SOME POSSIBLY USEFUL INFORMATION:

\[ N_A \text{ or } L = 6.022 \times 10^{23} \text{ mol}^{-1} \]
\[ h = 6.626 \times 10^{-34} \text{ J s} \]
\[ k = 1.38 \times 10^{-23} \text{ J K}^{-1} \]
\[ c = 2.998 \times 10^8 \text{ m s}^{-1} \]
\[ \text{H atom mass (1 amu or u) } = 1.66 \times 10^{-27} \text{ kg} \]
\[ \text{electron mass } = 9.11 \times 10^{-31} \text{ kg} \]
\[ R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \]

Planck: \[ E = hv \]
Schrodinger: \[ \hat{\psi} = E\psi \]
de Broglie: \[ \lambda = h/\rho \]

\( \hat{x} \) operator is multiply by \( x \)
\( \hat{p} \) operator is \[ h/(2\pi) \frac{d}{dx} \]
\( \hat{E}_k \) operator is \[ -\frac{\hbar^2}{2m} (\frac{d^2}{dx^2}) \]
\( \hat{V} \) operator is multiply by \( V \)

\[
\sin^2 x = \frac{1 - \cos 2x}{2} \\
\cos^2 x = \frac{1 + \cos 2x}{2} 
\]

\[
\int_0^\infty x^n e^{-ax} \, dx = \frac{n!}{a^{n+1}} \quad \text{vibrator:} \\
E = (\nu + 1/2)hv \quad \nu = (1/2\pi)\sqrt{\left(k/\mu\right)} 
\]

I.P. of one-electron atom proportional to \[ Z^2/\mu^2 \]. I.P. of H = 13.6 eV = \[ 2.18 \times 10^{-18} \text{ J} \].

Rotor: \[ J_z^2 = l(l + 1) \frac{\hbar^2}{(4\pi^2)} \]
\[ L_z = m_l \frac{\hbar}{(2\pi)} \]
1) 30 points

i) Sketch the shapes of the ground state wavefunction for a harmonic oscillator, and the wavefunction for the next highest energy. Label each curve with the corresponding vibrational quantum numbers.

ii) A diatomic molecule with a reduced mass of 7 u (i.e. 7 amu) has a force constant of 800 N m\(^{-1}\). What is the vibrational frequency in Hz?

iii) What is the energy of a photon whose energy matches the gap between the 3\(^{rd}\) and 4\(^{th}\) vibrational energy levels? Give your answer in cm\(^{-1}\).

*[If you have no answer to (ii) you may assume – incorrectly - that \(v = 2 \times 10^{13}\) Hz]*

\[
\mu = 7 \times 1.66 \times 10^{-27}\text{kg} = 1.162 \times 10^{-26}\text{kg}, \quad v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = 4.18 \times 10^{12}\text{Hz},
\]

\[
\Delta E = E_{v=4} - E_{v=2} = 4\frac{1}{2} \nu \frac{h}{2} - 3\frac{1}{2} \nu \frac{h}{2} = \nu \frac{h}{2} \quad \text{(constant gap between neighboring levels)}
\]

\[
\Delta E = \hbar \nu = h \nu \frac{c}{\lambda}, \quad \text{so} \quad \frac{1}{\lambda} = \frac{\Delta E}{h\nu} = \frac{4.18 \times 10^{12}\text{Hz}}{2.998 \times 10^{10}\text{cm}^{-1}} = 1.393 \text{cm}^{-1}.
\]
2) 40 points

i) A hypothetical spherically-symmetrical atomic orbital has the form \( \psi = N (3-r) \exp(-r/2) \). How many nodes do you expect in this wavefunction, and at what value(s) of \( r \)?

ii) At what value(s) of \( r \) is the electron most likely to be found?

iii) Determine the normalization constant \( N \).

iv) Find the average value of \( r \).

\[ \psi(r) = \frac{4\pi N^2}{r} \exp(-r/2) \]

\[ \psi_{\text{maxima or minima}} \]

\[ \frac{d\psi}{dr} = 4\pi N^2 \left[ \frac{r^2 (3-r)^2}{e^r} + \left( \frac{2}{e^r} \right) - \frac{r^2}{e^r} \right] \]

\[ = 4\pi N^2 e^{-r} \left[ -3r^2 (3-r)^2 + 6 - 2r^2 (3-r) \right] \]

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\[ = 0, 1, 2 \text{ or } 3. \]

\[ r = 0 \text{ and } 3 \text{ are minima (from the sketch), so } 0 = 1 \text{ and } 6 \text{ are maxima.} \]

\[ p_{\text{maxima}} = \int_0^\infty \psi^2 \, dr = \frac{4\pi N^2}{r} \int_0^\infty \left( r^2 e^{-r} \right) \, dr = 4\pi N^2 \left[ \int_0^\infty r^2 e^{-r} \, dr - 6 \int_0^\infty r e^{-r} \, dr + \int_0^\infty e^{-r} \, dr \right] \]

\[ = 4\pi N^2 \left[ 0.5 \right] = 2\pi N^2 \text{ so } N = \frac{1}{\sqrt{2\pi}}. \]

\[ \langle r^2 \rangle = \int_0^\infty r^2 \psi^2 \, dr = \int_0^\infty \frac{4\pi N^2}{r} \left( r^2 e^{-r} \right) \, dr \]

\[ = \frac{2\pi}{24\pi} \left[ 9 \int_0^\infty r^2 e^{-r} \, dr - 6 \int_0^\infty r e^{-r} \, dr + \int_0^\infty e^{-r} \, dr \right] \]

\[ = \frac{1}{6} \left[ 0.5 \right] = 5. \]
3) 30 points

i) Write out the electronic structure of a phosphorus atom (Z=15). What is the total spin \( S \) and the spin multiplicity?

ii) If an electron is in an f orbital, what is the magnitude of the orbital angular momentum in terms of \( \hbar \), and list all the allowed values of the z component of the orbital angular momentum?

iii) If a single electron occupies a p orbital, what are all the possible total angular momentum \( j \) values for this one electron? Explain briefly which of these has the lowest energy.

\[
\text{i) } 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^3 \quad \text{How are}\ 3p^- \ \text{arranged in these p orbitals?}
\]

Hund's rule gives \( t = \frac{1}{2} \).

\[
S = \frac{1}{2} + \frac{1}{2} = 1 \quad \text{Spin multiplicity} \quad J = 2, 1, 0, \quad \text{ spin} = 4, 3, 2, 1, 0.
\]

\[
\text{ii) For an f orbital} \quad l = 2, \quad l_z = \frac{1}{4}, \frac{5}{4}, \frac{9}{4}, \frac{13}{4}, \quad \text{so} \quad \left| l_z \right| = \sqrt{2}, \sqrt{2/\pi}, \quad \text{or} \quad 2, \sqrt{2/\pi}.
\]

\[
l_z = ml \quad \frac{1}{4} = -2, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \quad \text{(seven values)}.
\]

\[
\text{iii) Spin can be aligned mostly with or against the orbital angular momentum.}
\]

\[
1 \quad \begin{array}{c}
\downarrow \uparrow \\
S = l, s = \frac{3}{2}
\end{array}
\]

\[
1 \quad \begin{array}{c}
\downarrow \uparrow \\
S = l, s = \frac{1}{2}
\end{array}
\]

magnetic fields aligned
so lower energy

 magnetic fields opposed
- higher energy.