LCAO-MO, Basis Set & MO Diagrams

Outline of today’s lecture:

• LCAO-MO approach
• Basis set (H-like atom, STO, GTO, numerical)
• Examples (H₂ & N₂ re-visited) & MO diagram
References

• Molecular Quantum Mechanics, Atkins & Friedman (4th ed. 2005), Ch. 9.1-9.6


• Molecular Modeling, A. R. Leach (2nd ed. Prentice Hall, 2001) Ch. 2

• Introduction to Computational Chemistry, F. Jensen (2nd ed. 2006) Ch. 3

• Computational chemistry: Introduction to the theory and applications of molecular and quantum mechanics, E. Lewars (Kluwer, 2004) Ch. 5

• LCAO-MO: Hartree-Fock-Roothaan-Hall equation,
C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951)

• EMSL Basis Set Exchange http://gnode2.pnl.gov/bse/portal

• Basis Sets Lab Activity
http://www.shodor.org/chemviz/basis/teachers/background.html
So all we now need to do is to solve the one-electron Schrödinger equation:

\[ \hat{H}_1 \psi_a = \epsilon_a \psi_a \quad [1] \]

Effectively one-electron Hamiltonian and One-electron wavefunction, a molecular orbital.

Solving One-Electron Hartree-Fock Equations

\[ \hat{f}_i \chi_i = \epsilon_i \chi_i \quad i = 1, 2, \ldots, N \]

\[ \hat{f}_i = -\frac{1}{2} \nabla_i^2 - \sum_A A \frac{Z_A}{r_{iA}} + \sum_j \left( \hat{f}_j(\vec{x}_1) - \hat{K}_j(\vec{x}_1) \right) \]

\[ \hat{f}_j(\vec{x}_1) = \int |\chi_j(\vec{x}_2)|^2 \frac{1}{r_{12}} d\vec{x}_2 \quad \hat{K}_j(\vec{x}_1) \chi_i(\vec{x}_1) = \int \chi_j^*(\vec{x}_2) \frac{1}{r_{12}} \chi_i(\vec{x}_2) d\vec{x}_2 \chi_j(\vec{x}_1) \]

Coupled integro-differential equations

Purely numerical solution is too demanding for routine applications.
LCAO-MO Approximation
Linear Combination of Atomic Orbitals for Molecular Orbital

To actually do this we make one final approximation which

..... is the **linear combination of atomic orbitals (LCAO) approximation**.

This supposes that we can **construct molecular orbitals from linear superpositions of atomic orbitals centred on individual atoms.**

\[ \psi = \sum_i c_i \phi_i \]

i.e.

- Molecular orbital
- **Summation**
- **Mixing coefficient**
- An atomic orbital

**Atomic orbitals (AOs)**

**Molecular orbitals (MOs)**

- LCAO

**Figure:**

- LCAO process from atomic orbitals to molecular orbitals.
Linear Combination of Atomic Orbitals (LCAO-MO) Method

\[ \varphi_i = \sum_{\mu=1}^{L} c_{\mu i} \eta_\mu \quad \{ \eta_\mu \}: A \text{ set of L preset basis functions (complete if } L = \infty) \]

- Roothaan and Hall (1951) Rev. Mod. Phys. 23, 69
- Makes the one-electron HF equations \textbf{computationally} accessible
- Non-linear \(\rightarrow\) **Linear problem** (The coefficients \(\{c_{\mu i}\}\) are the variables)
LCAO-MO Example: Hydrogen (H₂) Molecule

Each hydrogen atom has a single valence orbital, this being the 1s orbital. Two molecular orbitals may be formed by the constructive and destructive overlap of these two atomic orbitals.

\[ 1s \pm 1s \]
\[ \phi_{1s,A} \quad \phi_{1s,B} \]  

Diagram showing the superposition of the two 1s atomic orbitals

\[ \downarrow \]

\[ 1s \sigma \]  
\[ (1\sigma_g) \]

Bonding molecular orbital
\[ \psi_+ = c_+ \phi_{1s,A} + c_+ \phi_{1s,B} = c_+ (\phi_{1s,A} + \phi_{1s,B}) \]

\[ \text{or} \]

\[ 1s \sigma^* \]  
\[ (1\sigma_u) \]

Antibonding molecular orbital
\[ \psi_- = c_- \phi_{1s,A} - c_- \phi_{1s,B} = c_- (\phi_{1s,A} - \phi_{1s,B}) \]
LCAO-MO Example: Hydrogen (H₂) Molecule

Note that in this instance two atomic orbitals give rise to two molecular orbitals - we shall see later that this is a general characteristic, i.e. linear combinations of \( n \) atomic orbitals give rise to \( n \) molecular orbitals.

**questions**

1. what are the values of the mixing coefficients ?
2. what are the exact energies of the molecular orbitals ?
LCAO-MO & HF Equation: Roothaan-Hall Equation

\[ \psi_i = \sum_{s=1}^{m} c_{si} \phi_s \quad i = 1, 2, 3, \ldots, m \text{ (m MOs)} \equiv \]

\[ \psi_1 = c_{11} \phi_1 + c_{21} \phi_2 + c_{31} \phi_3 + \cdots + c_{m1} \phi_m \]
\[ \psi_2 = c_{12} \phi_1 + c_{22} \phi_2 + c_{32} \phi_3 + \cdots + c_{m2} \phi_m \]
\[ \psi_3 = c_{13} \phi_1 + c_{23} \phi_2 + c_{33} \phi_3 + \cdots + c_{m3} \phi_m \]
\[ \vdots \]
\[ \psi_m = c_{1m} \phi_1 + c_{2m} \phi_2 + c_{3m} \phi_3 + \cdots + c_{mm} \phi_m \]

\[ \hat{F} \psi_i (1) = \varepsilon_i \psi_i (1) \quad \sum_{s=1}^{m} c_{s1} \hat{F} \phi_{sj} = \varepsilon_1 \sum_{s=1}^{m} c_{s1} \phi_s \]
\[ \hat{F} \psi_2 (1) = \varepsilon_2 \psi_2 (1) \quad \sum_{s=1}^{m} c_{s2} \hat{F} \phi_{sj} = \varepsilon_2 \sum_{s=1}^{m} c_{s2} \phi_s \]
\[ \vdots \]
\[ \hat{F} \psi_n (1) = \varepsilon_n \psi_n (1) \quad \sum_{s=1}^{m} c_{sn} \hat{F} \phi_{sj} = \varepsilon_n \sum_{s=1}^{m} c_{sn} \phi_s \]

Fock matrix \( \mathbf{F} \) & Overlap matrix \( \mathbf{S} \)

\[ F_{rs} = \int \phi_r \hat{F} \phi_s \, dv \quad \text{and} \quad S_{rs} = \int \phi_r \phi_s \, dv \]
Hartree-Fock-Roothaan-Hall Equation \( FC = SCE \)

\[
\hat{F}_{\mu v}^{KS} \varphi_i = \varepsilon_i \varphi_i \quad \& \quad \varphi_i = \sum_{\mu=1}^{L} c_{\mu i} \eta_{\mu} \rightarrow \hat{F}_{\mu v}^{KS}(\vec{r}_i) \sum_{v=1}^{L} c_{vi} \eta_{v}(\vec{r}_i) = \varepsilon_i \sum_{v=1}^{L} c_{vi} \eta_{v}(\vec{r}_i)
\]

\[
\sum_{v=1}^{L} c_{vi} \int \eta_{\mu}(\vec{r}_i) \hat{F}_{\mu v}^{KS}(\vec{r}_i) \eta_{v}(\vec{r}_i) d\vec{r}_i = \varepsilon_i \sum_{v=1}^{L} c_{vi} \int \eta_{\mu}(\vec{r}_i) \eta_{v}(\vec{r}_i) d\vec{r}_i \quad \text{for } 1 \leq i \leq L
\]

\[
F_{\mu v}^{KS} = \int \eta_{\mu}(\vec{r}_i) \hat{F}_{\mu v}^{KS}(\vec{r}_i) \eta_{v}(\vec{r}_i) d\vec{r}_i \\
S_{\mu v} = \int \eta_{\mu}(\vec{r}_i) \eta_{v}(\vec{r}_i) d\vec{r}_i
\]

Fock matrix **F**

\[
C = \begin{pmatrix}
c_{11} & c_{12} & \cdots & c_{1L} \\
c_{21} & c_{22} & \cdots & c_{2L} \\
\vdots & \vdots & \ddots & \vdots \\
c_{L1} & c_{L2} & \cdots & c_{LL}
\end{pmatrix}
\]

Overlap matrix **S**

\[
\varepsilon = \begin{pmatrix}
\varepsilon_1 & 0 & \cdots & 0 \\
0 & \varepsilon_2 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & \varepsilon_L
\end{pmatrix}
\]

\[
F_{\mu v}^{KS} C = S C \varepsilon
\]

Non-linear Integro-Differential equation \( \rightarrow \) **Linear Algebra Matrix equation**
$$\sum_{s=1}^{m} F_{rs} c_{si} = \sum_{s=1}^{m} S_{rs} c_{si} \varepsilon_i \quad r = 1, 2, 3, \ldots, m \quad \text{(for each } i = 1, 2, 3, \ldots, m) \equiv \mathbf{FC} = \mathbf{SC}\varepsilon$$

$$\mathbf{FC} = \begin{pmatrix}
F_{11} & F_{12} & F_{13} & \cdots & F_{1m} \\
F_{21} & F_{22} & F_{23} & \cdots & F_{2m} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
F_{m1} & F_{m2} & F_{m3} & \cdots & F_{mm}
\end{pmatrix}
\begin{pmatrix}
c_{11} & c_{12} & c_{13} & \cdots & c_{1m} \\
c_{21} & c_{22} & c_{23} & \cdots & c_{2m} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
c_{m1} & c_{m2} & c_{m3} & \cdots & c_{mm}
\end{pmatrix}
= \begin{pmatrix}
F_{11} c_{11} + F_{12} c_{21} + F_{13} c_{31} & \cdots & F_{11} c_{12} + F_{12} c_{22} + F_{13} c_{32} & \cdots & \vdots \\
F_{21} c_{11} + F_{22} c_{21} + F_{23} c_{31} & \cdots & F_{21} c_{12} + F_{22} c_{22} + F_{23} c_{32} & \cdots & \vdots \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
F_{m1} c_{11} + F_{m2} c_{21} + F_{m3} c_{31} & \cdots & F_{m1} c_{12} + F_{m2} c_{22} + F_{m3} c_{32} & \cdots & \vdots
\end{pmatrix}$$

$$\mathbf{SC}\varepsilon = \begin{pmatrix}
S_{11} & S_{12} & \cdots & S_{1m} \\
S_{21} & S_{22} & \cdots & S_{2m} \\
\vdots & \vdots & \ddots & \vdots \\
S_{m1} & S_{m2} & \cdots & S_{mm}
\end{pmatrix}
\begin{pmatrix}
c_{11} & c_{12} & \cdots & c_{1m} \\
c_{21} & c_{22} & \cdots & c_{2m} \\
\vdots & \vdots & \ddots & \vdots \\
c_{m1} & c_{m2} & \cdots & c_{mm}
\end{pmatrix}
\begin{pmatrix}
\varepsilon_{11} & 0 & \cdots & 0 \\
0 & \varepsilon_{22} & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & \varepsilon_{mm}
\end{pmatrix}
= \begin{pmatrix}
S_{11} c_{11} + S_{12} c_{21} + S_{13} c_{31} & \cdots & S_{11} c_{12} + S_{12} c_{22} + S_{13} c_{32} & \cdots & \vdots \\
S_{21} c_{11} + S_{22} c_{21} + S_{23} c_{31} & \cdots & S_{21} c_{12} + S_{22} c_{22} + S_{23} c_{32} & \cdots & \vdots \\
\vdots & \vdots & \ddots & \vdots & \varepsilon \\
\varepsilon (S_{11} c_{11} + S_{12} c_{21} + S_{13} c_{31} & \cdots & \varepsilon (S_{11} c_{12} + S_{12} c_{22} + S_{13} c_{32} & \cdots & \vdots \\
\varepsilon (S_{21} c_{11} + S_{22} c_{21} + S_{23} c_{31} & \cdots & \varepsilon (S_{21} c_{12} + S_{22} c_{22} + S_{23} c_{32} & \cdots & \vdots
\end{pmatrix}$$
Fock Matrix Elements I. \( \mathbf{h} \)

\[
\mathbf{h}_{\mu \nu} = \int \eta_\mu(\vec{r}_1) \left[ -\frac{1}{2} \nabla^2 - \sum_A ^M \frac{Z_A}{r_{1A}} \right] \eta_\nu(\vec{r}_1) d\vec{r}_1
\]

**One-electron integrals: easy** to evaluate

Fock Matrix Elements II. \( \mathbf{J} \) & \( \mathbf{K} \)

\[
P_{\mu \nu} = \sum_i ^N c_{\mu i} c_{\nu i} \quad \text{Density matrix} \ P
\]

\[
J_{\mu \nu} = \sum_\lambda ^L \sum_\sigma ^L P_{\lambda \sigma} \int \int \eta_\mu(\vec{r}_1) \eta_\nu(\vec{r}_1) \frac{1}{r_{12}} \eta_\lambda(\vec{r}_2) \eta_\sigma(\vec{r}_2) d\vec{r}_1 d\vec{r}_2
\]

**Classical Coulomb four-center-two-electron integrals**

\[
K_{\mu \nu} = \sum_\lambda ^L \sum_\sigma ^L P_{\lambda \sigma} \int \int \eta_\mu(\vec{x}_1) \eta_\lambda(\vec{x}_1) \frac{1}{r_{12}} \eta_\nu(\vec{x}_2) \eta_\sigma(\vec{x}_2) d\vec{x}_1 d\vec{x}_2
\]

**Exchange four-center-two-electron integrals**
Two Atomic Orbitals

\[ \psi = \sum_i (c_i \phi_i) \]

simplifies to

\[ \Rightarrow \quad \psi = c_1 \phi_1 + c_2 \phi_2 \]

The expression for \( E \) now becomes:

\[
E = \frac{\int \psi \hat{H} \psi \, d\tau}{\int \psi^2 \, d\tau} = \frac{\int (c_1 \phi_1 + c_2 \phi_2) \hat{H} (c_1 \phi_1 + c_2 \phi_2) \, d\tau}{\int (c_1 \phi_1 + c_2 \phi_2)^2 \, d\tau} \quad [3]
\]
(a) Consider first the top line of the fraction.

\[ \int \psi \hat{H} \psi \, d\tau = \int (c_1 \phi_1 + c_2 \phi_2) \hat{H} (c_1 \phi_1 + c_2 \phi_2) \, d\tau \]

\[ = c_1^2 \int \phi_1 \hat{H} \phi_1 \, d\tau + c_1 c_2 \int \phi_1 \hat{H} \phi_2 \, d\tau + c_1 c_2 \int \phi_2 \hat{H} \phi_1 \, d\tau + c_2^2 \int \phi_2 \hat{H} \phi_2 \, d\tau \]

An integral, \( \alpha_1 \), which corresponds to the energy of an electron in atomic orbital 1 (albeit in the molecular environment).

Two integrals, \( \beta_{12} \) and \( \beta_{21} \), whose size is a measure of the strength of the bonding interaction arising as a result of overlap of \( \phi_1 \) and \( \phi_2 \).

An integral, \( \alpha_2 \), which corresponds to the energy of an electron in atomic orbital 2 (albeit in the molecular environment).

\[ \int \psi \hat{H} \psi \, d\tau = c_1^2 \alpha_1 + c_1 c_2 \beta_{12} + c_1 c_2 \beta_{21} + c_2^2 \alpha_2 \]

\( \beta_{12} = \beta_{21} \)

\[ \int \psi \hat{H} \psi \, d\tau = c_1^2 \alpha_1 + 2c_1 c_2 \beta_{12} + c_2^2 \alpha_2 \]
(b) Now consider the bottom line of the fraction.

\[ \int \psi^2 d\tau = \int (c_1 \phi_1 + c_2 \phi_2)(c_1 \phi_1 + c_2 \phi_2) d\tau \]

\[ = c_1^2 \int \phi_1^2 d\tau + c_1 c_2 \int \phi_1 \phi_2 d\tau + c_1 c_2 \int \phi_2 \phi_1 d\tau + c_2^2 \int \phi_2^2 d\tau \]

\[ = 1 \; \text{since the atomic orbitals are "normalized"} \]

Two equal integrals; the integral is known as the "overlap integral" and denoted \( S \) (it is positive)

\[ = 1 \; \text{since the atomic orbitals are "normalized"} \]

i.e.

\[ \int \psi^2 d\tau = c_1^2 + c_2^2 + 2c_1 c_2 S \]
Substitution of the expressions for the integrals into eqn. [3] therefore gives:

\[
E = \frac{c_1^2\alpha_1 + 2c_1c_2\beta_{12} + c_2^2\alpha_2}{c_1^2 + c_2^2 + 2c_1c_2S} \tag{4}
\]

We now need to find the values of \( c_1 \), \( c_2 \) that minimize the value of \( E \).

**Summary of Terminology**

- \( \alpha_i \) is known as the *Coulomb integral* : it is equal to the energy of an electron in the corresponding atomic orbital, \( i \), albeit with the atom in the molecular environment - it is negative.

- \( \beta_{ij} \) is known as the *resonance integral* : it is a measure of the strength of the bonding interaction as a result of the overlap of orbitals \( i \) and \( j \) - it is negative for constructive overlap of orbitals.

- \( S \) is known as the *overlap integral* : is a measure of the effectiveness of overlap of the orbitals (its magnitude is always significantly less than one, i.e. \( S << 1 \)).
Consider the value of the product $\phi_1 \phi_2$ along a line passing through the two nuclei.

- **Orbitals overlap**
  - $\phi_1 \phi_2$ has finite value in the region of overlap.
  - $\therefore S \neq 0$

- **Orbitals do "not" overlap**
  - $\phi_1 \phi_2 = 0$ everywhere.
  - $\therefore S = 0$

The integral over all space is given by $S = \int \phi_1 \phi_2 \, d\tau$. The 1s orbitals are centred on nucleus 1 and nucleus 2.
The Secular Equations and Secular Determinant

Rearrangement of eqtn. [4] yields

\[ E(c_1^2 + c_2^2 + 2c_1c_2S) = c_1^2\alpha_1 + 2c_1c_2\beta_{12} + c_2^2\alpha_2 \]

To minimize \( E \) with respect to \( c_1 \) and \( c_2 \) we need to set both \( \frac{\partial E}{\partial c_1} = 0 \) and \( \frac{\partial E}{\partial c_2} = 0 \)

(See Appendix 1 for details)

Differentiation with respect to \( c_1 \) and setting the derivative equal to zero gives

\[ \Rightarrow \quad c_1(\alpha_1 - E) + c_2(\beta_{12} - ES) = 0 \quad [5] \]

Differentiation with respect to \( c_2 \) and setting the derivative equal to zero gives

\[ \Rightarrow \quad c_1(\beta_{12} - ES) + c_2(\alpha_2 - E) = 0 \quad [6] \]

Equations [5] and [6] are simultaneous equations in \( c_1 \) and \( c_2 \), known as the "secular equations". These equations need to be solved to obtain the appropriate values for \( c_1 \) and \( c_2 \).
Determinants and Simultaneous Equations

\[ a_{11}x_1 + a_{12}x_2 + \ldots + a_{1n}x_n = b_1 \]
\[ a_{21}x_1 + a_{22}x_2 + \ldots + a_{2n}x_n = b_2 \]
\[ a_{31}x_1 + a_{32}x_2 + \ldots + a_{3n}x_n = b_3 \]
\[ \text{etc.} \]

\[ AX = B \]
\[ A = \begin{pmatrix} a_{11} & a_{12} & \ldots & a_{1n} \\ a_{21} & a_{22} & \ldots & a_{2n} \\ a_{31} & a_{32} & \ldots & a_{3n} \\ \vdots & \vdots & \ddots & \vdots \end{pmatrix}, \quad X = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \end{pmatrix}, \quad B = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ \vdots \end{pmatrix} \]

\[ X = A^{-1}B \]

\[ A^{-1} = \frac{\text{adj}(A)}{|A|} \]

\text{adj}(A) \text{ is the adjoint matrix for the matrix } A.

\[ |A| \text{ (or } \text{det}(A) \text{) is the determinant of the matrix } A \]

What happens if \( B = 0 \) (i.e. all the \( b_i \) values are equal to zero)?

\[ X = A^{-1}B = \frac{\text{adj}(A)}{|A|} \cdot 0 \]

There are two possible solutions:

(i) \( X = 0 \) i.e. all the \( x_i \) values are equal to zero.

or

(ii) \( |A| = 0 \) i.e. the determinant is zero.
For non-trivial solutions (i.e. solutions other than $c_1 = c_2 = 0$) we require (see Appendix 2) that the corresponding "secular determinant" be equal to zero:

i.e.

\[
\begin{vmatrix}
\alpha_1 - E & \beta_{12} - ES \\
\beta_{12} - ES & \alpha_2 - E
\end{vmatrix} = 0
\]

[7]

Solving this equation will tell us for what values of $E$ we can get non-trivial solutions.

→ **Matrix diagonalization problem**
ab initio (First Principles) QM Calculation

*Ab Initio* (latin, “from the beginning”) Quantum Chemistry

Summary of approximations

- Born-Oppenheimer Approx.
- Non-relativistic Hamiltonian
- Use of trial functions, MOs, in the variational procedure
- Single Slater determinant
- Basis set, LCAO-MO approx.
- RHF, ROHF, UHF & post-HF (MP2, MP4, CI, etc.)
- Evaluate all the integrals (h, J, K)
Lower Level of Quantum Chemical Calculations

Semi-Empirical Molecular Orbital Theory

- only valence electrons: the core electrons are included in the nuclear core.
- minimal basis set: basis set contains only occupied atomic orbitals (s, p and d), e.g., for carbon STO-3G only 2s and 2p functions.
- parameterized integrals: many integrals obtained by fitting the results to experimental data or \textit{ab initio} calculations. Gives training set dependence.
- omission of some of the two electron integrals.

\[
\int \phi_i(1) \phi_j(1) \frac{e^2}{4\pi \varepsilon \alpha_{12}} \phi_k(2) \phi_l(2) \, d\tau_1 \, d\tau_2 \quad \phi_i(1) = \text{different atomic orbitals}
\]

- If your molecule is \textit{similar} to molecules in the training set, then the results \textit{may be very good}.
- If your molecule is \textit{significantly different} from anything in the training set, the results \textit{may be very poor}.
- Semi-empirical methods are not as sensitive to the parameterization set as molecular mechanics methods.
- Much caution is warranted for transition states and unstable molecules and ions.
\[ \int A(1) B(1) \frac{e^2}{4\pi \varepsilon_0 r_{12}} C(2) D(2) \, d\tau_1 \, d\tau_2 \]

**CNDO:** complete neglect of differential overlap
- zero unless \( A = B \), \( C = D \)
- two-center integrals only

**MNDO:** modified neglect of differential overlap
- zero unless \( A, B \) on same atom, \( C, D \) on same atom

**AM1:** more diverse training set; no d's for 3\(^{rd}\) period or metals.
**PM3:** more heteroatoms in training set, use for 3\(^{rd}\) period atoms and hydrogen bonding.
**MNDO/d, PM3/TM:** includes d orbitals for 3\(^{rd}\) period elements, metals
**ZINDO:** parameterized to reproduce electronic spectra
Basis Set to Expand the HF Orbitals

\{\eta_\mu\}: A set of L preset basis functions (complete if L = \infty)

\[ \varphi_i = \sum_{\mu=1}^{L} c_{\mu i} \eta_\mu \]

- Larger basis set give higher quality wavefunctions.
  (but more computationally-demanding)

**Candidates of Basis Functions**

- H-atom orbitals
- Slater type orbitals (STO; Slater)
- Gaussian type orbitals (GTO; Boys)
- Numerical basis functions
Each state is designated by four $(3+1)$ quantum numbers $n$, $l$, $m_l$, and $m_s$. 

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 e_0^2 \hbar^2 n^2} \text{ or } E_n = -\frac{Z^2}{2n^2} \text{ in atomic unit (hartree)}$$

Hydrogen-Like (1-Electron) Atom Orbitals
Hydrogen-Like (1-Electron) Atom Orbitals
STO Basis Functions

\[ \eta^{\text{STO}} = N r^{n-1} \exp[-\zeta r] \ Y_{lm}(\Theta, \phi) \]

- Correct cusp behavior (finite derivative) at \( r \to 0 \)
- Desired exponential decay at \( r \to \infty \)
- Correctly mimic the H atom orbitals
- Would be more natural choice
- No analytic method to evaluate the coulomb and exchange integrals

GTO Basis Functions

\[ \eta^{\text{GTO}} = N x^m y^n \exp[-\alpha r^2] \]

- **Wrong** cusp behavior (zero slope) at \( r \to 0 \)
- **Wrong** decay behavior (too rapid) at \( r \to \infty \)
- Analytic evaluation of the coulomb and XC (or exchange) integrals
  (The product of the gaussian "primitives" is another gaussian.)
\[ \eta^{\text{STO}} = N \ r^{n-1} \exp[-\zeta r] \ Y_{lm}(\Theta, \phi) \]

\[ \eta^{\text{GTO}} = N \ x^l y^m z^n \exp[-\alpha r^2] \]

how compact (large \( \alpha \)) or diffuse (small \( \alpha \))

\( L = l + m + n \)  
- s-functions (\( L = 0 \)), p-functions (\( L = 1 \)), d-functions (\( L = 2 \))

\(<\eta_\mu|\eta_\mu> = 1 \)

\(<\eta_\mu|\eta_\nu> \neq 0 \) for \( \mu \neq \nu \) (not orthogonal but normalized)

Slater Type Orbitals, STO

\[ \Psi_{n\ell m}(r) = N \ Y_{lm}(\Theta, \phi) \ r^{(n-1)} \ e^{-Z_{\text{eff}} r/ n a_0} \]

For He  \( Z_{\text{eff}} = 1.6875 \)

Slater Orbital Parameters \( Z_{\text{eff}} \leftrightarrow \alpha \) or \( \zeta \) above

<table>
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<th></th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
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<td>1.9120</td>
<td>2.5762</td>
<td>3.2166</td>
<td>3.8474</td>
<td>4.4916</td>
<td>5.1276</td>
</tr>
<tr>
<td>2p</td>
<td></td>
<td></td>
<td>2.4214</td>
<td>3.1358</td>
<td>3.8340</td>
<td>4.4532</td>
<td>5.1000</td>
</tr>
</tbody>
</table>

Smaller for Bigger shell (1s<2sp<3spd)
Contracted Gaussian Functions (CGF)

\[ \eta^\text{CGF}_\tau = \sum_a^A d_{\alpha \tau} \eta^\text{GTO}_a \]

- The product of the gaussian "primitives" is another gaussian.
- Integrals are easily calculated. Computational advantage.
- The price we pay is loss of accuracy.
- To compensate for this loss, we combine GTOs.
- By adding several GTOs, you get a good approximation of the STO.
- The more GTOs we combine, the more accurate the result.
- STO-nG (n: the number of GTOs combined to approximate the STO)

\[ \phi(\text{Slater}) = \left( \frac{r^3}{\pi} \right)^{1/2} e^{-\tau r} = 0.7790 e^{-1.24r} \quad \text{STO} \]
\[ \phi(\text{STO-1G}) = \left( \frac{2a}{\pi} \right)^{3/4} e^{-ar^2} = 0.3696 e^{-0.4166r^2} \quad \text{GTO primitive} \]
\[ \phi(\text{STO-3G}) = 0.4446 \left( \frac{2a}{\pi} \right)^{3/4} e^{-ar^2} + 0.5353 \left( \frac{2a}{\pi} \right)^{3/4} e^{-ar^2} + 0.1543 \left( \frac{2a}{\pi} \right)^{3/4} e^{-ar^2} \]
\[ = 0.0835 e^{-0.1689r^2} + 0.2678 e^{-0.6239r^2} + 0.2769 e^{-3.4233r^2} \quad \text{Minimal CGF basis set} \]
Extended Basis Set: Split Valence

* minimal basis sets (STO-3G)
  A single CGF for each AO up to valence electrons

• Double-Zeta ($\xi$: STO exponent) Basis Sets (DZ)
  - Inert core orbitals: with a single CGF (STO-3G, STO-6G, etc)
  - Valence orbitals: with a double set of CGFs

\[
\Phi_{2s}(r) = \Phi_{2s}^{STO}(r, \xi_1) + d\Phi_{2s}^{STO}(r, \xi_2)
\]

  - Slater Orbital 1
  - Slater Orbital 2

  core 1s orbital is sum of 3 gaussians
  valence shell 2s and 2p orbitals are split into two parts:
  inner part is sum of 2 gaussians
  outer part is 1 gaussian

  Pople’s 3-21G, 6-31G, etc.

• Triple-Zeta Basis Sets (TZ)
  - Inert core orbitals: with a single CGF
  - Valence orbitals: with a triple set of CGFs
  - Pople’s 6-311G, etc.
Double-Zeta Basis Set: Carbon 2s Example

The number of gaussian functions summed to describe the inner shell orbital

The number of gaussian functions summed in the second STO

3-21G

The number of gaussian functions that comprise the first STO of the double zeta

\[ \Phi_{1s}(r) = \sum_{i=1}^{3} d_{1i} \Phi_{1s}^{GF}(r, \alpha_{1s}) \]
\[ = 0.6176 \Phi_{1s}^{GF}(r, 172.256) + 0.3587 \Phi_{1s}^{GF}(r, 25.910) + 0.7007 \Phi_{1s}^{GF}(r, 5.533) \]

\[ \Phi_{2s}(r) = \sum_{i=1}^{3} d_{2s} \Phi_{2s}^{GF}(r, \alpha_{2s}) + d_{2s} \Phi_{2s}^{GF}(r, \alpha_{2s}') \]
\[ = -0.395 \Phi_{2s}^{GF}(r, 3.664) + 1.215 \Phi_{2s}^{GF}(r, 0.771) + 1.000 \Phi_{2s}^{GF}(r, 0.195) \]

\[ \Phi_{2p}(r) = \sum_{i=1}^{3} d_{2p} \Phi_{2p}^{GF}(r, \alpha_{2p}) + d_{2p} \Phi_{2p}^{GF}(r, \alpha_{2p}') \]
\[ = 0.236 \Phi_{2p}^{GF}(r, 3.664) + 0.860 \Phi_{2p}^{GF}(r, 0.771) + 1.000 \Phi_{2p}^{GF}(r, 0.195) \]

<table>
<thead>
<tr>
<th>CARBON</th>
<th>(6S,3P) -&gt; [3S,2P]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S 3</td>
<td>172.256000 0.6176E-01</td>
</tr>
<tr>
<td>2 25.910900 0.35879400</td>
<td></td>
</tr>
<tr>
<td>3 5.53335000 0.700713000</td>
<td></td>
</tr>
<tr>
<td>L 2</td>
<td>3.66498000 -0.395897000 0.23640000</td>
</tr>
<tr>
<td>2 0.770545000 1.21584000 0.860619000</td>
<td></td>
</tr>
<tr>
<td>L 1</td>
<td>0.195857000 1.000000000 1.000000000</td>
</tr>
</tbody>
</table>
Even though we are comparing the Gaussian orbitals with H-atom style orbitals, note that the H-atom orbitals are **not** the correct orbitals for **any** multi-electron atom.
Double-Zeta Basis Set: Example

**Lithium 3-21G basis set as listed in Gaussian94.**

<table>
<thead>
<tr>
<th>$\alpha_i$</th>
<th>$d_{si}$</th>
<th>$d_{xi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>0.368382</td>
<td>0.696686</td>
<td></td>
</tr>
<tr>
<td>0.548172</td>
<td>0.381346</td>
<td></td>
</tr>
<tr>
<td>0.111327</td>
<td>0.681702</td>
<td></td>
</tr>
<tr>
<td>SP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>0.540205</td>
<td>-0.263127</td>
<td>0.161546</td>
</tr>
<tr>
<td>0.102255</td>
<td>0.114339</td>
<td>0.915663</td>
</tr>
<tr>
<td>0.285645</td>
<td>0.100000</td>
<td>0.100000</td>
</tr>
</tbody>
</table>

3 for 1s (core)

21 for 2sp (valence)

\[ \Psi_{1s} = 0.0697 \, g_s(36.8,r) + 0.381 \, g_s(5.48,r) + 0.682 \, g_s(1.11,r) \]

\[ = 0.0697 \left( \frac{2 \cdot 36.8}{\pi} \right)^{3/4} e^{-36.8r^2} + 0.381 \left( \frac{2 \cdot 5.48}{\pi} \right)^{3/4} e^{-5.48r^2} + 0.682 \left( \frac{2 \cdot 1.11}{\pi} \right)^{3/4} e^{-1.11r^2} \]

\[ \Psi_{2s}(\text{inner}) = -0.263 \, g_s(0.540,r) + 1.14 \, g_s(0.102,r) \]

\[ \Psi_{2s}(\text{outer}) = 1.00 \, g_s(0.0286,r) \]

\[ \Psi_{2px}(\text{inner}) = 0.162 \, g_X(0.540,r) + 0.916 \, g_X(0.102,r) \]

\[ \Psi_{2px}(\text{outer}) = 1.00 \, g_X(0.0286,r) \]

\[ E(\text{Li,3-21G}) = -200.78 \, \text{eV} \]

Not so good agreement

\[ E(\text{exp.}) = -\text{IP}_1 - \text{IP}_2 - \text{IP}_3 = -202.42 \, \text{eV} \]
Triple-Zeta Basis Set: Example

6-311G basis set: core 1s orbital is sum of 6 gaussians
valence shell 2s and 2p orbitals are split into three parts:
contracted part is sum of 3 gaussians
more diffuse part is 1 gaussian
most diffuse part is 1 gaussian

Lithium 6-311G basis set as listed in Gaussian94.

<table>
<thead>
<tr>
<th>α_j</th>
<th>d_sj</th>
<th>d_xj</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>6 1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.9004600000D+03</td>
<td>0.2287040000D-02</td>
</tr>
<tr>
<td></td>
<td>0.1344300000D+03</td>
<td>0.1763500000D-01</td>
</tr>
<tr>
<td></td>
<td>0.3043650000D+02</td>
<td>0.8734340000D-01</td>
</tr>
<tr>
<td></td>
<td>0.8626390000D+01</td>
<td>0.2809770000D+00</td>
</tr>
<tr>
<td></td>
<td>0.2483320000D+01</td>
<td>0.6587410000D+00</td>
</tr>
<tr>
<td></td>
<td>0.3031790000D+00</td>
<td>0.1187120000D+00</td>
</tr>
<tr>
<td>SP</td>
<td>3 1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4868900000D+01</td>
<td>0.9332930000D-01</td>
</tr>
<tr>
<td></td>
<td>0.8569240000D+00</td>
<td>0.9430450000D+00</td>
</tr>
<tr>
<td></td>
<td>0.2432270000D+00</td>
<td>-0.2798270000D-02</td>
</tr>
<tr>
<td>SP</td>
<td>1 1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6350700000D-01</td>
<td>0.1000000000D+01</td>
</tr>
<tr>
<td></td>
<td>0.2436830000D-01</td>
<td>0.1000000000D+01</td>
</tr>
</tbody>
</table>

E(Li,6-311G) = -202.15eV  E(exp.) = IP_1 - IP_2 - IP_3 = -202.42eV

better agreement
Extended Basis Set: Polarization Function

- Functions of higher angular momentum than those occupied in the atom
- p-functions for H-He,
- d-functions for Li-Ca
- f-functions for transition metal elements
Extended Basis Set: Polarization Function

- The orbitals can distort and adapt better to the molecular environment.

(Example) Double-Zeta Polarization (DZP) or Split-Valence Polarization (SVP)

\[ 6-31G(d,p) = 6-31G^{**}, \ 6-31G(d) = 6-31G^* \] (Pople)

Polarization functions give more room for the electrons to get away from each other to minimize electron-electron repulsion.

For H add p functions

\[
\begin{align*}
\text{p} & + \lambda \text{ orbit} = \text{p orbit}
\end{align*}
\]

For Li-Ca add d functions

\[
\begin{align*}
\text{d} & + \lambda \text{ orbit} = \text{d orbit}
\end{align*}
\]
Polarization Functions. Good for Geometries

Figure 5.16. One basis function can be used to shift another in a given direction (to polarize it). In minimizing the energy, the program adjusts the relative contributions of the two functions to shift the electron density where it is needed to get the minimum energy. \( p \) Functions are also commonly used to polarize the \( s \) functions on hydrogen atoms, but the main use of polarization functions is the utilization of \( d \) functions on “heavy” atoms (atoms other than H and He).

Figure 5.14. Some STO-3G, STO-3G*, 3-21G and 3-21G(*) geometries.
Extended Basis Set: Diffuse Function

- Core electrons and electrons engaged in bonding are tightly bound.
  → Basis sets usually concentrate on the inner shell electrons.
  (The tail of wavefunction is not really a factor in calculations.)

- In anions and in excited states, loosely bond electrons become important.
  (The tail of wavefunction is now important.)
  → We supplement with **diffuse functions**
  (which has very small exponents to represent the tail).

- + when added to H
  ++ when added to others

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21 + G</td>
<td>hydrogen and helium</td>
</tr>
<tr>
<td>1s</td>
<td>3-21 + G basis set for carbon</td>
</tr>
<tr>
<td>2s'2p'2p'2p'</td>
<td></td>
</tr>
<tr>
<td>2s''2p''2p''</td>
<td></td>
</tr>
<tr>
<td>2s+, 2p+, 2p+, 2p+</td>
<td></td>
</tr>
<tr>
<td>3 basis functions</td>
<td>13 basis functions</td>
</tr>
</tbody>
</table>

![Wavefunction graph](image)
Dunning’s Correlation-Consistent Basis Set

- Augmented with functions with even higher angular momentum
- cc-pVDZ (correlation-consistent polarized valence double zeta)
- cc-pVTZ (triple zeta)
- cc-pVQZ (quadruple zeta)
- cc-pV5Z (quintuple zeta) \((14s8p4d3f2g1h)/[6s5p4d3f2g1h]\)

**Basis Set Sizes**

![Diagram of Carbone with 3-21G basis functions](image)

- STO-3G
- 3-21G
- 6-31G
- 6-31G*
- 6-31G**(6-31G(d,p))
- 6-311G**(6-31 1G(d,p))
- 6-31 1G(df,p)
- 6-31 1G(3df,3pd)
- 6-311++G(3df, 3pd)

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>5 + 1 + 1 = 7</td>
</tr>
<tr>
<td>3-21G</td>
<td>9 + 2 + 2 = 13</td>
</tr>
<tr>
<td>6-31G</td>
<td>15 + 2 + 2 = 19</td>
</tr>
<tr>
<td>6-31G*</td>
<td>15 + 5 + 5 = 25</td>
</tr>
<tr>
<td>6-31G**(6-31G(d,p))</td>
<td>18 + 6 + 6 = 30</td>
</tr>
<tr>
<td>6-311G**(6-31 1G(d,p))</td>
<td>25 + 6 + 6 = 37</td>
</tr>
<tr>
<td>6-31 1G(df,p)</td>
<td>35 + 17 + 17 = 69</td>
</tr>
<tr>
<td>6-31 1G(3df,3pd)</td>
<td>39 + 18 + 18 = 75</td>
</tr>
</tbody>
</table>

*Figure 5.15. Carbone, with 3-21G basis functions.*
Effective Core Potentials (ECP) or Pseudo-potentials

- From about the third row of the periodic table (K-)
  Large number of electrons slows down the calculation.
  Extra electrons are mostly core electrons.
  A minimal representation will be adequate.

- Replace the core electrons with analytic functions
  (added to the Fock operator) representing
  the combined nuclear-electronic core to the valence electrons.

- Relativistic effect (the masses of the inner electrons of heavy atoms are
  significantly greater than the electron rest mass) is taken into account by
  relativistic ECP.

- Hay and Wadt (ECP and optimized basis set) from Los Alamos (LANL)
# Accuracy of ab initio Quantum Chemistry Methods

## Ab initio Molecular Orbital Treatment for H₂

<table>
<thead>
<tr>
<th>Basis Set Type</th>
<th>HF</th>
<th>MP2</th>
<th>MP3</th>
<th>MP4</th>
<th>QCISD(T)</th>
<th>Full CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Split-valence</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarized</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffuse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High Ang Moment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **HF Limit**:  
- **Schroedinger Equation**: 

<table>
<thead>
<tr>
<th>Energy (E)</th>
<th>Method/Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>-308.4 kJ/mol</td>
<td>STO-3G</td>
</tr>
<tr>
<td>-322.8 kJ/mol</td>
<td>3-21G* 1s 1s'</td>
</tr>
<tr>
<td>-332.9 kJ/mol</td>
<td>6-31G* 1s 1s'</td>
</tr>
<tr>
<td>-344.9 kJ/mol</td>
<td>6-31G** 1s 1s' &amp; p</td>
</tr>
<tr>
<td>-347.7 kJ/mol</td>
<td>6-311G** 1s 1s' 1s'' &amp; p</td>
</tr>
<tr>
<td>-368.0 kJ/mol</td>
<td>MP2 3-21G(*)</td>
</tr>
<tr>
<td>-420.6 kJ/mol</td>
<td>MP2 6-311G**</td>
</tr>
<tr>
<td>-441.9 kJ/mol</td>
<td>CCSD 6-311G**</td>
</tr>
<tr>
<td>-450.9 kJ/mol</td>
<td>MP4 cc-pVTZ</td>
</tr>
<tr>
<td>-452.5 kJ/mol</td>
<td>CCSD cc-pVTZ</td>
</tr>
<tr>
<td>-458.1 kJ/mol</td>
<td>experimental</td>
</tr>
</tbody>
</table>
ab initio or DFT Quantum Chemistry Softwares

- Gaussian
- Jaguar (http://www.schrodinger.com): Manuals on website
- Turbomole
- DGAuss
- DeMon
- GAMESS
- ADF (STO basis sets)
- DMol (Numerical basis sets)
- VASP (periodic, solid state, Plane wave basis sets)
- PWSCF (periodic, solid state, Plane wave basis sets)
- CASTEP (periodic, solid state, Plane wave basis sets)
- SIESTA (periodic, solid state, gaussian basis sets)
- CRYSTAL (periodic, solid state, gaussian basis sets)
- etc.
Basis Set Selection in Quantum Chemistry Softwares

[Image of a software interface showing basis set selection options]

- **Molecule**
- **Theory**
- **SCF**
- **Properties**
- **Solvation**
- **Output**

**Symmetry:** Use if present

**Molecular state:**
- Use charge and multiplicity from Project Table
- Use these values:
  - Molecular charge: 0
  - Spin multiplicity (2S+1): 1

**Basis set:** 6-31G
- Polarization: **
- Diffuse: None

**Number of D functions:** 5D, 6D
120 basis functions.
Table 4.1. **Available basis sets that do not include effective core potentials**

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Atoms Included</th>
<th>Options</th>
<th>Method</th>
<th># of d fns.</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>H-Xe</td>
<td>* (Na-Xe)</td>
<td>analytic</td>
<td>5</td>
<td>67-71</td>
</tr>
<tr>
<td>3-21G</td>
<td>H-Xe</td>
<td>* (Na-Ar), + (Li-Ar), ++ (H-Ar)</td>
<td>H–Ar pseudospectral (analytic with + or ++), K–Xe analytic</td>
<td>6</td>
<td>72-74</td>
</tr>
<tr>
<td>4-21G</td>
<td>H-Ne</td>
<td>* , **</td>
<td>analytic</td>
<td>6</td>
<td>75</td>
</tr>
<tr>
<td>6-21G</td>
<td>H-Ar</td>
<td>* , **</td>
<td>analytic</td>
<td>6</td>
<td>72-74</td>
</tr>
<tr>
<td>4-31G</td>
<td>H-Ne</td>
<td>* , **</td>
<td>analytic</td>
<td>6</td>
<td>76-81</td>
</tr>
<tr>
<td>6-31G</td>
<td>H-Ar</td>
<td>* , **; +, ++</td>
<td>pseudospectral</td>
<td>6</td>
<td>77-82</td>
</tr>
<tr>
<td>6-311G</td>
<td>H-Ar</td>
<td>* , **; +, ++</td>
<td>H, Li, C-F, Na, Si-Cl pseudospectral, others analytic</td>
<td>5</td>
<td>84-87</td>
</tr>
<tr>
<td>6-311G(3d1f-3pd)</td>
<td>H-Ar</td>
<td>+, ++</td>
<td>analytic</td>
<td>5</td>
<td>84-87</td>
</tr>
<tr>
<td>6-31G(tm)</td>
<td>H-Zn</td>
<td>* , **; +, ++</td>
<td>H-Ar pseudospectral, K-Zn analytic</td>
<td>6</td>
<td>77-83</td>
</tr>
<tr>
<td>m6-31G(tm)</td>
<td>K-Zn</td>
<td>* , ** for H-Ar</td>
<td>analytic</td>
<td>6</td>
<td>88</td>
</tr>
<tr>
<td>D95V</td>
<td>H, Li-Ne</td>
<td>* , **</td>
<td>analytic</td>
<td>6</td>
<td>89</td>
</tr>
<tr>
<td>D95</td>
<td>H, Li-Ne, Al-Cl</td>
<td>* , **</td>
<td>H, Li, C-F, Si-Cl pseudospectral, others analytic</td>
<td>6</td>
<td>89</td>
</tr>
<tr>
<td>MSV</td>
<td>H-Ru, Pd-Xe</td>
<td></td>
<td>analytic</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>Basis Set</td>
<td>Atoms Included</td>
<td>Options</td>
<td>Method</td>
<td># of d fn.</td>
<td>Refs.</td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------------------</td>
<td>---------</td>
<td>-----------------------------------------------</td>
<td>-----------</td>
<td>-------</td>
</tr>
<tr>
<td>cc-pVDZ</td>
<td>H-He, B-Nc, Al-Ar</td>
<td>++</td>
<td>H, C-F, Si-Cl pseudospectral, others analytic; +, ++ analytic</td>
<td>5</td>
<td>91-94</td>
</tr>
<tr>
<td>cc-pVDZ(-d) (without d functions)</td>
<td>H-He, B-Nc, Al-Ar</td>
<td>++</td>
<td>H, C-F, Si-Cl pseudospectral, others analytic; +, ++ analytic</td>
<td>5</td>
<td>91-94</td>
</tr>
<tr>
<td>cc-pVTZ</td>
<td>H-Ar, Ca, Ga-Kr</td>
<td>++</td>
<td>H, C-F, Si-Cl, Br pseudospectral, others analytic</td>
<td>5</td>
<td>91-94</td>
</tr>
<tr>
<td>cc-pVTZ(-f) (without f functions)</td>
<td>H-Ar, Ca, Ga-Kr</td>
<td>++</td>
<td>H, C-Ne, Si-Ar, Br pseudospectral, others analytic</td>
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<td>91-94</td>
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<td>cc-pVQZ(-g) (without g functions)</td>
<td>H-F, Na-Ar, Ca, Ga-Kr</td>
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<td>H, C-O, pseudospectral, others analytic; +, ++ analytic</td>
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<td>MIDIX</td>
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<td>H, C-F, P-Cl pseudospectral; Li, Si, Br, I analytic</td>
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<tr>
<td>TZV</td>
<td>H-Kr</td>
<td><em>,</em>* (Sc-Zn p only)</td>
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<td>TZV(f)</td>
<td>H-Kr</td>
<td><em>,</em>* (Sc-Zn p and f)</td>
<td>analytic</td>
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<td>Basis Set</td>
<td>Atoms in ECP</td>
<td>Other Atoms</td>
<td>Options</td>
<td>Refs.</td>
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<tr>
<td>LAV1S</td>
<td>Na-La, Hf-Bi</td>
<td>H-Ne (STO-3G)</td>
<td>* (H-Ne)</td>
<td>99-100</td>
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<tr>
<td>LAV2D</td>
<td>Na-La, Hf-Bi</td>
<td>H, Li-Ne (D95V)</td>
<td>* , ** (H, Li-Ne)</td>
<td>99-100</td>
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<tr>
<td>LAV2P</td>
<td>Na-La, Hf-Bi</td>
<td>H-Ne (6-31G)</td>
<td>* , ** (H-Ne); +, ++ (H-Ne)</td>
<td>99-100</td>
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<td>LAV3D</td>
<td>Na-La, Hf-Bi</td>
<td>H, Li-Ne (D95V)</td>
<td>* , ** (H, Li-Ne)</td>
<td>99-100</td>
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<tr>
<td>LAV3P</td>
<td>Na-La, Hf-Bi</td>
<td>H-Ne (6-31G)</td>
<td>* , ** (H-Ne); +, ++ (H-Ne)</td>
<td>99-100</td>
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<tr>
<td>LACVD</td>
<td>K-Cu, Rb-Ag, Cs-La, Hf-Au</td>
<td>H, Li-Ne (D95V); Na-Ar, Zn-Kr, Cd-Xe, Hg-Bi (LAV3D)</td>
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<tr>
<td>LACVP</td>
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<td>H-Ar (6-31G); Zn-Kr, Cd-Xe, Hg-Bi (LAV3P)</td>
<td>* , ** (H-Ar); +, ++ (H-Ar)</td>
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<tr>
<td>LACV3P</td>
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<td>cc-pVTZ-pp</td>
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<td>H-Ar, Ca (cc-pVTZ)</td>
<td>+, ++</td>
<td>103-105</td>
<td></td>
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<tr>
<td>cc-pVTZ-pp(+f)</td>
<td>Ga-Kr, In-Xe</td>
<td>H-Ar, Ca (cc-pVTZ(+f))</td>
<td>+, ++</td>
<td>103-105</td>
<td></td>
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<tr>
<td>CSDZ</td>
<td>Ce-Lu</td>
<td>H-Ar (6-31G); Zn-Kr, Cd-Xe, Hg-Bi (LAV3P); K-Cu, Rb-Ag, Cs-La, Hf-Au (LACVP)</td>
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<td>106</td>
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<tr>
<td>ERMLR2</td>
<td>K-Lr</td>
<td>H-Ar; 6-31G</td>
<td>* , **; +, ++ (H-Ar, Ga-Kr, In-Xe, Tl-Rn)</td>
<td>107-114</td>
<td></td>
</tr>
</tbody>
</table>
MO Diagram of Homonuclear Diatomic Molecules

Atomic orbitals

Out-of-phase overlap (subtract)

In-phase overlap (add)

$\sigma_{1s}^{\text{b}}$ (bonding)

$\sigma_{1s}^{\text{a}}$ (antibonding)

Nodal plane

Energy
H₂

H₂

He₂

He₂

H₂

He₂

H₂

He₂

LUMO

HOMO

bond order = \frac{2 - 0}{2} = 1

stable molecule

bond order = \frac{2 - 2}{2} = 0

unknown molecule
Li₂

**LUMO**
σ₂\text{LUMO}\text{antibonding}

**HOMO**
σ₁\text{HOMO}\text{bonding MO}

\sigma₁\text{antibonding}

\frac{4 - 2}{2} = 1

**Li₂**
Bond order = 1

Li₂ is known in the gas phase

Be₂

**LUMO**
σ₂\text{LUMO}\text{antibonding}

**HOMO**
σ₂\text{HOMO}\text{bonding MO}

\sigma₁\text{antibonding}

\frac{4 - 4}{2} = 0

**Be₂**
Bond order = 0

Unknown species
The **head-on overlap** of two corresponding $p$ atomic orbitals on different atoms, such as $2p_x$ with $2p_x$, produces:

1. $\sigma_{2p_x}$ bonding orbital
2. $\sigma^*_{2p_x}$ antibonding orbital
Side-on overlap of two corresponding p atomic orbitals on different atoms (such as 2p$_y$ with 2p$_y$ or 2p$_z$ with 2p$_z$) produces:

1. $\pi_{2p_y}$ or $\pi_{2p_z}$ (both are bonding orbitals)

2. $\pi^*_{2p_y}$ or $\pi^*_{2p_z}$ (both are nonbonding orbitals)
H₂ through N₂

O₂ through Ne₂
**N₂**

**HOMO**

\[ \sigma_{2p_z} \]

\[ \sigma^*_{2p_z} \]

\[ \pi_{2p_x} \]

\[ \pi^*_{2p_x} \]

\[ \sigma_{1s} \]

\[ \sigma^*_{1s} \]

\[ \sigma_{2s} \]

\[ \sigma^*_{2s} \]

\[ 2p_y \]

**LUMO**

\[ \sigma_{2p_y} \]

\[ \sigma^*_{2p_y} \]

\[ \pi_{2p_z} \]

\[ \pi^*_{2p_z} \]

\[ \sigma_{1s} \]

\[ \sigma^*_{1s} \]

\[ \sigma_{2s} \]

\[ \sigma^*_{2s} \]

\[ 2p_x \]

Bond order for **N₂**:

\[ \frac{10 - 4}{2} = \frac{6}{2} = 3 \]

**Diradical**

**O₂**

**HOMO**

\[ \sigma_{2p_z} \]

\[ \sigma^*_{2p_z} \]

\[ \pi_{2p_x} \]

\[ \pi^*_{2p_x} \]

\[ \sigma_{1s} \]

\[ \sigma^*_{1s} \]

\[ \sigma_{2s} \]

\[ \sigma^*_{2s} \]

\[ 2p_y \]

**LUMO**

\[ \sigma_{2p_y} \]

\[ \sigma^*_{2p_y} \]

\[ \pi_{2p_z} \]

\[ \pi^*_{2p_z} \]

\[ \sigma_{1s} \]

\[ \sigma^*_{1s} \]

\[ \sigma_{2s} \]

\[ \sigma^*_{2s} \]

\[ 2p_x \]

Bond order for **O₂**:

\[ \frac{10 - 6}{2} = \frac{4}{2} = 2 \]

**Bond order**

\[ \text{bond order} = \frac{\text{number of electrons in bonding MOs}}{\text{number of electrons in anti-bonding MOs}} \]

N₂ is a stable molecule with a bond order of 3.

O₂ is a diradical with a bond order of 2.
The diagrams illustrate the molecular orbitals (MOs) and electron configurations of various diatomic molecules:

- **F₂**:
  - **HOMO**: $2s^2$ bonding
  - **LUMO**: $2p_z$ antibonding
  - Bond order: $\frac{10 - 8}{2} = 1$
  - Stable molecule

- **Ne₂**:
  - **HOMO**: $2s^2$ bonding
  - **LUMO**: $2p_z$ antibonding
  - Bond order: $\frac{10 - 10}{2} = 0$
  - Unknown species
Homonuclear Diatomics

Bond Order Measures

<table>
<thead>
<tr>
<th></th>
<th>H₂</th>
<th>Li₂</th>
<th>LiH</th>
<th>B₂*</th>
<th>C₂</th>
<th>N₂</th>
<th>O₂*</th>
<th>F₂</th>
<th>CN</th>
<th>CO</th>
<th>NO</th>
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</thead>
<tbody>
<tr>
<td>D₀  (kcal/mol)</td>
<td>104</td>
<td>25</td>
<td>58</td>
<td>69</td>
<td>144</td>
<td>225</td>
<td>118</td>
<td>36</td>
<td>188</td>
<td>256</td>
<td>151</td>
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<tr>
<td>D₀  (kJ/mol)</td>
<td>435</td>
<td>105</td>
<td>243</td>
<td>289</td>
<td>602</td>
<td>941</td>
<td>494</td>
<td>151</td>
<td>787</td>
<td>1070</td>
<td>632</td>
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<tr>
<td>r₀  (Å)</td>
<td>0.76</td>
<td>2.68</td>
<td>1.61</td>
<td>1.59</td>
<td>1.24</td>
<td>1.10</td>
<td>1.21</td>
<td>1.44</td>
<td>1.18</td>
<td>1.13</td>
<td>1.15</td>
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<tr>
<td>k₀  (mdyne/Å)</td>
<td>5.1</td>
<td>0.25</td>
<td>0.96</td>
<td>3.5</td>
<td>9.3</td>
<td>22.4</td>
<td>11.4</td>
<td>4.5</td>
<td>15.8</td>
<td>18.6</td>
<td>15.5</td>
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<tr>
<td>Bond Order</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>2.5</td>
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</tr>
</tbody>
</table>

D₀ = Dₑ - 1/2 hν₀  \quad Dₑ = \text{minimum in energy curve} \quad 1/2 hν₀ = \text{zero point energy}

r₀ = \text{internuclear distance at curve minimum}

k₀ = \text{force constant}

for an harmonic potential V = 1/2 k₀ (r-r₀)²  \quad \text{for a general potential} \quad k₀ = \left( \frac{∂²V}{∂r²} \right)
Koopman’s Theorem

• As well as the **total energy**, one also obtains a set of **orbital energies**.

\[ \epsilon_i = h_{ii} + \sum_j^n (J_{ij} - K_{ij}) \]

• Remove an electron from occupied orbital \( a \).

\[
E(\Psi^a) = V_{NN} + \sum_{i \neq a}^n h_{ii} + \sum_{i \neq a}^n \sum_{j > i, i \neq a}^n (J_{ij} - K_{ij}) \\
E(\Psi^0) = V_{NN} + \sum_i^1 h_{ii} + \sum_i^1 \sum_{j > i}^1 (J_{ij} - K_{ij}) \\
IE(M) \approx (E(\Psi^a) - E(\Psi^0)) = -h_{aa} - \sum_j (J_{aj} - K_{aj}) = -\epsilon_a
\]

**Orbital energy = Approximate ionization energy**
Koopman’s Theorem: Examples

<table>
<thead>
<tr>
<th></th>
<th>$IE_{exp}$</th>
<th>$-\epsilon_{HOMO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>1,490</td>
<td>1,570</td>
</tr>
<tr>
<td>$NH_3$</td>
<td>970</td>
<td>1,098</td>
</tr>
<tr>
<td>Benzene</td>
<td>890</td>
<td>870</td>
</tr>
<tr>
<td>Toluene</td>
<td>850</td>
<td>835</td>
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* Calculated according to Koopman’s theorem.