Your name: SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

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

Planck: \( E = \hbar \nu \)

Schrodinger: \( \hat{H} \psi = E \psi \)

de Broglie: \( \lambda = \hbar / p \)

The expectation or average value of an observable \( \hat{A} \) is \( \int \psi^* \hat{A} \psi \, d\tau / \int \psi^* \psi \, d\tau \)

Particle in 1-D box:
\( \psi_n = (2/a)^{1/2} \sin(n\pi x/a), \quad E_n = \hbar^2 n^2 / (8ma^2) \)

Harmonic oscillator:
\( E_V = (\nu + 1/2) \hbar \nu; \quad \nu = (k/\mu)^{1/2} / (2\pi) \)

Rigid rotor
\( |L^2| = l(l + 1) \hbar^2 / (4\pi^2) \)
\( L_z = m_i \hbar / (2\pi) \)
\( E = L^2 / (2I) \)

x operator is multiply by x

p operator is \( \hbar / (2\pi i) d/dx \)

E_K operator is \( -\hbar^2 / (8\pi^2 m) d^2 / dx^2 \)

V operator is multiply by V

radial distance r operator is multiply by r

Energy of 1-electron atom proportional to \(-Z^2 / n^2\).

\( \sin^2 x = (1 - \cos 2x) / 2 \)
\( \cos^2 x = (1 + \cos 2x) / 2 \)
\( \int_0^\infty x^n \exp(-ax) \, dx = \frac{n!}{a^{n+1}} \)
1) 30 points

i) Draw the electron configuration for the ground state of a sulfur atom, showing the orbitals in increasing order of energy, details of their occupation by electrons, and the arrangement of spins of these electrons. What is the spin multiplicity of this atom?

ii) Consider one electron in (a) an s orbital, and (b) an f orbital. Explain in which case(s) spin-orbit coupling occurs, what is the origin of the effect, and what j values are possible.

iii) Imagine an isolated H atom with its electron in the 4d orbital. What is the magnitude of the electron’s orbital angular momentum, and what are all the possible values of the z component of this orbital angular momentum? Leave \( \hbar \) in your answers. Experimentally, what would make these different states (corresponding to the different z components) have different energies?

\[
\begin{align*}
S &= \frac{1}{2} + \frac{1}{2} = 1 \\
\text{Multiplicity} &= 2S+1 = 3 \\
E &
\begin{array}{c}
\text{3p} \\
\text{2s} \\
\text{2p} \\
\text{1s} \\
\end{array}
\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}
\end{align*}
\]

ii) See notes. Total angular momentum \( J \) of an electron is \( L+S = J = \frac{1}{2} \).

For an f orbital \( L=3 \), so \( J = 2\frac{1}{2} \) or \( 3\frac{1}{2} \).

For an s orbital \( L=0 \) and there is no spin-orbit coupling. \( J = \frac{1}{2} \) only.

iii) \( L = 2 \). Magnitude of orbital angular momentum: 
\[
L^2 = \frac{(2\hbar)^2}{2\pi} = \hbar^2 \\
L = \sqrt{6} \cdot \hbar / 2\pi \\
\]

z-component \( L_z = m_L \cdot \frac{\hbar}{2\pi} = \frac{2\hbar}{2\pi}, \frac{\hbar}{2\pi}, 0, -\frac{\hbar}{2\pi}, -\frac{2\hbar}{2\pi} \).
2) 30 points

i) Sketch the shapes of the ground-state and first excited state wavefunctions of a harmonic oscillator, with $\psi$ on the vertical axis and carefully define the horizontal axis. Label your two $\psi$ curves with the value of the vibrational quantum number and the corresponding energy in terms of the classical frequency $\nu$.

ii) Consider the LiH diatomic molecule. The force constant is 800 N m$^{-1}$; what is its lowest possible energy, in J?

iii) What is the vibrational frequency in cm$^{-1}$?

\[ \psi(x) = \sqrt{\frac{M}{2\pi \hbar^2}} e^{-\frac{\sqrt{2M}x}{\hbar}} \]

\[ \varepsilon = \frac{\hbar \omega}{2} \]

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\[ \omega = \sqrt{\kappa \mu} = 1.18 \times 10^{14} \text{ Hz} \]

\[ \text{Zero-point energy} = \frac{1}{2} \hbar \omega = 3.91 \times 10^{-20} \text{ J} \]

\[ \nu = \frac{\hbar}{2\pi \mu} = 1.18 \times 10^{14} \text{ Hz} \]

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\[ \text{Vibrational frequency} = \frac{1.18 \times 10^{14}}{2.998 \times 10^{10}} \text{ cm}^{-1} = 39.36 \text{ cm}^{-1} \]
3) 20 points
A spherically symmetrical orbital in a hypothetical atom is given by

$$\psi = N r^2 \exp(-2r)$$

where \( r \) is the distance from the nucleus and \( N \) is the normalization constant. What is the average distance of the electron from the nucleus? **HINT:** it is not necessary to solve for \( N \) along the way although it is not wrong to do so.

$$\langle r^2 \rangle = \int_{0}^{\infty} 4\pi r^2 \psi^* \psi \, dr = \int_{0}^{\infty} N^2 r^4 e^{-2r} / 4\pi r^2 \, dr$$

$$\langle r^2 \rangle = \frac{\int_{0}^{\infty} 4\pi r^2 \psi^* \psi \, dr}{\int_{0}^{\infty} 4\pi r^2 \psi^* \psi \, dr} = \frac{9\pi}{4} \frac{81}{4^9} = \frac{9}{4}.$$
4) 20 points
On the same axes, sketch the radial distribution functions $P(r)$ for 2s and 2p orbitals. How do the $P(r)$ values compare for small values of $r$ and explain in as much detail as you can how this influences the energies of occupied 2s and 2p orbitals?

See notes about penetration and shielding.