一、單選題(每題 4 分，答錯每題倒扣 1.5 分，未作答 0 分)

1. Given that the ionization energy of hydrogen-atom ground state is 13.6 eV, how much energy in eV is required to remove an electron from the $3d_2$ orbital in a Be^{3+} ion?

(A) 6.8 eV　(B) 18.1 eV　(C) 24.2 eV　(D) 54.4 eV　(E) 61.2 eV

2. Consider a quantum particle of mass m trapped in a 3-dimensional cubic box. The potential energy is zero inside the box and infinity outside the box. The length on each side of the box is a. What is the degeneracy of the energy level of $E = \dfrac{14h^2}{8ma^2}$? (h = Planck constant)

(A) 1　(B) 2　(C) 4　(D) 6　(E) 8

3. In quantum mechanics, the measurements of two physical quantities, a and b, are represented by operators $\hat{A}$ and $\hat{B}$, respectively. If the two operators commute, which of the following statements is **NOT** true?

(A) It is possible to measure a and b precisely and simultaneously.

(B) The two operators possess a common set of eigenfunctions.

(C) The two operators possess a common set of eigenvalues.

(D) $\hat{A}\hat{B}f = \hat{B}\hat{A}f$, where f is a well-behaved function.

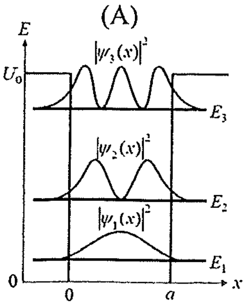
(E) $[\hat{A}, \hat{B}] = \hat{0}$.

4. Consider a quantum particle confined in a 1-D symmetric finite potential well defined as

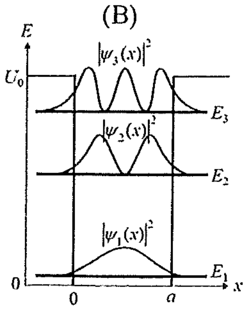
$$U(x) = \begin{cases} 0 & , 0 \le x \le a \\ U_0 & , x < 0 \text{ or } x > a \end{cases}$$

Which of the following schematic diagrams of the bound eigenstate energy distribution and probability density functions is most qualitatively correct in all aspects?

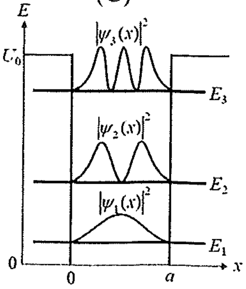
(A)



(B)



(C)



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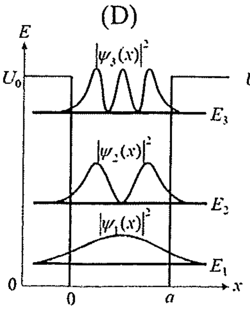
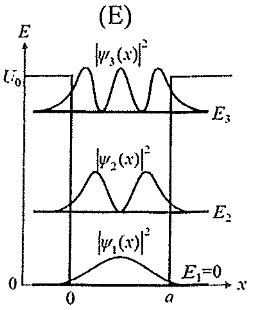


(E)



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5. A quantum harmonic oscillator (QHO) with a fundamental vibrational frequency ν is in a superposition state described by a wave function $\Psi(x)=\frac{1}{\sqrt{3}}\phi_0(x)+c_1\phi_1(x)+\frac{1}{\sqrt{3}}\phi_2(x)$, where $\phi_v(x)$'s are normalized eigenfunctions of the QHO (the subscripts "v" denote the vibrational quantum numbers) and c_1 is the expansion coefficient for $\phi_1(x)$. What is the average energy when a very large number of identically prepared QHO's in $\Psi(x)$ state are measured?

(A) $\frac{7}{2}h\nu$ (B) $2h\nu$ (C) $\frac{1}{2}h\nu$ (D) $\frac{3}{2}h\nu$ (E) $4h\nu$

6. The first excited state of helium (He) atom is described by electron configuration $1s^1 2s^1$. Which of the followings is the correct form of spin-orbital functions for He atom first excited-state wave function satisfying the Pauli Principle? (Note: $1S(i)$ and $2S(i)$ are the spatial orbitals; $\alpha(i)$ and $\beta(i)$ are the spin functions; i=1, 2 denotes the electron coordinates; N is the normalization constant)

(A) $N[1S(1)2S(2)-1S(2)2S(1)][\alpha(1)\beta(2)]$

(B) $N[1S(1)2S(2)+1S(2)2S(1)][\alpha(1)\alpha(2)]$

(C) $N[1S(1)\alpha(1)][2S(2)\beta(2)]$

(D) $N[1S(1)2S(2)+1S(2)2S(1)][\alpha(1)\beta(2)+\alpha(2)\beta(1)]$

(E) $N[1S(1)2S(2)-1S(2)2S(1)][\alpha(1)\beta(2)+\alpha(2)\beta(1)]$

7. Consider the variational method for the ground state of a two-electron atom. The simplest trial function is the Hartree product of the form $\Psi(r_1,r_2)=\phi_{1s}(r_1)\phi_{1s}(r_2)$, where $\phi_{1s}(r)=\frac{1}{\sqrt{\pi}}\left(\frac{\zeta}{a_0}\right)^{3/2}e^{-\zeta r/a_0}$ is the hydrogen-like $1s$ atomic orbital with an effective nuclear charge, ζ, as the variational parameter. The variational integral can be evaluated analytically to give $E_\Psi=E_h\left[-\zeta^2+2\zeta(\zeta-Z)+\frac{5}{8}\zeta\right]$, where Z is the true nuclear charge and E_h=27.2 eV is the Hartree energy. What is the ground state energy of Li^+ ion at this level of approximation?

(A) –77.5 eV (B) –196.5 eV (C) –54.4 eV (D) –108.8 eV (E) –98.2 eV

8. The hydrogen atomic wave functions can be expressed as $\Psi_{nlm}(r,\theta,\phi)=R_{nl}(r)Y_l^m(\theta,\phi)$, where

$$R_{10}=2\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0}\ ;\ R_{20}=\frac{1}{\sqrt{8}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}\ ;\ R_{21}=\frac{1}{\sqrt{24}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}$$

$$Y_0^0=\left(\frac{1}{4\pi}\right)^{1/2}\ ;\ Y_1^0=\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta\ ;\ Y_1^{\pm1}=\left(\frac{3}{8\pi}\right)^{1/2}(\sin\theta)e^{\pm i\phi}$$

An electron is in the $2p_0$ orbital of a H atom. What is the most probable radius (the radius where the radial distribution function is at maximum) of finding that electron?

(A) $5a_0$　(B) $4a_0$　(C) $3a_0$　(D) $2a_0$　(E) a_0

9. The complex form of H-atom wave functions for n=3, l=2, m=±1 states are $\Psi_{3d_{\pm1}}(r,\theta,\phi)=R_{3d}(r)Y_2^{\pm1}$, where $R_{3d}(r)$ is the radial function and $Y_2^{\pm1}=\left(\frac{15}{8\pi}\right)^{1/2}(\sin\theta\cos\theta)e^{\pm i\varphi}$ are spherical harmonic functions with l=2 and m=±1. A real form function ($3d_{xz}$ orbital) can be constructed with the linear combination of the two complex wave functions as $\Psi_{3d_{xz}}=\frac{1}{\sqrt{2}}\left(\Psi_{3d_{+1}}+\Psi_{3d_{-1}}\right)$. Which of the following statements about the $3d_{xz}$ orbital is **NOT** correct?

(A) $3d_{xz}$ wave function is an eigenfunction of H-atom $\hat{H}$ (Hamiltonian operator).

(B) $3d_{xz}$ wave function is an eigenfunction of H-atom $\hat{L}^2$ (operator for square of orbital angular momentum).

(C) $3d_{xz}$ wave function is an eigenfunction of H-atom $\hat{L}_z$ (operator for angular momentum along the z axis).

(D) The magnitude of orbital angular momentum is not zero.

(E) the average values of L_z is zero.

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10. Allyl radical (CH_2-CH-CH_2) is a planar molecular radical in which the three π electrons are delocalized. Hückel theory is a simplified molecular orbital (MO) theory describing the MOs of the π-electron system as linear combinations of the $2p_z$ atomic orbitals at each carbon atom involved in the delocalized system. The basic assumptions of Hückel theory are: All overlap integrals are set equal to zero; All resonance integrals between non-neighboring atoms are set equal to zero; All coulomb integrals are set equal to $\boldsymbol{\alpha}$; All resonance integrals between neighboring atoms are set equal to $\boldsymbol{\beta}$. What is the total energy of the three π electrons predicted by Hückel MO theory?

(A) $3\alpha + 2\sqrt{2}\beta$　(B) $2\alpha + 2\sqrt{2}\beta$　(C) $2\alpha - \sqrt{2}\beta$　(D) $2\alpha + 4\beta$　(E) $4\alpha + 4\beta$

11. The first excited electron configuration of HF is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^3(4\sigma*)^1$. What is (are) molecular term(s) that can arise from this excited configuration?

(A) $^1\Sigma$ and $^3\Sigma$　(B) $^1\Pi$ and $^3\Pi$　(C) $^3\Pi$ and $^1\Sigma$　(D) $^3\Pi$　(E) $^3\Delta$

12. The eigenfunctions of a diatomic rigid rotor are specified by two quantum numbers, l (angular momentum quantum number) and m (magnetic quantum number). Which of the following statements is correct for a diatomic rigid rotor?

(A) The rotational energy levels are equally spaced.

(B) The lowest rotational energy level has a nonzero energy called zero-point energy.

(C) Each rotational energy level has a degeneracy of $2(l+1)$.

(D) If a rigid rotor is measured to be in an eigenstate with $l = 2$ and $m = 0$, the direction of its angular momentum is accurately determined.

(E) Pure rotational transitions usually occur in the microwave region, and the transition lines are equally spaced in frequency.

13. If 2.019 g of ethanol $C_2H_5OH(l)$ is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 59.68 kJ. ΔH_f^0 for water(l) = –285.8 kJ mol^{-1} and for $CO_2(g)$ = –393.5 kJ mol^{-1}.

(A) $\Delta H^0_{combustion}$ for ethanol(l) at 298.15 K is 886.7 kJ mol^{-1}

(B) $\Delta H^0_{combustion}$ for ethanol(l) at 298.15 K is –886. kJ mol^{-1}

(C) ΔH_f^0 for ethanol(l) at 298.15 K is 210.5 kJ mol^{-1}

(D) ΔH_f^0 for ethanol(l) at 298.15 K is –210.5 kJ mol^{-1}

(E) ΔH_f^0 for ethanol(l) at 298.15 K is –280.4 kJ mol^{-1}

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14. The Joule coefficient is defined by $\left(\frac{\partial T}{\partial V}\right)_U = \left(\frac{1}{C_V}\right)\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right]$. The van der Waals gas of equation is: $P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$; a and b are constants.

(A) The joule coefficient for an ideal gas is $\left(\frac{1}{C_V}\right)$.

(B) The joule coefficient for an ideal gas is $-\left(\frac{1}{C_V}\right)$.

(C) The joule coefficient for a van der Waals gas is $\left(\frac{1}{C_V}\right)\frac{n^2a}{V^2}$.

(D) The joule coefficient for a van der Waals gas is $-\left(\frac{1}{C_V}\right)\frac{n^2a}{V^2}$.

(E) None of above is correct.

15. When the volume of 150.g of CO initially at 273 K and 1.00 bar increases by a factor of two. Take $C_{p,m}$ to be constant at the value of 29.16 J mol^{-1}K^{-1} and assume ideal gas behavior. The temperature of surroundings is 273 K. Which of the following statement is correct if the expansion occurs under that specific condition?

(A) In an adiabatic reversible expansion process, $\Delta S_{\text{system}} > 0$.

(B) In an adiabatic reversible expansion process, $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$

(C) In an expansion against $P_{\text{external}} = 0$, $\Delta S_{\text{system}} < 0$

(D) In an expansion against $P_{\text{external}} = 0$, $\Delta S_{\text{surroundings}} = 0$

(E) In an expansion against $P_{\text{external}} = 0$, $\Delta S_{\text{total}} = 0$

16. Consider the second-order reaction aA → products (which has a first half-life of 25 s). If the concentration of A after 17 s is 0.55 M, determine the initial concentration of A.

(A) 0.92 M　(B) 1.08 M　(C) 2.16 M　(D) 1.84 M　(E) 0.75 M

17. For the reaction: $2N_2O_5(g) \rightarrow O_2(g) + 4NO_2(g)$ the half-life is a constant 693 s at 45° C and the half-life at 65° C is a constant 70.7 s. Calculate the activation energy for this reaction. (ln(10) = 2.303)

(A) 5.0×10^2　(B) 7.0×10^2　(C) 3.0×10^2　(D) 2.0×10^2　(E) 1.0×10^2 kJ/mol.

18. G denotes Gibbs energy and A denotes Helmholtz energy. Following the Gibbs–Helmholtz equation, at constant pressure we obtain the relation of G/T vs. temperature. Similarly, the A/T vs. temperature for the equation $[\frac{\partial(\frac{A}{T})}{\partial(\frac{1}{T})}]_V = ?$

(A) entropy S　(B) enthalpy H　(C) –H　(D) internal energy U　(E) –U.

19. The critical pressure, molar volume and temperature denoted as P_c, T_c, and V_{mc}, respectively can be estimated from the van der Waals constants. Which of the following equations is correct for van der Waals gas?

(A) $P_c = a/(27b^2)$　(B) $V_{mc} = 2b$　(C) $T_c = 6a/(27Rb)$　(D) $z_c = P_cV_c/RT_c = 5/8$

(E) None of above is correct.

20. A gaseous system contains CO, CO_2, H_2, H_2O, and C_6H_6 in chemical equilibrium. The independent equations are: $CO_2 + H_2 \rightleftharpoons H_2O + CO$ and $12CO + 3H_2 \rightleftharpoons C_6H_6 + 6CO_2$. How many degrees of freedom are there in this system according to phase rule?

(A) 2　(B) 3　(C) 4　(D) 5　(E) 6

21. At 39.9°C, a solution of ethanol (molar fraction of component 1 in solution $x_1 = 0.9006$, vapor pressure of pure ethanol $P_1^* = 130.4$ torr) and isooctane ($P_2^* = 43.9$ torr) forms a vapor phase with $y_1 = 0.6667$ (molar fraction of component 1 in vapor) at a total pressure of 185.9 Torr. Which of the following statement is correct?

(A) The activity of component 1 $a_1 = 0.8501$

(B) The activity of component 2 $a_2 = 1.000$

(C) The activity coefficient of component 1 $\gamma_1 = 0.905$

(D) The activity coefficient of component 2 $\gamma_2 = 14.2$

(E) The total pressure of solution is 174.3 Torr if it were ideal solution.

22. Which of the following statement is correct

(A) The standard molar entropy of Ne is greater than that of Kr.

(B) At room temperature, the rotational partition function of HF is greater than that of CO.

(C) Classical statistical mechanics applies accurately to translations of molecules.

(D) At 500 K, the vibrational partition function of HF is already close to the classic limit.

(E) At 1500 K the vibrational partition function for Cl_2 is nearly unity.

23. Molecular oxygen populating the excited singlet state (${}^1\Delta_g$) can relax to the ground triplet state (${}^3\Sigma_g$) by emitting a 1280 nm (= 7812.5 cm^{-1}) photon.

(A) The partition function consist of these electronic states is $q = 1 + 3e^{-\beta(7812.5)}$, $\beta = 1/RT$ in $(cm^{-1})^{-1}$.

(B) Molecular oxygen a homonuclear diatom, shows no infared vibrational spectra. Hence, its vibrational partition function is zero.

(C) The translational partition function of molecular oxygen is function of volume.

(D) The rotational partition function of molecular oxygen is function of volume.

(E) None of above is correct.

24. A reaction is catalyzed by the bromide ion shown below:

$$H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow{Br^-} C_6H_5N_2^+ + 2H_2O.$$

A proposed mechanism is

(1) $H^+ + HNO_2 \rightleftharpoons H_2NO_2^+$

(2) $H_2NO_2^+ + Br^- \rightarrow ONBr + H_2O$

(3) $ONBr + C_6H_5NH_2 \rightarrow C_6H_5N_2^+ + H_2O + Br^-$

Symbol k_n denotes the rate constant for the step n.

(A) Assume that the second step is the rate-limiting. The rate law is $k_2[H_2NO_2^+][Br^-]$

(B) Assume that the second step is the rate-limiting. The rate law is $k_2[H^+][HNO_2][Br^-]$

(C) Assuming quasi-steady-state approximation, the rate law is $k_2[H_2NO_2^+][Br^-]$.

(D) Assuming quasi-steady-state approximation and excess $[Br^-]$, the rate law is $k_1[H^+][HNO_2]$

(E) Assuming quasi-steady-state approximation and excess $[Br^-]$, the rate law is

$(k_1/k_{-1})\, k_2[H^+][HNO_2][Br^-]$

25. In a cubic container with sides 1 cm in length that contains 1 atm of Ar at 298 K. What is the average velocity of Ar approximately? Mass of Ar = 40

(A) 2.0×10^2　(B) 2.0×10^3　(C) 4.0×10^2　(D) 4.0×10^3　(E) 6×10^2 m s^{-1}.