

# **CHEM 4301/5301: Theory of Chemical Bonding**

**© Erin R. Johnson**

**2025**

# Contents

<b>1</b>	<b>Atomic and Molecular Orbitals</b>	<b>5</b>
1.1	Review and Motivation . . . . .	5
1.2	Atomic Orbitals . . . . .	6
1.3	The Pauli Exclusion Principle . . . . .	8
1.4	The Helium Atom . . . . .	11
1.5	Many-Electron Atoms . . . . .	13
1.6	The Variational Principle . . . . .	14
<b>2</b>	<b>Simple Molecules: <math>\text{H}_2^+</math> and <math>\text{H}_2</math></b>	<b>18</b>
2.1	The Born-Oppenheimer Approximation . . . . .	18
2.2	MOs for $\text{H}_2^+$ . . . . .	18
2.3	MOs for $\text{H}_2$ . . . . .	21
<b>3</b>	<b>Qualitative MO Theory</b>	<b>23</b>
3.1	MO Diagrams . . . . .	23
3.2	Second-Period Diatomics . . . . .	25
3.3	Secondary Orbital Mixing . . . . .	26
3.4	MO Diagrams for Linear Polyatomic Molecules . . . . .	27

<i>CONTENTS</i>	3
3.5 MO Diagrams for Centro-Symmetric Molecules . . . . .	29
3.6 MOs versus Localized Hybrid Orbitals . . . . .	32
3.7 Jahn-Teller Distortions . . . . .	34
<b>4 Quantitative MO Theories</b>	<b>36</b>
4.1 Hückel Theory . . . . .	36
4.2 Extended Hückel Theory . . . . .	42
4.3 MO Theory for H <sub>2</sub> Revisited . . . . .	43
4.4 Configuration Interaction for H <sub>2</sub> . . . . .	46
4.5 Summary and Review . . . . .	47
<b>5 Introduction to Quantum-Chemical Calculations</b>	<b>49</b>
5.1 Overview of Electronic-Structure Methods . . . . .	49
5.2 Overview of Basis Sets . . . . .	50
5.3 Potential Energy Surfaces . . . . .	51
5.4 Overview of Calculation Types . . . . .	52
5.5 Input for a Gaussian Calculation . . . . .	52
5.6 Z-matrices . . . . .	52
5.7 Basis Sets . . . . .	55
5.8 Introduction to Statistical Mechanics . . . . .	57
5.9 Comparing Energies with Thermodynamic Data . . . . .	59
<b>6 Electronic-Structure Methods</b>	<b>61</b>

6.1	Hartree-Fock Theory . . . . .	61
6.2	The Roothan-Hall Method . . . . .	63
6.3	Restricted versus Unrestricted Spins . . . . .	64
6.4	Configuration Interaction . . . . .	65
6.5	Perturbation Theory . . . . .	67
6.6	Møller-Plesset Perturbation Theory . . . . .	69
6.7	Coupled-Cluster Theory . . . . .	70
<b>7</b>	<b>Density-Functional Theory (DFT)</b>	<b>72</b>
7.1	DFT Formalism . . . . .	72
7.2	Density-Functional Approximations . . . . .	74
7.2.1	The Local Density Approximation (LDA) . . . . .	74
7.2.2	Generalized Gradient Approximations (GGAs) . . . . .	74
7.2.3	meta-GGAs . . . . .	75
7.2.4	Hybrid Functionals . . . . .	75
7.2.5	Range-Separated Hybrid Functionals . . . . .	75
7.2.6	Double Hybrid Functionals . . . . .	76
7.3	Dispersion Methods . . . . .	76

# Chapter 1

## Atomic and Molecular Orbitals

### 1.1 Review and Motivation

The fundamental equation on which quantum chemistry is based is the time-independent Schrödinger equation:

$$\hat{H}\psi = E\psi$$

where  $\hat{H}$  is the Hamiltonian (or energy operator),  $\psi$  is the wavefunction, and  $E$  is the energy.

This is an eigenvalue problem, as in matrix algebra. The wavefunction  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  is a function of the positions of all  $N$  electrons in an atom or molecule.

The electron density

$$\rho(\mathbf{r}) = \int \cdots \int \psi^* \psi d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

describes the distribution of electrons in a molecule in 3D.

The Hamiltonian is a sum of the kinetic ( $\hat{T}$ ) and potential ( $\hat{V}$ ) energies of the electrons in the system

$$\hat{H} = \hat{T} + \hat{V}$$

The kinetic energy includes a sum of the kinetic energies of all the electrons and the potential energy is a sum of all electron-nuclear attraction and electron-electron repulsion terms.

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_A \frac{1}{r_{iA}} + \sum_{i < j} \frac{1}{r_{ij}}$$

However, the  $e^-e^-$  term is not separable into functions of the individual electron coordinates because

$$\frac{1}{r_{ij}} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

so the SE cannot be solved analytically for many- $e^-$  systems.

We want to solve the SE for molecules to determine their structure, energies, thermochemistry, reaction kinetics, vibrational spectra, absorption spectra, etc.

As a first approximation, we construct a set of molecular orbitals ( $\phi_i$ 's) from linear combinations of atomic orbitals ( $\chi_k$ 's)

$$\phi_i = \sum_k c_k \chi_k$$

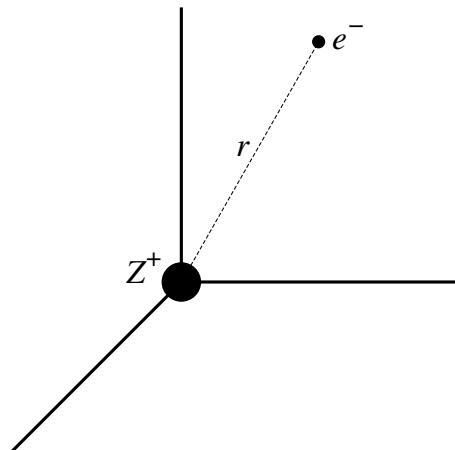
The MOs are the solutions to

$$\hat{H}\phi_i = \varepsilon_i \phi_i$$

where the  $\varepsilon_i$ 's are the molecular-orbital energies.

## 1.2 Atomic Orbitals

AOs are the solutions to the SE for the hydrogen atom.



The potential is  $V = -\frac{Z}{r}$  in atomic units and arises from the electrostatic attraction between the electron and nucleus.

The kinetic energy of the electron,  $\hat{T} = -\frac{1}{2}\nabla^2$ , is given in terms of the Laplacian, or second-derivative, operator. In Cartesian coordinates, the Laplacian is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

For the hydrogen atom, we work in spherical polar coordinates, where

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

The general solution for the H-atom wavefunctions is a product of radial and angular terms:

$$\psi_{nlm_\ell} = R_{nl}(r)Y_{\ell m_\ell}(\theta, \phi)$$

$n$  is the principle quantum number,  $\ell$  and  $m_\ell$  are angular momentum quantum numbers ( $\ell$  = total,  $m_\ell$  =  $z$ -component), and the  $Y_{\ell m_\ell}$ 's are the spherical harmonics.

## 1.2. Atomic Orbitals

7

The energies are  $E_n = -\frac{Z^2}{2n^2}$  in atomic units (Hartree).

Recall that  $n = 1, 2, 3, \dots$ ,  $\ell = 0, 1, \dots, n-1$ , and  $m_\ell = 0, \pm 1, \dots, \pm \ell$ .

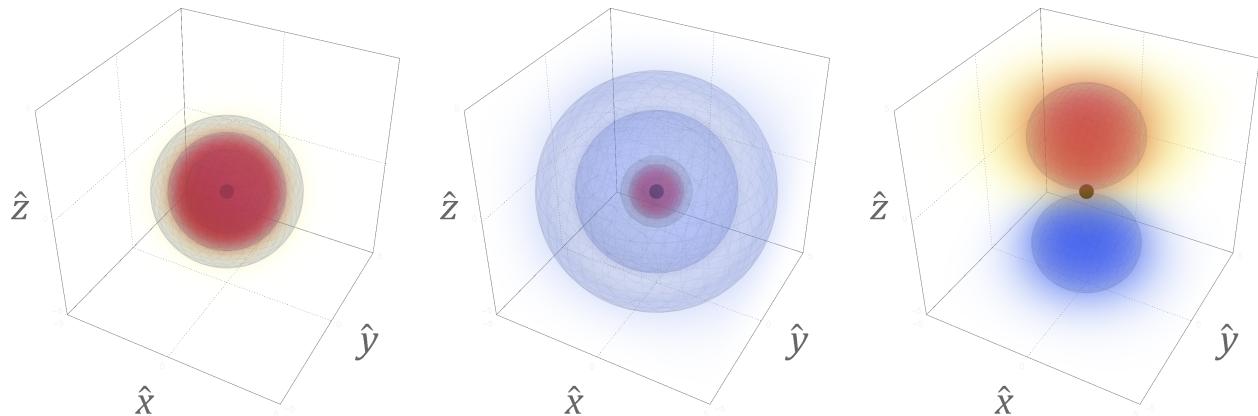
The general pattern of energy levels is:

	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	
$n = 4$	—	—	—	—	7 <i>f</i> orbitals, $m_\ell = 0, \pm 1, \pm 2, \pm 3$
$n = 3$	—	—	—	—	5 <i>d</i> orbitals, $m_\ell = 0, \pm 1, \pm 2$
$n = 2$	—	—	—	—	3 <i>p</i> orbitals, $m_\ell = 0, \pm 1$
$n = 1$	—	—	—	—	1 <i>s</i> orbital, $m_\ell = 0$

Complete H-atom wavefunctions for  $n = 1, 2$  are:

$$\begin{aligned}\psi_{100} &= \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Zr} \\ \psi_{200} &= \frac{1}{\sqrt{32\pi}} Z^{3/2} (2 - Zr) e^{-Zr/2} \\ \psi_{210} &= \frac{1}{\sqrt{32\pi}} Z^{3/2} Zr e^{-Zr/2} \cos \theta \\ \psi_{21\pm 1} &= \frac{1}{\sqrt{64\pi}} Z^{3/2} Zr e^{-Zr/2} \sin \theta e^{\pm i\phi}\end{aligned}$$

The first three orbitals can be plotted in 3D space:



However, the  $\psi_{21\pm 1}$  orbitals are complex valued – need to obtain real linear combinations:

For the positive linear combination, we have:

$$\begin{aligned}
 \frac{1}{\sqrt{2}}(\psi_{211} + \psi_{21-1}) &= \frac{1}{\sqrt{2}} \frac{1}{\sqrt{64\pi}} r \sin \theta (e^{i\phi} + e^{-i\phi}) e^{-r/2} \\
 &= \frac{1}{\sqrt{2}} \frac{1}{\sqrt{64\pi}} r \sin \theta [\cos \phi + i \sin \phi + \cos(-\phi) + i \sin(-\phi)] e^{-r/2} \\
 &= \frac{1}{\sqrt{32\pi}} r \sin \theta \cos \phi e^{-r/2} \\
 &= \frac{1}{\sqrt{32\pi}} x e^{-r/2} \\
 &= \psi_{2p_x}
 \end{aligned}$$

and similarly for the negative linear combination, we have:

$$\begin{aligned}
 -\frac{i}{\sqrt{2}}(\psi_{211} - \psi_{21-1}) &= -\frac{i}{\sqrt{2}} \frac{1}{\sqrt{64\pi}} r \sin \theta (e^{i\phi} - e^{-i\phi}) e^{-r/2} \\
 &= -\frac{i}{\sqrt{2}} \frac{1}{\sqrt{64\pi}} r \sin \theta [\cos \phi + i \sin \phi - \cos(-\phi) - i \sin(-\phi)] e^{-r/2} \\
 &= \frac{1}{\sqrt{32\pi}} r \sin \theta \sin \phi e^{-r/2} \\
 &= \frac{1}{\sqrt{32\pi}} y e^{-r/2} \\
 &= \psi_{2p_y}
 \end{aligned}$$

Additionally, these spatial orbitals are all doubly degenerate due to the electrons possibly having either  $\alpha$  or  $\beta$  spin. Recall that spin functions are orthonormal so that

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$

### 1.3 The Pauli Exclusion Principle

Before we can consider multi-electron systems, there is one further constraint we must impose on the wavefunction that arises from the indistinguishability of identical particles.

For a system of  $n$  identical particles, the wavefunction depends on their positions and spins. We will define the vector  $\mathbf{q} = (x, y, z, m_s)$  to give the spatial and spin coordinates. The wavefunction can then be written as

$$\psi = \psi(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_n)$$

We also define the permutation operator,  $\mathcal{P}_{ij}$  that interchanges the coordinates (both space and spin) of particles  $i$  and  $j$  so that

$$\mathcal{P}_{12}\psi(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_n) = \psi(\mathbf{q}_2, \mathbf{q}_1, \dots, \mathbf{q}_n)$$

Since the labeling is arbitrary, this permutation cannot affect the physical state of the system.

Two wavefunctions that correspond to the same state must be identical, to within a constant phase factor

$$\mathcal{P}_{ij}\psi = c\psi$$

so  $\psi$  is an eigenfunction of  $\mathcal{P}_{ij}$ . Also, application of  $\mathcal{P}_{ij}$  twice recovers the original wavefunction, so

$$\mathcal{P}_{ij}^2\psi = \psi$$

However,

$$\mathcal{P}_{ij}^2\psi = \mathcal{P}_{ij}(c\psi) = c^2\psi$$

Equating these two results means that  $c^2 = 1$ , so  $c = \pm 1$ . Therefore, the wavefunction must be either symmetric or antisymmetric with respect to interchange of any two particles.

To illustrate the consequences of this constraint, let's consider two non-interacting particles in a 1D box of width  $a$ . The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) \psi = E\psi$$

and the solution is a product of two particle in a box wavefunctions

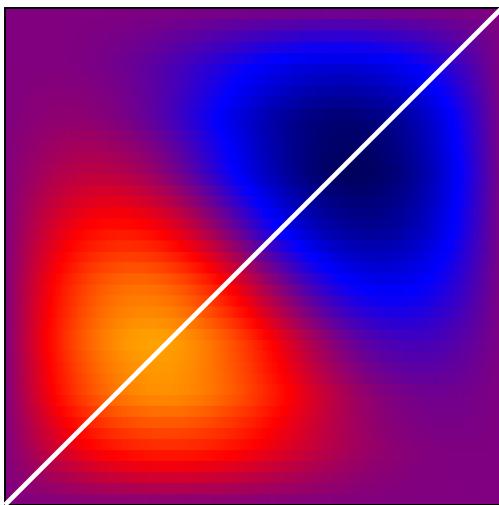
$$\psi_{mn}(x_1, x_2) = \psi_m(x_1)\psi_n(x_2)$$

Symmetric and antisymmetric wavefunctions can be constructed from the individual particle in a box wavefunctions for each particle and are

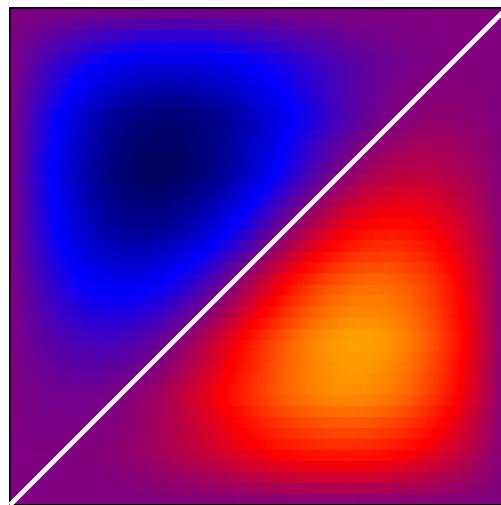
$$\psi_{mn}^S = \frac{1}{\sqrt{2}} [\psi_m(x_1)\psi_n(x_2) + \psi_m(x_2)\psi_n(x_1)]$$

$$\psi_{mn}^A = \frac{1}{\sqrt{2}} [\psi_m(x_1)\psi_n(x_2) - \psi_m(x_2)\psi_n(x_1)]$$

For the cases of  $\psi_{12}^S$  and  $\psi_{12}^A$ , the resulting probability densities are



$\psi_{12}^S$ : high probability of finding both particles at the same point.



$\psi_{12}^A$ : zero probability of finding both particles at the same point.

Experiment shows that there are two types of fundamental particles, with one type having each of the behaviours shown above:

- Fermions - antisymmetric with respect to interchange
- Bosons - symmetric with respect to interchange

and electrons are Fermions.

The **Pauli Exclusion Principle** states that the wavefunction of a system of electrons must be antisymmetric with respect to interchange of any two electrons.

An important consequence of this principle can be seen by considering the value of a wavefunction when two electrons have the same space and spin coordinates (i.e.  $\mathbf{q}_i = \mathbf{q}_j$ ). Then,

$$\psi = \psi(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_i, \mathbf{q}_i, \dots, \mathbf{q}_n)$$

but  $\psi$  must be antisymmetric with respect to interchange of  $i$  and  $j$ . This leads to  $\psi = -\psi$ , and this can only be true for  $\psi = 0$ .

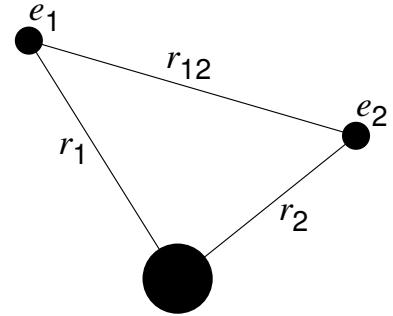
Therefore, another statement of the **Pauli Exclusion Principle** is that two electrons with the same spin have zero probability of being found at the same point in space.

## 1.4 The Helium Atom

The He-atom Hamiltonian, in atomic units, is

$$\mathcal{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

This resembles a repetition of the H-atom problem for electrons 1 and 2, except that the  $1/r_{12}$  term is not separable, so the Schrödinger equation cannot be solved analytically and approximate methods must be used.



Let us write the spatial wavefunction as the product of the hydrogen-like orbitals. For the ground state, this is

$$\psi^\circ = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) = 1s(1)1s(2)$$

We must also take spin into account (since there is more than one electron) and multiply this spatial wavefunction by a spin eigenfunction.

We will use the notation  $\alpha(i)$  or  $\beta(i)$  to indicate a state in which electron  $i$  is spin up or spin down, respectively.

There are four normalized spin eigenfunctions that satisfy the requirement of being either symmetric or antisymmetric with respect to exchange:

symmetric, “triplet” spin functions	$\begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \end{cases}$
-------------------------------------	---

antisymmetric, “singlet” spin function	$\begin{cases} \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \end{cases}$
--	---

According to the Pauli principle, the total wavefunction must be antisymmetric with respect to exchange. The spatial part is  $1s(1)1s(2)$ , which is symmetric. Therefore, the spin part must be antisymmetric and

$$\psi^\circ = 1s(1)1s(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

However, the spin terms will not affect the energy (since the Hamiltonian does not depend on spin, and the spin functionals are normalised), so we need consider only the spatial part.

The helium ground-state energy can be approximated as

$$\begin{aligned} E &= \left\langle 1s(1)1s(2) \left| -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right| 1s(1)1s(2) \right\rangle \\ &= \left\langle 1s(1) \left| -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} \right| 1s(1) \right\rangle \langle 1s(2)|1s(2)\rangle + \left\langle 1s(2) \left| -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} \right| 1s(2) \right\rangle \langle 1s(1)|1s(1)\rangle \\ &\quad + \left\langle 1s(1)1s(2) \left| \frac{1}{r_{12}} \right| 1s(1)1s(2) \right\rangle \end{aligned}$$

The first two terms correspond to the ground-state energy of  $\text{He}^+$ , which is  $E = -Z^2/2n^2$ , with  $Z = 2$  and  $n = 1$  for the  $1s$  orbital. The last term is called the Coulomb integral,  $J$ . It can be shown that  $J = \frac{5Z}{8}$  for the  $1s$  orbitals of a general hydrogen-like atom with nuclear charge  $Z$ . Thus, for the helium atom

$$E \approx -4 + J = -4 + \frac{5}{4} = -2.75 \text{ a.u.}$$

However, lower energies can be obtained by introducing flexibility in the orbital size as neutral He should have a much larger  $1s$  orbital than  $\text{He}^+$ .

The lowest-lying excited states for He have the electron configuration  $1s^12s^1$ . The spatial parts of these wavefunctions are

$$\begin{array}{lll} \psi_{\text{singlet}} = \frac{1}{\sqrt{2}} [1s(1)2s(2) + 1s(2)2s(1)] & 2s & \downarrow \quad 2s \quad \uparrow \\ \psi_{\text{triplet}} = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 1s(2)2s(1)] & 1s & \uparrow \quad 1s \quad \uparrow \\ & & \text{singlet} \quad \text{triplet} \end{array}$$

where  $\psi_{\text{singlet}}$  would be paired with the singlet spin function and  $\psi_{\text{triplet}}$  could be paired with any of the three triplet spin functions.

Using a general form of the spatial wavefunction

$$\psi = \frac{1}{\sqrt{2}} [1s(1)2s(2) \pm 1s(2)2s(1)]$$

it can be shown that the approximate energy is

$$E = -\frac{5}{2} + \left\langle 1s(1)2s(2) \left| \frac{1}{r_{12}} \right| 1s(1)2s(2) \right\rangle \pm \left\langle 1s(1)2s(2) \left| \frac{1}{r_{12}} \right| 1s(2)2s(1) \right\rangle$$

where the  $-5/2$  is the sum of the energies of the  $n = 1$  and  $n = 2$  states of  $\text{He}^+$ . The remaining two terms are the Coulomb integral ( $J$ ) and the exchange integral ( $K$ ).

$$E = -\frac{5}{2} + J \pm K$$

Since both  $J$  and  $K$  are positive, the triplet state is more stable. This is because there is zero probability of finding the electrons at the same point in space in the triplet, which reduces the extent of electron-electron repulsion, and lowers the energy. It is this additional stability that gives rise to Hund's rule of maximum electron unpairing.

## 1.5 Many-Electron Atoms

In general, for a  $N$ -electron atom, the Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}}$$

The wavefunction is approximated as a Slater determinant, with  $N$  electrons in  $N$  orbitals.

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix}$$

abbreviated as  $\psi = \frac{1}{\sqrt{N!}} |\phi_1 \ \phi_2 \ \cdots \ \phi_N|$

The  $\frac{1}{\sqrt{N!}}$  factor assures normalization. Properties of determinants cause the wavefunction to be antisymmetric (recall that the sign of a determinant flips if pairs of columns or rows change order) in accordance with the Pauli exclusion principle.

$\phi_1, \phi_2, \dots, \phi_N$  are spin orbitals, the order of which is chosen according to the AUFBAU (filling) principle.

EX. He atom

$$1s \quad \uparrow\downarrow \quad \psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} |1s\alpha \ 1s\beta|$$

EX. Li atom

$$\begin{array}{cc} 2s & \uparrow \\ 1s & \uparrow\downarrow \end{array} \quad \psi = \frac{1}{\sqrt{6}} |1s\alpha \ 1s\beta \ 2s\alpha|$$

EX. C atom

$$\begin{array}{cc} 2p & \uparrow\downarrow\uparrow\downarrow \\ 2s & \uparrow\downarrow \\ 1s & \uparrow\downarrow \end{array} \quad \psi = \frac{1}{\sqrt{6!}} |1s\alpha \ 1s\beta \ 2s\alpha \ 2s\beta \ 2p_x\alpha \ 2p_y\alpha|$$

Atomic states are described by their multiplicity ( $2S + 1$ ) (where  $S$  is the total spin), which is the number of unpaired electrons, plus 1. In atoms with all paired electrons, like He, the multiplicity is 1 - a singlet. Atoms with one unpaired electron, like Li are doublets. The ground state of the C atom is a triplet.

## 1.6 The Variational Principle

The molecular orbitals (MOs) are generally written as linear combinations of atomic orbitals (AOs)

$$\phi = \sum_{i=1}^n c_i \chi_i$$

where the coefficients are usually assumed to be real.

To optimize the coefficients in MO theory and minimize the ground-state energy, we turn to the variational theorem:

For a time-independent Hamiltonian with ground-state energy  $E_0$ , if  $\phi$  is any normalized, well-behaved function of the electron coordinates and satisfies the boundary conditions, then

$$E = \langle \phi | \hat{H} | \phi \rangle \geq E_0 \quad \left( \text{or } \int \phi^* \hat{H} \phi d\tau \geq E_0 \right)$$

this gives an upper bound to the ground-state energy.

Proof: expand  $\phi$  in terms of the eigenfunctions of  $\hat{H}$

$$\phi = \sum_i a_i \psi_i \quad \text{where} \quad \hat{H} \psi_i = E_i \psi_i$$

then

$$\begin{aligned} \langle \phi | \hat{H} | \phi \rangle &= \sum_i \sum_j a_i^* a_j \langle \psi_i | \hat{H} | \psi_j \rangle \\ &= \sum_i \sum_j a_i^* a_j E_j \langle \psi_i | \psi_j \rangle \\ &= \sum_i \sum_j a_i^* a_j E_j \delta_{ij} \\ &= \sum_j |a_j|^2 E_j \end{aligned}$$

and since  $E_0$  is the ground-state energy,  $E_j \geq E_0$

$$\therefore \langle \phi | \hat{H} | \phi \rangle \geq \sum_j |a_j|^2 E_0$$

and  $\phi$  is normalized, so  $\sum_j |a_j|^2 = 1$

$$\therefore \langle \phi | \hat{H} | \phi \rangle \geq E_0$$

Note that, if  $\phi$  is not normalized, this becomes

$$\frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \geq E_0$$

If the wavefunction,  $\phi$ , depends on an adjustable parameter,  $a$ , then the energy is minimized when

$$\frac{\partial E}{\partial a} = 0$$

We typically use the H AOs to build wavefunctions for many- $e^-$  atoms and molecules. However, the optimum size of the orbitals can be quite different depending on the nuclear charge and number of electrons (as noted above for He vs.  $\text{He}^+$ ). Thus,  $a$  is frequently the adjustable exponent in an atomic orbital, which allows the size of the AO to be optimized:

$$\phi = f(a) e^{-ar}$$

The drawback is that the exponent is a non-linear parameter. It is easier to fit linear parameters to minimize the energy.

For the case that  $\psi$  is a linear combination of basis functions (such as atomic orbitals),

$$\psi = \sum_i^n c_i \phi_i$$

assumed to be real, then

$$E = \frac{\langle \psi | \mathcal{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\sum_{ij} c_i c_j \langle i | \mathcal{H} | j \rangle}{\sum_{ij} c_i c_j \langle i | j \rangle}$$

where

$$\langle i | \mathcal{H} | j \rangle = \int \phi_i \mathcal{H} \phi_j d\tau = H_{ij}$$

are called the Hamiltonian “matrix elements” and

$$\langle i | j \rangle = \int \phi_i \phi_j d\tau = S_{ij}$$

are the “overlap” integrals. These are simply numbers that we can compute since we know the form of the Hamiltonian and the basis functions.

Rearranging the above

$$\sum_{ij} c_i c_j \langle i | \mathcal{H} | j \rangle = E \sum_{ij} c_i c_j \langle i | j \rangle$$

or more compactly,

$$\sum_{ij} c_i c_j H_{ij} = E \sum_{ij} c_i c_j S_{ij}$$

Grouping the terms together,

$$\sum_{ij} (H_{ij} - S_{ij}E) c_i c_j = 0$$

The energy will be minimized when  $\frac{\partial E}{\partial c_j} = 0$  for all  $c_j$ . Differentiating wrt  $c_j$

$$\sum_i (H_{ij} - S_{ij}E) c_i = 0$$

There will be  $n$  such equations, one for each choice of  $c_j$ :

$$(H_{11} - S_{11}E) c_1 + (H_{21} - S_{21}E) c_2 + \dots + (H_{n1} - S_{n1}E) c_n = 0$$

$$(H_{12} - S_{12}E) c_1 + (H_{22} - S_{22}E) c_2 + \dots + (H_{n2} - S_{n2}E) c_n = 0$$

⋮

$$(H_{1n} - S_{1n}E) c_1 + (H_{2n} - S_{2n}E) c_2 + \dots + (H_{nn} - S_{nn}E) c_n = 0$$

Thus, this is a set of  $n$  linear equations in  $n$  unknowns. In linear algebra, this is termed “homogeneous” system of linear equations and can be written in matrix form as

$$(\mathbf{H} - \mathbf{S}E)\mathbf{c} = 0$$

where  $\mathbf{c}$  is a column vector of the coefficients.

A homogeneous system of linear equations

$$\mathbf{A}\mathbf{c} = 0$$

will only have non-trivial solutions for  $\mathbf{c}$  if the determinant of  $\mathbf{A}$  is zero, i.e.  $|\mathbf{A}| = 0$

In our case, this means that

$$|\mathbf{H} - \mathbf{S}E| = 0$$

The term on the left is called the secular determinant. Writing it in full:

$$\begin{vmatrix} H_{11} - S_{11}E & H_{12} - S_{12}E & \cdots & H_{1n} - S_{1n}E \\ H_{21} - S_{21}E & H_{22} - S_{22}E & \cdots & H_{2n} - S_{2n}E \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - S_{n1}E & H_{n2} - S_{n2}E & \cdots & H_{nn} - S_{nn}E \end{vmatrix} = 0$$

Expanding this determinant gives a  $n$ th order polynomial in  $E$ , with  $n$  roots. The minimum value of these roots is the variational solution. Substituting the minimum energy back into the matrix equation will allow us to solve for the coefficients,  $c_i$ .

# Chapter 2

## Simple Molecules: $\text{H}_2^+$ and $\text{H}_2$

### 2.1 The Born-Oppenheimer Approximation

When attempting to solve the SE for molecules, we regard the nuclei as fixed in position – called the Born-Oppenheimer approximation. It is based on the fact that electrons are much lighter than nuclei, so they can respond almost instantly to changes in nuclear position. This is a good approximation for H and excellent for heavier elements.

The Hamiltonian is

$$\hat{H} = \hat{T}_e + \hat{T}_{\text{nuc}} + \hat{V}_{ee} + \hat{V}_{e-\text{nuc}} + \hat{V}_{\text{nuc}-\text{nuc}}$$

but  $\hat{T}_{\text{nuc}} = 0$  for fixed nuclei and  $\hat{V}_{\text{nuc}-\text{nuc}}$  is a constant, so we need consider only electronic terms and view the electrons as moving in a constant effective potential from the fixed nuclei.

### 2.2 MOs for $\text{H}_2^+$



The MOs are linear combinations of the 1s AOs on each nucleus

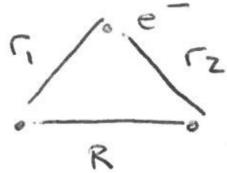
$$\phi = c_1\chi_1 + c_2\chi_2$$

Because this is a homonuclear bond, the system is symmetric and  $H_{11} = H_{22}$ . Also, the 1s orbitals are normalized, so  $S_{11} = S_{22} = 1$ . Then, the secular determinant is

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{11} - E \end{vmatrix} = 0$$

$$\begin{aligned}
 (H_{11} - E)^2 &= (H_{12} - ES)^2 \\
 E - H_{11} &= \pm(H_{12} - ES) \\
 E(1 \pm S) &= H_{11} \pm H_{12} \\
 E &= \frac{H_{11} \pm H_{12}}{1 \pm S} \quad (*)
 \end{aligned}$$

To evaluate the terms in (\*), consider the Hamiltonian for  $H_2^+$



$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}$$

$$\begin{aligned}
 H_{11} &= \left\langle \chi_1 \left| -\frac{1}{2}\nabla^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R} \right| \chi_1 \right\rangle \\
 &= \left\langle \chi_1 \left| -\frac{1}{2}\nabla^2 - \frac{1}{r_1} \right| \chi_1 \right\rangle + \left\langle \chi_1 \left| -\frac{1}{r_2} + \frac{1}{R} \right| \chi_1 \right\rangle \\
 &= -\frac{1}{2} + J
 \end{aligned}$$

$J = \langle \chi_1 | -\frac{1}{r_2} | \chi_1 \rangle + \frac{1}{R}$  is the Coulomb integral and corresponds to the Coulomb interaction between an electron in a  $1s$  orbital on nucleus 1 with nucleus 2 and the nuclear-nuclear Coulomb interaction.

Similarly,

$$\begin{aligned}
 H_{12} &= \left\langle \chi_1 \left| -\frac{1}{2}\nabla^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R} \right| \chi_2 \right\rangle \\
 &= \left\langle \chi_1 \left| -\frac{1}{2}\nabla^2 - \frac{1}{r_1} \right| \chi_2 \right\rangle + \left\langle \chi_1 \left| -\frac{1}{r_2} + \frac{1}{R} \right| \chi_2 \right\rangle \\
 &= -\frac{1}{2} \langle \chi_1 | \chi_2 \rangle + \left\langle \chi_1 \left| -\frac{1}{r_2} \right| \chi_2 \right\rangle + \frac{1}{R} \langle \chi_1 | \chi_2 \rangle \\
 &= -\frac{1}{2}S + K
 \end{aligned}$$

$K = \langle \chi_1 | -\frac{1}{r_2} | \chi_2 \rangle + \frac{S}{R}$  is the Exchange integral. It has the same form as the Coulomb integral, except with the electron switching orbitals.

Then, (\*) simplifies to

$$\begin{aligned} E &= \frac{-\frac{1}{2} + J \pm (-\frac{1}{2}S + K)}{1 \pm S} \\ &= \frac{-\frac{1}{2}(1 \pm S) + J \pm K}{1 \pm S} \\ &= -\frac{1}{2} + \frac{J \pm K}{1 \pm S} \end{aligned}$$

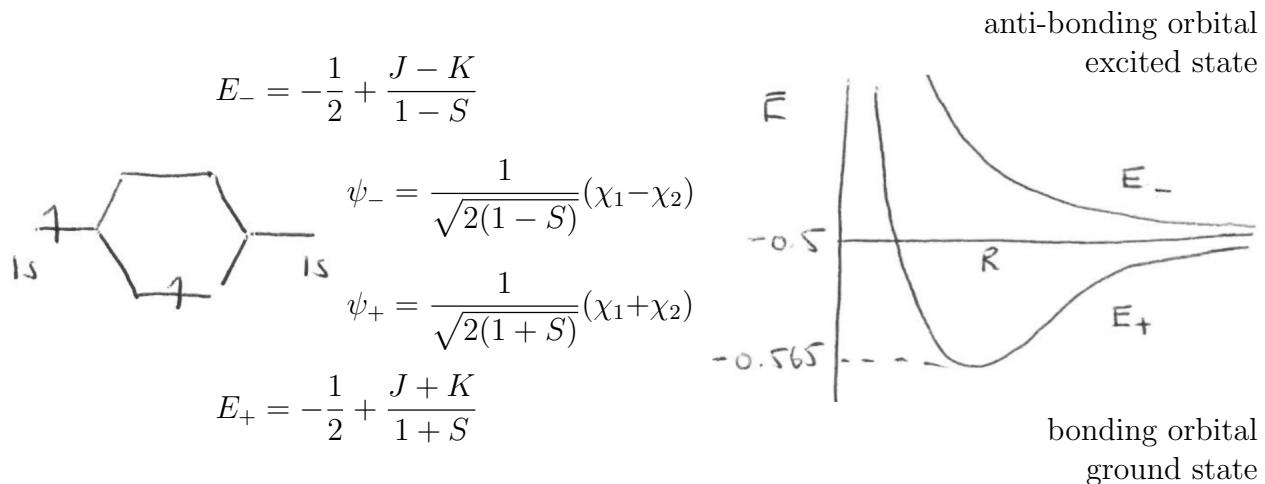
The first term is the H-atom energy and the second the bonding/anti-bonding term.

Since  $H_2^+$  is a one- $e^-$  system, the integrals  $S$ ,  $J$ , and  $K$  can be evaluated analytically and are found to be

$$\begin{aligned} S &= e^{-R} \left( 1 + R + \frac{R^2}{3} \right) \\ J &= e^{-2R} \left( 1 + \frac{1}{R} \right) \\ K &= e^{-R} \left( \frac{1}{R} - \frac{2}{3}R \right) \end{aligned}$$

Note that as  $R \rightarrow \infty$ ,  $J, K, S \rightarrow 0$  and  $E = -\frac{1}{2}$ . The dissociation limit is the energy of an infinitely-separated H atom and proton.

The orbital energies and potential energy curves are:



The exact result is a minimum ground-state energy of  $E = -0.602$  a.u. More accurate solutions can be obtained by adding more atomic orbitals (i.e.  $2p_z$ ) to the wavefunction.

## 2.3 MOs for $H_2$

As for  $H_2^+$ , the MOs are linear combination of the  $1s$  AOs.

$$\phi = c_1\chi_1 + c_2\chi_2$$

This wavefunction for  $H_2$  will yield the same secular determinant as for  $H_2^+$

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{11} - E \end{vmatrix} = 0$$

and the same expression for the orbital energies,

$$E = \frac{H_{11} \pm H_{12}}{1 \pm S}$$

However, since this is a  $2e^-$ -system, the integrals are much more difficult to evaluate. We will evaluate them later, but now, we will look at the more qualitative bonding/anti-bonding behaviour by expanding the energies in terms of the overlap,  $S$ .

Assuming that the overlap is  $S \ll 1$ , we use the Taylor expansion:

$$\frac{1}{1 \pm S} \approx 1 \mp S + S^2 + \dots$$

To second order in  $S$ ,

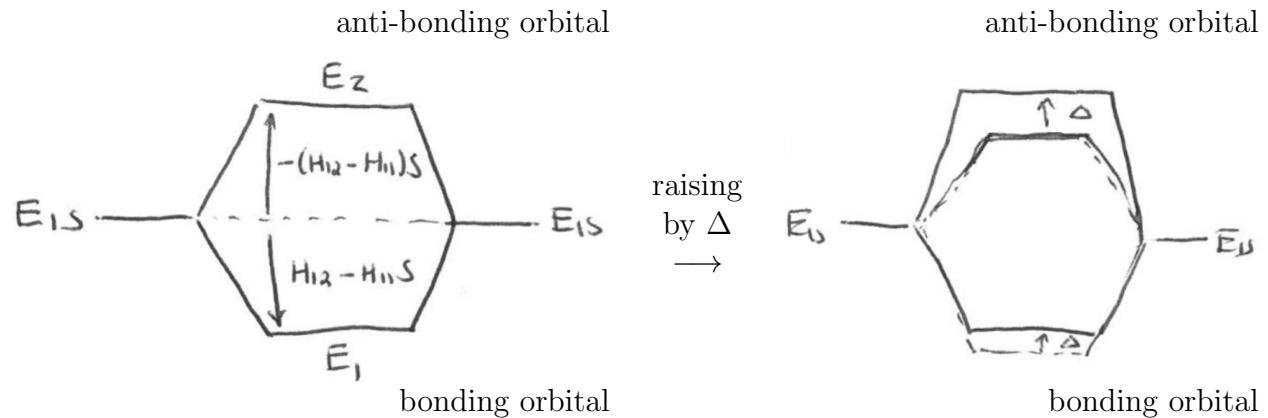
$$\begin{aligned} E_1 &= (H_{11} + H_{12})(1 - S + S^2 + \dots) \\ &= H_{11} + (H_{12} - H_{11}S) - (H_{12} - H_{11}S)S + \dots \end{aligned}$$

$$\begin{aligned} E_2 &= (H_{11} - H_{12})(1 + S + S^2 + \dots) \\ &= H_{11} - (H_{12} - H_{11}S) - (H_{12} - H_{11}S)S + \dots \end{aligned}$$

The first term,  $H_{11}$ , is negative and is the  $1s$  orbital energy for a non-interacting H atom.

$H_{12}$  is also negative, so the second term  $\pm(H_{12} - H_{11}S)$  lowers the energy of  $E_1$  and raises  $E_2$ . Both energies are raised slightly by the third term,  $\Delta = -(H_{12} - H_{11}S)S$ .

To first order:



To second order:

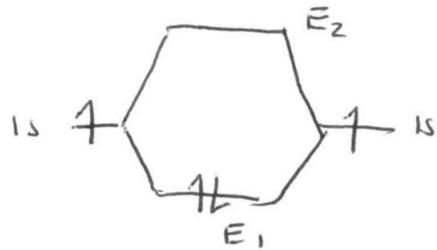
With respect to the non-interacting AO energies,  $E_2$  is raised more than  $E_1$  is lowered - this is why noble-gas dimers do not form bonds.

# Chapter 3

## Qualitative MO Theory

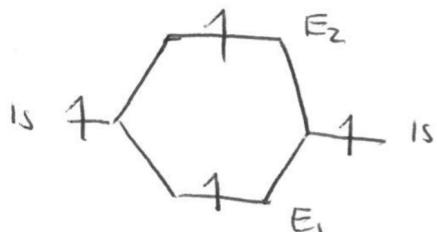
### 3.1 MO Diagrams

For H<sub>2</sub> in the ground state (singlet)



Bonding interaction, stabilizing

and in the excited state (triplet)



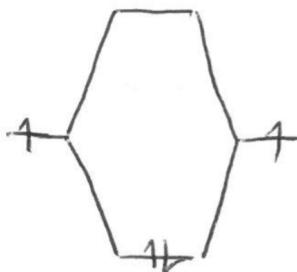
Destabilizing interaction.

The triplet state of H<sub>2</sub> is not bound (in the absence of dispersion).

Also, the amount of overlap between AOs determines the strength of the bond and the extent of stabilization/destabilization of the bonding and anti-bonding MOs.

Equilibrium bond length:

Stretched bond length:



high overlap, large stabilization

vs.

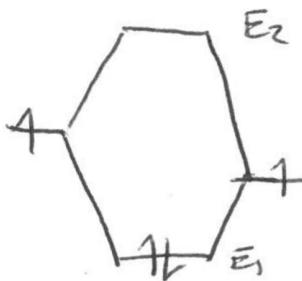


low overlap, small stabilization

For a heteronuclear diatomic, then  $H_{11} \neq H_{22}$  and the orbital energies are:

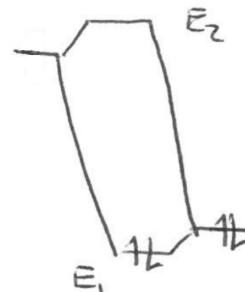
$$E_1 \approx H_{11} - \frac{(H_{12} - H_{11}S)^2}{H_{22} - H_{11}} \quad E_2 \approx H_{22} + \frac{(H_{12} - H_{11}S)^2}{H_{22} - H_{11}}$$

and the energy difference between the AOs affects the stabilization of the MOs.



small energy difference, large stabilization

vs.

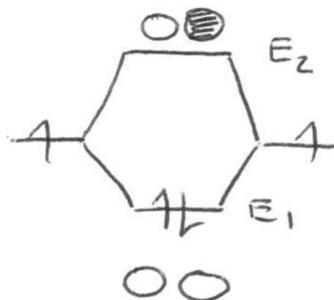


large energy difference, small stabilization

If the energy difference between the AOs is very large, then there is no stabilization and we say that the orbitals do not mix.

Thus, to form MOs, two (or more) AOs must have significant overlap and similar energies. Core overlap can be neglected and we consider overlap between valence orbitals only.

Returning to the MO coefficients, they will be equal in the homonuclear case:



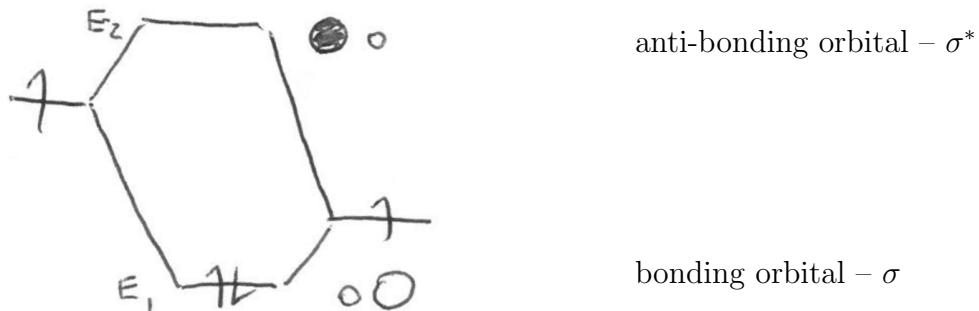
$$\phi_2 = c(\chi_1 - \chi_2)$$

negative linear combination  
anti-bonding orbital

$$\phi_1 = c(\chi_1 + \chi_2)$$

positive linear combination  
bonding orbital

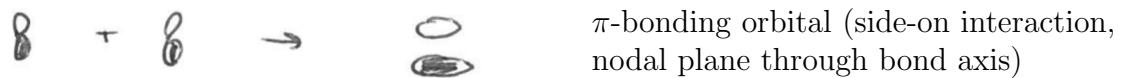
In the heteronuclear case, the bonding orbital will have a greater contribution from the lower-energy AO, while the anti-bonding will have a greater contribution from the higher-energy AO.



## 3.2 Second-Period Diatomics

Consider overlap of the  $p$  orbitals for atoms along the  $z$ -axis

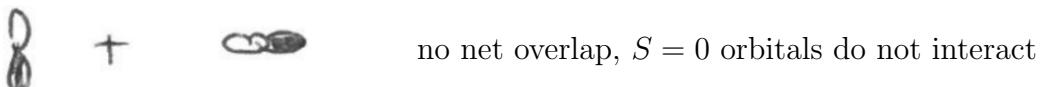
- positive overlap – resulting in a bonding orbital



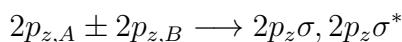
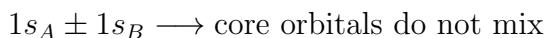
- negative overlap – resulting in an anti-bonding orbital



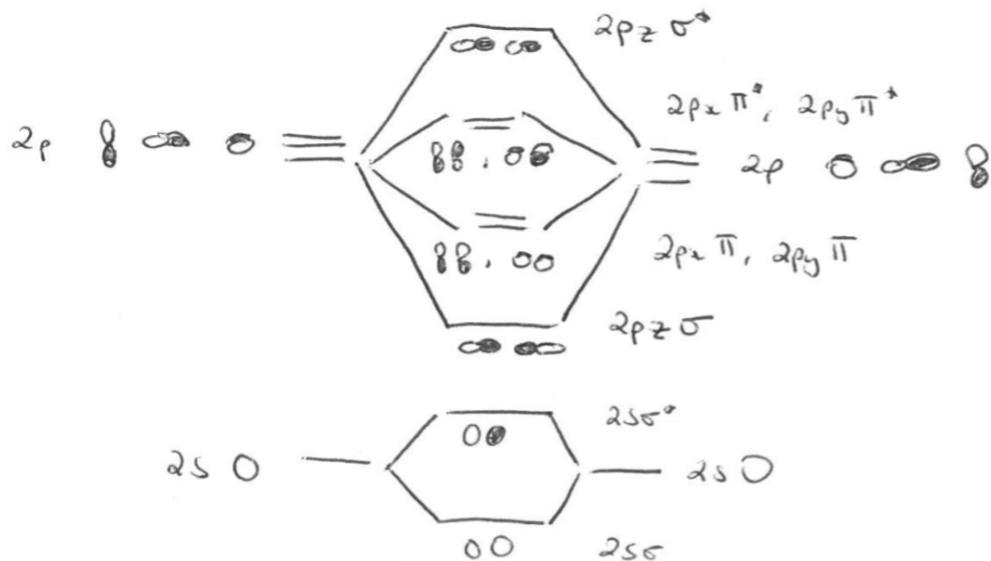
- zero overlap – resulting in non-bonding orbitals



The orbital interactions are:

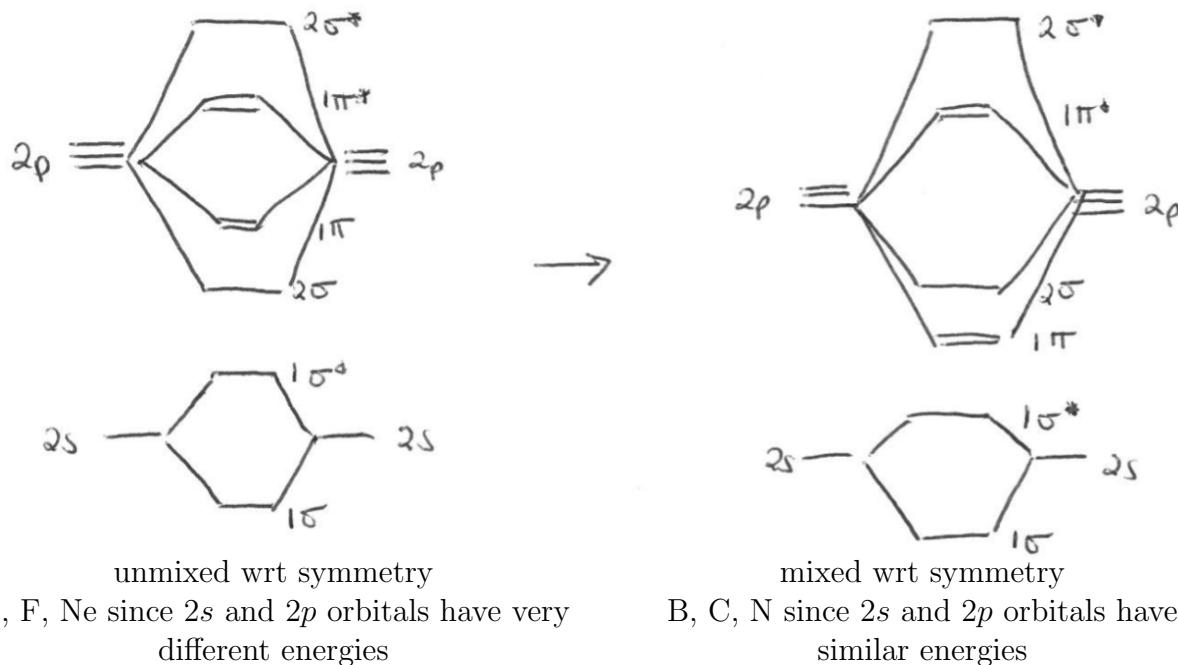


The MO diagram is:



### 3.3 Secondary Orbital Mixing

If orbitals have the same symmetry and similar energies, they can mix to provide greater stabilization. For example, the  $2s\sigma$  and  $2p_z\sigma$  can mix, causing the lower-energy  $\sigma$  orbital to become more stable and the higher-energy  $\sigma$  orbital to become less stable. The  $2s\sigma^*$  and  $2p_z\sigma^*$  can also mix.



To obtain the electronic configuration, follow Hund's rule of unpairing for degenerate orbitals.

The bond order is:

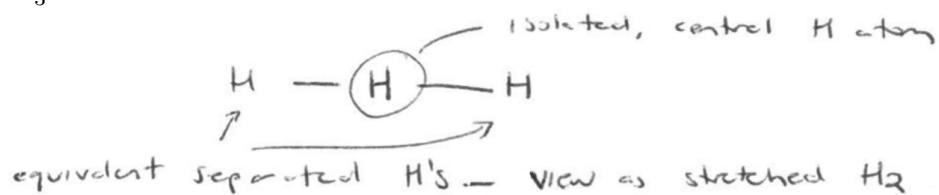
$$BO = \frac{1}{2} \left[ \left( \begin{array}{c} \#e^-'s \text{ in bonding} \\ \text{orbitals} \end{array} \right) - \left( \begin{array}{c} \#e^-'s \text{ in antibonding} \\ \text{orbitals} \end{array} \right) \right]$$

The HOMO is the highest occupied MO and the LUMO is the lowest unoccupied MO. Molecules with all paired electrons are diamagnetic, while molecules with unpaired electrons are paramagnetic.

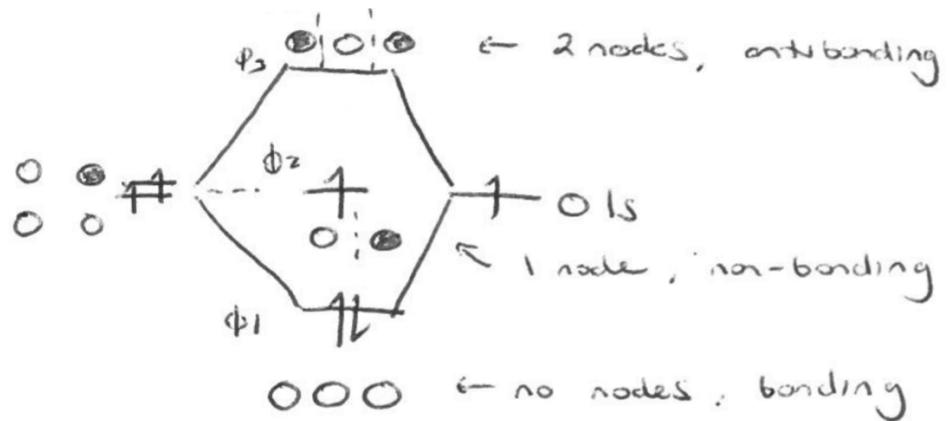
### 3.4 MO Diagrams for Linear Polyatomic Molecules

MOs for a larger molecules can be constructed by from the overlap of orbitals on smaller fragments. We make use of symmetry and consider overlap of a central atom or fragment with a collection of equivalent terminal atoms.

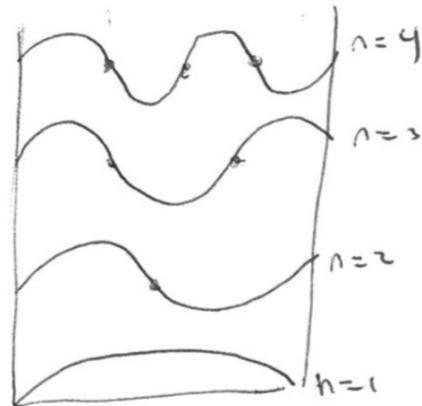
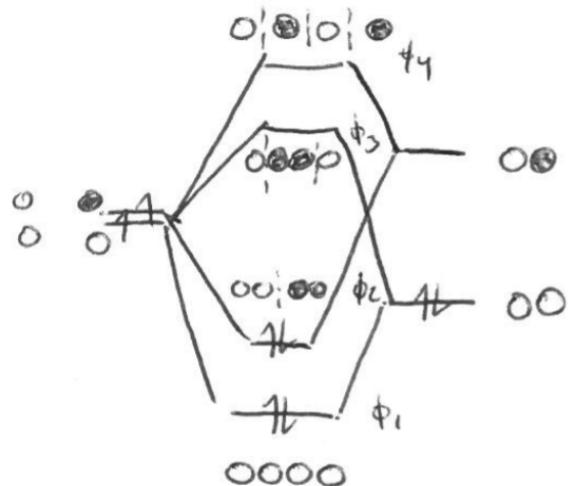
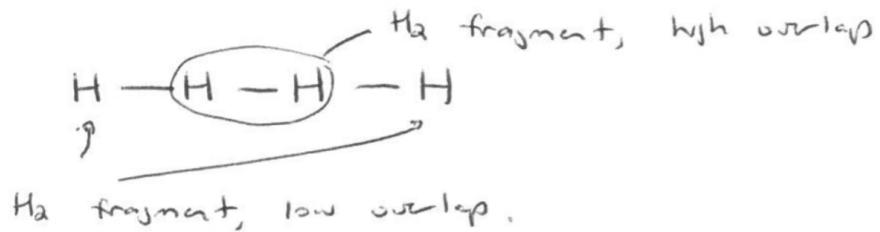
EX. Linear  $H_3$



Consider mixing of the  $\sigma$  and  $\sigma^*$  MOs of the  $H_2$  with the  $1s$  AO of the central H atom.



EX. Linear  $H_4$

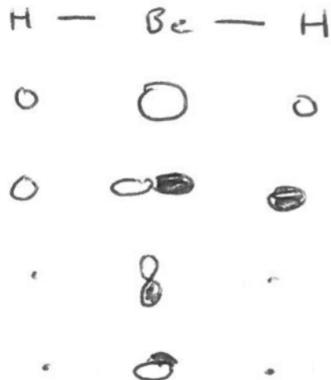


Higher-energy MOs have an increasing number of nodes perpendicular to the bond axis, resembling the particle-in-a-box wavefunctions.

### 3.5 MO Diagrams for Centro-Symmetric Molecules

Consider overlap of AOs on the central atom with those on the symmetry-equivalent terminal atoms.

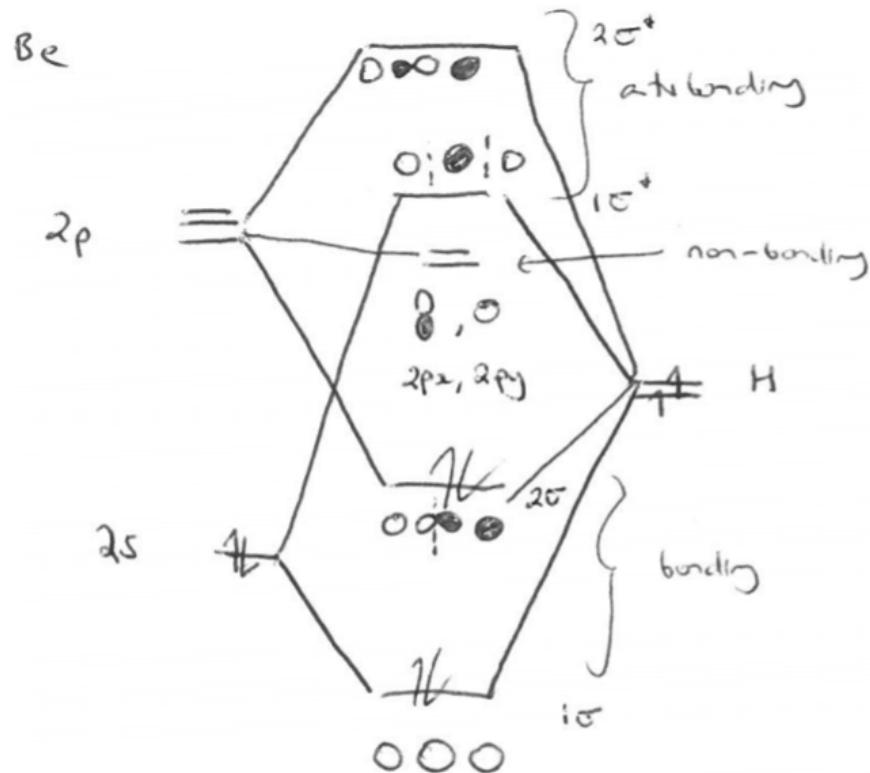
EX. BeH<sub>2</sub> (linear) – consider overlap of *s* and *p* orbitals of Be with the hydrogen 1*s* orbitals.



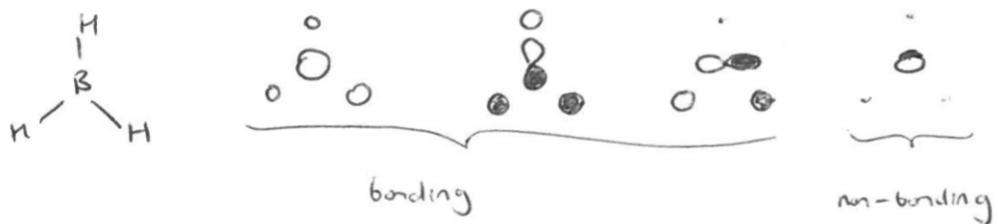
The anti-bonding MOs can be generated by changing the sign of the AO on the central atom.

Overlap between *s* orbitals will be greater than between *s* and *p* orbitals, giving greater stabilization.

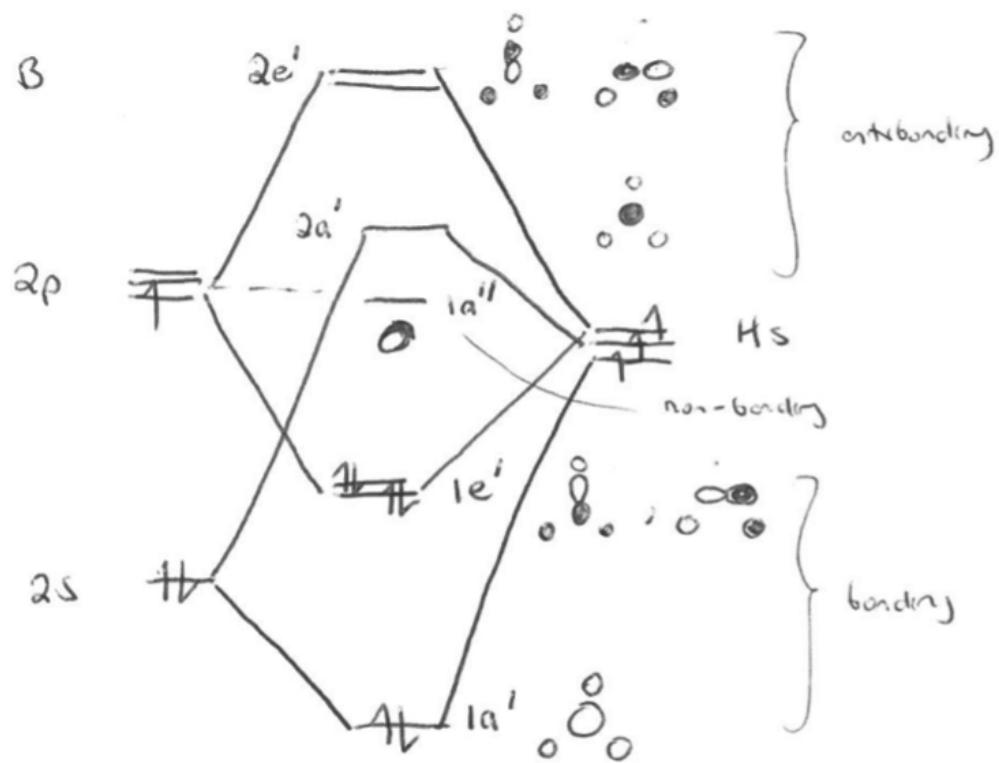
The MO diagram is:



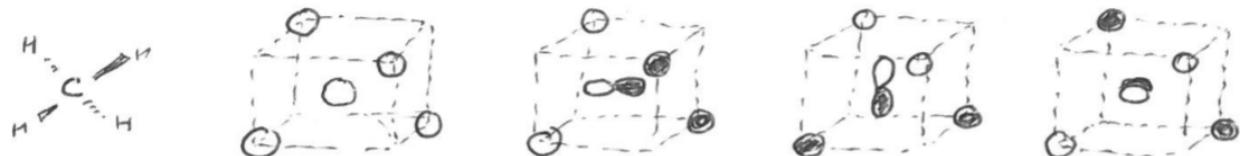
EX.  $\text{BH}_3$  (trigonal planar) – overlap of B  $s$  and  $p$  with H  $1s$  AOs.



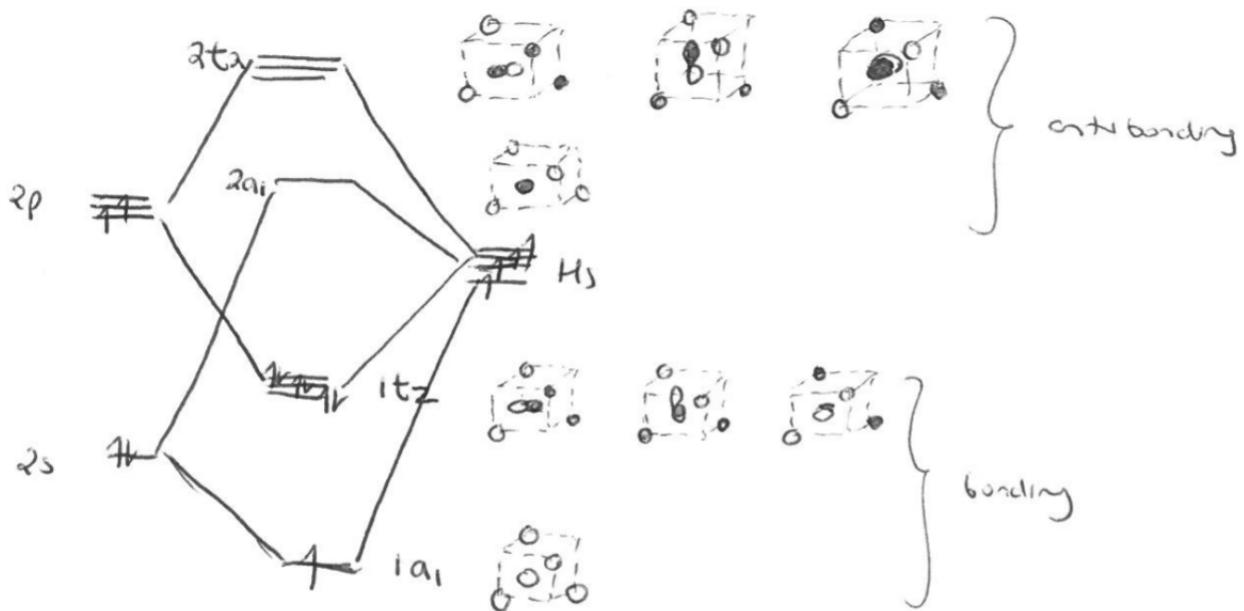
The MO diagram is:



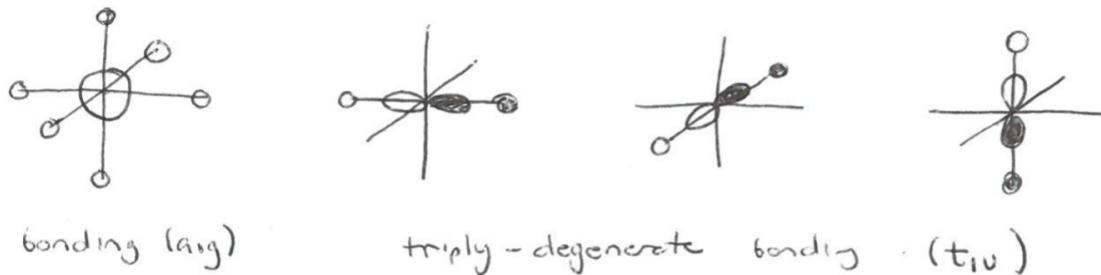
EX.  $\text{CH}_4$  (tetrahedral) – overlap of C  $s$  and  $p$  with H  $1s$  AOs.



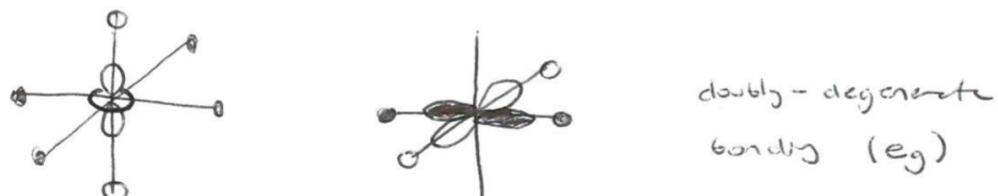
The MO diagram is:



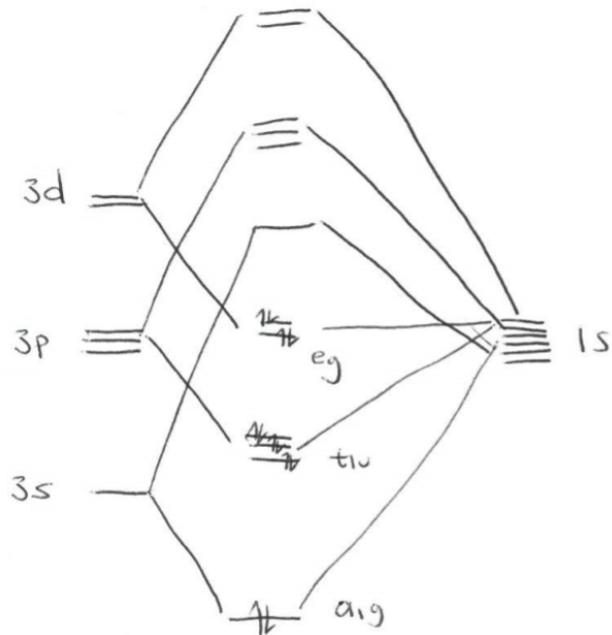
EX.  $\text{SH}_6$  (octahedral) – overlap of S  $s$ ,  $p$ , and  $d$  with H  $1s$  AOs.



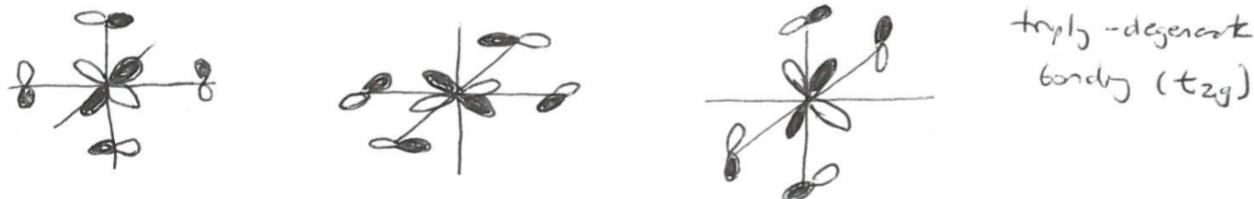
Need to involve some  $3d$  orbitals to form bonds to 6 ligands – use  $3d_{z^2}$  and  $3d_{x^2-y^2}$  since these are equivalent in  $O_h$  symmetry.



The MO diagram is:

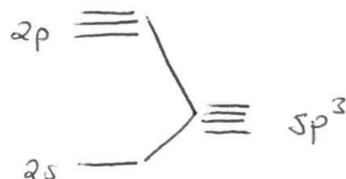


If the ligands also have *p* orbitals, then overlap with the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  AOs on the S would generate  $\pi$ -bonding MOs.



### 3.6 MOs versus Localized Hybrid Orbitals

Our MO theory diagram gives a picture of delocalized orbitals for methane, with unequal orbital energies. Alternatively, we can mix the  $2s$  and  $2p$  orbitals of the C atom to give 4 equivalent  $sp^3$  hybrid orbitals, with each forming a bond to a H  $1s$  AO.



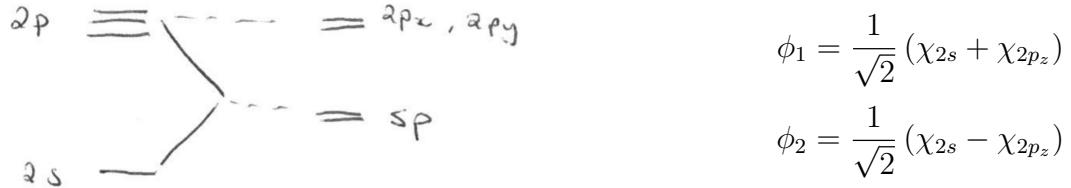
$$\phi_1 = \frac{1}{2} (\chi_{2s} + \chi_{2p_x} + \chi_{2p_y} + \chi_{2p_z})$$

$$\phi_2 = \frac{1}{2} (\chi_{2s} - \chi_{2p_x} + \chi_{2p_y} - \chi_{2p_z})$$

$$\phi_3 = \frac{1}{2} (\chi_{2s} + \chi_{2p_x} - \chi_{2p_y} - \chi_{2p_z})$$

$$\phi_4 = \frac{1}{2} (\chi_{2s} - \chi_{2p_x} - \chi_{2p_y} + \chi_{2p_z})$$

Similarly, for the BeH<sub>2</sub> example, we could mix the Be 2s and 2p<sub>z</sub> AOs to give 2 equivalent sp hybrid orbitals, with each forming a bond to a H 1s AO.



How can the delocalized and hybrid MO pictures be reconciled? They are related by a linear transformation, such that the total energy is unchanged.

Consider a linear transformation of the occupied MOs that satisfy the SE

$$\hat{H}\phi_i = E_i\phi_i$$

to another set of MOs

$$\phi'_i = \sum_k a_{ik} \phi_k$$

We require the new set of MOs to be orthogonal

$$\begin{aligned} \int \phi'_i \phi'_j d\tau &= \delta_{ij} \\ \int \left( \sum_m a_{im} \phi_m \right) \left( \sum_n a_{jn} \phi_n \right) d\tau &= \delta_{ij} \\ \sum_m \sum_n a_{im} a_{jn} \int \phi_m \phi_n d\tau &= \delta_{ij} \\ \sum_m \sum_n a_{im} a_{jn} \delta_{mn} &= \delta_{ij} \\ \sum_n a_{in} a_{jn} &= \delta_{ij} \end{aligned}$$

In matrix multiplication, the product  $\mathbf{A}\mathbf{A}$  is

$$AA_{ij} = \sum_n a_{in} a_{nj}$$

Thus, our result

$$\sum_n a_{in} a_{nj}^T = \delta_{ij}$$

can be written in matrix form as

$$\mathbf{A}\mathbf{A}^T = \mathbf{I}$$

where  $\mathbf{A}^T$  is the transpose of matrix  $\mathbf{A}$  and  $\mathbf{I}$  is the identity matrix. If the orbitals are also normalized, this is the definition of a unitary transformation.

The total electron density is not affected by this transformation

$$\begin{aligned}\rho' &= \sum_i (\phi'_i)^2 \\ &= \sum_i \left( \sum_m a_{im} \phi_m \right) \left( \sum_n a_{in} \phi_n \right) \\ &= \sum_m \sum_n \phi_m \phi_n \sum_i a_{im} a_{in} \\ &= \sum_m \sum_n \phi_m \phi_n \delta_{mn} \\ &= \sum_n \phi_n^2 \\ &= \rho\end{aligned}$$

It can be shown that the total energy is unchanged as well. Thus, any set of orthogonal MOs is equally valid for describing the total electron density and energy of a molecule. We say these properties are invariant wrt unitary orbital transformations. However, the individual orbital energies will differ.

Linear combinations of AOs yield delocalized MOs while linear combinations of hybrid AOs yield maximally localized MOs (LMOs). LMOs cannot be used to describe electronic spectroscopy because they are not eigenstates of  $\hat{H}$

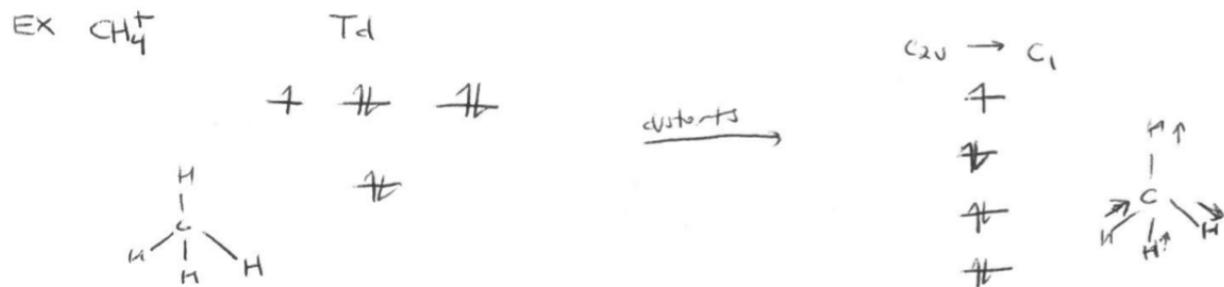
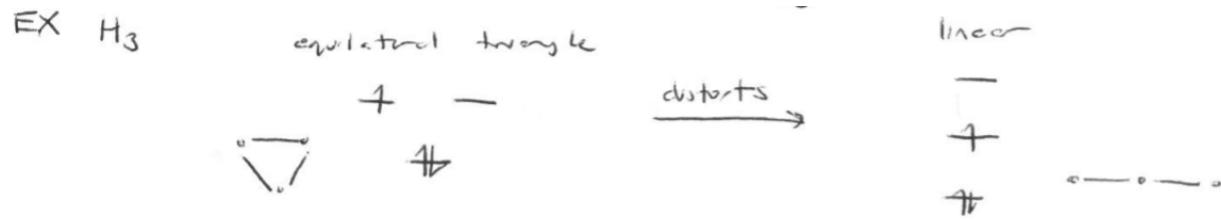
$$\hat{H}\phi'_i \neq E_i \phi'_i$$

Only the delocalized MOs are eigenstates of  $\hat{H}$  and have well-defined orbital energies. MOs must be used to describe electronic spectroscopy, although LMOs can be useful to interpret bonding (and in designing more efficient computational algorithms).

## 3.7 Jahn-Teller Distortions

The total electron density of a filled (or half-filled) set of degenerate orbitals has the same symmetry as the nuclear framework. For example, the filled  $p$ -shell for a noble-gas atom has spherical symmetry and the filled  $t_2$  MOs in methane gives the density tetrahedral symmetry

However, if a degenerate set of orbitals is not half-filled or filled, the molecule will distort to lower the energy.



# Chapter 4

## Quantitative MO Theories

### 4.1 Hückel Theory

This applies to conjugated polyenes and arenes. Treat the  $\pi$ -electrons as moving in a fixed effective potential from the  $\sigma$ -bonding framework.  $\pi$ -orbitals are delocalized over each of the carbon atoms.

Make the following assumptions when constructing the secular determinant:

- all overlap integrals are  $S_{ij} = \delta_{ij}$
- all diagonal Hamiltonian matrix elements are  $H_{ii} = \alpha$  (Coulomb integral)
- all off-diagonal Hamiltonian matrix elements are set equal to zero, except those between neighbouring atoms, which are assigned the same value  $\beta$  (resonance integral)

$\alpha$  and  $\beta$  are both negative.  $\beta$  is assigned the empirical value of -0.75 eV = -17 kcal/mol.

EX. Ethylene. Each C atom contributes a  $2p_z$  orbital to the  $\pi$  system.

$$\phi_\pi = c_1\chi_1 + c_2\chi_2$$

where  $\chi_1$  and  $\chi_2$  are the  $2p_z$  orbitals of each carbon.

The secular determinant is:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

#### 4.1. Hückel Theory

37

In the Hückel approximation, this becomes

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

$$(\alpha - E)^2 - \beta^2 = 0$$

$$\alpha - E = \pm \beta$$

$$E = \alpha \pm \beta$$

and the roots are  $E = \alpha \pm \beta$ .

To find the coefficients, solve the system of linear equations

$$(\alpha - E)c_1 + \beta c_2 = 0$$

$$\beta c_1 + (\alpha - E)c_2 = 0$$

and normalization requires that  $c_1^2 + c_2^2 = 1$ .

For  $E = \alpha - \beta$ ,

$$\beta c_1 + \beta c_2 = 0$$

$$c_1 = -c_2$$

and applying the normalization constraint,  $c_1 = \frac{1}{\sqrt{2}}$ ,  $c_2 = -\frac{1}{\sqrt{2}}$

For  $E = \alpha + \beta$ ,

$$-\beta c_1 + \beta c_2 = 0$$

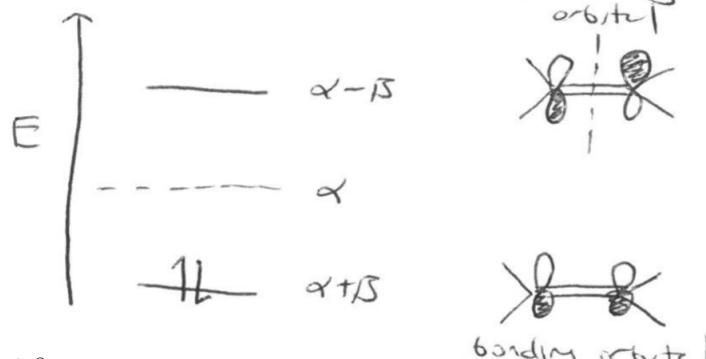
$$c_1 = c_2$$

and applying the normalization constraint,  $c_1 = \frac{1}{\sqrt{2}}$ ,  $c_2 = \frac{1}{\sqrt{2}}$

The energy-level diagram is

$$\phi_2 = \frac{1}{\sqrt{2}} (\chi_1 - \chi_2)$$

$$\phi_1 = \frac{1}{\sqrt{2}} (\chi_1 + \chi_2)$$



The  $\pi$ -electronic energy is  $E_\pi = 2\alpha + 2\beta$

EX. Butadiene. The MOs are linear combinations of four  $2p_z$  orbitals.

$$\phi_n = \sum_{i=1}^4 c_{in} \chi_i$$

The secular determinant within the Hückel approximation is

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

Factor  $\beta$  from each column and let  $x = \frac{\alpha-E}{\beta}$ , then

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

The secular equation is

$$x^4 - 3x^2 + 1 = 0$$

$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

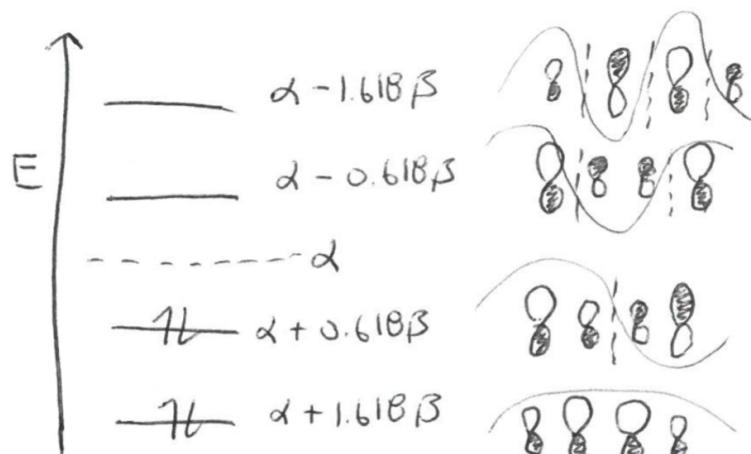
$$x = \pm \left( \frac{3 \pm \sqrt{5}}{2} \right)^{1/2}$$

$$E = \alpha \pm \left( \frac{3 \pm \sqrt{5}}{2} \right)^{1/2} \beta$$

The energy-level diagram is:

$$\begin{aligned} \phi_4 &= a\chi_1 - b\chi_2 + b\chi_3 - a\chi_4 \\ \phi_3 &= b\chi_1 - a\chi_2 - a\chi_3 + b\chi_4 \\ \phi_2 &= b\chi_1 + a\chi_2 - a\chi_3 - b\chi_4 \\ \phi_1 &= a\chi_1 + b\chi_2 + b\chi_3 + a\chi_4 \end{aligned}$$

$$a = 0.372, \quad b = 0.602$$



The total  $\pi$ -electronic energy is  $4\alpha + 2\sqrt{5}\beta$ . This is lower than the sum of two unconjugated  $\pi$ -bonds. The delocalization energy is:

$$\begin{aligned} E_\pi(\text{butadiene}) - 2E_\pi(\text{ethylene}) &= (4\alpha + 2\sqrt{5}\beta) - 2(2\alpha + 2\beta) \\ &= (2\sqrt{5} - 4)\beta \\ &= 0.472\beta \\ &= -8.2 \text{ kcal/mol} \end{aligned}$$

This is the additional stabilization due to  $\pi$ -conjugation in butadiene.

EX. Benzene. The MOs are linear combinations of six  $2p_z$  orbitals.

$$\phi_n = \sum_{i=1}^6 c_{in} \chi_i$$

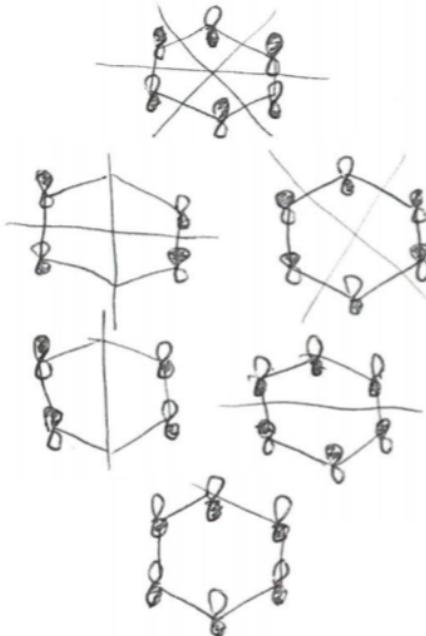
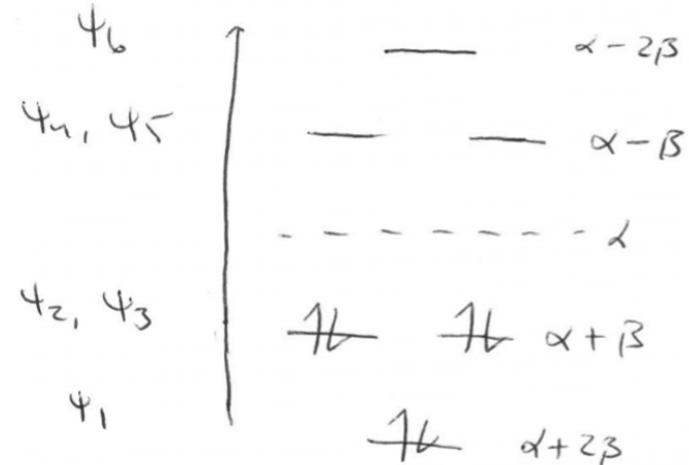
The secular determinant is

$$\left| \begin{array}{cccccc} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{array} \right| = 0$$

The six roots are

$$\begin{aligned} \phi_1 &= \frac{1}{\sqrt{6}} (\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6) \\ E_1 &= \alpha + 2\beta & \phi_2 &= \frac{1}{2} (\chi_2 + \chi_3 - \chi_5 - \chi_6) \\ E_2 &= E_3 = \alpha + \beta & \phi_3 &= \frac{1}{\sqrt{3}} \left( \chi_1 + \frac{\chi_2}{2} - \frac{\chi_3}{2} - \chi_4 - \frac{\chi_5}{2} + \frac{\chi_6}{2} \right) \\ E_4 &= E_5 = \alpha - \beta & \phi_4 &= \frac{1}{2} (\chi_2 - \chi_3 + \chi_5 - \chi_6) \\ E_6 &= \alpha - 2\beta & \phi_5 &= \frac{1}{\sqrt{3}} \left( \chi_1 - \frac{\chi_2}{2} - \frac{\chi_3}{2} + \chi_4 - \frac{\chi_5}{2} - \frac{\chi_6}{2} \right) \\ & & \phi_6 &= \frac{1}{\sqrt{6}} (\chi_1 - \chi_2 + \chi_3 - \chi_4 + \chi_5 - \chi_6) \end{aligned}$$

The energy-level diagram is:



The total  $\pi$ -electronic energy is

$$\begin{aligned} E_{\pi} &= 2(\alpha + 2\beta) + 4(\alpha + \beta) \\ &= 6\alpha + 8\beta \end{aligned}$$

The delocalization energy is

$$\begin{aligned} E_{\pi}(\text{benzene}) - 3E_{\pi}(\text{ethylene}) &= (6\alpha + 8\beta) - 3(2\alpha + 2\beta) \\ &= 2\beta \\ &= -34.6 \text{ kcal/mol} \end{aligned}$$

The stabilization due to  $\pi$ -conjugation in benzene is much greater than in butadiene, explained by the concept of aromaticity.

Hückel theory also allows a definition of bond order, between pairs of atoms  $j, k$

$$P_{jk} = \sum_i n_i c_{ji} c_{ki}$$

where the summation runs over each MO and  $n_i$  is the occupation number.

EX. Ethylene

$$\phi_1 = \frac{1}{\sqrt{2}}\chi_1 + \frac{1}{\sqrt{2}}\chi_2, \quad n_1 = 2$$

$$P_{12} = 2 \left( \frac{1}{\sqrt{2}} \right) \left( \frac{1}{\sqrt{2}} \right) = 1$$

which indicates a single  $\pi$ -bond. The total  $\sigma + \pi$  bond order for the C-C bond is 2.

EX. Benzene

$$P_{12} = 2 \left( \frac{1}{\sqrt{6}} \right) \left( \frac{1}{\sqrt{6}} \right) + 2(0) \left( \frac{1}{2} \right) + 2 \left( \frac{1}{\sqrt{3}} \right) \left( \frac{1}{2\sqrt{3}} \right) = \frac{1}{3} + \frac{1}{3} = \frac{2}{3}$$

$$P_{23} = 2 \left( \frac{1}{\sqrt{6}} \right) \left( \frac{1}{\sqrt{6}} \right) + 2 \left( \frac{1}{2} \right) \left( \frac{1}{2} \right) - 2 \left( \frac{1}{2\sqrt{3}} \right) \left( \frac{1}{2\sqrt{3}} \right) = \frac{1}{3} + \frac{1}{2} - \frac{1}{6} = \frac{2}{3}$$

Similarly,

$$P_{34} = P_{45} = P_{56} = P_{61} = \frac{2}{3}$$

The total  $\sigma + \pi$  bond order is  $1\frac{2}{3}$  and all bonds are equivalent.

Hückel theory can also be used to explain reactivity. Focus on the HOMO and LUMO of the reacting molecules – the “frontier” orbitals.



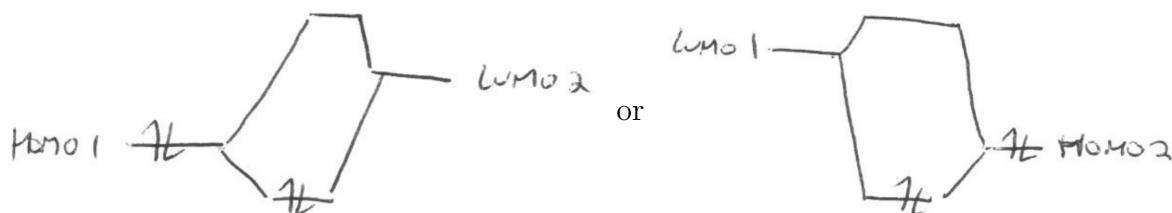
If the orbital symmetries are such that

- HOMO<sub>1</sub> overlaps HOMO<sub>2</sub>, then the reaction is symmetry forbidden and has a high barrier

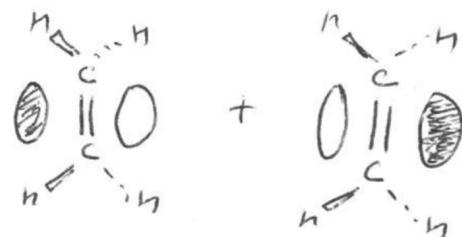


2-orbital, 4-e<sup>-</sup> interactions are destabilizing

- HOMO<sub>1</sub> overlaps LUMO<sub>2</sub> (or vice versa), then the reaction is symmetry allowed and has a low barrier.

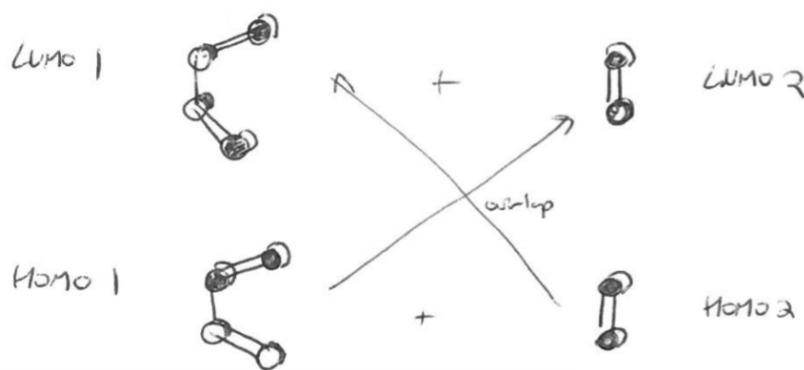


EX. Ethylene dimerization to cyclobutane



The HOMOs overlap, so the reaction cannot occur (although it can if one molecule is excited).

EX. Diels-Alder reaction



The HOMOs overlap with the LUMOs, so the reaction is symmetry allowed.

This approach forms the basis of the Woodward-Hoffmann rules.

## 4.2 Extended Hückel Theory

This method treats all valence  $e^-$ s for all atom types. One hydrogen-like AO or Slater-type orbital (STO) is assigned for each valence AO. Core AOs are neglected.

STOs have the form

$$\chi = N r^{n-1} e^{-\zeta r} Y_{\ell m}(\theta, \phi)$$

where the orbital exponent  $\zeta$  (zeta) is determined by Slater's rules for the effective nuclear charge.

When constructing the secular determinant, all overlap integrals,  $S_{ij}$ , are computed from integrating the STOs, but approximations are made for the Hamiltonian matrix elements.

The diagonal matrix elements,  $H_{ii}$ , are approximated as the negative of the corresponding free-atomic ionization potential, which should equal the AO energy in the free atom.

The off-diagonal matrix elements are approximated as

$$H_{ij} = \frac{1}{2} K (H_{ii} + H_{jj}) S_{ij}$$

called the Wolfsberg-Helmholz-Hoffmann formula.  $K$  is a constant with empirically determined value of  $K = 1.75$ . This formula ensures that  $H_{ij} \rightarrow 0$  as  $S_{ij} \rightarrow 0$  and the atoms are non-interacting.

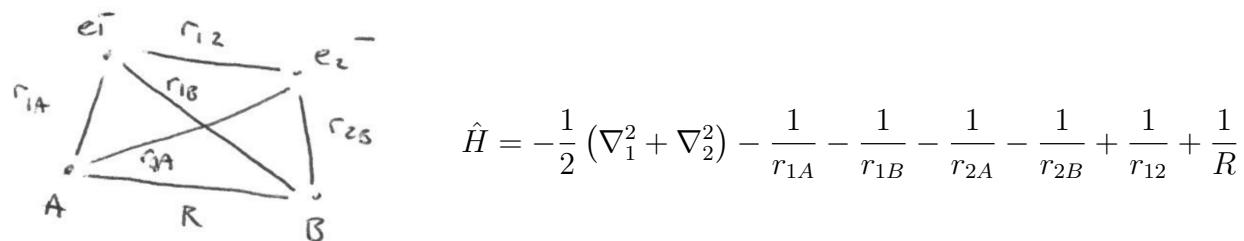
The MO energies are then evaluated computationally from the secular determinant.

Extended Hückel theory provides qualitatively correct results, but not quantitative chemical accuracy. It is commonly used as a “guess” for more expensive computational methods.

### 4.3 MO Theory for $H_2$ Revisited

To obtain quantitative chemical accuracy with MO theory, the solutions become complicated for many- $e^-$  systems.

Consider  $H_2$  as a relatively simple example

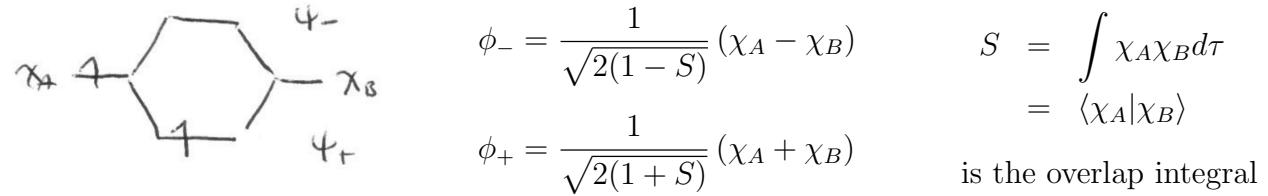


The  $\frac{1}{r_{12}}$  term is not separable into a product of terms depending only on  $e_1^-$  and  $e_2^-$ , so the problem cannot be solved analytically. We instead need to construct an approximate form for the wavefunction.

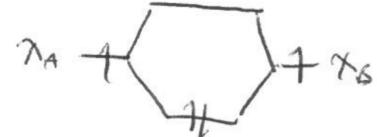
The MOs are linear combinations of the 1s AOs on each nucleus

$$\phi = c_A \chi_A + c_B \chi_B$$

Recall that, for  $\text{H}_2^+$ , the bonding and anti-bonding orbitals were



For  $\text{H}_2$ , both electrons will be paired in the bonding orbital



Recall also that, for a many- $e^-$  system, the wavefunction must be antisymmetric – use a Slater determinant (similar to He).

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_+(1)\alpha(1) & \phi_+(1)\beta(1) \\ \phi_+(2)\alpha(2) & \phi_+(2)\beta(2) \end{vmatrix}$$

This can be separated into a product of spatial and spin terms

$$\psi = \phi_+(1)\phi_+(2) \cdot \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

The energy depends only on the spatial part.

$$\begin{aligned} \psi &= \frac{1}{2(1+S)} [\chi_A(1) + \chi_B(1)][\chi_A(2) + \chi_B(2)] \\ &= \frac{1}{2(1+S)} [\chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2) + \chi_A(1)\chi_A(2) + \chi_B(1)\chi_B(2)] \end{aligned}$$

covalent terms –	ionic terms –
configurations with electrons	configurations with both
on different atoms	electrons on the same atom

The energy can be evaluated from

$$E = \langle \psi | \hat{H} | \psi \rangle = \int \int \psi \hat{H} \psi d\mathbf{r}_1 d\mathbf{r}_2$$

It can be shown that this wavefunction gives the energy

$$E = -1 + \frac{1}{R} - \frac{2j' + 2k'}{1+S} + \frac{j + 2k + 4\ell + m}{2(1+S)^2}$$

The electron-nuclear terms are:

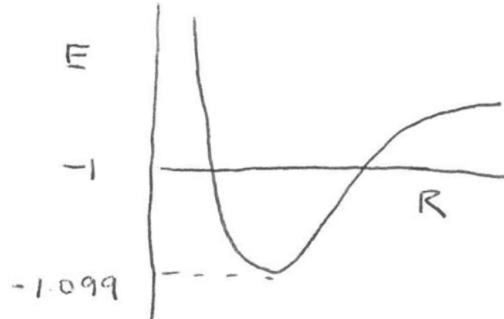
$$\begin{aligned} j' &= \int \frac{1}{r_B} \chi_A^2 d\mathbf{r} = \int \frac{1}{r_A} \chi_B^2 d\mathbf{r} \\ k' &= \int \frac{1}{r_A} \chi_A \chi_B d\mathbf{r} = \int \frac{1}{r_B} \chi_A \chi_B d\mathbf{r} \end{aligned}$$

and are analogous to the Coulomb and exchange integrals in  $H_2^+$ .

The electron-electron terms are:

$$\begin{aligned} j &= \int \int \frac{1}{r_{12}} \chi_A^2(1) \chi_B^2(2) d\mathbf{r}_1 d\mathbf{r}_2 = (AB|AB) \\ k &= \int \int \frac{1}{r_{12}} \chi_A(1) \chi_A(2) \chi_B(1) \chi_B(2) d\mathbf{r}_1 d\mathbf{r}_2 = (AA|BB) \\ \ell &= \int \int \frac{1}{r_{12}} \chi_A^2(1) \chi_A(2) \chi_B(2) d\mathbf{r}_1 d\mathbf{r}_2 = (AA|AB) \\ m &= \int \int \frac{1}{r_{12}} \chi_A^2(1) \chi_A^2(2) d\mathbf{r}_1 d\mathbf{r}_2 = (AA|AA) \end{aligned}$$

This gives the following potential energy curve:



The energy is higher than the exact energy at the minimum, which is  $-1.174$  a.u.  
(error of  $\sim 2$  eV)

There are two reasons for this:

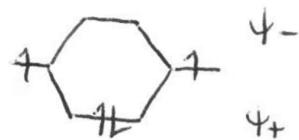
- the basis set is incomplete (only  $1s$  orbital)
- the form of the wavefunction is not sufficiently flexible – it is only a single Slater determinant – ionic and covalent terms have equal weighting

This also causes the dissociation limit to be higher in energy than the exact limit of  $-1$  a.u. (energy of two separated H atoms).

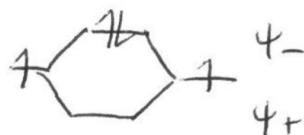
In the dissociation limit, the wavefunction should consist only of the covalent terms. This can be corrected by including more Slater determinants (or electronic configurations) in the wavefunction.

## 4.4 Configuration Interaction for H<sub>2</sub>

CI is an extension of MO theory to include excited-state electronic configurations in the wavefunction. For H<sub>2</sub>



ground electronic state, paired electrons in  $\phi_+$  (bonding MO)



excited electronic state, paired electrons in  $\phi_-$  (anti-bonding MO)

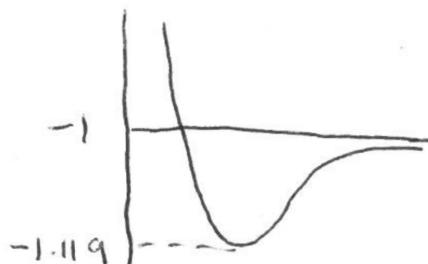
Write the wavefunction as a sum of Slater determinants with variable coefficients (the CI coefficients) to be optimized.

$$\begin{aligned}\psi &= \frac{c_1}{\sqrt{2}} \begin{vmatrix} \phi_+(1)\alpha(1) & \phi_+(1)\beta(1) \\ \phi_+(2)\alpha(2) & \phi_+(2)\beta(2) \end{vmatrix} + \frac{c_2}{\sqrt{2}} \begin{vmatrix} \phi_-(1)\alpha(1) & \phi_-(1)\beta(1) \\ \phi_-(2)\alpha(2) & \phi_-(2)\beta(2) \end{vmatrix} \\ &= [c_1\phi_+(1)\phi_+(2) + c_2\phi_-(1)\phi_-(2)] \cdot \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]\end{aligned}$$

Considering only the spatial part

$$\begin{aligned}\psi &= \frac{c_1}{2(1+S)} [\chi_A(1) + \chi_B(1)] [\chi_A(2) + \chi_B(2)] + \frac{c_2}{2(1-S)} [\chi_A(1) - \chi_B(1)] [\chi_A(2) - \chi_B(2)] \\ &= \frac{c_1(1-S) - c_2(1+S)}{2(1+S)(1-S)} [\chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2)] + \\ &\quad \frac{c_1(1-S) + c_2(1+S)}{2(1+S)(1-S)} [\chi_A(1)\chi_A(2) + \chi_B(1)\chi_B(2)] \\ &= c'_1 \psi_{\text{covalent}} + c'_2 \psi_{\text{ionic}}\end{aligned}$$

This gives a flexible weighting of the covalent and ionic terms (as opposed to the equal weighting with a single Slater determinant). The CI coefficients can be optimized at each value of the bond length to give the potential energy curve.



The minimum energy is -1.119 a.u., lower than before, but still above the exact result (by  $\sim 1.5$  eV) as expected from the variational principle.

The configuration mixing recovers the correct dissociation limit, where the wavefunction consists only of the covalent terms, which can be obtained from an even mixture of the two determinants.

This is actually represented as  $\uparrow \downarrow + \downarrow \uparrow$  or

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s_A(1)\alpha(1) & 1s_B(1)\beta(1) \\ 1s_A(2)\alpha(2) & 1s_B(2)\beta(2) \end{vmatrix} + \frac{c_2}{\sqrt{2}} \begin{vmatrix} 1s_A(1)\beta(1) & 1s_B(1)\alpha(1) \\ 1s_A(2)\beta(2) & 1s_B(2)\alpha(2) \end{vmatrix}$$

which will give the same electron density.

To obtain better approximations for the minimum energy, higher-lying AOs beyond  $1s$  (i.e.  $2p_z$ ) must be included. CI is exact in the limit of including all possible configurations (with a complete basis set) and models the physics of “electron correlation”.

## 4.5 Summary and Review

To model chemical bonding using molecular-orbital theory:

- Construct molecular orbital orbitals (MOs) as linear combinations of ( $s, p, d, \dots$ ) atomic orbitals (AOs) with variable coefficients

$$\phi_i = \sum_j c_{ij} \chi_j$$

- Use the variational principle to optimize the coefficients to minimize the energy. The variational principle provides an upper bound to the exact energy for suitable trial MOs/wavefunctions and minimizing the energy wrt any variable parameters will provide the best approximation to the ground-state energy.
- When the MOs are linear combinations of AOs, optimizing the coefficients involves solving the secular determinant for the MO energies.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{21} - ES_{21} & \cdots & H_{n1} - ES_{n1} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \cdots & H_{n2} - ES_{n2} \\ \vdots & \vdots & \ddots & \vdots \\ H_{1n} - ES_{1n} & H_{2n} - ES_{2n} & \cdots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$

- Sketch the MO diagram using the resulting MO energies and fill with electrons. The MO diagram will help you write the single-determinant wavefunction.

$$\psi_o = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix}$$

virtual  
 occupied  
 $\hat{H} \leftarrow \phi_1 \alpha,$   
 $\phi_1 \beta$

- More accurate wavefunctions can be constructed by adding more Slater determinants corresponding to excited electronic states. This adds in effects of electron correlation and improves the description of the dissociation limit for chemical bonds.

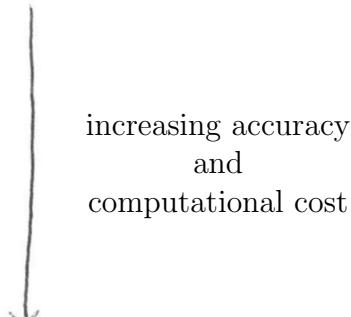
# Chapter 5

## Introduction to Quantum-Chemical Calculations

### 5.1 Overview of Electronic-Structure Methods

Since the  $\frac{1}{r_{ij}}$  term is not separable, the SE cannot be solved analytically for many- $e^-$  systems and we turn to a hierarchy of computational approximations.

- Semi-empirical
- Hartree-Fock
- Density-functional theory
- Perturbation theory
- Coupled-cluster theory
- Configuration interaction



increasing accuracy  
and  
computational cost

- Hartree-Fock (HF) is the simplest MO theory. It represents the wavefunction as a single Slater determinant and therefore treats exchange exactly. However, it neglects electron correlation – the correlation energy is defined as the difference between the exact energy and the HF energy. With HF, electronic energies are too high and molecules are severely underbound.
- Semi-empirical methods (extended Hückel, AM1) are based on HF, but some integrals are replaced by empirical parameters, fit to experiment. Typically give very poor energies, but very fast and good for geometries.
- Configuration interaction (CI) uses HF as a starting point and includes correlation

effects by adding contributions from many excited-state determinants to the wavefunction. It is exact in the limit of including all possible configurations (variational principle). Very accurate, but impractical for molecules with  $> 2 - 4$  atoms.

- Coupled-cluster theory (CCSD(T)) is based on HF and includes the majority of correlation effects by considering single, double, and (approximate) triple excitations. This “gold-standard” approach is exact for two electrons and quite accurate for larger systems, but is only practical for  $< 20$  atoms.
- Perturbation theory (MP2) treats electron correlation as a small perturbation to the HF energy. The correlation energy is evaluated from 2nd-order perturbation theory. This is the most efficient of the post-HF or “ab initio” methods, but the least accurate.
- Density-functional theory (DFT) is the most common approach used in computational chemistry since it frequently provides the best balance between computational time and accuracy. The energy is obtained as a function of the electron density,  $\rho$ , rather than the wavefunction. No exact form for  $E[\rho]$  is known, so many different forms have been proposed and there are many density-functional methods. The most popular in chemistry is B3LYP and the most popular in physics is PBE.

## 5.2 Overview of Basis Sets

The wavefunction (or electron density) is constructed from atomic orbitals that are approximated by linear combinations of Gaussian functions.

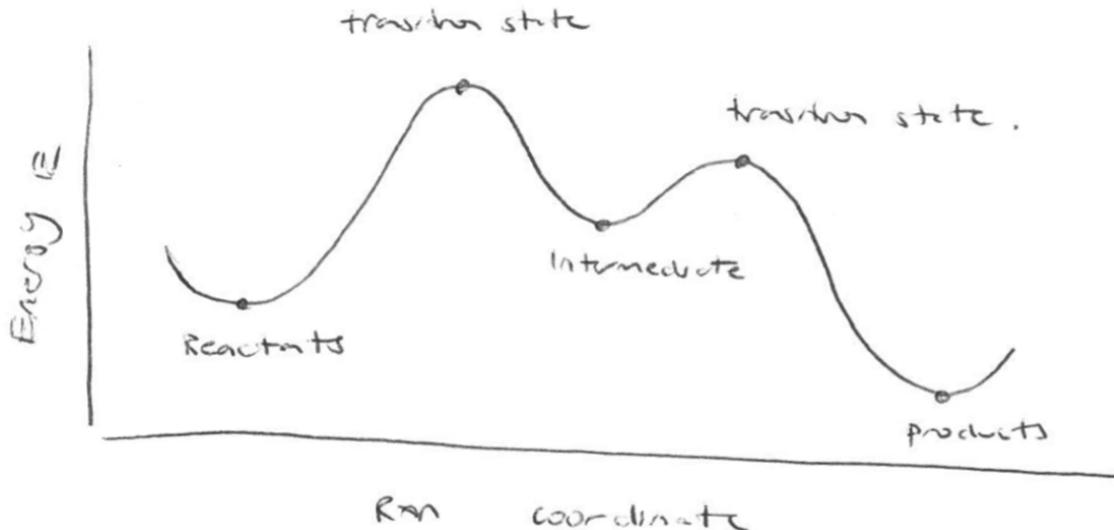


The more functions included in the basis set, the better the description of the orbitals and the lower the energy (variational principle).

Pople-style	Dunning-style	Ahlrichs-style	
• 6-31G*	• cc-pVDZ	• def2-SVP	
• 6-31+G**	• aug-cc-pVTZ	• def2-TZVPD	
• 6-311+G(2d,2p)	• aug-cc-pVQZ	• def2-QZVPPD	increasing accuracy and computational cost

## 5.3 Potential Energy Surfaces

The Born-Oppenheimer approximation allows construction of PES.



The energy can be viewed as a function of the nuclear coordinates

$$E = E(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \dots, \mathbf{q}_N)$$

The PES is therefore a  $3N$ -dimensional function of the nuclear positions.

The PES is characterized by “stationary points”, which are minima, maxima, or saddle points, where all first derivatives are zero.

$$\frac{\partial E}{\partial \mathbf{q}_i} = 0 \quad \forall \mathbf{q}_i$$

These derivatives are the forces on the nuclei due to the electrons. At the stationary points, all the forces are zero.

To differentiate between the types of stationary points, second derivatives of the energy,  $\frac{\partial^2 E}{\partial \mathbf{q}_i^2}$ , are needed.

The reactants, intermediates, and products are local minima on the PES and will have all  $\frac{\partial^2 E}{\partial \mathbf{q}_i^2} > 0$ .

The transition states are first-order saddle points on the PES and will have one  $\frac{\partial^2 E}{\partial \mathbf{q}_i^2} < 0$  in the direction of the intrinsic reaction coordinate (i.e. minimum energy in all directions but one).

## 5.4 Overview of Calculation Types

- A single-point energy calculation (default) evaluates the energy of a molecule at a fixed, input geometry with the specified method and basis set. The energy is quite sensitive to the level of theory. Recall that energies are given in Hartree atomic units and are relative to infinitely-separated electrons and nuclei.
- A geometry optimization (Opt) determines the optimum geometry (shape, bond lengths, angles, dihedrals) of the molecule. This sort of calculation will find the nearest stationary point on the PES where the forces (derivatives) are zero – can be a local minimum or saddle point.
- A frequency calculation (Freq) calculates the vibrational frequencies, which are obtained from the 2nd derivatives of the energy by assuming a harmonic potential. The frequencies can be used to verify that the geometry is optimized to a stable structure and not a saddle point.
- Other calculation types are also possible – NMR, excited states, etc.

## 5.5 Input for a Gaussian Calculation

- Route card – starts with #, specifies the type of calculation to be run, including method, basis set, and any other options (Opt, Freq, etc.).
- Title – note to yourself about the calculation.
- Charge and multiplicity – two integers to specify the electronic configuration.
- Molecular structure – positions of all nuclei, specified using either Cartesian coordinates or a Z-matrix.

## 5.6 Z-matrices

To perform a calculation on a chemical system, we must specify the atomic (nuclear) positions. This can be done within Cartesian coordinates, but it is hard to construct the geometry of non-linear molecules in Cartesians without molecule-building software. Instead, a Z-matrix defines the positions of all atoms based on bonding connectivity (bond lengths, angles, and dihedrals).

The form of a Z-matrix is:

Atom symbol

Atom symbol bonded to # bond length

Atom symbol bonded to # bond length angle with # angle

Atom symbol bonded to # bond length angle with # angle dihedral with # dihedral

The form of the last line is repeated for all subsequent atoms.

EX. H<sub>2</sub>O

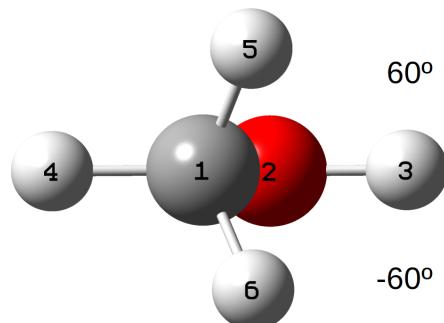
O
H 1 1.0
H 1 1.0 2 105.0

EX. NH<sub>3</sub>

N
H 1 1.0
H 1 1.0 2 109.47
H 1 1.0 2 109.47 3 120.0

EX. Methanol

C
O 1 1.4
H 2 1.0 2 109.47
H 1 1.1 2 109.47 3 180.0
H 1 1.1 2 109.47 3 60.0
H 1 1.1 2 109.47 3 -60.0



However, it is better to define the dihedrals of two of the CH<sub>3</sub> hydrogen atoms with respect to the other. This way, only one dihedral (instead of three) would need to be changed to rotate the methyl group:

C
O 1 1.4
H 2 1.0 2 109.47
H 1 1.1 2 109.47 3 180.0
H 1 1.1 2 109.47 4 120.0
H 1 1.1 2 109.47 4 -120.0

Note that angles cannot be  $0^\circ$  or  $180^\circ$ , so a dummy atom, X, is used in linear molecules.

EX. HCN

```

C
N 1 1.2
X 1 1.0 2 90.
H 1 1.1 2 90. 2 180.

```

Variables are often used in the Z-matrix, such as R1, A1, D1, with values specified below the Z-matrix. These can be separated into variables that are allowed to optimize and constraints that are kept fixed. This also allows users to scan over a particular variable.

EX. Dissociation curve for HF

```

H
F 1   R
R 0.5 S 20 0.1

```

EX. Rotation of the methyl group in methanol

```

C
O 1 R1
H 2 R2 2 A1
H 1 R3 2 A2 3 D1
H 1 R4 2 A3 4 D2
H 1 R5 2 A4 4 D3

R1 1.4
R2 1.0
R3 1.1
R4 1.1
R5 1.1
A1 109.47
A2 109.47
A3 109.47
A4 109.47
D2 120.
D3 -120.

D1 180. S 18 -10.

```

## 5.7 Basis Sets

Slater-type orbitals (STOs, H-atom wavefunctions) are the obvious choice, but the evaluation of the Coulomb and exchange (4-center,  $2-e^-$ ) integrals is impractical.

Calculations on large molecules were made feasible by use of Gaussian-type orbitals.

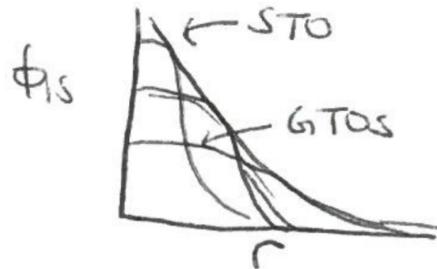
Gaussian basis functions have the form

$$g_{ijk}(\mathbf{r}) = Nx^i y^j z^k e^{-\alpha r^2}$$

where the origin of the coordinate system is the atomic nucleus.  $N$  is a normalization constant,  $\alpha$  is a positive exponent.

$$\begin{aligned} i = j = k = 0 &\longrightarrow s \text{ orbital} \\ i + j + k + 1 &\longrightarrow p \text{ orbital} \\ i + j + k + 2 &\longrightarrow d \text{ orbital} \end{aligned}$$

The problem with GTOs is that several Gaussians are needed to recover a good approximation to the nuclear cusps.



Several GTOs are combined to form contracted basis functions, which are fixed linear combinations of primitive Gaussians.

$$\chi_m = \sum_n d_{mn} g_n$$

The MOs are then expressed as linear combinations of the contracted Gaussians with variable coefficients.

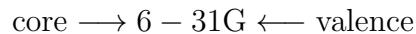
$$\phi_i = \sum_j c_{ij} \chi_j$$

Minimal basis sets have the notation

$$\text{STO} - nG$$

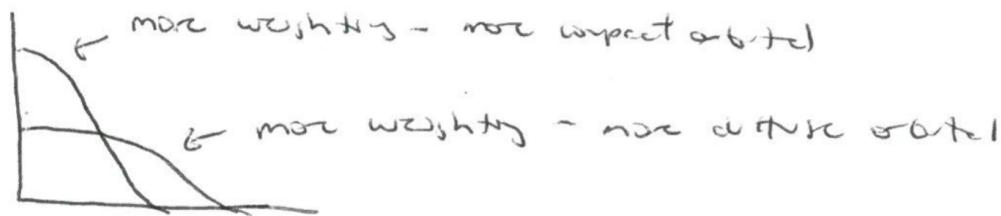
where each STO is represented by  $n$  (usually 3 or 6) Gaussians.

A simple (Pople-style) split-valence basis set is



For core electrons, each STO is represented by 6 Gaussian functions. For valence electrons, each orbital is represented by two contracted basis functions, one with 3 Gaussians, one with 1 Gaussian. This is called a double- $\zeta$  basis set, due to the two contracted basis functions for the valence.

Split-valence basis sets allow more flexibility because the valence orbitals can expand or contract depending on how the contracted functions are weighted.



6-31G\* or 6-31G(d) ← the \* or (d) indicates addition of higher angular momentum functions that can polarize the density. For  $p$ -block elements, polarization functions are a set of  $d$ -type Gaussians (actually 6 functions, instead of 5, for all combinations of  $i + j + k = 2$ ). For  $d$ -block elements, polarization functions are a set of  $f$ -type Gaussians.

6-31G(2d) ← the (2d) denotes 2 sets of higher angular momentum functions ( $d$  functions for  $p$ -block or  $f$  functions for  $d$ -block).

6-31G\*\* or 6-31G(d,p) ← the second \* or (,p) means addition of  $p$ -functions to H (or other  $s$ -block elements).

6-311G\* would be a triple- $\zeta$  basis set, with each valence orbital represented by 3 contracted basis functions.

6-31+G\* ← the + indicates addition of diffuse functions to all elements except the  $s$ -block. This is effectively going from double- to triple- $\zeta$ , but the extra basis functions are very diffuse, designed for anions, where the atomic size is much larger. A second + sign indicates addition of diffuse functions to H (and other  $s$ -block elements) as well.

Energies slowly converge to the basis-set limit as the number of basis functions increases (variational principle).

EX. For the C atom, need 1s, 2s, and 3 2p orbitals.

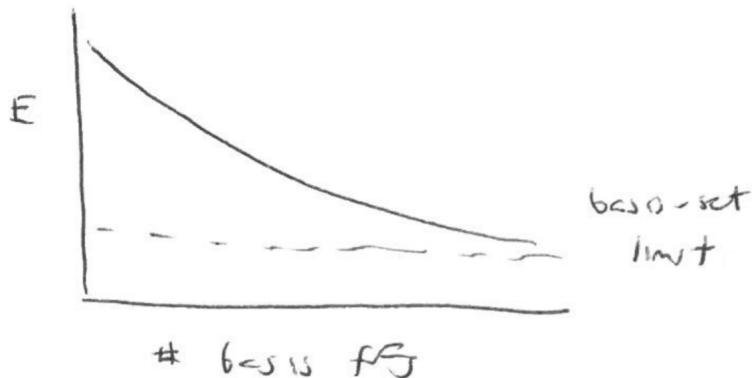
STO-3G    5 basis functions (1 per AO)  
 $3 \times 5 = 15$  primitive Gaussians

3-21G     $1(\text{core}) + 2 \cdot 4(\text{valence}) = 9$  basis functions  
 $3(\text{core}) + 3 \cdot 4(\text{valence}) = 15$  primitives

6-31G     $1(\text{core}) + 2 \cdot 4(\text{valence}) = 9$  basis functions  
 $6(\text{core}) + 4 \cdot 4(\text{valence}) = 22$  primitives

6-311G\*     $1(\text{core}) + 3 \cdot 4(\text{valence}) + 6(\text{polarization}) = 19$  basis functions  
 $6(\text{core}) + 5 \cdot 4(\text{valence}) + 6(\text{polarization}) = 32$  primitives

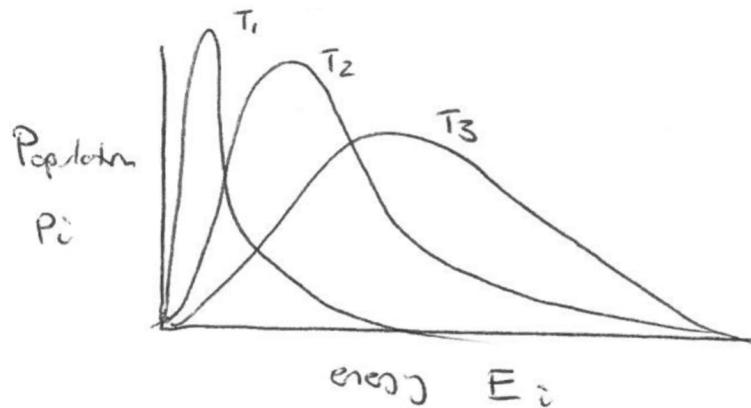
The energy will decrease variationally as more basis functions are added.



## 5.8 Introduction to Statistical Mechanics

MO theory tells us the electronic energies of molecules. However, we want to make a connection with thermochemical data (reaction enthalpies and free energies), which depend on temperature. This can be done via stat mech, which is a bridge between QM and thermodynamics.

At zero Kelvin, all systems will exit in their QM ground state, while at finite temperature, the population of possible energy levels is given by the Boltzmann distribution.



The fraction of particles in quantum state  $i$  is

$$P_i = \frac{n_i}{N} = \frac{1}{Q} e^{-E_i/kT}$$

where  $E_i$  is the energy of state  $i$ , obtained from a QM calculation.  $T$  is the temperature in Kelvin and  $k$  is Boltzmann's constant.

$$Q = \sum_i e^{-E_i/kT}$$

is the partition function. It is the central function in stat mech, analogous to the wavefunction in QM. Its magnitude is related to how many energy levels a system can access at a given  $T$ . If the energy levels involve degeneracy, the partition function can be written as

$$Q = \sum_i g_i e^{-E_i/kT}$$

where  $g_i$  is the degeneracy of the  $i$ th level. The ground state energy,  $E_0$  is set to zero by convention.

The thermodynamic functions  $U$  (energy),  $S$  (entropy),  $H$  (enthalpy),  $G$  (Gibbs free energy), and  $A$  (Helmholtz free energy) can all be determined from the partition function.

The energy at finite temperature is

$$\begin{aligned} U &= E_0 + \sum_i n_i E_i \\ &= E_0 + \frac{N}{Q} \sum_i E_i e^{-E_i/kT} \end{aligned}$$

$$\text{but } \frac{\partial Q}{\partial T} = \sum_i \frac{E_i}{kT^2} e^{-E_i/kT} \quad \text{so}$$

$$\begin{aligned} U &= E_0 + \frac{NkT^2}{Q} \left( \frac{\partial Q}{\partial T} \right) \\ &= E_0 + NkT^2 \left( \frac{\partial \ln Q}{\partial T} \right) \end{aligned}$$

For the particular case of a harmonic oscillator, the energy levels are  $E_n = E_0 + nh\nu$ , so the partition function is

$$Q = \sum_n e^{-nh\nu/kT}$$

this can be simplified to eliminate the sum over states by using the geometric series  $\sum_n x^n = \frac{1}{1-x}$  so

$$Q = \frac{1}{1 - e^{-h\nu/kT}}$$

$$\begin{aligned} U &= E_0 + \frac{NkT^2}{Q} \left( \frac{\partial Q}{\partial T} \right) \\ &= E_0 + NkT^2 \left( \frac{h\nu}{kT^2} \frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} \right) \\ &= E_0 + \frac{Nh\nu}{e^{h\nu/kT} - 1} \end{aligned}$$

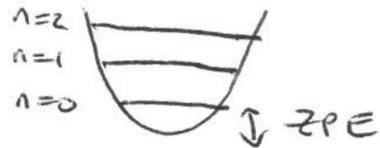
so the correction to the energy from thermal vibrations is

$$E_{\text{vib}}(T) = \frac{Nh\nu}{e^{h\nu/kT} - 1}$$

## 5.9 Comparing Energies with Thermodynamic Data

We must account for nuclear motion due to zero-point vibrations, as well as thermal motion from translation, rotation, and vibrations.

For a harmonic oscillator, the zero-point energy is the energy difference between the bottom of the well and the  $n = 0$  level.



$$E = \left( n + \frac{1}{2} \right) h\nu \quad \Rightarrow \quad E_{\text{ZPE}} = \frac{1}{2} h\nu$$

For a molecule, the ZPE is a sum over all the vibrational modes

$$E_{\text{ZPE}} = \sum_i \frac{1}{2} h\nu_i$$

At zero Kelvin, the electronic energy is corrected by the ZPE

$$E(O) = E_{\text{el}} + E_{\text{ZPE}}$$

At temperatures above zero Kelvin, use stat mech to determine the energy contributions from occupation of various rotational, translational, and vibrational levels:

$$E(T) = E_{\text{el}} + E_{\text{ZPE}} + E_{\text{vib}}(T) + E_{\text{trans}}(T) + E_{\text{rot}}(T)$$

For translation and rotation, the QM energy levels are so close together that we can assume the classical limit, and

$$E_{\text{trans}}(T) = \frac{3}{2}kT$$

$$E_{\text{rot}}(T) = \begin{cases} \frac{3}{2}kT & (\text{non-linear}) \\ kT & (\text{linear}) \end{cases}$$

Assuming harmonic vibrations,

$$E_{\text{vib}}(T) = \sum_i \frac{h\nu_i}{e^{h\nu_i/kT} - 1}$$

Finally, the enthalpy can be obtained from the thermally corrected energy by adding a pressure-volume correction:

$$H = E + kT$$

The thermal energy, enthalpy, and free-energy corrections are listed in the frequency section of the Gaussian output.

# Chapter 6

## Electronic-Structure Methods

### 6.1 Hartree-Fock Theory

HF is the simplest electronic-structure method for self-consistent numerical solution of the SE. The assumption is that the electrons move independently, i.e. that the wavefunction can be represented as a single  $N$ -electron Slater determinant.

$$\psi = \frac{1}{\sqrt{N!}} |\phi_1 \ \phi_2 \ \cdots \ \phi_N|$$

For a general polyatomic molecule, the Hamiltonian can be written as

$$\hat{H} = \sum_i \hat{h}_i + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

where  $\hat{h}_i$  is the one-electron Hamiltonian for electron  $i$

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N_{\text{nuc}}} \frac{Z_A}{r_{iA}}$$

and the factor of  $\frac{1}{2}$  prevents double-counting of  $e^-$ - $e^-$  interactions.

The HF energy is

$$\begin{aligned} E &= \langle \psi | \hat{H} | \psi \rangle \\ &= \left\langle \psi \left| \sum_i \hat{h}_i + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \right| \psi \right\rangle \end{aligned}$$

The one-electron integrals are:

$$\langle \psi | \sum_i \hat{h}_i | \psi \rangle = \sum_{i=1}^N \langle \phi_i | \hat{h}_i | \phi_i \rangle = \sum_{i=1}^N \langle i | \hat{h} | i \rangle$$

The two-electron integrals are:

$$\begin{aligned} \left\langle \psi \left| \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \right| \psi \right\rangle &= \frac{1}{2} \sum_{i \neq j} \left[ \left\langle \phi_i(1) \phi_j(2) \left| \frac{1}{r_{12}} \right| \phi_i(1) \phi_j(2) \right\rangle - \left\langle \phi_i(1) \phi_j(2) \left| \frac{1}{r_{12}} \right| \phi_j(1) \phi_i(2) \right\rangle \right] \\ &= \frac{1}{2} \sum_{i \neq j} (\langle ij | ij \rangle - \langle ij | ji \rangle) \end{aligned}$$

which is a difference of Coulomb and exchange integrals.

$$\therefore E = \sum_{i=1}^N \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i \neq j} (\langle ij | ij \rangle - \langle ij | ji \rangle)$$

To find the orthonormal set of spin orbitals,  $\phi_i$ , that give the minimum energy, apply the variational theorem. We want to minimize the energy by changing the orbitals (i.e.  $\frac{\partial E}{\partial \phi_i} = 0$  for each orbital). This gives the set of Fock equations:

$$\hat{f} \phi_i = \varepsilon_i \phi_i$$

where

$$\hat{f} = \hat{h}_i + \sum_j (\hat{J}_j - \hat{K}_j)$$

is the Fock operator.  $\hat{J}_j$  is the Coulomb operator,  $\hat{K}_j$  is the exchange operator, and the  $\varepsilon_i$  are the orbital energies.

These operators are defined such that the Coulomb integrals are

$$\langle ij | ij \rangle = \langle i | \hat{J}_j | i \rangle$$

and the exchange integrals are

$$\langle ij | ji \rangle = \langle i | \hat{K}_j | i \rangle$$

Note that the Coulomb and exchange operators depend on all the orbitals. This requires self-consistent solution of the HF equations.

An initial approximate form for the wavefunction (i.e. LCAOs, generalized Hückel) is used to evaluate the Coulomb and exchange integrals. The Fock equations are then solved to obtain improved orbitals and energies. The cycle is repeated until the wavefunction and energies are converged.

The HF orbital energies are

$$\begin{aligned}\varepsilon_i &= \langle i | \hat{h} | i \rangle + \sum_j \left( \langle i | \hat{J}_j | i \rangle - \langle i | \hat{K}_j | i \rangle \right) \\ &= \langle i | \hat{h} | i \rangle + \sum_j (\langle ij | ij \rangle - \langle ij | ji \rangle)\end{aligned}$$

So the sum of orbital energies is

$$\sum_{i=1}^N \varepsilon_i = \sum_{i=1}^N \langle i | \hat{h} | i \rangle + \sum_{i \neq j} (\langle ij | ij \rangle - \langle ij | ji \rangle)$$

which is not equal to the total HF energy because it counts all the  $e^-$ - $e^-$  interactions twice. The total energy, in terms of the orbital energies, is

$$E = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} (\langle ij | ij \rangle - \langle ij | ji \rangle)$$

The orbital energy is the energy required to remove an electron from that orbital, assuming that the remaining electron distribution is undisturbed. This gives Koopmans' theorem: the ionization energy  $I$  of an electron from orbital  $\phi_i$  is the negative of the orbital energy,  $\varepsilon_i$ , or

$$I = -\varepsilon_{\text{HOMO}}$$

This is only an approximation because the remaining  $N - 1$  electrons have a different set of HF orbital energies in the cation than in the neutral species. However, Koopmans' theorem would be exact if an exact electronic-structure method was used.

## 6.2 The Roothan-Hall Method

The HF procedure is straightforward for atoms due to their high symmetry, but more complex for molecules. The Roothan-Hall approach is used to transform the problem into a matrix equation.

Introduce a set of  $N_o$  basis functions,  $\chi_i$ . These can be thought of as AOs, but are usually Gaussian functions. Express each MO,  $\phi_n$ , in terms of these basis functions

$$\phi_n = \sum_{j=1}^{N_o} c_{nj} \chi_j$$

This expression is substituted into the Fock equations to give

$$\hat{f} \sum_{j=1}^{N_o} c_{nj} \chi_j = \varepsilon_n \sum_{j=1}^{N_o} c_{nj} \chi_j$$

To solve for the orbitals,  $\phi_n$ , we need only optimize the coefficients.

Multiply through by an arbitrary basis function,  $\chi_i$ , and integrate to give

$$\sum_{j=1}^{N_o} c_{nj} \langle i | \hat{f} | j \rangle = \varepsilon_n \sum_{j=1}^{N_o} c_{nj} \langle i | j \rangle$$

Let  $F_{ij}$  be the Fock matrix elements,  $F_{ij} = \langle i | \hat{f} | j \rangle$  and  $S_{ij}$  be the overlap matrix elements,  $S_{ij} = \langle i | j \rangle$ . Then,

$$\sum_{j=1}^{N_o} F_{ij} c_{nj} = \varepsilon_n \sum_{j=1}^{N_o} S_{ij} c_{nj}$$

and this is a set of  $N_o$  equations in  $N_o$  unknowns for the coefficients and orbital energies.

This can be written as a single matrix equation

$$\mathbf{FC} = \mathcal{E}\mathbf{SC}$$

where  $\mathbf{C}$  is the coefficient matrix, with elements  $c_{nj}$  and  $\mathcal{E}$  is a diagonal matrix of the orbital energies. This matrix equation is solved iteratively for the coefficient matrix.

An initial guess for  $\mathbf{C}$  is used to construct  $\mathbf{F}$ . The equation is then solved to obtain a new  $\mathbf{C}$  matrix and the orbital energies. The process is repeated until convergence is reached.

### 6.3 Restricted versus Unrestricted Spins

If all electrons in a molecule are paired, then one need only consider doubly occupied spatial orbitals in the SCF procedure – this is termed “spin-restricted” HF. However, if there are unpaired electrons, then one must solve for the  $\alpha$ -spin and  $\beta$ -spin orbitals separately, which is “spin-unrestricted” HF.

The problem with spin-unrestricted calculations is that they can give a wavefunction that is not a spin eigenfunction.

The expectation value of the total spin operator is

$$\langle S^2 \rangle = \left( \frac{N_\alpha - N_\beta}{2} \right) \left( \frac{N_\alpha - N_\beta}{2} + 1 \right)$$

This should be  $\langle S^2 \rangle = 0$  for a singlet,  $\langle S^2 \rangle = (1/2)(3/2) = 3/4$  for a doublet,  $\langle S^2 \rangle = 2$  for a triplet, etc.

However, by not having the  $\alpha$ -spin and  $\beta$ -spin orbitals equivalent for the paired electrons, the amount of spin polarisation can be magnified and the actual  $\langle S^2 \rangle$  from a HF calculation can be higher than the ideal values for a given multiplicity. This is called “spin contamination”.

## 6.4 Configuration Interaction

HF does not give the exact wavefunction. It considers only the average Coulomb interaction between electrons, ignoring correlation.

Basis sets with  $N_o$  functions give  $N_o$  MOs, but only the lowest-lying are occupied in HF theory, leaving  $N_o - \frac{1}{2}N_e$  unoccupied or “virtual” orbitals.

Let the ground-state have the (HF) wavefunction,  $\psi_o$

$$\psi_o = |\phi_1 \ \phi_2 \ \cdots \ \phi_a \ \phi_b \ \cdots \ \phi_n|$$

A singly-excited determinant is a wavefunction where a single electron has been excited from the occupied spin orbital  $\phi_a$  to the virtual spin orbital  $\phi_p$ .

$$\psi_a^p = |\phi_1 \ \phi_2 \ \cdots \ \phi_p \ \phi_b \ \cdots \ \phi_n|$$

A doubly-excited determinant is a wavefunction where two electrons have been excited from occupied spin orbitals  $\phi_a$  and  $\phi_b$  to virtual spin orbitals  $\phi_p$  and  $\phi_q$ .

$$\psi_{ab}^{pq} = |\phi_1 \ \phi_2 \ \cdots \ \phi_p \ \phi_q \ \cdots \ \phi_n|$$

Higher excitations can be generated in the same way.

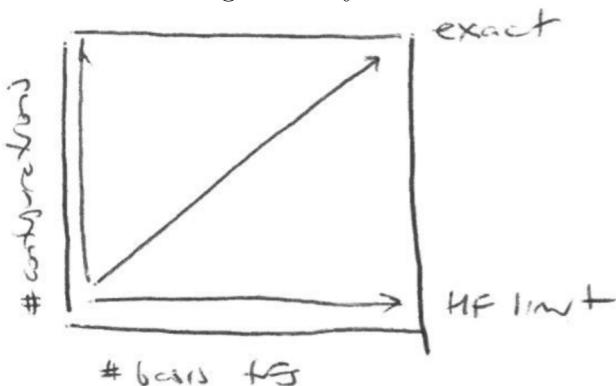
The exact ground-state wavefunction can be expressed as a linear combination of all possible  $N_e$ -electron Slater determinants (of the correct multiplicity) arising from a complete set of spin orbitals.

The CI wavefunction is

$$\psi = c_0\psi_0 + \sum_{a,p} c_a^p \psi_a^p + \sum_{\substack{a < b \\ p < q}} c_{ab}^{pq} \psi_{ab}^{pq} + \sum_{\substack{a < b < c \\ p < q < r}} c_{abc}^{pqr} \psi_{abc}^{pqr} + \dots$$

where the  $c$ 's are CI coefficients that are variationally optimized.

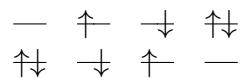
The difference between the exact energy and the HF limit is the correlation energy. CI accounts for the electron correlation neglected by HF.



CI calculations are very computationally demanding – in practise, only a limited number of configurations, differing from  $\psi_0$  by no more than a few spin orbitals are used. The most common is CISD (single and double excitations only).

CI calculations are variational, meaning that they can never obtain a lower energy than the exact ground-state energy. However, such truncated CI calculations are not size consistent, meaning that they can give a lower energy for two isolated atoms or molecules than for the infinitely separated complex.

EX.  $\text{He}_2$  with CISD



For a single He atom, CISD is full CI

However, configurations where the electrons on each He atom are doubly excited are missing from a CISD calculation on  $\text{He}_2$ , since that would be a quadruple excitation. This means that calculations on separate He atoms will give a lower energy than for the dimer. This is a problem for computing dissociation energies with CI. Size-consistent variants, called quadratic configuration interactions methods (QCI, QCISD) have been developed and are used in most computational chemistry packages.

## 6.5 Perturbation Theory

Assume we have solved the SE

$$\hat{H}^\circ \psi_n^\circ = E_n^\circ \psi_n^\circ$$

for a set of wavefunctions,  $\psi_n^\circ$ . Now, introduce a small perturbation term to the Hamiltonian,  $\hat{H}'$ , which will result in a different set of wavefunctions and energies.

The SE cannot be solved exactly for the new Hamiltonian

$$\hat{H} = \hat{H}^\circ + \hat{H}'$$

but because the perturbation is small, the solution should be similar to the unperturbed case.

The new (perturbed) problem to be solved is

$$\hat{H} \psi_n = E_n \psi_n \quad \text{where} \quad \hat{H} = \hat{H}^\circ + \lambda \hat{H}'$$

and  $\lambda$  is a coupling strength parameter used to keep track of the level of approximation.

$$\lambda = 0 \quad \Rightarrow \quad \hat{H}(\lambda) = \hat{H}^\circ$$

$$\lambda = 1 \quad \Rightarrow \quad \hat{H}(\lambda) = \hat{H}$$

The method of solution is to postulate

$$E_n = E_n^\circ + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

$$\psi_n = \psi_n^\circ + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots$$

Substituting into the SE gives

$$(\hat{H}^\circ + \lambda \hat{H}')(\psi_n^\circ + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots) = (E_n^\circ + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)(\psi_n^\circ + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots)$$

This must be true for every value of  $\lambda$  between 0 and 1, so it must be true order by order.

To order  $\lambda^0$ :  $\hat{H}^\circ \psi_n^\circ = E_n^\circ \psi_n^\circ \leftarrow$  idealized problem, known solution

To order  $\lambda^1$ :  $\hat{H}^\circ \psi_n^1 + \hat{H}' \psi_n^\circ = E_n^\circ \psi_n^1 + E_n^1 \psi_n^\circ \quad (*)$

To order  $\lambda^2$ :  $\hat{H}^\circ \psi_n^2 + \hat{H}' \psi_n^1 = E_n^\circ \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^\circ$

To find the first-order correction to the energy, multiply  $(*)$  by  $\psi_n^\circ$  and integrate. This gives

$$\langle \psi_n^\circ | \hat{H}^\circ | \psi_n^1 \rangle + \langle \psi_n^\circ | \hat{H}' | \psi_n^\circ \rangle = E_n^\circ \langle \psi_n^\circ | \psi_n^1 \rangle + E_n^1 \langle \psi_n^\circ | \psi_n^\circ \rangle$$

but  $\langle \psi_n^\circ | \hat{H}^\circ | \psi_n^1 \rangle = E_n^\circ \langle \psi_n^\circ | \psi_n^1 \rangle$  and  $\langle \psi_n^\circ | \psi_n^\circ \rangle = 1$ . Thus

$$E_n^1 = \langle \psi_n^\circ | \hat{H}' | \psi_n^\circ \rangle$$

is the first-order energy correction.

For the first-order correction to the wavefunction, let

$$\psi_n^1 = \sum_m c_{mn} \psi_m^\circ$$

substitute this definition into (\*) to give

$$(\hat{H}^\circ - E_n^\circ) \sum_m c_{mn} \psi_m^\circ = -(\hat{H}' - E_n^1) \psi_n^\circ$$

multiply through by  $\psi_\ell^\circ$  and integrate

$$\sum_m c_{mn} (E_\ell^\circ - E_n^\circ) \langle \psi_\ell^\circ | \psi_m^\circ \rangle = -\langle \psi_\ell^\circ | \hat{H}' | \psi_n^\circ \rangle + E_n^1 \langle \psi_\ell^\circ | \psi_n^\circ \rangle$$

$$c_{\ell n} (E_\ell^\circ - E_n^\circ) = -\langle \psi_\ell^\circ | \hat{H}' | \psi_n^\circ \rangle + E_n^1 \delta_{\ell n}$$

This gives two cases. If  $\ell = n$ , we recover the first-order energy correction. If  $\ell \neq n$ ,

$$c_{\ell n} = -\frac{\langle \psi_\ell^\circ | \hat{H}' | \psi_n^\circ \rangle}{E_\ell^\circ - E_n^\circ}$$

Returning to our definition of  $\psi_n^1$ , the first-order correction to the wavefunction is

$$\psi_n^1 = \sum_{m,m \neq n} \frac{\langle \psi_m^\circ | \hat{H}' | \psi_n^\circ \rangle}{E_n^\circ - E_m^\circ} \psi_m^\circ$$

Similarly, for the second-order correction to the energy, consider the order- $\lambda^2$  equation, multiply through by  $\psi_n^\circ$  and integrate:

$$\langle \psi_n^\circ | \hat{H}^\circ | \psi_n^2 \rangle + \langle \psi_n^\circ | \hat{H}' | \psi_n^1 \rangle = E_n^\circ \langle \psi_n^\circ | \psi_n^2 \rangle + E_n^1 \langle \psi_n^\circ | \psi_n^1 \rangle + E_n^2 \langle \psi_n^\circ | \psi_n^\circ \rangle$$

$$E_n^\circ \langle \psi_n^\circ | \psi_n^2 \rangle + \langle \psi_n^\circ | \hat{H}' | \psi_n^1 \rangle = E_n^\circ \langle \psi_n^\circ | \psi_n^2 \rangle + E_n^1(0) + E_n^2(1)$$

$$E_n^2 = \langle \psi_n^\circ | \hat{H}' | \psi_n^1 \rangle$$

Thus, the second-order energy correction is

$$E_n^2 = \sum_{m,m \neq n} \frac{|\langle \psi_m^\circ | \hat{H}' | \psi_n^\circ \rangle|^2}{E_n^\circ - E_m^\circ}$$

## 6.6 Møller-Plesset Perturbation Theory

CI improves on HF theory using the variational principle. Alternatively, we can improve on HF using perturbation theory.

In HF, the one-electron Fock operator is

$$\hat{f}_m = -\frac{1}{2}\nabla_m^2 - \sum_A \frac{Z_A}{r_{mA}} + \sum_{j=1}^n (\hat{J}_j - \hat{K}_j)$$

The MP unperturbed Hamiltonian is taken to be the sum of the Fock operators.

$$\hat{H}^\circ = \sum_{m=1}^n \hat{f}_m$$

The HF wavefunction is an eigenfunction of  $\hat{H}^\circ$  and the eigenvalue is the sum of the orbital energies.

$$\hat{H}^\circ \psi_\circ = \left( \sum_{m=1}^n \varepsilon_m \right) \psi_\circ$$

Let the perturbation  $\hat{H}'$  be the difference between the true  $e^-$ - $e^-$  repulsion and the average HF repulsion.

$$\hat{H}' = \hat{H} - \hat{H}^\circ = \sum_{m>\ell} \frac{1}{r_{\ell m}} - \sum_{m,j} (\hat{J}_j - \hat{K}_j)$$

The ground-state energy, to first order is:

$$\begin{aligned} E &= E^\circ + E^1 \\ &= \langle \psi_\circ | \hat{H}^\circ | \psi_\circ \rangle + \langle \psi_\circ | \hat{H}' | \psi_\circ \rangle \\ &= \langle \psi_\circ | \hat{H} | \psi_\circ \rangle \\ &= E^{\text{HF}} \end{aligned}$$

So first-order perturbation theory recovers the HF energy. To improve on HF, we must find the second-order energy correction.

$$E^2 = \sum_i \frac{|\langle \psi_i | \hat{H}' | \psi_\circ \rangle|^2}{E_\circ - E_i}$$

where the  $\psi_i$ 's are the unperturbed determinants for all possible excited configurations formed from the spin orbitals.

The matrix elements are non-zero only for doubly-excited configurations, so

$$E^{\text{MP2}} = E^{\text{HF}} + \sum_{\substack{a < b \\ p < q}} \frac{|\langle \psi_{ab}^{pq} | \hat{H}' | \psi_{\circ} \rangle|^2}{\varepsilon_p + \varepsilon_q - \varepsilon_a - \varepsilon_b}$$

MP2 is less computationally demanding than CISD. MP2 is size-consistent but, unlike CISD, it is not variational. This means that it can give an energy below the exact value. CI and MP calculations are termed post-HF or “ab initio”.

## 6.7 Coupled-Cluster Theory

The main limitation of truncated CI methods is that they are not size consistent. CC theory is similar in spirit of CI, but ensures size consistency by construction.

Define a set of operators that convert the ground-state HF wavefunction  $\psi_{\circ}$  (single Slater determinant) into linear combinations of excited-state determinants.

$$\hat{T}_1 \psi_{\circ} = \sum_{a,p} t_a^p \psi_a^p$$

$$\hat{T}_2 \psi_{\circ} = \sum_{\substack{a < b \\ p < q}} t_{ab}^{pq} \psi_{ab}^{pq}$$

and so forth. The  $t$  coefficients are called the CC amplitudes.

The “cluster” operator is a sum of single, double, etc. excitations

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_N$$

In practise,  $\hat{T}$  is truncated at some order. For CCSD (singles and doubles),

$$\hat{T} = \hat{T}_1 + \hat{T}_2$$

The fundamental premise of CC theory is that the wavefunction can be written as

$$\psi = e^{\hat{T}} \psi_{\circ}$$

The operator  $e^{\hat{T}}$  is defined by the Taylor series expansion

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots$$

The effect of this operator is to express the wavefunction as a linear combination of  $\psi_{\circ}$  and excited Slater determinants.

For the case of CCSD,

$$e^{\hat{T}} = e^{\hat{T}_1 + \hat{T}_2} = 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \dots$$

which includes higher-order excitations than CISD. The extra excitations included in the CCSD wavefunction restore size consistency and provide a more accurate description of the correlation energy.

The CCSD energy is given by

$$\hat{H} \left( e^{\hat{T}_1 + \hat{T}_2} \psi_o \right) = E_{\text{CCSD}} \left( e^{\hat{T}_1 + \hat{T}_2} \psi_o \right)$$

and is obtained by iteratively solving a set of non-linear equations for the CC amplitudes until self-consistence is reached.

CC methods are preferred over CI since they are more accurate while maintaining the same computational cost. However, the CC methods are not variational (although in practise they are quite close).

# Chapter 7

## Density-Functional Theory (DFT)

### 7.1 DFT Formalism

Given the number of electrons ( $N$ ), then the external potential  $V(\mathbf{r})$  (from the nuclei) generates the ground-state wavefunction,  $\psi$ , via the Hamiltonian,  $\hat{H}$

$$\hat{H} = \sum_i \left( -\frac{1}{2} \nabla_i^2 \right) + V + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

or  $V \rightarrow \hat{H} \rightarrow \psi \rightarrow E$  (and other observable properties). All properties can thus be considered functionals of the potential, but the wavefunction also generates the electron density

$$\rho = \int \cdots \int \psi^* \psi d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

so  $V \rightarrow \psi \rightarrow \rho$ . Hohenberg and Kohn showed that this mapping is one-to-one, so it is reversible and  $\rho \rightarrow V \rightarrow \psi \rightarrow E$  and all properties are unique functions of the electron density.

In particular, the kinetic and potential energies are functionals of  $\rho$ :

$$\begin{aligned} \text{kinetic:} \quad & \left\langle \psi \left| -\frac{1}{2} \sum_i \nabla_i^2 \right| \psi \right\rangle = T(\rho) \\ e^- - e^-: \quad & \left\langle \psi \left| \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \right| \psi \right\rangle = V_{ee}(\rho) \\ e^- - \text{nuc:} \quad & \langle \psi | V | \psi \rangle = \int V \rho(\mathbf{r}) d\mathbf{r} \end{aligned}$$

However, the Hohenberg-Kohn theorem is an existence proof only and we do not know simple  $\rho$ -dependent expressions for  $T(\rho)$  and  $V_{ee}(\rho)$ . Practical DFT calculations are based on Kohn-Sham theory.

Consider a system with the same electron density as the real system in which the electrons occupy orbitals that satisfy the simple Schrödinger equation

$$-\frac{1}{2}\nabla^2\psi_i + V_o\psi_i = \varepsilon_o\psi_i$$

where  $V_o$  is the effective potential and

$$\rho = \sum_{i=1}^N \psi_i^2$$

The kinetic energy using these orbitals

$$T_o = -\frac{1}{2} \sum_i \int \psi_i \nabla_i^2 \psi_i d\mathbf{r}$$

is likely a good approximation to the real kinetic energy.

We write the total energy as

$$E(\rho) = T_o(\rho) + \int V \rho d\mathbf{r} + J(\rho) + E_{XC}(\rho)$$

where the classical  $e^-$ - $e^-$  Coulomb repulsion is

$$J(\rho) = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

and  $E_{XC}$  defines the exchange-correlation energy

$$E_{XC} = [T(\rho) + V_{ee}(\rho)] - [T_o(\rho) + J(\rho)]$$

which is the difference between the exact and classical contributions to the energy and accounts for the QM effects of exchange and electron correlation.

As in HF, the DFT energy is minimized wrt the orbitals by self-consistent solution

$$-\frac{1}{2}\nabla^2\psi_i + \left( V + V_{el} + \frac{\delta E_{XC}}{\delta \rho} \right) \psi_i = \varepsilon_i \psi_i$$

where  $V_{el} = \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2$  is the Coulomb potential and  $\frac{\delta E_{XC}}{\delta \rho}$  is the XC potential.

However, the exact XC functional is unknown. There is no systematic route to obtain it and many forms have been proposed, none of which are variational.

Types of density-functional methods are usually classified according to Perdew's ladder.

## 7.2 Density-Functional Approximations

### 7.2.1 The Local Density Approximation (LDA)

In the LDA,  $E_{XC}$  depends only on  $\rho$ . The exchange energy is

$$E_X^{\text{LDA}} = c_X \int \rho^{4/3} d\mathbf{r}$$

There is no closed-form expression for the correlation energy – numerical parameterizations to Quantum Monte Carlo results for correlation energies of a uniform electron distribution are used instead.

The LDA strongly overbinds chemical systems (to roughly the same extent that HF underbinds).

### 7.2.2 Generalized Gradient Approximations (GGAs)

In GGAs,  $E_{XC}$  depends on  $\rho$  and the reduced density gradient,  $\chi$ :

$$\chi = \frac{|\nabla \rho|}{\rho^{4/3}}$$

Commonly, the GGA energy is split into separate exchange and correlation terms

$$\begin{aligned} E_X^{\text{GGA}} &= E_X^{\text{LDA}} + \int F_X(\chi) \rho^{4/3} d\mathbf{r} \\ E_C^{\text{GGA}} &= E_C^{\text{LDA}} + \int F_C(\chi) \rho^{4/3} d\mathbf{r} \end{aligned}$$

There are many possible forms for a GGA, which differ by the particular form chosen for the enhancement factor,  $F(\chi)$ . One common form for a GGA exchange enhancement factor is

$$F_X(\chi) = \beta \frac{\chi^2}{1 + \gamma \chi^2}$$

where  $\beta$  and  $\gamma$  are constants. The extra exchange term lowers the energy beyond the LDA, particular for regions where the reduced gradient is large, such as for free atoms, where the electron density distribution is roughly exponential.

GGAs give vastly improved bond energies compared to the LDA, with errors  $\sim 10$  kcal/mol. The most common GGAs are BLYP (in chemistry) and PBE (in physics).

### 7.2.3 meta-GGAs

Meta-GGAs are structurally similar to GGAs, but the enhancement factors now depend on  $\rho$ ,  $\nabla\rho$ ,  $\nabla^2\rho$ , and  $\tau = \sum_i |\nabla\psi_i|^2$ , which is the kinetic-energy density. meta-GGAs typically involve complicated functional forms with many empirical parameters and offer little advantage over GGAs. SCAN is a meta-GGA with growing popularity in physics.

### 7.2.4 Hybrid Functionals

Hybrids functionals include a mixture of density-functional and Hartree-Fock exchange:

$$E_{XC} = cE_X^{\text{HF}} + (1 - c)E_X^{\text{GGA}} + E_C^{\text{GGA}}$$

where  $c = 0.2 - 0.5$  in most cases. meta-GGAs can also be used in hybrids in the place of GGAs.

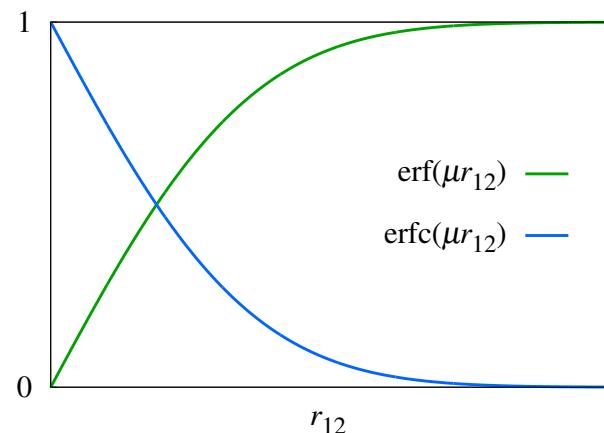
Proposed in 1993 by Axel Becke, hybrids remain the most common and most reliable class of density functionals (errors  $\sim 2 - 4$  kcal/mol for bond energies). The most popular are B3LYP (chemistry) and PBE0 (physics).

Hybrid functionals typically work well since HF is exact exchange, but no correlation, while GGAs approximate both exchange and correlation simultaneously. Thus, adding some amount of HF improves the treatment of exchange and improves chemical accuracy for many problems.

### 7.2.5 Range-Separated Hybrid Functionals

Hybrid functionals use a global mixing of HF and DFT exchange. Range-separated hybrids include a variable mixture of HF and DFT exchange that is dependent on the  $e^- - e^-$  interaction range  $r_{12}$ . This is done by splitting the Coulomb operator into short- and long-range components using the error function.

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}$$



For molecules, long-range HF exchange and short-range GGA exchange gives the best performance and reduces errors seen with conventional hybrids for charge transfer, but the optimal range-separation is highly system dependent. For solids, short-range HF exchange and long-range GGA exchange reduces the computational cost relative to conventional hybrids. Common methods are LC-BLYP and LC- $\omega$ PBE (chemistry) and HSE (physics).

### 7.2.6 Double Hybrid Functionals

Double hybrids are based on hybrid functionals, but also replace some fraction of the DFT correlation energy with the MP2 correlation energy:

$$E_{\text{XC}} = c_1 E_{\text{X}}^{\text{HF}} + (1 - c_1) E_{\text{X}}^{\text{GGA}} + c_2 E_{\text{C}}^{\text{MP2}} + (1 - c_2) E_{\text{C}}^{\text{GGA}}$$

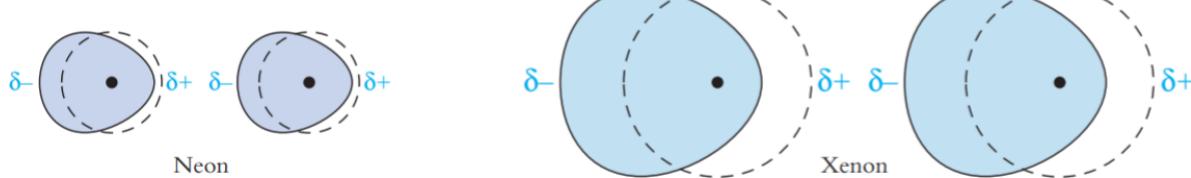
Due to the pairing of HF exchange and MP2 correlation, these functionals typically have  $c_1 = 0.5 - 0.8$ .

The use of MP2 correlation means that double hybrids depend on the virtual orbitals, so they are not “true” density functionals. As a result, they also have a much greater computational cost and poorer scaling than the other types of DFAs.

## 7.3 Dispersion Methods

London dispersion is responsible for condensation of non-polar species, like noble gases and hydrocarbons.

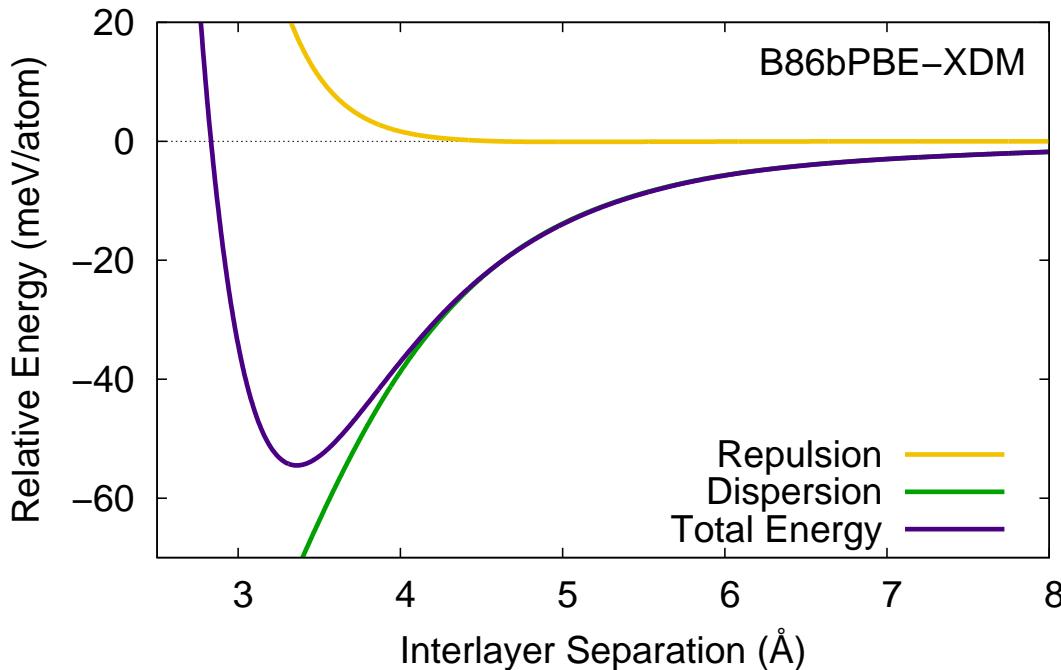
The strength of dispersion binding increases with polarizability and is due to interaction between instantaneous dipoles (and higher-order multipoles) that arise in the electron density distributions of atoms or molecules.



This long-range, non-local type of electron correlation is not captured by most density functionals (although double hybrids do partly account for dispersion via the MP2 correlation term).

The dispersion energy is commonly added as a post-SCF correction to a base density functional:

$$E = E_{\text{DFT}} + E_{\text{disp}}$$



The dispersion energy may be evaluated from 2nd-order perturbation theory and is written as a sum over all atom pairs:

$$E_{\text{disp}} = \sum_{i < j} \left( -\frac{C_{6,ij}}{R_{ij}^6} - \frac{C_{8,ij}}{R_{8,ij}^8} - \dots \right)$$

The  $C_6/R^6$  term comes from dipole-dipole interactions, while the  $C_8/R^8$  term comes from dipole-quadrupole interactions. Higher-order terms are also possible, but are quite small in magnitude, and so are rarely included.

Perturbation theory is accurate when the component atoms are weakly interacting (i.e. large  $R_{ij}$ ). In practice, the dispersion energy is damped at small  $R_{ij}$  to prevent divergence:

$$E_{\text{disp}} = \sum_{i < j} \left( -\frac{C_{6,ij}f_6(R_{ij})}{R_{ij}^6} - \frac{C_{8,ij}f_8(R_{ij})}{R_{8,ij}^8} - \dots \right)$$

where the  $f_n(R_{ij})$  terms are empirical damping functions.

There are several available dispersion corrections in the literature (D3, D4, XDM, MBD-rsSCS, and MBD-NL). These corrections are very quick to evaluate, so it is best practice to include a dispersion correction in all DFT calculations, but they are absolutely essential for studies of intermolecular chemistry with DFT.