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Chemistry 3502/4502

Exam III

March 28, 2005

1) Circle the correct answer on multiple-choice problems.

2) There is *one* correct answer to every multiple-choice problem. There is no partial credit. On the short-answer problems, show your work in full.

3) A table of useful integrals and other formulae is provided at the end of the exam. Calculators are not allowed.

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

5) There are 10 multiple-choice problems. Each is worth 6 points. The short-answer problems are worth 20 points each.

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. If you want 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. If Φ is a guess wave function that may or may not be normalized, 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) $\dfrac{\int \Phi^* H \Phi d\mathbf{r}}{\int \Phi^* \Phi d\mathbf{r}} \geq E_0$

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

(c) $H\Phi = E\Phi$

(d) all of the above

2. What is the Born-Oppenheimer approximation?

(a) Ignoring spin-orbit coupling in the Hamiltonian

(b) Assuming identical quantum mechanical particles to be indistinguishable from one another

(c) Assuming that spin can be included in an ad hoc fashion

(d) Assuming nuclear and electronic motions to be decoupled so that electronic energies can be computed for fixed nuclear positions

3. 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 $\Psi_1(x) = \sqrt{2}\sin(\pi x) \quad 0 \leq x \leq 1$ (assume all functions will be normalized)

(a) $\xi(x) = x(1-x)$

(b) $\xi(x;a,b) = x^a\left(1-x^b\right)$, a and b variational parameters

(c) $\xi(x;a,b,c) = \cos^a\left(bx^c\right)$, a, b, and c variational parameters

(d) $\xi(x;a) = x^a(1-x)$, a a variational parameter

4. In atomic units, what is the Hamiltonian for the Be^{2+} ion (atomic number 4)?

(a) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{4}{r_{12}}$

(b) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2}\nabla_3^2 - \frac{4}{r_1} - \frac{4}{r_2} - \frac{4}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$

(c) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{4}{r_1} - \frac{4}{r_2} + \frac{1}{r_{12}}$

(d) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{r_{12}}$

NAME: ____

5. 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) $\langle \mathbf{1}|T|\mathbf{1}\rangle < \langle \mathbf{2}|T|\mathbf{2}\rangle$

(b) $\left\langle \mathbf{1}\left|-\frac{1}{r}\right|\mathbf{1}\right\rangle > \left\langle \mathbf{2}\left|-\frac{1}{r}\right|\mathbf{2}\right\rangle$

(c) $< |\mathbf{1}|^2 > / < |\mathbf{2}|^2 > = 1$

(d) all of the above

6. Which of the below statements is/are *false*?

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

(b) A hydrogenic orbital can be represented to arbitrary accuracy by a (possibly infinite) linear combination of gaussian orbitals

(c) Gaussian s orbitals have a maximum at the nucleus that is a cusp

(d) A hydrogenic wave function optimized as a linear combination of a finite number of guassians may not satisfy the virial theorem

7. Which of the below statements is/are *true*?

(a) Fermions have integer spin

(b) Fermion wave functions must be symmetric

(c) $\Psi = a(1)b(2) - b(1)a(2)$ is a valid fermion wave function

(d) All of the above

NAME: ____

8. Given

$$\alpha = \begin{bmatrix}1\\0\end{bmatrix} \quad \text{and} \quad \beta = \begin{bmatrix}0\\1\end{bmatrix}$$

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

which of the below statements is/are *false*?

(a) $S_z\alpha = \frac{\hbar}{2}\alpha$

(b) $S_z\beta = \frac{\hbar}{2}\beta$

(c) $S_x\alpha = -iS_y\alpha$

(d) (b) and (c)

9. 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 the spatial function a is normalized?

(a) Its normalization constant is 2

(b) It is antisymmetric to particle swapping

(c) $< \Psi \mid S^2 \mid \Psi > = 0$

(d) It is a closed-shell singlet wave function

10. A ground-state Be atom (atomic number 4) has one electron removed from its 1s orbital and another from its 2s orbital. Which of the below statements about the resulting Be^{2+} configuration is/are false?

(a) $K_{1s2s} =$ $<1s(1)2s(1) \mid 1/r_{12} \mid 1s(2)2s(2)>$

(b) The singlet state lies below the triplet state in energy

(c) The singlet-triplet splitting is $2K_{1s2s}$

(d) $J_{1s2s} =$ $<1s(1)1s(1) \mid 1/r_{12} \mid 2s(2)2s(2)>$

NAME: ____

Perturbation Theory and the Harmonic Oscillator

Recall that the QMHO is subject to an external potential energy of $(1/2)kx^2$ where k is the force constant. In atomic units, the first two QMHO wave functions for an oscillator having a reduced mass of 1 and a force constant of 1 are

$$\Psi_0(x) = \left(\frac{1}{\pi}\right)^{1/4} e^{-x^2/2} \qquad \Psi_1(x) = \left(\frac{4}{\pi}\right)^{1/4} xe^{-x^2/2}$$

Prove that if the quadratic potential is perturbed by a small cubic term, εx^3, where ε is a constant, the energy correction to first order in perturbation theory is zero for both of these QMHO wave functions. For Ψ_0, what is the first-order correction if the perturbing potential is quartic, i.e., εx^4?

NAME: ____

NAME: ____

Real vs. Complex Wave Functions

Prove that $< p_x > = 0$ for any well behaved *real* (i.e., not complex) wave function $\Psi(x)$ over the interval $-\infty \le x \le \infty$. (Hint: Use integration by parts to move your integral along and then use the properties of well behaved wave functions to finish your proof.)

NAME: ____

NAME: ____

Some Potentially Useful Mathematical Formulae

Integrals

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

$$\int_a^b u\,dv = uv\Big|_a^b - \int_a^b v\,du$$

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

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

$$\int_0^\infty x^3e^{-ax^2}dx = \frac{1}{a^2}$$

$$\int_0^\infty x^n e^{-ax^2}dx = \begin{cases} \dfrac{(n-1)!}{2a^{(n+1)/2}}, & n \text{ odd} \\ \dfrac{1\bullet 3\bullet 5\bullet\bullet\bullet(n-1)}{2(2a)^{n/2}}\left(\dfrac{\pi}{a}\right)^{1/2}, & n \text{ even} \end{cases}$$

$$\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = 4\pi$$

Other

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

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

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

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

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

Some Operators

$x \equiv$ multiply by x

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

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

$$H = T + V$$

NAME: ____