# Week 8 Discussion Notes

## § Electron Configurations

Particles can have either 1/2 integer spin (1/2, 3/2, 5/2, etc) or integer spin (0, 1, 2, ...). We call the first type Fermions and Bosons have integer spin

Spin = 1/2, 3/2, 5/2 Fermions  Spin = 1, 2, .. Bosons

$e^-$ have spin 1/2 (recall last time). Now what this means is that a wavefunction that describes many electrons

$$\Psi(\vec{r}_1, \vec{r}_2) \qquad \vec{r}_i = (x, y, z, \sigma)$$

(x, y, z: spatial; $\sigma$: spin)

must be antisymmetric upon interchange of particles

$$\Psi(\vec{r}_1, \vec{r}_2) = -\Psi(\vec{r}_2, \vec{r}_1)$$

This is why Slater determinants are often used. Now, this antisymmetry forces no 2 electrons to have the same quantum numbers. Something fundamental.

Pauli Exclusion Principle: No two identical Fermions may have the same set of quantum numbers.

Begins to piece together how we can think of multi electron wavefunctions / build electron configurations. We also need:

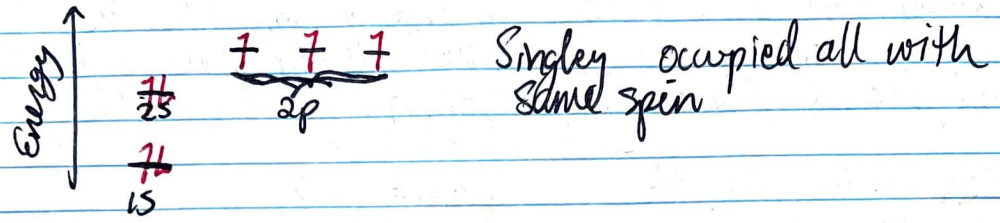
Aufbau Principle: lowest energy orbitals are filled 1st

Note: Not necessarily lowest "n"-value orbital. We fill the 4s before 3d since it is lower in energy.

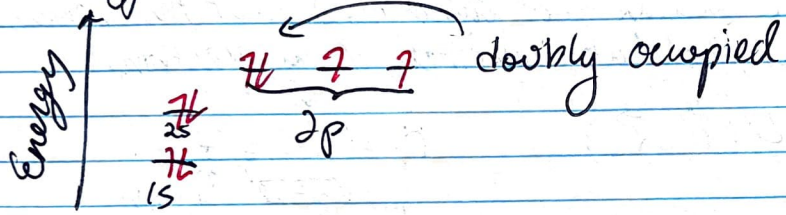
Hunds Rule: Prefer singly occupied orbitals first, with same spin to maximize angular momentum. Only after all orbitals are singly occupied do we begin to doubly occupy.

Let look at some examples

Ex: Nitrogen $Z=7 \Rightarrow$ 7 electrons

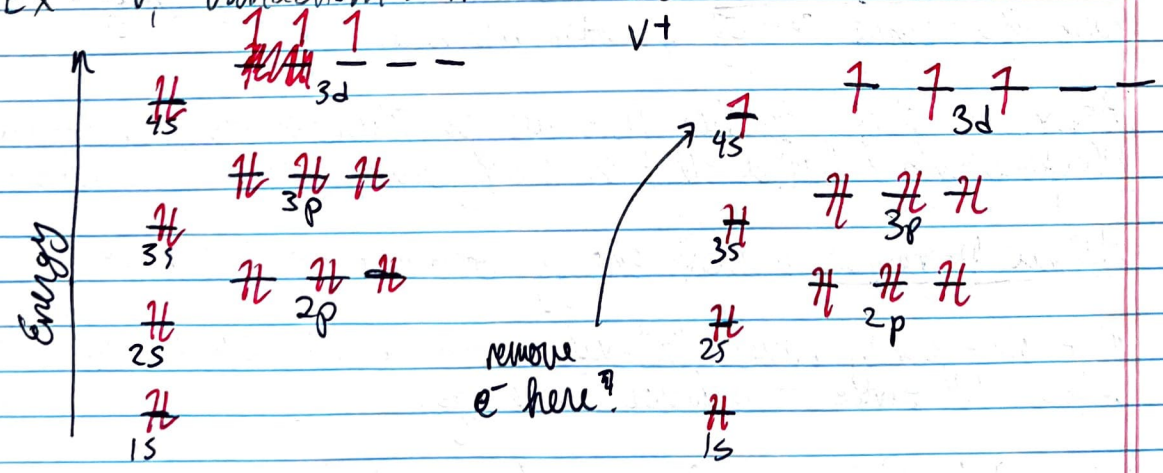



Ex: Oxygen $Z=8 \Rightarrow$ 8 electrons




Now we do have to deal with cations a bit differently. We will remove $e^-$ from the highest $n$ orbital first (since these $e^-$ are farther away from the nucleus). This does not always correspond with highest energy orbitals!

Ex: V, Vanadium. Atomic # 23.




Where would we remove the electron if we wanted $V^{2+}$? Can we write the noble gas configuration of these?

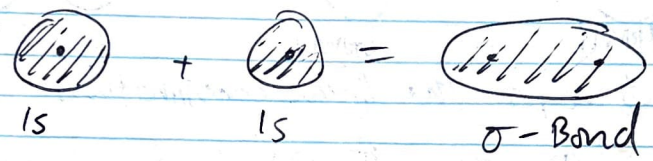
$V = [Ar]\, 4s^2 3d^3$ $\quad V^+ = [Ar]\, 4s^1 3d^3$

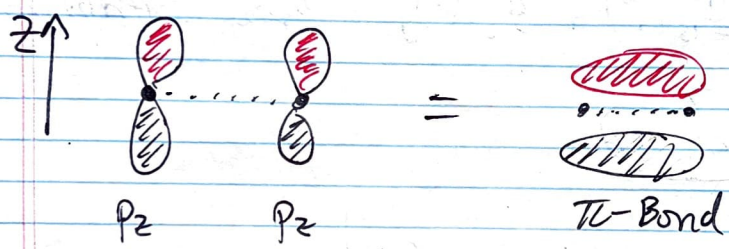
## § Bonding

σ- Bond: increased ρ (electron density) along the internuclear axis

π- Bond: increased electron density above & below the internuclear axis

Ex:



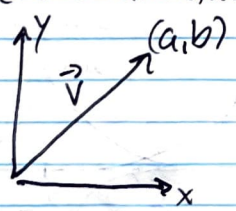

Lets look at practice problem 7 of the worksheet.

All of this leads nicely into the idea of linear combination of Atomic Orbitals to form Molecular orbitals

What is a linear combination? Can be thought of as a superposition. More generally it is something of the form

$$\sum_{?} a_i v_i$$

where the $a_i$ are called scalars, or coefficients, and the $v_i$ are called vectors (typically). Most common type of linear combination is a general vector




$$\vec{v} = \begin{bmatrix} a \\ b \end{bmatrix} = a\hat{e}_1 + b\hat{e}_2$$
$$= a\hat{i} + b\hat{j}$$

We can extend this notion to functions as well?

Say $\Psi_{1s}(\vec{r})$ is a 1s orbital centered on atom 1

$\tilde{\Psi}_{1s}(\vec{r})$ is a 1s orbital centered on atom 2

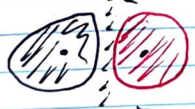
Now, lets adjust the linear combination

$\frac{1}{\sqrt{2}}\left[\Psi_{1s}(\vec{r}) + \tilde{\Psi}_{1s}(\vec{r})\right]$ equal contributions

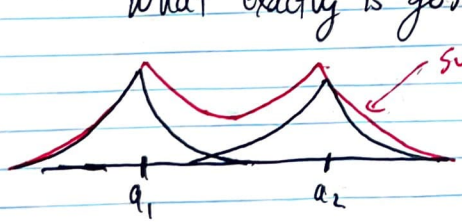
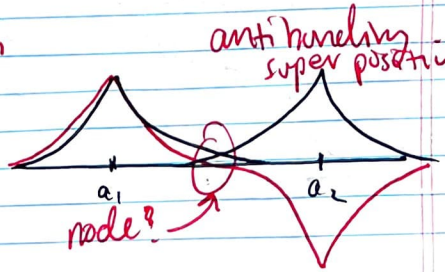
$\frac{1}{\sqrt{17}}\left[4\Psi_{1s}(\vec{r}) + \tilde{\Psi}_{1s}(\vec{r})\right]$

Heavily weighted towards the atom 1.

What if we introduce a negative sign?




$\frac{1}{\sqrt{2}}\left[\Psi_{1s}(\vec{r}) - \tilde{\Psi}_{1s}(\vec{r})\right]$

This is what constitutes an antibonding orbital?
A decrease in electron density between the 2 atoms.

What exactly is going on