

Molecular orbitals

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- From the viewpoint of the quantum mechanics, there is no chemical bonds! There are nuclei and electrons, and there is the wavefunction $\Psi(1,2,\dots,N)$, which bears all the information about the molecule.
- *Bonds*, as something linking two atoms (nuclei) in a molecule, is a chemical concept born long before the advent of quantum mechanics or the discovery of electron.
 - ▶ Still, *chemical bond* is a powerful, extremely useful concept central to chemistry.
 - ▶ Related concepts are also widely used in chemistry: atomic charges, bond orders (multiplicities), bond strengths (energies) – none of them has a clear quantum-mechanical counterpart.
- We often wish to extract some bonding information from the wavefunction obtained in a quantum-mechanical calculation.
 - ▶ No easy way! We have to invent extra methods (“tools”) to do so.

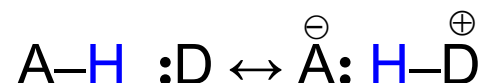
- *Covalent bond*: most universal bond type.
- *Ionic bond*: usually regarded as electrostatic interactions between two ions, but can be also seen as a limiting case of a polar covalent bond.
- *Donor-acceptor bond*: is also similar to and sometimes indistinguishable from a covalent bond. **Exercise**: consider the NH_4^+ example.
- *Ligand-metal bonds*: can be quite different, but usually described as donor-acceptor.
- *Hypervalent bonds*: still covalent.
- *Metallic bond*: a kind of highly delocalized bond in metals.
- *Charge-shift bond*: a special sort of covalent bond (such as F_2).
- There is no absolute limits between those bond types. They can be described as special cases of a covalent bond.

Weaker interactions:

(often called “non-covalent”)

- “Orbital” (i.e. in part covalent) interactions:

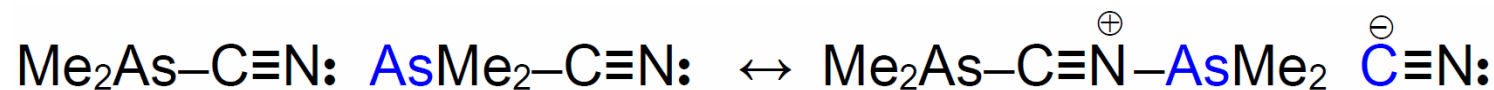
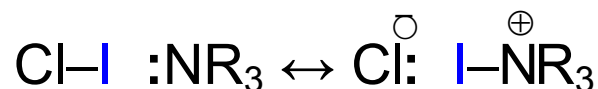
► *Hydrogen bond*: partly electrostatic, partly covalent. The stronger, the more covalent! (3-center 4-electron bond) $A-H \cdots D$



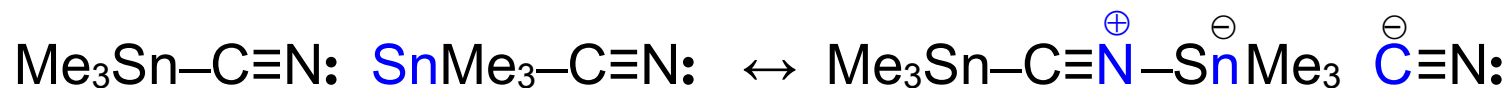
is an electron-withdrawing group.

MO description: $n(D) \rightarrow \sigma^*(A-H)$. **Exercise**: consider H_2O .

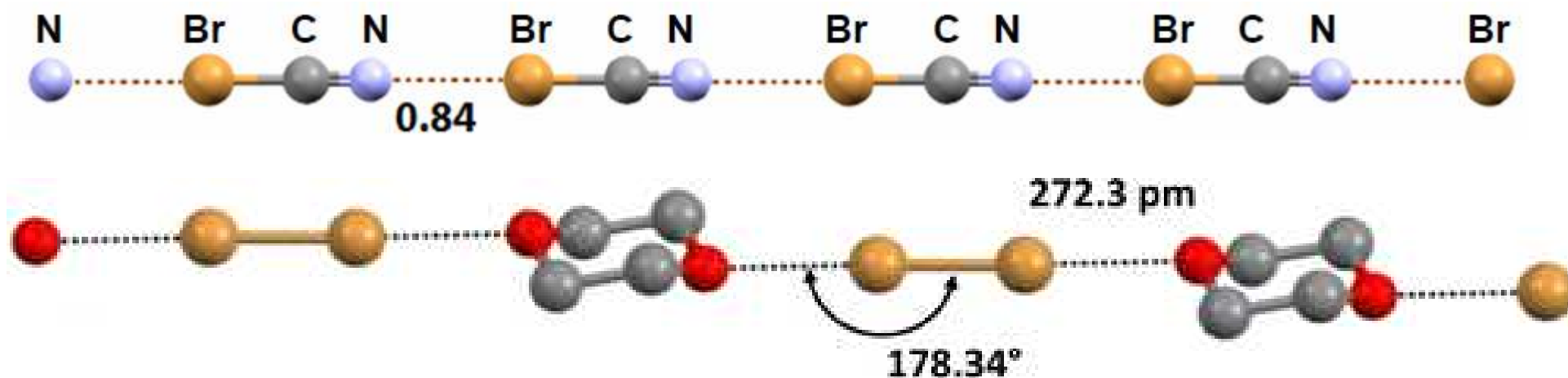
- *Halogen, chalcogen, and pnictogen* bonds:



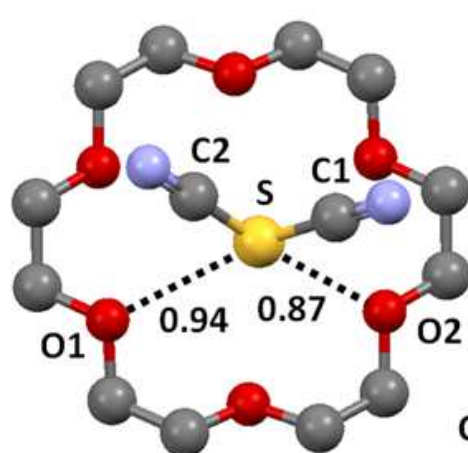
- Also *triel* and *tetrel* bonds (and others):



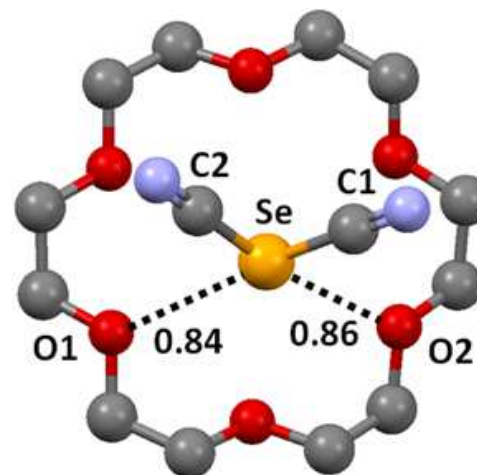
Halogen bond:



Chalcogen bond:

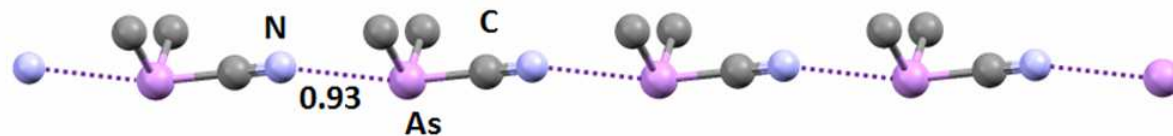
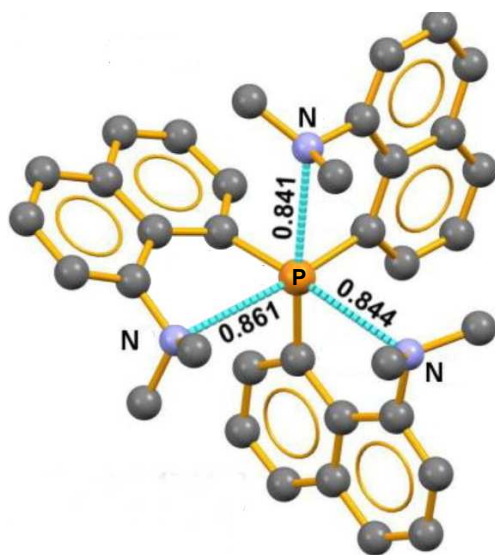


C1-S...O1 162.29°
C2-S...O2 173.41°

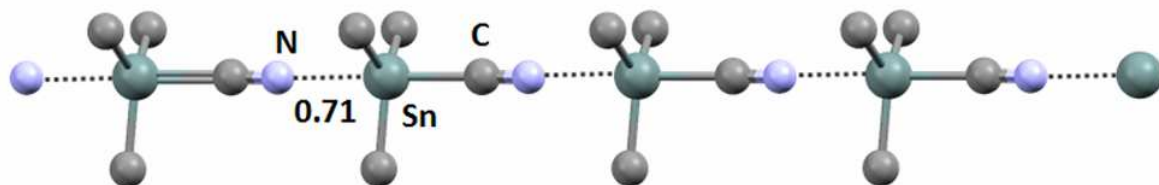


C1-Se...O1 167.25°
C2-Se...O2 161.24°

Pnictogen bond:



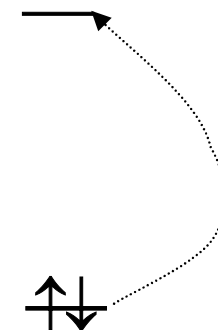
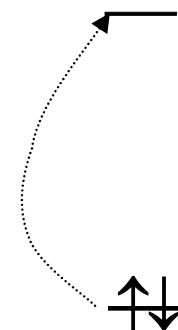
Tetrel bond:



Weaker interactions:

(often called “non-covalent”)

- “Orbital” (i.e. in part covalent) interactions:
 - ▶ *Hydrogen, halogen, chalcogen, pnictogen, triel, tetrel* bonds ...
- Non-orbital (non-covalent) interactions:
 - ▶ *Electrostatic interactions*: dipole-dipole, dipole-quadrupole, ...
Note: Dipole-induced dipole etc. are *not* purely electrostatic (polarization = induction)
 - ▶ *Dispersion interactions*: non-covalent: long-distance correlation effects.



- In general, a *molecular orbital* (MO) is a one-electron wavefunction of any kind.
 - ▶ For a many-electron system (atom or molecule), an MO is *not* the same as the total wavefunction. The latter depends on coordinates and spins of all N electrons in the system: $\Psi(1,2,...,N)$.
 - ▶ Terminology: a *spin-orbital* $\varphi(1)$ depends on coordinates and spins of one electron. A *spatial orbital* (or just an *orbital*) $\psi(\mathbf{r}_1)$ depends on coordinates only. They are related through a spin function:
 $\varphi(1) = \psi(\mathbf{r}_1)\alpha(\sigma_1)$, or $\varphi(1) = \psi(\mathbf{r}_1)\beta(\sigma_1)$, or $\varphi(1) = \psi_1(\mathbf{r}_1)\alpha(\sigma_1) + \psi_2(\mathbf{r}_1)\beta(\sigma_1)$
 Thus, $(1) = (\mathbf{r}_1, \sigma_1)$, where σ is the spin coordinate, α and β are spin eigenfunctions ($\hat{S}_z\alpha(\sigma) = 1/2\alpha(\sigma)$, “spin-up” \uparrow ; $\hat{S}_z\beta(\sigma) = -1/2\beta(\sigma)$, “spin-down” \downarrow).
 - ▶ Spin-orbitals are related to the total many-electron wavefunction $\Psi(1,2,...,N)$. In the Hartree–Fock approximation, Ψ is constructed from the spin-orbitals as a Slater determinant:

$$\Psi(1,2,...,N) = \frac{1}{\sqrt{N!}} \det[\varphi_i(j)] = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \dots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \dots & \varphi_2(N) \\ \dots & \dots & \dots & \dots \\ \varphi_N(1) & \varphi_N(2) & \dots & \varphi_N(N) \end{vmatrix}$$

- ▶ In the DFT, the meaning of orbitals is similar, but not identical.

- A well-known concept of an orbital occupied by *two* electrons is based on construction of two spin-orbitals from the same spatial orbitals, which is an additional approximation:

$$\varphi_1(1) = \psi(\mathbf{r}_1)\alpha(\sigma_1), \text{ or } \varphi_2(2) = \psi(\mathbf{r}_2)\beta(\sigma_2); \uparrow\downarrow$$

If there is an even number of electrons N , we need only $N/2$ doubly occupied spatial orbitals, giving rise to N spin orbitals. This corresponds to a Restricted closed-shell Hartree–Fock wavefunction. The orbitals are obtained as a solution of a one-electron equation (Hartree–Fock equation):

$$\hat{F}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

where \hat{F} is the one-electron Fock operator (Fockian) and ε_i is the eigenvalue (orbital energy).

Note: The sum of the occupied orbital energies is *not* equal to the total molecular energy.

Note: In the DFT, the molecular orbitals are eigenfunctions of another one-electron operator (Kohn–Sham operator), but work in a similar fashion.

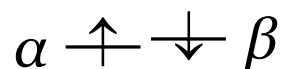
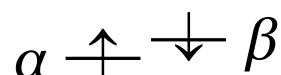
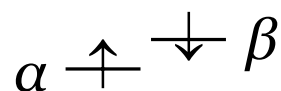
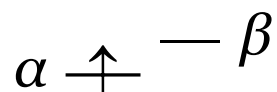
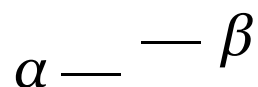
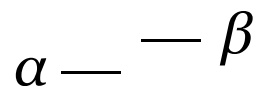
- Alternatively, we can use different orbitals for different spins (*DODS*, or *unrestricted* formalism). $\varphi_1(1) = \psi^\alpha(\mathbf{r}_1)\alpha(\sigma_1)$, $\varphi_2(2) = \psi^\beta(\mathbf{r}_2)\beta(\sigma_2)$, where in general, $\psi^\alpha \neq \psi^\beta$ and $\varepsilon^\alpha \neq \varepsilon^\beta$. ψ^α and ψ^β are eigenfunction of two different Fockians (or Kohn–Sham operators): $\hat{F}^\alpha \psi_i^\alpha(\mathbf{r}) = \varepsilon_i^\alpha \psi_i^\alpha(\mathbf{r})$; $\hat{F}^\beta \psi_i^\beta(\mathbf{r}) = \varepsilon_i^\beta \psi_i^\beta(\mathbf{r})$.
- Even if the numbers of α - and β -electrons are different, we can *force* the spatial α -spin-orbitals to be identical with β -spin-orbitals: $\psi_i^\alpha = \psi_i^\beta$. This is the *restricted open-shell* method. The formalism is quite complicated; there are special rules of constructing the Fockian depending on the spin state.

Note: The method is of little use nowadays. It is *not* used at all within the DFT.

RHF



UHF



ROHF



- The basic concept of the qualitative MO theory is that the MOs are composed from AOs (the *MO-LCAO approximation*). Mathematically, this means that the MOs are linear combination of AOs (atomic-centered *basis functions*) χ_μ :

$$\psi_i(\mathbf{r}) = \sum_{\mu}^{N_{bas}} c_{\mu i} \chi_{\mu}(\mathbf{r})$$

- ▶ Technically, basis functions $\chi_{\mu}(\mathbf{r})$ are not necessarily atomic eigenfunctions.
- ▶ The coefficients $c_{i\mu}$ are variationally adjustable: a self-consistent procedure to solve the Roothaan–Hall equations (RHF case):

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon} \qquad \sum_{\mu=1}^{N_{bas}} F_{\nu\mu} c_{\mu i} = \sum_{\mu=1}^{N_{bas}} S_{\nu\mu} c_{\mu i} \epsilon_i$$

where \mathbf{F} is the Fock matrix in an AO basis;

\mathbf{C} is the matrix of orbital coefficients (one MO is one column);

\mathbf{S} is the overlap matrix;

$\boldsymbol{\epsilon}$ is the diagonal matrix of orbital energies.

- ▶ A problem of the type $\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}$ is a *generalized eigenvalue problem*.

- *Electron density* (Hartree–Fock and DFT only) can be obtained from the orbitals as follows:

$$\rho(\mathbf{r}) = \sum_{k=1}^N \psi_k(\mathbf{r})^2 = \sum_{k=1}^{N_\alpha} \psi_k^\alpha(\mathbf{r})^2 + \sum_{k=1}^{N_\beta} \psi_k^\beta(\mathbf{r})^2$$

$$\rho(\mathbf{r}) = 2 \sum_{k=1}^{N/2} \psi_k(\mathbf{r})^2 \quad \text{for closed-shell case}$$

- Consider RHF for the H₂ molecule in a minimal basis set $\{\chi_a, \chi_b\}$,

- Solution for the 2×2 matrix giving two eigenvalue and two eigenfunctions:

$$\varphi_1 = \frac{1}{\sqrt{2(1+S)}}(\chi_a + \chi_b) \quad \varphi_2 = \frac{1}{\sqrt{2(1-S)}}(\chi_a - \chi_b)$$

- Electron density in the bonding orbital φ_1 :

$$\begin{aligned} \rho_{\text{bonding}}(\mathbf{r}) &= 2\varphi_1(\mathbf{r})^2 = \frac{1}{1+S}(\chi_a^2(\mathbf{r}) + \chi_b^2(\mathbf{r}) + 2\chi_a(\mathbf{r})\chi_b(\mathbf{r})) = \\ &= \frac{1}{1+S}(\rho_a(\mathbf{r}) + \rho_b(\mathbf{r}) + 2\chi_a(\mathbf{r})\chi_b(\mathbf{r})) \end{aligned}$$

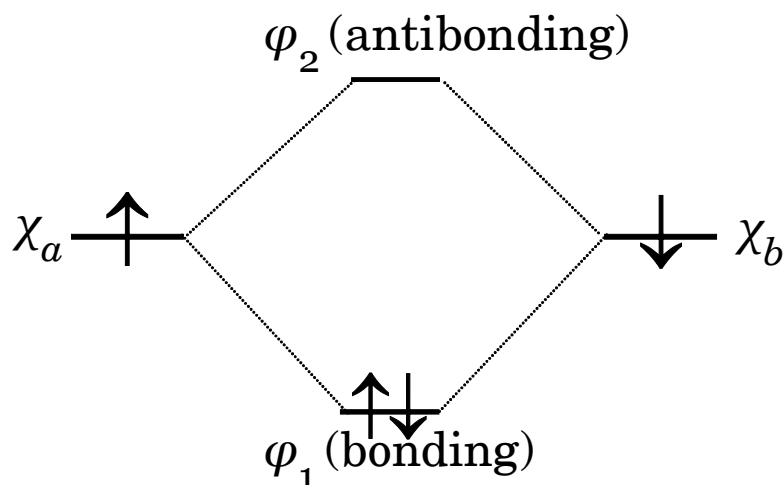
⇒ density *accumulation* in the internuclear area.

- Electron density in the anti-bonding orbital φ_2 :

$$\begin{aligned} \rho_{\text{anti-bonding}}(\mathbf{r}) &= 2\varphi_2(\mathbf{r})^2 = \frac{1}{1-S}(\chi_a^2(\mathbf{r}) + \chi_b^2(\mathbf{r}) - 2\chi_a(\mathbf{r})\chi_b(\mathbf{r})) = \\ &= \frac{1}{1-S}(\rho_a(\mathbf{r}) + \rho_b(\mathbf{r}) - 2\chi_a(\mathbf{r})\chi_b(\mathbf{r})) \end{aligned}$$

⇒ density *depletion* in the internuclear area.

- This is how a typical MO picture emerges:



- Mathematical origin for the MO splitting: off-diagonal Fock-matrix elements. If the diagonal elements $F_{aa} = F_{bb}$, then the eigenvalues of the Fockian matrix \mathbf{F} are $\varepsilon_1 = F_{aa} - |F_{ab}|$, $\varepsilon_2 = F_{aa} + |F_{ab}|$.

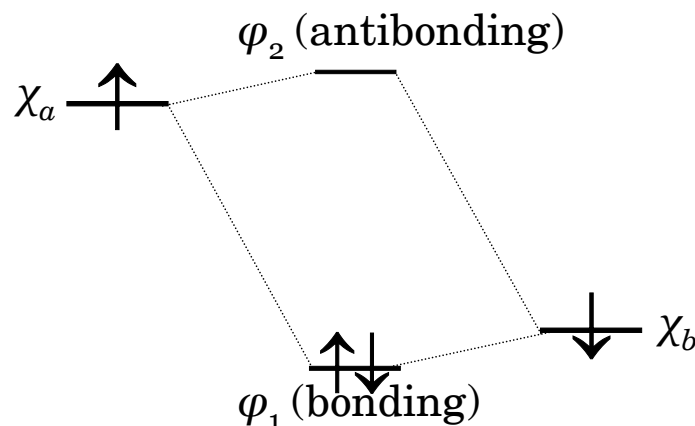
$$\mathbf{F} = \begin{pmatrix} F_{aa} & F_{ab} \\ F_{ba} & F_{bb} \end{pmatrix}$$

Thus, the splitting comes from the *orbital interaction*.

Note that F_{aa} and F_{bb} are related to energies of the atomic orbitals χ_a and χ_b .

Exercise: Express the eigenvalues ε_1 , ε_2 of matrix \mathbf{F} analytically for the case $F_{aa} = F_{bb}$ and demonstrate that $\varepsilon_1 = F_{aa} - |F_{ab}|$, $\varepsilon_2 = F_{aa} + |F_{ab}|$.

- This is how a typical MO picture emerges (e.g., HeH⁺ or LiH):



Question: *where is He⁺ and where is H on this diagram? Where is Li and where is H?*

In this case $F_{bb} < F_{aa}$, and the eigenvalues are:

$$\mathbf{F} = \begin{pmatrix} F_{aa} & F_{ab} \\ F_{ba} & F_{bb} \end{pmatrix} \quad \varepsilon_{2,1} = \frac{(F_{aa} + F_{bb}) \pm \sqrt{(F_{aa} - F_{bb})^2 + |2F_{ab}|^2}}{2}$$

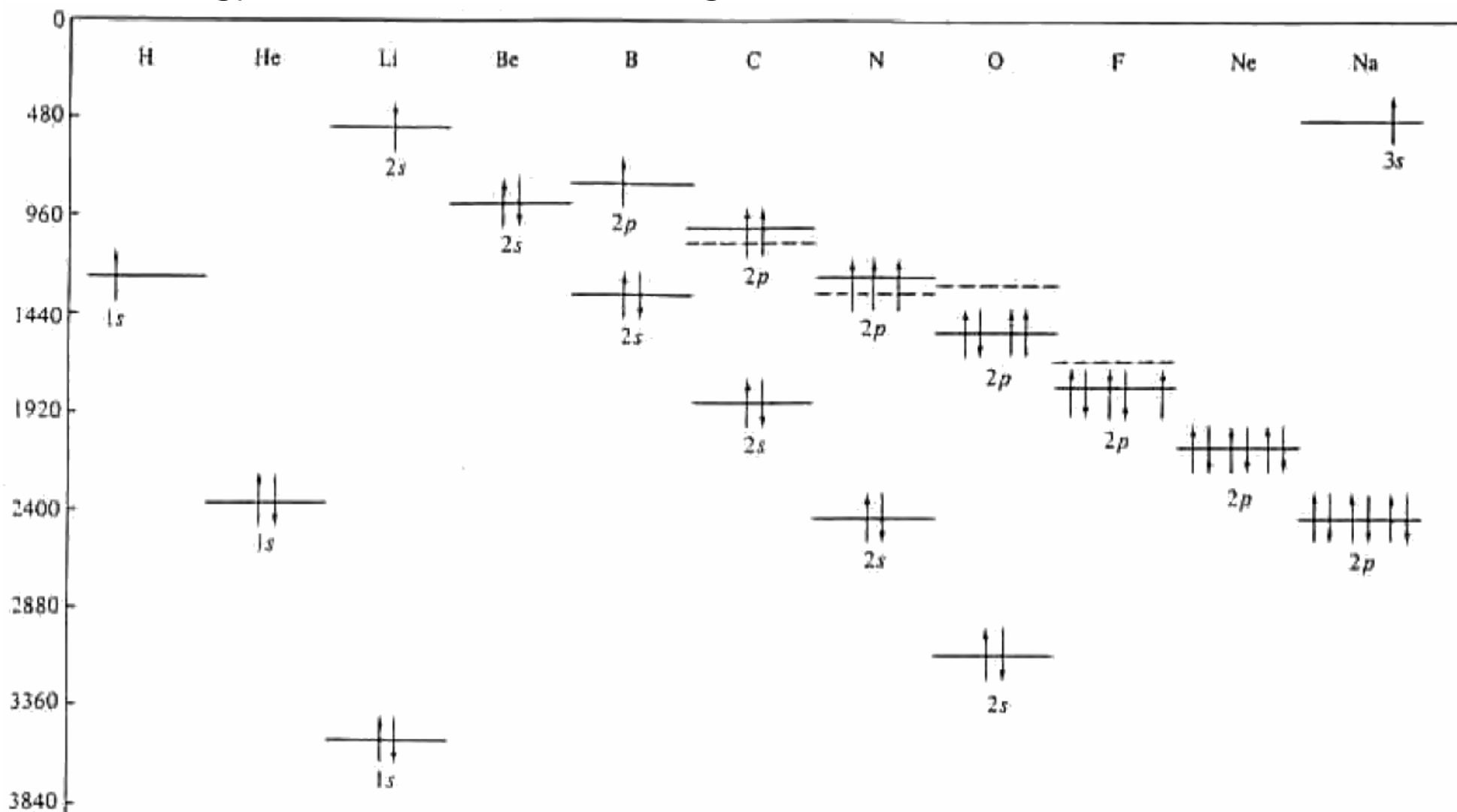
If $|F_{aa} - F_{bb}| \gg 2|F_{ab}|$ then $\varepsilon_1 \approx \varepsilon_b$, $\varepsilon_2 \approx \varepsilon_a$. Moreover, $\varphi_1 \approx \chi_b$, $\varphi_2 \approx \chi_a$.

► This is how an ionic bond emerges from the viewpoint of the MO theory!

Exercises: (a) Derive the equation for ε_1 , ε_2 above by analytically expressing the eigenvalues of matrix \mathbf{F} ; (b) Using the approximation $(1+x)^{1/2} \approx 1+x/2$ (valid if $x \ll 1$) obtain another approximation for ε_1 and ε_2 *without a square root*.

Molecular Orbitals – AO energy variation

- AO energy variation (orbital energies in $\text{kJ}\cdot\text{mol}^{-1}$):

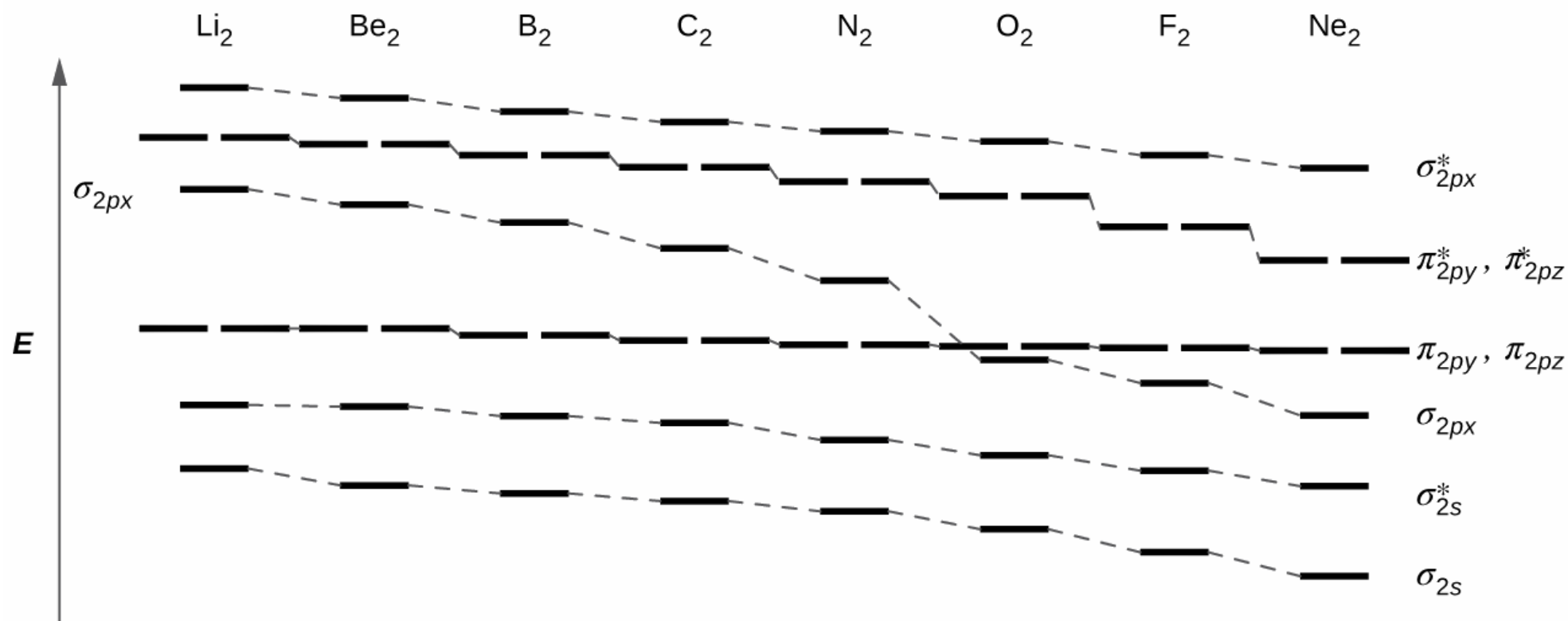


- All AO energies go down with increasing nuclear charge;
- The $s-p$ splitting increases with increasing nuclear charge.

Question: *what is the 2s–2p splitting for the hydrogen atom?*

Molecular Orbitals – homonuclear diatomic molecules

- MO energy variation:

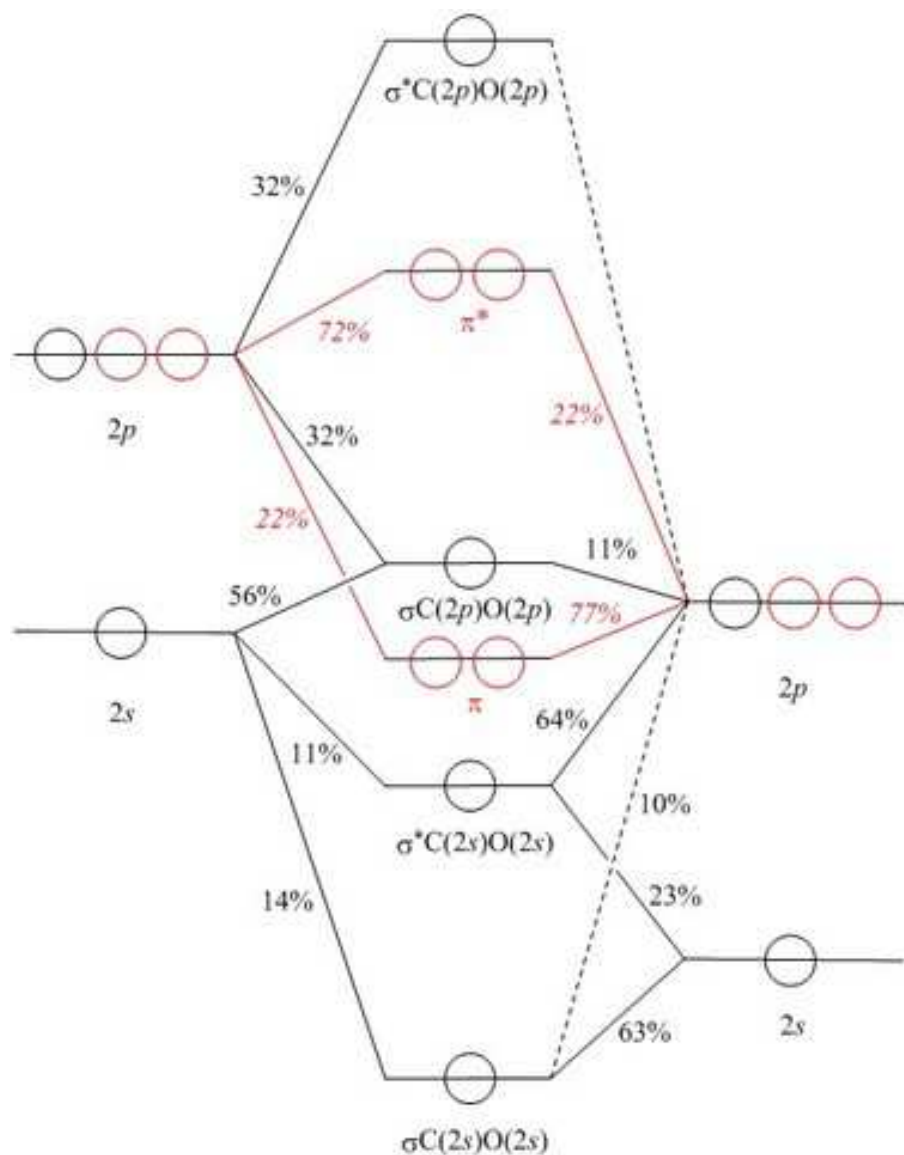


- Watch change in MO energy order $\text{F}_2 \rightarrow \text{O}_2 \rightarrow \text{N}_2$!
 - F_2 has ‘pure’ s- and p-contributions
 - N_2 , C_2 , B_2 ,... has more ‘hybride’ s- and p-contributions.

Question: *what happens with 1s orbitals?*

Molecular Orbitals – heteronuclear diatomic molecules

- CO molecule:



- HF molecule

