Problem Set PS05

ISSUED: 9/27/01 **Due: 10/4/01**

Prof. Darin J. Ulness Name ____________________

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

(b) $\begin{bmatrix} 2 & 0 \\ 3 & 1 \end{bmatrix}$

(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 3×3 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

$$\begin{bmatrix} 7 & 2 & 2 \\ 7 & 3 & 6 \\ 0 & 6 & 7 \end{bmatrix}$$

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 a general 3×3 matrix,

$$\begin{bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{bmatrix}.$$

You may want to 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) $\begin{bmatrix} x & y & z \\ a & b & c \\ a & b & c \end{bmatrix}$ (two rows are the same)

(b) $\begin{bmatrix} a & a & x \\ b & b & y \\ c & c & z \end{bmatrix}$ (two columns are the same)

Exercises

5. Consider the three electron systems Li and Be^+ whose first several energy levels are shown in the tables below. The only difference between these systems is the nuclear charge. Graph the energy levels for each system, comment on how they differ. Are the subshells equally effected by the change in nuclear charge? Note: the energys are given in wavenumbers and give the energy *below* the inonization energy. The best way to use these numbers is to set the ionization energy at zero then simply take the negative of the entries as the energy for the level. Note: for Be^+ the 2p and 3p states have been broken out into two levels each. Just graph the $J = \frac{1}{2}$ levels for each.

From: Atomic Energy States
R.F. Bacher and S. Goudsmit
Greenwood Press, NY 1968

Li I $\quad Z = 3$

3 electrons $\quad 1s^2\,2s\;^2S_{\frac{1}{2}}$

First ionization potential = 5.37 volts

The classification is taken from Fowler and Paschen-Götze. Only the first term of the p series has been resolved into a doublet. Its separation is 0.34 cm.$^{-1}$.

Two types of tables are given: first, one containing only the lowest terms, second, one containing the complete set of terms in series arrangement.

Configuration	Symbol	J	Term value
$2s$	^2S	$\frac{1}{2}$	43486.3
$2p$	$^2P^\circ$	$\frac{1}{2}, 1\frac{1}{2}$	*28582.5*
$3s$	^2S	$\frac{1}{2}$	16280.5
$3p$	$^2P^\circ$	$\frac{1}{2}, 1\frac{1}{2}$	*12560.4*
$3d$	^2D	$1\frac{1}{2}, 2\frac{1}{2}$	12203.1
$4s$	^2S	$\frac{1}{2}$	8475.2
$4p$	$^2P^\circ$	$\frac{1}{2}, 1\frac{1}{2}$	*7018.2*
$4d$	^2D	$1\frac{1}{2}, 2\frac{1}{2}$	6863.5
$4f$	$^2F^\circ$	$2\frac{1}{2}, 3\frac{1}{2}$	*6856.1*

Be II $\quad Z = 4$

3 electrons $\quad 1s^2\,2s\;^2S_{\frac{1}{2}}$

Ionization potential = 18.12 volts

These term values of the beryllium spark spectrum are from the work of Paschen and Kruger.

Reference

F. Paschen and P. G. Kruger, *Ann. d. Physik* **8,** 1005 (1931).

Configuration	Symbol	J	Term value	$\Delta\nu$
$1s^2 2s$	^2S	$\frac{1}{2}$	146881.7	
$2p$	$^2P^\circ$	$\frac{1}{2}$ $1\frac{1}{2}$	*114952.9* *114946.3*	6.6
$3s$	^2S	$\frac{1}{2}$	58650.5	
$3p$	$^2P^\circ$	$\frac{1}{2}$ $1\frac{1}{2}$	*50385.3* *50383.5*	1.8
$3d$	^2D	$1\frac{1}{2}, 2\frac{1}{2}$	48828.5	
$4s$	^2S	$\frac{1}{2}$	31416.5	
$4p$	$^2P^\circ$	$\frac{1}{2}, 1\frac{1}{2}$	*28122*	
$4d$	^2D	$1\frac{1}{2}, 2\frac{1}{2}$	27459.5	
$4f$	$^2F^\circ$	$2\frac{1}{2}, 3\frac{1}{2}$	*27437.1*	
$5s$	^2S	$\frac{1}{2}$	19545.6	
$5p$	$^2P^\circ$	$\frac{1}{2}, 1\frac{1}{2}$	*17911.5*	
$5d$	^2D	$1\frac{1}{2}, 2\frac{1}{2}$	17570.4	
$5f$	$^2F^\circ$	$2\frac{1}{2}, 3\frac{1}{2}$	*17559.8*	
$6s$	^2S	$\frac{1}{2}$	13322.6	

81

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

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

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

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

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

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

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?

7. Using mathematical exercise number 2 write out the ground state wavefunction for B^{2+} from its Slatter determinant.

Conceptual Problems

8. 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?

9. Pretend that the allowed values for magnetic orientation quatum number, m, are $0,1,2\cdots,l$ instead of $0,\pm1,\pm2\cdots,\pm l$ and that all other quantum numbers behave as they really do and all filling rules remain the same. Draw a new periodic table.

Reflective Exercises

10. 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. Write down the citation information; you do not need to turn in a copy of the article.

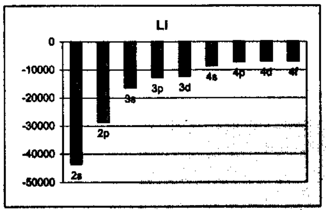
11. Use the internet to find out more about the stuff your intended career field expects new people to the field should know. For example, if you want to be a forensic chemistry for the FBI, what does the FBI expect you to know.

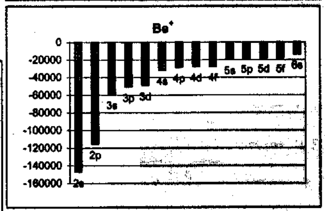
(1)

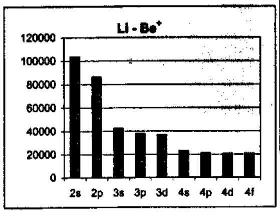
(a)
```
In[3]:= Det[{{4, 1}, {2, -1}}]
Out[3]= -6
```
(b)
```
In[4]:= Det[{{2, 0}, {3, 1}}]
Out[4]= 2
```
(c)
```
In[7]:= Simplify[Det[{{Cos[a], Sin[a]}, {-Sin[a], Cos[a]}}]]
Out[7]= 1
```
(d)
```
In[8]:= Det[{{Exp[I a / 2], -Exp[I a / 2]}, {Exp[-I a / 2], Exp[-I a / 2]}}]
Out[8]= 2
```
(2)
```
In[9]:= Det[{{7, 7, 2}, {7, 3, 6}, {0, 6, 7}}]
Out[9]= -364
```
(3)
```
In[12]:= A = Det[{{a, b, c}, {d, e, f}, {g, h, i}}]
Out[12]= -ceg + bfg + cdh - afh - bdi + aei
In[13]:= B = Det[{{d, e, f}, {a, b, c}, {g, h, i}}]
Out[13]= ceg - bfg - cdh + afh + bdi - aei
In[14]:= A === -B
Out[14]= True
In[18]:= F = Det[{{b, a, c}, {e, d, f}, {h, g, i}}]
Out[18]= ceg - bfg - cdh + afh + bdi - aei
In[19]:= A === -F
Out[19]= True
```
(4)
```
In[20]:= Det[{{x, y, z}, {a, b, c}, {a, b, c}}]
Out[20]= 0
In[21]:= Det[{{a, a, x}, {b, b, y}, {c, c, z}}]
Out[21]= 0
```


(5)

Li	Li	Be	
2s	-43486	-146881	103395
2p	-28582	-114952	86370
3s	-16280	-58650	42370
3p	-12560	-50385	37825
3d	-12203	-48828	36625
4s	-8475	-31416	22941
4p	-7018	-28122	21104
4d	-6863	-27459	20596
4f	-6856	-27437	20581
5s		-19545	
5p		-17911	
5d		-17570	
5f		-17559	
6s		-13322	







(6) $\psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)\psi_{1s}(2) \xrightarrow{1 \leftrightarrow 2} \psi_{1s}(2)\psi_{2s}(1) + \psi_{2s}(2)\psi_{1s}(1) = \psi_{12} + \psi_{21}$

$\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2) \xrightarrow{1 \leftrightarrow 2} \psi_{1s}(2)\psi_{2s}(1) - \psi_{2s}(2)\psi_{1s}(1) = -(\psi_{12} - \psi_{21})$

$\Psi_1 = (\psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)\psi_{1s}(2))(\alpha(1)\beta(2) - \alpha(2)\beta(1))$

$= \psi_{1s}(1)\psi_{2s}(2)\alpha(1)\beta(2) + \psi_{2s}(1)\psi_{1s}(2)\alpha(1)\beta(2) - \psi_{1s}(1)\psi_{2s}(2)\alpha(2)\beta(1) - \psi_{2s}(1)\psi_{1s}(2)\alpha(2)\beta(1)$

$= \psi_{1s}(1)\alpha(1)\psi_{2s}(2)\beta(2) + \psi_{2s}(1)\alpha(1)\psi_{1s}(2)\beta(2) - \psi_{1s}(1)\beta(1)\psi_{2s}(2)\alpha(2) - \psi_{2s}(1)\beta(1)\psi_{1s}(2)\beta(2)$

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

$\Psi_{2a} = \psi_{1s}(1)\psi_{2s}(2)\alpha(1)\alpha(2) - \psi_{2s}(1)\psi_{1s}(2)\alpha(1)\alpha(2)$

$= \psi_{1s}(1)\alpha(1)\psi_{2s}(2)\alpha(2) - \psi_{2s}(1)\alpha(1)\psi_{1s}(2)\alpha(2)$

$\Psi_{2b} = (\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2))(\alpha(1)\beta(2) + \alpha(2)\beta(1))$

$= \psi_{1s}(1)\psi_{2s}(2)\alpha(1)\beta(2) - \psi_{2s}(1)\psi_{1s}(2)\alpha(1)\beta(2) + \psi_{1s}(1)\psi_{2s}(2)\alpha(2)\beta(1) - \psi_{2s}(1)\psi_{1s}(2)\alpha(2)\beta(1)$

$= \psi_{1s}(1)\alpha(1)\psi_{2s}(2)\beta(2) - \psi_{2s}(1)\alpha(1)\psi_{1s}(2)\beta(2) + \psi_{1s}(1)\beta(1)\psi_{2s}(2)\alpha(2) - \psi_{2s}(1)\beta(1)\psi_{1s}(2)\alpha(2)$

$\Psi_{2c} = (\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2))\beta(1)\beta(2)$

$= \psi_{1s}(1)\beta(1)\psi_{2s}(2)\beta(2) - \psi_{2s}(1)\beta(1)\psi_{2s}(2)\beta(2)$

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

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

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

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

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

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

(7) Be^+ 3 elec $\frac{\uparrow}{\uparrow\downarrow}\ {}^{2s}_{1s}$

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

similarly for $\psi_{2s}(1)\beta(1)$

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

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

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

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

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

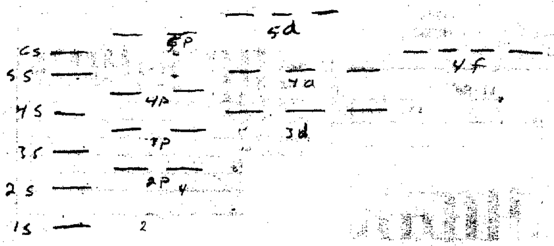
(8) Fe: $[Ar](4s)^2(3d)^6$ 3d $\uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow$
4s $\uparrow\downarrow$

Ni: $[Ar](4s)^2(3d)^8$ 3d $\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow$ magnetic
$\uparrow\downarrow$

Zn: $[Ar](4s)^2(3d)^{10}$ 3d $\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow$ no magnet
$\uparrow\downarrow$

(9)

n=1 l=0 m=0
n=2 l=1 m=0,1
l=0 m=0
n=3 l=2 m=2,1,0
l=1 m=1,0
l=0 m=0



1	H 1											He 2
22	Li 3	Be 4							B 5	C 6	N 7	O 8
3	F 9	Ne 10							Na 11	Mg 12	Al 13	Si 14
4	P 15	S 16	Cl 17	Ar 18	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26
5	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36	Rb 37	Sr 38
6	Y 39	Zr 40	Nb 41	Sn 50	Sb 51	Te 52	I 53	Xe 54	Cs 55	Ba 56	La 57	Ce 58
7	Pr 59	Nd 60	Pm 61	Yb 70	Lu 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78
8	Au 79	Hg 80	Tl 81	Fm 100	Md 101	No 102	Lr 103	Rf 104	Db 105	Sg 106	Bh 107	Hs 108
	Mt 109											

Mo 42	Te 43	Ru 44	Rh 45	Pd 46	Ag 47	Ca 48	In 49
Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69

Pb 82	Bi 83	Po 84	At 85	Rn 86	Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99