Exam 2 and Answers

1. Determine quantum numbers \( n_1 \) and \( n_2 \) for \( \text{any} \) transition of \( \text{He}^+ \) in the visible region.

For \( \text{He}^+ \), \( Z = 2 \) 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 \( \lambda = 469 \text{ nm} \), 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

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

\[
\Delta r = \sqrt{3 - \left( \frac{3}{2} \right)^2} = \frac{\sqrt{3}}{2} \quad \Delta p_r = \hbar \quad \Delta r \Delta p_r = \frac{\sqrt{3}}{2} \hbar
\]

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 \(\text{H}^-\) (in hartrees).

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

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

This is minimized for

\[
\alpha = Z - \frac{5}{16} = \frac{11}{16} \quad \text{giving} \quad E = -\frac{11^2}{16} = -0.473 \text{ hartree}
\]

This might seem to indicate that \(\text{H}\) is unstable since \(\text{H}\) has an energy of \(-0.5\) hartree. A more accurate calculation gives an energy of \(-0.5284\)
hartree, showing that \( H \) is stable. The hydride ion is involved in the action of NAD-linked dehydrogenases.

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

\[
\Psi(1, 2) = \frac{1}{\sqrt{2}} \left( 1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2) \right)
\]

and the corresponding energy is

\[
E = 2I_{1s} + J_{1s,1s}
\]

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

\[
\Psi(1, 2, 3) = \frac{1}{\sqrt{3!}} \left| \begin{array}{ccc}
1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\
1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\
1s\alpha(3) & 1s\beta(3) & 2s\alpha(3)
\end{array} \right|
\]

\[
= \frac{1}{\sqrt{6}} \left( 1s\alpha(1)1s\beta(2)2s\alpha(3) + 1s\beta(1)2s\alpha(2)1s\alpha(3) + 2s\alpha(1)1s\alpha(2)1s\beta(3) \\
-2s\alpha(1)1s\beta(2)1s\alpha(3) - 1s\beta(1)1s\alpha(2)2s\alpha(3) - 1s\alpha(1)2s\alpha(2)1s\beta(3) \right)
\]

\[
E = 2I_{1s} + I_{2s} + J_{1s,1s} + 2J_{1s,2s} - K_{1s,2s}
\]

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

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

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$_3$E 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$_3$E$_2$ in trigonal bipyramid. E’s both go to equatorial positions leaving distorted T-shape.