Solutions to assignment 4

1. (a) In this case, the energy eigenvalues are

$$E_{n_1n_2n_3} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}+\frac{n_3^2}{L_3^2}\right) = \frac{h^2}{8m}\left(\frac{n_1^2}{L^2}+\frac{n_2^2}{4L^2}+\frac{n_3^2}{9L^2}\right),$$

the lowest of which is

$$E_{111} = \frac{h^2}{8mL^2}\left(1+\frac{1}{4}+\frac{1}{9}\right) \equiv \frac{49}{36}E_0.$$

The lowest ten in order are

n_1	n_2	n_3	$E_{n_1n_2n_3}/E_0$
1	1	1	1.361
1	1	2	1.694
1	2	1	2.111
1	1	3	2.250
1	2	2	2.444
1	2	3	3.000
1	1	4	3.028
1	3	1	3.360
1	3	2	3.472
1	2	4	3.778

(b) The wavefunctions for the five lowest-energy states are

$$\psi_{111} = A\sin\frac{\pi x}{L}\sin\frac{\pi y}{2L}\sin\frac{\pi z}{3L}$$
$$\psi_{112} = A\sin\frac{\pi x}{L}\sin\frac{\pi y}{2L}\sin\frac{2\pi z}{3L}$$
$$\psi_{121} = A\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{\pi z}{3L}$$
$$\psi_{113} = A\sin\frac{\pi x}{L}\sin\frac{\pi y}{2L}\sin\frac{\pi z}{L}$$
$$\psi_{122} = A\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{2\pi z}{3L}$$

(c) The energy eigenvalues are now

$$E_{n_1n_2n_3} = \frac{h^2}{8m}\left(\frac{n_1^2}{L^2}+\frac{n_2^2}{4L^2}+\frac{n_3^2}{16L^2}\right),$$

the lowest of which is

$$E_{111} = \frac{h^2}{8mL^2}\left(1+\frac{1}{4}+\frac{1}{9}\right) \equiv \frac{84}{64}E_0.$$

The lowest ten in order are

n_1	n_2	n_3	$E_{n_1n_2n_3}/E_0$
1	1	1	1.313
1	1	2	1.500
1	1	3	1.813
1	2	1	2.063
1	1	4	<u>2.250</u>
1	2	2	<u>2.250</u>
1	2	3	2.563
1	1	5	2.813
1	2	4	3.000
1	3	1	3.313
1	1	6	<u>3.500</u>
1	3	2	<u>3.500</u>

(d) There are no degenerate levels when $L_3 = 3L_1$, but when $L_3 = 4L_1$ the 114 and 122 states and the 116 and 132 states (underlined in the table) are degenerate (meaning that they have the same energy).

2. (a) For $n = 2$, $l = 0, 1$. For $l = 0$, $m_l = 0$ with two spin states ($m_S = -1/2, 1/2$). For $l = 1$, $m_l = -1, 0, 1$, each with two spin states. The total number of states is $2 + 6 = 8$.

(b) For $n = 4$, $l = 0, 1, 2, 3$. In addition to those found in part (a), we now have $l = 2$ with $2l+1 = 5$ possible m_l values and two possible m_S values; and $l = 3$ with $2l + 1 = 7$ possible m_l values and two possible m_S values. The total is 2+6+10+14=32.

3. (a) The electrostatic potential between a charge q_1 and a charge q_2 separated a distance r is

$$U = \frac{1}{4\pi\epsilon_0}\frac{q_1q_2}{r}.$$

If there is a charge transfer of one electron between the X and Y atoms, then we are left with a line of ions have unit charge and alternating sign

$$\cdots + - + - + - + - + \cdots$$

Therefore, the electrostatic energy felt between one X^+ ion and all the other ions is

$$U = \frac{e}{4\pi\epsilon_0}\left[\cdots + \frac{-e}{3a}+\frac{e}{2a}+\frac{-e}{a}+\frac{-e}{a}+\frac{e}{2a}+\frac{-e}{3a}+\cdots\right] = \frac{2e^2}{4\pi\epsilon_0 a}\left[-1+\frac{1}{2}-\frac{1}{3}+\frac{1}{4}+\cdots\right] = -\frac{e^2\ln 2}{2\pi\epsilon_0 a}.$$

(The last line follows from the hint.)

For the charge transfer to be energetically favourable, it must be that

$$-\frac{e^2 \ln 2}{2\pi\epsilon_0 a} + E_1 < 0.$$

(b) If there is a charge transfer of z electrons between the X and Y atoms, the electrostatic energy felt between one X^{z+} ion and all the other ions is

$$\begin{aligned} U &= \frac{ze}{4\pi\epsilon_0}\left[\cdots + \frac{-ze}{3a} + \frac{ze}{2a} + \frac{-ze}{a} + \frac{-ze}{a} + \frac{ze}{2a} + \frac{-ze}{3a} + \cdots\right] \\ &= \frac{2z^2e^2}{4\pi\epsilon_0 a}\left[-1 + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} + \cdots\right] \\ &= -\frac{z^2e^2(2\ln 2)}{4\pi\epsilon_0 a}. \end{aligned}$$

The stable configuration is the one that minimizes

$$-z^2(2\ln 2)\frac{e^2}{4\pi\epsilon_0 a} + E_z$$

for $z = 0, 1, 2, 3, 4$. In units where $e^2/4\pi\epsilon_0 a = 0.2\,\text{eV}$, we have

z	E_z [eV]	E_{tot} [eV]
0	0	0
1	0.1	−0.1773
2	0.5	−0.6090
3	2.5	0.00467
4	10	5.56

Clearly, the minimum value occurs at $z = 2$, meaning that the $X^{2+}Y^{2-}$ configuration is stable.