Molecular Structure and Molecular Spectroscopy (CY61044/CY61228)
Problem Set – 2

1. What is orbital approximation? Justify and formulate the introduction of effective nuclear charge in the Hamiltonian of multi-electron systems.

2. What would be the results of Stern-Gerlach experiments if the experimental atoms have one valance electron in a) s orbital, b) p_x orbital, c) p_z orbital, and d) d_{z^2} orbital.

3. Answer the following questions on exchange or interchange operation.

   a. Define exchange operator ($\widehat{\mathrm{P}}_{\mathrm{ij}}$) using suitable example. Show that a system of multiple identical spinless particles is defined by either symmetric or anti-symmetric wavefunction.
   b. Show that $\widehat{\mathrm{P}}_{\mathrm{ij}}$ is a linear operator.
   c. Show that $\widehat{\mathrm{P}}_{\mathrm{ij}}^{\,2}$ is an identity operator.
   d. For a system of identical quantum particles, show that $\widehat{\mathrm{P}}_{\mathrm{ij}}$ commutes with the Hamiltonian operator.
   e. Consider the following wavefunction of a multiparticle system

   $$\psi(x_1, x_{2,} x_3, x_4) = \frac{10x_4}{x_2^2 x_3} e^{-ix_1}$$

   Find out $[\widehat{\mathrm{P}}_{12}, \widehat{\mathrm{P}}_{14}]$, $[\widehat{\mathrm{P}}_{12}, \widehat{\mathrm{P}}_{21}]$, and $[\widehat{\mathrm{P}}_{12}, \widehat{\mathrm{P}}_{34}]$.

4. State Symmetrization Postulate. Derive Pauli's exclusion principle from this postulate.

5. Three non-interacting particles are placed in a 1D infinite potential well of box length L. Find out the energy and wave function of the ground state and first excited state of the system if the particles are a) spinless and distinguishable of same mass, b) spinless and distinguishable having $\mathrm{m}_3 > \mathrm{m}_2 = \mathrm{m}_1$, b) indistinguishable and spin ½, and c) indistinguishable and spin 1.

6. Consider a system of two non-interacting identical electrons of mass m is moving along a 1D harmonic oscillator. The state of the system is defined as:

   $$\psi(x_1, x_2) = \sqrt{\frac{2}{\pi}\frac{1}{x_0^2}}(x_2 - x_1)exp\left(-\frac{x_1^2 + x_2^2}{x_0^2}\right)\omega(s_1, s_2)$$

   Where x_1, x_2 are spatial coordinates and s_1, s_2 are spin coordinates. $\omega(s_1, s_2)$ is the spin state of the particles.

   a. Is $\omega(s_1, s_2)$ singlet or triplet state? Justify.
   b. What is the energy of the above state? Justify.

7. Discuss Bose-Einstein condensation using the example of superconductivity of ^{4}He and its applications as cyrocooler such as in NMR and MRI instruments where liquid helium is used to cool down the magnet.

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8. A researcher wants to calculate the ground state energy of a quartic oscillator (mass = μ) whose potential energy is given by $V(x) = \lambda x^4$ using variational method. She used the following trial function: $\varphi(x) = e^{-\frac{\alpha x^2}{2}}$.

   a. Identify the variational parameter(s).
   b. Write down the functional form of the numerator of E_φ with proper integration limits.
   c. Write down the functional form of the denominator of E_φ with proper integration limits.
   d. The solutions of the numerator and denominator of E_φ are $\left(\frac{\hbar^2}{\mu}\sqrt{\alpha\pi} + \frac{3\lambda\sqrt{\pi}}{4\alpha^{5/2}}\right)$ and $\sqrt{\frac{\pi}{\alpha}}$ respectively. Find the value of $E_{\varphi,min}$.

9. Two students are asked to define their own trial functions for simple harmonic oscillator model for the applications of variational principle. Their trial functions are (i) $\varphi(x) = (1 + \beta x^2)^{-1}$ and (ii) $\varphi(x) = cos\lambda x$.

   a. Identify the variational parameters in each of the trial functions.
   b. Write down the normalized integrals for the estimation of E_φ for each trial functions. Provide proper limits of the integral.
   c. For the trial function (i), the numerator and denominator of E_φ are $\left(\frac{\hbar^2}{\mu}\left(\frac{\pi}{8}\right)\beta^{1/2} + \frac{k\pi}{4\beta^{3/2}}\right)$ and $\frac{\pi}{2\beta^{1/2}}$ respectively. Find the value of $E_{\varphi,min}$.
   d. For the trial function (ii), the numerator and denominator of E_φ are $\left(\frac{\hbar^2\lambda}{\mu}\left(\frac{\pi}{4}\right) + \frac{k}{\lambda^3}\left(\frac{\pi^3}{48} - \frac{\pi}{8}\right)\right)$ and $\frac{\pi}{2\lambda}$ respectively. Find the value of $E_{\varphi,min}$.
   e. Compare the $E_{\varphi,min}$ values obtained from the above trial functions with the zero-point energy of a simple harmonic oscillator having force constant of k and reduced mass of μ. Find out the error in the determination of energy for each trial function?

10. The allyl cation $\mathrm{CH_2 = CH - CH^+}$ has a delocalized π network that can be described by the Hückel method. Derive the MO energy levels of this species and place the electrons in the levels appropriate for the ground state. Using the butadiene MOs as an example, sketch what you would expect the MOs to look like. Classify the MOs as bonding, antibonding, or nonbonding.