Problem Set 11 Answers
Electronic configurations of many-electron atoms

1. (a) Suppose you have a recipe for determining $(Z_{eff})_i$ for each electron in the atom, the solutions to

$$\mathcal{H} = \sum_{i=1}^{electrons} \{-(\hbar^2/2\mu)\nabla^2{}_i - (Z_{eff})_i e^2/r_i\}$$

where the Laplacian $\nabla^2{}_i = \{\partial^2/\partial x_i^2 + \partial^2/\partial y_i^2 + \partial^2/\partial z_i^2\}$ when transformed to spherical coordinates becomes

$$\nabla^2{}_i = \partial^2/\partial r_i^2 + (2/r_i)\,\partial/\partial r_i + \{r_i^2\sin\theta_i)^{-1}\partial/\partial\theta_i(\sin\theta_i\,\partial/\partial\theta_i) + \{r_i^2\sin^2\theta_i)^{-1}(\partial^2/\partial\phi_i^2)$$

can be found by separation of variables. Let the functions Ψ be written as a simple product of one-electron functions:

$$\Psi(1,2,3,4,...) = \psi(1)\bullet\psi(2)\bullet\psi(3)\bullet\psi(4)\bullet\psi(5)\bullet\psi(6)\bullet...$$

If we substitute this into the Schrödinger equation:

$$\sum_{i=1}^{electrons} \{-(\hbar^2/2\mu)\nabla^2{}_i - (Z_{eff})_i e^2/r_i\}\psi(1)\bullet\psi(2)\bullet\psi(3)\bullet\psi(4)\bullet\psi(5)\bullet\psi(6)\bullet...$$
$$= E\psi(1)\bullet\psi(2)\bullet\psi(3)\bullet\psi(4)\bullet\psi(5)\bullet\psi(6)\bullet... ,$$

and perform the operations, we will get

$$\psi(2)\bullet\psi(3)\bullet\psi(4)\bullet\psi(5)\bullet\psi(6)\bullet...\{-(\hbar^2/2\mu)\nabla^2{}_1 - (Z_{eff})_1 e^2/r_1\}\psi(1)$$
$$+\psi(1)\bullet\psi(3)\bullet\psi(4)\bullet\psi(5)\bullet\psi(6)\bullet...\{-(\hbar^2/2\mu)\nabla^2{}_2 - (Z_{eff})_2 e^2/r_2\}\psi(2)$$
$$+\psi(1)\bullet\psi(3)\bullet\psi(4)\bullet\psi(5)\bullet\psi(6)\bullet...\{-(\hbar^2/2\mu)\nabla^2{}_3 - (Z_{eff})_2 e^2/r_3\}\psi(3) + ...$$
$$=E\psi(1)\bullet\psi(2)\bullet\psi(3)\bullet\psi(4)\bullet\psi(5)\bullet\psi(6)\bullet... ,$$

Now divide both sides by $\psi(1)\bullet\psi(2)\bullet\psi(3)\bullet\psi(4)\bullet\psi(5)\bullet\psi(6)\bullet...$
To get

$$\frac{\{-(\hbar^2/2\mu)\nabla^2{}_1 - (Z_{eff})_1 e^2/r_1\}\psi(1)}{\psi(1)} + \frac{\{-(\hbar^2/2\mu)\nabla^2{}_2 - (Z_{eff})_2 e^2/r_2\}\psi(2)}{\psi(2)} + ... = E$$

Since E is a constant, the only possibility of ending up with a sum of numbers such that for any coordinates chosen independently for particle 1, for particle 2, and so on, the sum is always equal to the constant E, is for each of the terms to be individually equal to constants. Call the constants E_1, E_2, ...That is,

$$\frac{\{-(\hbar^2/2\mu)\nabla^2{}_1 - (Z_{eff})_1 e^2/r_1\}\psi(1)}{\psi(1)} = E_1 \qquad \frac{\{-(\hbar^2/2\mu)\nabla^2{}_2 - (Z_{eff})_2 e^2/r_2\}\psi(2)}{\psi(2)} = E_2$$

So now all we have to do is solve each equation to find the functions $\psi(1)$ and the constants E_1, etc. That is, we need to solve $\{-(\hbar^2/2\mu)\nabla^2{}_1 - (Z_{eff})_1 e^2/r_1\}\psi(1) = E_1\,\psi(1)$, for example. Note that all the equations are hydrogen atom types of equations. Therefore,

$$\psi(1) = R_{n\ell}(r)\bullet\Theta_{\ell m}(\theta)\bullet\Phi_m(\phi) ,$$

the hydrogen functions except that we have $(Z_{eff})_1$ instead of Z=1. The energies E_1 are also known: They are $-[(Z_{eff})_1/n]^2 e^2/2a_0$.

Therefore the functions for the many-electron atom with this hamiltonian are of the form

$\Psi(1,2,3,4,...) = R_{n1\ell 1}(r_1) \bullet \Theta_{\ell 1 m1}(\theta_1) \bullet \Phi_{m1}(\phi_1) \bullet R_{n2\ell 2}(r_2) \bullet \Theta_{\ell 2 m2}(\theta_2) \bullet \Phi_{m2}(\phi_2) \bullet ...$

(b) The energies are
$E = E_1 + E_2 + E_3 + ... = -[(Z_{eff})_1/n_1]^2 e^2/2a_0 - [(Z_{eff})_2/n_2]^2 e^2/2a_0 - (Z_{eff})_3/n_3]^2 e^2/2a_0 ...$
Introduce the m_s quantum number for each electron, which is either +½ or –½, corrresponding to having z component of the spin angular momentum equal to either $+½\hbar$ or $–½\hbar$. Thus, every one of the electrons can have either one of these m_s values, subject only to the **restriction that no more than one electron may have exactly the same set of quantum numbers n, ℓ, m_ℓ, m_s.** Specifying the set of four quantum numbers n, ℓ, m_ℓ, m_s to each hydrogen-like function $\Psi_{n, \ell, m\ell, ms}(r_i,\theta_i,\phi_i)$ is sufficient to define the function $\Psi_{n, \ell, m\ell, ms}(r_i,\theta_i,\phi_i)$ itself.
The energy of the Li atom in its lowest (ground) energy level can be calculated
Li Z = 3, electronic configuration: $1s^2 2s$

electron	n_i	ℓ_i	$(Z_{eff})_i/n_i$ C&R	$(Z_{eff})_i/n_i$ Slater
1	1	0	2.6905	2.70
2	1	0	2.6905	2.70
3	2	0	0.6396	0.65

$E_{grd} = \{- 2(2.6905)^2 - 1(0.6396)^2\} \bullet 13.6$ eV
The electronic configuration of the lowest energy state of Na atom is $1s^2 2s^2 2p^6 3s$.
(c) (i) Energy of the ground state of He atom is $- 2(1.6875)^2 (e^2/2a_0)$
(ii) Li atom states $1s^2 2s$, $1s^2 2p$, $1s^2 3s$, $1s^2 3p$ not including spin-orbit coupling.
The energies of the excited states are different, but the Clementi & Raimondi effective Z have only been determined for the ground state. On the other hand, the Slater rules make the approximation that each electron in a subshell has the same contribution to the screening, which is incorrect, since electrons in s and p orbitals have distributions in space that are quite dissimilar, leading to larger screening from s than from p.
Using Slater's rules,
Li Z = 3, electronic configuration: $1s^2 2s$

Li $1s^2 2s$ electron	n	ℓ	screening from others 1	2	3	$s_{n\ell}$	Z-$s_{n\ell}$
1	1	0	self	0.30	0	0.30	2.70
2	1	0	0.30	self	0	0.30	2.70
3	2	0	0.85	0.85	self	1.70	1.30

$E_{grd} = \{- 2(2.70)^2 - 1(0.65)^2\} \bullet 13.6$ eV

Li Z = 3, electronic configuration: $1s^2 2p$

Li $1s^2 2p$ electron	n	ℓ	screening from others 1	2	3	$s_{n\ell}$	Z-$s_{n\ell}$

1	1	0	self	0.30	0	0.30	2.70
2	1	0	0.30	self	0	0.30	2.70
3	2	1	0.85	0.85	self	1.70	1.30

Because of the approximations used, $E_{first\ exc}$ is indistinguishable from energy of $1s^2 2s$

Li Z = 3, electronic configuration: $1s^2 3s$

Li $1s^2 3s$ electron	n	ℓ	screening from others			$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3		
1	1	0	self	0.30	0	0.30	2.70
2	1	0	0.30	self	0	0.30	2.70
3	3	0	1	1	self	2.0	1. 0

$E_{second\ exc} = \{- 2(2.70)^2 - 1(1)^2\}\bullet 13.6$ eV

Li Z = 3, electronic configuration: $1s^2 3p$

Li $1s^2 3p$ electron	n	ℓ	screening from others			$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3		
1	1	0	self	0.30	0	0.30	2.70
2	1	0	0.30	self	0	0.30	2.70
3	3	1	1	1	self	2.0	1. 0

Because of the approximations used, $E_{third\ exc}$ is indistinguishable from energy of $1s^2 3s$

First ionization potential of Li atom corresponding to the process

Li(ground state) $\rightarrow$ Li^+ ion (ground state).

Li^+ Z = 3, electronic configuration: $1s^2$

Li^+ electron	n	ℓ	screening from others			$s_{n\ell}$	Z-$s_{n\ell}$
			1	2			
1	1	0	self	0.30		0.30	2.70
2	1	0	0.30	self		0.30	2.70

In units of $e^2/2a_0$, $E_{Li+} = - 2(2.70)^2$

$IP_1 = - 2(2.70)^2 - \{- 2(2.70)^2 - 1(0.65)^2\} = 1(0.65)^2 = 0.4225$

Li^{++} Z = 3, electronic configuration: 1s

electron	n	ℓ	screening from others			$s_{n\ell}$	Z-$s_{n\ell}$
			1				
1	1	0	self			0	3

$E_{Li++} = - 3^2$

$IP_2 = - 3^2 - \{- 2(2.70)^2 \} = 5.58$ much, much larger than first ionization potential

(iii) The first ionization potentials have periodic behavior

Ionization He $1s^2 \rightarrow 1s$

He electron	n	ℓ	screening from others			$s_{n\ell}$	Z-$s_{n\ell}$
			1	2			
1	1	0	self	0.30		0.30	1.70
2	1	0	0.30	self		0.30	1.70

$IP = -2^2 - [-2(1.70)^2] = 1.78$

Li $1s^2 2s \rightarrow 1s^2$

we have done this one: $IP_1 = - 2(2.70)^2 - \{- 2(2.70)^2 - (0.65)^2\} = 1(0.65)^2 = 0.4225$

Be $1s^2 2s^2 \rightarrow 1s^2 2s$

Be electron	n	ℓ	screening from others				$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4		
1	1	0	self	0.30	0	0	0.30	3.70
2	1	0	0.30	self	0	0	0.30	3.70
3	2	1	0.85	0.85	self	0.35	2.05	1.95
4	2	1	0.85	0.85	.35	self	2.05	1.95

Be^+ electron	n	ℓ	screening from others				$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3			
1	1	0	self	0.30	0		0.30	3.70
2	1	0	0.30	self	0		0.30	3.70
3	2	1	0.85	0.85	self		1.7	2.3

Note the $1s^2$ is unchanged in going from Be to Be^+ ion. So only need to consider the change in energy coming from those electrons in the subshell from which the electron is ejected. In units of $e^2/2a_0$: $\{-(2.3/2)^2 - [-2 (1.95/2)^2]\} = -1.322 + 1.901 = 0.69$

B $1s^2 2s^2 2p \rightarrow 1s^2 2s^2$

B electron	n	ℓ	screening from others					$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5		
1	1	0	self	0.30	0	0	0	0.30	4.70
2	1	0	0.30	self	0	0	0	0.30	4.70
3	2	0	0.85	0.85	self	.35	.35	2.05	2.95
4	2	0	0.85	0.85	.35	self	.35	2.05	2.95
5	2	1	0.85	0.85	.35	.35	self	2.05	2.95

B^+ electron	n	ℓ	screening from others				$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4		
1	1	0	self	0.30	0	0	0.30	4.70
2	1	0	0.30	self	0	0	0.30	4.70
3	2	0	0.85	0.85	self	.35	2.4	2.6
4	2	0	0.85	0.85	.35	self	2.4	2.6

Note the $1s^2$ is unchanged in going from B to B^+ ion. So only need to consider the change in energy coming from those electrons in the subshell from which the electron is ejected. In units of $e^2/2a_0$: $\{-2(2.95/2)^2 - [-3\,(2.6/2)^2]\} = -4.351 + 5.07 = 0.719$

C $1s^2 2s^2 2p^2 \rightarrow 1s^2 2s^2 2p$

C electron	n	ℓ	screening from others						$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5	6		
1	1	0	self	0.30	0	0	0	0	0.30	5.70
2	1	0	0.30	self	0	0	0	0	0.30	5.70
3	2	0	0.85	0.85	self	.35	.35	.35	2.75	3.25
4	2	0	0.85	0.85	.35	self	.35	.35	2.75	3.25
5	2	1	0.85	0.85	.35	.35	self	.35	2.75	3.25
6	2	1	0.85	0.85	.35	.35	.35	self	2.75	3.25

C^+ electron	n	ℓ	screening from others						$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5			
1	1	0	self	0.30	0	0	0		0.30	5.70
2	1	0	0.30	self	0	0	0		0.30	5.70
3	2	0	0.85	0.85	self	.35	.35		2.4	3.6
4	2	0	0.85	0.85	.35	self	.35		2.4	3.6
5	2	1	0.85	0.85	.35	.35	self		2.4	3.6

Note the $1s^2$ is unchanged in going from C to C^+ ion. So only need to consider the change in energy coming from those electrons in the subshell from which the electron is ejected. In units of $e^2/2a_0$: $\{-3(3.6/2)^2 - [-4\,(3.25/2)^2]\} = -9.72 + 10.562 = 0.842$

N $1s^2 2s^2 2p^3 \rightarrow 1s^2 2s^2 2p^2$

N electron	n	ℓ	screening from others							$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5	6	7		
1	1	0	self	0.30	0	0	0	0	0	0.30	6.70
2	1	0	0.30	self	0	0	0	0	0	0.30	6.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	3.1	3.9

4	2	0	0.85	0.85	.35	self	.35	.35	.35	3.1	3.9
5	2	1	0.85	0.85	.35	.35	self	.35	.35	3.1	3.9
6	2	1	0.85	0.85	.35	.35	.35	self	.35	3.1	3.9
7	2	1	0.85	0.85	.35	.35	.35	.35	self	3.1	3.9

N^+ electron	n	ℓ	screening from others						$s_{n\ell}$	$Z-s_{n\ell}$
			1	2	3	4	5	6		
1	1	0	self	0.30	0	0	0	0	0.30	6.70
2	1	0	0.30	self	0	0	0	0	0.30	6.70
3	2	0	0.85	0.85	self	.35	.35	.35	2.75	4.25
4	2	0	0.85	0.85	.35	self	.35	.35	2.75	4.25
5	2	1	0.85	0.85	.35	.35	self	.35	2.75	4.25
6	2	1	0.85	0.85	.35	.35	.35	self	2.75	4.25

Note the $1s^2$ is unchanged in going from N to N^+ ion. So only need to consider the change in energy coming from those electrons in the subshell from which the electron is ejected. In units of $e^2/2a_0$: $\{-4(4.25/2)^2 - [-5\ (3.9/2)^2]\} = -18.0625 + 19.0125 = 0.95$

O $1s^22s^22p^4 \rightarrow 1s^22s^22p^3$

O electron	n	ℓ	screening from others								$s_{n\ell}$	$Z-s_{n\ell}$
			1	2	3	4	5	6	7	8		
1	1	0	self	0.30	0	0	0	0	0	0	0.30	7.70
2	1	0	0.30	self	0	0	0	0	0	0	0.30	7.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	3.45	4.55
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	3.45	4.55
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	3.45	4.55
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	3.45	4.55
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	3.45	4.55
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	3.45	4.55

O^+ electron	n	ℓ	screening from others							$s_{n\ell}$	$Z-s_{n\ell}$
			1	2	3	4	5	6	7		
1	1	0	self	0.30	0	0	0	0	0	0.30	7.70
2	1	0	0.30	self	0	0	0	0	0	0.30	7.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	3.1	4.9
4	2	0	0.85	0.85	.35	self	.35	.35	.35	3.1	4.9
5	2	1	0.85	0.85	.35	.35	self	.35	.35	3.1	4.9
6	2	1	0.85	0.85	.35	.35	.35	self	.35	3.1	4.9
7	2	1	0.85	0.85	.35	.35	.35	.35	self	3.1	4.9

Note the $1s^2$ is unchanged in going from O to O^+ ion. So only need to consider the change in energy coming from those electrons in the subshell from which the electron is ejected. In units of $e^2/2a_0$: $\{-5(4.9/2)^2 - [-6(4.55/2)^2]\} = -30.0125 + 31.05375 = 1.04$

F $1s^2 2s^2 2p^5 \rightarrow 1s^2 2s^2 2p^4$

F electron	n	ℓ	screening from others 1	2	3	4	5	6	7	8	9	$s_{n\ell}$	Z-$s_{n\ell}$
1	1	0	self	0.30	0	0	0	0	0	0	0	0.30	8.70
2	1	0	0.30	self	0	0	0	0	0	0	0	0.30	8.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	.35	3.8	5.2
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	.35	3.8	5.2
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	.35	3.8	5.2
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	.35	3.8	5.2
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	.35	3.8	5.2
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	.35	3.8	5.2
9	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	self	3.8	5.2

F^+ electron	n	ℓ	screening from others 1	2	3	4	5	6	7	8	$s_{n\ell}$	Z-$s_{n\ell}$
1	1	0	self	0.30	0	0	0	0	0	0	0.30	8.70
2	1	0	0.30	self	0	0	0	0	0	0	0.30	8.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	3.45	5.55
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	3.45	5.55
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	3.45	5.55
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	3.45	5.55
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	3.45	5.55
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	3.45	5.55

Note the $1s^2$ is unchanged in going from F to F^+ ion. So only need to consider the change in energy coming from those electrons in the subshell from which the electron is ejected. In units of $e^2/2a_0$: $\{-6(5.55/2)^2 - [-7(5.2/2)^2]\} = -46.20 + 47.32 = 1.12$

Ne $1s^2 2s^2 2p^6 \rightarrow 1s^2 2s^2 2p^5$

Ne electron	n	ℓ	screening from others 1	2	3	4	5	6	7	8	9/10	$s_{n\ell}$	Z-$s_{n\ell}$
1	1	0	self	0.30	0	0	0	0	0	0	0	0.30	9.70
2	1	0	0.30	self	0	0	0	0	0	0	0	0.30	9.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	.35	4.15	5.85
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	.35	4.15	5.85

5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	.35	4.15	5.85
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	.35	4.15	5.85
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	.35	4.15	5.85
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	.35	4.15	5.85
9	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	self	4.15	5.85
10	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	.35	4.15	5.85

Ne^+ electron	n	ℓ	screening from others									$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5	6	7	8	9		
1	1	0	self	0.30	0	0	0	0	0	0	0	0.30	9.70
2	1	0	0.30	self	0	0	0	0	0	0	0	0.30	9.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	.35	3.8	6.2
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	.35	3.8	6.2
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	.35	3.8	6.2
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	.35	3.8	6.2
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	.35	3.8	6.2
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	.35	3.8	6.2
9	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	self	3.8	6.2

Note the $1s^2$ is unchanged in going from Ne to Ne^+ ion. So only need to consider the change in energy coming from those electrons in the subshell from which the electron is ejected. In units of $e^2/2a_0$: $\{-7(6.2/2)^2 - [-8(5.85/2)^2]\} = -67.27 + 68.445 = 1.175$

Na $1s^2 2s^2 2p^6 3s \rightarrow 1s^2 2s^2 2p^6$

Na electron	n	ℓ	screening from others									$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5	6	7	8	9/10		
1	1	0	self	0.30	0	0	0	0	0	0	0	0.30	10.70
2	1	0	0.30	self	0	0	0	0	0	0	0	0.30	10.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	.35	4.15	6.85
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	.35	4.15	6.85
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	.35	4.15	6.85
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	.35	4.15	6.85
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	.35	4.15	6.85
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	.35	4.15	6.85
9	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	self	4.15	6.85
10	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	.35	4.15	6.85
11	3	0	1.0	1.0	.85	.85	.85	.85	.85	.85	.85	8.80	2.2

11th electron does not screen any of the others

Na^+ electron	n	ℓ	screening from others									$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5	6	7	8	9/10		
1	1	0	self	0.30	0	0	0	0	0	0	0	0.30	10.70
2	1	0	0.30	self	0	0	0	0	0	0	0	0.30	10.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	.35	4.15	6.85
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	.35	4.15	6.85
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	.35	4.15	6.85
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	.35	4.15	6.85
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	.35	4.15	6.85
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	.35	4.15	6.85
9	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	self	4.15	6.85
10	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	.35	4.15	6.85

Note the $1s^2$ and the $2s^2 2p^6$ are unchanged in going from Na to Na^+ ion. So only need to consider the change in energy coming from those electrons in the subshell from which the electron is ejected. In units of $e^2/2a_0$: - [-(2.2/3)^2]} = 0.538

The trend in calculated IP mimics that of experiments:

H	He	Li	Be	B	C	N	O	F	Ne	Na			
1	1.78	.42	.69	.719	.842	.95	1.04	1.12	1.175	.538			

(d) (i) Transfer of one electron from F to Na

$Na + F \rightarrow Na^{+} + F^{-}$

F^{-} ion $1s^2 2s^2 2p^6$

F- ion electron	n	ℓ	screening from others									$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5	6	7	8	9/10		
1	1	0	self	0.30	0	0	0	0	0	0	0	0.30	8.70
2	1	0	0.30	self	0	0	0	0	0	0	0	0.30	8.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	.35	4.15	4.85
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	.35	4.15	4.85
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	.35	4.15	4.85
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	.35	4.15	4.85
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	.35	4.15	4.85
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	.35	4.15	4.85
9	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	self	4.15	4.85
10	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	.35	4.15	4.85

Note the $1s^2$ is unchanged in going from F to F^{-} ion. So only need to consider the change in energy coming from those electrons in the subshell to which the electron is added. In units of $e^2/2a_0$: $\{-8(4.85/2)^2 - [-7(5.2/2)^2]\} = -47.63 + 47.32 = -0.31$

$Na + F \rightarrow Na^{+} + F^{-}$ $\quad 0.467 + (-0.31) = +0.16$ in units of $e^2/2a_0$.

According to this approximate calculation, energy is absorbed.

(ii) The energy of the x-ray emitted when a 2s electron falls into the hole left in the 1s shell of a Na atom.

$Na^{+}\ 1s\ 2s^2 2p^6\ 3s \rightarrow Na^{+}\ 1s^2\ 2s\ 2p^6\ 3s$

Na^{+} electron	n	ℓ	screening from others									$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5	6	7	8	9/10		
1	1	0	self	0	0	0	0	0	0	0	0	0	11
2	2	0	0.85	self	.35	.35	.35	.35	.35	.35	.35	3.3	7.7
3	2	0	0.85	.35	self	.35	.35	.35	.35	.35	.35	3.3	7.7
4	2	1	0.85	.35	35	self	.35	.35	.35	.35	.35	3.3	7.7
5	2	1	0.85	.35	.35	.35	self	.35	.35	.35	.35	3.3	7.7
6	2	1	0.85	.35	.35	.35	.35	self	.35	.35	.35	3.3	7.7
7	2	1	0.85	.35	.35	.35	.35	.35	self	.35	.35	3.3	7.7
8	2	1	0.85	.35	.35	35	.35	.35	.35	self	.35	3.3	7.7
9	2	1	0.85	.35	.35	.35	.35	.35	.35	.35	self	3.3	7.7
10	3	0	1	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	7.80	3.20

10th electron does not screen any of the others

$1s\ 2s^2 2p^6\ 3s$: $-\{(11/1)^2 + 8(7.7/2)^2 + (3.2/3)^2\} = -\{121 + 118.58 + 1.141\} = -240.72$

Na^+ electron	n	ℓ	screening from others									$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5	6	7	8	9/10		
1	1	0	self	0.30	0	0	0	0	0	0	0	0.30	10.70
2	1	0	0.30	self	0	0	0	0	0	0	0	0.30	10.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	.35	4.15	6.85
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	.35	4.15	6.85
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	.35	4.15	6.85
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	.35	4.15	6.85
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	.35	4.15	6.85
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	.35	4.15	6.85
9	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	self	4.15	6.85
10	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	.35	4.15	6.85

$1s^2\ 2s\ 2p^6\ 3s$: $-\{2(10.7/1)^2 + 8(6.85/2)^2\} = -\{228.98 + 93.845\} = -322.825$

$Na^+\ 1s\ 2s^2 2p^6\ 3s \rightarrow Na^+\ 1s^2\ 2s\ 2p^6\ 3s$:

$-322.825-(-240.72) = -82.1\ e^2/2a_0 = 1116.6$ eV x-ray emitted.

(iii) EA (F): F $1s^2 2s^2 2p^6 \rightarrow F^-$ ion $1s^2\ 2s^2 2p^6\ 3s$ (already calculated) = -0.31 Definition of EA is E(neutral) - E(-ion) = +0.31 for F

IP (F) F $1s^2 2s^2 2p^6 \rightarrow F^+$ ion $1s^2\ 2s\ 2p^5$ (already calculated) = +1.12 absorbed

Electronegativity (F) = ½(EA + IP), EA + IP = 1.43 in $e^2/2a_0$ units

EA(Li) Li $1s^2 2s \rightarrow Li^-$ ion $1s^2\ 2s^2$

Li^- ion electron	n	ℓ	screening from others				$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4		
1	1	0	self	0.30	0	0	0.30	2.70
2	1	0	0.30	self	0	0	0.30	2.70
3	2	1	0.85	0.85	self	0.35	2.05	0.95
4	2	1	0.85	0.85	.35	self	2.05	0.95

E (Li^-) = $-\{2(2.70)^2 + 2(.95/2)^2\}$

E (Li) already calculated = $-\{2(2.70)^2 + 1(0.65)^2\}$

EA = $-1(0.65)^2 + 2(0.95/2)^2 = -0.4225 + 0.226 = -0.20$

IP (Li) already calculated: 0.4225

Electronegativity (Li): EA + IP = 0.226 in $e^2/2a_0$ units

EA (Na) Na $1s^2 2s^2 2p^6 3s \rightarrow Na^-$ ion $1s^2 2s^2 2p^6 3s^2$

Na^- ion electron	n	ℓ	screening from others									$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5	6	7	8	9/10		
1	1	0	self	0.30	0	0	0	0	0	0	0	0.30	10.70
2	1	0	0.30	self	0	0	0	0	0	0	0	0.30	10.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	.35	4.15	6.85
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	.35	4.15	6.85
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	.35	4.15	6.85
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	.35	4.15	6.85
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	.35	4.15	6.85
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	.35	4.15	6.85
9	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	self	4.15	6.85
10	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	.35	4.15	6.85
11	3	0	1.0	1.0	.85	.85	.85	.85	.85	.85	.85	9.15	1.85
12	3	0	1.0	1.0	.85	.85	.85	.85	.85	.85	.85	9.15	1.85

11 and 12th electron do not screen any others except each other by 0.35.

EA: E(Na)- E(Na^-) $-(2.20/3)^2 - \{-2(1.85/3)^2\} = -.5375+.761 = +0.22$

IP (Na) already calculated 0.538

Electronegativity (Na): EA + IP = +0.22+0.54 = 0.76

O $1s^2 2s^2 2p^4 \rightarrow O^-$ ion $1s^2 2s^2 2p^5$

O- electron	n	ℓ	screening from others									$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3	4	5	6	7	8	9		
1	1	0	self	0.30	0	0	0	0	0	0	0	0.30	7.70
2	1	0	0.30	self	0	0	0	0	0	0	0	0.30	7.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	.35	3.8	4.2
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	.35	3.8	4.2
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	.35	3.8	4.2
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	.35	3.8	4.2
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	.35	3.8	4.2
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	.35	3.8	4.2
9	2	1	0.85	0.85	.35	.35	.35	.35	.35	.35	self	3.8	4.2

EA O atom = $-6(4.55/2)^2 - [-\{7(4.20/2)^2\}] = -31.05375+30.87 = -0.18$

IP O atom already calculated: 1.04

Electronegativity (O): EA + IP = -0.18 + 1.04 = 0.86 in units of $e^2/2a_0$

C^- ion $1s^2 2s^2 2p^3$

C-electron	n	ℓ	screening from others							$s_{n\ell}$	Z-s $_{n\ell}$
			1	2	3	4	5	6	7		
1	1	0	self	0.30	0	0	0	0	0	0.30	5.70
2	1	0	0.30	self	0	0	0	0	0	0.30	5.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	3.1	2.9
4	2	0	0.85	0.85	.35	self	.35	.35	.35	3.1	2.9
5	2	1	0.85	0.85	.35	.35	self	.35	.35	3.1	2.9
6	2	1	0.85	0.85	.35	.35	.35	self	.35	3.1	2.9
7	2	1	0.85	0.85	.35	.35	.35	.35	self	3.1	2.9

EA C atom = $-4(3.25/2)^2 - [-\{5(2.9/2)^2\}] = -10.56 + 10.51 = -0.05$

IP C atom alreaedy calculated = 0.842

Electronegativity (C): EA + IP = -0.05+0.84 = 0.79

H- ion $1s^2$

H-electron	n	ℓ	screening from others			$s_{n\ell}$	Z-s $_{n\ell}$
			1	2			
1	1	0	self	0.30		0.30	.70
2	1	0	0.30	self		0.30	.70

$E(H-) = -2(0.70/1)^2 = -0.98$

EA (H) = -1 -[-0.98] = -0.02

IP (H) = 1

Electronegativity (Hatom): EA+ IP = 0.96 in units of $e^2/2a_0$

N- ion $1s^2 2s^2 2p^4$

N- ion electron	n	ℓ	screening from others								$s_{n\ell}$	Z-s $_{n\ell}$
			1	2	3	4	5	6	7	8		
1	1	0	self	0.30	0	0	0	0	0	0	0.30	6.70
2	1	0	0.30	self	0	0	0	0	0	0	0.30	6.70
3	2	0	0.85	0.85	self	.35	.35	.35	.35	.35	3.45	3.55
4	2	0	0.85	0.85	.35	self	.35	.35	.35	.35	3.45	3.55
5	2	1	0.85	0.85	.35	.35	self	.35	.35	.35	3.45	3.55
6	2	1	0.85	0.85	.35	.35	.35	self	.35	.35	3.45	3.55
7	2	1	0.85	0.85	.35	.35	.35	.35	self	.35	3.45	3.55
8	2	1	0.85	0.85	.35	.35	.35	.35	.35	self	3.45	3.55

$E(N-) = -\{2(6.70/1)^2 + 6(3.55/2)^2\}$ $E(N) = -\{2(6.70/1)^2 + 5(3.9/2)^2\}$

$EA(N) = -5(3.9/2)^2 + 6(3.55/2)^2 = -19.01 + 18.90 = -0.11$

IP (N) already calculated = 0.95

Electronegativity (N): EA + IP = -0.11 + 0.95=0.84 in units of $e^2/2a_0$

The electronegativity :

F	O	N	C	Li	Na	H
1.43	0.86	0.84	0.79	0.23	0.76	0.96

Results are disappointing, but considering the approximations in the Slater rules for screening, it is probably too much to ask that these energy differences be sufficiently accurate. Nevertheless, F is found to be the most electronegative atom.

3. Energy of the Ar atom in its ground state:
Ar: $1s^22s^22p^63s^23p^6$
1s screen each other by 0.30 leads to Z_{eff} = 18-0.3 = 17.7
(2s,2p) are screened by 1s by 0.85 twice and screen each other 7 times by 0.35, Z_{eff} = 18-4.15 = 13.85
(3s,3p) are screened by 1s by 1.0 twice and screened by (2s,2p) 8 times by 0.85, and screen each other 7 times by 0.35, Zeff = 18- 11.25= 6.75
$E = -\{2(17.7/1)^2 + 8(13.85/2)^2 + 8(6.75/3)^2\} = -\{626.58 + 383.64 + 40.5\} = -1050.7$ in units of $e^2/2a_0$ = -14289.86 eV

Removing one electron from the (3s,3p) subshell
In Ar + ion, (3s,3p) are screened by 1s by 1.0 twice and screened by (2s,2p) 8 times by 0.85, and screen each other 6 times by 0.35, Zeff = 18- 10.90= 7.1
would require $-7(7.1/3)^2 - [-8(6.75/3)^2]$ or -39.26+ 40.5 = 1.24 in units of $e^2/2a_0$
or 16.82 eV. Compare with expt value 29.2, 16 and 15.5 eV

Removing one electron from the (2s,2p) subshell
In Ar + ion, (2s,2p) are screened by 1s by 0.85 twice and screen each other 6 times by 0.35, Zeff = 18- 3.8= 14.2. The (3s,3p) are screened by 1s by 1.0 twice and screened by (2s,2p) 7 times by 0.85, and screen each other 7 times by 0.35, Zeff = 18- 10.45= 7.55.
The energy of the ion is $-2(17.7/1)^2 - 7(14.2/2)^2 - 8(7.6/3)^2$ while the energy of the atom is $-\{2(17.7/1)^2 + 8(13.85/2)^2 + 8(6.75/3)^2\}$. The energy required is $-7(14.2/2)^2 - 8(7.6/3)^2 - [-8(13.85/2)^2 - 8(6.75/3)^2]$ or -404.14 + 424.14 = 20 in units of $e^2/2a_0$ or 272 eV.
Compare with expt value 326.3 , 250.5, 238.5 eV.

Removing one electron from the (1s) subshell
In Ar + ion 1s is unscreened so Zeff = 18. The (2s,2p) are screened by 1s by 0.85 and screen each other 7 times by 0.35, Zeff = 18- 3.3= 14.72. The (3s,3p) are screened by 1s by 1.0 twice and screened by (2s,2p) 8 times by 0.85, and screen each other 7 times by 0.35, Zeff = 18- 10.25= 7.75. The energy of the ion is $-1(18/1)^2 - 8(14.72/2)^2 - 8(7.75/3)^2$ while the energy of the atom is $-\{2(17.7/1)^2 + 8(13.85/2)^2 + 8(6.75/3)^2\}$. or -810.68 + 1050.72 = 240 in units of $e^2/2a_0$ or 3264 eV. Compare with experimental value 3206 eV.

eV	1s	2s	2p	3s	3p
EXPT	3206	326.3	250.5, 238.5	29.2	16, 15.5
Calculated	3264	272	272	16.82	16.82

The results are in reasonable agreement with experiment. Deficiencies of the Slater rules are that the 2s and 2p screening are treated equivalently whereas this experiment shows they have different energies. Ditto with 3s and 3p. Also, the additional splittings seen in the spectra are due to coupling of electron spin and electron orbital angular momenta, which are of course not included in our calculations.