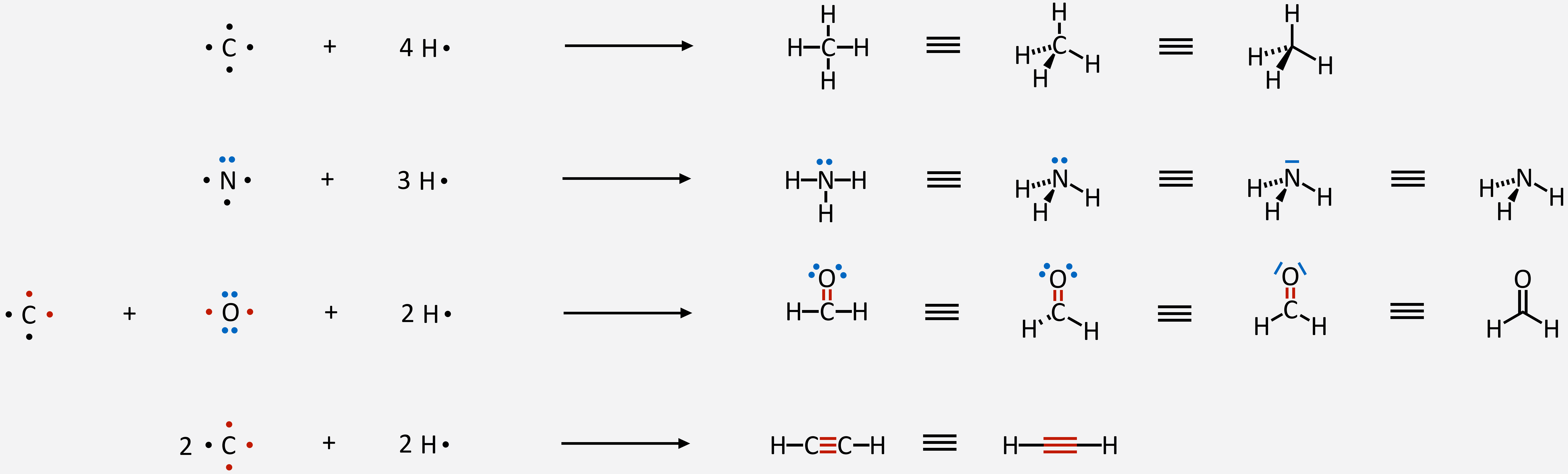
2.3 Formation of Single Bonds

Reading Recommendations

- Clayden, Greeves, Warren, *Organic Chemistry*, Oxford University Press, 2nd ed., **2012**, *pp* 88–106.
- Jamart, Bodiguel, Brosse, *Les cours de Paul Arnaud - Cours de chimie organique*, Dunod, 19th ed., **2015**, *pp* 79–86.

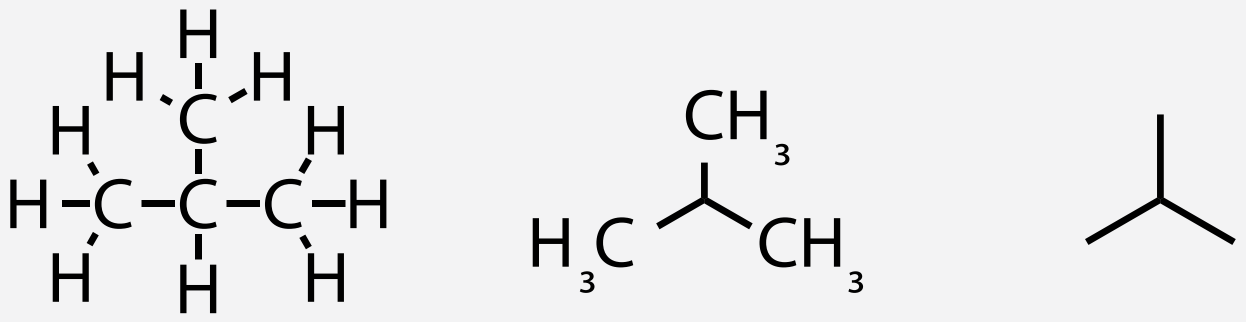
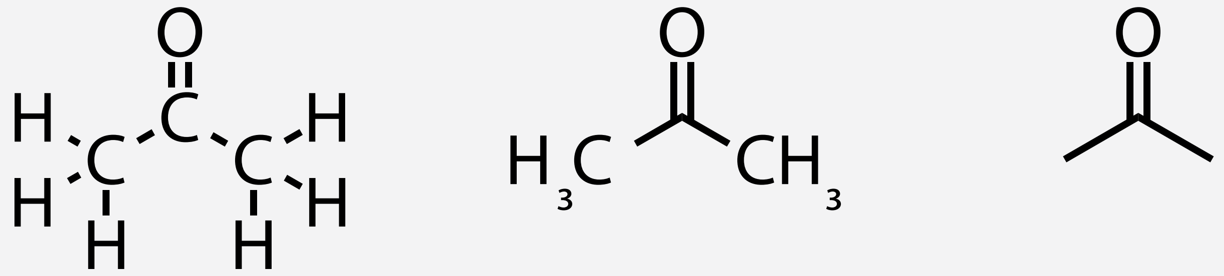
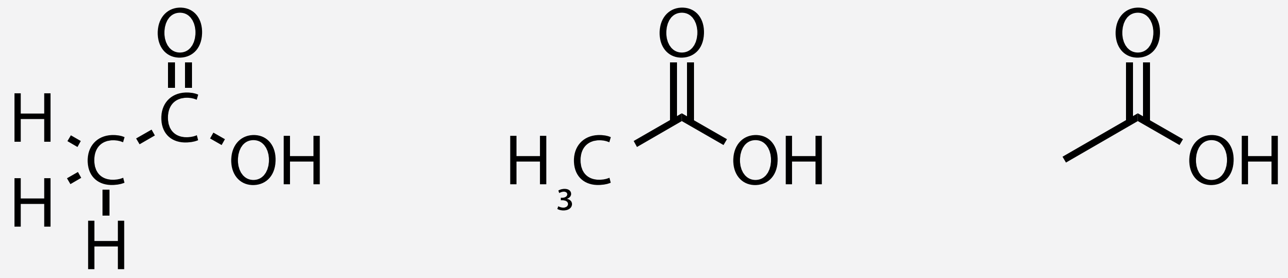
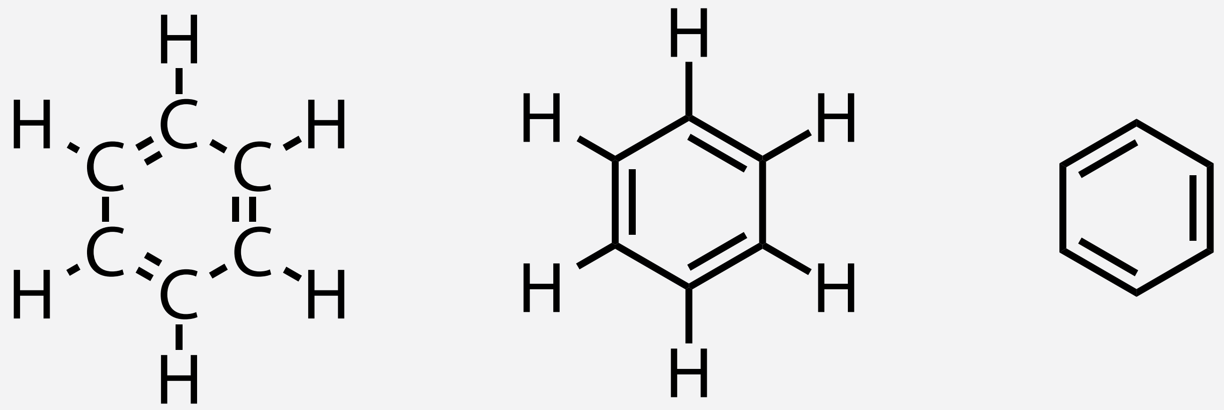
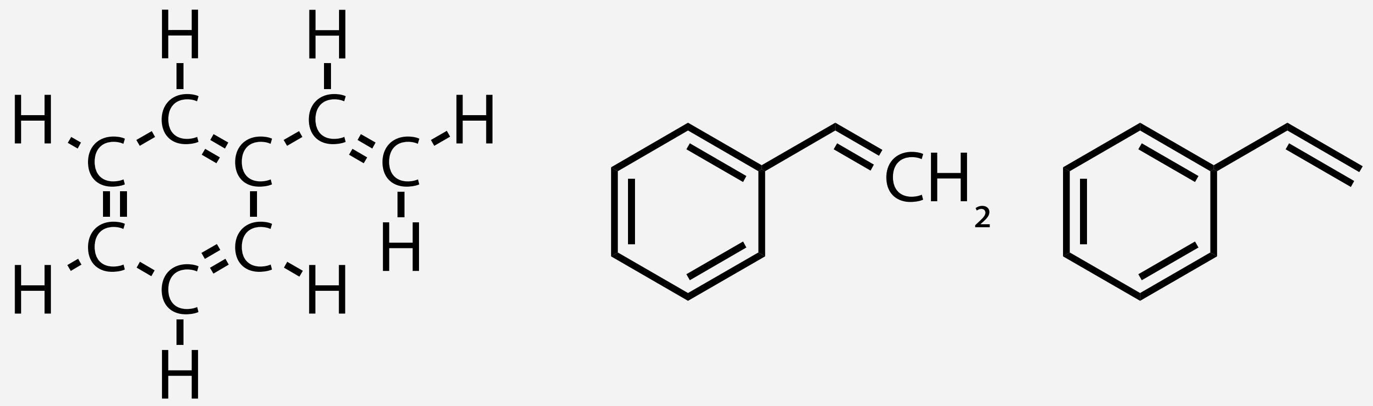
Covalent Bond Formation, Lewis Structure Formulae & Valency

- assumption: all elements need to complete their valence shell by pairing up electrons with others
  - hydrogen completes first shell (maximum one electron pair)
  - carbon, nitrogen, oxygen, fluorine complete second shell (maximum four electron pairs, octet rule)



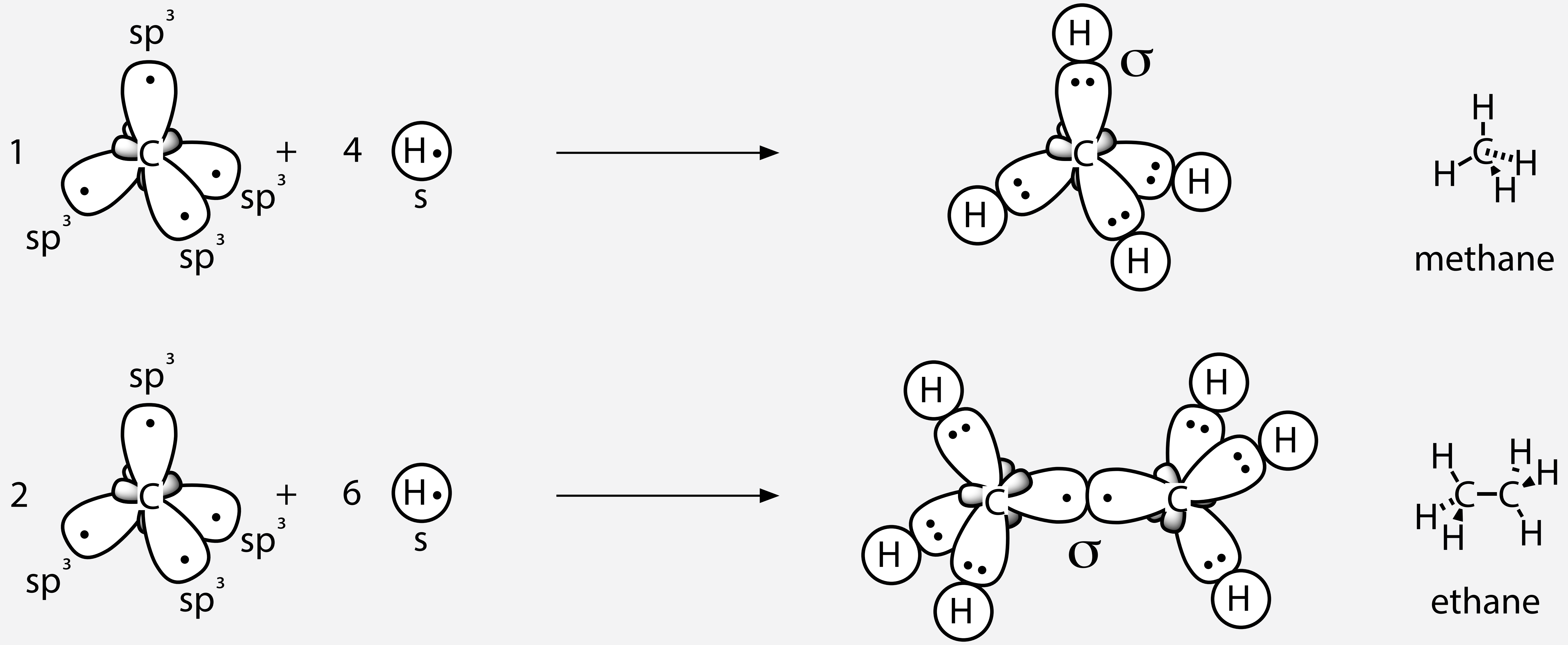
- **Lewis structure formulae show unpaired electrons as dot and electron pairs as lines**
- **electron pairs can be covalent bonds between two atoms or lone pairs assigned to one atom**
- **I mostly use double dots for lone pairs for purely practical reasons (drawing software limitation)**
- **atoms can be connected by single, double, or triple bonds (one, two or three electron pairs)**
- **carbon, nitrogen, oxygen, fluorine strictly fulfill octet rule; carbon is always tetravalent**

Different Types of Chemical Formulae

trivial name	IUPAC name	molecular formula	condensed formula	Lewis structure formulae
isobutane	2-methylpropane	C_4H_{10}	CH_3 -CH(CH_3)-CH_3	
acetone	propan-2-one	$C_3H_6O_6$	CH_3 -C(O)-CH_3	
acetic acid	ethanoic acid	$C_2H_4O_2$	CH_3-C(O)-OH CH_3COOH	
benzene	benzene	C_6H_6	C_6H_6	
styrene	1-phenylethene	C_8H_8	C_6H_5-CH=CH_2	

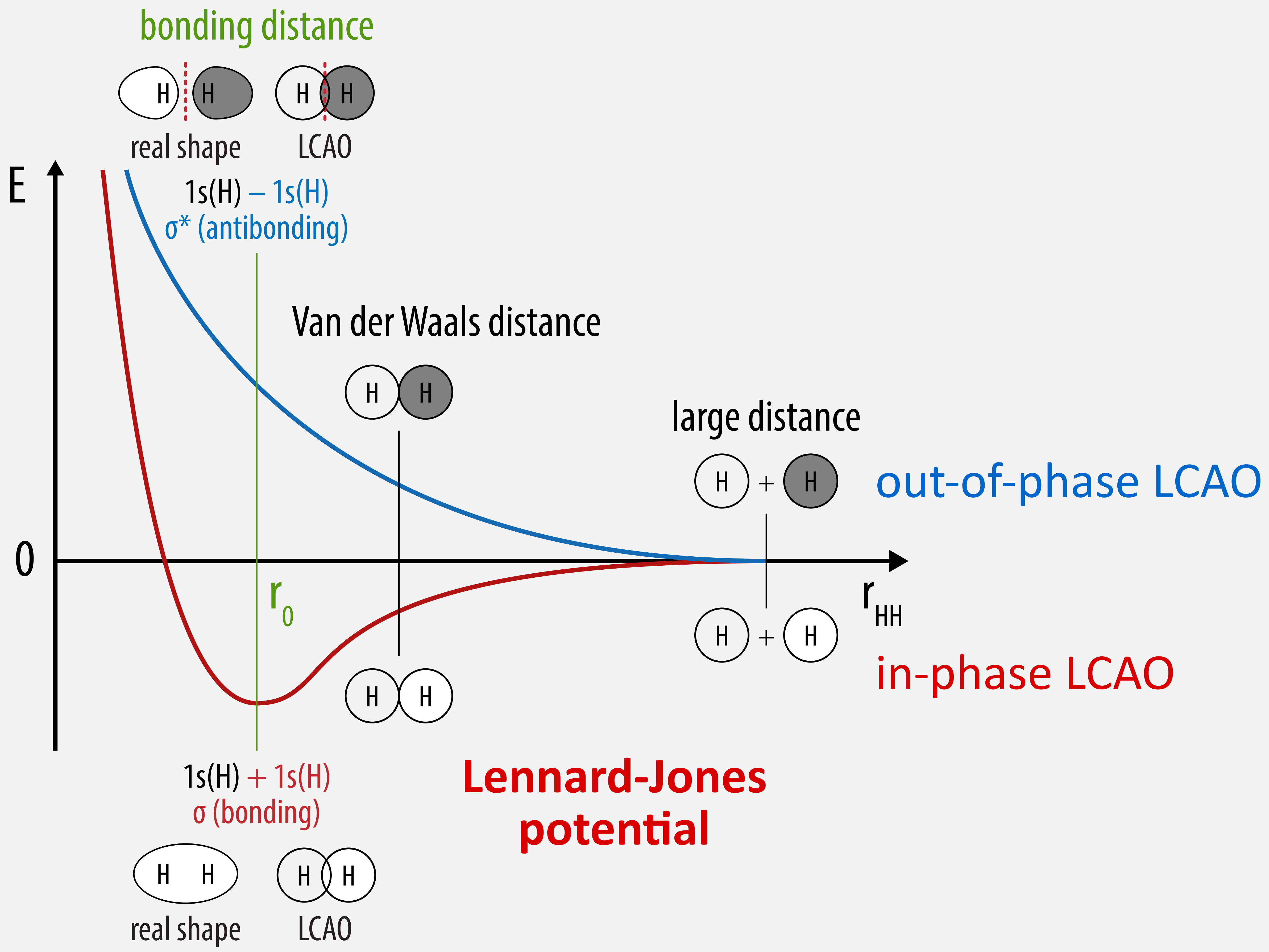
Formation of Single Bonds (Valence Bond Model)

- according to valence bond model, covalent bonds form by pairing electrons of atomic orbitals



- **in-phase combination of atomic or hybrid orbitals**
- **single bonds are σ-bonds (rotational symmetry) between sp³, sp², sp, or s orbitals**
- **due to rotational symmetry of the σ-orbital, rotation is free without breaking the bond**

Interaction of Atomic Orbitals upon Approach

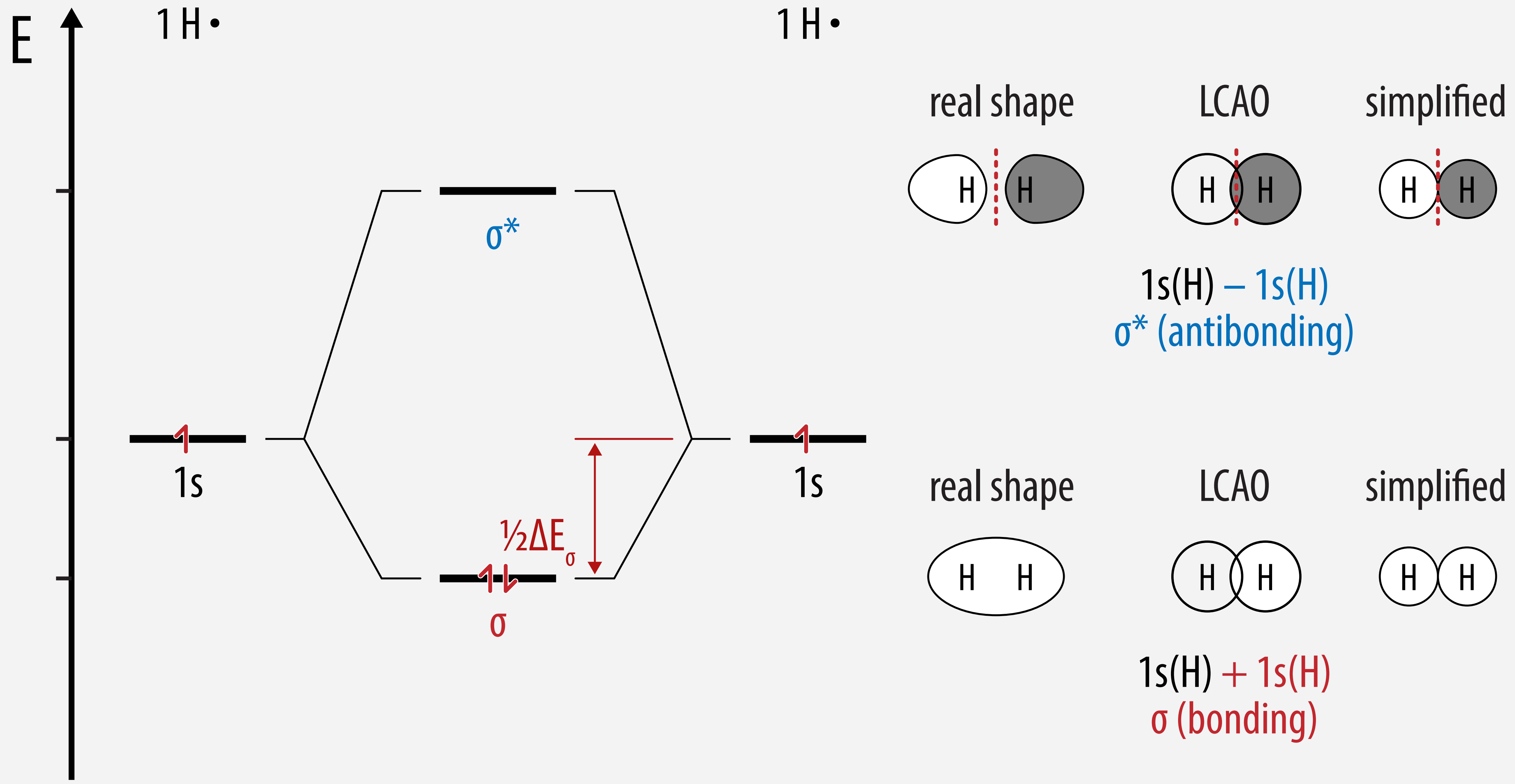


Lennard-Jones potential

- **upon decreasing the interatomic distance, atomic orbitals interact and split energetically**
- **number of orbitals conserved, LCAO with one in-phase LCAO and one out-of-phase LCAO**
- **energy in fact not quite conserved, overall raise of both levels due to electrostatic repulsion**

Molecular Orbital Energy Diagrams

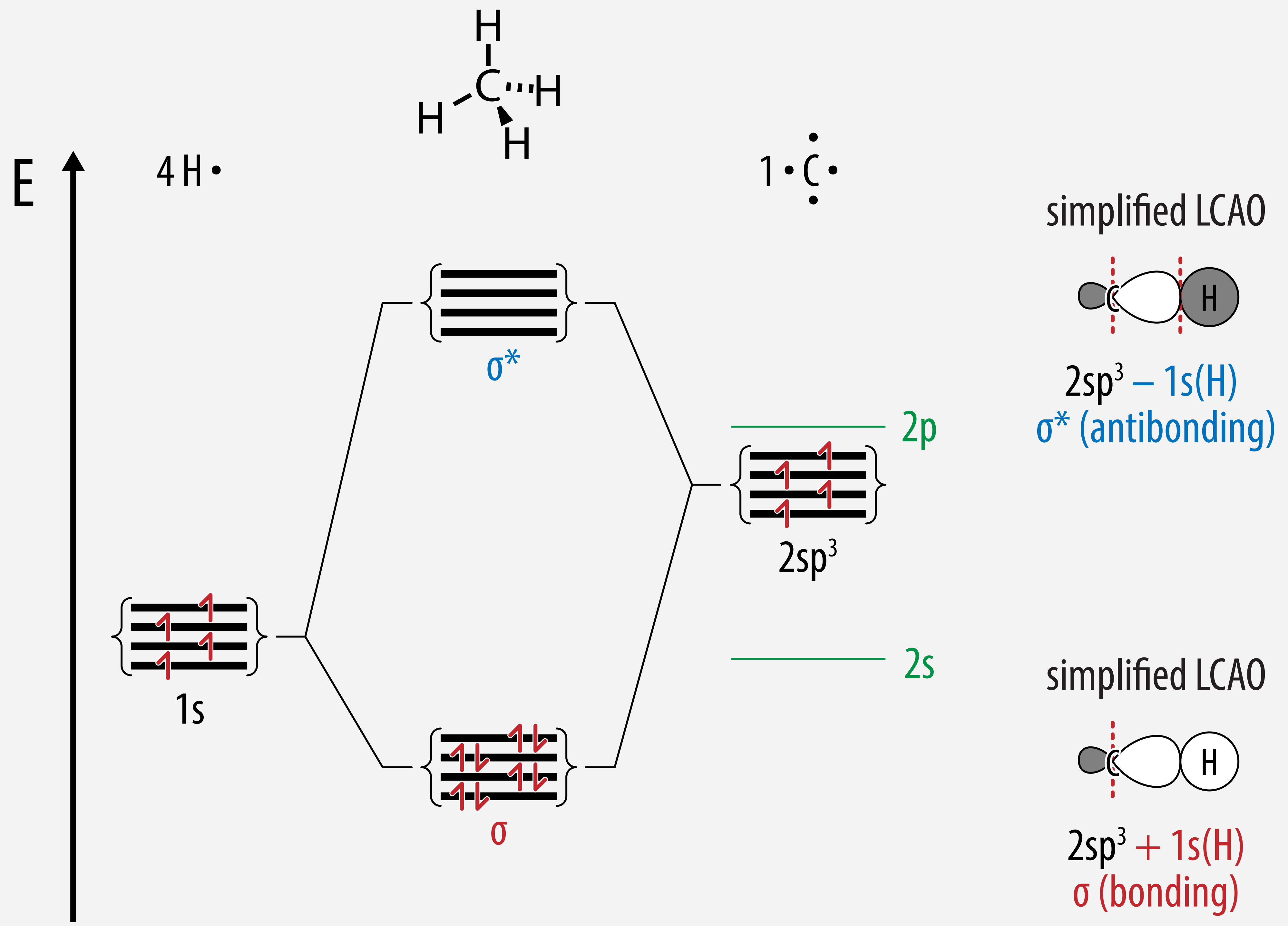
- schematic molecular orbital energy diagram for a symmetric diatomic molecule (such as H_2)



- **energy splitting increases with atomic orbital overlap**
- **number of orbitals preserved but sum of orbital energies (electron density) increases**
- **bond energy is stabilization of filled bonding orbital σ (due to electron delocalization)**
- **antibonding orbital σ* is energetically destabilized but remains empty (but relevant for reactivity!)**

Molecular Orbital View of the Covalent Bond in Multiatom Molecules

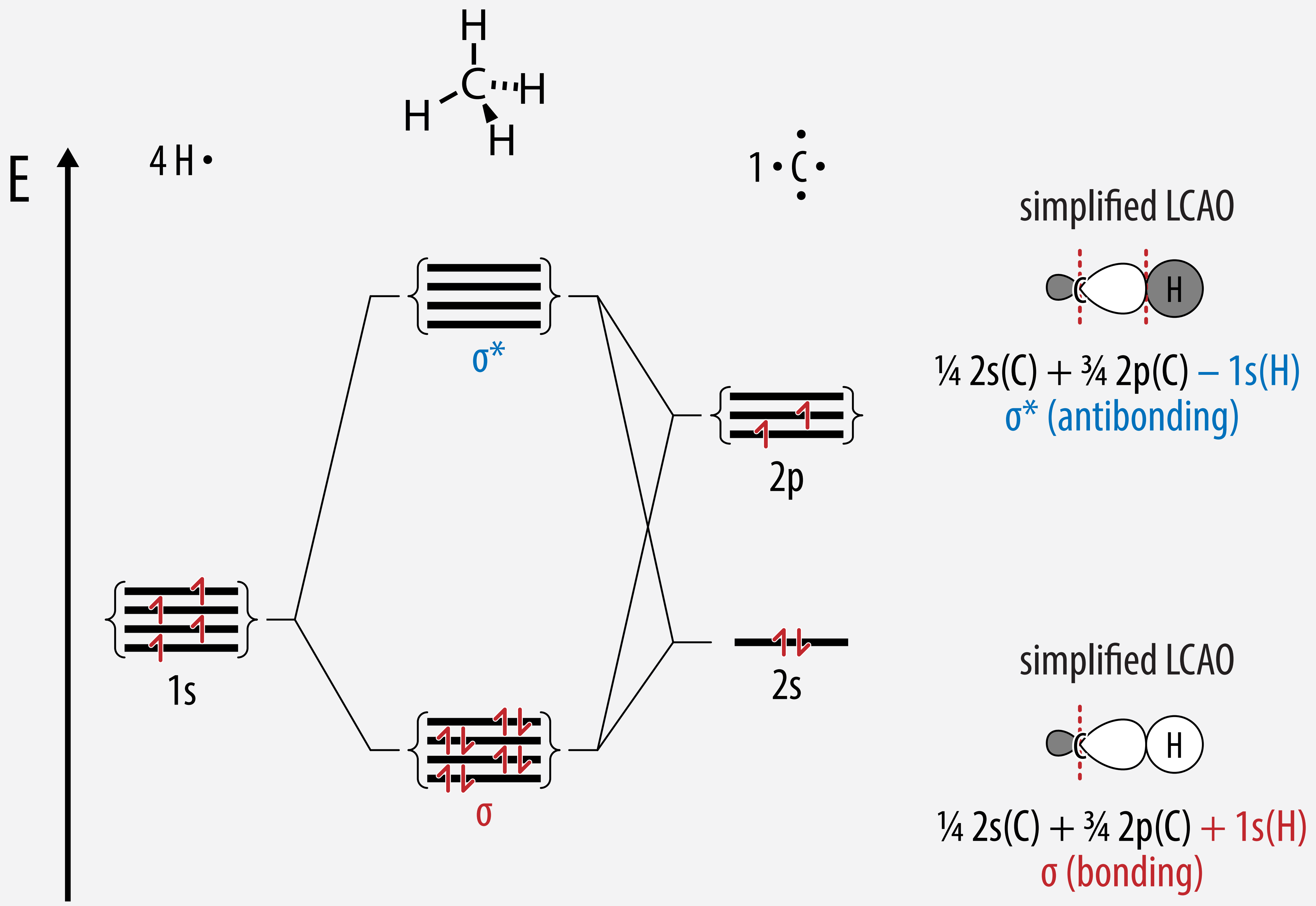
- simplified and schematic molecular orbital energy diagram of the methane molecule



- **linear combination of atomic orbitals may start from LCAO hybrid orbitals**
- **interactions between orbitals or orbital sets of matching symmetry**

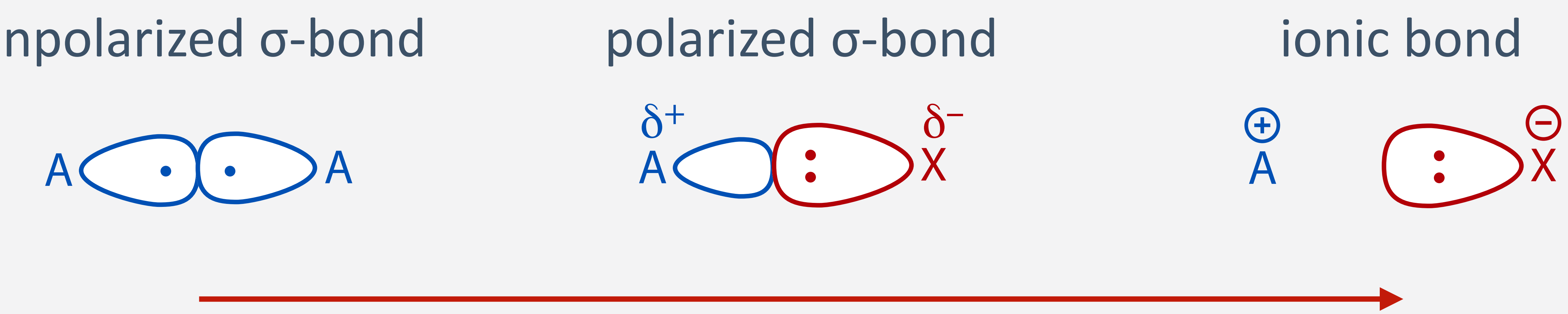
Molecular Orbital View of the Covalent Bond in Multiatom Molecules

- simplified and schematic molecular orbital energy diagram of the methane molecule



- **a more correct approach would start from atomic orbitals instead of hybrid orbitals**
- **result will be (almost) the same due to “mixing” of orbitals**
- **VSEPR model and hybridization are useful and valid simplifications**

Polarization of Covalent Bonds



unpolarized σ-bond

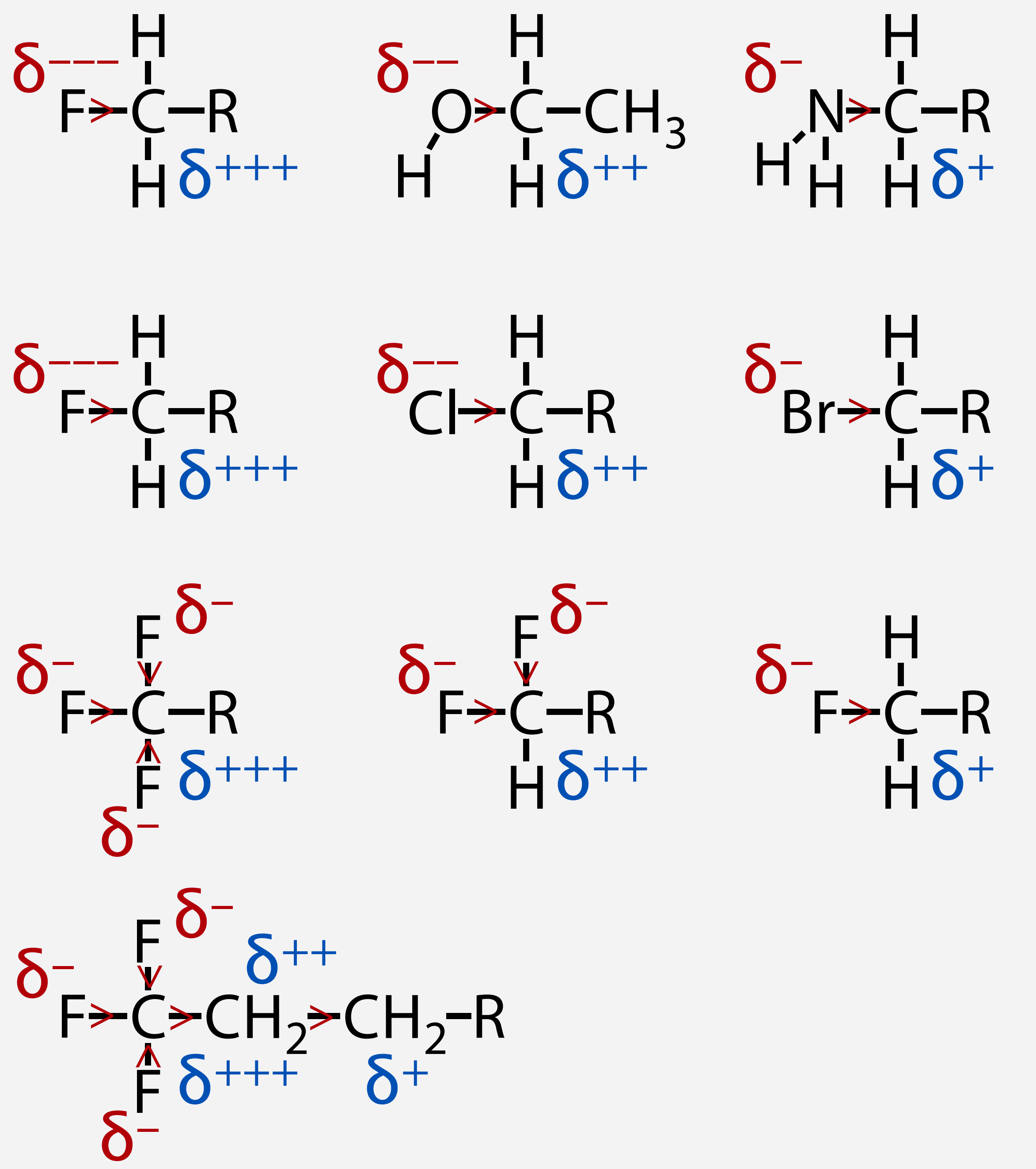
polarized σ-bond

ionic bond

increasing electronegativity (of X and Y)

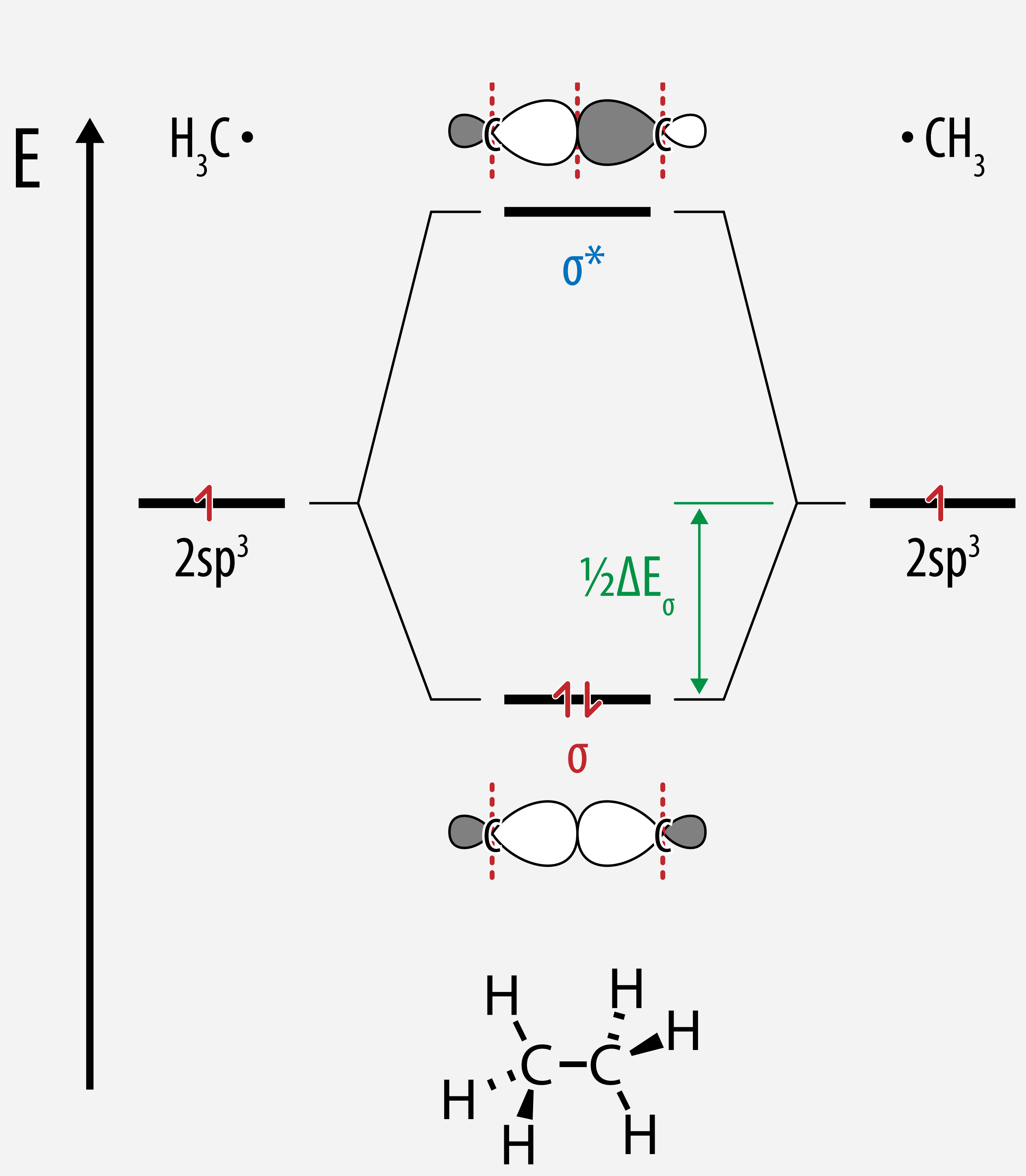
IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	**Be** 1.5			**B** 2.0	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0
Na 0.9	**Mg** 1.2			**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0
K 0.8	**Ca** 1.0							**Br** 2.8
								I 2.5

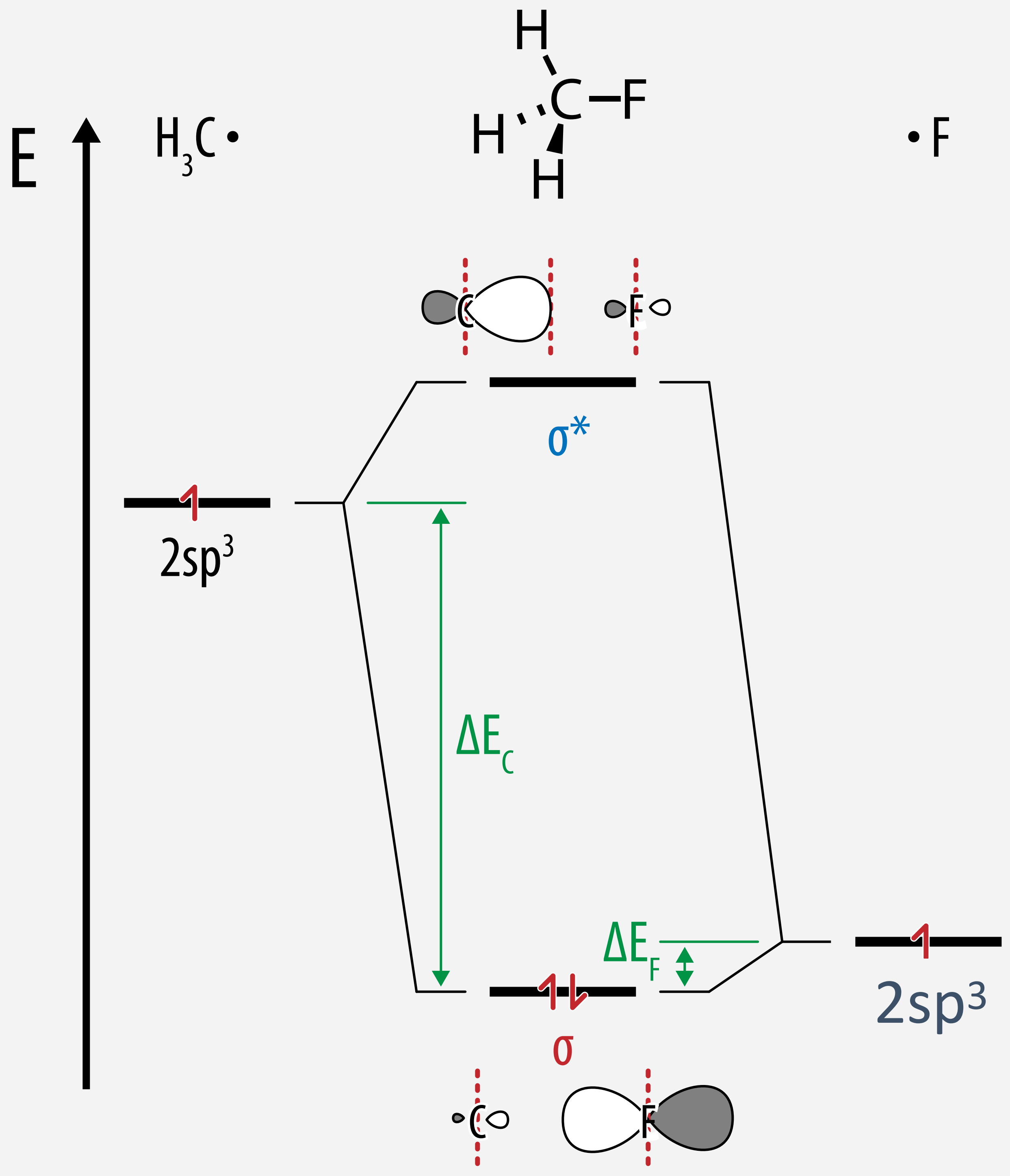
negative inductive Effect (–I effect)



Molecular Orbital Representation of Polarized Bonds

- simplified and schematic molecular orbital diagrams of the C–C and the C–F bond





- **atomic orbitals of more electronegative atoms lower in energy (higher electron affinity)**
- **increasing energy difference between bonding partners implies less electronic interaction**
- **bonding MO closer in energy to, “look more like” AO from more electronegative element**

Learning Outcomes

- covalent bond can be described by linear combination of atomic orbitals
- interactions only between orbitals or orbital sets of matching symmetry
- number of orbitals preserved but sum of all orbital energies increases
- bond energy is stabilization of bonding orbital σ (electron delocalization)
- antibonding orbital σ* energetically destabilized but remains empty