P \text{ with levels } ^1P_1, ^3P_2, ^3P_1, ^3P_0. \]

**Energies:** \(^3P_0 < ^3P_1 < ^3P_2 < ^1P_1 \) [Hund rules]

\[ ^2p^1^3p^1 : L = 2, 1, 0; S = 0, 1; \text{ hence } ^3D, ^1D, ^3P, ^1P, ^3S, ^1S. \]

**Energies:** \(^3D_1 < ^3D_2 < ^3D_3 < ^3P_0 < ^3P_1 < ^3P_2 \)

\[ < ^3S_1 < ^1D_2 < ^1P_1 < ^1S_0 \]

\[ ^3p^1^3d^1 : L = 3, 2, 1; S = 0, 1; \text{ hence } ^3F, ^1F, ^3D, ^1D, ^3P, ^1P. \]

**Energies:** \(^3F_2 < ^3F_3 < ^3F_4 < ^3D_1 < ^3D_2 < ^3D_3 \)

\[ < ^3P_0 < ^3P_1 < ^3P_2 < ^1F_3 < ^1D_2 < ^1P_1 \]
**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 \(^1\)G, \(^3\)F, \(^1\)D, \(^3\)P, \(^1\)S arise.

(b) \(f^2\): \(L = (3 \times 3) = 6 + 5 + \ldots + 0; S = 1, 0\). Pauli forbids 3I etc.; hence \(^1\)I, \(^3\)H, \(^1\)G, \(^3\)F, \(^1\)D, \(^3\)P, \(^1\)S 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 \(d^2\): \(\Gamma^{(2)} \times \Gamma^{(2)} = \Gamma^{(4)} + \left[ \Gamma^{(3)} \right] + \Gamma^{(2)} + \left[ \Gamma^{(1)} \right] + \Gamma^{(0)}\)

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

Since \(\left[ \Gamma^{(0)} \right]\) 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 \(\left[ \Gamma^{(3)} \right]\) (an F state) and antisymmetric \(\left[ \Gamma^{(1)} \right]\) (a P state) must be triplets.

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

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

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

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

\[\Delta E^{(1)} = \mu_B \beta; \Delta \tilde{v} = (\mu_B/\hbar c)\beta\]

Therefore, \(\beta = h c \Delta \tilde{v} / \mu_B = 2.14 \text{ T}\) when \(\tilde{v} = 1 \text{ cm}^{-1}\).

**Exercise:** Calculate the magnetic field required to produce a splitting of 1 cm\(^{-1}\) between the states of a \(^1\)D\(_2\) 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) \( J_{\text{max}} = L + S \),

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

\[ = 1 + \frac{S}{L+S} \]

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

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

\[ = 1 - \frac{S}{L-S+1} \]

**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 \( ^1F \to ^1D \) is a transition between singlets, the normal Zeeman effect will be observed: the transition splits into three lines with separation \( \Delta \bar{v} = (\mu_B/\hbar)cB = 1.87 \text{ cm}^{-1} \) for \( B = 4.0 \text{ T} \) [use first part of Problem 7.19].

**Exercise:** How many lines will be observed in a magnetic field of 4.0 T for a \( ^1F \to ^1P \) transition?

**7.22** For the \( ^3P \to ^3S \) transition we must distinguish the levels and calculate their respective \( g \)-factors:

\[ g_A(L = S) = 1 + \left[ \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right]_{L=S} \]

\[ = 1 + \frac{1}{2} = \frac{3}{2} \]
Therefore, \( g_3^J(3P) = \frac{3}{2} \) for \( J = 0, 1, 2 \).

\[
g_3^J(3S_1) = 1 + \frac{J(J+1) + S(S+1)}{2J(J+1)} = 1 + 1 = 2
\]

At \( B = 4 \) T,

\[
\Delta \tilde{\nu} = g_J \mu_B B / h c = g_J \times (1.87 \text{ cm}^{-1}) = \begin{cases} 
2.80 \text{ cm}^{-1} & \text{for } g_J = \frac{3}{2} \\
3.74 \text{ cm}^{-1} & \text{for } g_J = 2 
\end{cases}
\]

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 \( ^4F \rightarrow ^4D \) 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 $\chi$:

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

where

$$x = \alpha r$$
with

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

The density \( \rho \) is given in terms of the function \( \chi \) by eqn 7.62. To proceed, assume far from the nucleus that \( \chi \) is proportional to \( x^m \). Taking,

\[
\frac{d^2\chi}{dx^2} = am(m - 1)x^{m-2}
\]

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

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

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

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

\[
\frac{6144Z^2}{a^{6\pi^3}} = \frac{6144Z^2(3\pi)^4}{\pi^32^64^4Z^2} = \frac{497664\pi}{16384} = 30.375\pi
\]

Problems

7.1

\[ \langle n'lm'|\mu_m|nlm_l \rangle \propto \int R_{n'\ell'\ell'^*}rY_{l+m_l}^*RY_{l_m}r^2dr \sin \theta d\theta d\phi \]

[The proportionality factor is irrelevant; but because \( z = 2(\pi/3)^{1/2}rY_{l0} \) and \( x \pm iy = \mp \)

\[ 2(2\pi/3)^{1/2}rY_{1,\pm1}, \] with \( \mu_0 = \mu_e \) and \( \mu_{\pm1} = \mp(\mu_e \pm i\mu_e)/\sqrt{2}, \] it is equal to \(-2(\pi/3)^{1/2}e\).] Then
Because

\[ Y_{l'm'}^* Y_{lm} Y_{l'm} \propto \exp\{i(m_l + m - m')\phi}\]

the integral vanishes unless \( m' = m_l + m \); therefore \( \Delta m_l = m = 0, \pm 1 \). Since the spherical harmonics are bases for \( \Gamma^{(0)}, \Gamma^{(1)}, \text{and} \Gamma^{(0)} \) 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 \( Y_{lm} \) under inversion is \(-1\). Therefore \( Y_{l'm'} \) and \( Y_{lm} \) must be of mutually opposite parity. Consequently \( l' = l \) is excluded, and we conclude that \( \Delta l = \pm 1 \). 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 \( xx, xy, \text{etc.}, \) which themselves are proportional to the \( Y_{2m} \).]

7.4

\[ \hbar c \zeta_m = \hbar^2 \int_0^\infty \xi(r)R_m^2(r)r^2dr \quad \text{[eqn 7.15]} \]

\[ = (Ze^2\hbar^2/8\pi\varepsilon_0m_e^2c^2)\int_0^\infty (1/r)R_m^2(r)dr \quad \text{[eqn 7.16]} \]

\[ = (Ze^2\hbar^2/8\pi\varepsilon_0m_e^2c^2)(Z^3/a_0^3n^3l(l+\frac{1}{2})(l+1)) \]
[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 $1/\langle r^3 \rangle$ for an electron in a hydrogenic orbital.

$$E_{so}(j) - E_{so}(j - 1) = \frac{1}{2} \hbar c \zeta_{nl} \{j(j + 1) - (j - 1)j\}$$

$$= jhc \zeta_{nl}$$

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

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

$$= -(1/2\mu c^2) \langle \text{nlml}|E_{\text{nlml}}^2 + V^2 - 2VE_{\text{nlml}}|\text{nlml} \rangle$$

$$= -(1/2\mu c^2) \{E_{\text{nlml}}^2 + \langle \text{nlml}|V^2|\text{nlml} \rangle - 2\langle \text{nlml}|V|\text{nlml} \rangle E_{\text{nlml}}\}$$

From the virial theorem

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

Consequently

$$\langle \text{nlml}|H^{(1)}|\text{nlml} \rangle = -(1/2\mu c^2) \{ \langle \text{nlml}|V^2|\text{nlml} \rangle - 3E_{\text{nlml}}^2 \}$$

$$V^2 = (\epsilon^2/4\pi \epsilon_0)^2(1/r^2); \quad E_{\text{nlml}}^2 = (\hbar c R_{\text{H}})^2/n^4$$

$$\langle \text{nlml}|(1/r^3)|\text{nlml} \rangle = (1/a^2) \{1/(l + \frac{1}{2}) n^3\}$$
\[ \langle nlm|H^{(1)}|nlm\rangle = -(1/2\alpha^2)^2 \left\{ \frac{(\epsilon^2/4\pi\varepsilon_0 a)^2}{(l+\frac{1}{2})n^3} - \frac{3(hcR_n)^2}{n^4} \right\} \]

\[ = -\frac{1}{2} \alpha^4 \mu e^2 \left\{ \frac{1}{(l+\frac{1}{2})n^3} - \frac{3}{4n^4} \right\} \]

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

\[ E^{(1)} = \langle 100|H^{(1)}|100\rangle = -\frac{5}{8} \alpha^4 \mu e^2 = -1.450 \times 10^{-22} \text{ J} (-7.299 \text{ cm}^{-1}) \]

**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 \(\varphi_a\) and \(\varphi_b\); 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 \(\Omega_1 = \Omega(1) + \Omega(2)\).
\[ \langle \Psi | \Omega_1 | \Psi \rangle = \frac{1}{2} (a(1)b(2) - a(2)b(1)|\Omega(1) + \Omega(2)|a(1)b(2) - a(2)b(1)) \\
= \frac{1}{2} [(a(1)|\Omega(1)|a(1)) + (a(2)|\Omega(2)|a(2)) + (b(1)|\Omega(1)|b(1)) + (b(2)|\Omega(2)|b(2))] = \langle a(1)|\Omega(1)|a(1) \rangle + \langle b(1)|\Omega(1)|b(1) \rangle \\
\]

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 \( \Omega_2 = \Omega(1,2) \):

\[ \langle \Psi | \Omega_2 | \Psi \rangle = \frac{1}{2} (a(1)b(2) - a(2)b(1)|\Omega(1,2)|a(1)b(2) - a(2)b(1)) \\
= \frac{1}{2} [(a(1)b(2)|\Omega(1,2)|a(1)b(2)) + (a(2)b(1)|\Omega(1,2)|a(2)b(1)) \]

\[ - (a(1)b(2)|\Omega(1,2)|a(2)b(1)) - (a(2)b(1)|\Omega(1,2)|a(1)b(2)) ] \]

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:

\[ \psi_1^e(1,2) = \frac{1}{\sqrt{2}} \{ a(1)c(2) - a(2)c(1) \} \]

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

\[ \langle \Psi | \Omega_1 | \psi_1^e \rangle = \frac{1}{2} (a(1)b(2) - a(2)b(1)|\Omega(1) + \Omega(2)|a(1)c(2) - a(2)c(1)) \\
= \frac{1}{2} [(b(2)|\Omega(2)|c(2)) + (b(1)|\Omega(1)|c(1)) = \langle b(1)|\Omega(1)|c(1) \rangle \]

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

\[ \langle \Psi | \Omega_2 | \psi_1^e \rangle = \frac{1}{2} (a(1)b(2) - a(2)b(1)|\Omega(1,2)|a(1)c(2) - a(2)c(1)) \\
= \frac{1}{2} [(a(1)b(2)|\Omega(1,2)|a(1)c(2)) + (a(2)b(1)|\Omega(1,2)|a(2)c(1)) \]

\[ - (a(1)b(2)|\Omega(1,2)|a(2)c(1)) - (a(2)b(1)|\Omega(1,2)|a(1)c(2))] \]

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

\[
\langle \Psi | \Omega_2 | \Psi_{ab}^{cd} \rangle = \frac{1}{2} \{a(1)b(2) - a(2)b(1)\Omega(1,2)|c(1)d(2) - c(2)d(1)\} \\
= \frac{1}{2} \{(a(1)b(2)|\Omega(1,2)|c(1)d(2)) + (a(2)b(1)|\Omega(1,2)|c(2)d(1)) \\
- (a(1)b(2)|\Omega(1,2)|c(2)d(1)) - (a(2)b(1)|\Omega(1,2)|c(1)d(2))\} \\
= \{a(1)b(2)|\Omega(1,2)|c(1)d(2)) - (a(1)b(2)|\Omega(1,2)|c(2)d(1))\}
\]

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]

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

Therefore,

\[ K_{1s^12s^1}/hc = 3211 \text{ cm}^{-1} \ (0.3981 \text{ eV}) \]

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

Therefore,

\[ K_{1s^13s^1}/hc = 814 \text{ cm}^{-1}(0.1009 \text{ eV}) \]

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

\[
\langle \langle 1s(1) \ldots 2\bar{\sigma}(4) | H | 1s(1) \ldots 2\bar{\sigma}(4) \rangle \rangle = (1/4!)^{1/2}[\langle 1s(1) 1\bar{\sigma}(2) 2s(3) 2\bar{\sigma}(4) \rangle - \langle 1s(1) 1\bar{\sigma}(2) 2s(3) 2\bar{\sigma}(4) \rangle]
\]

\[
- \langle 1s(1) 2s(2) 1\bar{\sigma}(3) 2\bar{\sigma}(4) \rangle + \langle 1s(1) 2s(2) 1\bar{\sigma}(3) 2\bar{\sigma}(4) \rangle
\]

\[
+ \langle 1s(1) 2\bar{\sigma}(2) 1\bar{\sigma}(3) 2s(4) \rangle - \langle 1s(1) 2\bar{\sigma}(2) 1\bar{\sigma}(3) 2s(4) \rangle
\]

\[
- \langle 1\bar{\sigma}(1) 1s(2) 2s(3) 2\bar{\sigma}(4) \rangle + \langle 1\bar{\sigma}(1) 1s(2) 2s(3) 2\bar{\sigma}(4) \rangle
\]

\[
+ \langle 1\bar{\sigma}(1) 2s(2) 1s(3) 2\bar{\sigma}(4) \rangle - \langle 1\bar{\sigma}(1) 2s(2) 1s(3) 2\bar{\sigma}(4) \rangle
\]

\[
- \langle 1\bar{\sigma}(1) 2\bar{\sigma}(2) 1s(3) 2s(4) \rangle + \langle 1\bar{\sigma}(1) 2\bar{\sigma}(2) 1s(3) 2s(4) \rangle
\]

\[
+ \langle 2s(1) 1s(2) 1\bar{\sigma}(3) 2\bar{\sigma}(4) \rangle - \langle 2s(1) 1s(2) 1\bar{\sigma}(3) 2\bar{\sigma}(4) \rangle
\]

\[
- \langle 2s(1) 1\bar{\sigma}(2) 1s(3) 2\bar{\sigma}(4) \rangle + \langle 2s(1) 1\bar{\sigma}(2) 1s(3) 2\bar{\sigma}(4) \rangle
\]

\[
+ \langle 2s(1) 2\bar{\sigma}(2) 1s(3) 1\bar{\sigma}(4) \rangle - \langle 2s(1) 2\bar{\sigma}(2) 1s(3) 1\bar{\sigma}(4) \rangle
\]

\[
- \langle 2\bar{\sigma}(1) 1s(2) 1\bar{\sigma}(3) 2s(4) \rangle + \langle 2\bar{\sigma}(1) 1s(2) 1\bar{\sigma}(3) 2s(4) \rangle
\]

\[
+ \langle 2\bar{\sigma}(1) 2\bar{\sigma}(2) 1s(3) 2s(4) \rangle - \langle 2\bar{\sigma}(1) 2\bar{\sigma}(2) 1s(3) 2s(4) \rangle
\]

\[
- \langle 2\bar{\sigma}(1) 2s(2) 1s(3) 1\bar{\sigma}(4) \rangle + \langle 2\bar{\sigma}(1) 2s(2) 1s(3) 1\bar{\sigma}(4) \rangle
\]

\[
\times \left[ T_1 + T_2 + T_3 + T_4 + V_1 + V_2 + V_3 + V_4 + V_{12} + V_{13} + V_{14} + V_{23} + V_{24} + V_{34} \right]
\]
\[ \times \det |1s(1) \ldots 2s(4)\rangle \]

\[ = 2E_{1s} + 2E_{2s} + \langle ls(1)ls(2) | V_{12}^2 | ls(1)ls(2) \rangle \]

\[ + 4\langle ls(1)2s(2) | V_{12}^2 | ls(1)2s(2) \rangle \]

\[ + \langle 2s(1)2s(2) | V_{12}^2 | 2s(1)2s(2) \rangle \]

\[ - 2\langle ls(1)2s(2) | V_{12}^2 | ls(1)ls(2) \rangle \]

[many terms are identical in value], with

\[ \langle ls(1)ls(2) | V_{12}^2 | ls(1)ls(2) \rangle = j_0 \int \psi_{ls}^2 (1)(1/r_{12}) \psi_{ls}^2 (2) d\tau_1 d\tau_2 \]

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

\[ \langle ls(1)2s(2) | V_{12}^2 | ls(1)2s(2) \rangle = j_0 \int \psi_{ls}^2 (1)(1/r_{12}) \psi_{2s}^2 (2) d\tau_1 d\tau_2 \]

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

\[ \langle ls(1)2s(2) | V_{12}^2 | ls(1)ls(2) \rangle = j_0 \int \psi_{ls}^2 (1)\psi_{ls}^2 (2)(1/r_{12}) \psi_{ls}^2 (2) d\tau_1 d\tau_2 \]

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

\[ E = 2E_{1s} + 2E_{2s} + \{(2J_{1s1s} - K_{1s1s}) + (2J_{2s2s} - K_{2s2s}) \]

\[ + (2J_{1s2s} - K_{1s2s}) + (2J_{2s1s} - K_{2s1s}) \}\]

\[ = 2E_{1s} + 2E_{2s} + \{J_{1s1s} + J_{2s2s} + 4J_{1s2s} - 2K_{1s1s} \} \]

\[ = 2E_{1s} + 2E_{2s} \]

\[ + \langle ls(1)ls(2) | V_{12}^2 | ls(1)ls(2) \rangle + \langle 2s(1)2s(2) | V_{12}^2 | 2s(1)2s(2) \rangle \]

\[ + 4\langle ls(1)2s(2) | V_{12}^2 | ls(1)2s(2) \rangle - 2\langle ls(1)2s(2) | V_{12}^2 | 2s(1)ls(2) \rangle \]

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),

\[
\mu = \frac{5}{3} C \rho(r)^{2/3} - j_0 \frac{Z}{r} + j_0 \int \frac{\rho(r_1)}{|r - r_1|} \, dr_1
\]

To impose the additional constraint

\[
j_0 \int e^{-2kr} \nabla^2 \rho(r) \, dr < \infty
\]

we introduce a Lagrange multiplier \( \lambda \) for the additional constraint, producing

\[
\mu = \frac{5}{3} C \rho(r)^{2/3} - j_0 \frac{Z}{r} + j_0 \int \frac{\rho(r_1)}{|r - r_1|} \, dr_1 - \lambda j_0 \nabla^2 \left( e^{-2kr} \right)
\]

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

\[
\nabla^2 \left( e^{-2kr} \right) = 4k^2 e^{-2kr} - \frac{4ke^{-2kr}}{r}
\]

we find, by setting \( 4kJ = Z \),

\[
\mu = \frac{5}{3} C \rho(r)^{2/3} - j_0 \frac{Z}{r}
\]

\[
+ j_0 \int \frac{\rho(r_1)}{|r - r_1|} \, dr_1 - \frac{Zj_0}{4k} \left( 4k^2 e^{-2kr} - \frac{4ke^{-2kr}}{r} \right)
\]

\[
= \frac{5}{3} C \rho(r)^{2/3} - j_0 \frac{Z}{r} \left( 1 - e^{-2kr} \right) + j_0 \int \frac{\rho(r_1)}{|r - r_1|} \, dr_1 - Zj_0k e^{-2kr}
\]

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