Problem Set PS05

Issued: 9/26/02 Due: 10/3/02

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Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. The determinant of a matrix, $\mathcal{M}$, is notated as $|\mathcal{M}|$. For a 2×2 matrix $\mathcal{M} = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix}$, the determinant is given by

$$\begin{vmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{vmatrix} = m_{11}m_{22} - m_{12}m_{21}.$$

   evaluate the determinant for the following matrices (simplify your answers).

   (a) $\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

   (b) $\begin{bmatrix} 1 & 8 \\ 3 & 9 \end{bmatrix}$

   (c) $\begin{bmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{bmatrix}$

2. The determinant of a 3×3 matrix is given by

$$\begin{vmatrix} m_{11} & m_{12} & m_{13} \\ m_{21} & m_{22} & m_{23} \\ m_{31} & m_{32} & m_{33} \end{vmatrix} = m_{11} \begin{vmatrix} m_{22} & m_{23} \\ m_{32} & m_{33} \end{vmatrix} - m_{12} \begin{vmatrix} m_{21} & m_{23} \\ m_{31} & m_{33} \end{vmatrix} + m_{13} \begin{vmatrix} m_{22} & m_{23} \\ m_{32} & m_{33} \end{vmatrix}$$

   evaluate the determinant for

$$\begin{bmatrix} 6 & 2 & 8 \\ 1 & 4 & 5 \\ 6 & 4 & 7 \end{bmatrix}$$

3. Determinants have the property that if any two rows or any two column are exchanged, the value of the determinant changes sign. Verify this for the determinants of the above two problems (you may use Mathematica).

4. Determinants have the property that if any two rows or any two column are the same, the value of the determinant is zero. Show that this is verified for the following determinants

(a) $\begin{bmatrix} x & y & z \\ a & b & c \\ a & b & c \end{bmatrix}$

(b) $\begin{bmatrix} a & a & x \\ b & b & y \\ c & c & z \end{bmatrix}$

Exercises

5. In the notes we obtained the ground state of helium which was

$$\Psi_{\mathsf{g}} = \psi_{\mathsf{1s}}(1)\psi_{\mathsf{1s}}(2)\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right].$$

As a short-hand representation of this state one uses the notation $(1s)^2$ which is read as the product of two $1s$ hydrogenic states. Also, it is automatically understood that the Pauli exclusion principle applies and the electrons have opposite spins. This is the one and only ground state, so one says the ground state is a "singlet." Let us consider one particular excited state $(1s)^1(2s)^1$. This is an excited state of helium where one electron is in the $1s$ state and the other is in the $2s$ state. The spatial part of the wavefunction for this state could be

$$\psi_{\mathsf{12}} = \psi_{\mathsf{1s}}(1)\psi_{\mathsf{2s}}(2)$$

or

$$\psi_{\mathsf{21}} = \psi_{\mathsf{2s}}(1)\psi_{\mathsf{1s}}(2),$$

but neither of these are symmetric or antisymmetric. So we must make linear combinations of these two wavefunction as,

$$\psi_{\mathsf{12}} + \psi_{\mathsf{21}} = \psi_{\mathsf{1s}}(1)\psi_{\mathsf{2s}}(2) + \psi_{\mathsf{2s}}(1)\psi_{\mathsf{1s}}(2) = \psi_{\text{sym}}$$

and

$$\psi_{\mathsf{12}} - \psi_{\mathsf{21}} = \psi_{\mathsf{1s}}(1)\psi_{\mathsf{2s}}(2) - \psi_{\mathsf{2s}}(1)\psi_{\mathsf{1s}}(2) = \psi_{\text{anti}}.$$

Verify that these wavefunctions have the denoted symmetry. The spin part of the wavefunction for this state could be

$$\alpha(1)\alpha(2),$$

$$\beta(1)\beta(2),$$

$$\alpha(1)\beta(2)$$

or

$$\alpha(2)\beta(1).$$

The first two possibilities are symmetric but the last two are neither symmetric nor antisymmetric. The properly symmetric spin wavefunctions are

$$\chi_{\text{sym}} = \begin{cases} \alpha(1)\alpha(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \\ \beta(1)\beta(2) \end{cases}.$$

The properly antisymmetric spin wavefunction is

$$\chi_{\text{anti}} = \alpha(1)\beta(2) - \alpha(2)\beta(1).$$

Now, according to the Pauli exclusion principle the total wavefunction must be antisymmetric. This leads to

$$\Psi_1 = \psi_{\text{sym}}\chi_{\text{anti}}$$

and

$$\Psi_2 = \psi_{\text{anti}}\chi_{\text{sym}}.$$

Write out these wavefunctions. Ψ_1 is a single state just as the ground state was. It is therefore called a "singlet" excited state. Ψ_2 is actually three states. It is therefore called a "triplet" excited state. Use horizontal lines to represent the 1s and 2s states and use arrows to represent the electrons and their spin state. Draw all the possible ways that you can have one electron in each state. Do this first by labelling the electrons and then do it again with out labelling the electrons. How does labelling the electrons affect the number of states. Can you correspond your pictures to the wavefunctions?

6. Using mathematical exercise number 2 explicitly write out one of the ground state wavefunctions for Li from its Slatter determinant.

7. Give the shorthand notation for the ground state wavefunctions for C, Al, Sr, and As.

8. If the electrons in helium did not interact as we assume in our qualitative approach to the helium atom the first ionization energy of helium would be $4\mathcal{R}$ where $\mathcal{R}$ is the Rydberg constant. In reality the first ionization energy is about $1.8\mathcal{R}$. This is because the presence of another electron shields the full nuclear charge from the electron being ionized away. What is the effective nuclear charge felt by the electrons in helium?

Conceptual Problems

9. Pretend the quantum number $s = \frac{3}{2}$ instead of $\frac{1}{2}$ for electrons. If this was the case which elements would constitute the noble gases? Which element would be most electronegative? Which elements would constitute the "d block." How many rows would the periodic table have?

10. Pretend that for any given n the allowed values of the quantum number l is $l = 0, 1, 2, \cdots, n$ (rather than $l = 0, 1, 2, \cdots, n-1$) and that all other quantum numbers behave as they really do. If this was the case which elements would constitute the noble gases? Which element would be most electronegative? Which elements would constitute the "d block." How many rows would the periodic table have?

Reflective Exercises

11. List the major journals in your field of interest (e.g., New England Journal of Medicine, Journal of the American Chemical Society, Physical Review, etc.). Go to the library (or the internet if applicable) and find an article that deals in some way with physical chemistry. If you simply can't find anything to do with physical chemistry then find something to do with chemistry. You do not need to turn in a copy of the paper; just report the reference (with title)

12. I think that the type of people who end-up pursuing science degrees generally have a strong work ethic and an above average drive to do their best. For the most part striving for excellence is highly valued here at Concordia, but once you leave here and are engaged in your career things could be different. Supervisors, co-workers and other people related to you job might not recognize and value your effort. How will you handle such a situation. In some cases you might find that your effort and pursuit of excellence is not only not valued but in fact resisted. That is, institutional or informal social/political barriers hinder your pursuit of excellence. How might you handle this situation? Consider the question from both the point of view of your career goals and of your interpersonal relationships with your co-workers.

① (a) $1(-1) - 0 = -1$

(b) $1(4) - 3(8) = 15$

(c) $\cos^2\alpha + \sin^2\alpha = 1$

② $6(4(7)-4(5)) - 2(1(7)-6(5)) + 8(1(4) - 6(4))$

$6(8) - 2(-23) + 8(-20) = -66$

③ Use Mathematica

④ (a) $x\begin{vmatrix} b & c \\ b & c \end{vmatrix}^{\to 0} - y\begin{vmatrix} a & c \\ a & c \end{vmatrix}^{0} + z\begin{vmatrix} b & c \\ b & c \end{vmatrix}^{0} = 0$ ✓

(b) $a\begin{vmatrix} x & y \\ c & z \end{vmatrix} - a\begin{vmatrix} b & y \\ c & z \end{vmatrix} + x\begin{vmatrix} b & c \\ b & c \end{vmatrix}^{0} = 0$ ✓

⑤ see last year's soln's

⑥ $\psi = \begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(1)\beta(1) & \psi_{2s}(1)\alpha(1) \\ \psi_{1s}(2)\alpha(2) & \psi_{1s}(2)\beta(2) & \psi_{2s}(2)\alpha(2) \\ \psi_{1s}(3)\alpha(3) & \psi_{1s}(3)\beta(3) & \psi_{2s}(3)\alpha(3) \end{vmatrix}$

$= \psi_{1s}(1)\alpha(1)\left(\psi_{1s}(2)\beta(2) - \psi_{2s}(3)\alpha(3)\right)$

$- \psi_{1s}(1)\beta(1)\left(\psi_{1s}(2)\alpha(2)\psi_{2s}(3)\alpha(3) - \psi_{1s}(3)\alpha(3)\psi_{2s}(2)\alpha(2)\right)$

$+ \psi_{2s}(1)\alpha(1)\left(\psi_{1s}(2)\alpha(2)\psi_{1s}(3)\beta(3) - \psi_{1s}(3)\alpha(3)\psi_{1s}(2)\beta(2)\right)$

⑦ C: $[He](2s)^2(2p)^2$

Al: $[Ne](3s)^2(3p)^1$

Sr: $[Kr](5s)^2$

As: $[Ar](3d)^{10}(4s)^2(4p)^3$

⑧ $E_{ion} = Z^2 R \qquad 1.8R = Z^2 R \qquad Z^2 = 1.8 \qquad Z = 1.34$

⑨

4P Pm ... Hf

3d Nb ... → Nd

4S Rb Sr Y Zr

3P Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

3S Sc Ti V Cr

2P F Ne Na Mg Al Si P S Cl Ar K Ca

2S B C N O

1S H He Li Be

Noble gases: Be, Ca, Kr, Hf
"most electronegative": K
"d block" Nb – Nd, Zr – Cm

⑩ 3f Sb Te I Xe Cs Ba La Ce Pr Nd Pm Sm Eu Gd

3d Nb Mo Tc Ru Rh Pd Ag Cd In Sn

4S Kr Rb

3P Zn Ga Ge As Se Br.

3S Co Ni

2d Cl Ar K Ca Sc Ti V Cr Mn Fe

2P Na Mg Al Si P S

2S F Ne

1P Li Be B C N O

1S H He

Noble gases: He, O, S, Br
most electronegative N
"d block" Cl – Fe, Nb – Sn

11, 12 your words