Problem Set 1

#1 (a)

Atomic orbitals are often named after the cartesian description of the angular part, obtained by transforming the spherical polar form.

Symbol	Angular function
s	no angular dependence
p_x	$\sin\theta\cos\phi$
p_y	$\sin\theta\sin\phi$
p_z	$\cos\theta$
$d_{3z^2-r^2}$ or d_{z^2}	$3\cos^2\theta-1$
$d_{x^2-y^2}$	$\sin^2\theta\cos 2\phi$
d_{xy}	$\sin^2\theta\sin 2\phi$
d_{xz}	$\sin\theta\cos\theta\cos\phi$
d_{yz}	$\sin\theta\cos\theta\sin\phi$
$f_{x(5x^2-3r^2)}$ or f_{x^3}	$\sin\theta\cos\phi(5\sin^2\theta\cos^2\phi-3)$
$f_{y(5y^2-3r^2)}$ or f_{y^3}	$\sin\theta\sin\phi(5\sin^2\theta\sin^2\phi-3)$
$f_{z(5z^2-3r^2)}$ or f_{z^3}	$5\cos^3\theta-3\cos\theta$
$f_{x(z^2-y^2)}$	$\sin\theta\cos\phi(\cos^2\theta-\sin^2\theta\sin^2\phi)$
$f_{y(z^2-x^2)}$	$\sin\theta\sin\phi(\cos^2\theta-\sin^2\theta\cos^2\phi)$
$f_{z(x^2-y^2)}$	$\sin^2\theta\cos\theta\cos 2\phi$
f_{xyz}	$\sin^2\theta\cos\theta\sin 2\phi$

ALREADY IN REAL FORM

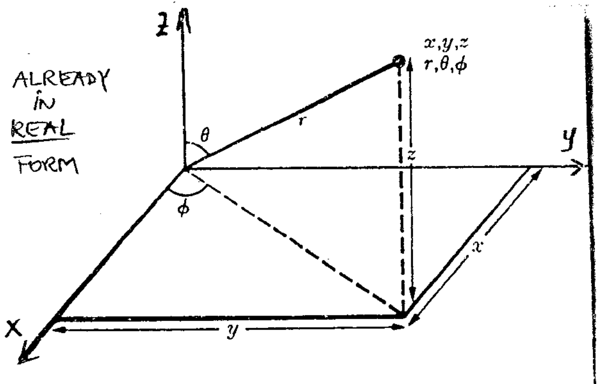


FIG. 11-2.1. The coordinate system for atomic orbitals.

Since in spherical coordinates

$$\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases},$$

we write the angular part of the 5 atomic orbitals as a function of the cartesian coordinates x, y & z

$$d_{xz} \Rightarrow \sin\theta\cos\theta\cos\phi = \underbrace{\sin\theta\cos\phi}_{x/r}\cdot\underbrace{\cos\theta}_{z/r} = \frac{xz}{r^2} \propto xz$$

$$d_{yz} \Rightarrow \sin\theta\cos\theta\sin\phi = \underbrace{\sin\theta\sin\phi}_{y/r}\,\underbrace{\cos\theta}_{z/r} = \frac{yz}{r^2} \propto yz$$

$$d_{xy} \Rightarrow \sin^2\theta\sin 2\phi = 2\sin\phi\cos\phi\sin^2\theta = 2\,\underbrace{\sin\theta\cos\phi}_{x/r}\,\underbrace{\sin\theta\sin\phi}_{y/r}$$

$$= \frac{2xy}{r^2} \propto xy$$

$$d_{x^2-y^2} = \sin^2\theta\cos 2\phi = \sin^2\theta\left[\cos^2\phi-\sin^2\phi\right] = \underbrace{(\sin\theta\cos\phi)^2}_{\left(\frac{x}{r}\right)^2} - \underbrace{(\sin\theta\sin\phi)^2}_{(y/r)^2}$$

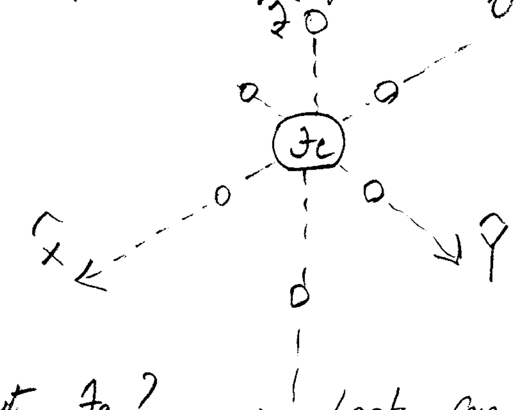
$$\propto x^2-y^2$$

$$d_{z^2} \text{ or } d_{2z^2-r^2} = 3\cos^2\theta-1 = 3\cos^2\theta-\cos^2\theta-\sin^2\theta = 2\,\underbrace{\cos^2\theta}_{(z/R)^2} - \underbrace{\sin^2\theta}_{\frac{(x^2+y^2)}{r^2}} \propto 2z^2-x^2-y^2$$

(b)

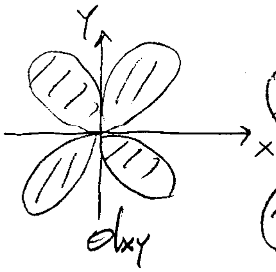
Here the main idea is to look for orbitals which overlapp the <u>most</u>. Overlapping of wave-function is in fact what the bonding is

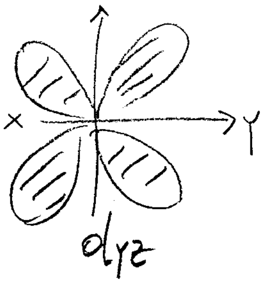
Now, if the Fe ion is sorrounded by 6 oxygen located @ ±x, ±y and ±z, the Fe ion will tend to form bonds along ±x, ±y and ±z, since these are the directions (and orientations) along which the 2p orbitals of the oxygen atoms are pointing towards

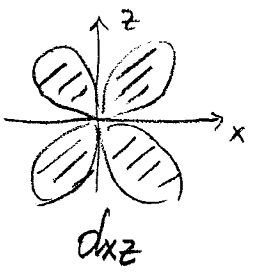


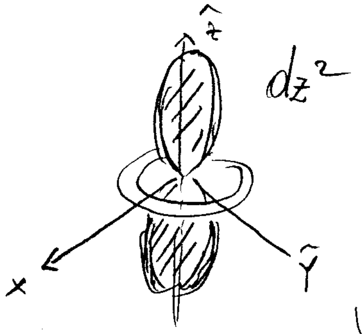
along $\hat{x}$ ⇒ p_x orbitals for oxygen
" $\hat{y}$ ⇒ p_y orbitals for oxygen
" $\hat{z}$ ⇒ p_z orbitals for oxygen

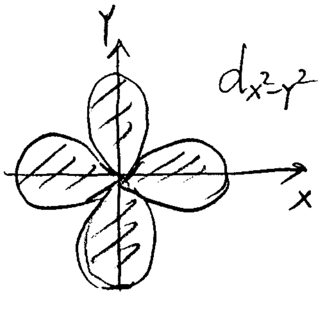
How about Fe? ⇒ Look for the orbitals which are directed mainly along $\hat{x}, \hat{y}$ and $\hat{z}$



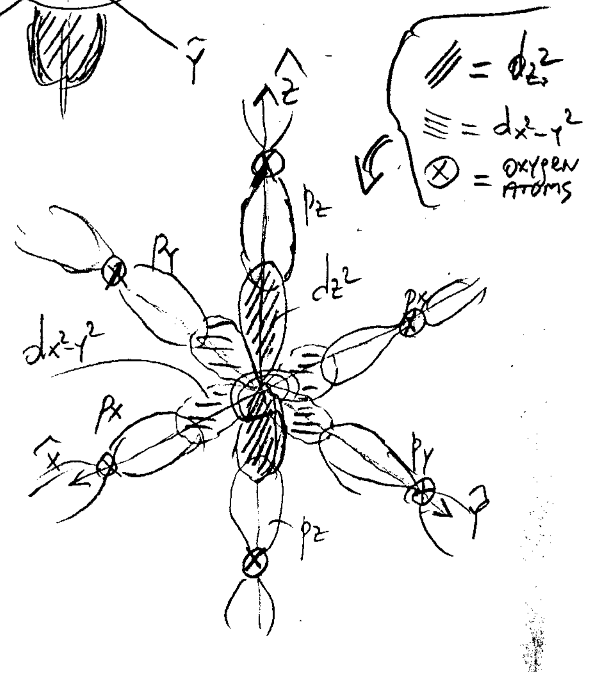








By inspection, the orbitals which points mostly towards $\underbrace{\hat{x}\ \hat{y}}_{d_{x^2-y^2}}$ and $\underbrace{\hat{z}}_{d_{z^2}}$ are



Problem # 2

The easiest way to approach the problem is To refer to the anti-symmetric property of a fermion wave function

Consider $\Psi(1,2)$, where by "1" we denote the set of quantum numbers for electron 1, "2"
" " " " " " 2

In other words $\Psi(\underbrace{\underbrace{r_1}_{\text{pos'n}}\underbrace{\omega_1}_{\text{spin}}}_{\text{elec 1}}, \underbrace{r_2\omega_2}_{\text{elec 2}})$

<u>ANTISYMMETRIC</u> MEANS $\Psi(1,2) = -\Psi(2,1)$ OR

$$\Psi(r_1\omega_1, r_2\omega_2) = -\Psi(r_2\omega_2, r_1\omega_1)$$

Now, if the two electron have the same spin and are in the same position, $\omega_1 = \omega_2 = \omega$, $r_1 = r_2 = r$ so that

$$\Psi(r_1\omega_1, r_2\omega_2) = -\Psi(r_2\omega_2, r_1\omega_1)$$ becomes

$$\Psi(r\omega, r\omega) = -\Psi(r\omega, r\omega) \Rightarrow \Psi = 0$$

This is more like a "proof" or a check for Pauli's principle. Full credit is given to who approached the problem in this way, but for a true understanding of the exchange interaction it may be instructive to look at the following derivation.

First, let's write the generic expression for the wavefunction (wf) of the 2 electrons making sure to satisfy the antisymmetry requirement (here we mean antisymmetric with respect to the interchange of the labels for electron 1 and 2)
This is accomplished by writing a Slater's determinant,

$$\Psi(1,2) = \underset{\substack{\uparrow \\ \text{normalization} \\ \text{coefficient}}}{\frac{1}{\sqrt{2}}} \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left\{ \chi_1(\underset{\substack{\text{electron} \\ 1}}{1})\, \chi_2(\underset{\substack{\text{elec.} \\ 2}}{2}) - \chi_2(\underset{\substack{\text{elec.} \\ 1}}{1})\, \chi_1(\underset{\substack{\text{elec.} \\ 2}}{2}) \right\}$$

__nb.__ : 1) The subscripts 1 & 2 denote two different sets of quantum numbers

2) Any determinant is invariant under transposing the matrix, or in other words, if you consider the transposed matrix $\begin{vmatrix} \chi_1(1) & \chi_1(2) \\ \chi_2(1) & \chi_2(2) \end{vmatrix}$, you still get the correct expression for the determinant.

__Step 2__ : The reason why we write χ is because we don't have to forget the spin.
χ is infact a spinor, meaning that it describes __both__ the spatial wf __and__ the spin of the electron.
the spin notation differs among the authors, you can use ↑↓, $m_s = \pm 1/2$, $\alpha(\omega)$ and $\beta(\omega)$, that's up to your preference.

If we denote by ω_1 and ω_2 the spin variables for electron 1 and 2 respectively, we can write

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \left\{ \psi_1(r_1)\alpha(\omega_1)\psi_2(r_2)\alpha(\omega_2) - \psi_2(r_1)\alpha(\omega_1)\psi_1(r_2)\alpha(\omega_2) \right\},$$

with the understanding that we already assigned the <u>Same</u> spin (α = up or DOWN) to <u>both</u> electrons

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<u>nb</u>: if you are not happy with this notation, you can write

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\left\{\psi_1(r_1)\begin{pmatrix}1\\0\end{pmatrix}_1 \psi_2(r_2)\begin{pmatrix}1\\0\end{pmatrix}_2 - \psi_2(r_1)\begin{pmatrix}1\\0\end{pmatrix}_1 \psi_1(r_2)\begin{pmatrix}1\\0\end{pmatrix}_2\right\} \Rightarrow \underset{\text{spin for elec 1}}{(\ )_1} \text{ and } \underset{\text{spin for elec 2}}{(\ )_2}$$

if you think $\underset{m_s = +1/2}{\alpha = \text{up}}$, or use $\begin{pmatrix}0\\1\end{pmatrix}$ if you think $\underset{m_s = -1/2}{\alpha = \text{down}}$

<u>Step 3</u> at this point you can complete the exercise in two different ways:

<u>method 1</u>: you can take $|\Psi(1,2)|^2 dr_1 dr_2$, but you must integrate (<u>i.e.</u> average) over the spin variables, that is

if $$\Psi(1,2) = \frac{1}{\sqrt{2}}\left\{\psi_1(r_1)\alpha(\omega_1)\psi_2(r_2)\alpha(\omega_2) - \psi_2(r_1)\alpha(\omega_1)\psi_1(r_2)\alpha(\omega_2)\right\}$$

$$P(r_1,r_2)dr_1dr_2 = \int d\omega_1 d\omega_2 |\Psi(1,2)|^2 dr_1 dr_2$$, with the integration to be performed only on the spin variables

Note that in general the ψ's are complex function, therefore care must be taken in evaluating $|\psi(1,2)|^2$

$|\psi(1,2)|^2 = \psi^*(1,2)\psi(1,2)$, so that

$$|\Psi(1,2)|^2 = \frac{1}{2}\Big\{\psi_1(r_1)\alpha(\omega_1)\psi_2(r_2)\alpha(\omega_2)\psi_1^*(r_1)\alpha^*(\omega_1)\psi_2^*(r_2)\alpha^*(\omega_2) +$$
$$+ \psi_2(r_1)\alpha(\omega_1)\psi_1(r_2)\alpha(\omega_2)\psi_2^*(r_1)\alpha^*(\omega_1)\psi_1^*(r_2)\alpha^*(\omega_2) - \psi_1(r_1)\alpha(\omega_1)\psi_2(r_2)\alpha(\omega_2)\psi_2^*(r_1)\alpha^*(\omega_1)\psi_1^*(r_2)\alpha^*(\omega_2)$$
$$- \psi_2(r_1)\alpha(\omega_1)\psi_1(r_2)\alpha(\omega_2)\psi_1^*(r_1)\alpha^*(\omega_1)\psi_2^*(r_2)\alpha^*(\omega_2)\Big\},$$

where we used the property of complex numbers according to which

$$|a-b|^2 = |a|^2 + |b|^2 - ab^* - ba^*$$

Now that you have the 4 terms, just integrate over the spin just recalling that

$$\langle\alpha|\alpha\rangle = \int d\omega\, \alpha^*(\omega)\alpha(\omega) = 1$$, paying attention not to mix the spin variables

Therefore, $P(r_1,r_2)\,dr_1 dr_2 = \int d\omega_1 d\omega_2 \, |\Psi(1,2)|^2 \, dr_1 dr_2$

The first term in the integration gives $|\psi_1(r_1)|^2 |\psi_2(r_2)|^2$, the second term gives $|\psi_2(r_1)|^2 |\psi_1(r_2)|^2$ the third gives $-\psi_1(r_1)\psi_2(r_2)\psi_2^*(r_1)\psi_1^*(r_2)$ the fourth one gives $-\psi_2(r_1)\psi_1(r_2)\psi_1^*(r_1)\psi_2^*(r_2)$, so that

$$P(r_1,r_2)\,dr_1 dr_2 = \frac{1}{2}\Big\{|\psi_1(r_1)|^2|\psi_2(r_2)|^2 + |\psi_2(r_1)|^2|\psi_1(r_2)|^2 - $$
$$- \left[\psi_1(r_1)\psi_2^*(r_1)\psi_2(r_2)\psi_1^*(r_2) + \psi_1^*(r_1)\psi_2(r_1)\psi_2^*(r_2)\psi_1(r_2)\right]\Big\}\, dr_1 dr_2$$

The term in the squared brakets makes the probability correlated, meaning that $P(r_1,r_2)$ is not given just by products of independent probabilities expressed as $|\psi|^2$

Evaluating now $P(r_1,r_2)$ with $\underbrace{r_1 = r_2}_{\text{i.e. same position}}$ we get $P(r,r)\,dr_1 dr_2 = 0$ cvd,

// —————————————— //

method 2

one of the basic postulates of QM states that if you have a QM. STATE $|\psi\rangle$ and want to find the probabilities that a certain observable A has values between a and $a+da$, you must calculate $\Rightarrow da\,|\langle a|\psi\rangle|^2$

in our case, A is the position and spin of the qm particle

example: if $A \equiv x$, position, $P(x)dx = |\langle x|\psi\rangle|^2 dx = |\psi(x)|^2 dx$

in this case the problem requires to be carefull because of the presence of the spin.

In this case $P(r_1,r_2)\,dr_1 dr_2 = \Big\{\underbrace{\iint |\langle r_1\omega_1, r_2\omega_2|\Psi(1,2)\rangle|^2 d\omega_1 d\omega_2}_{\text{integration over spin only}}\Big\}\, dr_1 dr_2$

therefore you have to take the state $\Psi(1,2)$ and project it onto the spin eigenvectors, and then $| \; |^2$ and sum.

Take for ex,

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \left\{ \underbrace{\psi_1(r_1)\uparrow}_{\text{elec } 1} \; \underbrace{\psi_2(r_2)\uparrow}_{\text{elec } 2} - \underbrace{\psi_2(r_1)\uparrow}_{\text{elec } 1} \; \underbrace{\psi_1(r_2)\uparrow}_{\text{elec } 2} \right\}$$

where elect. 1 and 2 have the <u>same</u> spin (can be $\downarrow$, doesn't matter)

Projecting onto the $\downarrow$ STATE gives you ZERO, while projecting onto the $\uparrow$ state (for <u>both</u> spins!) gives you

$$\frac{1}{\sqrt{2}} \left\{ \psi_1(r_1)\psi_2(r_2) - \psi_2(r_1)\psi_1(r_2) \right\}$$

At this point take $| \; |^2$ and get the same expression as before ...

<u>nb</u>: we want to note that writing <u>without</u> taking account the spin $\left| \frac{1}{\sqrt{2}} \left\{ \psi_1(r_1)\psi_2(r_2) - \psi_2(r_1)\psi_1(r_2) \right\} \right|^2$ does not give you a general correct answer.
In fact, as an exercise, consider the same problem, this time allowing <u>different</u> spins.
In this case,

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \left\{ \psi_1(r_1)\alpha(\omega_1)\psi_2(r_2)\beta(\omega_2) - \psi_1(r_2)\alpha(\omega_2)\psi_2(r_1)\beta(\omega_1) \right\} \quad \text{OR}$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \left\{ \underbrace{\psi_1(r_1)\uparrow}_{\text{elec } 1} \; \underbrace{\psi_2(r_2)\downarrow}_{\text{elec } 2} - \underbrace{\psi_1(r_2)\uparrow}_{\text{elec } 2} \; \underbrace{\psi_2(r_1)\downarrow}_{\text{elec } 1} \right\}$$

project now onto the spin states; there are 4 cases:
$\uparrow\uparrow$, $\downarrow\downarrow$, $\uparrow\downarrow$, $\downarrow\uparrow$

$$\therefore \quad P(r_1,r_2)\,dr_1 dr_2 = \int d\omega_1 d\omega_2 \left|\langle r_1\omega_1 r_2\omega_2 | \Psi(1,2)\rangle\right|^2 dr_1 dr_2 =$$

$$\left\{ \left|\langle \uparrow\downarrow | \Psi(1,2)\rangle\right|^2 + \left|\langle \downarrow\uparrow | \Psi(1,2)\rangle\right|^2 \right\} dr_1 dr_2 =$$

$$= \frac{1}{2}|\psi_1(r_1)|^2|\psi_2(r_2)|^2 + \frac{1}{2}|\psi_2(r_1)|^2|\psi_1(r_2)|^2$$

Take now $r_1 = r_2$ $\Rightarrow$

$$P(r,r)\,dr_1 dr_2 = \frac{1}{2}\left[|\psi_1(r)|^2|\psi_2(r)|^2 + |\psi_2(r)|^2|\psi_1(r)|^2\right]$$

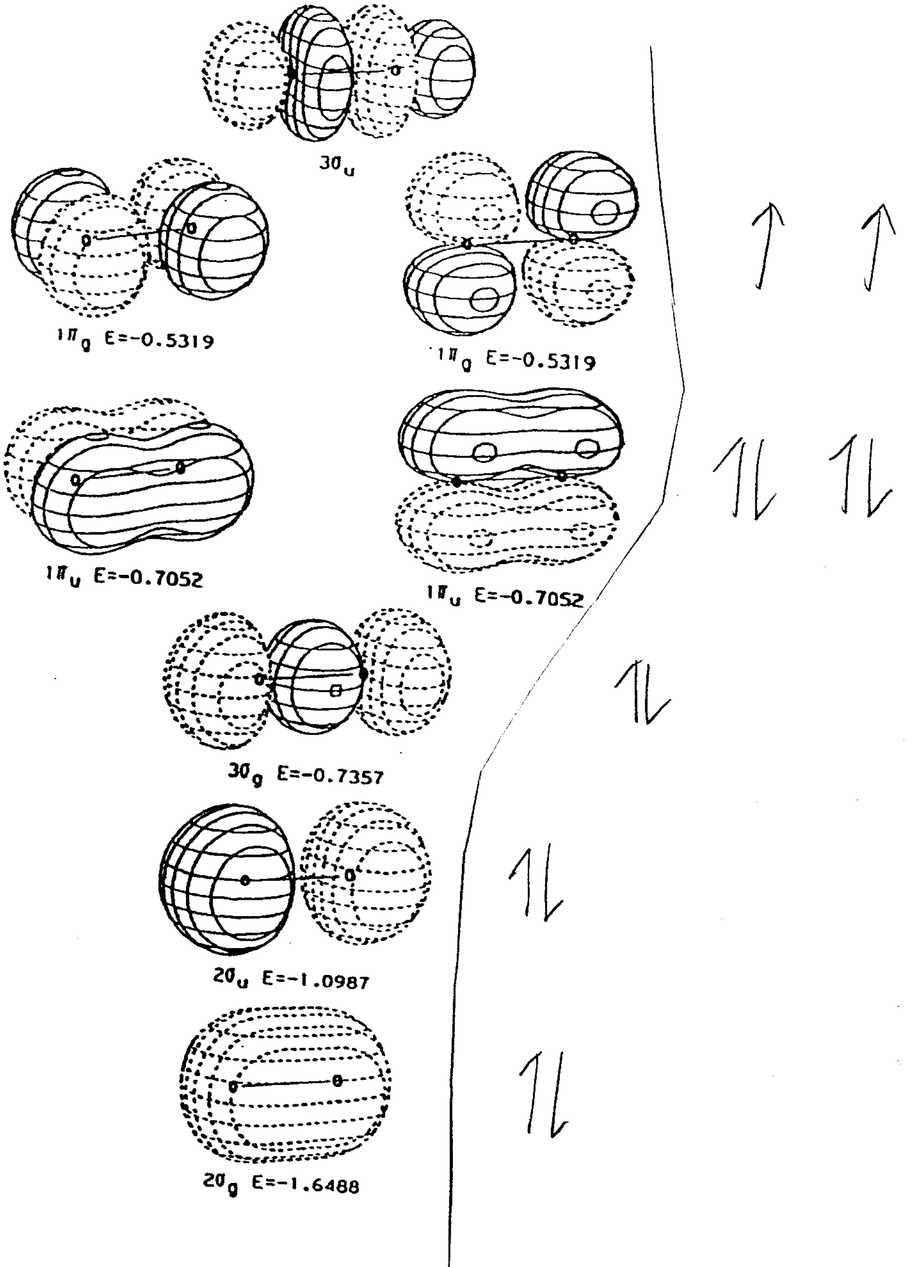
$$= |\psi_1(r)|^2|\psi_2(r)|^2 \neq 0 \Longrightarrow$$ Finite probability of finding two e's with opposite spin @ the same point in space

also note that in this case the probabilities are NOT correlated or, in other words, the fact that the probabilities are expressed as $|\psi|^2$ means that electron 1 "doesn't care" of what electron 2 does and viceversa.

Problem # 3

The electron configuration for the O_2 molecule is :

$$\underbrace{1S_A^2\ 1S_B^2}_{\text{CORE ELECTRONS}}\quad 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^2$$



+ CORE e⁻'s

In order to make the system stable, each orbital must have the same number of electrons, that's what dictates the filling order of the molecular orbitals.

The outermost energy levels, ($\pi_g 2p$), must accomodate 2 electrons (there are two $1\pi_g$ orbitals).

Since the two orbitals have different positions, the electrons can have the same spin or a different one.

Now the question is : do they prefer to have the same spin or not ?

→ YES! ⇒ in fact, if you read the text of ⇒ problem # 2, you'll find "energy LOWERING exchange interactions"

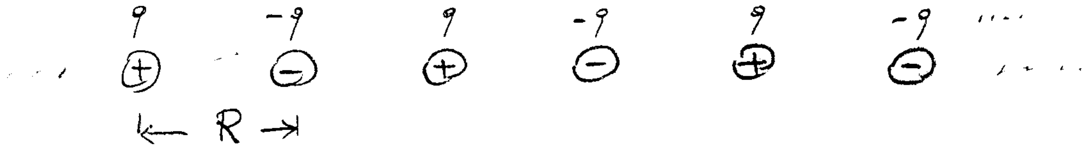
Electrons like to have the same spin and be away from each other, in order to minimize the Coulomb repulsion

↑ ↑ has a lower energy than

↑ ↓

This is also why in Transition metals, where you have 3d shells open, the spins tend to align parallel to each other ⇒ MAGNETISM

#4



Taking any arbitrary ion as a refrence,
The expression for the Madelung constant is

$$M = \sum_{i=1}^{\infty} \frac{(\pm)\, n_i}{\alpha_i},$$

where n_i is the number of ions located at a distance $r_i = \alpha_i R$ from the reference, R is the smallest distance between two ions.

For this particular case, n_i is always 2 and $\alpha_i = 1, 2, 3, \dots, n, \dots$

Therefore we have

$$M = \sum_i \frac{(\pm)\, n_i}{\alpha_i} = 2 \sum_i \frac{(\pm 1)}{\alpha_i} = 2\left\{ \frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right\}$$

where we took $n_i = 2$ outside the summation since it is a constant

The series in the curly brakets is equal to ln2
In fact, $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$
so taking $x = 1$ proves our statement.

Remarks : note that the Madelung constant is characteristic of the crystalline structure (ions arrangment, in this case), and it does not depend on the distance between the ions.
The Madelung constant is positive, since the Coulomb energy of a crystalline arrangement of 2N ions is written as
$E = -\frac{Ne^2}{R} M$, and it is negative $\Rightarrow$ Cohesion

The Madelung constant is a number, does not have dimensions!

#5 1.14(a)

$$\frac{dE}{dr} = \frac{d}{dr}\left(N\frac{A}{R^n} - N\frac{\alpha e^2}{4\pi\varepsilon_0 R} \right) =$$

$$= -\cancel{N} n \frac{A}{R^{n+1}} + \cancel{N}\frac{\alpha e^2}{4\pi\varepsilon_0 R^2} = 0 \Rightarrow$$

$$\Rightarrow \quad R^{n-1} = \frac{4\pi\varepsilon_0 n A}{\alpha e^2}$$

b)

$$R^n = \frac{4\pi\varepsilon_0 n A}{\alpha e^2} R$$

$$E = N\cancel{A}\frac{\alpha e^2}{4\pi\varepsilon_0 n \cancel{A} R} - N\frac{\alpha e^2}{4\pi\varepsilon_0 R} = \frac{\alpha e^2 N}{4\pi\varepsilon_0 R}\left(\frac{1}{n} - 1\right)$$

c)

$$\frac{4\pi\varepsilon_0 R E}{\alpha e^2 N} = \frac{1}{n} - 1 \quad \Rightarrow \quad \frac{4\pi\varepsilon_0 R}{\alpha e^2}\cdot\frac{E}{N} + 1 = \frac{1}{n} \Rightarrow$$

$$\Rightarrow \quad n = \left(1 + \frac{4\pi\varepsilon_0 R}{\alpha e^2}\cdot\frac{E}{N} \right)^{-1} \approx \qquad \left(E<0,\ R=\frac{a}{2}\right)$$

R from Table 1.2

$$\approx 9$$

Error in Omar, 1.83 kcal/mole Should be 183.3 kcal/mole, So using 7.95 eV/molecule is necessary to get the correct exponent. The other gives a ridiculous no. like 1.4 x 10^{-38}!!