# Exam 2 and Answers

1. Determine quantum numbers $n_1$ and $n_2$ for *any* transition of He$^+$ in the visible region.

For He$^+$, $Z = 2$ and the Rydberg formula can be written

$$\frac{1}{\lambda} = Z^2 R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where $R = 10973700 \text{ m}^{-1}$.

$n_1 = 3, n_2 = 4$ gives $\lambda = 469$ nm, which is in the visible region (400-700 nm).

2. For the ground state of the hydrogen atom:

(i), (ii) Calculate $\langle r \rangle$ and $\langle r^2 \rangle$. Use atomic units, of course.

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi}} e^{-r}$$

$$\langle r \rangle = \int_0^\infty r \left( \frac{1}{\sqrt{\pi}} e^{-r} \right)^2 4\pi r^2 dr = 4 \int_0^\infty e^{-2r} r^3 \, dr = 4 \times \frac{3!}{2^4} = \frac{3}{2}$$

$$\langle r^2 \rangle = \int_0^\infty r^2 \left( \frac{1}{\sqrt{\pi}} e^{-r} \right)^2 4\pi r^2 dr = 4 \int_0^\infty e^{-2r} r^4 \, dr = 4 \times \frac{4!}{2^5} = 3$$

The radial momentum operator is defined by

$$\hat{p}_r = -i\hbar \frac{1}{r} \frac{\partial}{\partial r} r$$

(iii), (iv) Calculate $\langle p_r \rangle$ and $\langle p_r^2 \rangle$.

$$\langle p_r \rangle = \int_0^\infty \frac{1}{\sqrt{\pi}} e^{-r} \left\{ -i\hbar \frac{1}{r} \frac{d}{dr} r \right\} \frac{1}{\sqrt{\pi}} e^{-r} \, 4\pi r^2 dr$$

$$= -4i\hbar \int_0^\infty e^{-r} \frac{1}{r} (e^{-r} - re^{-r}) \, r^2 \, dr = -4i\hbar \left( \frac{1!}{2^2} - \frac{2!}{3^2} \right) = 0$$

$$\langle p_r^2 \rangle = \int_0^\infty \frac{1}{\sqrt{\pi}} e^{-r} \left\{ -\hbar^2 \frac{1}{r} \frac{d^2}{dr^2} r \right\} \frac{1}{\sqrt{\pi}} e^{-r} \, 4\pi r^2 dr = \hbar^2$$

(v) Calculate the uncertainty product $\Delta r \Delta p_r$ in the ground state of the hydrogen atom. Recall that

$$\Delta a = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

$$\Delta r = \sqrt{3 - \left( \frac{3}{2} \right)^2} = \frac{\sqrt{3}}{2} \qquad \Delta p_r = \hbar \qquad \Delta r \Delta p_r = \frac{\sqrt{3}}{2} \hbar$$

Note that this is $> \hbar/2$, just as Heisenberg said.


3. Using the best approximate method at your immediate disposal, calculate the ground state energy of the hydride ion H$^-$ (in hartrees).

Use the variational function $\psi(r_1, r_2) = e^{-\alpha(r_1 + r_2)}$ just like helium. We found the energy

$$E(\alpha) = \alpha^2 - 2Z\alpha + \frac{5}{8}\alpha \qquad \text{where} \quad Z = 1$$

This is minimized for

$$\alpha = Z - \frac{5}{16} = \frac{11}{16} \qquad \text{giving} \qquad E = -\frac{11}{16}^2 = -0.473 \, \text{hartree}$$

This might seem to indicate that H is unstable since H has an energy of $-0.5$ hartree. A more accurate calculation gives an energy of $-0.5284$

4. For the ground state of the helium atom, the Slater determinant for the
approximate wavefunction can be written, in abbreviated notation,

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\Big(1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2)\Big)$$

and the corresponding energy is

$$E = 2I_{1s} + J_{1s,1s}$$

Write the analogous formulas for the ground state of lithium atom.

$$\Psi(1,2,3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

$$= \frac{1}{\sqrt{6}}\Big(1s\alpha(1)1s\beta(2)2s\alpha(3) + 1s\beta(1)2s\alpha(2)1s\alpha(3) + 2s\alpha(1)1s\alpha(2)1s\beta(3)$$

$$-2s\alpha(1)1s\beta(2)1s\alpha(3) - 1s\beta(1)1s\alpha(2)2s\alpha(3) - 1s\alpha(1)2s\alpha(2)1s\beta(3)\Big)$$

$$E = 2I_{1s} + I_{2s} + J_{1s,1s} + 2J_{1s,2s} - K_{1s,2s}$$

5. The energy of interaction between two atoms can be approximated by
the Lennard-Jones potential:

$$E(R) = \frac{A}{R^{12}} - \frac{B}{R^6}$$

Find $D_e$ and $R_e$ in terms of the parameters $A$ and $B$.

The minimum of the function is found from

$$E'(R) = -12AR^{-13} + 6BR^{-7} = 0$$

This gives

$$R_e = (2A/B)^{1/6} \qquad \text{and} \qquad E(R_e) = -\frac{B^2}{4A}$$

Since $E(\infty) = 0$, $D_e = B^2/4A$.

6. On the basis of the valence-shell model, predict the geometry of each of the following trifluorides:

(i) $BF_3$

B has 3 valence electrons, 3B–F bonds in trigonal planar arrangement.

(ii) $NF_3$

N has 5 valence electrons, 3N–F bonds plus lone pair. Tetrahedral $NF_3E$ with 3 bonds making trigonal pyramid, like $NH_3$.

(iii) $ClF_3$

Cl has 7 valence electrons, 3Cl–F bonds plus 2 lone pairs. $ClF_3E_2$ in trigonal bipyramid. E's both go to equatorial positions leaving distorted T-shape.