Solution Key, Hour Exam 2, Chem. 1410, 11/07

1) Note the general formula for hydrogenic atom energy levels: $E_n = -Z^2 R_H / n^2$, where Z is the atomic number, $n = 1, 2, ...$ is the principal quantum number, and R_H is the Rydberg constant for the hydrogen atom: numerically, $R_H = 13.6 eV$. So ...

a) i)(8 points) Ignoring the "other electron", the tagged electron feels the bare (unscreened) Z=+2 helium nucleus. Thus if it is in a 1s orbital (n=1), $E_1^{He} = -4R_H = -54.4 eV$.

ii) (8 points) Assuming that the other (inner lying) electron effectively reduces the bare helium nucleus charge by one unit to Z=1 (effectively, an H-atom nucleus), then if the tagged electron is in a 1s orbital, $E_1^H = -R_H = -13.6 eV$.

b) (6 points) The true situation for a He atom lies somewhere between the extremes considered in i) and ii) above: the other electron *partially (but not completely) shields* the tagged electron from the nucleus, so the tagged electron experiences an effective nuclear charge that lies somewhere between Z=1 and Z=2, resulting in a binding energy E_{bind} in the range $13.6 eV < E_{bind} < 54.4 eV$. [Note: the experimentally measured first ionization potential for ground state He is ~25eV.]

(c) (8 points) From PS7, we know that for a hydrogenic atom in an l=0 state, $<r>_n = \dfrac{3n^2 a_0}{2Z}$, where n, Z have the same meaning as above, and a_0 is the hydrogen atom Bohr radius; numerically, $a_0 = 0.53$ Å. Following the reasoning above, in the extreme case that the tagged electron does not feel the other electron's presence at all (because the tagged electron lies inside the other electron at all times), then the effective value of Z is 2, and $<r>_{1s}^{He} = \dfrac{3a_0}{4} = 0.4$ Å. In the other extreme case that the tagged electron is always farther away from the nucleus than the other electron, then the tagged electron sees a Z=1 nucleus, and $<r>_{1s}^H = \dfrac{3a_0}{2} = 0.8$ Å. We expect that for an electron in the true ground electronic state of the helium atom, the average radial distance from the nucleus r_{av} will be bracketed by these extreme values, i.e., 0.4 Å $< r_{av} < 0.8$ Å.

2) a) (12.5 points) Note: $dv^{eff}(r)/dr = kr - \dfrac{\hbar^2 l(l+1)}{\mu r^3}$

The minimum of v^{eff} occurs at r_m s.t. $dv^{eff}(r_m)/dr = 0$. Thus: $r_m = \left[\dfrac{\hbar^2 l(l+1)}{\mu k} \right]^{1/4}$, QED.

b) (12.5 points) Differentiating again: $d^2 v^{eff}(r)/dr^2 = k + \dfrac{3\hbar^2 l(l+1)}{\mu r^4}$.

Thus: $\boxed{d^2 v^{eff}(r_m)/dr^2 = 4k}$

c) (10 points) Expanding $v^{eff}(r)$ in a Taylor series about r_m:

$$v^{eff}(r) = v^{eff}(r_m) + \frac{1}{2}\frac{d^2 v^{eff}(r_m)}{dr^2}(r - r_m)^2 + ...$$

Note: the first order term in the expansion vanishes because $dv^{eff}(r_m)/dr = 0$.

Neglecting cubic and higher terms in the Taylor series expansion, then $v^{eff}(r) \cong v^{quad}(r)$, with

$$v^{quad}(r) = v^{eff}(r_m) + \frac{1}{2}\tilde{k}(r - r_m)^2, \quad \tilde{k} \equiv 4k \quad .$$

As sketched in Fig. A1, v^{quad} is a parabolic ("harmonic oscillator") potential. Its quantum mechanical energy eigenvalues are characterized by a constant spacing between any adjacent pair of energy levels, namely, $\Delta E = \hbar \tilde{\omega}$, with $\tilde{\omega} = \sqrt{\tilde{k}/\mu} = 2\sqrt{k/\mu}$. Thus, the difference between the lowest two energy levels in this well is $\boxed{E_1 - E_0 = 2\hbar\sqrt{k/\mu}}$.

3) a) (12 points) In region I, the Schrödinger Eq. reads:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

Its solutions (modulo normalization) are $\sin kx, \cos kx$, with $k(E)$ stated in the problem. Only the sin solution obeys the boundary condition that $\psi(0) = 0$; thus, the cos solution must be discarded.

In region II, the Schrödinger Eq. reads:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x)$$

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For $E < V_0$ the solutions of this differential equation (modulo normalization) are $\exp(\kappa x), \exp(-\kappa x)$, with $\kappa(E)$ stated in the problem. The solution $\exp(\kappa x)$ blows up as $x \to \infty$, and thus must be discarded.

Note: We can arbitrarily normalize the solution in region I (with the understanding that we will normalize the complete energy eigenfunction once it has been fully determined). This then implies a scale constant A in region II which is chosen as follows:

b) (12 points) Match $\psi_I(L) = \psi_{II}(L)$, i.e.,: $\qquad\qquad \sin kL = Ae^{-\kappa L}$ $\qquad\qquad$ [i]

$\qquad$ Match $d\psi_I(L)/dx = d\psi_{II}(L)/dx$, i.e.: $\quad k\cos kL = -\kappa Ae^{-\kappa L}$ $\qquad$ [ii]

Dividing [ii]/[i], we obtain for the quantization condition: $\cot kL = -\kappa/k$, or, equivalently:

$$\cot\left(\frac{\sqrt{2mE}\,a}{\hbar}\right) = -\sqrt{\frac{V_0 - E}{E}} \quad , QED.$$

c) Using the equivalent form for the quantization condition stated in Eq. 2 of the Exam, and consulting Fig. 2 of the exam:

i) (5 points) There are 4 intersections of the l.h.s. and the r.h.s. of Eq. 2 in the energy range $0 < E < V_0$. Thus there are 4 bound states in this well.

iii) (6 points) Counting the lowest energy bound state as "state 1", then state 3 corresponds to the intersection at $\varepsilon \cong 7.5$. In the case of an infinitely deep box ($V_0 = \infty$), this intersection would move to the value of ε at the 3rd vertical line from the left, namely, $\varepsilon = 9$. (Note: this is the $n = 3$ solution of the standard particle in a box of width a.)

[Question: Can you provide a simple reason why the energy of this state goes *down* when V_0 is reduced from ∞ to a finite value?]