CHEM356: Physical Chemistry II
Homework Set IV - due 18^{th} of April, 5.00 pm
Each problem is worth 5 points, 25 pts in total.

Instructor: Dr. Mateusz Marianski
Room#: HN-1321B
email: *mmarians@hunter.cuny.edu*
Office hours: Thu, 5-7 pm, HN-1321B

Problem I

Matrix determinats, as defined during the lecture, have number of useful properties that make them useful in writing the wave function of many-electron systems. Using the shorthand equation for the determinant of 3x3 matrix:

$$det(A) = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}a_{22}a_{33} + a_{12}a_{23}a_{31} + a_{13}a_{21}a_{32} - a_{13}a_{22}a_{31} - a_{12}a_{21}a_{33} - a_{11}a_{23}a_{32}$$

prove following properties for given matrices:

1. For matrix `A` show that the determinant is unchanged if rows are made into columns in the same order (the determinant of the transposed matrix)

$$\begin{vmatrix} -3 & 4 & 0 \\ 2 & 1 & 1 \\ 2 & 0 & 3 \end{vmatrix} = \begin{vmatrix} -3 & 2 & 2 \\ 4 & 1 & 0 \\ 0 & 1 & 3 \end{vmatrix}$$

2. If any two rows or columns are the same, the value of the determinant is zero.

$$\begin{vmatrix} -3 & 4 & -3 \\ 2 & 1 & 2 \\ 2 & 0 & 2 \end{vmatrix} = 0$$

3. If any two rows or columns are interchanged, the sign of the determinant is changed.

$$\begin{vmatrix} -3 & 4 & 0 \\ 2 & 0 & 3 \\ 2 & 1 & 1 \end{vmatrix} = \begin{vmatrix} -3 & 4 & 0 \\ 2 & 1 & 1 \\ 2 & 0 & 3 \end{vmatrix}$$

4. If every element in a row or column is multiplied by a factor k, the value of the determinant is multiplied by k

$$\begin{vmatrix} -3 & 4 & -6 \\ 2 & 1 & 4 \\ 2 & 0 & 4 \end{vmatrix} = 2 \begin{vmatrix} -3 & 4 & -3 \\ 2 & 1 & 2 \\ 2 & 0 & 2 \end{vmatrix}$$

5. If any row or column is written as the sum or difference of two or more terms, the determinant can be written as the sum of difference of two or more determinats:

$$\begin{vmatrix} -3 & 4 & -6 \\ 2 & 1 & 4 \\ 2 & 0 & 4 \end{vmatrix} = \begin{vmatrix} -3 & 4 & -2 \\ 2 & 1 & 1 \\ 2 & 0 & 1 \end{vmatrix} + \begin{vmatrix} -3 & 4 & -4 \\ 2 & 1 & 3 \\ 2 & 0 & 3 \end{vmatrix}$$

6. The value of the determinant is unchanged if one row or column is added or subtracted to another:

$$\begin{vmatrix} -3 & 4 & -6 \\ 2 & 1 & 4 \\ 2 & 0 & 4 \end{vmatrix} = \begin{vmatrix} -3 & 4 & -2 \\ 2 & 1 & 5 \\ 2 & 0 & 4 \end{vmatrix}$$

Which of the properties is the mathematical notation of Pauli's Exclusion Principle?

Problem II

Compute the energy of hydrogen atom using $e^{-\alpha r^2}$ trial function, where α is a variational parameter. The function do not have any angular dependence hence your hamiltonian simplifies to:

$$\hat{H} = -\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{e^2}{4\pi\epsilon_0 r}$$

Still, you have the 4π factor coming from integration over θ and ϕ angles and the volume element $r^2 dr \sin\theta d\theta d\phi$. Next, minimize the expression with respect to the α parameter and confirm that the variational principle holds.

Problem III

Derive ground-state term symbols for ns^1np^1, p^4 and d^2 electronic configurations.

Problem IV

- Consider the 1s np $^3P \rightarrow$ 1s nd ^3D transition in helium atom. Draw an energy-level diagram and show the allowed transtions.
- The first ionization potential of helium atom is 24.6 eV and the transition wavelenght to 1s2p ^1P state is 58.44 nm. What is the ionization energy of excited [1s2p] helium atom?
- The transition $Al[Ne]3s^2 3p^1 \rightarrow Al[Ne]3s^2 4s^1$ has two lines given by $\widetilde{\nu} = 25354.8$ cm^{-1} and $\widetilde{\nu} = 25242.7$ cm^{-1}. The transition $Al[Ne]3s^2 3p^1 \rightarrow Al[Ne]3s^2 3d^1$ has three lines given by 32444.8, 32334.0 and 32332.7 cm-1. Sketch an enenrgy diagram and explain the source of the lines.

Problem V

- Sketch the molecular orbital energy diagram for the radical OH and compare it with a diagram for HF. Show HOMO, LUMO and eventual nonbonding orbitals.
- The bond dissociation energies follow the trend $CF^+ > NO > CF^-$. Explain the trend using MO theory.
- Calculate the bond order of following diatomic molecules Li_2, C_2, O_2 and F_2. Next, calculate the bond order of negatively and positively charged ions of these species and explain, using MO's theory, the changing bond order.