

Chemistry 3502/4502

Exam III

All Hallows Eve/Samhain, 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

NAME:

1. Which of the following terms is/are *not* quantitatively important in the typical molecular Hamiltonian?
- | | |
|---|---|
| (a) Kinetic energy of the electrons | (e) Coulomb repulsion of the nuclei |
| (b) Coulomb attraction between the nuclei and the electrons | (f) Gravitational attraction between the nuclei |
| (c) Coulomb repulsion of the electrons | (g) (a) and (d) |
| (d) Kinetic energy of the nuclei | (h) (b) and (f) |
2. Which of the following statements about a many-particle Hamiltonian and its eigenfunctions is/are true?
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|--|--|
| (a) There may be infinitely many eigenfunctions | (e) Exact eigenfunctions are unknown for cases with 3 or more moving particles |
| (b) The total energy does not depend on the choice of coordinate system (e.g., cartesian, spherical polar, etc.) | (f) (a) and (d) |
| (c) The set of all eigenfunctions forms a complete basis for all functions of the particle coordinates | (g) (a), (c), (d), and (e) |
| (d) Non-degenerate eigenfunctions will be orthonormal | (h) All of the above |
3. If Φ is a guess wave function, H is the Hamiltonian, and E_0 is the ground-state energy, which of the following is/are *always* true as a consequence of the variational principle?
- | | |
|--|--|
| (a) $\int \Phi^* H \Phi d\mathbf{r} \geq E_0$ | (e) $\frac{\int \Phi^* H \Phi d\mathbf{r}}{\int \Phi^* \Phi d\mathbf{r}} \geq E_0$ |
| (b) $\langle \Phi H \Phi \rangle \geq E_0$ if Φ is normalized | (f) (a) and (b) |
| (c) The expectation value of H over Φ will be less than E_0 | (g) (b) and (e) |
| (d) The expectation value of H over Φ will be greater than $E_0 + 1/2$ a.u. | (h) (a), (b), and (e) |

NAME:

4. What is the Born-Oppenheimer approximation?
- | | |
|---|--|
| (a) Assuming nuclear and electronic motions to be decoupled so that electronic energies can be computed for fixed nuclear positions | (e) Assuming identical quantum mechanical particles to be indistinguishable from one another |
| (b) Ignoring spin-orbit coupling in the Hamiltonian | (f) Assuming that spin can be included in an ad hoc fashion |
| (c) Leaving zero-point vibrational energy out of the potential energy surface | (g) Mistaking Max Born for Robert Oppenheimer |
| (d) Assuming electrons to be lighter than nuclei | (h) All of the above |
5. Which of the following statements about the secular determinant is/are true?
- | | |
|--|---|
| (a) The secular determinant is $N \times N$ where N is the number of basis functions | (e) In each element, $0 \leq S_{ij} \leq 1$ |
| (b) Each element of the secular determinant involves a resonance integral, an overlap integral, and a molecular orbital energy | (f) In the absence of degeneracy, there will be N values of E_j each one of which will have associated with it basis set coefficients a_{ij} for an associated molecular orbital. |
| (c) It must be set equal to one in order to find molecular orbital coefficients | (g) (a), (b), (e), and (f) |
| (d) In each element, $H_{ij} > S_{ij}$ | (h) All of the above |
6. If the approximate energy of a wave function is given by $\langle H \rangle = a^4 - 4a^3 - 8a^2 + 4$ where a is a variational parameter, what value of a will minimize the energy?
- | | |
|--------|---|
| (a) 4 | (e) -124 |
| (b) 5 | (f) 1 |
| (c) -1 | (g) The function has no finite minima |
| (d) 0 | (h) There are infinitely many values of a |

NAME:

7. For a particle in a box of length 1, which of the following trial wave functions would be likely to yield the best approximation to the exact ground state wave function $\Psi_1(x) = \sqrt{2} \sin(\pi x)$ $0 \leq x \leq 1$ (assume all functions will be normalized)

- (a) $\xi(x) = x(1-x)$ (e) $\xi(x;a,b,c) = x^a(1-x^b)(1-x^c)$, a , b , and c variational parameters
- (b) $\xi(x;a) = x^a(1-x)$, a a variational parameter (f) $\xi(x;a,b) = \sin^a(bx)$, a and b variational parameters
- (c) $\xi(x;a) = x^a(1-x^2)$, a a variational parameter (g) $\xi(x;a,b,c) = \cos^a(bx^c)$, a , b , and c variational parameters
- (d) $\xi(x;a,b) = x^a(1-x^b)$, a and b variational parameters (h) None of the above

8. In atomic units, what is the Hamiltonian for the He atom?

- (a) $H = \frac{1}{2} \nabla_1^2 + \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$ (e) $H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}$
- (b) $H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$ (f) $H = T$
- (c) $H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} - \frac{1}{r_{12}}$ (g) There are infinitely many Hamiltonians for He
- (d) $H = -\frac{1}{2} L_1^2 - \frac{1}{2} L_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$ (h) None of the above

9. If we take a two-electron wave function for the He atom as $\Psi(1,2) = \psi(1)\psi(2)$ where each one-electron wave function ψ is given by $\psi_{100}(r, \theta, \phi) = \frac{\eta^{3/2}}{\sqrt{\pi}} e^{-\eta r}$ and η is a variational parameter, which value for η of those listed below would provide the lowest expectation value for the energy?

- (a) 0 (e) 2
- (b) 1.69 (f) 2.5
- (c) 1 (g) π
- (d) 0.5 (h) It depends on the He isotope

NAME:

10. What is the expectation value in a.u. of the momentum operator p_x for the harmonic oscillator wave function $\Psi_0(x) = \left(\frac{1}{\pi}\right)^{1/4} e^{-x^2/2}$?
- (a) $1/2$ (e) 2π
 (b) $i\hbar$ (f) It depends on the He isotope
 (c) η (g) It cannot be determined from the information provided
 (d) 0 (h) None of the above
11. What is $\langle -1/r \rangle$ in a.u. for the one-electron wave function $\psi_{1s}(r, \theta, \phi; \alpha) = e^{-\alpha r^2}$?
- (a) 0 (e) $\pi / 2\alpha$
 (b) π / α (f) α
 (c) 1 (g) 2α
 (d) $1/2$ (h) None of the above
12. Given two gaussian functions **1** and **2** on the same nucleus defined as $\mathbf{1} = \left(\frac{2\alpha_1}{\pi}\right)^{3/4} e^{-\alpha_1 r^2}$ and $\mathbf{2} = \left(\frac{2\alpha_2}{\pi}\right)^{3/4} e^{-\alpha_2 r^2}$ with $\alpha_1 > \alpha_2$, which of the below statements is/are true?
- (a) $\langle \mathbf{1} | T | \mathbf{1} \rangle > \langle \mathbf{2} | T | \mathbf{2} \rangle$ (e) $S_{12} = \langle \mathbf{1} | \mathbf{2} \rangle$
 (b) $\left\langle \mathbf{1} \left| -\frac{1}{r} \right| \mathbf{1} \right\rangle < \left\langle \mathbf{2} \left| -\frac{1}{r} \right| \mathbf{2} \right\rangle$ (f) (a) and (b)
 (c) $|\mathbf{1}|^2 + |\mathbf{2}|^2 = 1$ (g) (a), (b), and (e)
 (d) **1** and **2** are complex valued (h) All of the above
13. Which of the below statements is/are false?
- (a) Gaussian orbitals fall off in amplitude more rapidly with distance than do hydrogenic orbitals (e) A hydrogenic orbital can be represented to arbitrary accuracy by a (possibly infinite) linear combination of gaussian orbitals
 (b) Gaussian s orbitals have a maximum at the nucleus that is not a cusp (f) Hydrogenic s orbitals have a cusp at the nucleus
 (c) Any optimized linear combination of gaussians satisfies the virial theorem (g) (b) and (e)
 (d) For one-electron atoms, hydrogenic orbitals satisfy the virial theorem (h) (a), (b), and (d)

NAME:

14. Which of the below statements is/are true?

- | | |
|--|--|
| (a) Fermions have half-integer spin | (e) $\Psi = a(1)b(2) - b(1)a(2)$ is a valid fermion wave function |
| (b) Fermion wave functions must be antisymmetric | (f) Boson wave functions do not vanish when two particles have identical one-particle wave functions |
| (c) Bosons have integer spin | (g) (a), (b), (c), and (e) |
| (d) Boson wave functions are symmetric | (h) All of the above |

15. Given $\alpha = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ and $\beta = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$ which of the below statements is/are true?

$S_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$ and $S_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$ and $S_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

- | | |
|---|-------------------------------|
| (a) $S_z\alpha = \frac{\hbar}{2}\alpha$ | (e) $S_x\alpha \neq S_y\beta$ |
| (b) $S_z\beta = -\frac{\hbar}{2}\beta$ | (f) (b) and (d) |
| (c) α and β are orthogonal | (g) (a) and (c) |
| (d) $[S_x, S_y] = i\hbar S_z$ | (h) All of the above |

16. Which of the below statements about a many-electron wave function Ψ composed of 3 α electrons and 4 β electrons is/are true?

- | | |
|---|--|
| (a) Ψ must be antisymmetric | (e) Ψ can be a quartet |
| (b) Ψ can be a singlet | (f) Ψ cannot be an eigenfunction of S^2 |
| (c) M_S for Ψ can be $\pm(1/2)\hbar$ | (g) (b) and (e) |
| (d) In the absence of a magnetic field, the energy of the system could remain unchanged by flipping one electron from β to α | (h) (a), (d), and (e) |

NAME:

17. Which of the below statements about the wave function $\Psi(1,2) = \begin{vmatrix} a(1)\alpha(1) & a(1)\beta(1) \\ a(2)\alpha(2) & a(2)\beta(2) \end{vmatrix}$ is/are false if a is normalized?

- | | |
|---|--|
| (a) Its normalization constant is $1/2$ | (e) $\langle S^2 \rangle = 0$ |
| (b) It is antisymmetric | (f) It is a closed-shell wave function |
| (c) It is a singlet | (g) (d) and (e) |
| (d) Its M_S value is zero | (h) (c), (d), and (e) |

18. For a normalized two-electron wave function Ψ , $\langle \Psi | S^2 | \Psi \rangle = 1$. Which of the below statements about Ψ is/are true?

- | | |
|---|----------------------|
| (a) The quantum number $S = 1$ | (e) $ \Psi ^2 = 2$ |
| (b) Ψ is a pure spin state | (f) (a) and (e) |
| (c) Ψ is an equal mixture of a singlet and a triplet state | (g) (c) and (d) |
| (d) Ψ cannot be antisymmetric | (h) All of the above |

19. A He atom has one electron in its 1s orbital and one electron in its 2s orbital. Which of the below statements about this system is/are false?

- | | |
|---|--|
| (a) The spin state may be either singlet or triplet | (e) The singlet-triplet splitting is $2K_{1s2s}$ |
| (b) The triplet state lies below the singlet state in energy | (f) (b) and (c) |
| (c) $K_{1s2s} = \langle 1s(1)2s(2) 1/r_{12} 1s(2)2s(1) \rangle$ | (g) (d) and (e) |
| (d) $J_{1s2s} = \langle 1s(1)2s(2) 1/r_{12} 1s(1)2s(2) \rangle$ | (h) None of the above |

20. A particle in a box of length 1 is subject to a perturbing potential of $(x - 0.5)$. What is the first-order perturbation-theory correction to the ground-state energy given an unperturbed ground-state wave function of $\Psi = \sqrt{2} \sin(\pi x)$?

- | | |
|---|-----------------|
| (a) 2 | (e) 1 |
| (b) $\langle \Psi (x - 0.5) \Psi \rangle$ | (f) 0 |
| (c) $\pi/2$ | (g) (a) and (b) |
| (d) $1/2$ | (h) (b) and (c) |

NAME:

Some Potentially Useful Mathematical Formulae

Trigonometric Relations

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

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

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

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

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

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

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

Integrals

$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a} \right)^{1/2}$$

$$\int_0^{\infty} x e^{-ax^2} dx = \frac{1}{2a}$$

$$\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4a} \left(\frac{\pi}{a} \right)^{1/2}$$

Some Operators

$x \equiv$ multiply by x

$$T = -\frac{1}{2r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - L^2 \right) \text{ [spherical polars]}$$

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

$$H = T + V$$

Other

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - cb$$

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} \begin{bmatrix} e \\ f \end{bmatrix} = \begin{bmatrix} ae + bf \\ ce + df \end{bmatrix}$$

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} \begin{bmatrix} e & f \\ g & h \end{bmatrix} = \begin{bmatrix} ae + bg & af + bh \\ ce + dg & cf + dh \end{bmatrix}$$

volume element in spherical polar coordinates: $r^2 \sin \theta dr d\theta d\phi$

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

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

NAME: