S13102 Photobiochemistry

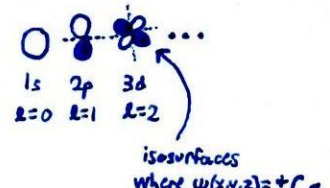
L1: Quantization and Structure

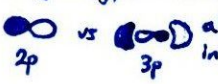
1. Atoms, molecules and extended solids are equipped with a structure much like the shelves in a kitchen or library: an array of different levels for electrons to occupy, ordered by "height" (increasing energy).

i. For the simplest species, H_2^+ with ground state (lowest-energy) configuration $[1s^1]$, possible ways for the electron to orbit the nucleus make up the familiar set of s, p, d, f... "orbitals" with characteristic shapes and orientations that pop out when certain quantum numbers (n, ℓ, m_ℓ) are inserted into the underlying equation for ψ, a mathematical "wavefunction" for the sole electron.

(unpaired electron or "radical"; singly occupied is)

- n: indicates increasing energy and extension outward from nucleus
- ℓ: shape; = # of nodes or zeroes that cut the function (angular nodes)
- m_ℓ: orientation in space, $m_\ell = -\ell, -\ell+1, \ldots, \ell-1, \ell$





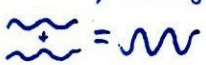
along with $(n-\ell-1)$ internal "radial" nodes

isosurfaces where $\psi(x,y,z) = \pm C$ (some constant number value)

ii. ψ says everything there is to know about a certain electron; its energy, its average location and momentum, etc. It is rarely calculable exactly and cannot be directly measured – it is a function $\psi(x,y,z,t)$ of both 3D position and time that outputs complex pure numbers which can have an imaginary part.

a. $|\psi^2|$ is identified with the probability that an electron is at some place at some time.

b. Traditionally, the color that graphical depictions of ψ are shaded with is an indication of the phase, which controls how they add together, like ordinary waves.



1D cosine waves in phase sum to bigger wave

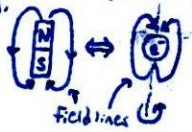
1D cosine waves out of phase (π radian shift) cancel out

c. Two electrons cannot share one state ψ. (Pauli exclusion principle)

A fourth number m_s is present, corresponding to the alignment of the "spin" of an electron, as an additional degree of freedom allowing two electrons to pair up in one orbital, schematically depicted $\uparrow\downarrow$.

The "spin" is an intrinsic property of the e^- making it act as though it is always rotating on its axis in addition to orbiting the nucleus, generating a small magnetic field.

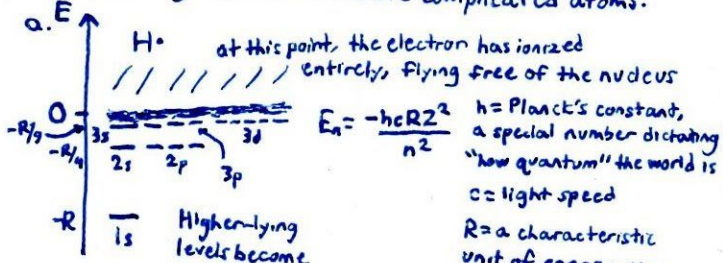
"spin up" $m_s = \frac{1}{2}$
"spin down" $m_s = -\frac{1}{2}$



d. For ψ which rigorously have a defined energy, E, their shapes do not change with time and these are "stationary states". All proper orbitals are such states.

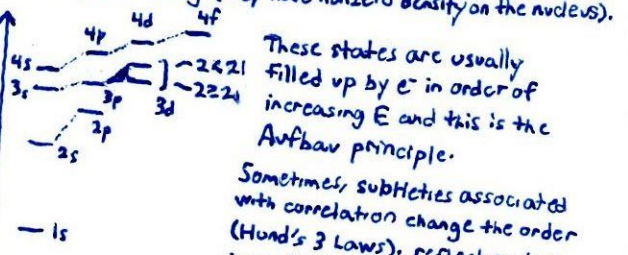
iii. Electrons repel each other, an unfavorable interaction that leads them to try to avoid each other (this dance is called correlation). So for multi-electron atoms, the hydrogenic orbitals perfectly valid for H· are not precisely accurate, as they do not incorporate this effect; really, there should be a many-body $\psi(x_1, y_1, z_1, \ldots, x_n, y_n, z_n, t)$ and separating the electrons into individual orbitals is an approximation ignoring their collective motion. Often, however, it is very valid to use hydrogen-like ψ for describing heavier and more complicated atoms.

a.



Higher-lying levels become quite densely packed up until the energy 0, defined to be an unbound e^-. Below it are "bound" orbitals.

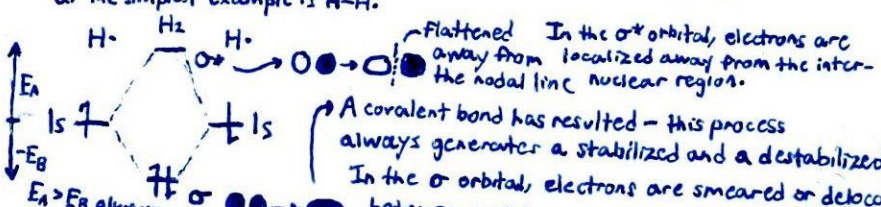
b. For a multielectron atom, however, single electrons can be considered to move in an environment consisting of the nucleus and the smeared-out average negative charge from the other e^-. This allows the return of the orbital model, except now different ℓ-states differ in their energies because they are differently shielded from the nuclear charge by other e^- clouds, which they penetrate to varying degrees. Roughly, $ns < np < nd < nf$ in E as s-orbitals are most core-penetrating (they have nonzero density on the nucleus).



Sometimes, subtleties associated with correlation change the order (Hund's 3 Laws), reflecting the imperfection of this approximation.

iv. The addition and subtraction of atomic orbitals (AOs) produces molecular orbitals (MOs), which are one-electron states of a multi-nuclear system. This is bonding and antibonding from wave interaction.

a. The simplest example is H–H.



Flattened away from the internodal line

In the σ^* orbital, electrons are localized away from the internuclear region.

A covalent bond has resulted – this process always generates a stabilized and a destabilized MO.

In the σ orbital, electrons are smeared or delocalized between nuclei.

$E_A > E_B$ always

The antibond is more destabilized than the bonding orbital is stabilized. If two e^- would be introduced, the molecule would prefer to blow apart.

b. Delocalization is inherently stabilizing because of Heisenberg's uncertainty principle (formally, $\Delta x \Delta p \geq \frac{h}{4\pi}$). The more smeared out a particle, the higher its positional uncertainty Δx and the lower its momentum uncertainty Δp. Consequently the chance that an e^- is moving very fast declines and its kinetic energy is lower on average (stabilizing).

This is part of why electrons do not collapse into nuclei. It would localize them too much.

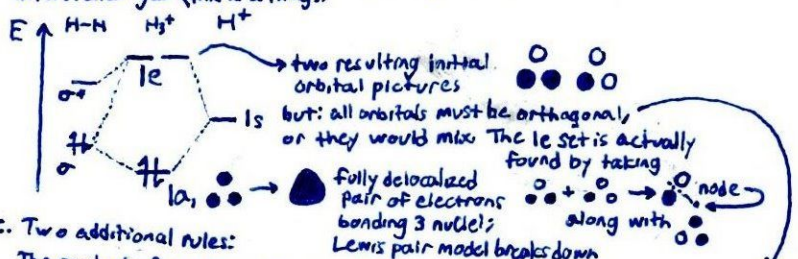
L1.

Key takeaway:

By understanding overlap, relative energies and the combination of atoms of small molecules, almost any MO problem can be reduced to interacting two sets of orbitals and real molecules can be derived.

v. This approach readily extends to more complicated examples. The key is to apply the fact that the gaps in energy produced by orbital mixing are larger when orbitals overlap to a large extent in space and are similar in energy to begin with (prior to considering their interaction).

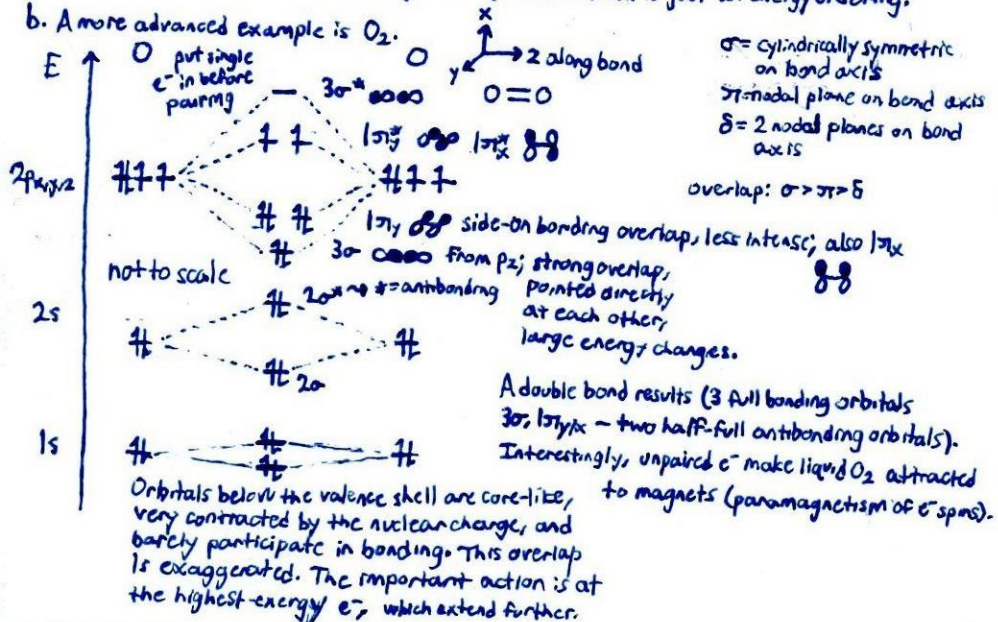
a. Adding a proton (H^+) to H_2 produces $\left[\begin{smallmatrix} H \\ H-H \end{smallmatrix}\right]^+$, found in interstellar gas (this is a thing).



α. Two additional rules:
The product of any two orbitals, added up over all space, must be 0. [orthogonality]
$|\psi^2|$ added up over all space must equal 1. So ψ_σ of H_2 is not $\psi_{1s}(\text{left H}) + \psi_{1s}(\text{right H})$. It's $\approx \frac{1}{\sqrt{2}}(\psi_{1s}(L) + \psi_{1s}(R))$, which avoids pulling extra e^- from thin air when the orbital is described. $\left(\left(\frac{1}{\sqrt{2}}\right)^2 + \left(\frac{1}{\sqrt{2}}\right)^2 = 1\right)$

β. Orbitals are given labels (σ, π, δ if characterized completely by how their shape relates to a bond axis, various labels like e, a_{1g}, t_{2g} which are a notation describing fundamental aspects of their shape and symmetry). Fully describing this is the bulk of an advanced semester course. For our purposes it is enough to know that two orbitals must have the same label to mix, but having the same label does not guarantee there will be any advantage to mixing. The H in front is just an energy ordering.

b. A more advanced example is O_2.



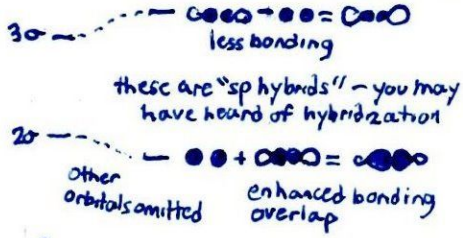
σ = cylindrically symmetric on bond axis
π = nodal plane on bond axis
δ = 2 nodal planes on bond axis

overlap: σ > π > δ

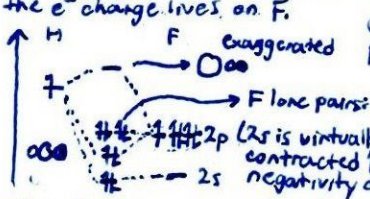
A double bond results (3 full bonding orbitals 3σ, $1\pi_{y/x}$ – two half-full antibonding orbitals). Interestingly, unpaired e^- make liquid O_2 attracted to magnets (paramagnetism of e^- spins).

Orbitals below the valence shell are core-like, very contracted by the nuclear charge, and barely participate in bonding. This overlap is exaggerated. The important action is at the highest-energy e^-, which extend further.

c. Actually, there is a symmetry-allowed possibility of mixing 2σ with 3σ and $2\sigma^*$ with $3\sigma^*$. For O and F the s/p energy separation (these orbitals have s and p parentage respectively) is too large, but for the other diatomics it occurs and raises 3σ above the π set.

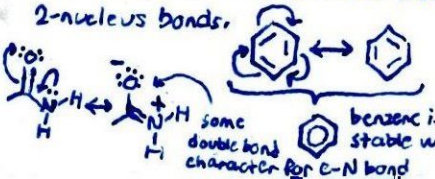


d. HF is a very polarized molecule where most of the e^- charge lives on F.



Orbitals look more like the parent orbitals near them in energy. Notice that the bond is weighted heavily on F, but the antibonding puts e^- in a disfavored position (high weight on H).

e. Resonance structures are in some sense an attempt to recapture the inherently delocalized nature of e^- in MO theory with a Lewis picture of lone pairs and 2-e^- 2-nucleus bonds.



↗ = formal, not literal, movement of 2 e^-
↿ = 1 e^- movement (e.g. radicals)

} "arrow pushing" used to describe bond forming and bond breaking processes in organic chemistry