Example 2
   OPCl$_3$

   A-central atom
(there are two odd ones, but the least electronegative
one is the central atom)

O	6e⁻		6e⁻
P	5e⁻		5e⁻
Cl	7e⁻ x 3	=	21e⁻
			32e⁻

O   6e⁻   6e⁻
P   5e⁻   5e⁻
Cl   7e⁻ x 3   =   <u>21e⁻</u>
                        32e⁻

$$:\ddot{O}: $$

$$:\ddot{Cl}—P—\ddot{Cl}:$$

$$:\ddot{Cl}:$$
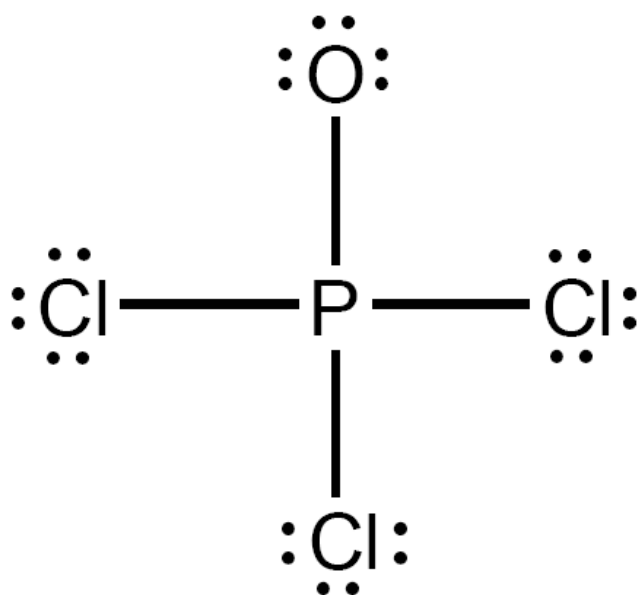
P usually has 8e⁻
or 10e⁻ around
the central atom

Lewis Structure
(a possible one that works but you need to check it)

2) occupancy factor

   $OPCl_3$ AB_3B'
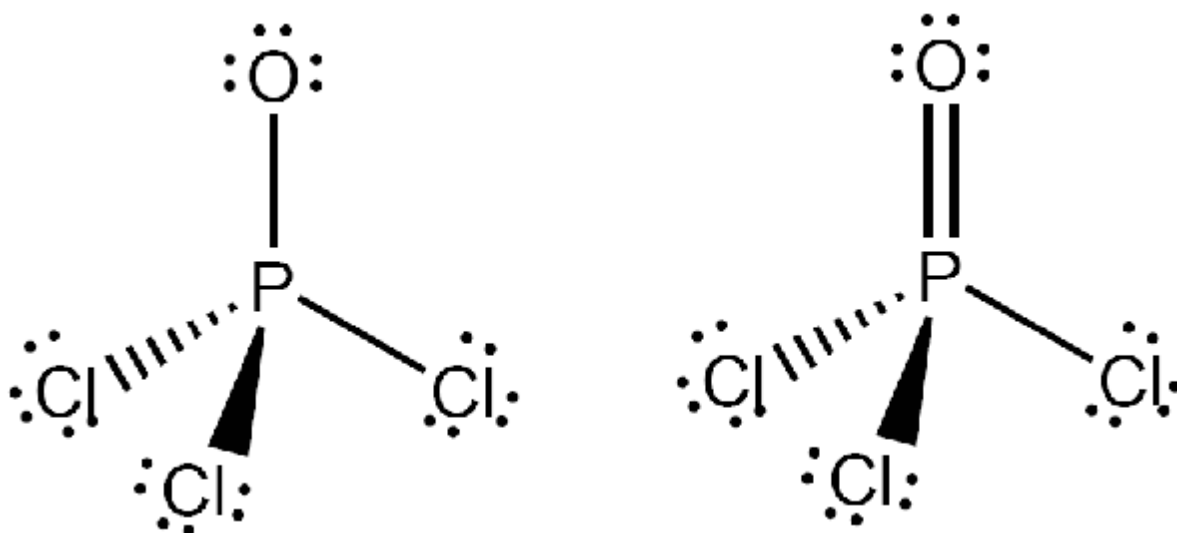
   $(x+y) = 4$

3) for an occupancy factor of 4, sp^3 works well for P

4) VSEPR predicts tetrahedral

*<u>formal charge</u> is often invoked to help choose the correct Lewis Structure. It works sometimes, but it is not always accurate.

Why?

Because it <u>assumes</u> that all <u>atoms</u> <u>have</u> the <u>same EN</u>.

Do formal charge calculation on the above two structures. Which one is the best structure?

Q. Does formal charge ever fail to make sense?

A. Yes!   Look at CO

Lewis structure of CO
C   4e⁻
O   6e⁻   = 10 valence e⁻

:C≡O: is the only way to have a
complete octet (1 σ, 2π bonds)

Formal Charge $\overset{-1}{:}C \equiv \overset{+1}{O}:$ but O is more
                                                                E.N. than C!

This formal charge implies a huge dipole moment

$$:C \equiv O:$$
$$\longleftarrow +$$

but, in fact, CO has one of the smallest dipole
moments of any molecule (0.12 Debye units)

Bond lengths and Covalent radii

Covalent radius

In X-X molecules, if the bond distance is 1.988 A° as it is for C1 – C1, the underline covalent bonding radius would be ½ of this number.

Table 3-2 on page 97. (in A°)

H 0.28	C 0.77	N 0.70	O 0.66	F 0.64
	Si 1.77	P 1.10	S 1.04	Cl 0.99
	Ge 1.22	As 1.21	1.17	Br 1.14
	Sh 1.40	Sb 1.41	1.37	I 1.33

These were obtained in a similar manner to Cl-Cl.

From this table, then, we can predict bond lengths:

C-Si   0.77 + 1.17   =   1.94 A°
                                (1.87 A°) experiment
P-Cl   1.10 + 0.99   =   2.09 A°
                                (2.04 A°) experiment
Etc.,

- <u>Multiple Bonds</u> are <u>shorter</u> than single bonds:
    N≡N (1.10 A˚)
    N=N (1.25 A˚)
    N-N (1.45 A˚)

- also <u>hybridization affects covalent radii</u>
s orbitals have better overlap at short distances so
the bonds get shorter with more s orbital character

<u>van der Waals Radii</u>
These are not covalent or ionic
These distances are the closest approach between
atoms that are not bonded. Occurs in the liquid and
solid states. There is a limit of contact based on
repulsive forces.

Table 3-3

Table 3-3 van der Waals Radii of Nonmetallic Atoms (in Å)

H	1.1–1.3					He	1.40
N	1.5	O	1.40	F	1.35	Ne	1.54
P	1.9	S	1.85	Cl	1.80	Ar	1.92
As	2.0	Se	2.00	Br	1.95	Kr	1.98
Sb	2.2	Te	2.20	I	2.15	Xe	2.18

Radius of a methyl group, 2.0 Å
Half-thickness of an aromatic ring, 1.85 Å

The van der Waals distances values reflect a combination of attractive <u>and</u> repulsive forces.

Three contributions:

a) Dipole ···· Dipole
b) Dipole ···· Induced dipole
c) Fluctuating dipoles or London Forces

Delocalized Bonding
Molecular Orbital Theory

Main aspects:

(1) bonds exist when orbitals on different atoms overlap so as to concentrate electron density between the atoms

(2) electron density and not electron pairs is emphasized

(3) allows for three types of orbital overlap:
   (a) positive overlap – bonding
   (b) negative overlap – antibonding
   (c) zero overlap - nonbonding

1.40
1.54
1.92
1.98
2.18

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Example

Positive overlap

$s + s$

$p_z + s$

$p_x + p_x$

$d_{zx} + p_x$

Negative overlap

$p_z + p_z$

$-p_z + s$

$p_x - p_x$

$d_{zx} - p_x$

Zero overlap

s p_x or p_y

s d_{xy}

p_y $d_{x^2 - y^2}$

p_x p_y

Figure 3-15   Some common types of orbital interaction leading to positive, negative, and zero overlap.

Consider H_2^+ Molecule

$1e^-$

Two ways to describe overlap (which is proportional to $(e^-$ density$)^2$)

(1) Simple "sum of the squares" of the atomic orbitals

or

(2) "Square of the sums" of the atomic orbitals

Localized versus Molecular Orbital approach

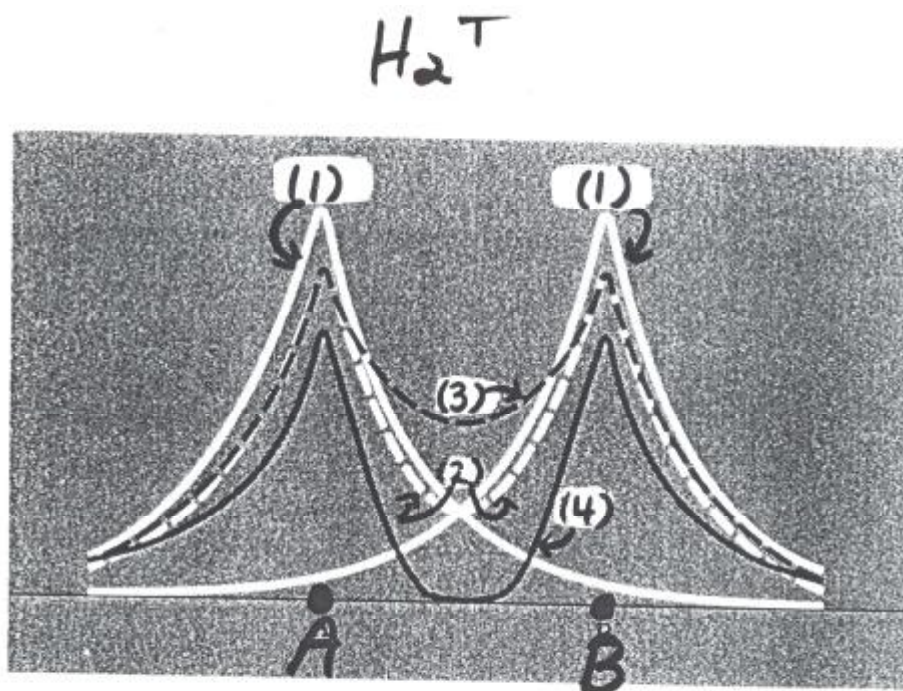Φ_A Φ_B Atomic wavefunctions
For H 1s orbitals

Φ_A^2 Φ_B^2 Squares of the wavefunctions
are proportional to overlap

Bonding then is either proportional to
(1) $(\Phi_A^2 + \Phi_B^2)/2$ or
(2) $(\Phi_A + \Phi_B)^2/2$ à $\Phi_A^2 + \Phi_A \Phi_B + \Phi_B^2$

(2) is > (1) by $\Phi_A \Phi_B$

H_2^+

These plots depict the electron density in the region of space between atoms A and B

Atomic Orbitals   (1) white curves are individual atomic wavefunctions Φ_A, Φ_B

Localized Bonding   (2) dotted white curve represents the "sum of the squares" $\Phi_A{}^2 + \Phi_B{}^2/2$
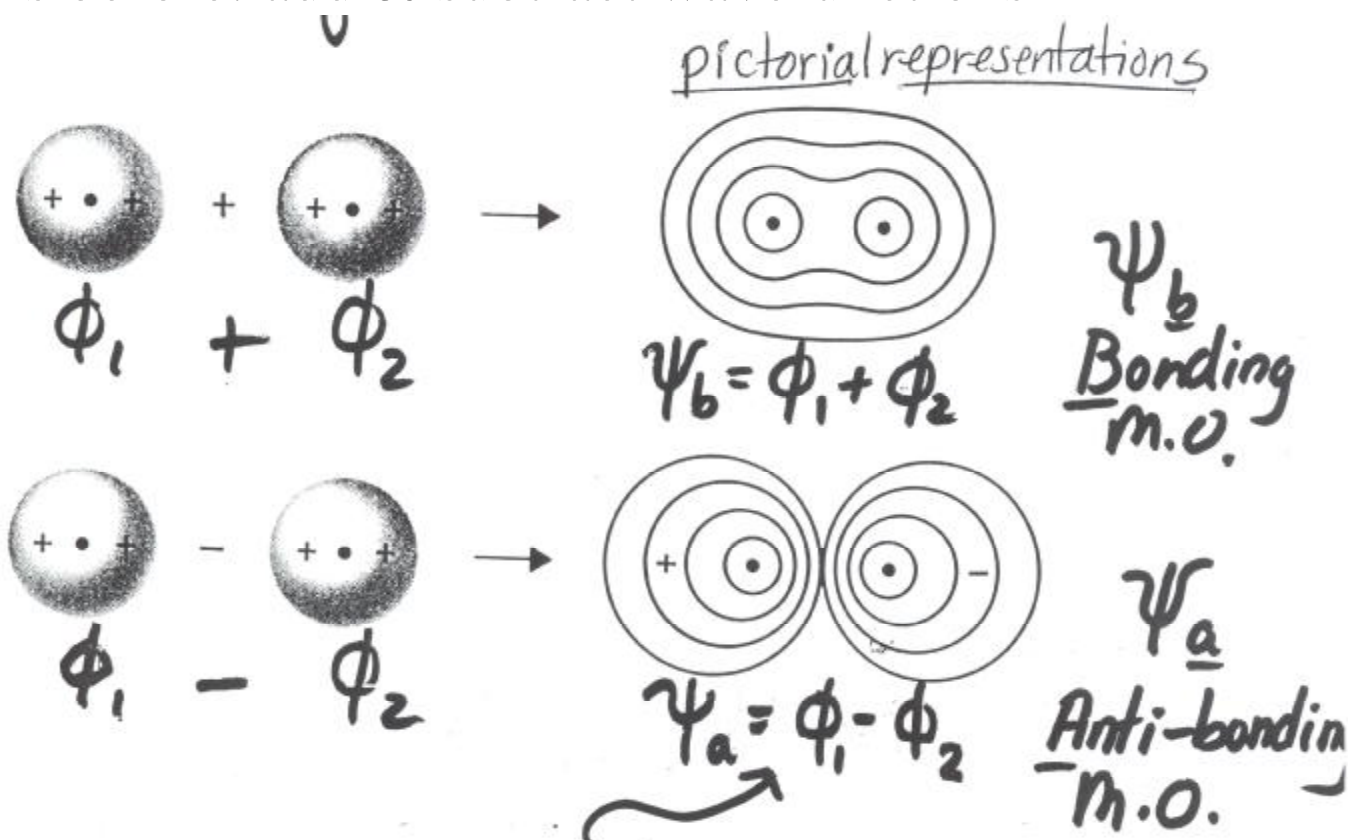
M.O. Bonding   (3) dotted black curve represents the "square of the sum" of $\Phi_A + \Phi_B$ namely, $(\Phi_A + \Phi_B)^2/2$

M.O. Antibonding   (4) solid black curve represents the square of the difference $(\Phi_A - \Phi_B)^2/2$

H_2^+

These plots depict the electron density in the region of space between atoms A and B

Atomic Orbitals (1) white curves are individual atomic wavefunctions Φ_A, Φ_B

Localized Bonding (2) dotted white curve represents the "sum of the squares" $\Phi_A{}^2 + \Phi_B{}^2/2$

M.O. Bonding (3) dotted black curve represents the "square of the sum" of $\Phi_A + \Phi_B$ namely, $(\Phi_A + \Phi_B)^2/2$

M.O. Antibonding (4) solid black curve represents the square of the difference $(\Phi_A - \Phi_B)^2/2$

Molecular Orbital Treatment
Diatomic Molecules …. continued

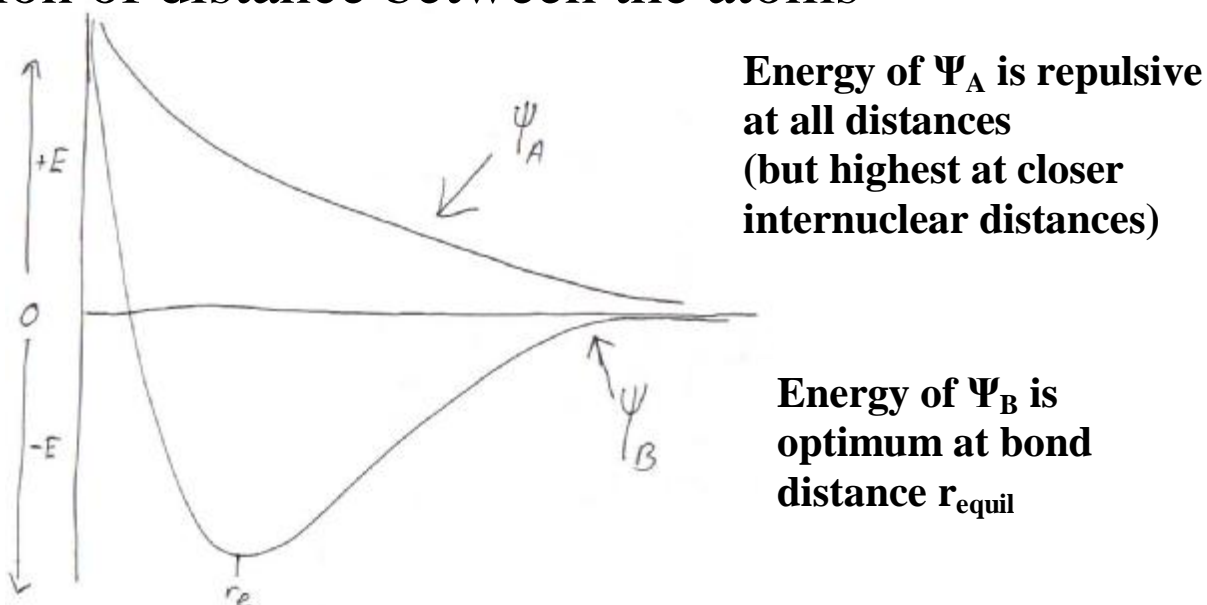## H_2 and He_2

As before: add & subtract wavefunctions

pictorial representations

$\phi_1 + \phi_2 \rightarrow$ $\Psi_b = \phi_1 + \phi_2$ Ψ_b **Bonding** m.o.

$\phi_1 - \phi_2 \rightarrow$ $\Psi_a = \phi_1 - \phi_2$ Ψ_a **Anti-bonding** m.o.

The sign changes here
Between the nuclei $\rightarrow$ nodal
plane where e^- density is zero

Now:
Put electrons into Ψ_b and Ψ_a just as we do for atomic orbitals.

What are the relative energies of Ψ_a and Ψ_b?
Once can represent this by a plot of the energies as a
function of distance between the atoms

**Energy of Ψ_A is repulsive
at all distances
(but highest at closer
internuclear distances)**

**Energy of Ψ_B is
optimum at bond
distance r_{equil}**

There is another, preferred, method for depicting the
energies of M.O.'s than the above diagram

→   Molecular Orbital Diagrams

M.O. Diagrams
(1) Put the relative energies of the atomic orbitals on
opposite sides of the diagram
(group "like" atoms together if there is more than one)

(2) The Diagram shows the energies of the molecular
orbitals at only one energy, namely r_e.

$E_a = E_b$ for interactions of two orbitals at same starting energy

à
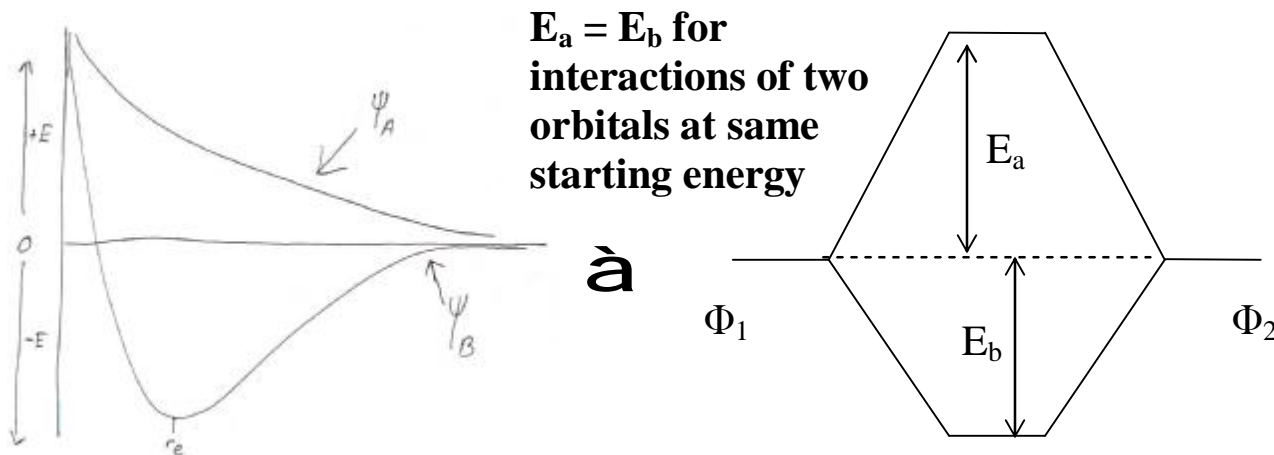
(3) Put electrons into the Molecular Orbitals following the same rules as for atomic filling (Pauli Exclusion Principle, Hund's rule)

Electrons are denoted by arrows ↑ or dots ¨

Contrast the Molecular Orbital Energy Level Diagrams for H$_2$ and He$_2$: Φ_1 & Φ_2 are 1s atomic orb.
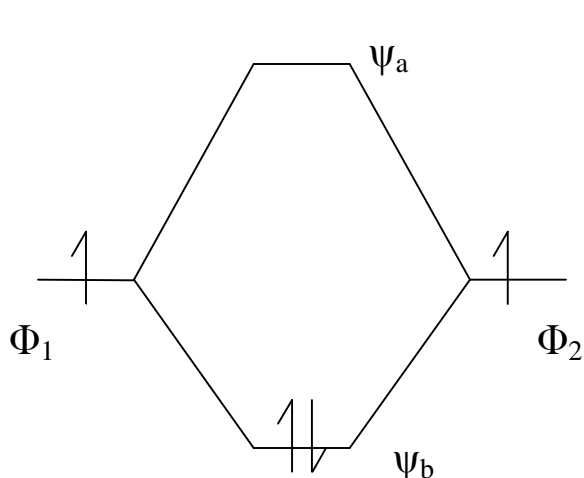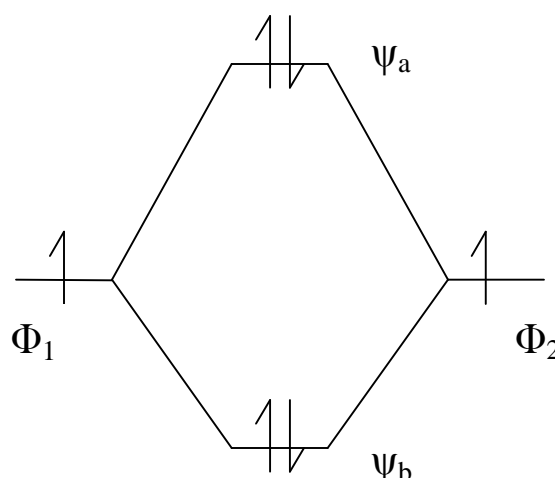
H$_2$ 2e$^-$
Stable, forms
a single bond:
H-H
$\Psi_b{}^2 \Psi_a{}^\circ$ is
Electronic conf.

He$_2$ 4e$^-$
Unstable, no bond:
He X He
(same number of
bonding electrons and
antibonding e$^-$)