$\mathcal{NAME}$________________________________

CHEMISTRY 461

FINAL EXAMINATION **JUNE 17, 2002**

This examination consists of 40 multiple choice questions. Circle the best answer to each problem: A, B, C, D or E.

A 100 W sodium-vapor lamp emits yellow light of wavelength of 550 nm.

1. The frequency of the radiation is

(A) 3.00×10^8 (B) 5.50×10^{11} (C) 5.45×10^{14} (D) 1.83×10^{15}
(E) 5.14×10^{16} Hz

2. The wavenumber of the radiation is

(A) 1100 (B) 2.34×10^3 (C) 8.66×10^3 (D) 1.81×10^4 (E) 5.50×10^9 cm^{-1}

3. The energy of one of the emitted photons equals

(A) 3.61×10^{-19} (B) 5.07×10^{-15} (C) 3.29×10^{-10} (D) 0.0100 (E) 100 J

4. The number of photons emitted per second equals

(A) 100 (B) 8.01×10^{15} (C) 1.60×10^{19} (D) 2.77×10^{20} (E) 6.02×10^{23}

5. The atomic transition producing this radiation is

(A) $2p \rightarrow 1s$ (B) $3p \rightarrow 3s$ (C) $2s \rightarrow 1s$ (D) $3d \rightarrow 1s$ (E) $3d \rightarrow 4s$

6. The energy of this transition in eV equals

(A) 2.25 (B) 3.98 (C) 13.6 (D) 54.4 (E) 100

7. To be physically acceptable, a quantum-mechanical wavefunction must be

(A) single-valued (B) finite everywhere (C) continuous (D) any of A, B, C (E) all of A, B, C.

8. Consider a quantum-mechanical eigenvalue equation

$$\hat{A}\psi_n = a_n \psi_n$$

The operator $\hat{A}$ *must* be

(A) the Hamiltonian (B) the angular momentum (C) the linear momentum (D) expressed in spherical polar coordinates (E) Hermitian.

9. The eigenvalue a_n *must* be

(A) an integer (B) a multiple of $\hbar$ (C) a real number (D) a quantum number (E) part of a continuum.

10. The physical significance of the eigenvalue a_n is

(A) a possible result of measurement of the dynamical variable $\hat{A}$ (B) the uncertainty in the measurement of $\hat{A}$ (C) the statistical average of a large number of measurements of $\hat{A}$ (D) the square of the wavefunction ψ_n
(E) the relative probability of the value a_n.

11. *All but one* of the following statements about the eigenfunctions is true:

(A) Eigenfunctions belonging to different eigenvalues are orthogonal.
(B) No two eigenfunctions can have the same eigenvalue.
(C) An eigenfunction is normalized if $\int \psi_n^* \psi_n \, d\tau = 1$.
(D) A constant multiplied by an eigenfunction is still an eigenfunction.
(E) All the eigenfunctions must be single-valued, finite and continuous.

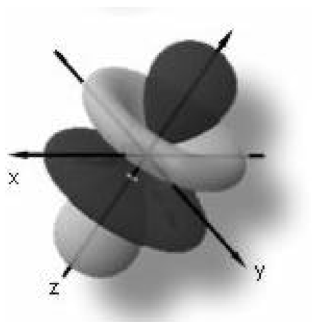
12. Suppose the commutator of two operators $\hat{A}$ and $\hat{B}$ equals zero. This implies that

(A) $\hat{A}$ and $\hat{B}$ are equal (B) $\Delta a \Delta b \geq \hbar/2$ (C) Simultaneous measurements of $\hat{A}$ and $\hat{B}$ are incompatible. (D) There exist simultaneous eigenfunctions of $\hat{A}$ and $\hat{B}$. (E) One of these operators is the Hamiltonian.

13. The commutator between the x-components of linear momentum and angular momentum equals

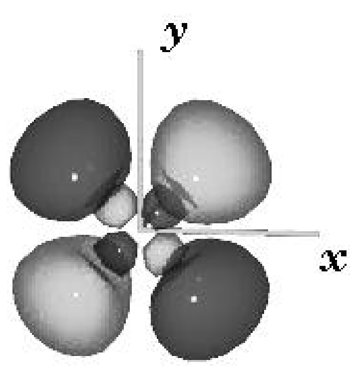
(A) 0 (B) 1 (C) $\hbar$ (D) $i\hbar$ (E) x

14. Identify the pictured atomic orbital. The different shadings represent positive and negative regions of the wavefunction.



(A) $4f_0$ (B) $4p_0$ (C) $4d_0$ (D) sp^3 (E) $1\pi_u$

15. Identify this atomic orbital:



(A) $4d_{z^2}$ (B) $3d_{x^2-y^2}$ (C) $3d_{xy}$

(D) $4d_{x^2-y^2}$ (E) $4d_{xy}$

16. For an atom in a ^2D state, the possible values of J are

(A) 3/2, 5/2 (B) +1/2, −1/2 (C) $-2, -1, 0, +1, +2$

(D) $-3/2, -1/2, +1/2, +3/2$ (E) 0, 1/2, 1, 3/2, 2

17. Another exotic hydrogenlike species is a muonic atom, consisting of a negative muon and a proton. The mass of the muon is 207 times that of an electron. The radius of the "first Bohr orbit" for this system equals approximately

(A) 2.6×10^{-13} (B) 2.4×10^{-12} (C) 5.3×10^{-11} (D) 1.0×10^{-10}
(E) 1.1×10^{-8} meters

18. Nitrogen is trivalent and can form molecules such as NH_3. Phosphorus, just below nitrogen in the periodic table, can be pentavalent as well as trivalent, forming stable compounds including both PF_3 and PF_5. Why is this?

(A) The phosphorus atom can access *d*-orbitals (B) Elemental phosphorus is a solid at room temperature (C) Deviations from the exclusion principle for larger values of nuclear charge (D) Excited vibrational states of trigonal bipyramid (E) Spin-orbit coupling

19. Which of the following triatomic molecules is *not* linear

(A) CO_2 (B) BeF_2 (C) HCN (D) H_2S (E) XeF_2

20. Which of the following molecular species is *not* tetrahedral

(A) BF_4^- (B) CF_4 (C) NH_4^+ (D) SO_4^{-2} (E) XeF_4

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

$$\hat{A} = \frac{\partial}{\partial r} + \frac{1}{r}$$

(A) e^{-r} (B) e^{-r^2} (C) $\frac{1}{r}e^{-r}$ (D) re^{-r} (E) $e^{-r} + \frac{1}{r}$

22. The corresponding eigenvalue equals (A) -1 (B) 0 (C) 1 (D) $i\hbar$ (E) 1/r

23. The commutator $[\hat{A}, \hat{A}]$ equals

(A) 0 (B) 1 (C) $-1/r^2$ (D) $1/r$ (E) $i\hbar$

24. The LCAO MO approximation for the ground state of the hydrogen molecule can be written

(A) $\Big(1s_A(1) + 1s_B(1)\Big)\Big(1s_A(2) + 1s_B(2)\Big)$

(B) $\Big(1s_A(1) + 1s_A(2)\Big)\Big(1s_B(1) + 1s_B(2)\Big)$

(C) $\Big(1s_A(1) + 1s_B(2)\Big)\Big(1s_B(1) + 1s_A(2)\Big)$

(D) $1s_A(1) + 1s_B(1) + 1s_A(2) + 1s_B(2)$

(E) $1s_A(1)1s_B(2)$

25. The tetrahedral molecule CH_4 has how many modes of vibration

(A) 5 (B) 6 (C) 7 (D) 8 (E) 9

26. The linear molecule HC≡CH has how many modes of vibration

(A) 4 (B) 5 (C) 6 (D) 7 (E) 8

For the ^{7}Li^{1}H molecule, $\tilde{\nu}$=1405.6 cm^{-1}, $\tilde{\nu}x_e$ = 23.2 cm^{-1} and B = 7.513 cm^{-1}. Calculate the following quantities:

27. R_e (in pm) (A) 98 (B) 102 (C) 149 (D) 160 (E) 188

28. The force constant (in Nm^{-1}) (A) 98 (B) 102 (C) 149 (D) 160 (E) 188

29. The wavenumber of the $J = 2$ to $J = 3$ transition (in cm^{-1})

(A) 7.5 (B) 15 (C) 30 (D) 45 (E) 60

30. Taking account of anharmonicity, the wavenumber of the $v = 1$ to $v = 2$ transition (in cm^{-1}) (A) 1313 (B) 1360 (C) 1382 (D) 1406 (E) 1499

31. As $R \to 0$ (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

32. The term symbol for the ground electronic state of the superoxide ion O_2^- is (A) ${}^2\Sigma_g$ (B) ${}^4\Delta_g$ (C) ${}^2\Sigma_u$ (D) ${}^2\Pi_g$ (E) ${}^2\Pi_u$

33. The term symbol for the ground electronic state of the peroxide ion O_2^{-2} is (A) ${}^1\Sigma_g$ (B) ${}^1\Sigma_u$ (C) ${}^3\Sigma_g$ (D) ${}^3\Sigma_u$ (E) ${}^1\Pi_g$

34. The vibrational energy for an anharmonic oscillator can be represented by the formula

$$hcE_v = (v + \tfrac{1}{2})\tilde{\nu} - (v + \tfrac{1}{2})^2\tilde{\nu}x$$

The highest possible vibrational quantum number for the stable molecule can be estimated by the condition $dE_v/dv = 0$. The best approximation to v_{max} is therefore

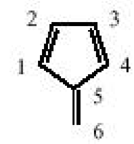
(A) x (B) $2\tilde{\nu}x$ (C) $\dfrac{1}{x}$ (D) $\dfrac{1}{2x} - \dfrac{1}{2}$ (E) $\dfrac{1}{\sqrt{x}} - \dfrac{1}{2}$

35. This is acrylonitrile (a recently suspected carcinogen found in bread and french fries):

$$CH_2{=}CH{-}C{\equiv}N$$

The molecule exhibits all but one of the following features [two choices]

(A) sp^3 hybridization (B) sp^2 hybridization (C) sp hybridization (D) a π orbital (E) a π^* orbital

36. A Hückel molecular-orbital computation on fulvene 

gives the following secular determinant [3,4 element corrected to 1]

(A) $\begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 0 & 1 & x \end{vmatrix}$

(B) $\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix}$

(C) $\begin{vmatrix} x & 1 & 0 & 0 & 1 & 0 \\ 1 & x & 1 & 0 & 0 & 1 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 1 & 0 & 0 & 1 & x & 1 \\ 0 & 1 & 0 & 0 & 1 & x \end{vmatrix}$

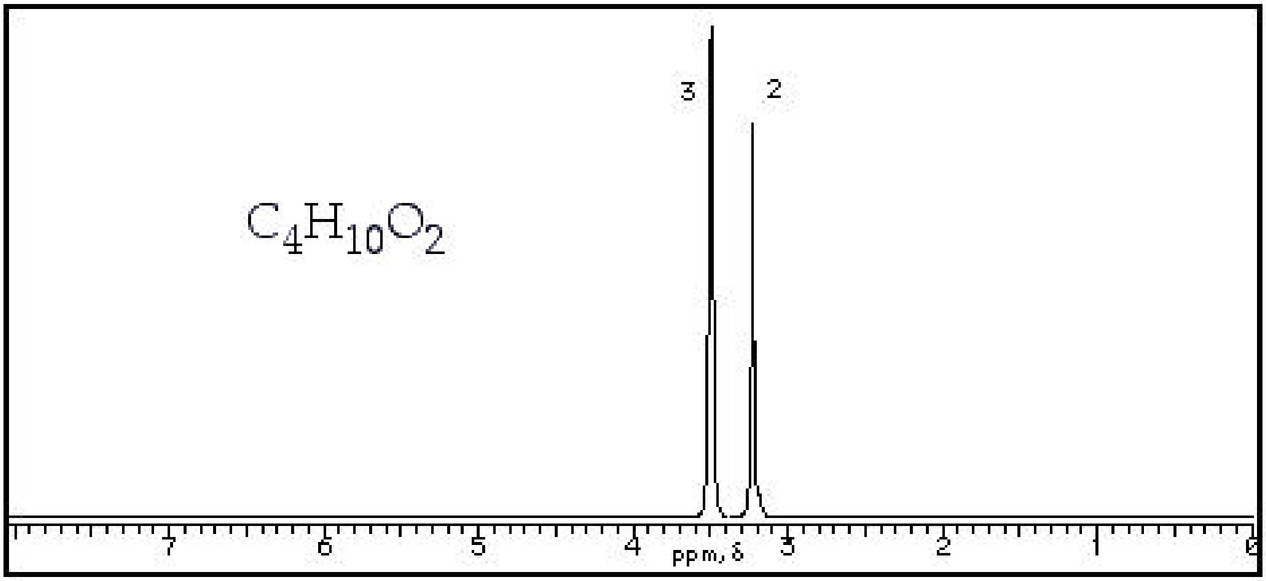
(D) $\begin{vmatrix} x & 1 & 0 & 0 & 1 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 1 & 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 0 & 1 & x \end{vmatrix}$

(E) $\begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 1 \\ 0 & 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 1 & 1 & x \end{vmatrix}$

37. A top-of-the-line NMR spectrometer operates at a frequency of 900 MHz. The proton resonance will occur in a magnetic field of

(A) 0.05 (B) 1.0 (C) 8.3 (D) 11 (E) 21 T

38. Identify this compound from its proton NMR spectrum. The relative intensities of the two peaks is 3:2

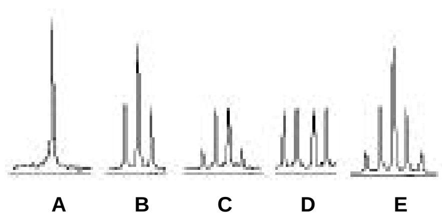


(A) CH_3–CH_2–O–O-CH_2–CH_3 (B) CH_3–CH(OCH_3)$_2$

(C) CH_3–CH_2–O–CH_2–O–CH_3 (D) CH_3–O–CH_2–CH_2–O–CH_3

(E) CH_3–O–CH–O–CH_3
|
CH_3

Following are five different observed NMR spectra



39. Which is the spectrum of Si(CH_3)$_4$ (A) (B) (C) (D) (E)

40. Which spectrum shows the splitting a nucleus with 4 equivalent protons on its neighboring atoms (A) (B) (C) (D) (E)