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Chemistry 3502/4502

Exam IV

November 24, 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) Atomic numbers are: H, 1; C, 6; O, 8; F, 9.**
- 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. Which of the following statements is/are *false* about a Hamiltonian that is separable into a sum of one-electron operators?

- | | |
|---|--|
| (a) Its eigenfunctions can be normalized | (e) Its eigenvalues can be determined from the eigenvalues of the one-electron operators |
| (b) Its eigenfunctions can be made to be antisymmetric | (f) Its eigenfunctions are formed from Hartree products of the one-electron eigenfunctions |
| (c) It can include electron-electron repulsion only in an average way | (g) (c) and (f) |
| (d) It cannot include the kinetic energy operator | (h) None of the above |

2. An operator $H = h_1 + h_2 + h_3$ where $h_1\psi_1 = 3\psi_1$, $h_2\psi_2 = 3\psi_2$, and $h_3\psi_3 = 2\psi_3$. If ψ_1 , ψ_2 , and ψ_3 are normalized, what is $\langle \psi_1\psi_2\psi_3 | H | \psi_1\psi_2\psi_3 \rangle$?

- | | |
|-----------|-----------------------|
| (a) -2 | (e) π |
| (b) 0 | (f) 8 |
| (c) 1 | (g) 18 |
| (d) 2 2/3 | (h) None of the above |

3. Which of the below is *not* the Coulomb integral J_{ab} between an electron in orbital a and another electron in orbital b ?

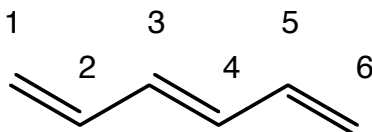
- | | |
|--|--|
| (a) $\iint a^*(1)b^*(2)\frac{1}{r_{12}}a(1)b(2)d\mathbf{r}_1d\mathbf{r}_2$ | (e) $\iint a^*(1)b^*(1)\frac{1}{r_{12}}a(2)b(2)d\mathbf{r}_1d\mathbf{r}_2$ |
| (b) $\iint \frac{1}{r_{12}} a(1) ^2 b(2) ^2d\mathbf{r}_1d\mathbf{r}_2$ | (f) $(aa bb)$ |
| (c) $\iint a^*(1)a(1)b^*(2)b(2)\frac{1}{r_{12}}d\mathbf{r}_1d\mathbf{r}_2$ | (g) $\iint a(1) ^2\frac{1}{r_{12}} b(2) ^2d\mathbf{r}_1d\mathbf{r}_2$ |
| (d) $\iint a^*(1)b(2)\frac{1}{r_{12}}a(1)b^*(2)d\mathbf{r}_1d\mathbf{r}_2$ | (h) None of the above |

4. When is the Coulomb integral J_{ab} equal to the exchange integral K_{ab} ?

- | | |
|---|---|
| (a) When a and b have the same angular momentum | (e) When a and b are infinitely separated |
| (b) When $a = b$ | (f) (b) and (e) |
| (c) When a and b are orthogonal | (g) (b), (d), and (e) |
| (d) When $S_{ab} = 1$ | (h) The two are never equal |

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For the next three questions, consider a Hückel theory calculation on planar neutral 1,3,5-hexatriene with carbon atoms numbered as indicated.



5. Which of the following statements is/are *not true* about Hückel theory in general?
- | | |
|--|---|
| (a) The Hückel theory many-electron wave function is the Hartree product of the molecular orbitals | (e) All resonance integrals in the secular determinant are replaced by either zero or empirically determined values |
| (b) Hückel theory is an iterative self-consistent field procedure | (f) The final MOs are expressed as a linear combination of AOs |
| (c) The basis set is one p orbital per carbon atom, with all p orbitals parallel | (g) (a) and (d) |
| (d) For any two basis functions $S_{ij} = \delta_{ij}$ | (h) (b) and (f) |
6. Which of the following statements is/are *not true* about a Hückel theory calculation for 1,3,5-hexatriene?
- | | |
|---|-----------------------|
| (a) There are four occupied MOs in the final wave function | (e) $H_{14} = S_{14}$ |
| (b) $H_{23} = H_{56}$ | (f) (a) and (c) |
| (c) $H_{11} = S_{11}$ | (g) (a) and (e) |
| (d) The terms in the secular determinant have dimension 6 x 6 | (h) (b) and (e) |
7. Which of the following statements is/are *true* about a Hückel theory calculation on 1,3,5-hexatriene?
- | | |
|---|---|
| (a) The only node in the lowest energy MO will be the plane of the molecule | (e) If there were no interaction between any of the 3 formal double bonds, the total energy would be $6\alpha + 6\beta$ |
| (b) No MO will use all 6 basis functions | (f) The secular determinant would not change if we connected atom 1 to atom 6 to make benzene |
| (c) MOs with more nodes will have lower kinetic energies | (g) (a) and (e) |
| (d) $H_{22} = \alpha / 2$ | (h) (c), (d), and (e) |

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8. What distinguishes the Hartree-Fock (HF) method from the Hartree method?
- | | |
|---|---|
| (a) HF wave functions are antisymmetric and Hartree wave functions are not | (e) Only the HF method uses basis functions |
| (b) Only the HF method requires exchange integrals | (f) Only the HF method requires a self-consistent-field iterative procedure |
| (c) Only the HF method forms molecular orbitals as linear combinations of atomic orbitals | (g) (a) and (b) |
| (d) Only the HF method accounts for the correlation between electron movements | (h) (b) and (f) |
9. How do gaussian orbital basis functions differ from Slater orbital basis functions?
- | | |
|--|---|
| (a) Gaussian orbitals cannot be normalized but Slaters can | (e) Only gaussian orbitals are exact solutions of the Schrödinger equation for one-electron atoms |
| (b) There is always an analytic solution to $(\mu\nu \lambda\sigma)$ when all basis functions are gaussians, but not necessarily when they are Slaters | (f) Gaussian p orbitals cannot be anywhere negative but Slater p orbitals can |
| (c) Only gaussians have a cusp at the nucleus | (g) (a) and (c) |
| (d) Gaussian orbitals have a slower radial decay than Slater orbitals | (h) (b) and (f) |
10. Consider the molecule HF (hydrogen fluoride). What is the minimum number of atomic-orbital basis functions required for a Hartree-Fock calculation on HF?
- | | |
|-------|--------|
| (a) 1 | (e) 5 |
| (b) 2 | (f) 6 |
| (c) 3 | (g) 7 |
| (d) 4 | (h) 10 |

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11. Which of the below statements about the density matrix \mathbf{P} in Hartree-Fock calculations is/are true?
- | | |
|--|--|
| (a) The matrix is $N \times N$ where N is the number of basis functions | (e) If \mathbf{P} is unchanged after a self-consistent-field step, the HF calculation is converged |
| (b) The matrix elements depend on the coefficients of only the occupied molecular orbitals | (f) (c) and (e) |
| (c) For all m, n , $P_{mn} = P_{nm}$ | (g) (a), (d), and (e) |
| (d) To start an HF calculation, one uses a guess to construct the density matrix | (h) All of the above |
12. Given two normalized basis functions μ and ν where $\mu \neq \nu$, which of the below statements is/are always true?
- | | |
|---|---------------------------------|
| (a) $\left\langle \mu \left -\frac{1}{2} \nabla^2 \right \mu \right\rangle > 0$ | (e) $-1 \leq S_{\mu\nu} \leq 1$ |
| (b) $\left\langle \mu \left -\frac{1}{2} \nabla^2 \right \mu \right\rangle > \left\langle \mu \left -\frac{1}{2} \nabla^2 \right \nu \right\rangle$ | (f) (a) and (c) |
| (c) $\left\langle \mu \left -\frac{1}{2} \nabla^2 \right \nu \right\rangle > 0$ | (g) (a), (b), and (e) |
| (d) $0 \leq S_{\mu\nu} \leq 1$ | (h) All of the above |
13. In a restricted Hartree-Fock calculation on methane (CH_4), how many occupied MOs will be used to construct the HF wave function?
- | | |
|-------|-------|
| (a) 1 | (e) 5 |
| (b) 2 | (f) 6 |
| (c) 3 | (g) 7 |
| (d) 4 | (h) 8 |
14. The Hartree-Fock wavefunction for a molecule of 4 atoms is to be computed using 12 basis functions. How many one-electron integrals need to be evaluated ignoring any symmetry from the molecule or the turnover rule?
- | | |
|---|---|
| (a) $(12^2) + (4 \times 12^2) + (12^4)$ | (e) $(12) + (4 \times 12)$ |
| (b) 2×12^2 | (f) $(12^2) + (4 \times 12^2) + (12^4) / 2$ |
| (c) $(12^2) + (4 \times 12^2)$ | (g) π |
| (d) 1 | (h) 4×12 |

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15. If each basis function in problem 14 is a contracted gaussian basis function formed from 5 primitive gaussian functions, by what factor will the total number of one-electron integrals over primitive functions exceed the number of one-electron integrals over contracted functions?

- | | |
|--------|--------|
| (a) 1 | (e) 25 |
| (b) 4 | (f) 36 |
| (c) 9 | (g) 49 |
| (d) 16 | (h) 64 |

16. Consider the water molecule with all atoms in the yz plane (just as in class). Which of the below integrals involving gaussian AO basis functions is/are equal to zero?

- | | |
|---|---------------------------------------|
| (a) $\left\langle 1s_O \left -\frac{1}{2} \nabla^2 \right 1s_{H_a} \right\rangle$ | (e) $\langle 2p_{x,O} 1s_O \rangle$ |
| (b) $\langle 2s_O 1s_O \rangle$ | (f) (a) and (e) |
| (c) $\langle 1s_{H_b} 1s_{H_a} \rangle$ | (g) (d) and (e) |
| (d) $\langle 2p_{x,O} 1s_{H_a} \rangle$ | (h) All of the above |

17. What is the name for *any* kind of surface defined by $|\Psi|^2 = C$ where C is a constant?

- | | |
|---------------------------|---------------------------|
| (a) van der Waals surface | (e) Lennard-Jones surface |
| (b) isopotential surface | (f) isoenergy surface |
| (c) isodensity surface | (g) isotired surface |
| (d) isometric surface | (h) reentrant surface |

18. Which of the below sets of Mulliken atomic partial charges is most reasonable from a Hartree-Fock calculation on the molecule HOF (hypofluoric acid)?

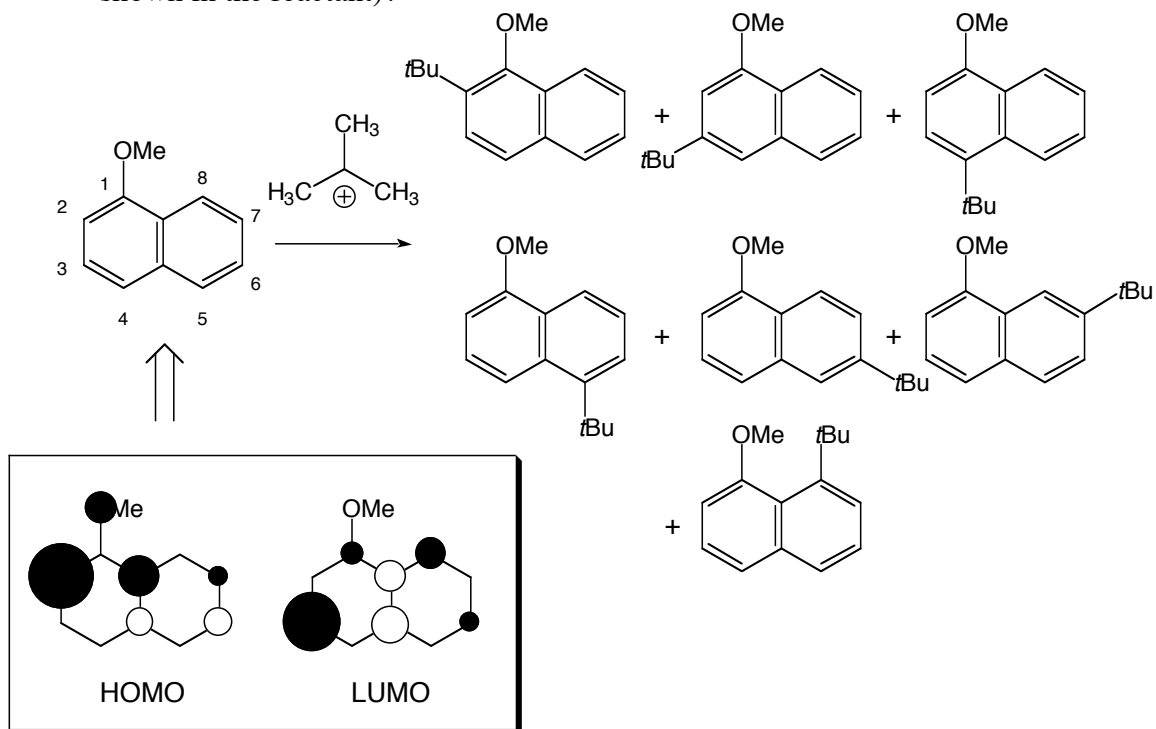
- | | |
|---|---|
| (a) $q_H = 0.7, q_O = -0.7, q_F = 0.0$ | (e) $q_H = 0.1, q_O = 0.6, q_F = -0.5$ |
| (b) $q_H = 0.3, q_O = -0.7, q_F = -1.7$ | (f) $q_H = 0.0, q_O = 0.0, q_F = 0.0$ |
| (c) $q_H = -0.7, q_O = 0.7, q_F = 1.0$ | (g) $q_H = 1.5, q_O = -1.0, q_F = -0.5$ |
| (d) $q_H = 0.8, q_O = -0.3, q_F = -0.5$ | (h) $q_H = 1.0, q_O = 1.0, q_F = 1.0$ |

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19. An HF/STO-3G calculation provides the following energies (a.u.) for the molecular orbitals of a molecule with 10 electrons: -21.5 , -1.6 , -0.7 , -0.7 , -0.4 , 0.6 , 0.8 , 1.1 . Based on Koopmans' theorem, what is the ionization potential of the most weakly bound electron in a.u.?

- | | | | |
|-----|-----|-----|--------|
| (a) | 1.6 | (e) | 1.0 |
| (b) | 0.7 | (f) | 0.0 |
| (c) | 0.6 | (g) | π |
| (d) | 0.4 | (h) | -0.6 |

20. The π aromatic system of 1-methoxynaphthalene can act as a nucleophile to trap the *t*-butyl cation, resulting in *t*-butyl substitution after loss of a proton from the ring position at which trapping occurs. Shown below are the HOMO and LUMO of 1-methoxynaphthalene (viewed from directly above, so you are looking at the top of the p orbitals of the π system—the size of a circle indicates the importance of that AO's contribution to the MO). Which *t*-butylated stereoisomer do you expect to predominate based on these orbitals (the ring numbering scheme is shown in the reactant)?



- | | | | |
|-----|---|-----|---|
| (a) | 2- <i>t</i> -butyl-1-methoxynaphthalene | (e) | 6- <i>t</i> -butyl-1-methoxynaphthalene |
| (b) | 3- <i>t</i> -butyl-1-methoxynaphthalene | (f) | 7- <i>t</i> -butyl-1-methoxynaphthalene |
| (c) | 4- <i>t</i> -butyl-1-methoxynaphthalene | (g) | 8- <i>t</i> -butyl-1-methoxynaphthalene |
| (d) | 5- <i>t</i> -butyl-1-methoxynaphthalene | | |

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