# Chemistry 3502/4502

# Final Exam Part I

# May 14, 2005

1.      For which of the below systems is *<H>* = *<T>* where *H* is the Hamiltonian operator and *T* is the kinetic-energy operator?

(a)     The free particle                    (e)     The one-electron atom
(b)     The particle in a box               (f)     (a) and (d)
(c)     The rigid rotator                     (g)     (a), (b), and (c)
(d)     The harmonic oscillator          (h)     All of the above

2.      Which of the below statements about computed molecular vibrational frequencies is/are true?

(a)     They may be used to verify the nature of stationary points (as minima, transition-state structures, etc.)

(e)     At the HF level, they are systematically about 10% too large in magnitude compared to measured infrared spectra

(b)     The vibrational partition function may be computed from them

(f)     (a) and (d)

(c)     There are in general 3*N*–6 of them where *N* is the number of atoms

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

(d)     They may be used to compute the zero-point vibrational energy as

$$ZPVE = \sum_{i}^{\substack{\text{normal} \\ \text{modes}}} \frac{1}{2}h\nu_i \quad \text{where } h \text{ is}$$

Planck's constant and $\nu$ is a frequency

(h)     All of the above

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3. Given a particle of mass $m$ in a box of length $L$ having the wave function $\Psi(x) = \sqrt{\dfrac{2}{L}}\sin\left(\dfrac{n\pi x}{L}\right)$, what is the energy of the level corresponding to n = 2?

(a) Since this wave function is not an eigenfunction of the Hamiltonian the question cannot be answered

(e) $\dfrac{16\pi^2\hbar^2}{L^2}$

(b) 4 times the energy of the ground state

(f) (c) and (d)

(c) $< \Psi \mid p_x^2 \mid \Psi >$

(g) (b) and (e)

(d) $8\hbar^2/mL$

(h) None of the above


4. For the diatomic molecule HeH$^+$, where He has atomic mass 4 and H has atomic mass 1, what is the reduced mass?

(a) 1 / 5

(e) 5 / 4

(b) 1 / 4

(f) It depends on the angular momentum

(c) 4 / 5

(g) Cannot be determined from information given

(d) 1

(h) None of the above


5. Which of the following statements is/are *true* for the quantum mechanical harmonic oscillator?

(a) The ground state energy is equal to the energy at the bottom of the potential

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

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

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

(c) As the force constant goes to zero, the entropy goes to zero

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

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

(h) All of the above

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

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

(b) Rigid rotator, $l = 4$

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

(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) (b) and (e) have the same degeneracy which is greater than all of the others

(h) (a) through (f) are all singly degenerate

7. Which of the below statements is false?

(a) Gaussian orbitals fall off in amplitude more rapidly with distance than do hydrogenic orbitals

(b) Tunneling is a quantum mechanical phenomenon that permits particles to penetrate finite potential barriers over which the particles do not have sufficient energy otherwise to pass; tunneling becomes more probable as the particle becomes lighter

(c) When two operators commute, the Heisenberg uncertainty principle says that we may not simultaneously measure their respective expectation values to infinite accuracy

(d) For one-electron atoms, hydrogenic orbital eigenfunctions of the Hamiltonian satisfy the virial theorem $<V> = -2<T>$

(e) The variational principle permits the expectation value of the energy of a variational wave function to be judged as: the lower in energy it is, the more accurate it is.

(f) The concept of the potential energy surface derives from the Born-Oppenheimer approximation, which decouples nuclear and electronic motion

(g) The particle in a box and the quantum mechanical harmonic oscillator have zero-point energy, while the free particle and the rigid rotator do not.

(h) If $\left\langle \Psi_i | \mu | \Psi_f \right\rangle = 0$ where $\Psi_i$ is an initial state, $\Psi_f$ is a final state, and $\mu$ is the dipole moment operator, then absorption of radiation cannot induce a transition from $\Psi_i$ to $\Psi_f$

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) None of the above

9. Which of the following statements about molecular hydrogen ($H_2$) is/are true?

(a) Bonding occurs because electrons in the σ bond repel each other less than if they were in their respective unmixed 1s orbitals

(b) Given a minimal basis set, the ground-state CID wave function is composed of eight determinants

(c) There are ionic terms in the RHF ground-state wave function

(d) The RHF ground-state wave function has two occupied orbitals

(e) An analytic solution of the Schrödinger equation is available for the molecule

(f) (b) and (c)

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

(h) All of the above

10. Which of the below statements about correlated levels of electronic structure theory is/are *true*?

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

(b) MP4 is size consistent

(c) CISD is variational

(d) MP2 scales more favorably with respect to basis set size than CISD

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

(f) (a) and (d)

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

(h) All of the above

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# Final Exam Part II Key

### TWO ELECTRONS IN TWO ORBITALS

1) Provide the name of an organic functional group whose reactivity is well explained by a 2-electron-in-2-orbital model.

    Nitrene (carbene is also acceptable)

2) What are the allowed eigenvalues of $S^2$ for a 2-electron-in-2-orbital wave function?

    0 and 2

3) Consider the 1s and 2s orbitals of the He ($Z = 2$) atom, which, with 2 electrons, is an uncharged 2-electron-in-2-orbital system:

  a) How many different electronic states may this system have?

    6 (3 degenerate triplets and 3 unique singlets)

  b) In shorthand notation, list all of these states from lowest to highest in energy.

$$^1\left|1s^2\right\rangle < {}^3\left|1\bar{s}2\bar{s}\right\rangle = {}^3\left|1s2\bar{s}\right\rangle = {}^3\left|1s2s\right\rangle < {}^1\left|1s2\bar{s}\right\rangle < {}^1\left|2s^2\right\rangle$$

  c) Write any two possible determinants for this system in full algebraic detail (i.e., not just a shorthand representation).

    Some acceptable answers are below (others are possible)

$$\frac{1}{\sqrt{2}}\left\{1s(1)1s(2)\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]\right\} \qquad \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$$

$$\frac{1}{2}\left\{\left[1s(1)2s(2) + 1s(2)2s(1)\right]\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]\right\} \qquad \frac{1}{\sqrt{2}}\left\{\left[1s(1)2s(2) - 1s(2)2s(1)\right]\left[\beta(1)\beta(2)\right]\right\}$$

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

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d) What is the full Hamiltonian for He (in a.u.)?

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

e) In terms of one-electron orbital energies $\varepsilon_{1s}$ and $\varepsilon_{2s}$ and Coulomb and exchange integrals $J_{ij}$ and $K_{ij}$ (where $i$ and $j$ may each be either 1s or 2s), what is the energy difference between the states $^1| 1s^2 >$ and $^1| 2s^2 >$?

$$2(\varepsilon_{2s} - \varepsilon_{1s}) + (J_{2s2s} - J_{1s1s})$$

f) Which is larger, $J_{1s1s}$ or $J_{2s2s}$? Explain why.

$J_{1s1s}$ is larger; since the 1s orbital is more compact than the 2s orbital, the two electrons in it repel each other more.

g) What is the configuration interaction (CI) matrix element $H_{mn}$ between the states $^1| 1s^2 >$ and $^1| 2s^2 >$?

$K_{1s2s}$

h) List any two states (shorthand notation is fine) whose corresponding CI matrix element will be zero *because of Brillouin's theorem.*

$$^1\left|1s^2\right\rangle \text{ and } {}^1\left|1s2\bar{s}\right\rangle$$

i) List any two states (shorthand notation is fine) whose corresponding CI matrix element will be zero for a reason *other* than Brillouin's theorem. Explain your choice.

$^1\left|1s^2\right\rangle$ and $^3\left|1s2\bar{s}\right\rangle$ or indeed any singlet state with any triplet state. Since the He Hamiltonian contains no spin operators, every integral in such a matrix element will involve the overlap of an alpha spin with a beta spin and will therefore be made to vanish.

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