PH 253 / LeClair   Spring 2010

Problem Set 9: Solutions

1. *Hydrogen-like systems.* Assuming a ^{3}Li atom to be hydrogen-like, determine the ionization energy of the 2s electron. Explain qualitatively the difference from the experimental value of 5.39 eV. *Hint: two approximations are to: a) neglect the inner electrons, or b) presume they shield the nucleus. These approximations bound the correct answer.*

If we neglect the inner electrons, then the outer electron feels a nuclear charge of $Ze = 3e$. The energy of the outer electron in the $n=2$ state is then

$$E_n = -\frac{Z^2 E_o}{n^2} = -\frac{9}{4}E_o \approx -30.6\,\text{eV} \qquad \text{(neglect inner electrons)} \tag{1}$$

Here E_o is the ground state Bohr energy, $-13.6\,\text{eV}$. If we assume the inner electrons perfectly screen the nucleus, then the outer electron feels a nuclear charge of only $(Z-2)e = e$. It is then effectively in a hydrogen-like environment, and the energy is simply

$$E_n = -\frac{E_o}{n^2} = -\frac{1}{4}E_o \approx -3.40\,\text{eV} \qquad \text{(perfect screening by inner electrons)} \tag{2}$$

These two extreme estimates bound the actual value of $-5.39\,\text{eV}$.

2. *Energetics of diatomic systems I.* The dissociation energy of KI is 3.33 eV. Calculate the bond length (interionic distance) for KI given that the electron affinity of I is 3.06 eV and the ionization energy of K is 4.34 eV. (The measured bond length is 0.323 nm.) *Hint: the dissociation energy is the sum of the electrostatic energy required to separate the two species and the electron affinity, minus the ionization energy.*

The electrostatic energy required to separate KI into K^+ and I^- is the work required to move bound charges of e and $-e$ an infinite distance apart from an initial separation of r_o, ke^2/r_o. The dissociation energy can thus be written as

$$\text{(dissociation energy)} = \frac{ke^2}{r_o} + \text{(electron affinity)} - \text{(ionization energy)} \tag{3}$$

Solving for r_o,

$$r_o = \frac{ke^2}{\Delta E} \approx 0.312\,\text{nm} \quad \text{with} \quad \Delta E = \text{(dissociation energy)} + \text{(ionization energy)} - \text{(electron affinity)}$$

3. *Energetics of diatomic systems II.* An approximate expression for the potential energy of two ions as a function of their separation is

$$U(r) = -\frac{ke^2}{r} + \frac{b}{r^9} \tag{5}$$

The first term is the usual Coulomb interaction, while the second term is introduced to account for the repulsive effect of the two ions at small distances. **(a)** Find b as a function of the equilibrium spacing r_o. **(b)** Calculate the potential energy of KCl at its equilibrium spacing ($r_o = 0.279\,\text{nm}$).

The equilibrium spacing will be characterized by the net force between the ions being zero, or equivalently, the potential energy being zero:

$$F(r_o) = -\frac{dU}{dr}\bigg|_{r=r_o} = 0 = \frac{ke^2}{r_o^2} - \frac{9b}{r_o^{10}} \tag{6}$$

$$ke^2 r_o^8 = 9b \tag{7}$$

$$b = \frac{1}{9}ke^2 r_o^8 \tag{8}$$

Substituting this result back into our potential energy expression,

$$PE = U(r) = -\frac{ke^2}{r} + \frac{ke^2 r_o^8}{9r^9} \tag{9}$$

Evaluating at equilibrium,

$$U(r_o) = -\frac{ke^2}{r_o} + \frac{ke^2}{9r_o} = -\frac{8ke^2}{9r_o} \approx -4.59\,\text{eV} \tag{10}$$

4. *Energetics of diatomic systems III.* An expression for the potential energy of two neutral atoms as a function of their separation r is given by the *Morse potential,*

$$PE = U(r) = P_o \left[1 - e^{-a(r-r_o)}\right]^2 \tag{11}$$

(a) Show that r_o is the atomic spacing and P_o the dissociation energy. **(b)** Calculate the force constant for small oscillations about $r = r_o$.

As in the previous problem, equilibrium is characterized by $dU/dr = 0$.

$$\frac{dU}{dr} = 2P_o \left[1 - e^{-a(r-r_o)}\right] \left(ae^{-a(r-r_o)}\right) = 0 \tag{12}$$

Either of the terms in brackets could be zero. The latter only leads to the trivial solution of $r \to \infty$, meaning there is no molecule in the first place. Setting the former term in brackets to zero,

$$0 = 1 - e^{-a(r-r_o)} \qquad \Longrightarrow \qquad r = r_o \tag{13}$$

The dissociation energy is defined as the amount of energy required to take the system from equilibrium at $r = r_o$ to complete breakup for $r \to \infty$. Thus,

$$(\text{dissociation energy}) = \left[\lim_{r \to \infty} U(r)\right] - U(r_o) = P_o - 0 = P_o \tag{14}$$

In other words, an amount of work P_o is required to bring about an infinite separation of the atoms, and this defines the dissociation energy.

If we wish to calculate a force constant, it is necessary to show that the force at least approximately obeys Hooke's law for small displacements, i.e., for a small displacement δ from equilibrium, $\delta = r - r_o$, $F(r_o + \delta) \approx k\delta$ where k is the force constant.[i] We have already calculated the force versus displacement:

$$F(r) = -\frac{dU}{dr} = -2P_o \left[1 - e^{-a(r-r_o)}\right] \left(ae^{-a(r-r_o)}\right) = -2P_o a \left(e^{-a(r-r_o)} - e^{-2a(r-r_o)}\right)$$
$$F(r_o + \delta) = -2P_o a \left(e^{-a\delta} - e^{-2a\delta}\right) \tag{15}$$

For small δ, we may make use of the approximation $e^\delta \approx 1 + \delta + \frac{1}{2}\delta^2 + \cdots$. Retaining terms only up to first order,

$$F(r_o + \delta) \approx -2P_o a \left(1 - a\delta - 1 + 2a\delta\right) = -\left(2P_o a^2\right)\delta \qquad \Longrightarrow \qquad k = 2P_o a^2 \tag{16}$$

Thus, for small displacements from equilibrium, we may treat the molecule as a mass-spring system, with an effective force constant k.

5. *Energetics of diatomic systems IV.* In the potassium iodide molecule, presume that the K and I atoms bond ionically by the transfer of one electron from K to I. **(a)** The ionization energy of K is 4.34 eV, and the electron affinity of I is 3.06 eV. What energy is needed to transfer an electron

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[i]Equivalently, we could show $U(\delta) \approx \frac{1}{2}k\delta^2$.

from K to I, to form K^+ and I^- ions from neutral atoms? This is sometimes called the activation energy E_a. **(b)** Another model potential energy function for the KI molecule is the Lennard-Jones potential:
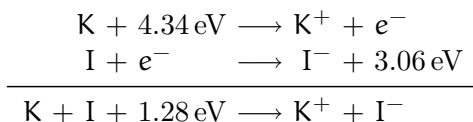
$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + E_a \tag{17}$$

where r is the internuclear separation distance, and σ and ϵ are adjustable parameters. The E_a term is added to ensure correct asymptotic behavior at large r. At the equilibrium separation distance $r = r_o = 0.305\,\text{nm}$, $U(r)$ is a minimum, and $U(r_o) = -3.37\,\text{eV}$ is the negative of the dissociation energy. Evaluate σ and ϵ. **(c)** Calculate the force needed to break up a KI molecule. **(d)** Calculate the force constant for small oscillations about $r = r_o$. *Hint: Set $r = r_o + \delta$, where $\delta/r_o \ll 1$ and expand $U(r)$ in powers of δ/r_o up to second-order terms.*

In order to transfer an electron, we must add the ionization energy of K to remove its electron, but we will gain back the electron affinity of I once it has an extra electron. Thus, the net energy required is

$$\text{(ionization energy K)} - \text{(electron affinity I)} = 4.34\,\text{eV} - 3.06\,\text{eV} = 1.28\,\text{eV} \tag{18}$$

Put another way, the following two reactions must occur and balance:

$$\begin{aligned} K + 4.34\,\text{eV} &\longrightarrow K^+ + e^- \\ I + e^- &\longrightarrow I^- + 3.06\,\text{eV} \\ \hline K + I + 1.28\,\text{eV} &\longrightarrow K^+ + I^- \end{aligned}$$

Thus, an activation energy of $1.28\,\text{eV}$ is required.

We can find σ by enforcing the condition $\frac{dU}{dr}\big|_{r=r_o} = 0$:

$$\frac{dU}{dr}\bigg|_{r=r_o} = 4\epsilon \left[\frac{12\sigma^{12}}{r_o^{13}} - \frac{6\sigma^6}{r_o^7} \right] = 0 \tag{19}$$

$$\frac{12\sigma^{12}}{r_o^{13}} = \frac{6\sigma^6}{r_o^7} \tag{20}$$

$$2\sigma^6 = r_o^6 \tag{21}$$

$$\sigma = 2^{-1/6} r_o \approx 0.272\,\text{nm} \tag{22}$$

Knowing σ, we can find ϵ by evaluating $U(r_o)$, since we are given $U(r_o) = -E_{\text{diss}} = -3.37\,\text{eV}$.

$$U(r_o) = 4\epsilon\left[\left(2^{-1/6}\right)^{12} - \left(2^{-1/6}\right)^{6}\right] + E_a = -\epsilon + E_a = -E_{\text{diss}} \tag{23}$$

$$\implies \quad \epsilon = -\left(E_{\text{diss}} + E_a\right) \approx 4.65\,\text{eV} \tag{24}$$

In order to find the force required to break up the molecule, we should first calculate the maximum restoring force that the molecule is able to respond with. If we exceed that force, the molecule will be broken.

$$F = -\frac{dU}{dr} = 4\epsilon\left[\frac{12\sigma^{12}}{r^{13}} - \frac{6\sigma^6}{r^7}\right] \tag{25}$$

This function has a clear maximum, which we can find by setting $dF/dr = 0$:

$$\frac{dF}{dr} = 4\epsilon\left[\frac{-156\sigma^{12}}{r^{14}} + \frac{42\sigma^6}{r^8}\right] = \frac{4\epsilon}{\sigma^2}\left[-156\left(\frac{\sigma}{r}\right)^{14} + 42\left(\frac{\sigma}{r}\right)^{8}\right] = 0$$

$$\implies \quad r = \left(\frac{156}{42}\right)^{1/6}\sigma \approx 0.338\,\text{nm} \tag{26}$$

Applying the second derivative test, or quick graph, will verify that this is a maximum. Thus,

$$F_{\text{max}} = F\left(\left(\frac{156}{42}\right)^{1/6}\sigma\right) = 4\epsilon\left[12\left(\frac{42}{156}\right)^{13/6} - \left(\frac{42}{156}\right)^{7/6}\right] \approx 6.55\,\text{nN} \tag{27}$$

Thus, the molecule can apply a maximum restoring force of about 6.55 nN, so exceeding this force will break up the molecule.

In order to find the force constant for small oscillations, we must either show that $F(r_o + \delta) \approx -k\delta$ or $U(r_o + \delta) \approx \frac{1}{2}k\delta^2$ for small displacements δ from equilibrium. The basic tactic is always the same: if the displacement is small compared to the equilibrium distance, $\delta/r_o \ll 1$, then we should write the potential or force in such a way to use an expansion in δ/r_o.

Starting from the potential:

$$U(r_o + \delta) = 4\epsilon\left[\left(\frac{\sigma}{r_o + \delta}\right)^{12} - \left(\frac{\sigma}{r_o + \delta}\right)^{6}\right] + E_a = 4\epsilon\left[\left(\frac{2^{-1/6}r_o}{r_o + \delta}\right)^{12} - \left(\frac{2^{-1/6}r_o}{r_o + \delta}\right)^{6}\right] + E_a$$

$$= 4\epsilon\left[\frac{1}{4}\left(\frac{r_o}{r_o + \delta}\right)^{12} - \frac{1}{2}\left(\frac{r_o}{r_o + \delta}\right)^{6}\right] + E_a$$

$$= 4\epsilon\left[\frac{1}{4}\left(\frac{1}{1 + \frac{\delta}{r_o}}\right)^{12} - \frac{1}{2}\left(\frac{1}{1 + \frac{\delta}{r_o}}\right)^{6}\right] + E_a \tag{28}$$

Since $\delta/r_o \ll 1$, we may use the binomial expansion to simplify, viz., $(1+\delta/r_o)^n \approx 1 + n\delta/r_o + \frac{1}{2}n(n-1)\delta^2/r_o^2$, keeping terms up to 2nd order.

$$U(r_o + \delta) = 4\epsilon \left[\frac{1}{4}\left(\frac{1}{1+\frac{\delta}{r_o}}\right)^{12} - \frac{1}{2}\left(\frac{1}{1+\frac{\delta}{r_o}}\right)^6 \right] + E_a$$

$$\approx 4\epsilon \left[\frac{1}{4}\left(1 - 12\frac{\delta}{r_o} + \frac{12\cdot 11}{2}\frac{\delta^2}{r_o^2}\right) - \frac{1}{2}\left(1 - 6\frac{\delta}{r_o} + \frac{6\cdot 5}{2}\frac{\delta^2}{r_o^2}\right) \right] + E_a$$

$$\approx \epsilon \left[-1 + 36\frac{\delta^2}{r_o^2} \right] + E_a = (E_a - \epsilon) + \frac{1}{2}\left(\frac{72\epsilon}{r_o^2}\right)\delta^2 = U(r_o) + \frac{1}{2}\left(\frac{72\epsilon}{r_o^2}\right)\delta^2 \qquad (29)$$

Thus, $k = 72\epsilon/r_o^2 \approx 3600\,\text{eV/nm} \approx 576\,\text{N/m}$. One can just as easily start with the force expression to arrive at the same result, except that now we need only keep terms to first order in the binomial expansion:

$$F(r_o + \delta) = 4\epsilon \left[\frac{12\sigma^{12}}{(r_o+\delta)^{13}} - \frac{6\sigma^6}{(r_o+\delta)^7} \right] = 4\epsilon \left[12\frac{\frac{1}{4}r_o^{12}}{(r_o+\delta)^{13}} - 6\frac{\frac{1}{2}r_o^6}{(r_o+\delta)^7} \right]$$

$$= 4\epsilon \left[\frac{3}{r_o}\left(1+\frac{\delta}{r_o}\right)^{-13} - \frac{3}{r_o}\left(1+\frac{\delta}{r_o}\right)^{-7} \right]$$

$$\approx 4\epsilon \left[\frac{3}{r_o}\left(1 - 13\frac{\delta}{r_o}\right) - \frac{3}{r_o}\left(1 - 7\frac{\delta}{r_o}\right) \right] = -\left(\frac{72\epsilon}{r_o^2}\right)\delta \qquad (30)$$

Again, the conclusion is $k = 72\epsilon/r_o^2$.

6. *Crystal lattice energy.* Consider a one-dimensional chain of alternating positive and negative ions. Show that the potential energy associated with one of the ions and its interactions with the rest of this hypothetical crystal is

$$U(r) = -k_e \alpha \frac{e^2}{r} \qquad (31)$$

where the Madelung constant is $\alpha = 2\ln 2$ and r is the interionic spacing. *Hint: the series expansion for $\ln(1+x)$ may prove useful in evaluating an infinite sum.*

Pick any positive ion $+e$ as the origin. Immediately to the right at a distance r, we have a negative ion $-e$. The potential energy of this pair is $-ke^2/r$. One more lattice spacing to the right, a distance $2r$ from the origin, is another negative ion, whose potential energy with the ion at the origin is $ke^2/2r$. Continuing in this way, all ions to the right-hand side of the ion at the origin give us a potential energy

$$U_{\text{RHS}} = -\frac{ke^2}{r} + \frac{ke^2}{2r} - \frac{ke^2}{3r} + \ldots = \frac{ke^2}{r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n} = -\frac{ke^2}{r}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} \qquad (32)$$

To the left-hand side of the origin, there are just as many ions in the same arrangement, giving us the same contribution to the potential energy. Thus,

$$U_{tot} = 2U_{RHS} = -2\frac{ke^2}{r}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} \tag{33}$$

The series we must evaluate is then

$$\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} \tag{34}$$

This is known as the *alternating harmonic series*, and is known to evaluate to $\ln 2$. This can be seen readily from the Taylor expansion for $\ln(1+x)$:

$$\ln(1+x) = \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}x^n \quad\Longrightarrow\quad \ln(2) = \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} \tag{35}$$

Thus, the potential energy is

$$U_{tot} = 2U_{RHS} = -2\frac{ke^2}{r}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} = -k_e\alpha\frac{e^2}{r} \quad\text{with}\quad \alpha = 2\ln 2 \tag{36}$$

7. *Free-electron gas I.* **(a)** Obtain an expression for the Fermi energy at $T=0\,K$ for an electron gas in a metal in terms of the total number of electrons, the volume, and fundamental constants. **(b)** At $T=0\,K$, what is the rms speed, in terms of the Fermi energy, of an electron gas in a metal?

The Fermi energy at $T=0$ is given by

$$E_F\big|_{T=0}\frac{\hbar^2}{2m}\left(\frac{3\pi^2N}{V}\right)^{2/3} \tag{37}$$

where N is the number of electrons in a volume V. A derivation may be found here:

`http://en.wikipedia.org/wiki/Fermi_energy`

This is the energy of the highest-energy electrons in a metal at $T=0$. If all this energy is available as kinetic energy,

$$E_f = \frac{1}{2}mv^2 \quad\Longrightarrow\quad v = \sqrt{\frac{2E_F}{m}} \tag{38}$$

8. *Free-electron gas II.* Show that the average kinetic energy of a conduction electron in a metal at $0\,\mathrm{K}$ is $E_{av} = \frac{3}{5} E_F$. *Hint: in general, the average kinetic energy is*

$$E_{av} = \frac{1}{n_e} \int E\, N(E)\, dE \tag{39}$$

where n_e is the density of particles, $N(E)\, dE$ is the number of electrons per unit volume that have energies in $[E, E + dE]$, and the integral is over all possible values of energy.

The Fermi energy, the energy of the highest occupied quantum state in a system of fermions at absolute zero temperature, is a function of the number of fermions as found in the last problem. If there are N particles in a volume V, then the highest occupied state has an energy

$$E_F(T = 0) = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \tag{40}$$

Thus, as more and more particles are added, it takes more and more energy to add the last particle. The total energy of the system, if there are enough particles to consider the distribution of states to be quasi-continuous, is given by

$$E_{tot} = \int_0^N E_F(N')\, dN' \tag{41}$$

The average energy is simply the total energy divided by the number of particles:

$$E_{avg} = \frac{1}{N} \int_0^N E_F(N')\, dN' = \frac{1}{N} \int_0^N \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N'}{V} \right)^{2/3} dN' = \frac{1}{N} \frac{\hbar^2}{2m} \left(\frac{3\pi^2}{V} \right)^{2/3} \left(\frac{3}{5} N^{5/3} \right) = \frac{3}{5} E_F \tag{42}$$

9. *Ohmic conduction.* An aluminum wire with a cross-sectional area of $4.00 \times 10^{-6}\,\mathrm{m^2}$ carries a current of $5.00\,\mathrm{A}$. Find the drift speed of the electrons in the wire. The density of aluminum is $2.70\,\mathrm{g/cm^3}$; assume each Al atom provides a single electron for conduction. *Hint: how many atoms per unit volume are there? Use your periodic table.*

Each aluminum atom donates one mobile electron for conducting electricity. Therefore, finding the number of carriers per unit volume n is equivalent to finding the number of aluminum atoms per unit volume - easily found from the density and molar mass of aluminum and Avogadro's number:

$$n = \left[2.70\,\frac{\text{g}}{\text{cm}^3}\right] \left[\frac{100\,\text{cm}}{1\,\text{m}}\right]^3 \left[\frac{1\,\text{mol}}{27\,\text{g}}\right] \left[6.02 \times 10^{23}\,\frac{\text{atoms}}{\text{mol}}\right] \left[1\,\frac{\text{electron}}{\text{atom}}\right] \tag{43}$$

$$= 6.02 \times 10^{28}\,\frac{\text{electrons}}{\text{m}^3} \tag{44}$$

Now we have the carrier density n, and we further know the current I and conductor area A. Since the conduction is stated as due to electrons, we also know the charge per carrier $q = e$. This is as much as we need to find the drift velocity:

$$v_d = \frac{I}{nqA} = \frac{5.00\,\text{A}}{\left(6.02 \times 10^{28}\,\frac{\text{electrons}}{\text{m}^3}\right)\left(1.60 \times 10^{-19}\,\frac{\text{C}}{\text{electron}}\right)\left(4.00 \times 10^{-6}\,\text{m}^2\right)} \tag{45}$$

$$= 1.3 \times 10^{-4}\,\frac{\text{A} \cdot \text{m}}{\text{C}} = 1.3 \times 10^{-4}\,\text{m/s} \tag{46}$$

If we remember that one Ampere is one Coulomb per second, the units come out just fine.