IISER Kolkata – End-Semester Examinations

CH-3103- Quantum Chemistry II

Total marks = 50 Duration: 3 hour

Note: Answer all questions. Each question contains 5 marks.

1. Calculate $\langle r \rangle$ for the ground state of the Hydrogen atom. Wave function for 1s state of H atom is given by $\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} \exp\left(-\frac{r}{a_0}\right)$.
2. Consider a particle in a spherical box of radius a. The ground state Hamiltonian is given by $H = -\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)$, where $0 \le r \le a$. Use $\psi(r) = a - r$ to calculate an upper bound to the ground state energy of the system.
3. Consider a one-particle, one dimensional system with $V = 0$ for $0 \le x \le l$ and $V = \frac{20\hbar^2}{ml^2}$ elsewhere. Use the variation function $\psi(x) = \sin[\pi(x+c)/(l+2c)]$ for $-c \le x \le l+c$ and $\psi(x) = 0$ elsewhere, where c is a positive variational parameter. Find the value of c which minimize the variational integral W and find the expression for the minimum value of W.
4. (a) For a particle in a square box of length l with origin at x = 0, y = 0, write down the wave functions and energy levels. (b) If this system is perturbed by $H' = b$ for $\frac{l}{4} \le x \le \frac{3l}{4}$ and $\frac{l}{4} \le y \le \frac{3l}{4}$ where b is a constant and $H' = 0$ elsewhere, find the first order correction values to Energy ($E^{(1)}$) for the ground state and for the first excited energy level.
5. Calculate the first-order correction to the ground state energy of a hydrogen atom in an external electric field of strength E, where perturbation is given by $H' = eEr\cos\theta$.
6. Using the Condon-Slater rule show that ground state energy for the Li atom is given $E = E^{(0)} + J_{1s1s} + 2J_{1s2s} - K_{1s2s}$, where $E^{(0)}$ is the energy ignoring electron repulsions. J and K are Coulomb and exchange integrals, respectively.
7. Using Valence-Bond Theory show that ground state energy of H_2 molecule (in Hartree unit) is given by $W_1 = -1 + \frac{Q+A}{1+S_{ab}^2}$. Q and A are Coulomb and exchange integrals, respectively. S_{ab} is the overlap integral of 1s orbitals of the two H atoms.
8. Show that MO wavefunction of the ground state H_2 molecule underestimates electronic correlation whereas VB wavefunction for the ground state H_2 molecule overestimates electronic correlation.
9. State and prove the quantum-mechanical Virial theorem.
10. Using generalized Hellmann-Feynman theorem, show that for hydrogen like atom $\left\langle \frac{1}{r} \right\rangle = \frac{Z}{n^2}\left(\frac{1}{a}\right)$. Here Z is the nuclear charge, n is the principal quantum number, and a is the Bohr radius.

06/12/18