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Chemistry 3502/4502

Final Exam
May 10, 2006

1) For Part I of the exam, fill in the blank on each question with the correct answer, by letter, from the list provided on the last page of the exam. There is *one* correct answer to every question. There is no partial credit. No answer will be used more than once. There *are* answers that are *not* used, however.

2) Part II is multiple choice. Circle the correct answer. There is *one* correct answer to every problem. There is no partial credit.

3) On the various parts of the short-answer problems, which constitute Part III of the exam, show your work in full. Partial credit will be awarded in Part III.

4) Atomic numbers are: H, 1; He, 2; Li, 3; O, 8.

5) There is no penalty for guessing in Parts I and II.

6) Please write your name at the bottom of each page. ID numbers are *not* required

7) 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

Part I (50 points)

For the following 10 problems, answer by letter from the list provided at the back of the exam. You may tear the list off the exam if you like.

1. A quantum mechanical phenomenon that permits particles to penetrate finite potential barriers over which the particles otherwise do not have sufficient energy to pass _______

2. For a molecule that is not subject to an external potential, the total potential energy is equal to the negative of twice the kinetic energy. The proof of this statement is known as _______

3. The singlet-triplet splitting in a helium atom with one electon in the 1s orbital and the other in the 2s orbital _______

4. We may not know more than one cartesian component of the angular momentum because the component operators L_x, L_y, and L_z fail to commute. The proof that one cannot in general measure the expectation values of two non-commuting operators to perfect accuracy is known as _______

5. The ionization potential of a molecule is well approximated by the negative of the Hartree-Fock energy of the highest occupied molecular orbital. This is a consequence of _______

6. A wave function for which $\langle S^2 \rangle = 2$ _______

For the remaining 4 problems, identify an eigenfunction of *H* corresponding to

7. A harmonic oscillator (reduced mass and force constant of 1 a.u.) _______

8. A particle in a box (mass and box length of 1 a.u.) _______

9. A rigid rotator _______

10. Li^{2+} _______

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Part II (50 points)

11. Which one of the below quantum mechanical systems has a ground-state energy of zero?

(a) The one-electron atom
(b) The particle in a box
(c) The rigid rotator
(d) The harmonic oscillator

12. What does 2-PPE stand for?

(a) 2-particle positron emission
(b) 2-point polynomial equation
(c) 2-photon photoelectron spectroscopy
(d) twice polymerized polyethylene

13. Which of the below statements about computed molecular vibrational frequencies is true?

(a) There are in general $3N$ of them where N is the number of atoms
(b) They may be used to verify the nature of stationary points (as minima, transition-state structures, etc.)
(c) At the HF level, they are systematically about 50% too large in magnitude compared to measured infrared spectra
(d) They may be used to compute the zero-point vibrational energy as $ZPVE = \sum_{i}^{\text{normal modes}} h\nu_i$ where h is Planck's constant and ν is a frequency

14. For restricted Hartree-Fock theory, it is always the case that $\langle \Psi_{\mathrm{HF}} | H | \Psi_a^r \rangle = 0$ where H is the Hamiltonian and Ψ_a^r is any wave function generated from the ground-state wave function Ψ_{HF} by exciting one electron from occupied orbital a to virtual orbital r. This result is known as

(a) Brillouin's theorem
(b) Koopmans' theorem
(c) Limited configuration interaction
(d) The Hartree-Fock limit

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

(a) $(1/2)Z^2$ a.u.

(b) The negative of the energy of the electron in the 1s orbital

(c) The energy required to infinitely separate the nucleus and electron

(d) all of the above

16. Which of the below statements about correlated levels of electronic structure theory is *false*?

(a) Full CI with an infinite basis set is equivalent to an exact solution of the Schrödinger equation

(b) MP2 scales less favorably with respect to basis set size than CISD

(c) MCSCF theory optimizes the orbitals for wave functions expressed as more than a single Slater determinant

(d) CISD is variational

17. If Φ is a guess wave function, H is the Hamiltonian, and E_0 is the ground-state energy, which of the following is *always* true as a consequence of the variational principle?

(a) $\int \Phi^* H \Phi d\mathbf{r} \geq E_0$ if Φ is normalized

(b) $\langle \Phi | H | \Phi \rangle = E_0$

(c) $\dfrac{\int \Phi^* H \Phi d\mathbf{r}}{\int \Phi^* \Phi d\mathbf{r}} \leq E_0$

(d) The expectation value of H over Φ will be less than E_0

18. Which of the below functions is an eigenfunctions of the parity operator Π with eigenvalue –1?

(a) $\sin x$

(b) x^2

(c) e^{ix}

(d) $\cos x$

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19. Order the following wave functions from smallest to largest degeneracy:

V: Spin-free hydrogenic wave function, $n = 2$
W: Particle in a box, level $n = 4$
X: Rigid rotator, $l = 2$
Y: Relativistic free electron at rest
Z: Spin-free hydrogenic wave function, $n = 6$, $l = 1$

(a) $Y < Z < W < X < V$
(b) $W < Y < Z < V < X$
(c) $X < Y < Z < W < V$
(d) $Z < X < Y < V < W$

20. Which of the following statements about the HF/STO-3G wave function for water at its minimum energy geometry is false?

(a) There are six occupied orbitals
(b) The two lone pairs have different molecular orbital energies
(c) The dipole moment is non-zero
(d) The Mulliken charge on the oxygen atom is negative

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Part III (50 points)

The normalized 1s wave function for a one-electon atom in atomic units is

$$\Psi_{100}(r,\theta,\phi) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Zr}$$

where Z is the atomic number.

a) The expectation value of what operator would correspond to the average value, in a.u., that you would obtain after a very, very large number of measurements of the distance of the 1s electron from the nucleus in the hydrogen atom?

b) Would the value for the same measurement be larger or smaller for He^+? Explain your answer.

c) Now, prove that the average distance of the 1s electron from the proton in the hydrogen atom is 1.5 a.u. You may find the following integral useful: $\int_0^\infty r^n e^{-2r} dr = \frac{n!}{2^{n+1}}$. You may also find it useful to recall that the spherical polar volume element is $r^2 dr \sin\theta d\theta d\phi$.

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d) Instead of using the exact Slater 1s function, consider if we were to use a single normalized Gaussian function of the form $\Phi_{100}(r,\theta,\phi;\alpha)=\left(\frac{2\alpha}{\pi}\right)^{3/4}e^{-\alpha r^2}$. If we want to have $< \Phi_{100} \mid r \mid \Phi_{100} > = 3/2$ (the exact result), prove that α is equal to $(32/9\pi)$. You may find the following integral useful: $\int_0^\infty r^3 e^{-ar^2}dx = \frac{1}{a^2}$

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e) When we use $(32/9\pi)$ for α in the 1s gaussian, will $< \Phi_{100} \mid H \mid \Phi_{100} >$ be less than, equal to, or greater than $< \Psi_{100} \mid H \mid \Psi_{100} >$ where Ψ_{100} is the exact 1s function defined at the beginning of this problem? Explain your reasoning.

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A: Brillouin's theorem

B: $2\iint 1s(1)1s(1)\frac{1}{r_{12}}2s(2)2s(2)d\mathbf{r}(1)d\mathbf{r}(2)$

C: Ballistic momentum

D: Koopmans' theorem

E: $\Psi(\theta,\phi)=\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{-2i\phi}$

F: $\Psi(x)=\sqrt{2}\sin(4\pi x)$

G: The virial theorem

H: $\Psi(1,2)=\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$

I: $2\iint 1s(1)2s(1)\frac{1}{r_{12}}1s(2)2s(2)d\mathbf{r}(1)d\mathbf{r}(2)$

J: $\Psi(x)=\tan x$

K: $\Psi(r,\theta,\phi)=\frac{3^{5/2}}{8\sqrt{\pi}}r\sin\theta e^{-i\theta}e^{-3r/2}$

L: Tunneling

M: $\Psi(1,2)=\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix}$

N: Wave-particle duality

O: $\Psi(x)=\cos(2\pi x)$

P: The Heisenberg uncertainty principle

Q: The Born-Oppenheimer approximation

R: $\Psi(x)=\left(\frac{1}{4\pi}\right)^{1/4}2xe^{-x^2/2}$

S: Schrödinger's cat

T: $\Psi(x)=1+x+\frac{1}{2!}x^2+\frac{1}{3!}x^3+\cdots$

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