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Chemistry 3502/4502

Exam II

October 10, 2003

1) This is a multiple choice exam. Circle the correct answer.

2) There is *one* correct answer to every problem. There is no partial credit.

3) A table of useful integrals and other formulae is provided at the end of the exam.

4) You should try to go through all the problems first, saving harder ones for later.

5) There are 20 problems. Each is worth 5 points.

6) There is no penalty for guessing.

7) Please write your name at the bottom of each page.

8) Please mark your exam with a pen, not a pencil. Do not use correction fluid to change an answer. Cross your old answer out and circle the correct answer. Exams marked with pencil or correction fluid will not be eligible for regrade under any circumstances.

Score on Next Page after Grading

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1. How many nodes does the QMHO wave function $\Psi(x) = \left(\frac{\sqrt{k\mu}}{147456\hbar\pi}\right)^{1/4}\left[16\left(\frac{\sqrt{k\mu}}{\hbar}\right)^2 x^4 - 48\left(\frac{\sqrt{k\mu}}{\hbar}\right)x^2 + 12\right]e^{-\sqrt{k\mu}x^2/2\hbar}$ have?

(a) 0
(b) 1
(c) 2
(d) 3
(e) 4
(f) It depends on *k*
(g) It depends on μ
(h) (f) and (g)

2. For the diatomic molecule BeO, where Be has atomic mass 9 and O has atomic mass 16, what is the reduced mass?

(a) (9 x 16) / (9 + 16)
(b) 9
(c) 16
(d) (9 + 16) / (9 x 16)
(e) 1
(f) It depends on *k*
(g) It depends on the vibrational energy
(h) None of the above

3. Which of the following statements is/are true about $\langle x^2 \rangle$ evaluated for one-dimensional QMHO wave functions over the same potential *V*?

(a) Parity requires it to be zero for levels where *n* is odd
(b) It increases with increasing *n*
(c) It is equal to $\langle x \rangle^2$
(d) It is always positive
(e) It is equal to $2\langle V \rangle / k$ where *k* is the oscillator force constant
(f) (b) and (c)
(g) (c) and (d)
(h) (b), (d), and (e)

4. Which of the following statements about chemically equivalent CH vs. CD bonds is/are *true*?

(a) The CD bond has the smaller zero-point vibrational energy
(b) The CH bond has the smaller vibrational frequency
(c) The CH bond has the smaller force constant *k* by a factor of 2
(d) Both bonds absorb photons at the same IR frequency
(e) The CH bond has the larger reduced mass
(f) All of the above
(g) (a), (b) and (e)
(h) (c) and (d)

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5. Which of the following statements is/are true for a given set of QMHO wave functions corresponding to the same harmonic potential V?

(a) The ground state energy is above the bottom of the potential

(b) The number of nodes is equal to n+1, where n is the energy level

(c) $\langle T\rangle_n = \langle V\rangle_n = (1/2)\langle E\rangle_n$

(d) The wave functions have zero amplitude beyond the classical turning points

(e) The wave functions are eigenfunctions of the parity operator

(f) The selection rule for spectroscopic transitions is $n \to n \pm 1$

(g) (a), (c), (e), and (f)

(h) All of the above

6. What is $[L_x,L_y]$ when $|\mathbf{L}|^2 > 0$?

(a) 0

(b) $i\hbar$

(c) $i\hbar L_z$

(d) $i\hbar\left(L_x - L_y\right)$

(e) $i\hbar\left(L^2 - L_x^2 - L_y^2\right)^{1/2}$

(f) 1

(g) (c) and (e)

(h) None of the above

7. Which of the following statements about angular momentum operators, eigenvalues, and eigenfunctions is/are *false*?

(a) $L_+ = (L_-)^*$

(b) $\langle L^2\rangle = \langle L_z\rangle^2$ if $m_l = l$

(c) For each value of l there are $2l + 1$ possible values of m_l

(d) $L_+Y_{l,l} = 0$

(e) $L_-Y_{l,l} = 0$

(f) (b) and (e)

(g) (b), (d) and (e)

(h) None of the above

8. Which of the following statements about the spherical harmonics Y is/are *true*?

(a) The number of nodes in Y_{l,m_l} is l

(b) $\langle Y_{l,0}|T|Y_{l,0}\rangle > \langle Y_{l',0}|T|Y_{l',0}\rangle$ if $l > l'$

(c) The *real* spherical harmonics are not all eigenfunctions of L_z

(d) The *complex* spherical harmonics are not all eigenfunctions of L^2

(e) $Y_{0,0}$ is a constant everywhere in space

(f) (a) and (e)

(g) (a), (b), (c) and (e)

(h) All of the above

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9. What is the eigenvalue of $\left(L_x^2 + L_y^2\right)$ for Ψ if the eigenvalue of L^2 for Ψ is $12\hbar^2$ and the eigenvalue of L_z for Ψ is $2\hbar$?

(a) The Heisenberg uncertainty principle dictates that Ψ cannot be an eigenfunction for $\left(L_x^2 + L_y^2\right)$
(b) $10\hbar^2$
(c) $8\hbar^2$
(d) $4\hbar$
(e) $10\hbar$
(f) 0
(g) π
(h) None of the above

10. The frequency for the ground- to first-excited-state rotational transition in HO (m_H = 1; m_O = 16) is 100 cm^{-1}. What is the frequency for the same transition in DS (m_D = 2; m_S = 32) if HO and DS have exactly the same bond length?

(a) 400 cm^{-1}
(b) 200 cm^{-1}
(c) 100 cm^{-1}
(d) 50 cm^{-1}
(e) 25 cm^{-1}
(f) It depends on the bond length
(g) It cannot be determined from the information provided
(h) (f) and (g)

11. For a diatomic molecule, what is the rotational constant *B*?

(a) The eigenvalue of L^2
(b) The eigenvalue of L_z
(c) 0
(d) *J* + *K*
(e) $\hbar^2 / 2\mu R^2$ where μ is the reduced mass and *R* is the bond length
(f) $\hbar^2 / I$ where *I* is the moment of inertia
(g) (e) and (f)
(h) None of the above

12. What are the diffuse interstellar bands?

(a) Groups of widely separated wandering alien musicians
(b) Absorption or emission peaks in the otherwise uniform cosmic spectrum
(c) Gas clouds of CO
(d) The stripes on Schrödinger's cat
(e) Nebulae connecting one star to another
(f) Regions of anomalous space-time
(g) Cosmic radio stations that are very difficult to tune in to
(h) None of the above

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13. For a spin-free hydrogenic wave function, which of the below relationships between quantum numbers is/are always true?

(a) $n = l > m_l$
(b) $n > l > m_l$
(c) $n > l + m_l$
(d) $n > l \geq m_l$
(e) $n = l + m_l$
(f) (b) and (c)
(g) (b) and (e)
(h) None of the above

14. What is the ground-state ionization potential for a one-electron atom having atomic number Z?

(a) Z^2 a.u.
(b) The negative of the energy of the electron in the 1s orbital
(c) $(1/2)Z^2$ a.u.
(d) $2Z^2$ a.u.
(e) 1 a.u.
(f) The energy required to infinitely separate the nucleus and electron
(g) (b), and (d)
(h) (b), (c), and (f)

15. Which of the following is not equal to 1.0 in atomic units?

(a) $\hbar$
(b) $4\pi\varepsilon_0$
(c) The charge of the electron
(d) The mass of the electron
(e) 0.529 Å
(f) The speed of light
(g) Twice the ionization potential of the ground-state H atom
(h) None of the above

16. Which of the below statements about electron spin is/are true?

(a) Spin is a necessary property if relativity is included in the electronic Schrödinger equation
(b) Spin couples with orbital angular momentum according to $\mathbf{J} = \mathbf{L} + \mathbf{S}$
(c) For a single electron, the only eigenvalues of S_z are $\pm(1/2)\hbar$
(d) Stern and Gerlach discovered electron spin by studying the magnetic moments of Ag atoms
(e) Spin-orbit coupling is proportional to the 4th power of the atomic number
(f) (a) and (c)
(g) (a), (c), and (d)
(h) All of the above

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17. An electron of spin β is in a 4f orbital. Which of the below sets of quantum numbers (n, l, m_l, m_s) might describe such an electron?

(a) (4, 4, 4, 4)
(b) (4, 3, 2, 1/2)
(c) (4, 3, 0, –1/2)
(d) (4, 3, 0, 7/2)
(e) (4, 4, 3, –1/2)
(f) (c) and (e)
(g) (b), (c), (d) and (e)
(h) None of the above

18. Which of the following statements is/are true for a one-electron atom placed in a uniform magnetic field in the z direction?

(a) Given a strong enough magnetic field, a $3^2P_{3/2}$ state can be lower in energy than a $3^2P_{1/2}$ state
(b) The magnetic field lifts the degeneracy of levels otherwise differing only in m_j
(c) The phenomenon in answer (b) is called the Zeeman effect
(d) New spectroscopic transitions will become available according to the selection rule $\Delta m_j = 0$ or ± 1
(e) The proper Schrödinger equation includes the magnetic field strength
(f) (b), (c), and (d)
(g) (b), (c), (d), and (e)
(h) All of the above

19. The Landé g factor is $g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$. What g factors are possible for an α electron in a 3p orbital?

(a) 1
(b) 2
(c) 5/3
(d) 2 and 5/2
(e) 2/3 and 4/3
(f) It depends on the magnetic field strength
(g) Insufficient information is supplied in order to answer the question
(h) An infinite number of g factors

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20. Which of the following wave functions has the greatest degeneracy?

(a) Particle in a box, level $n = 8$

(b) Quantum mechanical harmonic oscillator, level $n = 25$

(c) Rigid rotator, $l = 5$

(d) Spin-free hydrogenic wave function, $n = 6$, $l = 1$

(e) Spin-free hydrogenic wave function, $n = 3$

(f) Relativistic free electron at rest

(g) All of the above are singly degenerate

(h) (deliberately left blank)

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Some Potentially Useful Mathematical Formulae

Trigonometric Relations

$$\sin\alpha\sin\beta = \frac{1}{2}\left[\cos(\alpha-\beta)-\cos(\alpha+\beta)\right]$$

$$\cos\alpha\cos\beta = \frac{1}{2}\left[\cos(\alpha-\beta)+\cos(\alpha+\beta)\right]$$

$$\sin\alpha\cos\beta = \frac{1}{2}\left[\sin(\alpha-\beta)+\sin(\alpha+\beta)\right]$$

$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \sin\beta\cos\alpha$$

$$\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$

$$\frac{d}{dx}\sin x = \cos x$$

$$\frac{d}{dx}\cos x = -\sin x$$

Some Operators

$x \equiv$ multiply by x

$\mathbf{r} \equiv$ multiply by $\mathbf{r}$

$$p_x \equiv -i\hbar\frac{d}{dx}$$

$$H = T + V$$

$$\boldsymbol{\mu} \equiv e\mathbf{r}$$

$$\mathbf{L} \equiv \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ -i\hbar\frac{\partial}{\partial x} & -i\hbar\frac{\partial}{\partial y} & -i\hbar\frac{\partial}{\partial z} \end{vmatrix}$$

$L_+ = L_x + iL_y$ and $L_- = L_x - iL_y$

Integrals

$$\int_0^L \sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx = \frac{L}{2}\delta_{mn}$$

$$\int x\cos(ax)dx = \frac{x}{a}\sin ax + \frac{\cos ax}{a^2}$$

$$\int x^2\cos(ax)dx = \frac{2x\cos ax}{a^2} + \frac{a^2x^2-2}{a^3}\sin ax$$

Complex Relations

$$\sqrt{-1} = i = -\frac{1}{i}$$

$$e^{i\theta} = \cos\theta + i\sin\theta$$

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