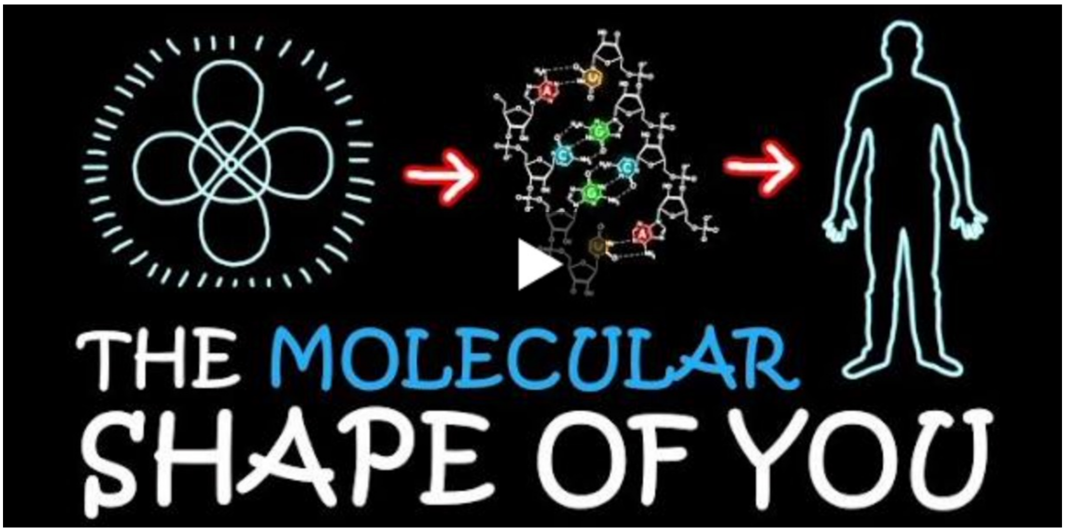
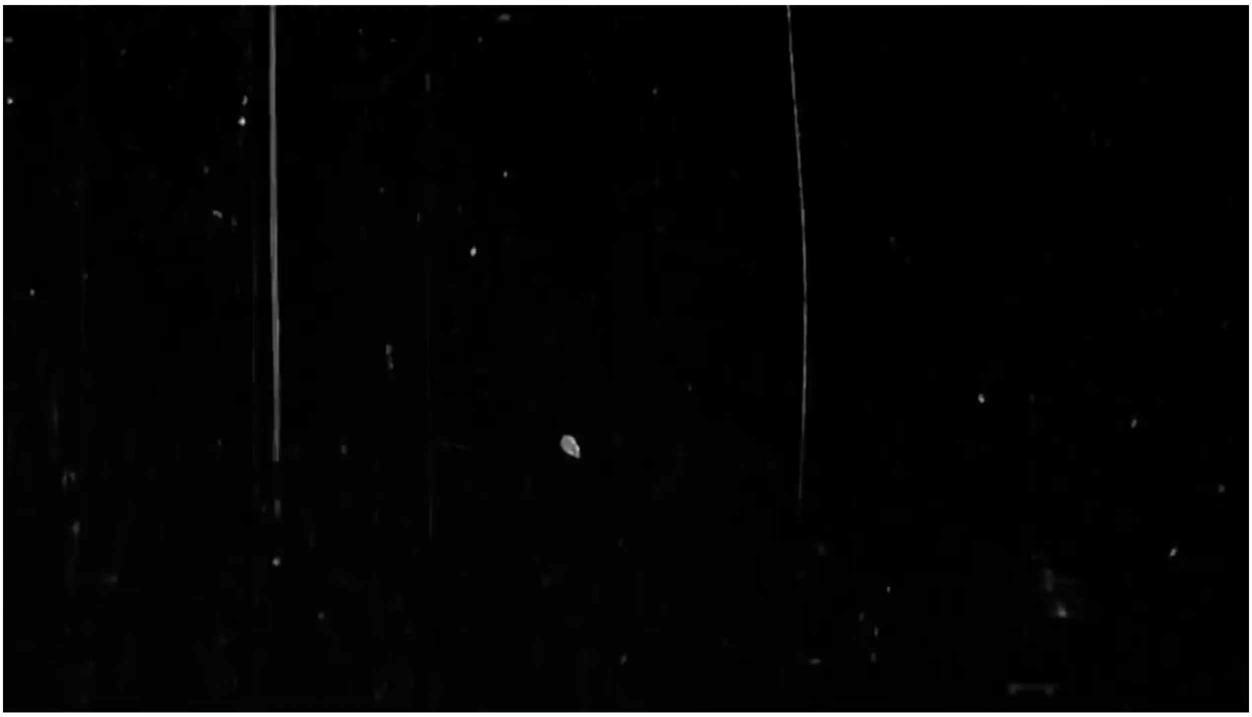
MSE 423 Fall 2025 – Week 7

From atoms to molecules



MSE 423 Fall 2024 – Week 7

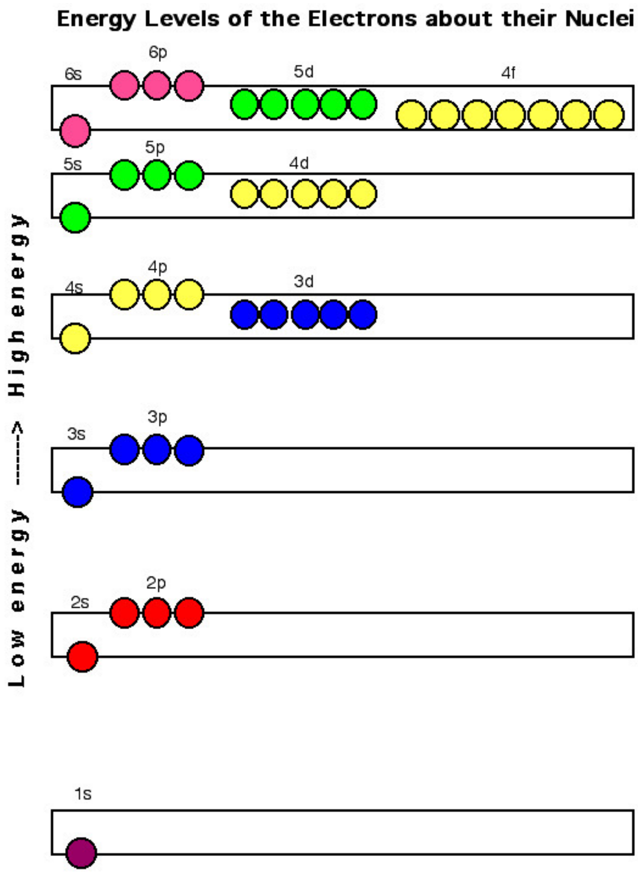


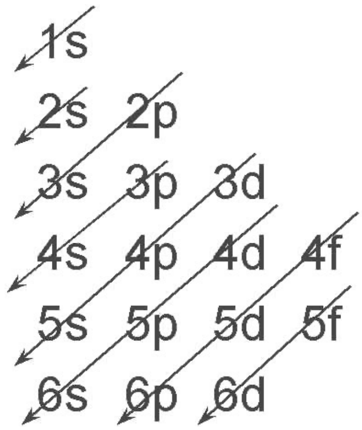
Exam: (double check in Dec/Jan): Tuesday 20 Jan 2026 15h15 to 18h15 (AAC 2 31)

Last week

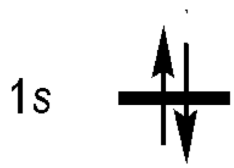
- Spin - S^2 and S_z
- Atomic units
- Two-electron atom and many-electron atom
- Energy of a collection of atoms
- Hartree ansatz and equations
- Spin-statistics connection
- Slater determinants and Hartree-Fock equations
- Pauli exclusion principle

Auf-bau





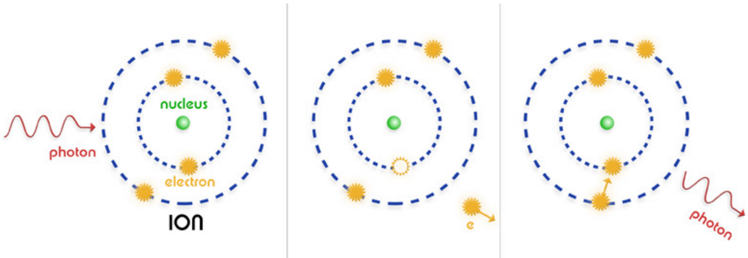
One more complexity – spin orbitals

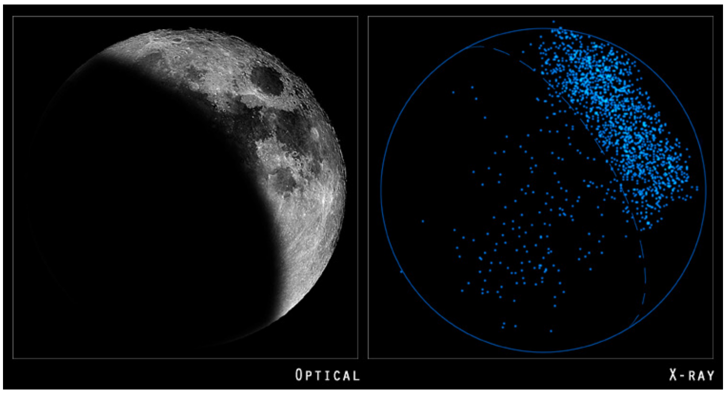


$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) \end{vmatrix}$$

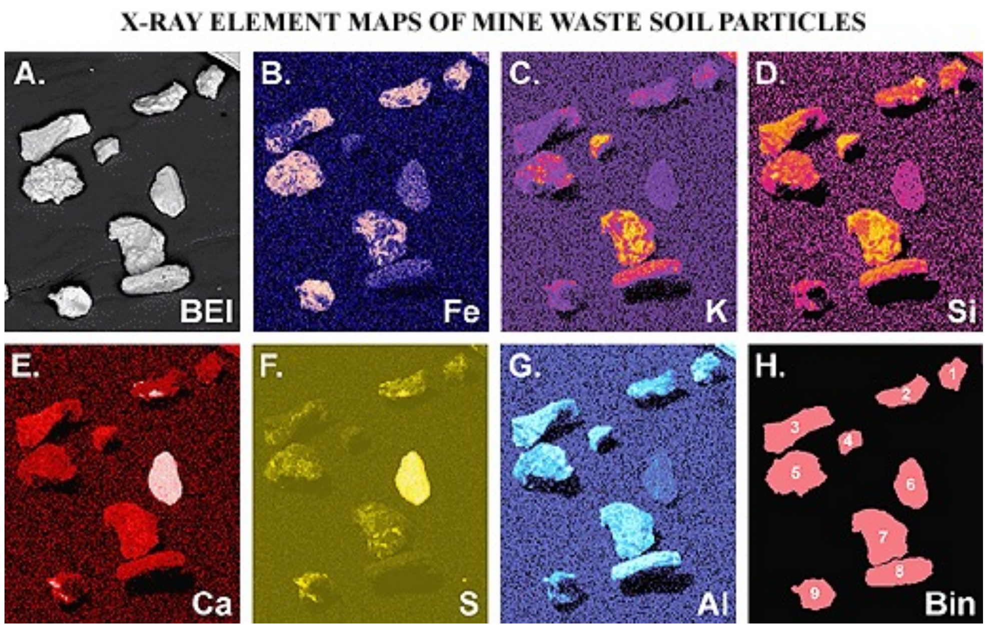
$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \underbrace{[\varphi_{1s}(1)\varphi_{1s}(2)]}_{\text{spatial component}} \underbrace{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{spin component}}$$

XPS in Materials





Composition Analysis



Hydrogen Molecular Ion H_2^+

- Born-Oppenheimer approximation: the electron is always in the ground state corresponding to the instantaneous ionic positions

$$\left[-\frac{1}{2}\nabla^2 + \left(\frac{1}{\left|\vec{R}_{H_1} - \vec{R}_{H_2}\right|} - \frac{1}{\left|r - \vec{R}_{H_1}\right|} - \frac{1}{\left|r - \vec{R}_{H_2}\right|}\right)\right]\psi(\vec{r}) = E\psi(\vec{r})$$

Linear Combination of Atomic Orbitals

- Most common approach to find out the ground-state solution – it allows a meaningful definition of “hybridization”, “bonding” and “anti-bonding” orbitals.
- Also knows as LCAO, LCAO-MO (for molecular orbitals), or tight-binding (for solids)
- Trial wavefunction is a linear combination of atomic orbitals – the variational parameters are the coefficients:

$$\Psi_{trial} = c_1 \Psi_{1s}\left(\vec{r} - \vec{R}_{H_1}\right) + c_2 \Psi_{1s}\left(\vec{r} - \vec{R}_{H_2}\right)$$

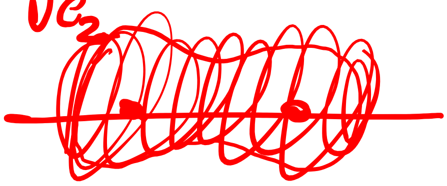
How do we find the two coefficients?

$\psi_{TRIAL} = c_1 \psi_{1s}(\vec{r} - H_1) + c_2 \psi_{1s}(\vec{r} - H_2)$

$E[\psi_{TRIAL}] = \frac{\langle \psi_{TRIAL} | \hat{H}_{H_2^+} | \psi_{TRIAL} \rangle}{\langle \psi_{TRIAL} | \psi_{TRIAL} \rangle}$ MINIMIZED

$\Downarrow$ $E(c_1, c_2)$ $\frac{\partial E}{\partial c_1}$ $\frac{\partial E}{\partial c_2}$ $\|\psi_{TRIAL}\|^2 = 1$

AT THE MINIMUM $c_1 = c_2$



Bonding and Antibonding (I)

$\psi_{TRIAL} = c_1 1sA + c_2 1sB$

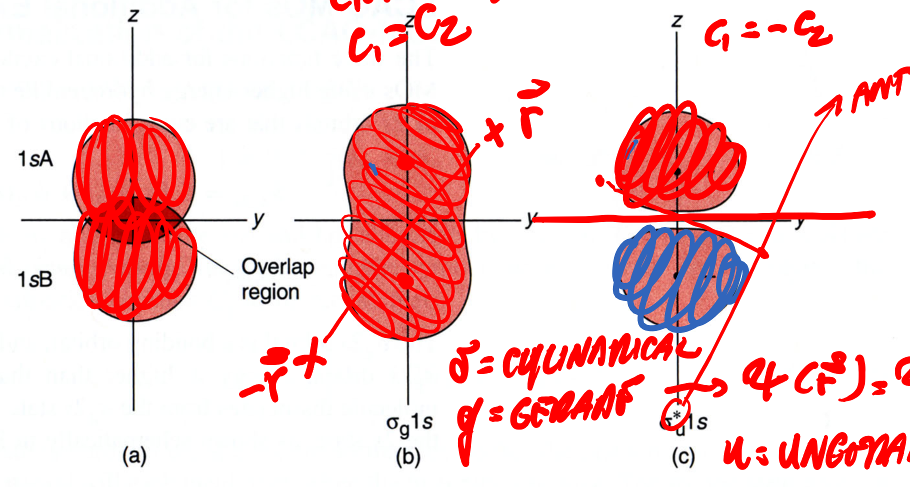
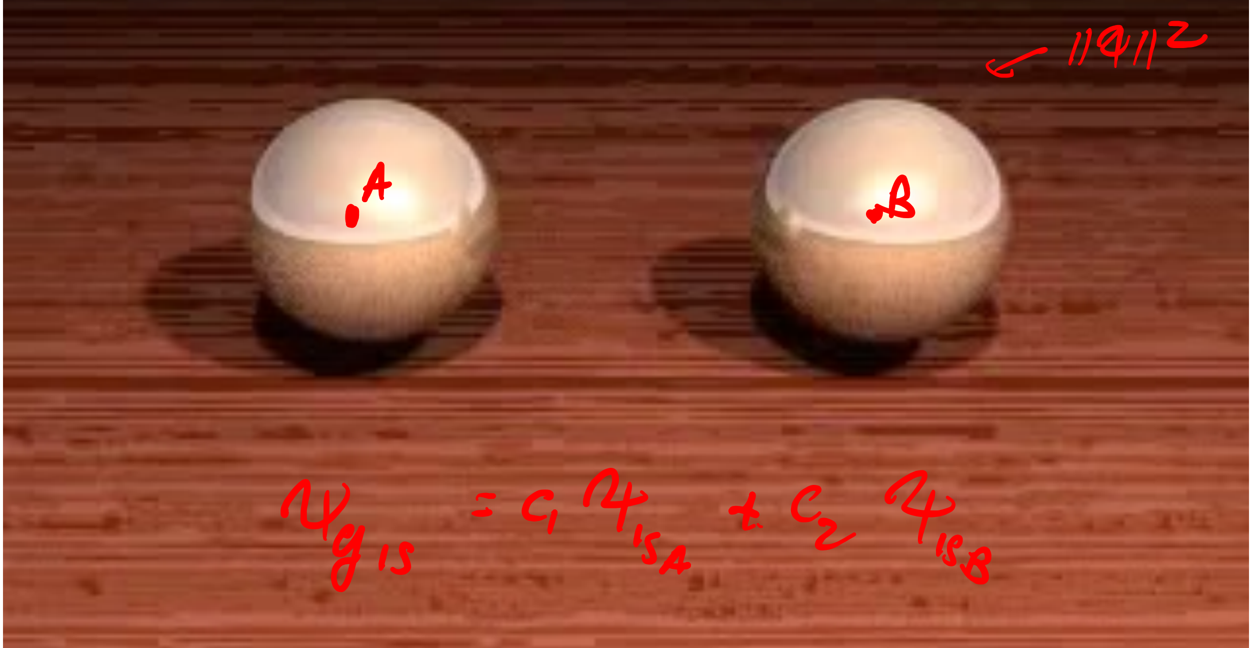


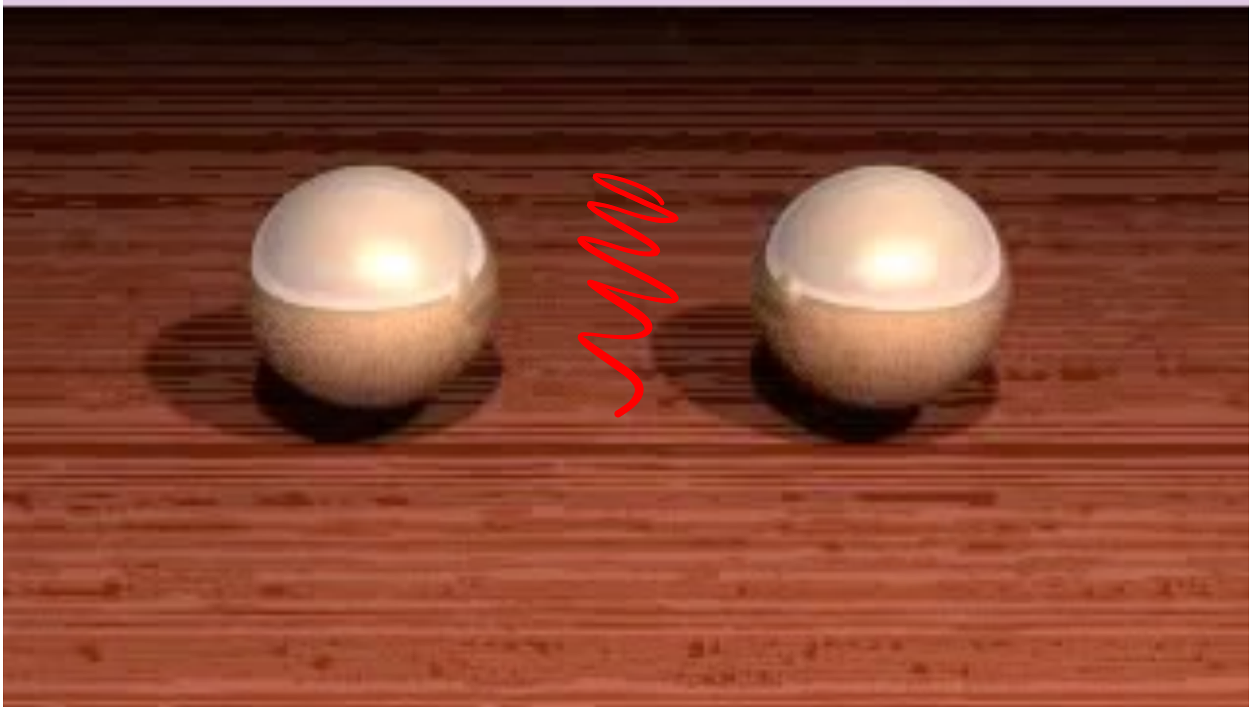
Figure 18.7 The Orbital Region for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. (a) The overlapping orbital regions of the 1sA and 1sB atomic orbitals. (b) The orbital region of the $\sigma_g 1s$ LCAO-MO. (c) The orbital Region of the $\sigma_u^* 1s$ LCAO-MO. The orbital regions of the LCAO molecular orbitals have the same general features as the "exact" Born Oppenheimer orbitals whose orbital regions were depicted in Figure 18.4.

Formation of a Bonding Orbital

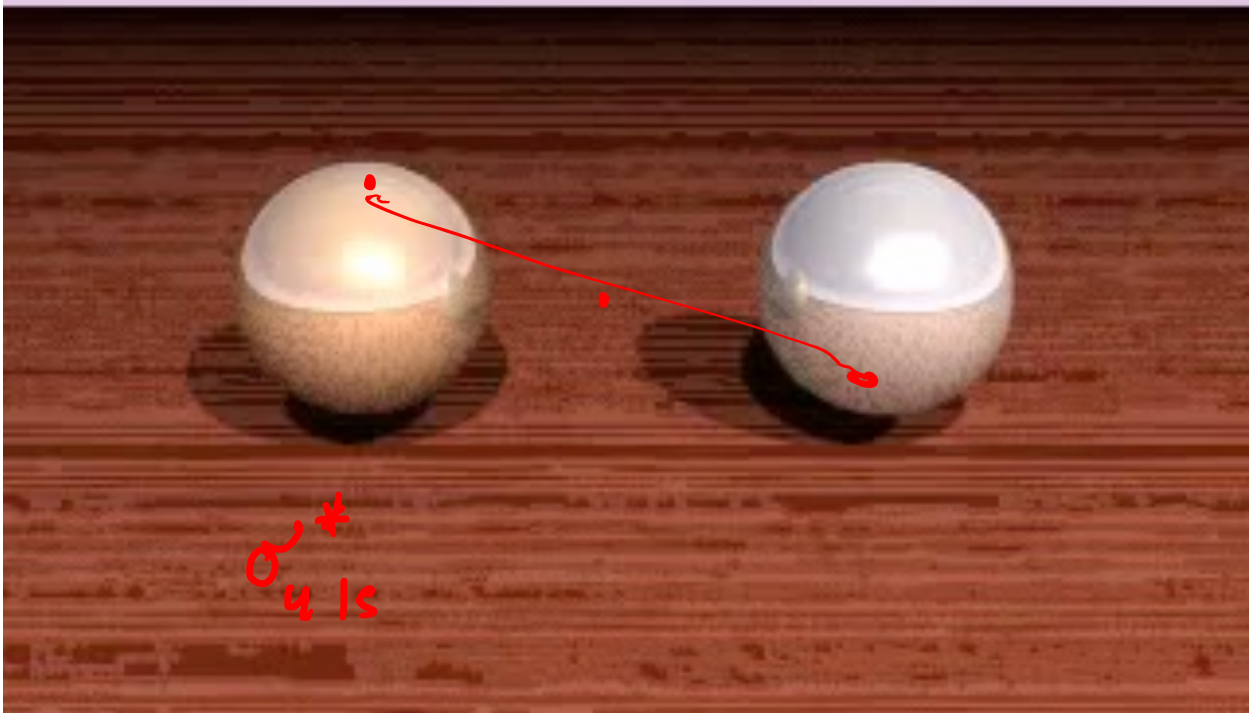
http://winter.group.shef.ac.uk/orbitron/



Formation of a Bonding Orbital



Formation of an Antibonding Orbital



MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

Formation of an Antibonding Orbital

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Bonding and Antibonding (II)

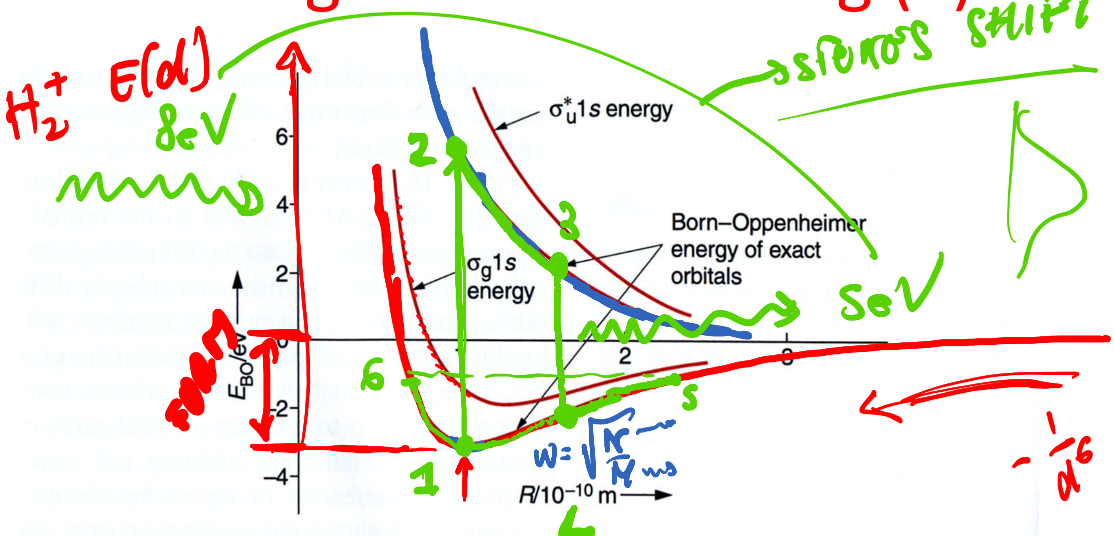


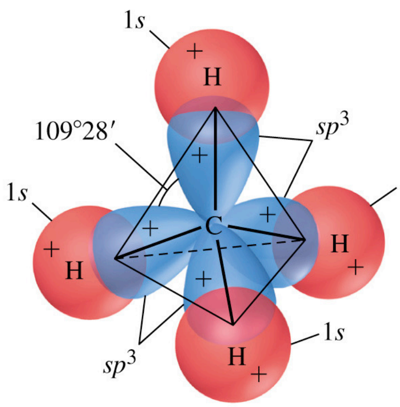
Figure 18.8 The Orbital Energies for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. This diagram shows qualitatively how the Born–Oppenheimer energies of the LCAO molecular orbitals compare with the Born Oppenheimer energies of the "exact" orbitals. The approximate orbital energies must lie above the corresponding exact energies for all internuclear distances.

More complex molecules: LCAO

$$\Psi_{trial} = \sum_{I,(nlm)} c^I_{(nlm)} \Psi^I_{(nlm)}\left(\vec{r} - \vec{R}_I\right)$$

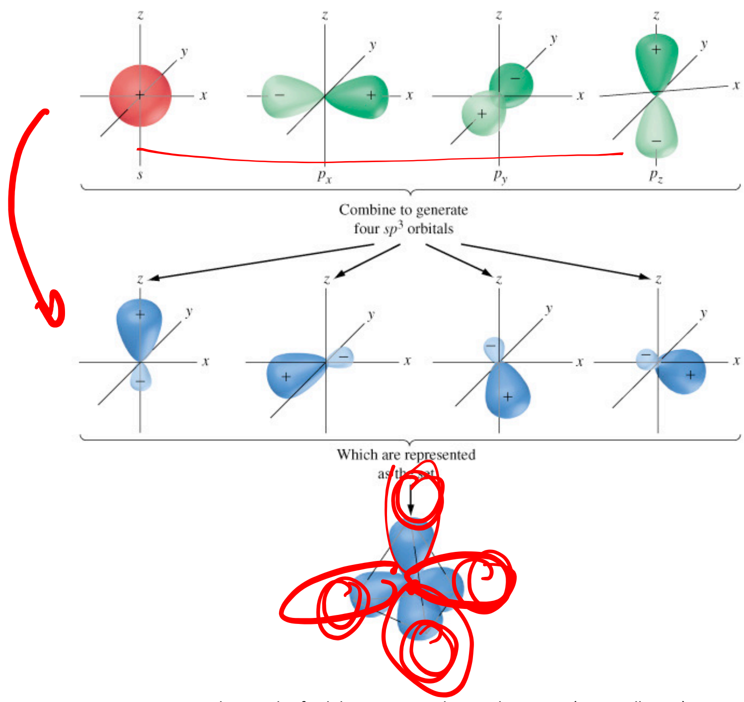
$$E_{LCAO} = \min \frac{\left\langle \Psi_{trial} \middle| \hat{H} \middle| \Psi_{trial} \right\rangle}{\left\langle \Psi_{trial} \middle| \Psi_{trial} \right\rangle}$$

More complex molecules: LCAO

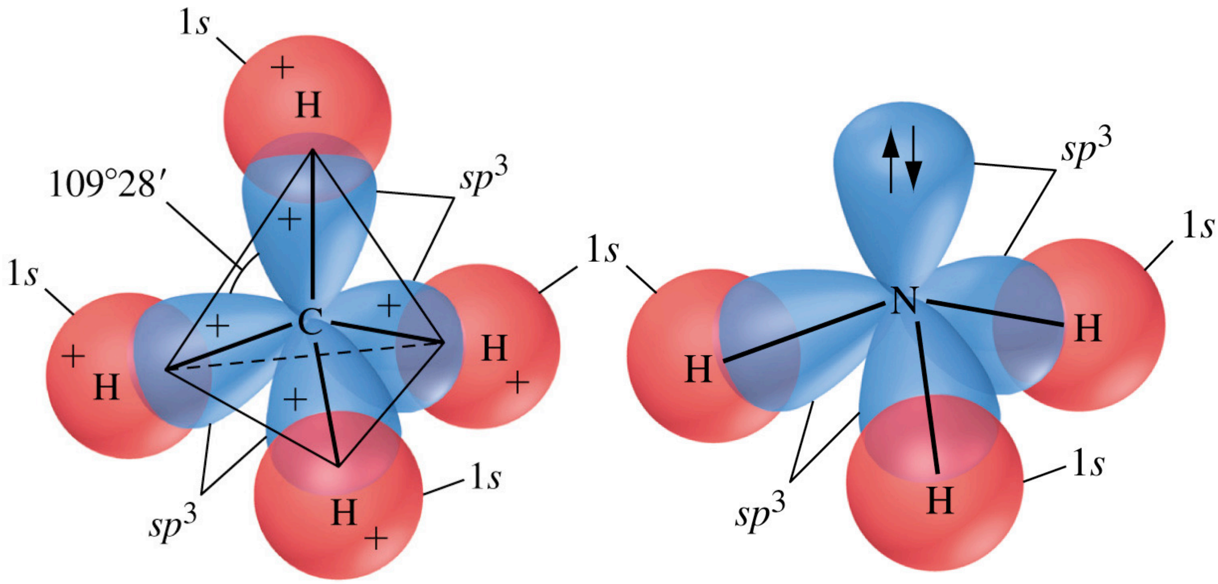


$$\Psi_{trial} = c_1\Psi_{1s,H_a} + c_2\Psi_{1s,H_b} + c_3\Psi_{1s,H_c} + c_4\Psi_{1s,H_d}$$
$$+ c_5\Psi_{2s,C} + c_6\Psi_{2p_x,C} + c_7\Psi_{2p_y,C} + c_8\Psi_{2p_z,C}$$

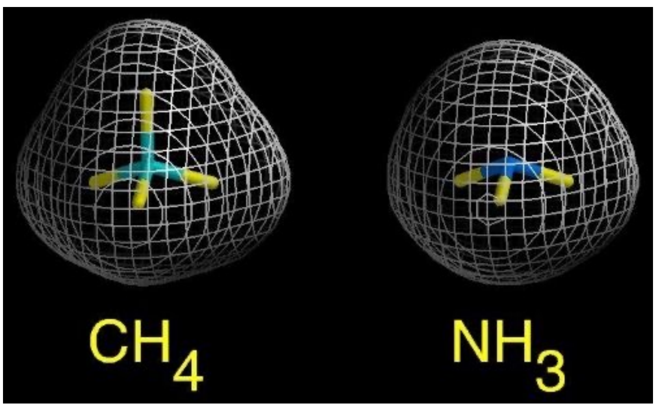
sp^3 hybridization

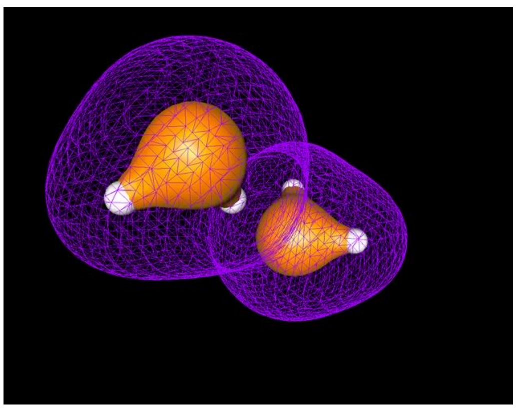


sp^3 hybridization

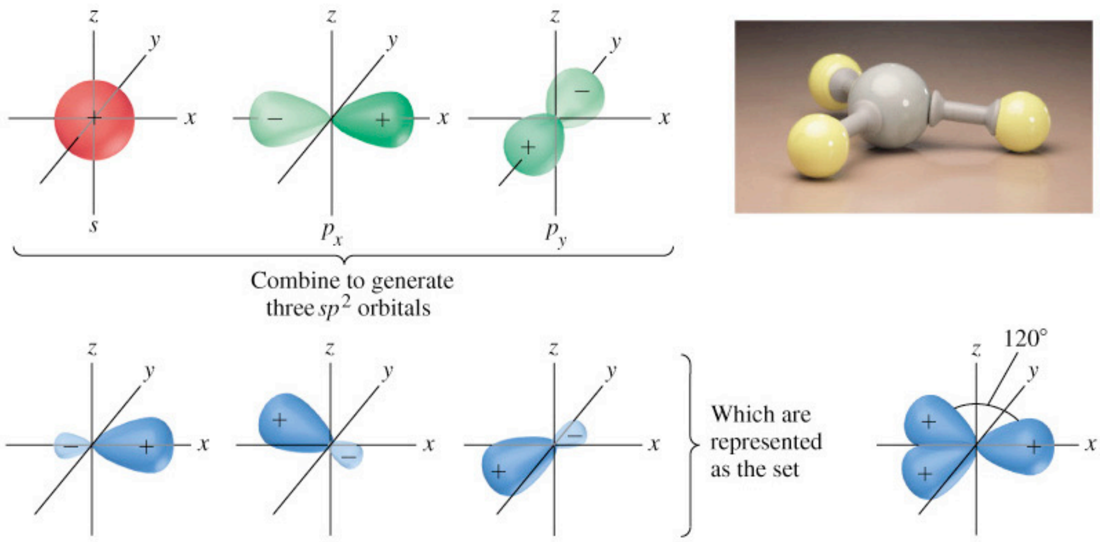


Great gases and liquids

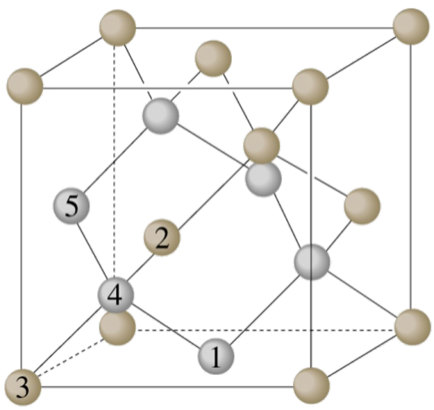


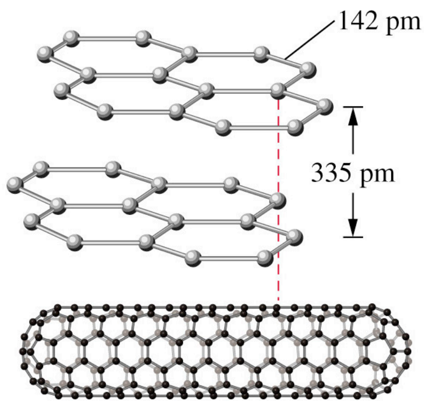


sp² hybridization

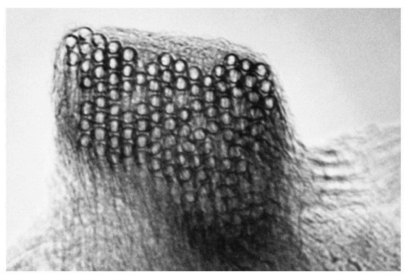


Carbon compounds



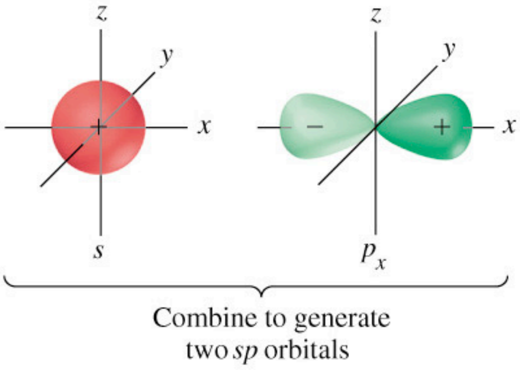


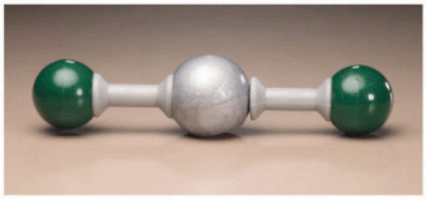
(a)

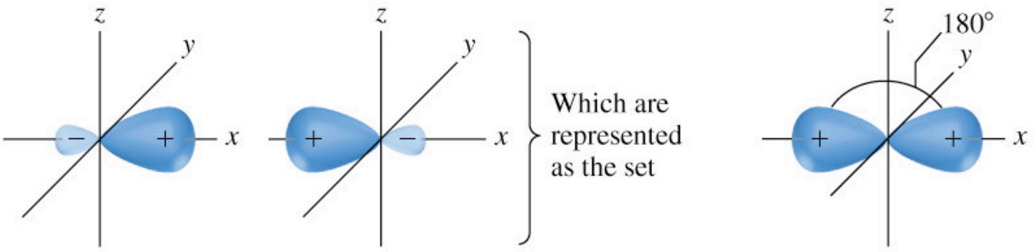


(b)

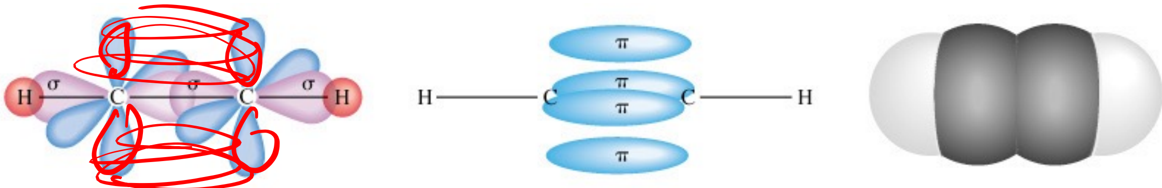
sp hybridization







Ethyne (Acetylene)

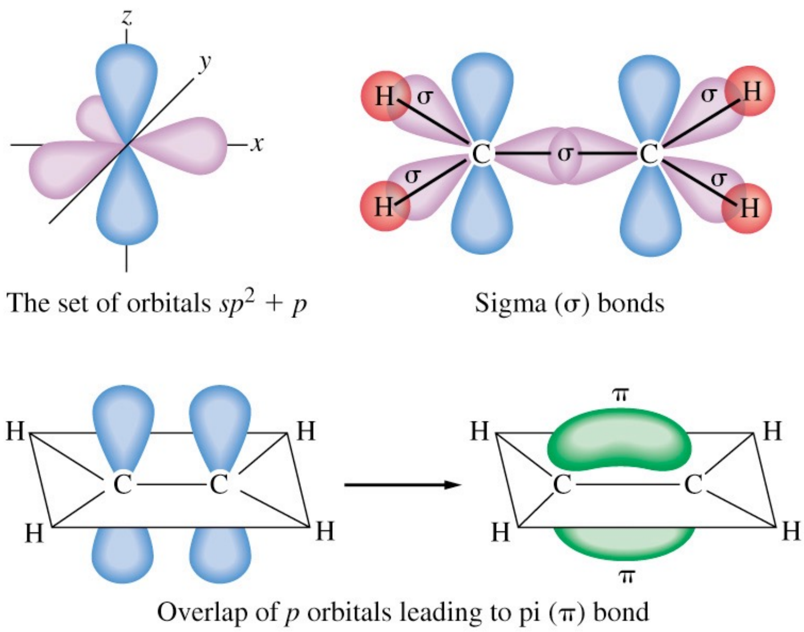


Formation of σ bonds

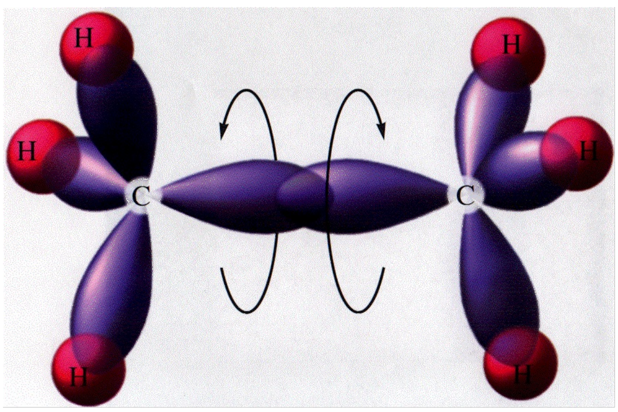
Formation of π bonds

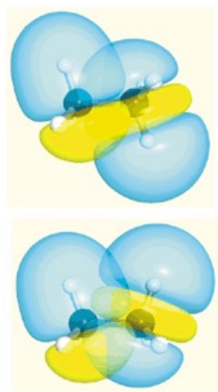
Space-filling model

Ethene (Ethylene)



Ethane (saturated)





Goodman *et al.* Nature (2001)

Bond Lengths and Bond Energies

TABLE 11.2 Some Average Bond Lengths[a]

Bond	Bond Length, pm	Bond	Bond Length, pm	Bond	Bond Length, pm
H—H	74.14	C—C	154	N—N	145
H—C	110	C=C	134	N=N	123
H—N	100	C≡C	120	N≡N	109.8
H—O	97	C—N	147	N—O	136
H—S	132	C=N	128	N=O	120
H—F	91.7	C≡N	116	O—O	145
H—Cl	127.4	C—O	143	O=O	121
H—Br	141.4	C=O	120	F—F	143
H—I	160.9	C—Cl	178	Cl—Cl	199
				Br—Br	228
				I—I	266

[a] Most values (C—H, N—H, C—H, . . .) are averaged over a number of species containing the indicated bond and may vary by a few picometers. Where a diatomic molecule exists, the value given is the actual bond length in that molecule (H_2, N_2, HF, . . .) and is known more precisely.

TABLE 11.3 Some Average Bond Energies[a]

Bond	Bond Energy, kJ/mol	Bond	Bond Energy, kJ/mol	Bond	Bond Energy, kJ/mol
H—H	436	C—C	347	N—N	163
H—C	414	C=C	611	N=N	418
H—N	389	C≡C	837	N≡N	946
H—O	464	C—N	305	N—O	222
H—S	368	C=N	615	N=O	590
H—F	565	C≡N	891	O—O	142
H—Cl	431	C—O	360	O=O	498
H—Br	364	C=O	736[b]	F—F	159
H—I	297	C—Cl	339	Cl—Cl	243
				Br—Br	193
				I—I	151

[a] Although all data are listed with about the same precision (three significant figures), some values are actually known more precisely. Specifically, the values for the diatomic molecules: H_2, HF, HCl, HBr, HI, N_2 (N≡N), O_2 (O=O), F_2, Cl_2, Br_2, and I_2 are actually bond-dissociation energies, rather that average bond energies.
[b] The value for the C=O bonds in CO_2 is 799 kJ/mol.

Homonuclear Diatomic Levels (I)