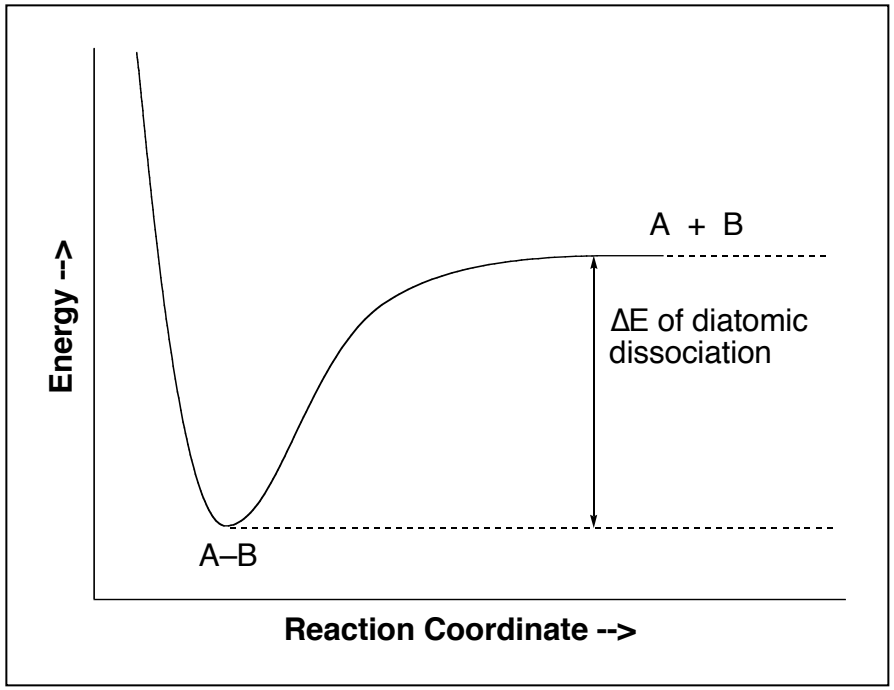
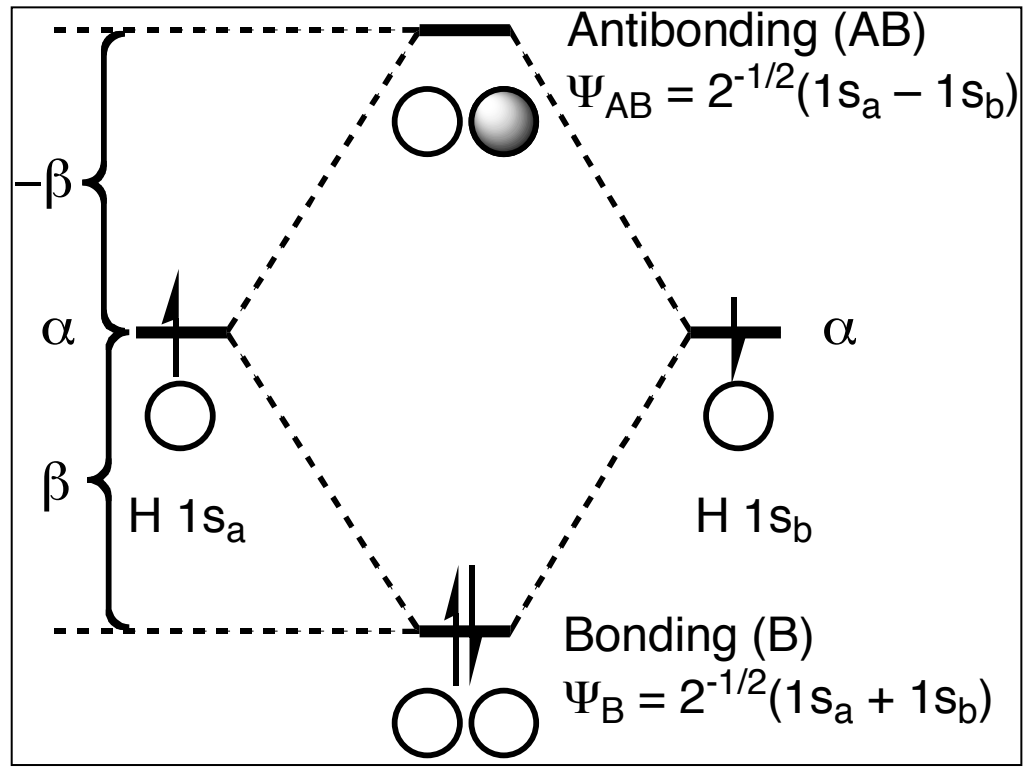
What is a Bond?

- Simplest definition focuses on stability, observability, energy
- Bond concept predates knowledge of the electron or atomic structure
- Columbia Encyclopedia: "There is a chemical bond between two atoms or groups of atoms when the forces acting between them are strong enough to lead to the formation of an aggregate with sufficient stability to be regarded as an independent species."
- Most commonly encountered in organic systems is the covalent (Lewis electron pair) bond.



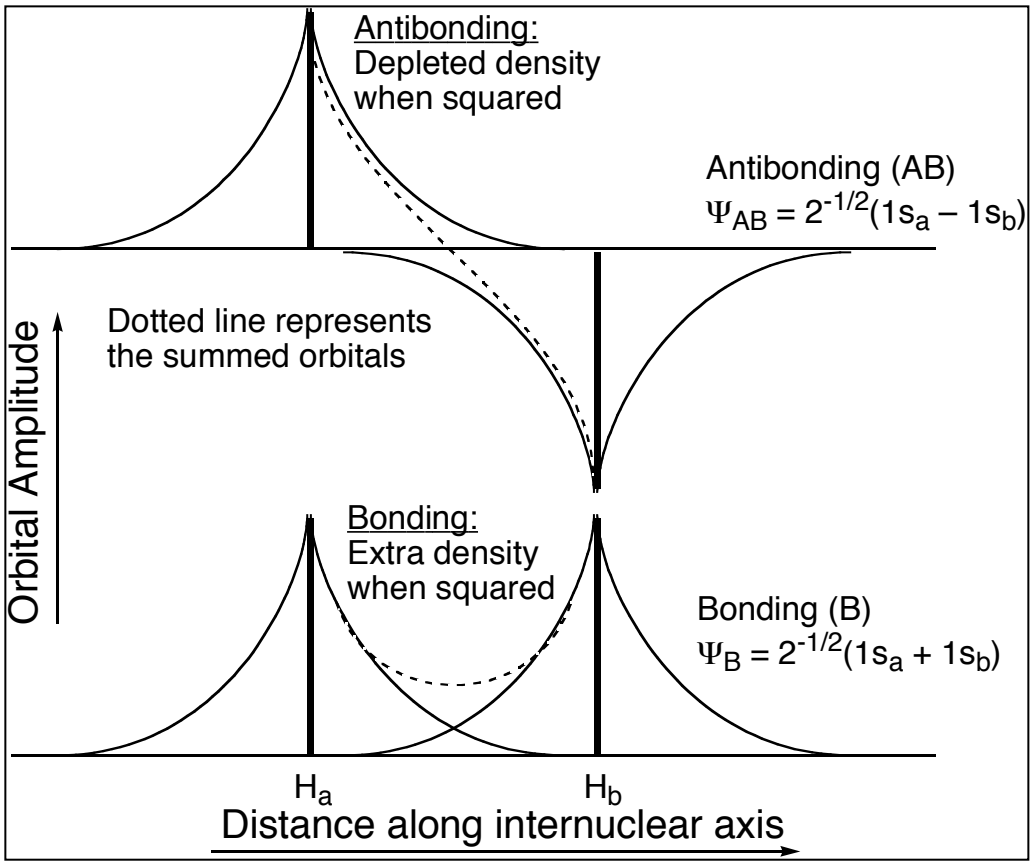
Building MOs of Polyatomics

- The $2e^-$ bond in H_2, Hückel picture:
- α is E of AO
- β is ΔE due to intxn
- Both α & β are <0
- Ψ_B enhances ρ_{e-} between protons
- Ψ_{AB} depletes interproton charge ρ_{e-}



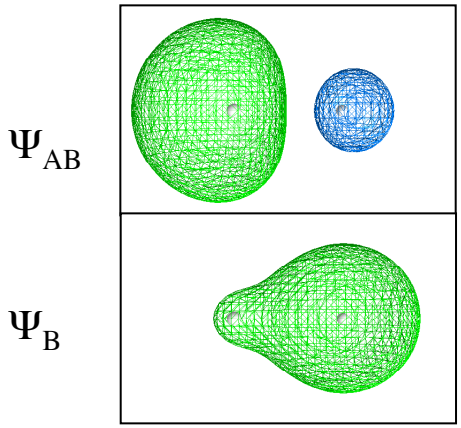
MOs and Electron Density

- Ψ^2 = orb. e^- density ρ_e
- Ψ_{AB} has a node ($\rho_e = 0$) beween atoms where H $1s_a$ and H $1s_b$ are equal and cancel each other because $0^2 = 0$
- More nodes --> higher E orbitals

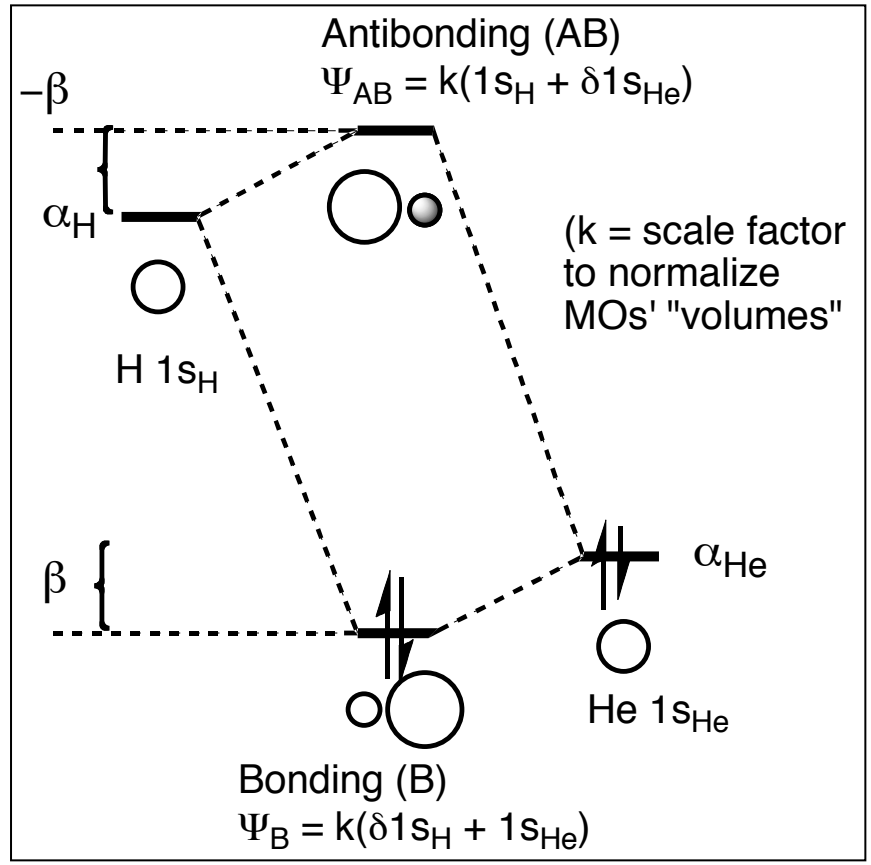


A Polar Bond: HHe^+

- Lower E AO $1s_{He}$ contributes more than $1s_H$ to Ψ_B, the lower E MO, so this orbital's e^- pair is polarized toward He
- Ψ_{AB} is the opposite; an electron pair there would be polarized toward H

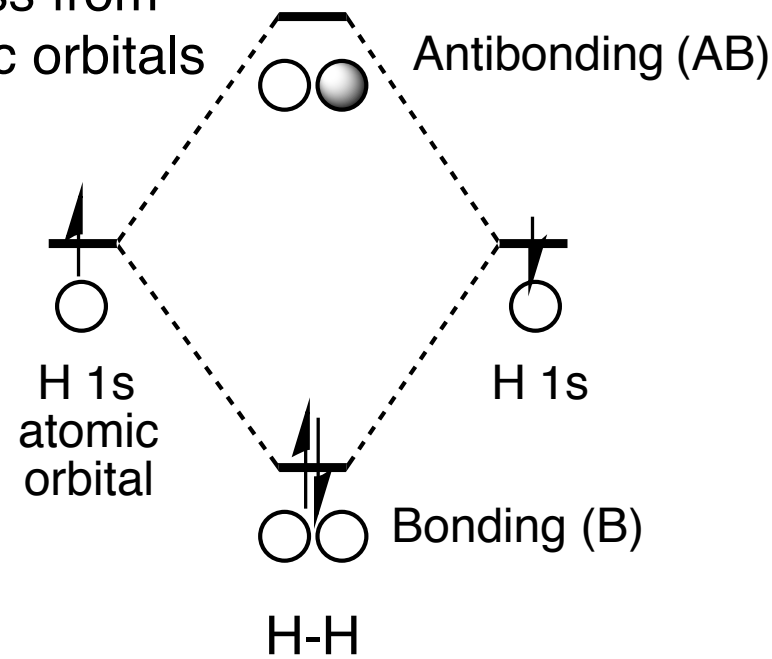


- $\beta \propto$ overlap and $1/(a_H - a_{He})$ so less bonding than in H_2 (BDE 42.5 vs. 104.2 kcal/mol)



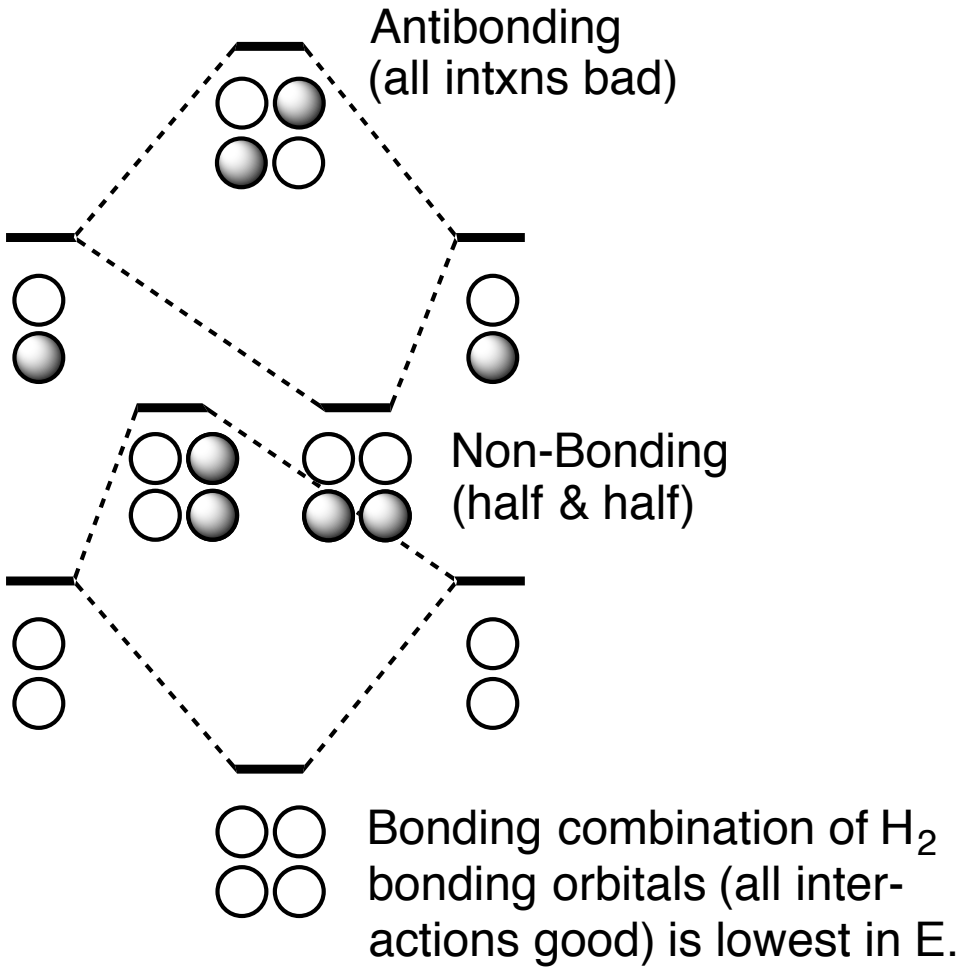
Building Methane's Orbitals

1. "Make" H_2 as in class from two H atoms' 1s atomic orbitals

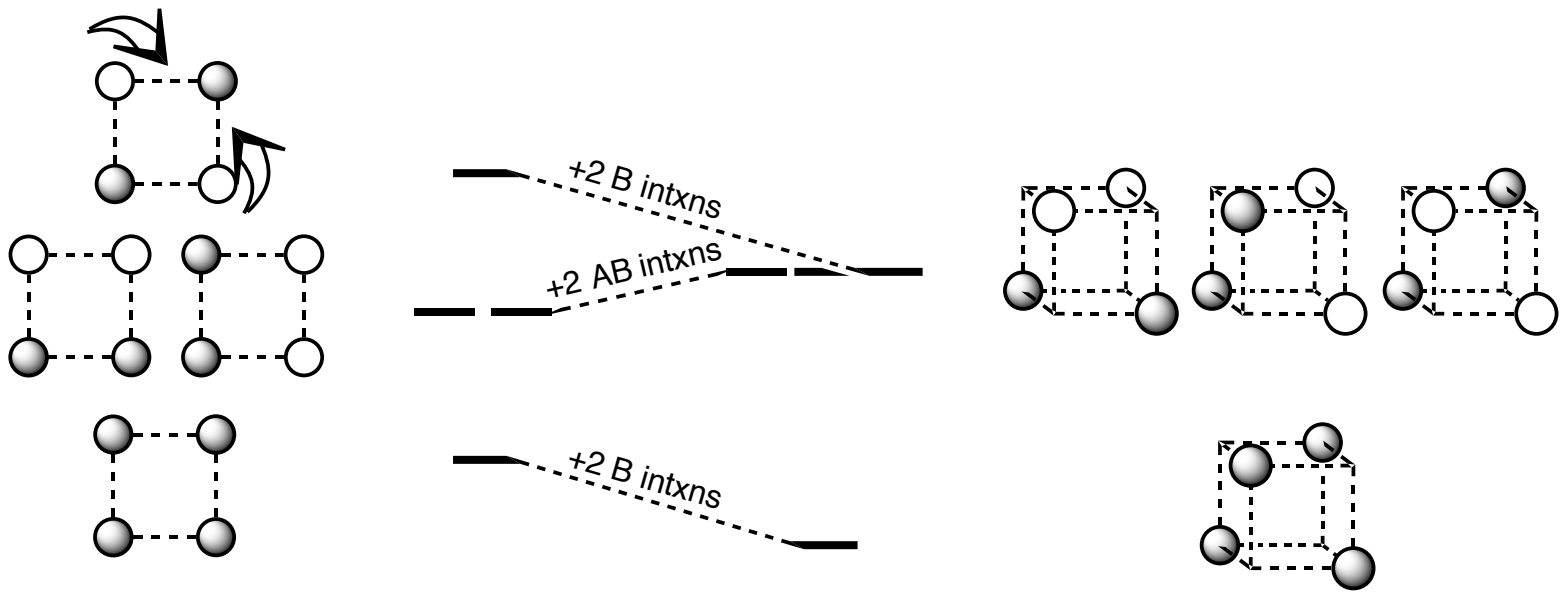


2. Combine two H_2 fragments in a square arrangement. Symmetry allows only B-B and AB-AB (see step 1) interactions, but note that the bonding combo of H_2 AB orbitals and the antibonding combo of H_2B orbitals yield symmetry-related orbitals* at the non- bonding level (two good, two bad interactions).

*This is analogous to the three 2p orbitals on an atom--they have the same shape, same E, but they are orthogonal



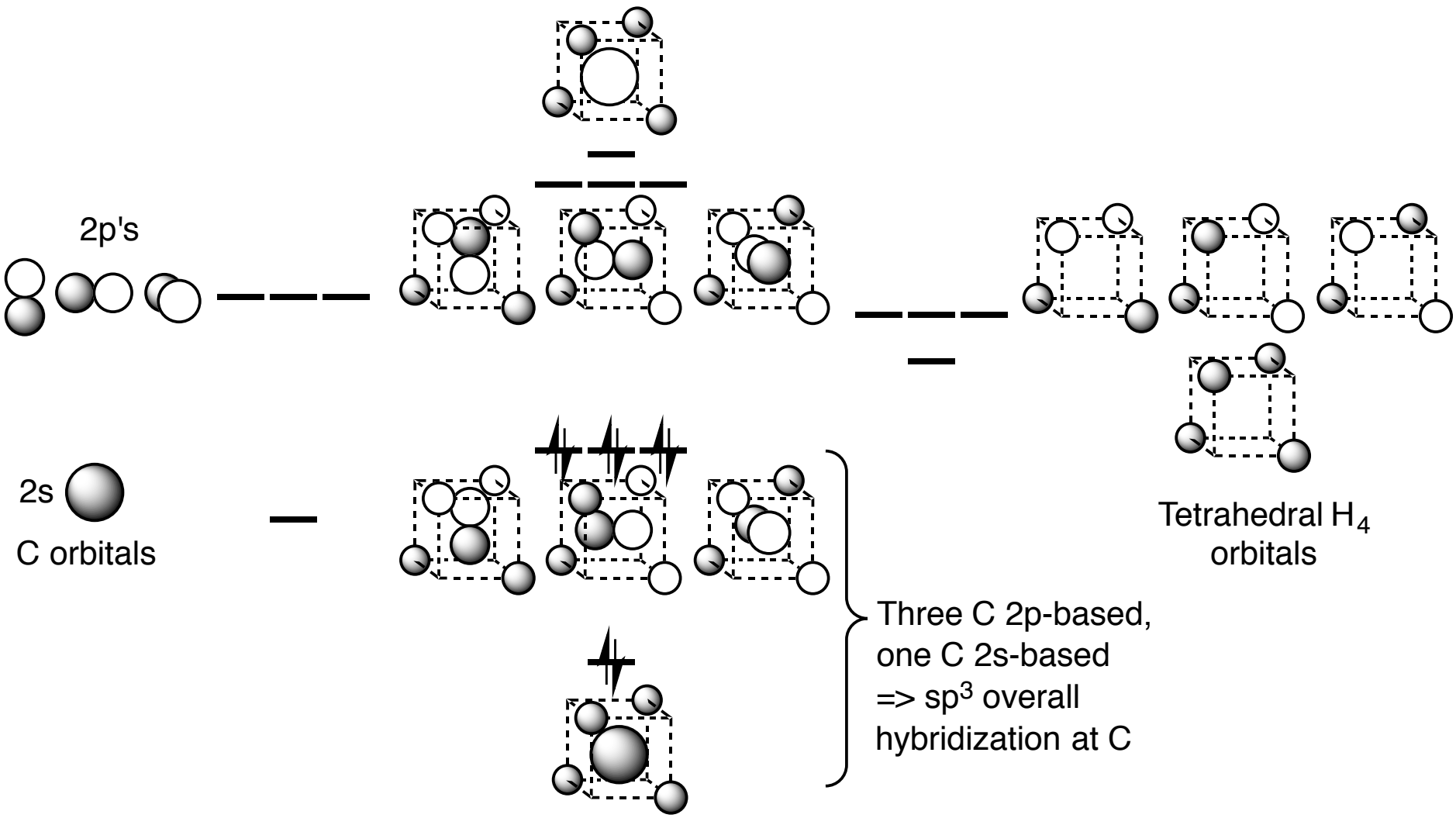
3. Fold Square H_4 to Tetrahedral H_4 by pulling up opposite corners



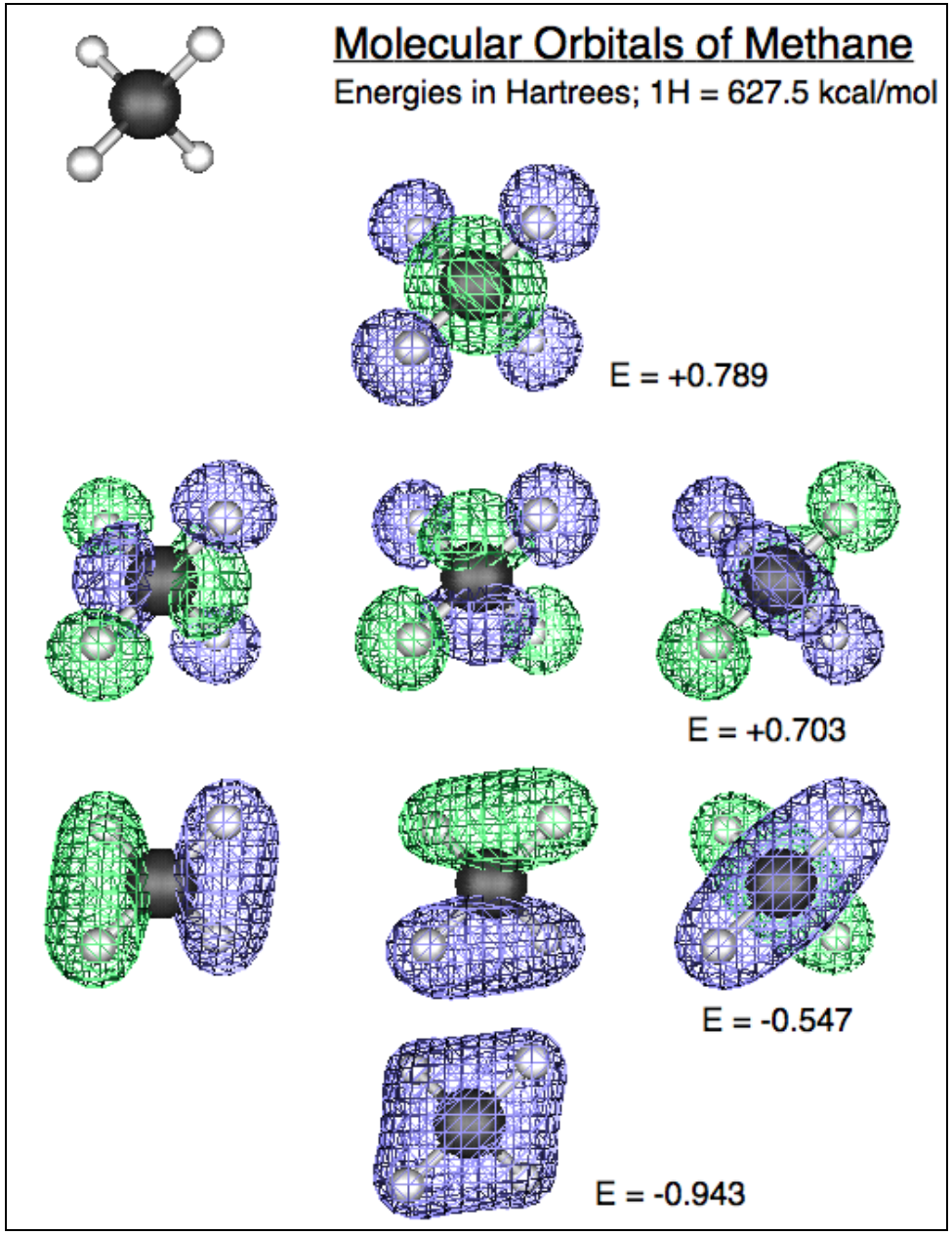
Square H_4 orbitals

Tetrahedral H_4 orbitals

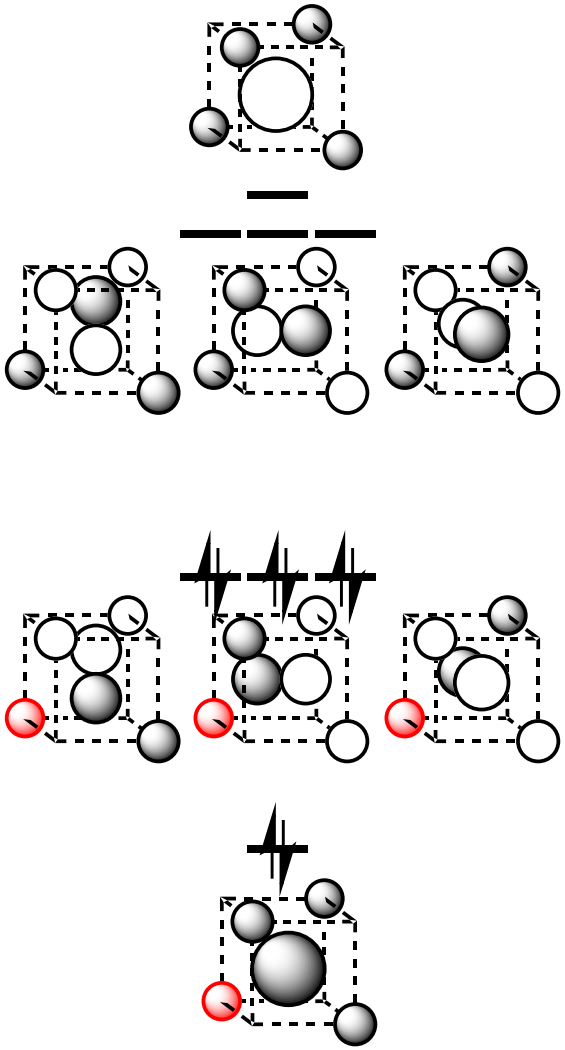
4. Turn on interactions between Symmetry-paired Orbitals

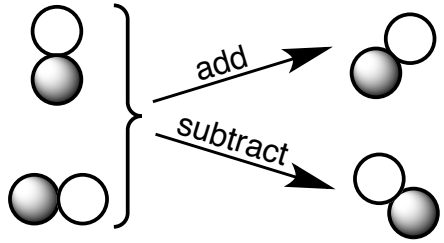


MOs of tetrahedral methane from a modern, quite accurate simulation built on quantum physics (known as Ab Initio calculations). Note how large the energy values are. Negative energies represent how tightly the electrons in the bonding (bottom four) orbitals are held; positive energies of the empty levels mean an electron in there would not "stick" – i.e. that CH_4 has a negative EA.

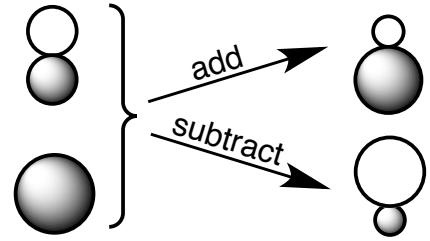


5. To understand hybridization, consider the sum of all these orbitals' contributions to bonding to one H atom.



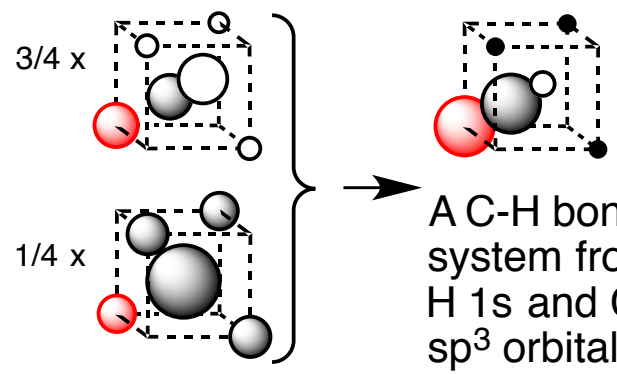


Note that mixing (by adding and subtracting) two 2p orbitals *on the same atom* center simply produces two rotated 2p orbitals, as shown above.



Mixing some 2s orbital into a 2p (*same atom*) enhances one p lobe and depletes the other (see above), making a hybrid.

Mixing the reoriented 2p-centered with the 2s-centered orbital in 3:1 proportions gives a "sp^3 hybrid" that lets us focus on the C-H bond as a local, two-orbital interaction like that in H_2. Equivalent hybrids can be derived for the other three H's.



A C-H bond system from H 1s and C sp^3 orbitals.