Final Exam   Name _____
CHE 525
May 14, 2021

PLEASE CAREFULLY READ THE DIRECTIONS BEFORE PROCEEDING

Directions: This is a take-home final, **due to be turned in via Blackboard by 10:45 am on Friday, May 14, 2021**. Late work will not be accepted. You **may** use any written material, including but not limited to course texts, other books, or your notes. You **may** use anything that you find on the internet, including but not limited to the course lecture videos, other videos, other online references, etc. You **may not** discuss this exam with each other or with any other person (whether in person or on the internet). Working together or discussing with others constitutes academic dishonesty, and may result in failure of the course.

True/False Instructions: Next to each statement, circle T if that statement is true or F if that statement is false. (2 points each)

1.   T   F   A converged geometry optimization always finds the global minimum on the potential energy surface.

2.   T   F   The aug-cc-pVDZ basis set for carbon contains diffuse functions.

3.   T   F   6-311G is a valence double-zeta basis set.

4.   T   F   The exchange interaction between electrons is a consequence of the antisymmetry of many-electron wavefunctions.

5.   Suppose that two Hartree-Fock calculations are performed on the same system using different basis sets. One uses the 6-31G** basis set and the other uses 6-31++G.

     T   F   If the 6-31G** calculation results in a more negative absolute energy than 6-31++G, then the variational theorem tells us that the 6-31G** energy is closer to the exact absolute energy of the system.

6. T F In a configuration interaction calculation, the many-electron wavefunction is approximated as a single Slater determinant.

7. T F The CCSD method is size extensive.

8. T F The MP2 method is variational.

9.   Suppose that two DFT calculations are performed on the same system using the same basis set, but using different density functionals: B3LYP and PBE.

    T F If the B3LYP calculation predicts a more negative absolute energy than the PBE calculation, then the second Hohenberg-Kohn theorem tells us that the B3LYP energy is closer to the exact absolute energy of the system.

10. T F In principle, Kohn-Sham DFT is an exact theory for predicting the ground state energy of a many-electron system.

Free Response Instructions: Answer all questions **completely, clearly, and legibly** to receive credit. Use the **vocabulary** we learned in class to receive full credit.

11. (5 points) When approximating a many-electron wavefunction, what is the advantage of a Slater determinant relative to a Hartree product?

12. (10 points) Describe a reasonable computational protocol (method and basis set) that would allow you to accurately calculate the energy of two krypton atoms as a function of the distance between them. Justify your answer using vocabulary we learned in class. (Full CI does not constitute a reasonable method in this context because it is too computationally expensive.)

13. (15 points) Suppose that you compute the potential energy surface of F_2 as a function of distance between fluorine atoms using three different methods: restricted Hartree-Fock, MP2, and CASSCF (with all 14 valence electrons and all 8 valence bonding and antibonding molecular orbitals included in the active space of the CASSCF calculation). All calculations are performed with the 6-31g* basis set. Draw a picture of what you would expect the three curves to look like. Explain in complete sentences why each curve looks the way that it does. Which of these three methods do you expect would provide the most accurate prediction of the bond dissociation energy and why? (Use vocabulary we learned in class.)

14. (10 points) Suppose that you do two single point energy calculations at the same level of theory using the same basis set. In the first calculation you compute the energy of a single ammonia molecule at its ground state minimum energy geometry, $E(\text{NH}_3)$. In the second calculation, you compute the energy of two ammonia molecules at the same geometry as above separated by an infinite distance, $E(2\,\text{NH}_3)$. Name a method for which $2E(\text{NH}_3) \neq E(2\,\text{NH}_3)$. Explain your answer using vocabulary you learned in class.

15. (15 points). Consider a two-level system with Hamiltonian $\hat{H}$, described by the density operator.

$$a \left|\psi_0\right\rangle \left\langle\psi_0\right| + b \left|\psi_0\right\rangle \left\langle\psi_1\right| + c \left|\psi_1\right\rangle \left\langle\psi_0\right| + d \left|\psi_1\right\rangle \left\langle\psi_1\right|$$

Where ψ_1 and ψ_0 are eigenstate of the Hamiltonian with energy eigenvalues E_1 and E_0 with $E_1 > E_0$. Or in matrix form

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

Explain the physical meaning of the coefficients a, b, c, and d.

If the density matrix of the system is initially, at $t = 0$, given by

$$\rho(t = 0) = \begin{pmatrix} 0.9 & 0.09 \\ 0.09 & 0.1 \end{pmatrix}$$

Does this describe a pure state or a mixed state? Describe the free evolution of this density matrix with time in a typical chemical environment (i.e. what is the time evolution of the four components (a, b, c, d) when *not* driven with an external EM field).

For the question below **circle all that apply** (2 points each)

16. To try to understand the spectrum $FeCl_2$ dissolved in water, you run an excited-state quantum chemistry calculation on a gas-phase Fe^{2+} atomic ion. Which of the following quantities regarding the Fe^{2+} in the solution might be reasonable to estimate from your calculation. Circle all that apply.

The wavelengths at which the Fe^{2+} absorbs light.

The dipole matrix elements between the different electronic states of the aqueous Fe^{2+}

The oscillator strength of the transitions

The accuracy of your calculation via the Thomas-Reiche-Kuhn sum rule.

The peak absorption coefficient of the aqueous Fe^{2+}

The spontaneous emission rate for an excited Fe^{2+} ion

The lifetime of an excited state of the Fe^{2+}