# BONDING IN MOLECULES

The future of electronics ? A pentacene molecule deposited on $SiO_2$ as a thin film

Image removed for copyright reasons.

# Homework for Wed Oct 19

- Study: 24.2, 24.4-6

- Read math supplement of Engel-Reid (A.7 and A.8, working with determinants and working with matrices)

# Last time:

1. Stability determined by the interplay of n-n, e-e-, e-n interactions and the quantum kinetic energy

2. Many-electron wavefunction as product of single-particle orbitals (each one LCAO)

3. Many-atom Hamiltonian

4. sp, $sp^2$ and $sp^3$ hybridizations – bond lengths and bond energies

# Complexity of the many-body Ψ

"...Some form of approximation is essential, and this would mean the construction of tables. The tabulation function of one variable requires a page, of two variables a volume and of three variables a library; but the full specification of a single wave function of neutral iron is a function of 78 variables. It would be rather crude to restrict to 10 the number of values of each variable at which to tabulate this function, but even so, full tabulation would require 10**78 entries."

$$\psi = \psi(\vec{r}_1, ..., \vec{r}_n)$$

# Mean-field approach

- Independent particle model (Hartree): each electron moves in an effective potential, representing the attraction of the nuclei and the average effect of the repulsive interactions of the other electrons

- This average repulsion is the electrostatic repulsion of the average charge density of all other electrons

# Hartree Equations

•The Hartree equations can be obtained directly from the variational principle, once the search is restricted to the many-body wavefunctions that are written – as above – as the product of single spin-orbitals (i.e. we are working with independent electrons)

$$\psi(\vec{r}_1,...,\vec{r}_n) = \varphi_1(\vec{r}_1)\,\varphi_2(\vec{r}_2)\cdots\varphi_n(\vec{r}_n)$$

# Hartree Equations

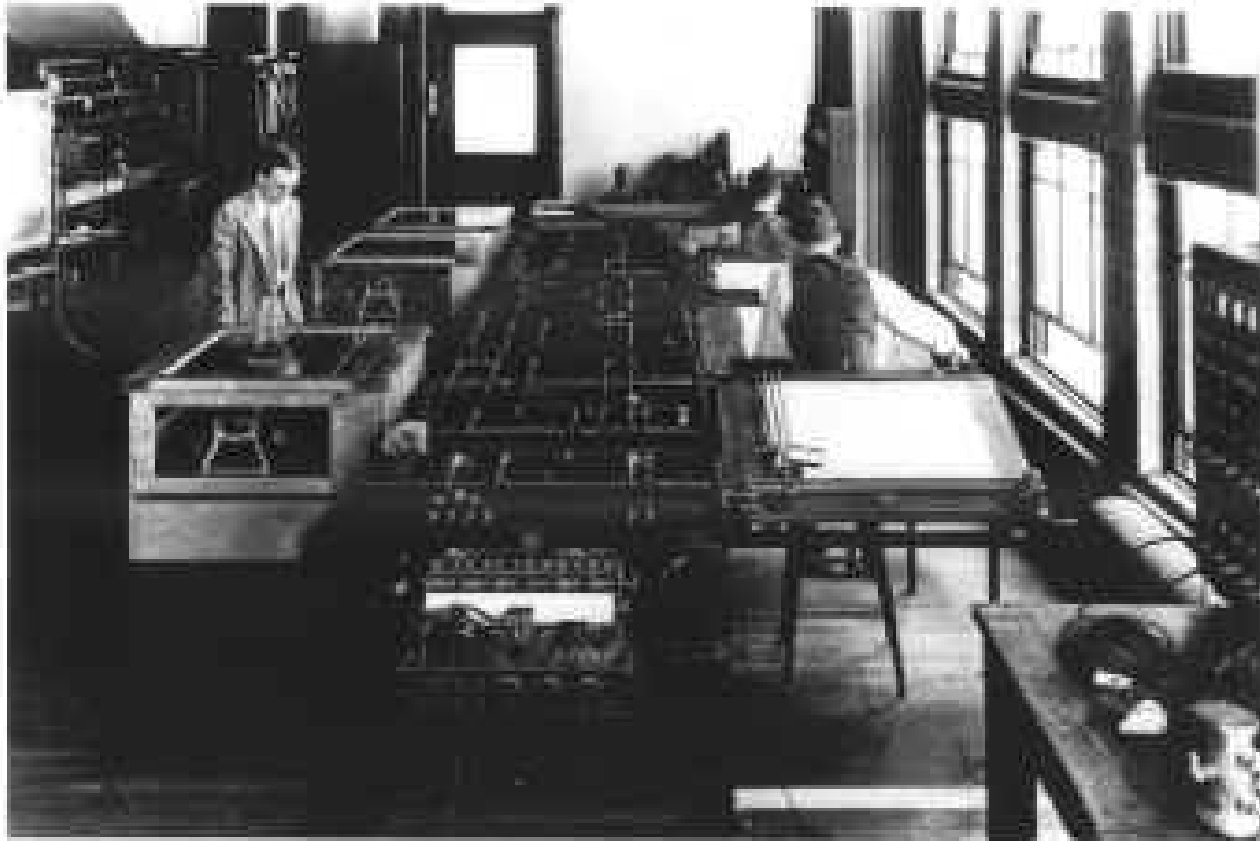$$\left[ -\frac{1}{2}\nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \sum_{j \neq i} \int \left\| \varphi_j(\vec{r}_j) \right\|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

# The self-consistent field

- The single-particle Hartree operator is self-consistent ! I.e., it depends in itself on the orbitals that are the solution of all other Hartree equations

- We have $n$ simultaneous integro-differential equations for the $n$ orbitals

- Solution is achieved iteratively

# Differential Analyzer



Vannevar Bush and the Differential Analyzer.
Courtesy of the MIT Museum. Used with permission.

3.012 Fundamentals of Materials Science: Bonding - Nicola Marzari (MIT, Fall 2005)

# Spin-Statistics

- All elementary particles are either fermions (half-integer spins) or bosons (integer)

- A set of identical (indistinguishable) fermions has a wavefunction that is antisymmetric by exchange

$$\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_j, ..., \vec{r}_k, ..., \vec{r}_n) = -\psi(\vec{r}_1, \vec{r}_2, ..., r_k, ..., \vec{r}_j, ..., \vec{r}_n)$$

- For bosons it is symmetric

# Slater determinant

- An antisymmetric wavefunction is constructed via a Slater determinant of the individual orbitals (instead of just a product, as in the Hartree approach)

$$\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_n) = \frac{1}{\sqrt{n!}} \begin{Vmatrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) & \cdots & \varphi_\nu(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) & \cdots & \varphi_\nu(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_\alpha(\vec{r}_n) & \varphi_\beta(\vec{r}_n) & \cdots & \varphi_\nu(\vec{r}_n) \end{Vmatrix}$$

# Pauli principle

- If two states are identical, the determinant vanishes (i.e. we can't have two electrons in the same quantum state)

# Hartree-Fock Equations

•The Hartree-Fock equations are, again, obtained from the variational principle: we look for the minimum of the many-electron Schrödinger equation in the class of all wavefunctions that are written as a single Slater determinant

$$\left[ -\frac{1}{2}\nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) \right]\varphi_\lambda(\vec{r}_i) +$$

$$\left[ \sum_\mu \int \left\| \varphi_\mu(\vec{r}_j) \right\|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right]\varphi_\lambda(\vec{r}_i) -$$

$$\sum_\mu \left[ \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_i)\varphi_\lambda(\vec{r}_j) d\vec{r}_j \right] = \varepsilon\varphi_\lambda(\vec{r}_i)$$

$$\psi(\vec{r}_1,...,\vec{r}_n) = \left\| Slater \right\|$$

# Example: two electrons in $H_2$

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left\| \begin{matrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) \end{matrix} \right\| = \frac{1}{\sqrt{2}} \left[ \varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2) - \varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1) \right]$$

$\varphi_{\alpha,\beta}(\vec{r})$ = full solution of (integro-differential) Hartree-Fock equations, or

$$\varphi_\alpha(\vec{r}) = \left( c_1 \Psi_{1s}(\vec{r} - \vec{R}_A) + c_2 \Psi_{1s}(\vec{r} - \vec{R}_B) \right) \times \left( spin - up \right)$$

$$\varphi_\beta(\vec{r}) = \left( c_1 \Psi_{1s}(\vec{r} - \vec{R}_A) + c_2 \Psi_{1s}(\vec{r} - \vec{R}_B) \right) \times \left( spin - down \right)$$
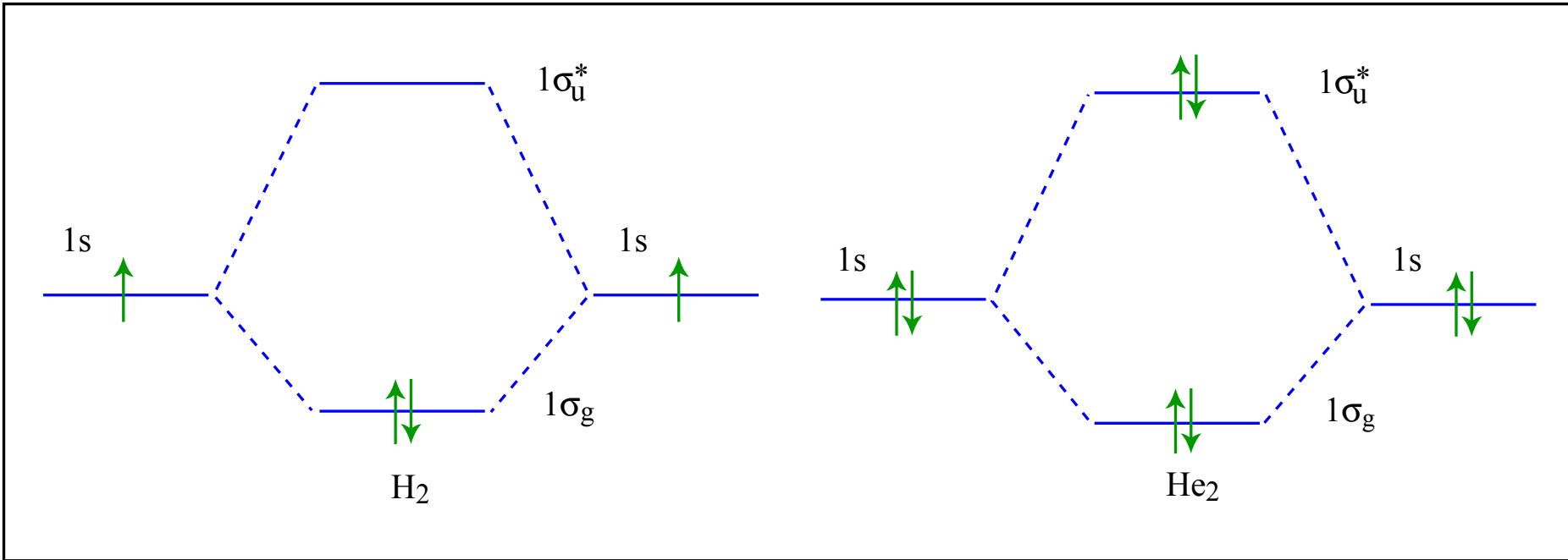
# H$_2$ and He$_2$



Figure by MIT OCW.

# Symmetries

- Rotation along molecular axis → σ

- Nodal plane containing molecular axis → π

- Parity upon inversion:

$$\vec{r} \rightarrow -\vec{r} \Rightarrow \Psi\left(\vec{r}\right) = \Psi\left(-\vec{r}\right)$$

$$\Psi\left(\vec{r}\right) = -\Psi\left(-\vec{r}\right)$$

# Formation of a π Bonding Orbital

See animation at
http://winter.group.shef.ac.uk/orbitron/MOs/N2/2px2px-pi/index.html

# Symmetries

Contour plots of several bonding and antibonding orbitals of $H_2^+$.
Images removed for copyright reasons.
See p. 528, figure 24.4 in Engel, T., and P. Reid. *Physical Chemistry*. Single volume ed. San Francisco, CA: Benjamin Cummings, 2005.

# Homonuclear Diatomic Levels (I)

Diagram of Orbital Regions for 2*p* atomic orbitals and LCAO molecular orbitals made from them removed for copyright reasons.
See p. 667, figure 18.11 in Mortimer, R. G. *Physical Chemistry*. 2nd ed. San Diego, CA: Elsevier, 2000.
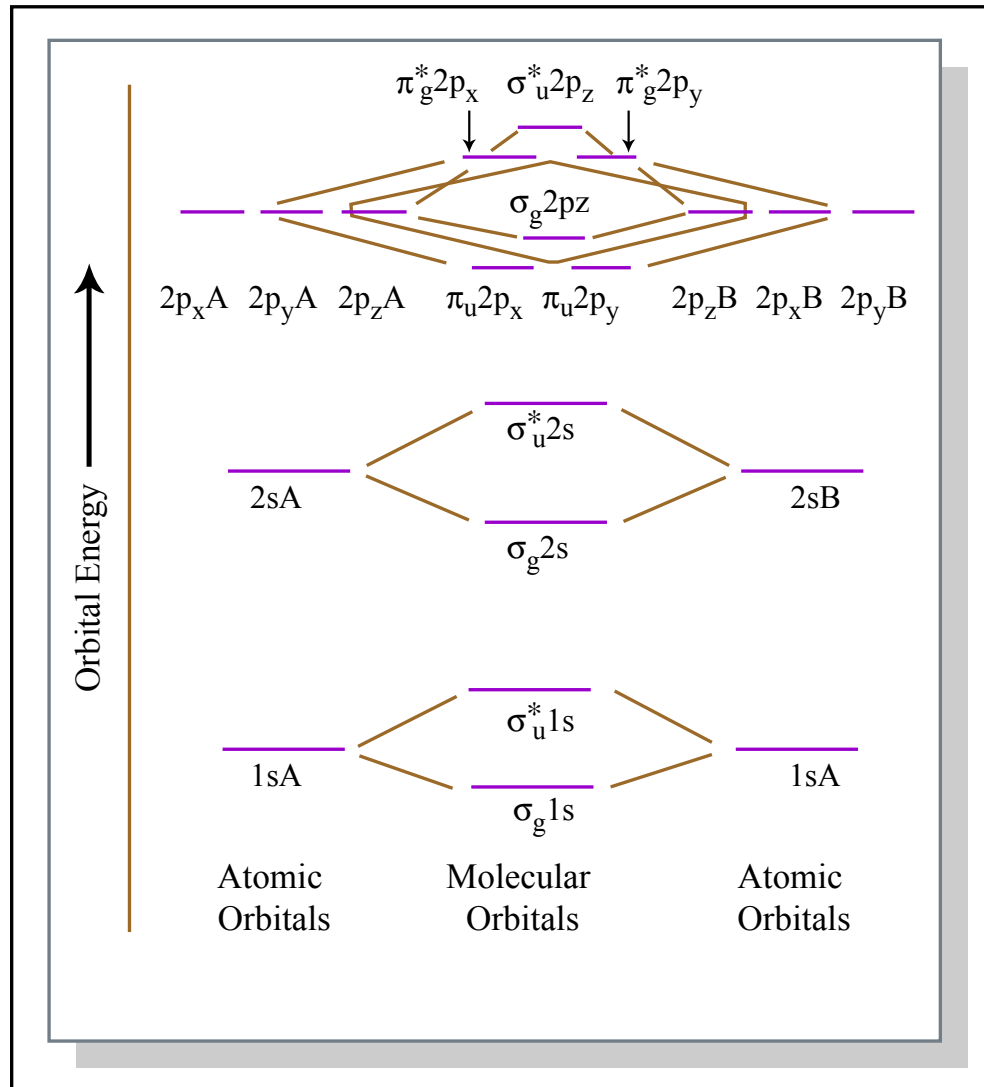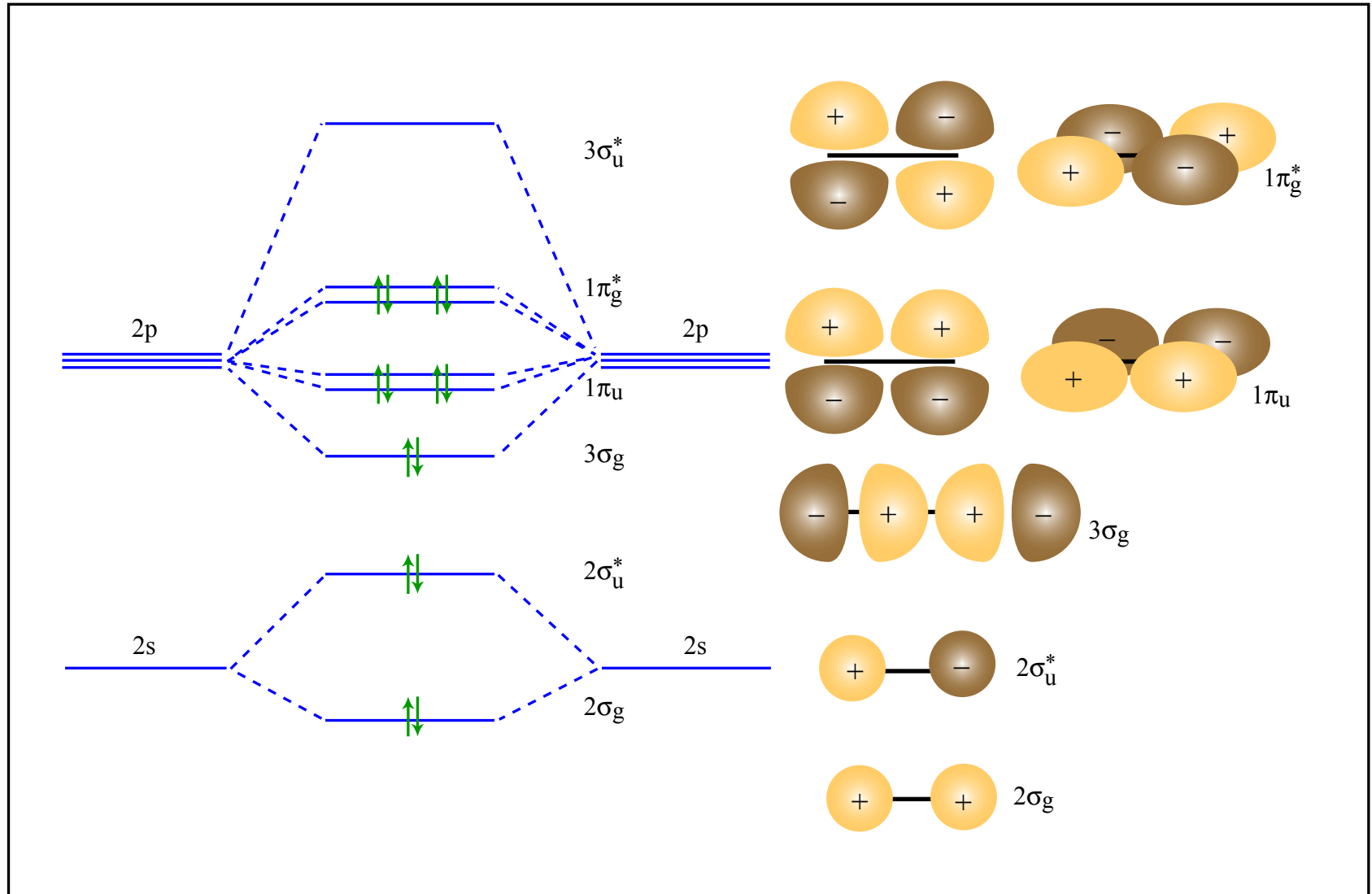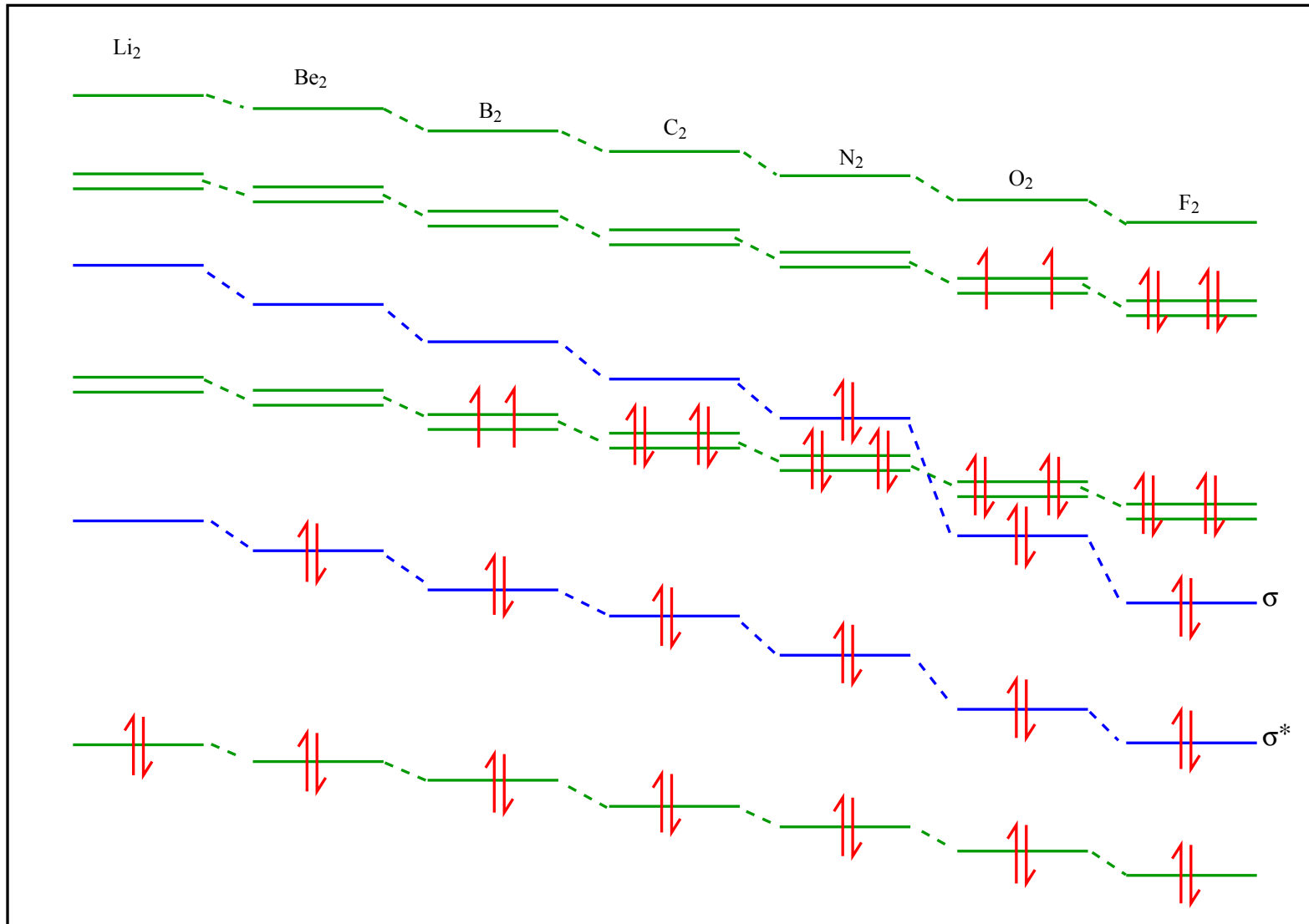
# Homonuclear Diatomic Levels (II)



Figure by MIT OCW.

# Fluorine dimer $F_2$

# Homonuclear Diatomic Levels (III)

Figure by MIT OCW.

# Bond Order

Graph of bond order, bond energy, bond length, and force constant against number of electrons. Removed for copyright reasons.
See p. 535, figure 24.11 in Engel, T., and P. Reid. *Physical Chemistry*. Single volume ed. San Francisco, CA: Benjamin Cummings, 2005.

Bond order = ½ of [bonding electrons - antibonding electrons]

# Advanced Reading Material

Further readings (from less to more advanced):

- Atkins *Physical Chemistry* Freeman & Co (2001)

- Thaller *Visual Quantum Mechanics* Telos (2000)

- Bransden & Joachain *Quantum Mechanics* (2nd ed) Prentice Hall (2000)

- Bransden & Joachain *Physics of Atoms and Molecules* (2nd ed) Prentice Hall (2003)