

## Problem Set PS05

ISSUED: 9/28/00 Due: 10/5/00

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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  $2 \times 2$  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)  $\begin{bmatrix} 4 & 2 \\ 7 & 1 \end{bmatrix}$

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

(d)  $\begin{bmatrix} e^{i\frac{\alpha}{2}} & -e^{i\frac{\alpha}{2}} \\ e^{-i\frac{\alpha}{2}} & e^{-i\frac{\alpha}{2}} \end{bmatrix}$

2. The determinant of a  $3 \times 3$  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

$$\begin{bmatrix} 3 & 2 & 2 \\ 8 & 4 & 9 \\ 1 & 4 & 1 \end{bmatrix}$$

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

$$\Psi_g = \psi_{1s}(1)\psi_{1s}(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)].$$

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

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

or

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

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

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

and

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

**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.**  $\Psi_1$  is a single state just as the ground state was. It is therefore called a “singlet” excited state.  $\Psi_2$  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?

- Using mathematical exercise number 2 write out the ground state wavefunction for  $\text{Be}^+$  from its Slater determinant.

### Conceptual Problems

- Iron can be made into a magnet if the spins of the unpaired electrons for the iron atoms in macroscopic regions can be made to more or less align. The alignment process can be done by melting the iron in a magnetic field which aligns the spins and letting it freeze into place. Show via an energy level diagram that iron has the necessary unpaired electrons to be useful as a magnet. (Note: a rule of thumb is that if electron are not in the same subshell they tend to fill spin parallel.) Could one make a magnet out of nickel? How about zinc?
- Pretend that for any given  $n$  the allowed value of the quantum number  $l$  is  $l = n - 1$  (rather than  $l = 0, 1, 2, \dots, n - 1$ ) 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

- 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.
- Use the internet to find out more about the stuff your intended career field expects new people to the field should know. For example, if you want to be a forensic chemistry for the FBI, what does the FBI expect you to know.

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

(b)  $\begin{vmatrix} 4 & 2 \\ 7 & 1 \end{vmatrix} = (4)(1) - (7)(2) = -10$

(c)  $\begin{vmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{vmatrix} = \cos^2 \alpha + \sin^2 \alpha = 1$

(d)  $\begin{vmatrix} e^{i\alpha} & e^{-i\alpha} \\ e^{-i\alpha} & e^{i\alpha} \end{vmatrix} = e^{i\alpha} e^{i\alpha} - (e^{-i\alpha} e^{-i\alpha}) = 2$

(2)  $\begin{vmatrix} 3 & 2 & 2 \\ 8 & 4 & 9 \\ 1 & 4 & 1 \end{vmatrix} = 3 \begin{vmatrix} 4 & 9 \\ 4 & 1 \end{vmatrix} - 2 \begin{vmatrix} 8 & 9 \\ 1 & 1 \end{vmatrix} + 2 \begin{vmatrix} 8 & 4 \\ 1 & 4 \end{vmatrix}$   
 $= 3(4(1) - 4(9)) - 2(8(1) - 9(1)) + 2(8(4) - 1(4))$   
 $= 3(-32) - 2(-1) + 2(28)$   
 $= -96 + 2 + 56 = -38$

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

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

(5)  $\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2) \xrightarrow{1 \leftrightarrow 2} \psi_1(2)\psi_2(1) + \psi_2(2)\psi_1(1) = \psi_1\psi_2$   
 $\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2) \xrightarrow{1 \leftrightarrow 2} \psi_2(2)\psi_1(1) - \psi_1(2)\psi_2(1) = -(\psi_1 - \psi_2)$

$\Psi_1 = (\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)) \alpha(1)\beta(2) + \alpha(2)\beta(1)$   
 $= \psi_1(1)\psi_2(2) \alpha(1)\beta(2) + \psi_2(1)\psi_1(2) \alpha(1)\beta(2) - \psi_1(1)\psi_2(2) \alpha(2)\beta(1) - \psi_2(1)\psi_1(2) \alpha(2)\beta(1)$   
 $= \psi_1(1)\psi_2(2) \alpha(1)\beta(2) + \psi_2(1)\psi_1(2) \alpha(1)\beta(2) - \psi_1(1)\psi_2(2) \alpha(2)\beta(1) - \psi_2(1)\psi_1(2) \alpha(2)\beta(1)$

cont

$\Psi_2 = (\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)) \begin{pmatrix} \alpha(1)\beta(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \\ \alpha(1)\beta(2) \end{pmatrix}$

$\Psi_{2a} = \psi_1(1)\psi_2(2) \alpha(1)\beta(2) - \psi_2(1)\psi_1(2) \alpha(1)\beta(2)$   
 $= \psi_1(1)\psi_2(2) \alpha(1)\beta(2) - \psi_2(1)\psi_1(2) \alpha(1)\beta(2)$

$\Psi_{2b} = (\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)) (\alpha(1)\beta(2) + \alpha(2)\beta(1))$   
 $= \psi_1(1)\psi_2(2) \alpha(1)\beta(2) - \psi_2(1)\psi_1(2) \alpha(1)\beta(2) + \psi_1(1)\psi_2(2) \alpha(2)\beta(1) - \psi_2(1)\psi_1(2) \alpha(2)\beta(1)$   
 $= \psi_1(1)\psi_2(2) \alpha(1)\beta(2) - \psi_2(1)\psi_1(2) \alpha(1)\beta(2) + \psi_1(1)\psi_2(2) \alpha(2)\beta(1) - \psi_2(1)\psi_1(2) \alpha(2)\beta(1)$

$\Psi_{2c} = (\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)) \alpha(1)\beta(2)$   
 $= \psi_1(1)\psi_2(2) \alpha(1)\beta(2) - \psi_2(1)\psi_1(2) \alpha(1)\beta(2)$

$\frac{\uparrow 1}{\uparrow 2} \quad \frac{\uparrow 2}{\uparrow 1} \quad \frac{\downarrow 1}{\downarrow 2} \quad \frac{\downarrow 2}{\downarrow 1} \quad \frac{\uparrow 1}{\downarrow 2} \quad \frac{\uparrow 2}{\downarrow 1} \quad \frac{\downarrow 1}{\uparrow 2} \quad \frac{\downarrow 2}{\uparrow 1}$

$\Psi_1 = \frac{\uparrow 1}{\uparrow 1} + \frac{\uparrow 1}{\downarrow 2} - \frac{\uparrow 2}{\downarrow 1} - \frac{\downarrow 1}{\downarrow 2}$

$\Psi_{2a} = \frac{\uparrow 2}{\uparrow 1} - \frac{\uparrow 1}{\uparrow 2}$

$\Psi_{2b} = \frac{\downarrow 2}{\uparrow 1} - \frac{\uparrow 1}{\downarrow 2} + \frac{\uparrow 2}{\downarrow 1} - \frac{\downarrow 1}{\downarrow 2}$

$\Psi_{2c} = \frac{\downarrow 2}{\downarrow 1} - \frac{\downarrow 1}{\downarrow 2}$

(6) Be<sup>+</sup> 3 eled  $\frac{1}{1s} \frac{2s}{1s}$

$\begin{vmatrix} \psi_1(1)\alpha(1) & \psi_2(1)\beta(1) & \psi_3(1)\alpha(1) \\ \psi_1(2)\alpha(2) & \psi_2(2)\beta(2) & \psi_3(2)\alpha(2) \\ \psi_1(3)\alpha(3) & \psi_2(3)\beta(3) & \psi_3(3)\alpha(3) \end{vmatrix}$  similarly for  $\psi_2(1)\beta(1)$

$= \psi_1(1)\alpha(1) \begin{vmatrix} \psi_2(2)\beta(2) & \psi_3(2)\alpha(2) \\ \psi_2(3)\beta(3) & \psi_3(3)\alpha(3) \end{vmatrix} - \psi_2(1)\beta(1) \begin{vmatrix} \psi_1(2)\alpha(2) & \psi_3(2)\alpha(2) \\ \psi_1(3)\alpha(3) & \psi_3(3)\alpha(3) \end{vmatrix}$   
 $+ \psi_3(1)\alpha(1) \begin{vmatrix} \psi_1(2)\alpha(2) & \psi_2(2)\beta(2) \\ \psi_1(3)\alpha(3) & \psi_2(3)\beta(3) \end{vmatrix}$

$= \psi_1(1)\alpha(1) (\psi_2(2)\beta(2)\psi_3(3)\alpha(3) - \psi_3(2)\beta(2)\psi_2(3)\alpha(3))$   
 $- \psi_2(1)\beta(1) (\psi_1(2)\alpha(2)\psi_3(3)\alpha(3) - \psi_3(3)\alpha(3)\psi_1(2)\alpha(2))$   
 $+ \psi_3(1)\alpha(1) (\psi_1(2)\alpha(2)\psi_2(3)\beta(3) - \psi_2(3)\beta(3)\psi_1(2)\alpha(2))$

(7) Fe: [Ar] (4s)<sup>2</sup> (3d)<sup>6</sup> 3d  $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$   
 4s  $\uparrow \uparrow$

Ni: [Ar] (4s)<sup>2</sup> (3d)<sup>8</sup> 3d  $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$  magnetic

Zn: [Ar] (4s)<sup>2</sup> (3d)<sup>10</sup> 3d  $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$  no magnet  
 4s  $\uparrow \uparrow$

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	<u>elect in shell</u>	<u>total elect.</u>
1s	2	2
2p	6	8
3d	10	18
4f	14	32
5g	18	50
6h	22	72
7i	26	98

Noble gases He, O, Ar, Ge, Sn, Hf, Cf

most electronegative: N

"d block": F  $\rightarrow$  Ar

Now 8 rows in periodic table the 8<sup>th</sup> row is mostly undiscovered.

⑨ } your work  
⑩ }