Serial No. PCH-16- **ISLAMIC UNIVERSITYOF SCIENCE & TECHNOLOGY**
DEPARMENT OF CHEMISTRY
M Sc. (2^{nd} Semester) (Mid term) **Max. Marks: 30**
Course Title: Quantum Chemistry and Electrochemistry (PCH-CC-203) **Time: 40min**
Rollno:

1. The Shrodinger equation can be solved exactly for the H atom but not for the Li atom. This is because the Hamiltonian for Li has:
   a) three Laplacian terms.
   b) three electron-electron repulsion terms.
   c) two electron-electron repulsion terms.
   d) three electron-nucleus attraction terms.

2. Out of the trial wave functions: $\phi_1 = \exp(-\alpha . r)$ & $\phi_2 = \exp(-\alpha . r^2)$, which function gives the more accurate value of energy for the ground state of hydrogen atom?
   a) ϕ_1
   b) ϕ_2
   c) both ϕ_1 and ϕ_2
   d) none of these

3. The variational treatment of a multi-electron system gives:
   a) an upper bound to its ground state energy.
   b) a lower bound to its ground state energy.
   c) The result depends upon which trial function is used.
   d) Every trial function leads to the same value of energy

4. The Hamiltonian operator for the particle in a box with varying potential is $-\frac{\hbar^2}{2m}\nabla^2 + \frac{Vx}{L}$, where L is the length of the box and $-\frac{\hbar^2}{2m}\nabla^2$ is the unperturbed hamiltonian. The perturbation is maximum at :
   a) x = 0
   b) x = L
   c) x = L/2
   d) x =V

5. The average ground state energy for the above problem is :
   a) $h^2/8mL^2$
   b) $h^2/8mL^2 + V$
   c) $h^2/8mL^2 + V/2$
   d) $h^2/8mL^2 + V/L$

6. Which are the correct Hamiltonians $H^{(0)}$ and $H^{(1)}$ for an oscillator with potential :

   $$U(x) = \tfrac{1}{2} kx^2 + 1/6\, \gamma x^3 + 1/24\, bx^4$$

   i. $H^{(0)} = -1/2\nabla^2$
   ii. $H^{(0)} = -1/2\ \nabla^2 + \tfrac{1}{2} kx^2$
   iii. $H^{(1)} = \tfrac{1}{2} kx^2 + 1/6\, \gamma x^3$
   iV. $H^{(1)} = 1/6\, \gamma x^3 + 1/24\, bx^4$
   a) (i) & (iii)
   b) (i) & (iv)
   c) (ii) & (iii)
   d) (ii) & (iv)

7. For a two electron system with Hamiltonian :

   $$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} + \frac{1}{R}$$

   identify $H^{(0)}$ if the system is to be treated by the perturbation method.
   a) $1/R$
   b) $1/r_{12}$
   c) $1/R + 1/r_{12}$
   d) none of these

Signature of Student **Signature of Invigilator**

8. One of the secular equations for a multi-electron system is :

$$C_1(H_{11}-ES_{11}) + c_2 (H_{12}-ES_{12}) + C_3 (H_{13}- ES_{13}) = 0$$

Which is the correct statement about the system?

a) The MO is LCAO of 2 AOs
b) The MO is LCAO of 3 AOs
c) $S_{12} = S_{13}$
d) H_{11} = resonance integral

9. In solving the H_2^+ problem using a wave function that is a linear combination of two 1s AOs, the matrix element H_{AB} is equal to :

a) $<1s_A|1s_B>$
b) $<1s_A|H|1s_B>$
c) $<1s_B|H|1s_A>$
d) both (b) & (c)

10. Given $\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$, the value of the integral $\int 1s\hat{H}1s\,d\tau$ is:

a) 1/2 a.u
b) -1/2 a.u
c) 2 a. u
d) 0

11. The ionic strength of:
(i) A solution which is 0.1 molal in KCl and 0.2 molal in K_2SO_4.
(ii) 0.2 molal $BaCl_2$ solution.

a) (i) =0.7; (ii) = 0.6
b) (i) =0.6; (ii) = 0.7
c) (i) =0.5; (ii) = 0.4
d) (i) =0.1; (ii) = 0.2

12. The mean ionic activity coefficient $f_{\pm}$ of NaCl at a molality of 0.01 at 25 ^{0}C is:

a) 0.889
b) 0.998
c) 0.989
d) 0.908

13. The chemical potential change in an ionic solution in going from the standard state to the final state involved is:

a) $\mu - \mu_0 = RT \ln x_i + RT \ln f_i$
b) $\mu - \mu_0 = RT \ln f_i$
c) $\mu - \mu_0 = RT \ln x_i$
d) None

14. The ion-dipole interaction energy is given by:

a) $U_{I-D} = \dfrac{-z_i e_0 \mu \cos\theta}{r^2}$
b) $U_{I-D} = \dfrac{z_i e_0 \mu \cos\theta}{r^2}$
c) $U_{I-D} = \dfrac{-z_i e_0 \mu}{r^2}$
d) $U_{I-D} = \dfrac{-z_i e_0}{r^2}$

15. When a negative ion is considered, the water molecule turns around through π radians, and one obtains by an argument an equation for interaction energy similar to that for positive ions is given by:

a) $U_{I-Q} = \dfrac{-z_i e_0 \mu}{r^2} - \dfrac{z_i e_0 p_w}{2r^3}$
b) $U_{I-Q} = \dfrac{-z_i e_0 \mu}{r^2} + \dfrac{z_i e_0 p_w}{2r^3}$
c) $U_{I-Q} = \dfrac{z_i e_0 \mu}{r^2} - \dfrac{z_i e_0 p_w}{2r^3}$
d) None

16. According to the Debye-Huckel theory, the chemical-potential

change $\Delta\mu_{i-I}$ arising from the ion-ion interactions is given by:

a) $\Delta\mu_{i-I} = \frac{-N_A(z_i e_0)^2}{2\varepsilon\kappa^{-1}}$
b) $\Delta\mu_{i-I} = \frac{(z_i e_0)^2}{2\varepsilon\kappa^{-1}}$
c) $\Delta\mu_{i-I} = \frac{-N_A(z_i e_0)^2}{2\varepsilon}$
d) None

17. For 1:1 electrolytes with $Z_+ = Z_- = 1$ $\log f_\pm =$?
a) $-Ac^{1/2}$
b) $Ac^{1/2}$
c) $-A^{1/2}$
d) None

18. The Born term in the ion-ion interaction in a solution is:
a) $\Delta G_{Born} = \frac{(z_i e_0)^2}{2r_i\varepsilon} - \frac{(z_i e_0)^2}{2r_i}$
b) $\Delta G_{Born} = \frac{(z_i e_0)^2}{2r_i\varepsilon} + \frac{(z_i e_0)^2}{2r_i}$
c) Both
d) None

19. The effects of mole fraction and activity coefficients on the free energy are:
a) Multiplicative
b) Additive
c) Both
d) None

20. There are a number of fundamental difficulties with the Born equation:
(i) Behind the idea of the work of charging is an assumption that the charging occurs slowly, so that all parts of the system concerned are arranged in their equilibrium configuration.
(ii) Although the Born charging energy differs from either the ionization energy or the electron affinity, its values for simple ions are not unreasonable.
(iii) The thinking behind the deduction of Born's equation is pre-quantal. In reality, atoms do not charge up by the aggregation of a series of infinitesimally small amounts of charge.
a) (i) and (ii) are correct
b) (ii) and (iii) are correct
c) Only (iii) is correct
d) All the above are true