Simon
5,2

a) $\varepsilon_n = -\frac{az^2}{n}$ $a = 13,6\,eV$

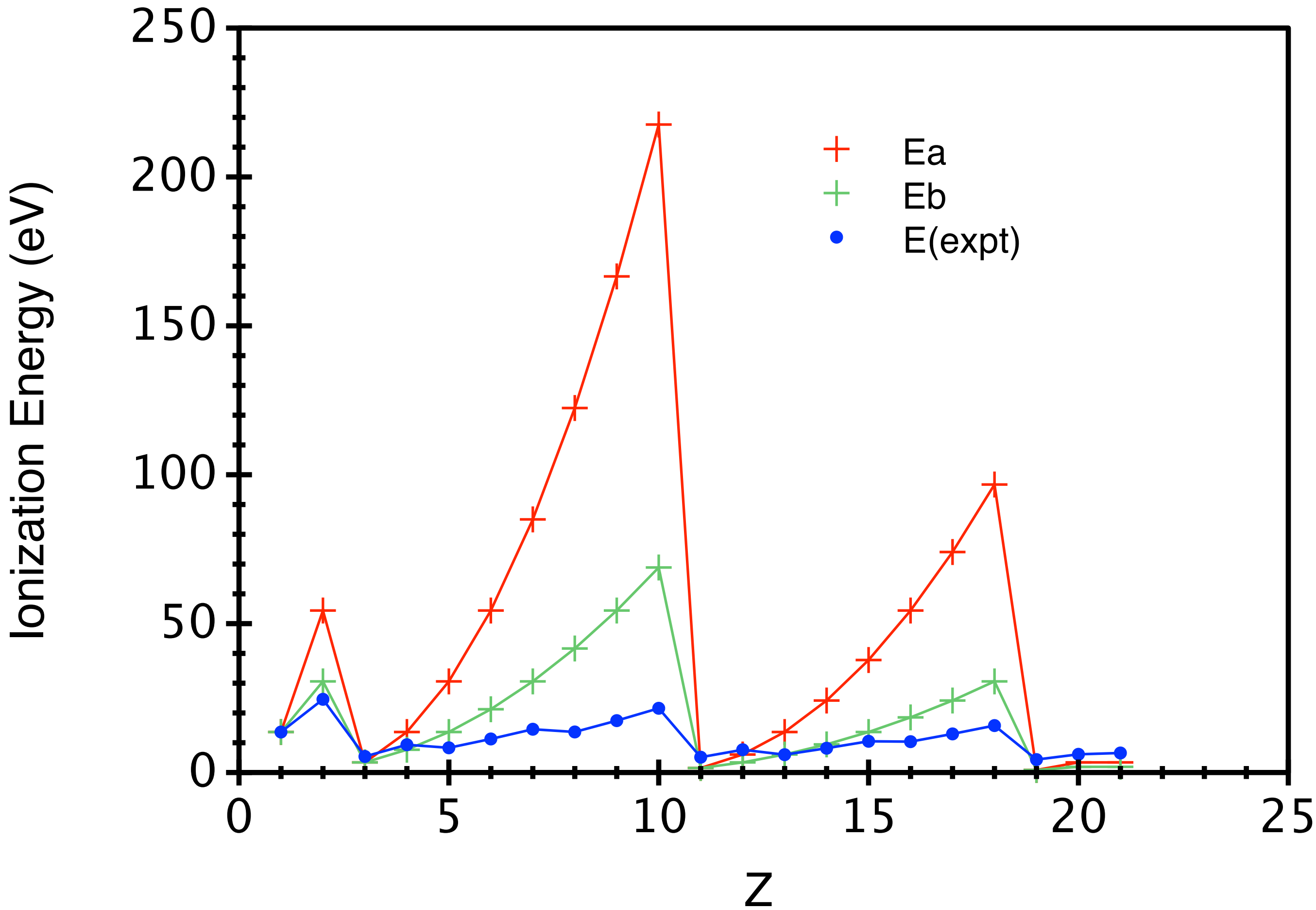
$$\varepsilon_{ion} = 0 - \frac{-az^2}{n^2} = \frac{az^2}{n^2}$$

b) $z = Z_{Nuc} - N_{inside}$ assumes all other electrons with $n' < n$ are inside the orbital of the electron being considered. The inner electrons are assumed to partially cancel the nuclear charge.

$z = Z_{Nuc} - N_{inside} - \frac{(N_{same} - 1)}{2}$ Assumes electrons with $n' < n$ (partially) cancel the nuclear charge, but those in the nth shell only $\frac{1}{2}$-cancels the nuclear charge

Table 1

	n	Znuc	Ninside	Nsame	Za=Znuc-Nsame	Zb=Znuc-Ninside-(Nsame-1)/2	Ea(ion)	Eb(ion)	Eion(eV)	Eion(expt) from http://www.sciencegeek.net/tables/IonizationNRG.pdf
	1	1	0	1	1	1	13.6	13.6	13.5980413	1312
	1	2	0	2	2	1.5	54.4	30.6	24.5842637	2372
	2	3	2	1	1	1	3.4	3.4	5.38946759	520
	2	4	2	2	2	1.5	13.6	7.65	9.32792468	900
	2	5	2	3	3	2	30.6	13.6	8.30185296	801
	2	6	2	4	4	2.5	54.4	21.25	11.2660601	1087
	2	7	2	5	5	3	85	30.6	14.5308337	1402
	2	8	2	6	6	3.5	122.4	41.65	13.6187700	1314
	2	9	2	7	7	4	166.6	54.4	17.4224904	1681
	2	10	2	8	8	4.5	217.6	68.85	21.5682347	2081
	3	11	10	1	1	1	1.511111111111	1.511111111111	5.14072293	496
	3	12	10	2	2	1.5	6.04444444444	3.4	7.64889824	738
	3	13	10	3	3	2	13.6	6.04444444444	5.99060051	578
	3	14	10	4	4	2.5	24.1777777777	9.44444444444	8.15675191	787
	3	15	10	5	5	3	37.7777777777	13.6	10.4887330	1012
	3	16	10	6	6	3.5	54.4	18.5111111111	10.3643607	1000
	3	17	10	7	7	4	74.0444444444	24.1777777777	12.9658153	1251
	3	18	10	8	8	4.5	96.7111111111	30.6	15.7641927	1521
	4	19	18	1	1	1	0.85	0.85	4.34266715	419
	4	20	18	2	2	1.5	3.4	1.9125	6.11497284	590
	4	21	19	2	2	1.5	3.4	1.9125	6.56064036	633



250
200
150
100
50
0
Ionization Energy (eV)
0
5
10
15
20
25
Z
Ea
Eb
E(expt)

Simon

6.2 a) $E = \dfrac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \dfrac{\sum_{ij} \phi_i^* H_{ij} \phi_j}{\sum_i \phi_i^* \phi_i}$

$$0 = \frac{\partial E}{\partial \phi_K^*} = \frac{\left(\sum_i \phi_i^* \phi_i\right)\left(\sum_{ij} \delta_{iK} H_{ij} \phi_j\right) - \left(\sum_i \delta_{iK} \phi_i\right)\left(\sum_{ij} \phi_i^* H_{ij} \phi_j\right)}{\left(\sum_i \phi_i^* \phi_i\right)^2}$$

$$0 = \left(\sum_i \phi_i^* \phi_i\right)\left(\sum_j H_{Kj} \phi_j\right) - \left(\phi_K\right)\left(\sum_{ij} \phi_i^* H_{ij} \phi_j\right)$$

$$\sum_j H_{Kj} \phi_j = \underbrace{\frac{\left(\sum_{ij} \phi_i^* H_{ij} \phi_j\right)}{\left(\sum_i \phi_i^* \phi_i\right)}}_{\varepsilon} \phi_K$$

$$\underset{\sim}{H} \phi = \varepsilon \phi$$

b) $V_{cross} = \int d^3r \, \phi_1^*(\vec{r}) V_2(\vec{r}) \phi_1(\vec{r}) \overset{?}{=} \int d^3r \, \phi_2^*(\vec{r}) \underline{V_1}(\vec{r}) \phi_2(\vec{r})$

ϕ can be taken real & $\phi_1(\vec{r}) = \phi(\vec{r}-\vec{R}_1)$ $\phi_2(\vec{r}) = \phi(\vec{r}-\vec{R}_2)$
$V_1(\vec{r}) = V(\vec{r}-\vec{R}_1)$ $V_2(\vec{r}) = V(\vec{r}-\vec{R}_2)$

$$\int d^3r \, \phi(\vec{r}-\vec{R}_1) V(\vec{r}-\vec{R}_2) \phi(\vec{r}-\vec{R}_1) \overset{?}{=} \int d^3r \, \phi(\vec{r}-\vec{R}_2) V(\vec{r}-\vec{R}_1) \phi(\vec{r}-\vec{R}_2)$$

COV $\vec{r} \to \vec{r} + \vec{R}_2$ COV $\vec{r} \to \vec{r} + \vec{R}_1$

$$\int d^3r \, \phi(\vec{r}-(\vec{R}_1-\vec{R}_2)) V(\vec{r}) \phi(\vec{r}-(\vec{R}_1-\vec{R}_2)) \overset{?}{=} \int d^3r \, \phi(\vec{r}-(\vec{R}_2-\vec{R}_1)) V(\vec{r}) \phi(\vec{r}-(\vec{R}_2-\vec{R}_1))$$

Simon
6.2:
(cont.)

b) $\begin{pmatrix} \epsilon + V_c & -t \\ -t & \epsilon + V_c \end{pmatrix} V = \lambda V \rightarrow \det \begin{pmatrix} \epsilon + V_c - \lambda & -t \\ -t & \epsilon + V_c - \lambda \end{pmatrix} = 0$

$$(\epsilon + V_c - \lambda)^2 - t^2 = 0$$

$$\lambda^2 + \lambda(-2(\epsilon + V_c)) + (\epsilon + V_c)^2 - t^2 = 0$$

$$\lambda = \frac{+2(\epsilon + V_c) \pm \sqrt{4(\epsilon + V_c)^2 - 4 \cdot 1[(\epsilon + V_c)^2 - t^2]}}{2}$$

$$= \frac{2(\epsilon + V_c) \pm \sqrt{4t^2}}{2} = \epsilon + V_c \pm |t|$$

Simon
6.2
(cont.)

define $\vec{R} \equiv \vec{R}_1 - \vec{R}_2$)

$$\int d^3r\, \phi(\vec{r}-\vec{R})\, V(\vec{r})\, \phi(\vec{r}-\vec{R}) \stackrel{?}{=} \int d^3r\, \phi(\vec{r}+\vec{R})\, V(\vec{r})\, \phi(\vec{r}+\vec{R})$$

$$V(\vec{r}) = V(-\vec{r})$$

$$\int d^3r\, \phi(-\vec{r}-\vec{R})\, V(\vec{r})\, \phi(-\vec{r}-\vec{R}) \stackrel{?}{=} \quad \vdots$$

$\&$ $\phi(\vec{r}) = \pm\phi(-\vec{r})$

$$\int d^3r\, \phi(\vec{r}+\vec{R})\, V(\vec{r})\, \phi(\vec{r}+\vec{R}) \stackrel{\checkmark}{=} \int d^3r\, \phi(\vec{r}+\vec{R})\, V(\vec{r})\, \phi(\vec{r}+\vec{R})$$

$$t = -\int d^3r\, \phi(\vec{r}-\vec{R}_1)\, V(\vec{r}-\vec{R}_2)\, \phi(\vec{r}-\vec{R}_2) \stackrel{?}{=} -\int d^3r\, \phi(\vec{r}-\vec{R}_1)\, V(\vec{r}-\vec{R}_1)\, \phi(\vec{r}-\vec{R}_2$$

$\vec{r} \to \vec{r} + \vec{R}_2$ $\quad (\vec{R} \equiv \vec{R}_1 - \vec{R}_2)$ $\qquad r \to \vec{r} + \vec{R}_1$

$$\int d^3r\, \phi(\vec{r}-\vec{R})\, V(\vec{r})\, \phi(\vec{r}) \stackrel{?}{=} \int d^3r\, \phi(\vec{r})\, V(\vec{r})\, \phi(\vec{r}+\vec{R})$$

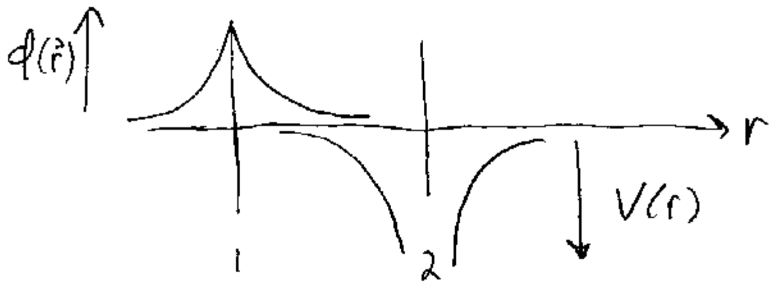
$\vec{r} \to -\vec{r}$, $V(\vec{r}) = V(-\vec{r})$

$$\int d^3r\, \phi(-\vec{r}-\vec{R})\, V(\vec{r})\, \phi(-\vec{r}) \stackrel{?}{=}$$

$$\phi(\vec{r}) = \pm\phi(-\vec{r})$$

$$\int d^3r\, \phi(\vec{r}+\vec{R})\, V(\vec{r})\, \phi(\vec{r}) \stackrel{\checkmark}{=} \int d^3r\, \phi(\vec{r})\, V(\vec{r})\, \phi(\vec{r}+\vec{R})$$

Simon
6.2
(cont.)



$$V_{cross} = \int d^3r\, \phi^2(\vec{r}-\vec{R}_1)\, V(\vec{r}-\vec{R}_2)$$

as shown in the graph above $\phi(\vec{r}-\vec{R}_1)$ is peaked around $\vec{R}_1$ so V_{cross} is approximately the Colomb energy for an electron at $\vec{R}_1$ in the nuclear potential centered on $\vec{R}_2$, & $V_{cross} < 0$. The Coulomb interaction between nuclei is $V_{Nuc} = \frac{+e^2}{4\pi\epsilon_0 |\vec{R}_1-\vec{R}_2|}$ since the nuclei are located precisely at $\vec{R}_1$ & $\vec{R}_2$. So, V_{cross} approximately cancels V_{Nuc}.

As $|\vec{R}_1-\vec{R}_2| \to 0$ $\int d^3r\, \phi^2(\vec{r}-\vec{R}_1) V(\vec{r}-\vec{R}_2) \to \int d^3r\, \phi^2(\vec{r}) V(\vec{r})$

so $\lim_{|\vec{R}_1-\vec{R}_2|\to 0} V_{cross} = \int d^3\, \phi^2(r) V(r)$ which is finite.

however $V_{Nuc} \to \infty$ as $|\vec{R}_1-\vec{R}_2| \to 0$ so the cancelation breaks down.

Simon

6.3

$$\det\begin{pmatrix} \epsilon_1+V_c-\lambda & -t \\ -t & \epsilon_2+V_c-\lambda \end{pmatrix} = (\lambda-\epsilon_1-V_c)(\lambda-\epsilon_2-V_c)-t^2$$

$$= \lambda^2 - \lambda(\epsilon_1+V_c+\epsilon_2+V_c) + (\epsilon_1+V_c)(\epsilon_2+V_c) - t^2 = 0$$

$$\begin{vmatrix} a-\lambda & c \\ c & b-\lambda \end{vmatrix} = (a-\lambda)(b-\lambda)-c^2 = \lambda^2-(a+b)\lambda+ab-c^2=0$$

$$\lambda = \frac{(a+b) \pm \sqrt{(a+b)^2-4(ab-c^2)}}{2} = \frac{(a+b)\pm\sqrt{a^2+b^2-2ab-4c^2}}{2}$$

$$\begin{pmatrix} a & c \\ c & b \end{pmatrix}\begin{pmatrix} V \\ 1 \end{pmatrix} = \lambda\begin{pmatrix} V \\ 1 \end{pmatrix} = \begin{pmatrix} aV+c \\ cV+b \end{pmatrix} \rightarrow \quad \lambda = cV+b$$

$$V = \frac{\lambda-b}{c}$$

$$V = \frac{(a+b)\pm\sqrt{a^2+b^2-2ab-4c^2}}{2c} - \frac{2b}{2c} = \frac{(a-b)\pm\sqrt{a^2+b^2-2ab-4c^2}}{2c}$$

w/ $\begin{pmatrix} a & c \\ c & b \end{pmatrix} \rightarrow \begin{pmatrix} \epsilon_1+V_c & -t \\ -t & \epsilon_2+V_c \end{pmatrix}$

$$\rightarrow V = \frac{(\epsilon_1-\epsilon_2)\pm\sqrt{(\epsilon_1+V_c)^2+(\epsilon_2+V_c)^2-2(\epsilon_1+V_c)(\epsilon_2+V_c)-4t^2}}{2(-t)}$$

$$V = \frac{(\epsilon_1-\epsilon_2)\pm\sqrt{\epsilon_1^2+\cancel{V_c^2}+\cancel{2\epsilon_1V_c}+\epsilon_2^2+\cancel{V_c^2}+\cancel{2\epsilon_2V_c}-2\epsilon_1\epsilon_2-\cancel{2V_c^2}-\cancel{2\epsilon_1V_c}-\cancel{2\epsilon_2V_c}-4t^2}}{-2t}$$

$$= \frac{(\epsilon_1-\epsilon_2)\pm\sqrt{\epsilon_1^2+\epsilon_2^2-2\epsilon_1\epsilon_2-4t^2}}{-2t} = \frac{(\epsilon_2-\epsilon_1)\pm\sqrt{(\epsilon_2-\epsilon_1)^2-4t^2}}{2t}$$

Simon
6.4

$$\Delta E_{Na, Cl \to NaCl} = E_{ionization}(Na) - E_{affinity}(Cl) - E_{binding}(NaCl)$$

$$= 5.14\,eV - 3.62\,eV - \frac{27.2\,eV}{r/a_0}$$

$$= 5.14\,eV - 3.26 - \frac{27.2\,eV}{0.236\,nm / 0.0529\,nm}$$

$$= (5.14\,eV - 3.26 - 6.1)\,eV = -4.22\,eV$$

This is the change in energy of the Na + Cl system, so the binding energy is +4.22eV. which is very close to the experimental value +4.26 eV. (i.e. the real NaCl is bound more tightly.) In our calculation we assumed the binding energy is purely Coulombic, but in fact There is some covalent bonding as well which is why the actual binding energy is greater.

Simon

6.5

a)

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{ij} \phi_i^* H_{ij} \phi_j}{\sum_{ij} \phi_i^* S_{ij} \phi_j}$$

$$\partial_{\phi_k^*} E = \frac{\left(\sum_{ij} \phi_i^* S_{ij} \phi_j\right)\left(\sum_{ij} \delta_{ik} H_{ij} \phi_j\right) - \left(\sum_{ij} \delta_{ik} S_{ij} \phi_j\right)\left(\sum_{ij} \phi_i^* H_{ij} \phi_j\right)}{\left(\sum_{ij} \phi_i^* S_{ij} \phi_j\right)^2}$$

$$\left(\sum_{ij} \phi_i^* S_{ij} \phi_j\right)\left(\sum_j H_{kj} \phi_j\right) = \left(\sum_j S_{kj} \phi_j\right)\left(\sum_{ij} \phi_i^* H_{ij} \phi_j\right)$$

$$\sum_j H_{kj} \phi_j = \underbrace{\frac{\left(\sum_{ij} \phi_i^* H_{ij} \phi_j\right)}{\left(\sum_{ij} \phi_i^* S_{ij} \phi_j\right)}}_{E} \sum_j S_{kj} \phi_j$$

$$\rightarrow \quad \underset{\sim}{H}\, \phi = E\, \underset{\sim}{S}\, \phi$$

b) s-orbitals have no nodes, so the orbital can be chosen to be positive everywhere.

$$\int d^3r\, \phi_1(r)\, V_1(r)\, \phi_2(r) < 0$$ since ϕ_1 & $\phi_2 > 0$ everywhere & $V_1(r) < 0$ everywhere

Simon
6.5
(cont)

$$\underset{\sim}{H} V = \varepsilon \underset{\sim}{S} V$$

$$\underset{\sim}{S}^{-1} \underset{\sim}{H} V = \varepsilon V \qquad S = \begin{pmatrix} 1 & c \\ c & 1 \end{pmatrix} \quad H = \begin{pmatrix} \epsilon + V_c & -t \\ -t & \epsilon + V_c \end{pmatrix}$$

$$S^{-1} = \frac{\mathrm{cof}(S)_{ij}}{\det S} = \frac{1}{1-c^2} \begin{pmatrix} 1 & -c \\ -c & 1 \end{pmatrix}$$

$$S^{-1} H = \frac{1}{1-c^2} \begin{pmatrix} 1 & -c \\ -c & 1 \end{pmatrix} \begin{pmatrix} a & -t \\ -t & a \end{pmatrix} = \frac{1}{1-c^2} \begin{pmatrix} a + ct & -ac - t \\ -ac - t & a + ct \end{pmatrix}$$

$$a \equiv \epsilon + V_c$$

eigenvalues of $\begin{pmatrix} A & B \\ B & A \end{pmatrix}$ are $A \pm B$

So $$\varepsilon = \frac{1}{1-c^2} \left(a + ct \pm (ac + t) \right)$$

$$= \frac{1}{1-c^2} \left[\epsilon + V_c + ct \pm \left[(\epsilon + V_c) c + t \right] \right]$$

$$= \frac{1}{1-c^2} \left[\epsilon + V_c + ct \pm (\epsilon + V_c) c \pm t \right]$$