

Physical Chemistry

FINAL EXAMINATION

This examination consists of 40 multiple choice questions. Mark the best answer A, B, C, D or E on the Answer Sheet. No penalty for wrong guesses.

1. Planck's constant has the same units as
 (A) angular momentum (B) the Hamiltonian (C) frequency (D) quantum number (E) de Broglie wavelength

(A) Recall relation like $L_z = m\hbar$.

2. Which of the following is known as the Schrödinger equation

(A) $E = h\nu$ (B) $E = mc^2$ (C) $\lambda = h/p$ (D) $\hat{H}\psi = E\psi$ (E) $-\frac{\hbar^2}{2m}\nabla^2$

(D)

3. Which of the following is NOT a correct consequence of the Heisenberg uncertainty principle:

(A) The shorter the lifetime of an excited state of an atom, the less accurately can its energy be measured. (B) An electron in an atom cannot be described by a well-defined orbit. (C) The momentum of an electron cannot be measured exactly. (D) Measurement of one variable in an atomic system can affect subsequent measurements of other variables. (E) A harmonic oscillator possesses a zero-point energy.

(C) Yes it CAN be measured exactly, but then uncertainty in position is infinite.

4. Which of the following is NOT a solution of the differential equation $y''(x) + k^2y(x) = 0$

(A) $\exp(-ikx)$ (B) $\exp(-kx)$ (C) $\sin kx$ (D) $\cos kx$

(E) $\sin(kx - \alpha)$ ($\alpha = \text{const}$) (B)

5. Which of the following is an eigenfunction of the operator

$$\hat{p}_r = -i\hbar r^{-1} \partial/\partial r r$$

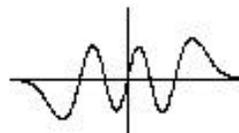
(A) $\exp(ikr)$ (B) $\sin(kr)$ (C) $r^{-1} \exp(ikr)$ (D) $r \exp(ikr)$

(E) $\exp(-kr^2)$ (C)

6. The corresponding eigenvalue equals (A) 0 (B) $\hbar k$ (C) $i\hbar k$ (D) $\hbar^2 k^2$ (E) $\hbar^2 k^2/2$ (B)

7. The energy levels of the linear harmonic oscillator are (A) all nondegenerate (B) n -fold degenerate (C) $(n + \frac{1}{2})$ -fold degenerate (D) $(2n + 1)$ -fold degenerate (E) n^2 -fold degenerate (A)

8. The illustrated wavefunction represents the state of the linear harmonic oscillator with



$n =$ (A) 1 (B) 2 (C) 3 (D) 4 (E) 5
(E) 5 nodes. Count em!

9. A hydrogen atom radiates a photon as it falls from a $2p$ level to the $1s$ level. The wavelength of the emitted radiation equals (A) 22.8 (B) 91.2 (C) 121.6 (D) 182.4 (E) 364.7 nm (C)

10. Spherical polar coordinates are used in the solution of the hydrogen atom Schrödinger equation because (A) the Laplacian operator has its simplest form in spherical polar coordinates. (B) cartesian coordinates would give particle-in-a-box wavefunctions. (C) the Schrödinger equation is then separable into 3 ordinary differential equations. (D) otherwise the atomic orbitals would violate the Pauli exclusion principle. (E) Schrödinger first used this coordinate system; any other coordinate system would be equally convenient.

(C)

11. The atomic orbital illustrated on the right is of what type:
(A) $2p$ (B) $3s$ (C) $3p$ (D) $3d$ (E) $s-p$ hybrid

(D) $3d_{z^2}$



12. For the hydrogen atom, which of the following orbitals has the lowest energy

(A) $4s$ (B) $4p$ (C) $4d$ (D) $4f$ (E) They all have the same energy (E)

13. The orbital degeneracy (excluding spin) of hydrogen atom energy levels equals (A) $n - 1$ (B) n (C) $n + 1$ (D) $2n + 1$ (E) n^2 (E)

14. For real atomic orbitals with quantum numbers n , ℓ , the total number of nodal surfaces, radial plus angular, equals (A) n (B) $n - 1$ (C) $n - \ell - 1$ (D) $n + \ell$ (E) $2\ell + 1$ (B)

15. Which of the following statements about the hydrogen atom ground state is INCORRECT: (A) It is described by the quantum numbers $n = 1$, $\ell = 0$, $m = 0$. (B) The electron's angular momentum equals \hbar . (C) The wavefunction is spherically symmetrical. (D) The wavefunction decreases exponentially as a function of r . (E) The radial distribution function has its maximum at the Bohr radius.

(B) Bohr theory was wrong!

16. The expectation value of $1/r$ in the ground state of the hydrogen atom equals

(A) a_0 (B) $(3/2)a_0$ (C) $a_0/4\pi$ (D) $1/a_0$ (E) h/mc (D)

17. The ionization energy for hydrogen atom is 13.6 eV. The ionization energy for the ground state of Li^{++} is approximately

(A) 13.6 (B) 27.2 (C) 40.8 (D) 54.4 (E) 122.4 eV

(E) $Z^2 \times 13.6 = 122.4 \text{ eV}$

18. The lowest excited state of the helium atom has the term symbol

(A) $2s^2$ (B) 1S_0 (C) 3S_1 (D) $^1\Sigma_g^+$ (E) He^+ (C)

19. The ground state of the ozone molecule O_3 has the following shape

(A) linear (B) bent (C) equilateral triangle (D) tetrahedral (E) trigonal bipyramid (B)

20. Sulfur apparently shows a valence of 6 in the molecule SF_6 , whereas oxygen, just above it in the periodic table, has only a valence of 2. Why is this?

(A) The sulfur atom can access d -orbitals (B) Breakdown of the Pauli principle (C) Breakdown of the Born-Oppenheimer approximation (D) Excited vibrational states (E) Excited rotational states (A)

21. Which of the following is NOT a correct aspect of the Born-Oppenheimer approximation (A) The electrons in a molecule move much faster than the nuclei. (B) Excited electronic states have the same equilibrium internuclear distance as the ground electronic state. (C) The electronic and vibrational motions of a molecule are approximately separable. (D) Electronic energy curves serve as potential energy functions for nuclear vibrational

motion. (E) The typical amplitude of nuclear vibration is much smaller than that characterizing the motion of electrons. (B)

22. Molecules are known to absorb radiation in which region of the electromagnetic spectrum: (A) ultraviolet (B) visible (C) infrared (D) microwave (E) all of the above (E)

23. As $R \rightarrow 0$ (not ∞) the $1\pi_g$ MO of H_2^+ turns into which AO of He^+ : (A) 2s (B) 2p (C) 3p (D) 3d (E) sp hybrid (D)

24. The $1\sigma_g$ MO of H_2 is best approximated by
 (A) $1s_A + 1s_B$ (B) $1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)$ (C) $1\pi_g + 1\pi_u$
 (D) $\exp[-\alpha(r_1 + r_2)]$ (E) $D_e\{1 - e^{-a(R-R_e)}\}^2$
 (A) This is LCAO approx for orbital.

25. Which of the following molecules belongs to the same symmetry group as NH_3
 (A) BF_3 (B) CH_4 (C) CH_3OH (D) $CHCl_3$ (E) NH_4Cl (D)

26. A certain symmetry group of order 8 has 5 irreducible representations. What is the highest possible degeneracy of its quantum states
 (A) 1 (B) 2 (C) 3 (D) 5 (E) 8
 (B) $1^2 + 1^2 + 1^2 + 1^2 + 2^2 = 8$

27. Allowed electronic transitions in a homonuclear diatomic molecule obey the following selection rules: $\Delta S = 0$ and $g \leftrightarrow u$; $\Sigma \leftrightarrow \Sigma$, $\Sigma \leftrightarrow \Pi$ and $\Pi \leftrightarrow \Pi$ are all allowed. The lowest excited state of N_2 which can be attained by absorption of radiation from the ground state (not necessarily the lowest excited state!) is predicted to be (A) $^1\Sigma_g$ (B) $^1\Pi_g$ (C) $^3\Pi_g$ (D) $^1\Pi_u$ (E) $^3\Pi_u$ (D)

The spectroscopic constants assigned for the NO molecule are $D_0 = 6.48$ eV, $\tilde{\nu} = 1904 \text{ cm}^{-1}$, $B = 1.705 \text{ cm}^{-1}$

28. For NO, the $J = 0$ to $J = 1$ transition occurs at (A) 1.705 (B) 3.410 (C) 6.820 (D) 121 (E) 1904 cm^{-1}
 (B) $\Delta E = 2B$

29. The equilibrium internuclear distance in NO equals (A) 115 (B) 121 (C) 140 (D) 171 (E) 229 pm (A)

30. The force constant in NO equals (A) 1125 (B) 1235 (C) 1410 (D) 1595 (E) 1735 N/m (D)

31. The lowest energy orbital for the ammonia molecule is designated
 (A) $1s$ (B) $1\sigma_g$ (C) $1a_1$ (D) C_{3v} (E) N-H (C)

32. The benzene molecule C_6H_6 has how many vibrational modes
 (A) 6 (B) 12 (C) 24 (D) 30 (E) 36
 (D) $3 \times 12 - 6 = 30$

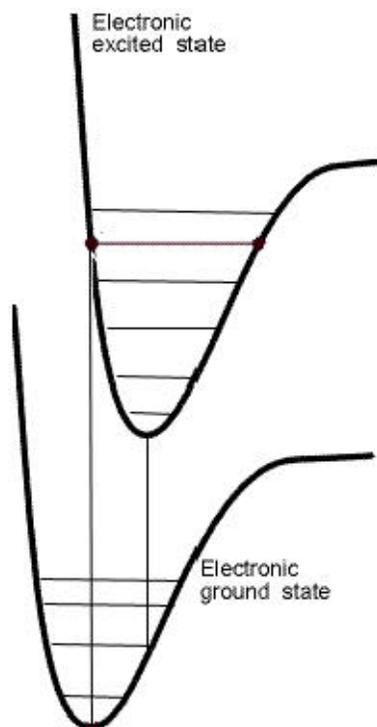
33. The Lennard-Jones potential for the interaction of two atoms has the form

$$V(R) = V_0 \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

The value of R_e is given by

(A) σ (B) $2^{1/6}\sigma$ (C) $\sigma^{12} - \sigma^6$ (D) $V_0/4\sigma^2$ (E) $(1 - e^{-\sigma/2})^2$
 (B) From solution of $V'(R) = 0$

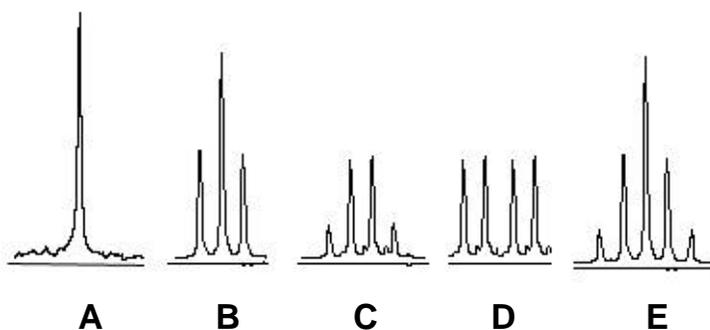
34. In the electronic transition pictured below, the molecule starts in its ground vibrational level. The most probable vibrational quantum number of the excited state is (A) 1 (B) 2 (C) 3 (D) 4 (E) 5 (D) 5th level, $v = 4$



35. Which of the following is a true statement about the fluorescence of a molecule whose ground state is a singlet:

(A) Its dissociation must proceed by a unimolecular mechanism. (B) The excited state must be a triplet (C) The excited state must have the same geometry as the ground state. (D) Fluorescence can occur in the visible region after absorption in the ultraviolet. (E) Intersystem crossing must have occurred. (D)

36. Which of the following represents the NMR spectrum of $^{12}\text{CH}_4$



(A) equivalent nuclei

37. Which of the following is most likely to be violated:

(A) the Pauli principle (B) the uncertainty principle (C) conservation of energy (D) the antisymmetry principle (E) the Born-Oppenheimer approximation (E) It's just an approximation!

38. All but one of the following abbreviations is likely to be used in quantum chemistry:

(A) NMR (B) LCAO (C) HOMO (D) LUMO (E) RSVP

(E) But don't forget to RSVP your invitations.

39. All but one of the following scientists made an important contribution to quantum mechanics:

(A) Heinrich Aufbau (B) Albert Einstein (C) Werner Heisenberg (D) Wolfgang Pauli (E) Erwin Schrödinger

(A) Aufbau means "building up." I'm sure Heinrich would have been a jolly fellow though.

40. "Now I need a drink, alcoholic of course, after the heavy sessions involving quantum mechanics." This is a mnemonic for which famous constant

(A) π (B) \hbar (C) mc^2 (D) a_0 (E) \mathcal{R}_∞ (A) Count the letters!