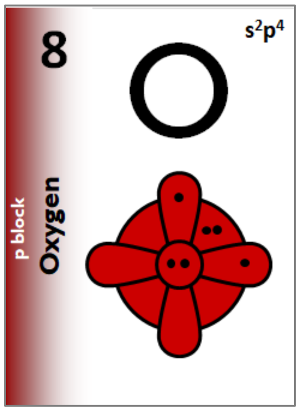
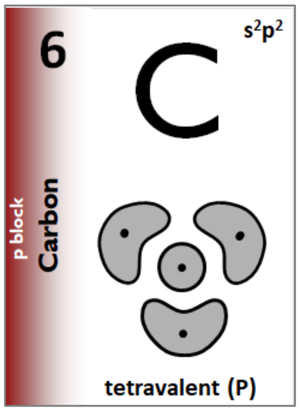
Using orbital coupling diagrams in physical chemistry courses



David E. Woon

or

“Glyph-based Chemistry”



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ILLINOIS

Keywords (in lieu of an outline)

Quantum Chemistry

Chemical Intuition

Atom-By-Atom

Alternative Iconography

Atoms, Bonding, & Molecules

Inquiry-Based

Compelling
Narrative

Fun?

Ownership

Define "glyph"…

Glyphs

Egyptian Hieroglyphs

https://commons.wikimedia.org/wiki/File:Minnakht_01.JPG

Geoglyphs

https://commons.wikimedia.org/wiki/File:Líneas_de_Nazca,_Nazca,_Perú,_2015-07-29,_DD_54.JPG

Modern Language Glyphs

abcdefg ABCDEFG :”;.’

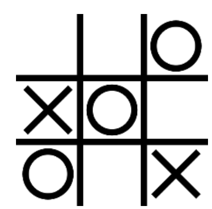
原子

Math Glyphs

0123456789 + –

$$\int \Psi^* \Psi d\tau = 1$$

Game Glyphs



(marked up)

Glyphs for Chemistry?

Atoms – The Foundations

- **Quantum phenomena**

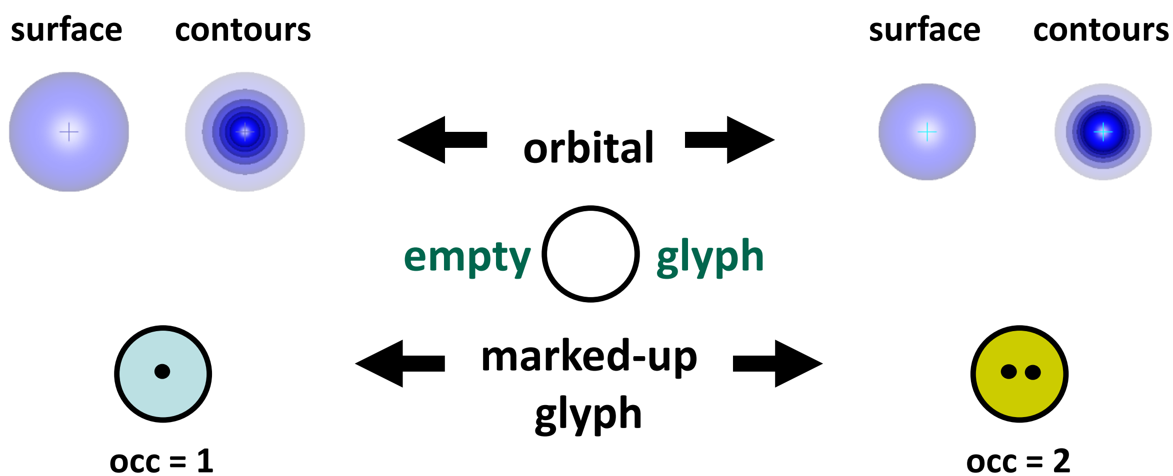
Fraunhofer absorption lines

- **Schrödinger Equation** $$\hat{H}\Psi = E\Psi$$

- **Pauli Principle (antisymmetry)** $$\alpha\beta \text{ in orbital } \varphi$$

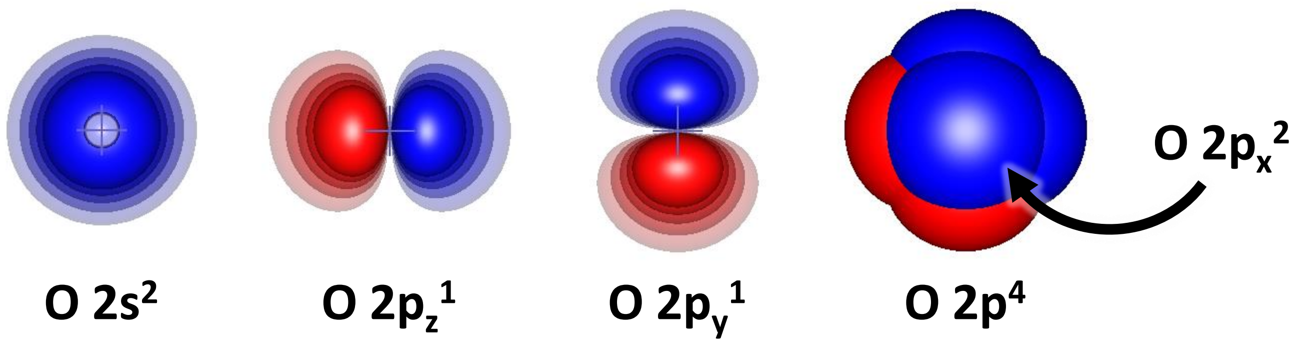
- **Atomic Ground and Excited State Electronic Configurations**

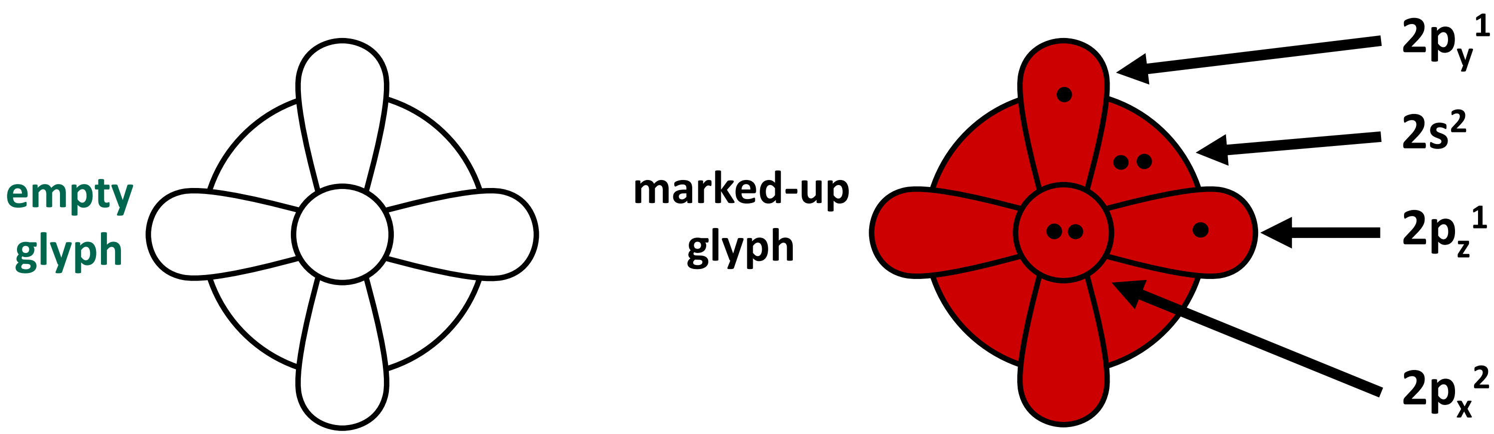
H: $1s^1$ spin: $\alpha + \beta$ **He: $1s^2$** spin: $\alpha\beta - \beta\alpha$



Atoms – The Foundations

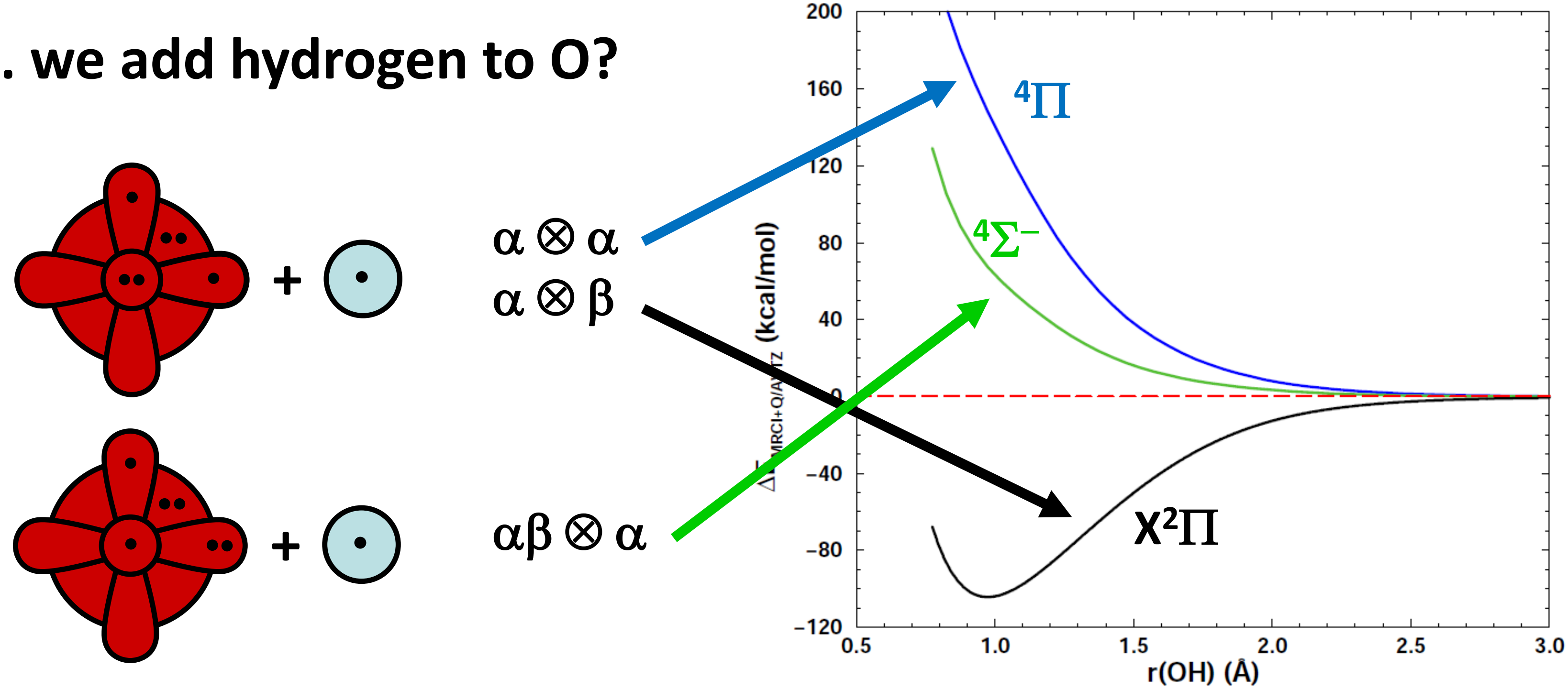
O ground state: $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ (triplet spin)



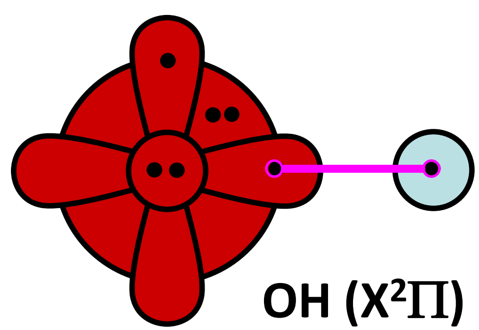


What Happens If…

… we add hydrogen to O?



The bound state of OH has a polar covalent bond:

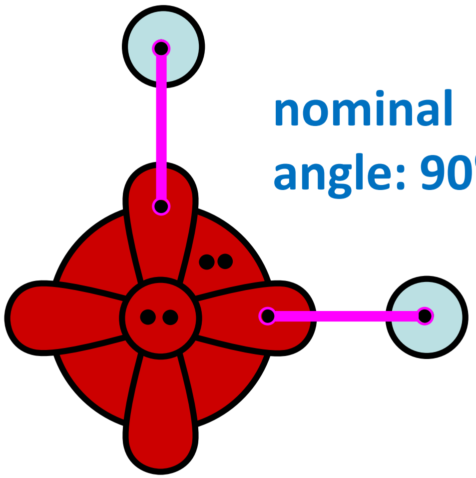


OH ($X^2\Pi$)

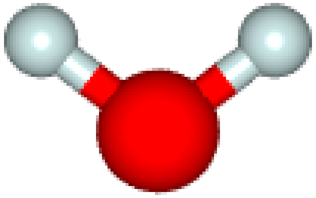
coupling diagram (singlet coupled bond pair)

What Happens If…

… we add a second hydrogen to OH? What nominal bond angle would we expect?



nominal angle: 90⁰



H_2O
r_{OH}=0.948 Å
∠HOH = 104.4°

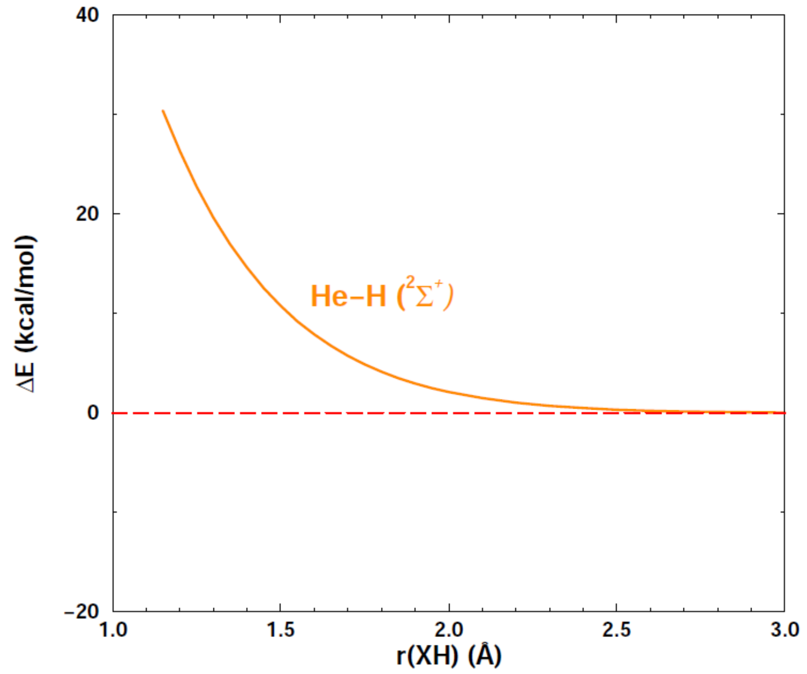
The bond angle increases due to Pauli repulsion between the two bond pairs, with additional Coulombic repulsion between the two protonic hydrogens.

What Happens If…

… we allow H to interact with He or Be atoms?

$H(1s^1) \otimes He(1s^2) \rightarrow 1\sigma_B^{\,2}\ 2\sigma_A^{\,1}$

Antibonding is bad, no bond forms.



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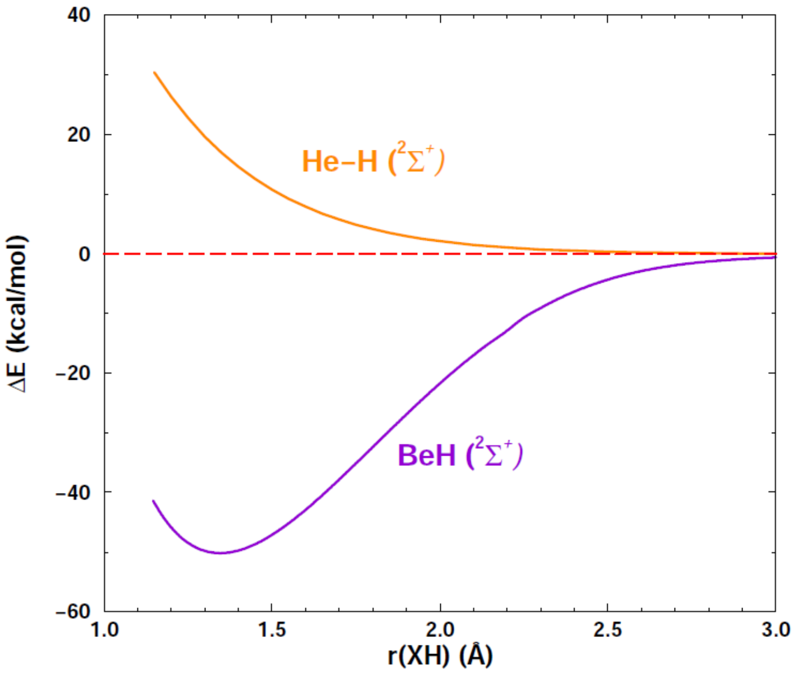
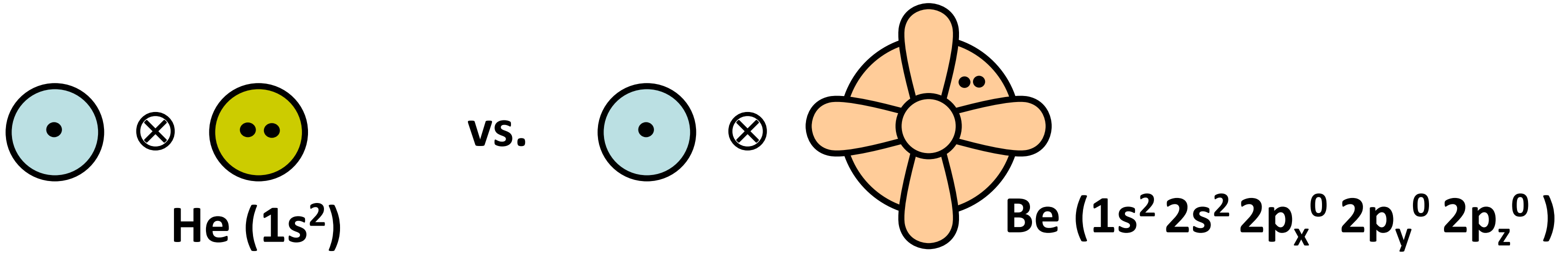
Antibonding is bad: no bond forms.

$H(1s^1) \otimes Be(1s^2 2s^2) \rightarrow 1\sigma^2\ 2\sigma_B^2\ 3\sigma_A^1$

A bond forms. Why is BeH so different?





Why do the 2p orbitals make a difference in BeH?

We can expand the wavefunctions of He and Be by adding the next orbital (closest in energy): 2s for He, 2p for Be.

$$\text{He:}\quad \Psi = \hat{A}(c_1 1\text{s}^2 + c_2 2s^2)\,\alpha\beta$$

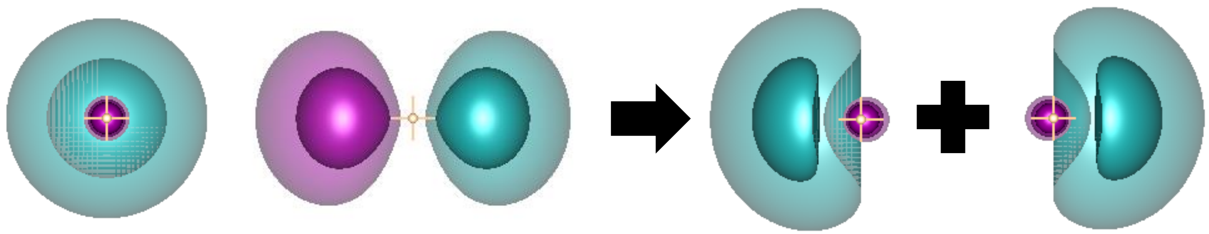
$$\text{Be:}\quad \Psi = \hat{A}(c_1 1\text{s}^2 2\text{s}^2 + c_2 1\text{s}^2 2\text{p}_\text{x}^2 + c_2 1\text{s}^2 2\text{p}_\text{y}^2 + c_2 1\text{s}^2 2\text{p}_\text{z}^2)\,\alpha\beta\alpha\beta$$

All three of the Be 2p orbitals need to be included in its Ψ. The coefficients are the same due to symmetry.

Atom	c_1^2 (weight)	c_2^2 (weight)
He	99.6% $1s^2$	0.4% $2s^2$
Be	90.2% $2s^2$	9.8% $2p_x^2+2p_y^2+2p_z^2$

Why do the 2p orbitals make a difference in BeH?

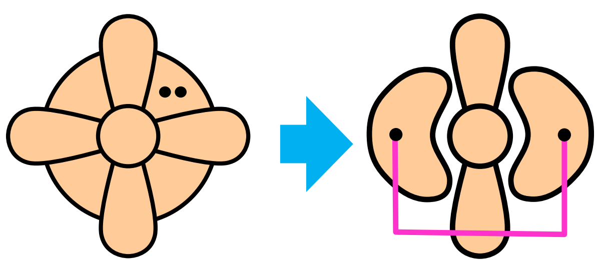
The coefficients for the 2s and 2p orbitals can be used to create new orbitals that better represent the electron pair:



$0.95\ 2s^2$ $\pm 0.18\ 2p_z^2$ σ_L^1 σ_R^1

"lobe orbitals"
2s-2p hybrids

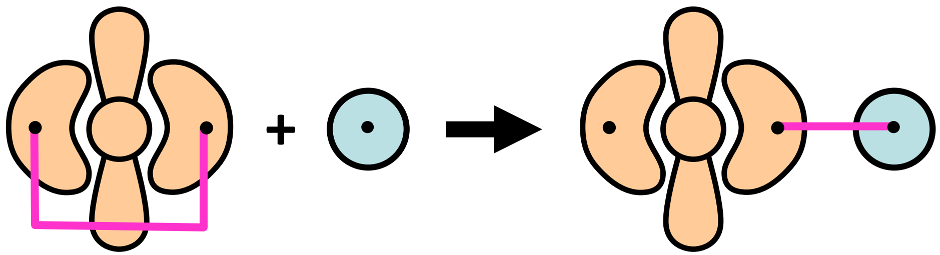
The glyph we previously used for Be is inadequate.



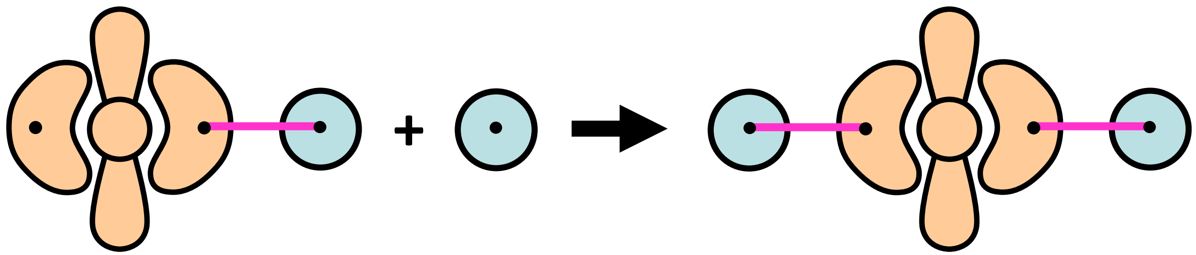
In the new glyph we use lobe shapes to represent the lobe orbitals and explicitly couple them with a coupling bar.

Why do the 2p orbitals make a difference in BeH?

Now we can construct a coupling diagram for BeH:



We can also anticipate the structure of BeH_2:

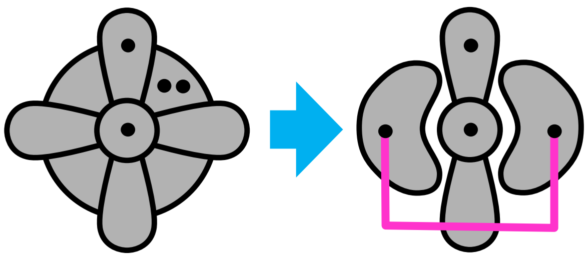


The bonding in BeH is known as recoupled pair bonding.

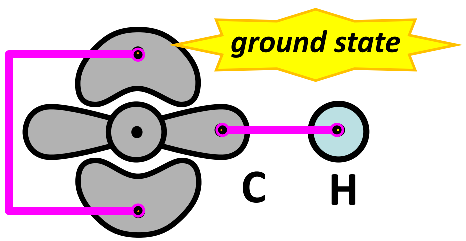
Recoupling also occurs in a far more important element…

Recoupled Pair Bonding in Carbon

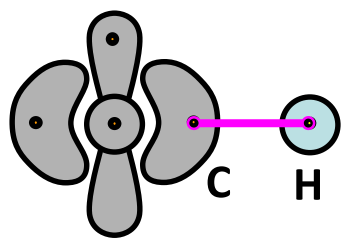
Like Be, C has an unused 2p orbital that can hybridized with the $2s^2$ pair:



H can interact with one of the singly occupied 2p orbitals to form a covalent bond, but it can also recouple the lobe pair.

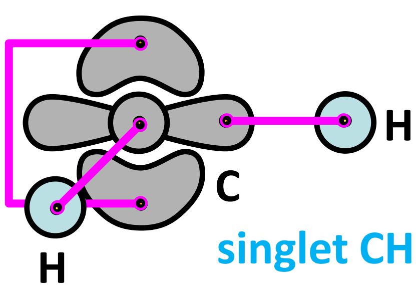


covalent CH

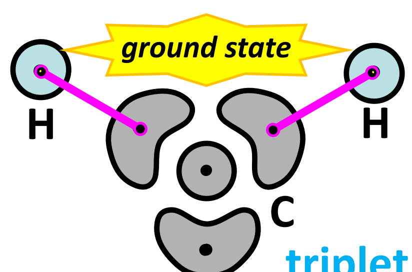


recoupled pair CH

The state with the covalent bond is more stable, but the ordering changes when a second H is added.



singlet CH_2
90° nominal angle

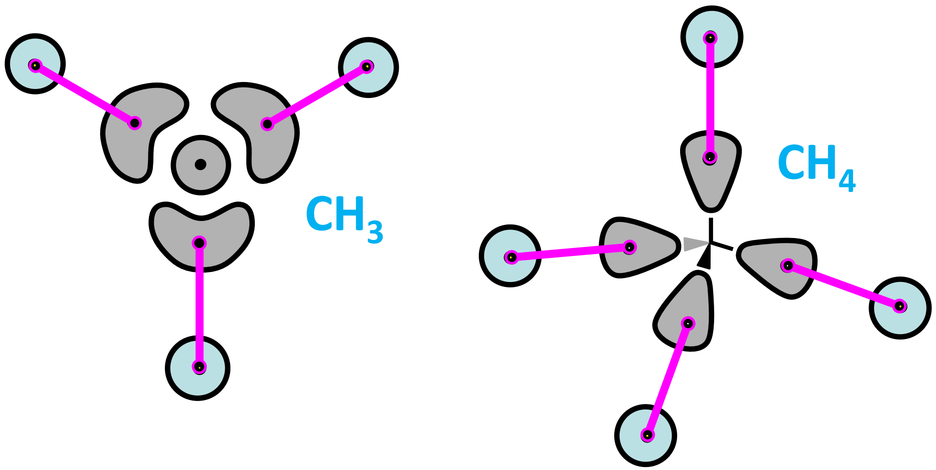


triplet CH_2
120° nominal angle

The new glyph accounts for hybridization of the 2s and two 2p orbitals.

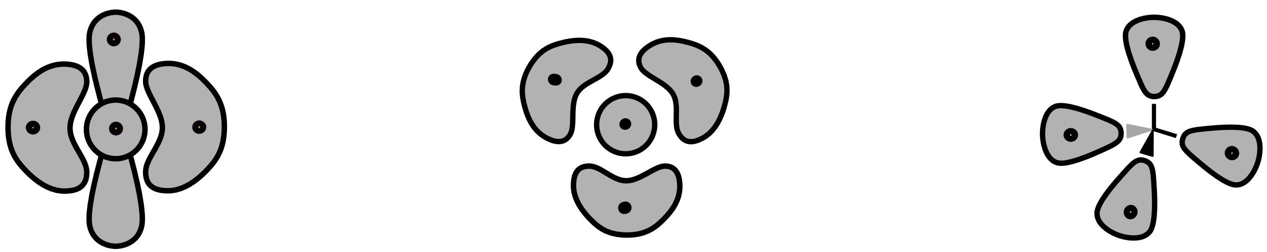
Recoupled Pair Bonding in Carbon

The methyl radical and methane follow sequentially.



The glyph for CH_4 accounts for hybridization of the 2s and all three 2p orbitals.

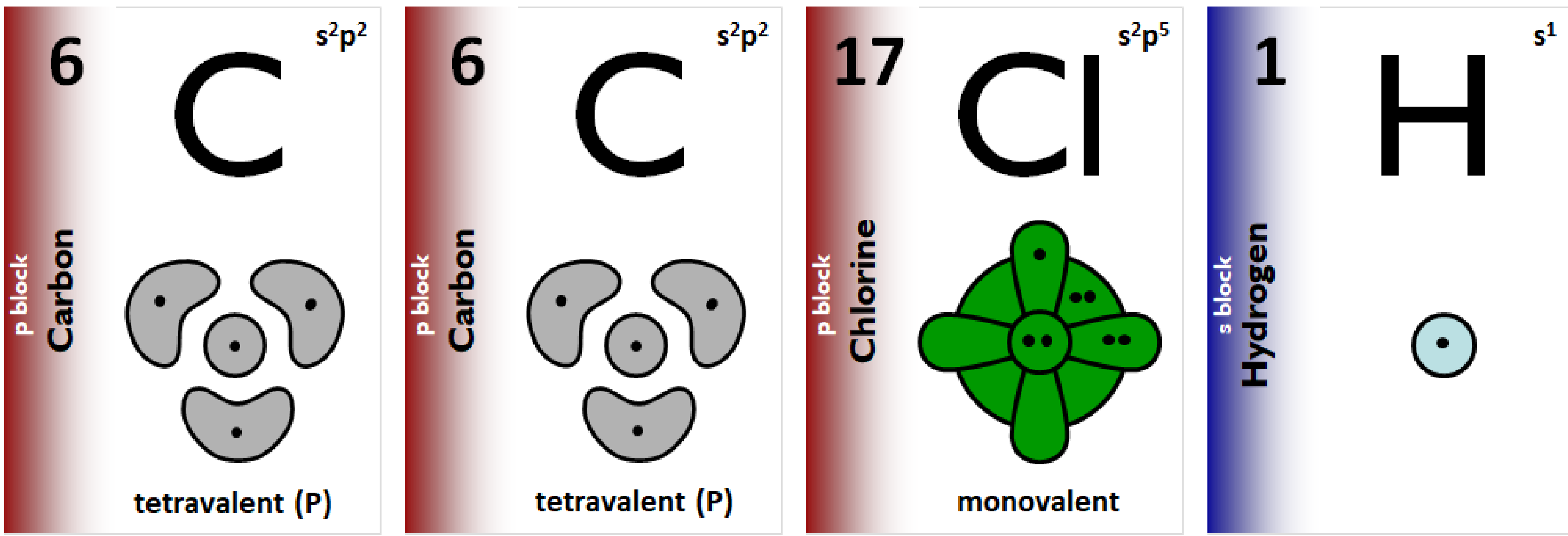
The three glyphs can be used to construct many compounds.



linear C (180°) planar C (120°) tetrahedral C (109.5°)

The Fun Part

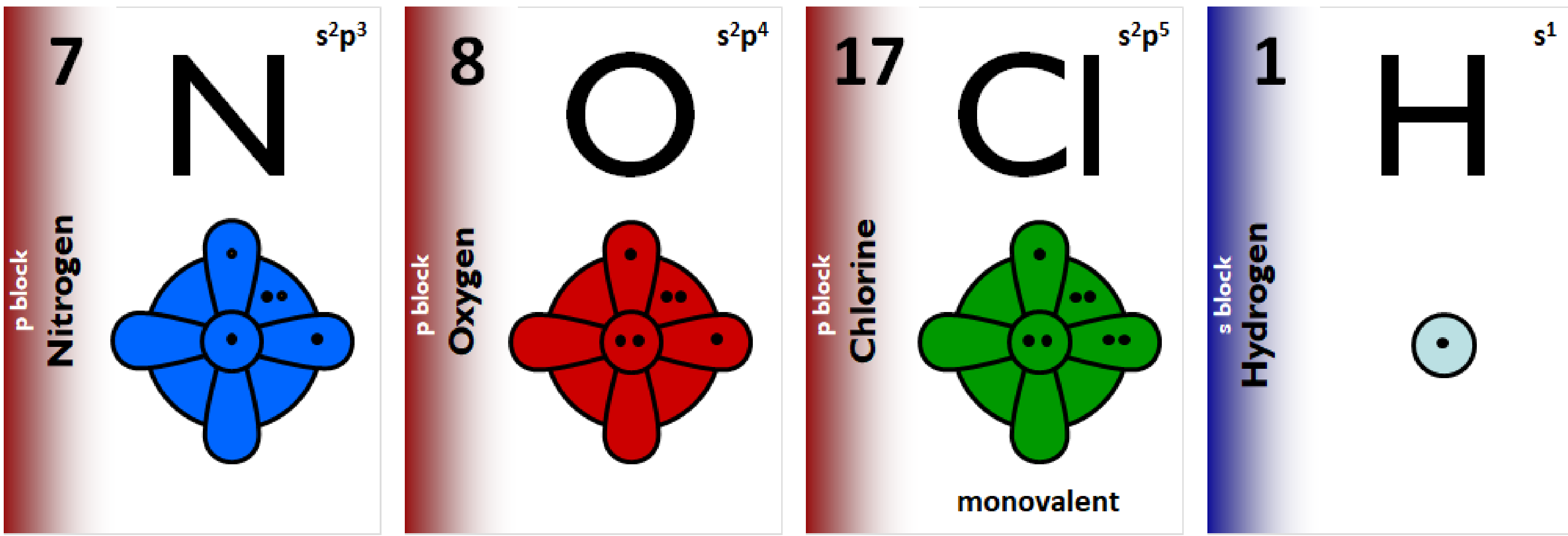
Students receive randomized trading cards and build molecules from them.



backbone cards (σ + π bond) (must be used)	monovalent atoms (to complete your molecule; H is optional)

The Fun Part

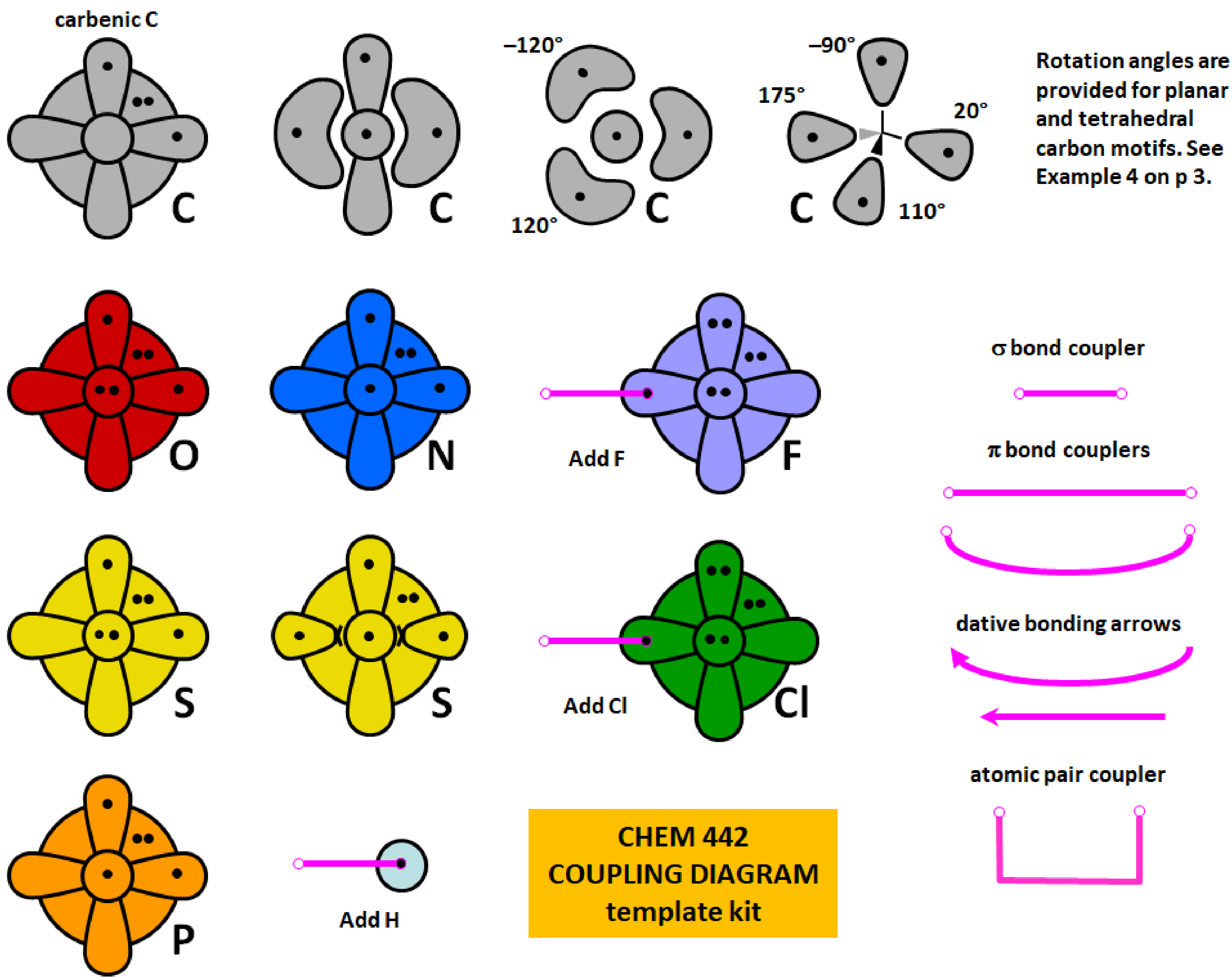
Students receive randomized trading cards and build molecules from them.



backbone cards (σ bond)
(must be used)

monovalent atoms
(to complete your molecule; H is optional)

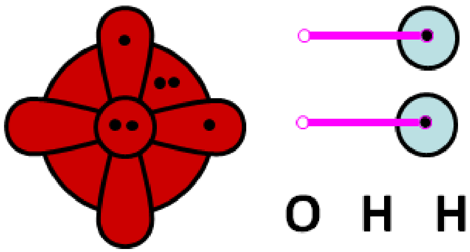
Templates and examples are provided.



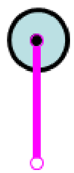
Templates and examples are provided.

Example 1: How to build H_2O

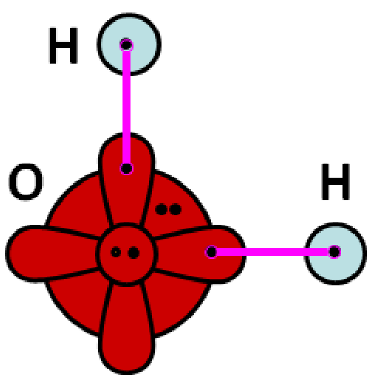
1. Copy the parts you need: O, 2H, and labels.



2. Rotate one H by –90°.

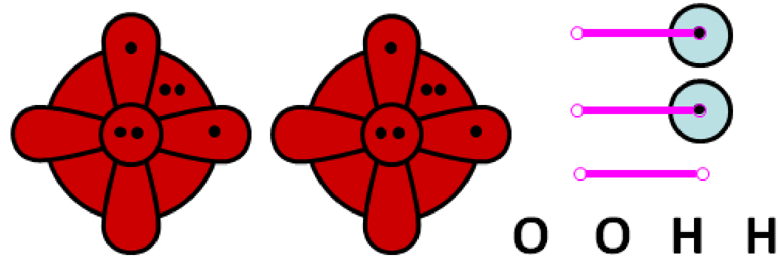


3. Move H atoms until couplers are aligned with singly occupied 2p orbitals on O. Add labels.

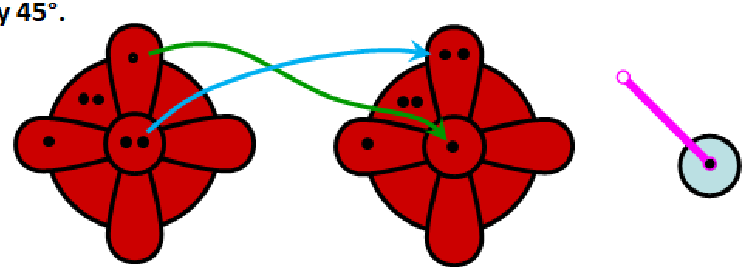


Example 2: How to build HOOH

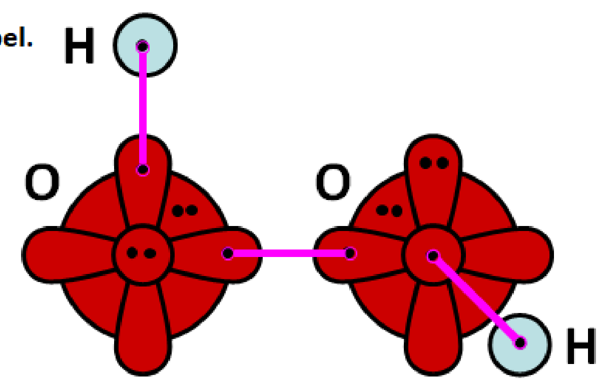
1. Copy the parts you need: 2O, 2H, 1 σ bond coupler, and labels.



2. Flip one O horizontally, then move the dots in the out-of-plane and vertical 2p orbitals to where they're needed. Also rotate one H by 45°.



3. Assemble and label.

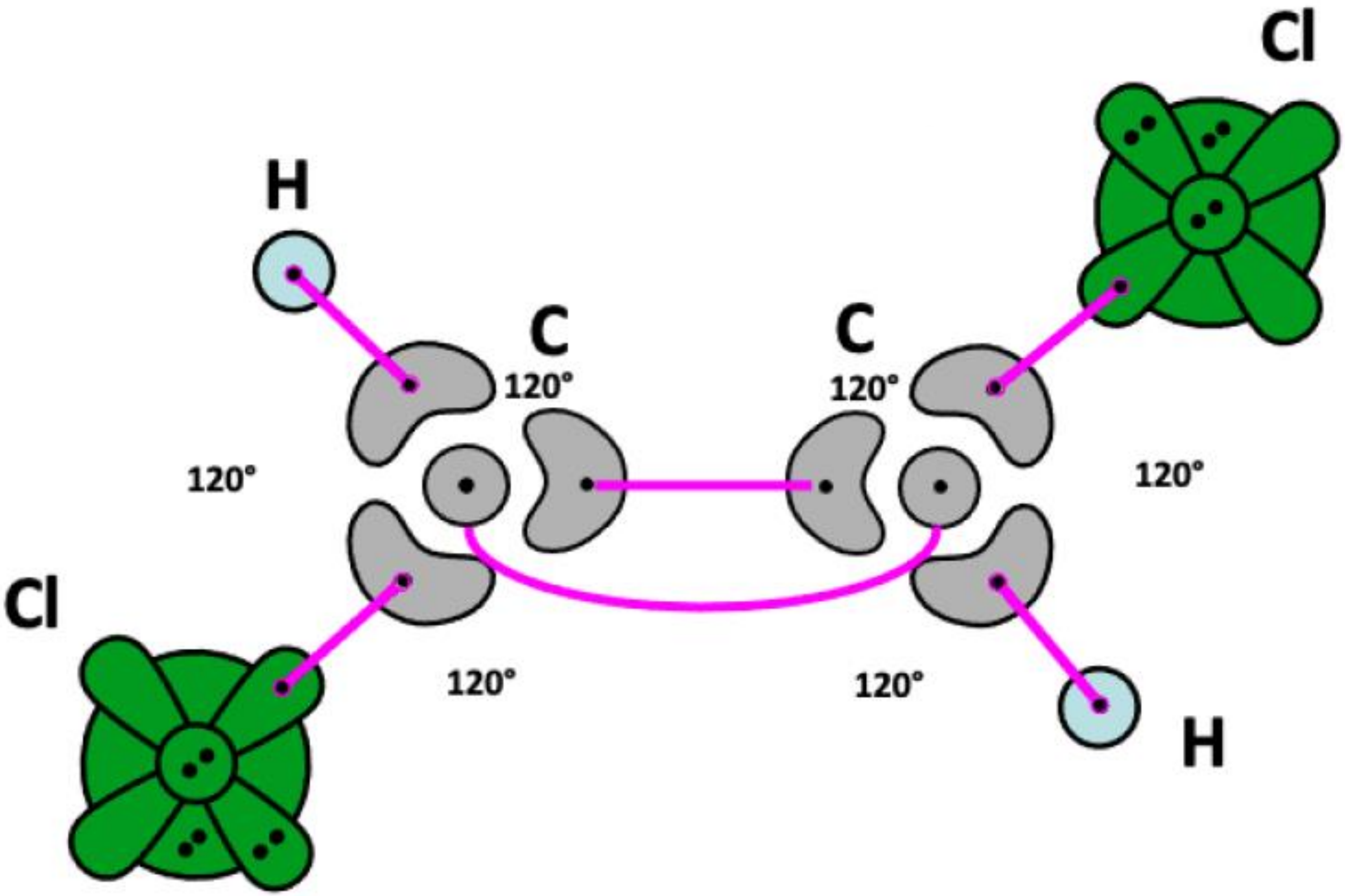


Molecule Projects

In Principles of Physical Chemistry, I provide the students with calculated properties of their molecules (structure, rotational constants, and vibrational frequencies).

In Physical Chemistry I, I provide the students with sample input files and let them run their molecules on the ChemCompute website (chemcompute.org). In addition to structure, rotational constants, and vibrational frequencies, they can generate orbitals.

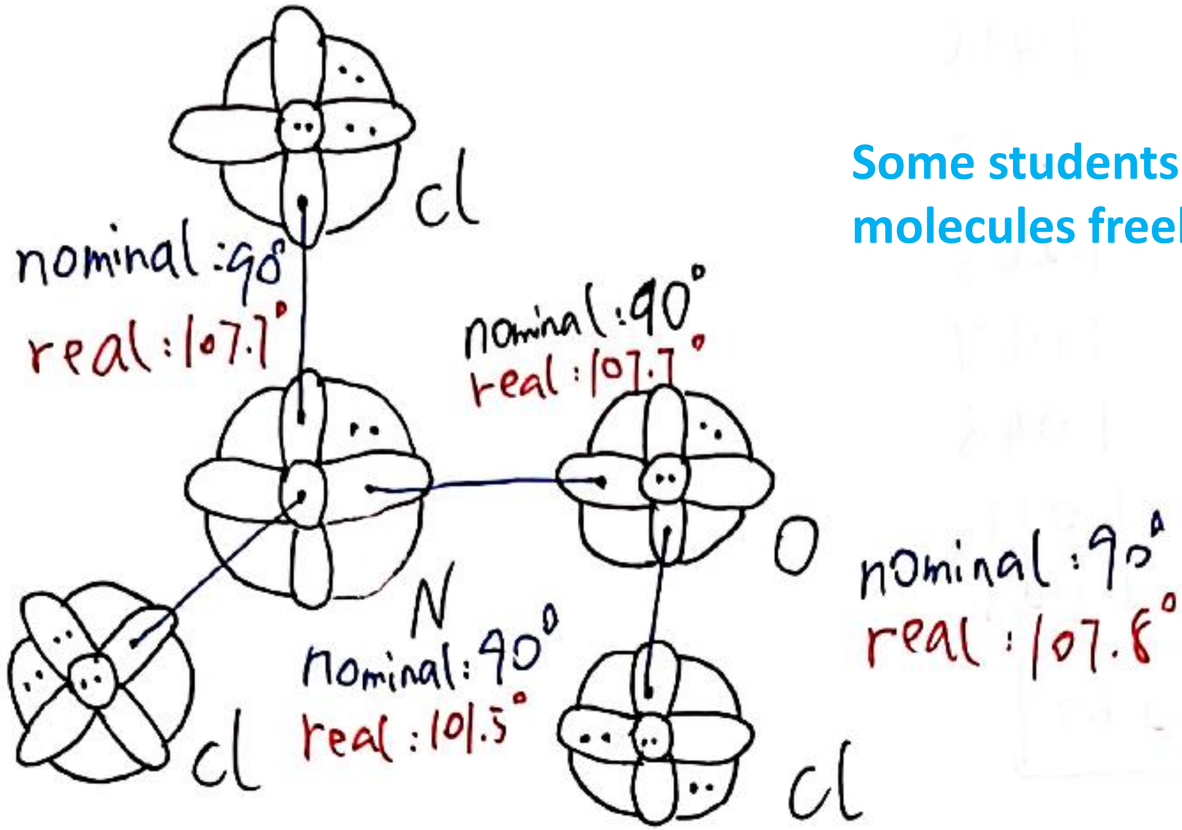
Representative Student Coupling Diagrams



Some students use the template set that I provide to generate their coupling diagrams.

Representative Student Coupling Diagrams

Some students draw their molecules freehand.

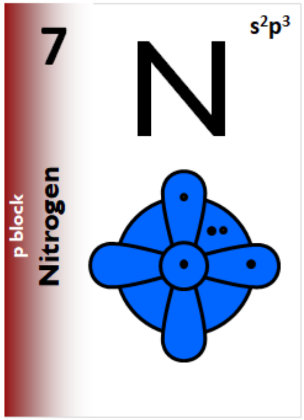


Coupling diagram consistent with the actual structure.

Additional Material

With limited time, there's much I couldn't talk about today:

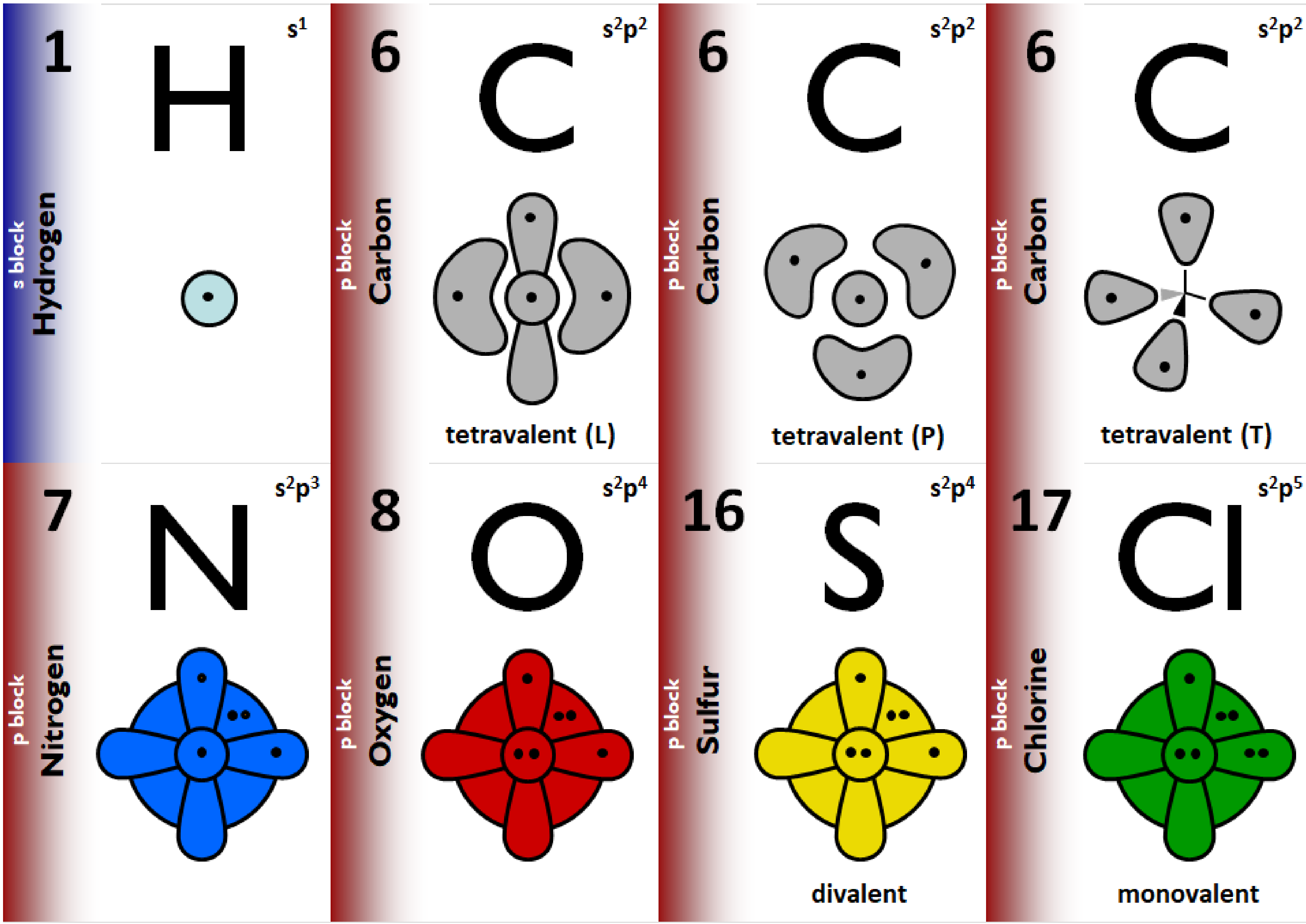
- **Use of Generalized Valence Bond orbitals in P Chem**
- **Orbital changes during bond formation (animations)**
- **Multiple bonds**
- **Ionic and dative bonding**
- **Resonance with coupling diagrams**
- **Foundations of coupling diagrams**



URL on back of sample cards

Visit http//astrochymist.org/glyphs for more information and downloads!

Thank you!



1
H
s^1
s block
Hydrogen
6
C
s^2p^2
p block
Carbon
tetravalent (L)
6
C
s^2p^2
p block
Carbon
tetravalent (P)
6
C
s^2p^2
p block
Carbon
tetravalent (T)
7
N
s^2p^3
p block
Nitrogen
8
O
s^2p^4
p block
Oxygen
16
S
s^2p^4
p block
Sulfur
divalent
17
Cl
s^2p^5
p block
Chlorine
monovalent