CHEM 4301/5301: Theory of Chemical Bonding

© Erin R. Johnson

2019

Contents

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), ψ is the wavefunction, and E is the energy.

This is an eigenvalue problem, as in matrix algebra. The wavefunction $\psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N})$ 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

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

$$\hat{V} = \text{electron-nuclear attraction} + \text{electron-electron repulsion}$$

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

However, the e^--e^- term is not separable into functions of the individual electron coordinates (because of the $1/r_{ij}$ term), so the SE cannot be solved analytically for many-e^- systems.

As a first approximation, we construct a set of molecular orbitals (ϕ_i's) from linear combinations of atomic orbitals (χ_k's)

$$\phi_i = \sum_k c_k \chi_k$$
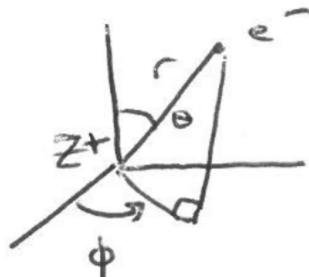
The MOs are the solutions to

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

where the ε_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.

The general solution is a product of radial and angular terms:

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

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

The energies are $E_n = -\frac{Z^2}{2n^2}$ in atomic units (Hartree).
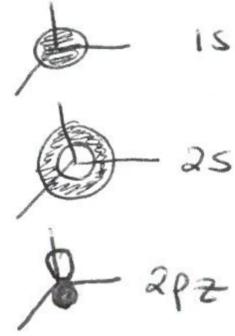
Recall that $n = 1, 2, 3, \ldots$, $\ell = 0, 1, \ldots, n-1$, and $m_\ell = 0, \pm 1, \ldots, \pm \ell$.

The general pattern of energy levels is:

	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	
$n = 4$	— $4s$	— $4p$	— $4d$	— $4f$	7 f orbitals, $m_\ell = 0, \pm 1, \pm 2, \pm 3$
$n = 3$	— $3s$	— $3p$	— $3d$		5 d orbitals, $m_\ell = 0, \pm 1, \pm 2$
$n = 2$	— $2s$	— $2p$			3 p orbitals, $m_\ell = 0, \pm 1$
$n = 1$	— $1s$				1 s orbital, $m_\ell = 0$
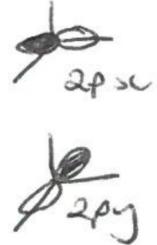
Complete H-atom wavefunctions for $n = 1, 2$ are:

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_\circ} \right)^{3/2} e^{-\frac{Zr}{a_\circ}}$$

$$\psi_{200} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_\circ} \right)^{3/2} \left(2 - \frac{Zr}{a_\circ} \right) e^{-\frac{Zr}{2a_\circ}}$$

$$\psi_{210} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_\circ} \right)^{3/2} \frac{Zr}{a_\circ} e^{-\frac{Zr}{2a_\circ}} \cos\theta$$

$$\psi_{21\pm1} = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_\circ} \right)^{3/2} \frac{Zr}{a_\circ} e^{-\frac{Zr}{2a_\circ}} \sin\theta e^{\pm i\phi}$$

These are complex valued – need to obtain real linear combinations:

$$\psi_{2p_x} = \frac{1}{\sqrt{2}} \left(\psi_{211} + \psi_{21-1} \right) = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_\circ} \right)^{3/2} \frac{Zr}{a_\circ} e^{-\frac{Zr}{2a_\circ}} \sin\theta \cos\phi$$

$$\psi_{2p_y} = \frac{i}{\sqrt{2}} \left(\psi_{211} - \psi_{21-1} \right) = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_\circ} \right)^{3/2} \frac{Zr}{a_\circ} e^{-\frac{Zr}{2a_\circ}} \sin\theta \sin\phi$$

Additionally, these spatial orbitals are all doubly degenerate – α or β spin.

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

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

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

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

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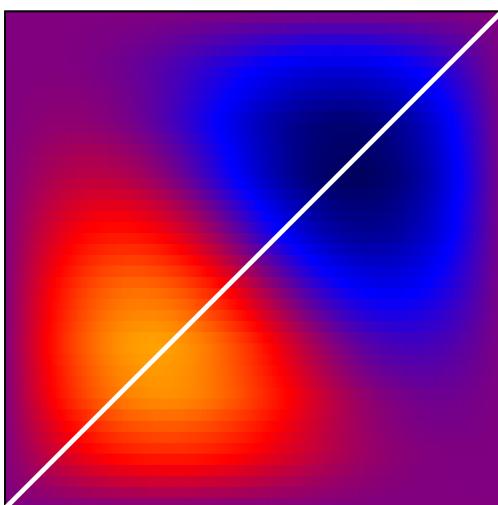
$$\psi_{mn}(x_1, x_2) = \psi_m(x_1)\psi_n(x_2)$$

Symmetric and antisymmetric wavefunctions can be constructed from the individual particle in a box wavefunctions for each particle and are
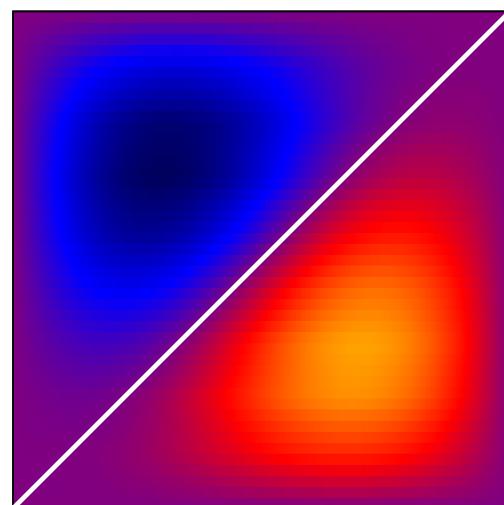
$$\psi_{mn}^{\mathrm{S}} = \frac{1}{\sqrt{2}}\left[\psi_m(x_1)\psi_n(x_2) + \psi_m(x_2)\psi_n(x_1)\right]$$

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

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

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

ψ_{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 ψ 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 Laplacian Operator

∇^2 is the Laplacian, or second-derivative, operator. It appears in determination of the kinetic energy, $\hat{T} = -\frac{1}{2m}\nabla^2$. In one dimension, the Laplacian is

$$\nabla^2 = \frac{d^2}{dx^2}$$

and in three dimensions,

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

In spherical polar coordinates,

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

1.5 The Helium Atom

The He-atom Hamiltonian, in atomic units, is

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

The first two terms are the kinetic energies of electrons 1 and 2, respectively. The next two terms are the attractive electrostatic interactions of electrons 1 and 2 with the nucleus (charge $Z = 2$). The last term is the repulsive electrostatic interaction between the two electrons.

This resembles a repetition of the H-atom problem for electrons 1 and 2, except that the last term

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

is not separable into functions of the individual electron coordinates. This means that the Schrödinger equation cannot be solved analytically for this system and approximate methods must be used. This is true for all atoms or molecules with two or more electrons.

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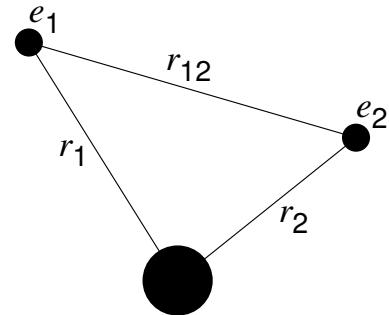
There are four normalized spin eigenfunctions that satisfy the requirement of being either symmetric or antisymmetric with respect to exchange:

$$\text{symmetric, "triplet" spin functions} \begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right] \end{cases}$$

$$\text{antisymmetric, "singlet" spin function} \left\{ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right] \right.$$

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

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

The lowest-lying excited states for He have the electron configuration $1s^1 2s^1$. The spatial parts of these wavefunctions are

$$\psi_{\text{singlet}} = \frac{1}{\sqrt{2}}\big[1s(1)2s(2) + 1s(2)2s(1)\big]$$

$$\psi_{\text{triplet}} = \frac{1}{\sqrt{2}}\big[1s(1)2s(2) - 1s(2)2s(1)\big]$$

$2s$	↓	$2s$	↑
$1s$	↑	$1s$	↑
	singlet		triplet

where ψ_{singlet} would be paired with the singlet spin function and ψ_{triplet} could be paired with any of the three triplet spin functions.

1.6   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 $\psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1 & \phi_2 & \cdots & \phi_N \end{vmatrix}$

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.

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

EX. He atom

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

EX. Li atom

$2s$ ↿
$1s$ ⇅ $$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s\alpha & 1s\beta & 2s\alpha \end{vmatrix}$$

EX. C atom

$2p$ ↿ ↿ —
$2s$ ⇅ $$\psi = \frac{1}{\sqrt{6!}} \begin{vmatrix} 1s\alpha & 1s\beta & 2s\alpha & 2s\beta & 2p_x\alpha & 2p_y\alpha \end{vmatrix}$$
$1s$ ⇅

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.

1.7   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.

The 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 ϕ 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 ϕ 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

$$\langle\phi|\hat{H}|\phi\rangle = \sum_i \sum_j a_i^* a_j \langle\psi_i|\hat{H}|\psi_j\rangle$$

$$= \sum_i \sum_j a_i^* a_j E_j \langle\psi_i|\psi_j\rangle$$

$$= \sum_i \sum_j a_i^* a_j E_j \delta_{ij}$$

$$= \sum_j |a_j|^2 E_j$$

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

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

Note that, if ϕ is not normalized, this becomes

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

If the wavefunction, ϕ, 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. 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 ϕ is a linear combination of fixed AOs

$$\phi = \sum_i c_i \chi_i$$

(or other basis functions), again assumed to be real, then

$$E = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\int \left(\sum_{i=1}^{n} c_i \chi_i \right) \hat{H} \left(\sum_{j=1}^{n} c_j \chi_j \right) d\tau}{\int \left(\sum_{i=1}^{n} c_i \chi_i \right) \left(\sum_{j=1}^{n} c_j \chi_j \right) d\tau}$$

rearranging

$$\sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j \int \chi_i \hat{H} \chi_j d\tau = E \sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j \int \chi_i \chi_j d\tau$$

We introduce the simplifying notation

$$\langle \chi_i | \hat{H} | \chi_j \rangle = \int \chi_i \hat{H} \chi_j d\tau = H_{ij} \qquad \text{(the Hamiltonian "matrix elements")}$$

$$\langle \chi_i | \chi_j \rangle = \int \chi_i \chi_j d\tau = S_{ij} \qquad \text{(the "overlap" integrals)}$$

then

$$\sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j H_{ij} = E \sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j S_{ij}$$

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

Differentiating wrt c_i

$$\sum_{j=1}^{n} c_j H_{ij} = E \sum_{j=1}^{n} c_j S_{ij}$$

and there will be n such equations, one for each c_i. Thus, this is a set of n linear equations in n unknowns, and can be represented in matrix form:

$$\begin{bmatrix} H_{11} & H_{12} & \cdots & H_{1n} \\ H_{21} & H_{22} & \cdots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} & H_{n2} & \cdots & H_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1n} \\ S_{21} & S_{22} & \cdots & S_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ S_{n1} & S_{n2} & \cdots & S_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix}$$

$$\mathbf{Hc} = E\mathbf{Sc}$$

This can be rewritten as

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

which is a "homogeneous" system of linear equations and will only have non-trivial solutions for $\mathbf{c}$ if the secular determinant is zero

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

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

Expanding this determinant gives a nth order polynomial in E, which will give the set of MO energies as roots. Substituting each root, E_i, back into the matrix equation

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

gives the expansion coefficients for each MO, ϕ_i

$$\phi_i = \sum_{j=1}^{n} c_j \chi_j$$

1.8   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

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

but $\hat{T}_{\text{nuc}} = 0$ for fixed nuclei and $\hat{V}_{\text{nuc-nuc}}$ 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.

1.9   MOs for H_2^+

The MOs are linear combinations of the $1s$ AOs on each nucleus
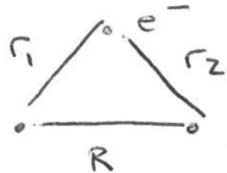
$$\phi = c_1\chi_1 + c_2\chi_2$$

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

$$
\begin{aligned}
E &= \frac{-\frac{1}{2} + J \pm \left(-\frac{1}{2}S + K\right)}{1 \pm S} \\
&= \frac{-\frac{1}{2}(1 \pm S) + J \pm K}{1 \pm S} \\
&= -\frac{1}{2} + \frac{J \pm K}{1 \pm S}
\end{aligned}
$$
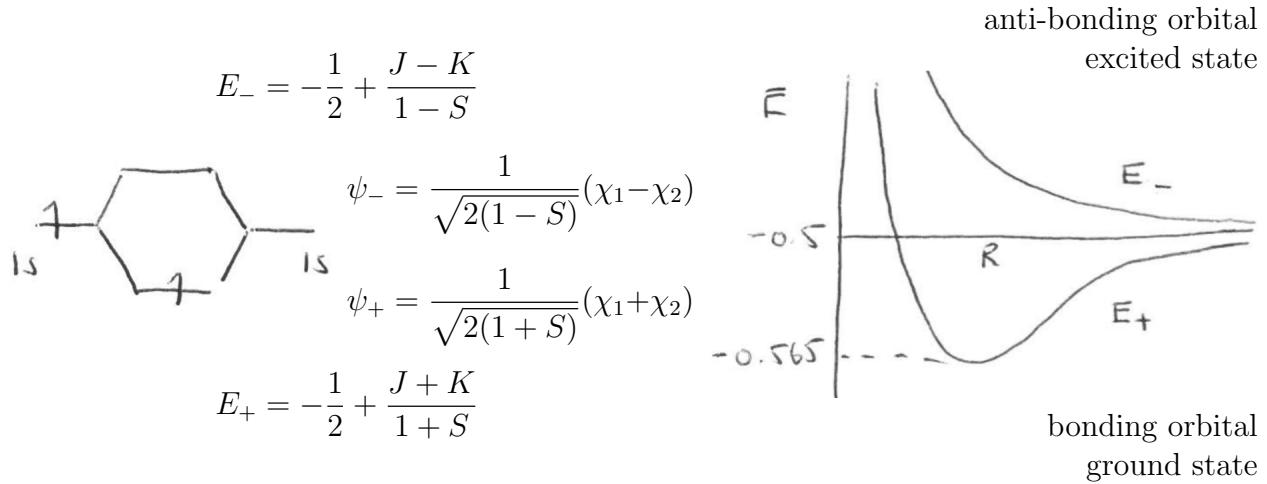
The first term is the H-atom energy and the second the bonding/anti-bonding term.

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

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

Note that as $R \to \infty$, $J, K, S \to 0$ 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:

anti-bonding orbital
excited state

$$E_- = -\frac{1}{2} + \frac{J - K}{1 - S}$$

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

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

$$E_+ = -\frac{1}{2} + \frac{J + K}{1 + S}$$

bonding orbital
ground state

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.

Chapter 2

Qualitative MO Theory

2.1 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 $S << 1$, we use the Taylor expansion:

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

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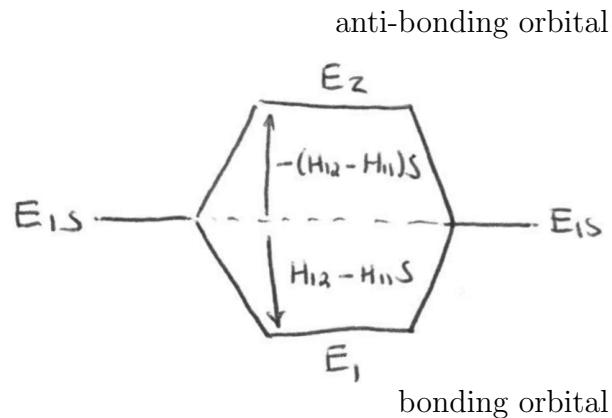
$$\begin{aligned} E_1 &= (H_{11} + H_{12})(1 - S + S^2 + \dots) \\ &= H_{11} + (H_{12} - H_{11}S) - (H_{12} - H_{11}S)S + \dots \end{aligned}$$

$$
\begin{aligned}
E_2 &= (H_{11} - H_{12})(1 + S + S^2 + \ldots) \\
&= H_{11} - (H_{12} - H_{11}S) - (H_{12} - H_{11}S)S + \ldots
\end{aligned}
$$
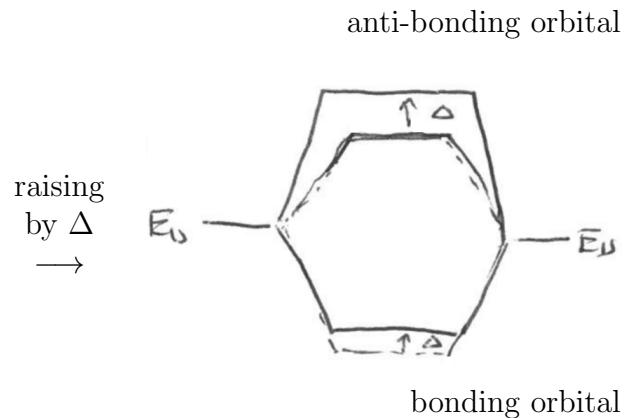
The first term, H_{11}, is negative and is the $1s$ orbital energy for a non-interacting H atom.

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:

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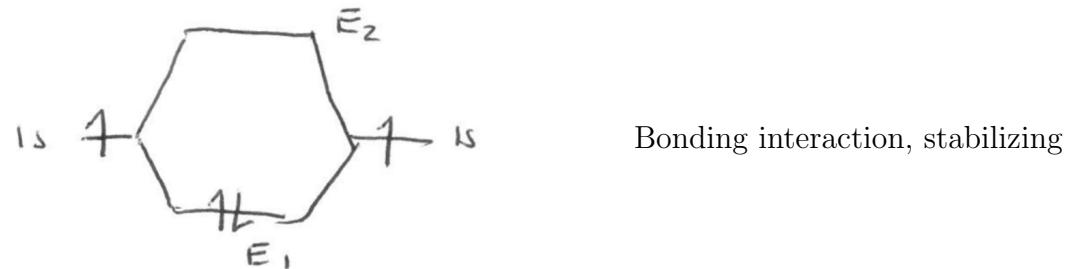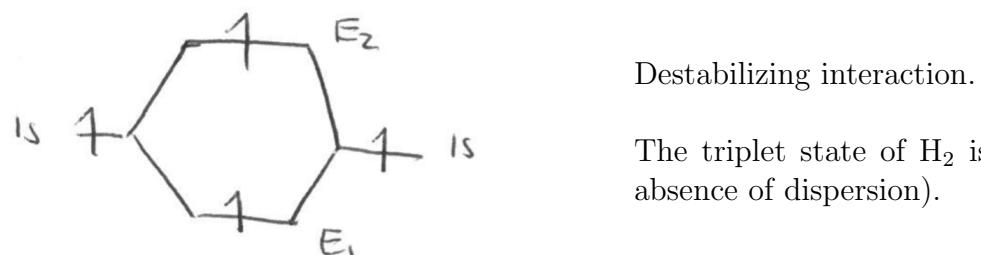
With respect to the non-interacting AO energies, E_2 is raised more than E_1 is lowered - this is why noble-gas dimers do not form bonds.

For H$_2$ in the ground state (singlet)

Bonding interaction, stabilizing
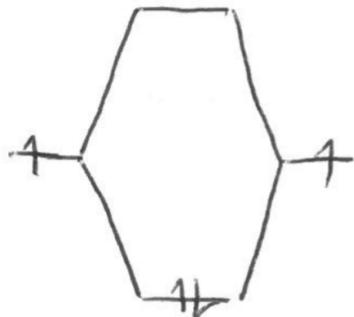
and in the excited state (triplet)

Destabilizing interaction.

The triplet state of H$_2$ 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:

vs.

high overlap, large stabilization   low overlap, small stabilization
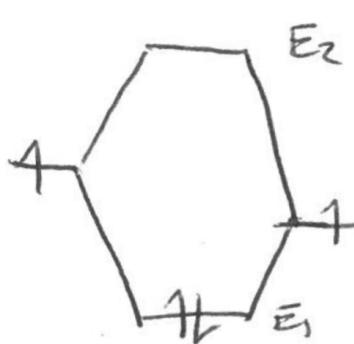
2.2   Heteronuclear Diatomics

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

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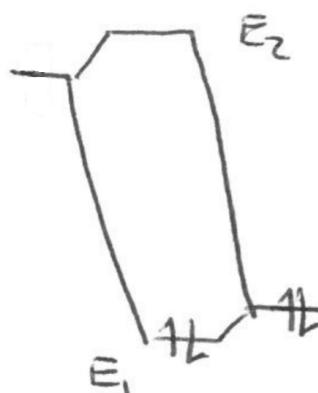
$$E_2 \approx H_{22} + \frac{(H_{12} - H_{11}S)^2}{H_{22} - H_{11}}$$

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

vs.

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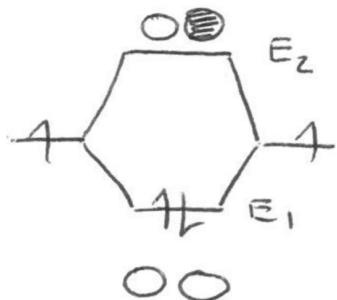
If the energy difference between the AOs is very large, then there is no stabilization and we say that the orbitals do not mix.

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:
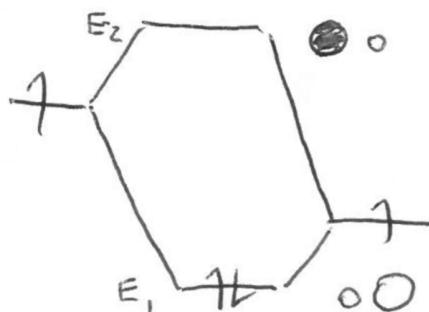
$$\phi_2 = c(\chi_1 - \chi_2)$$ negative linear combination
anti-bonding orbital

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

anti-bonding orbital $- \sigma^*$

bonding orbital $- \sigma$

2.3   2nd-Period Diatomics

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

- positive overlap – resulting in a bonding orbital

σ-bonding orbital (end-on interaction, density accumulation along the bond)
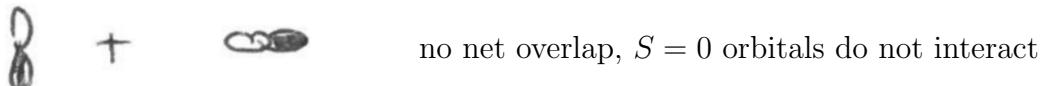
π-bonding orbital (side-on interaction, nodal plane through bond axis)

- negative overlap – resulting in an anti-bonding orbital
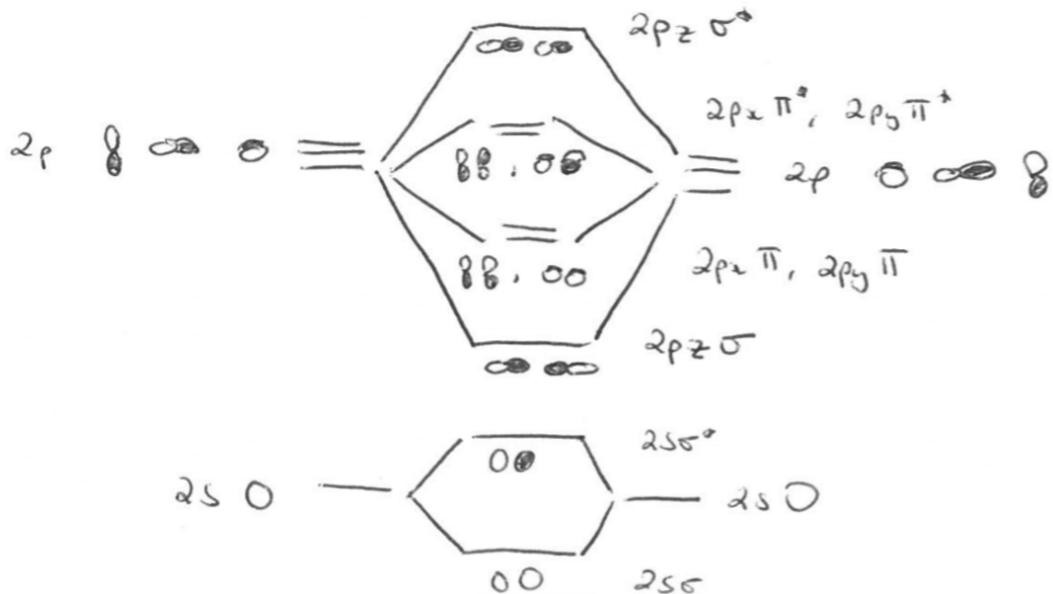
σ^* orbital

π^* orbital

- zero overlap – resulting in non-bonding orbitals

no net overlap, $S = 0$ orbitals do not interact

The orbital interactions are:

$$1s_A \pm 1s_B \longrightarrow \text{core orbitals do not mix}$$

$$2s_A \pm 2s_B \longrightarrow 2s\sigma, 2s\sigma^* \qquad\qquad 2p_{x,A} \pm 2p_{x,B} \longrightarrow 2p_x\pi, 2p_x\pi^*$$

$$2p_{z,A} \pm 2p_{z,B} \longrightarrow 2p_z\sigma, 2p_z\sigma^* \qquad\qquad 2p_{y,A} \pm 2p_{y,B} \longrightarrow 2p_y\pi, 2p_y\pi^*$$
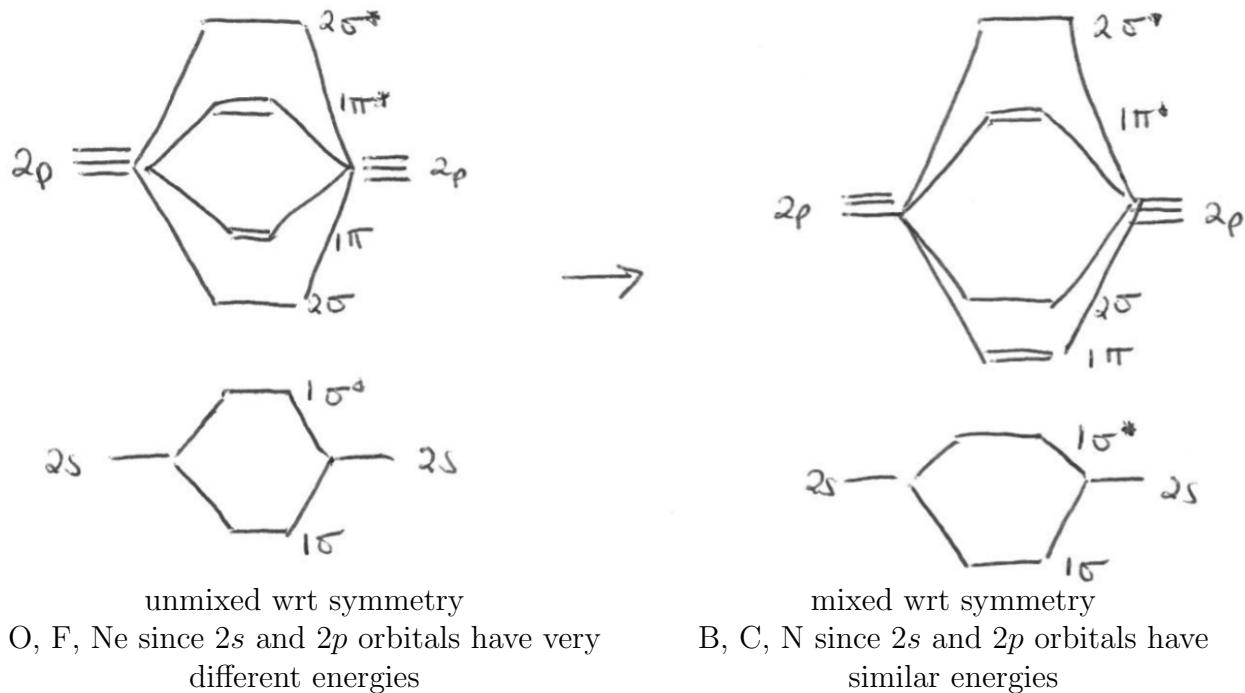
The MO diagram is:

2.4   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 σ orbital to become more stable and the higher-energy σ orbital to become less stable. The $2s\sigma^*$ and $2p_z\sigma^*$ can also mix.

| unmixed wrt symmetry	mixed wrt symmetry
O, F, Ne since $2s$ and $2p$ orbitals have very different energies	B, C, N since $2s$ and $2p$ orbitals have similar energies

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

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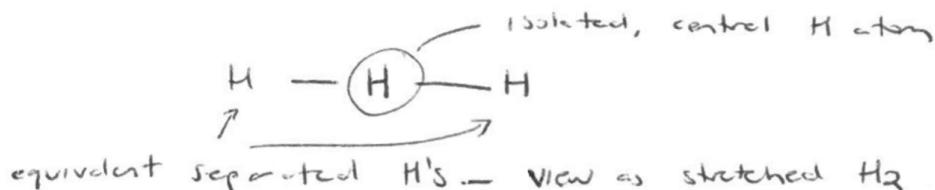
$$\text{BO} = \frac{1}{2}\left[\left(\begin{array}{c}\#e^{-}\text{'s in bonding}\\ \text{orbitals}\end{array}\right) - \left(\begin{array}{c}\#e^{-}\text{'s in antibonding}\\ \text{orbitals}\end{array}\right)\right]$$

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.
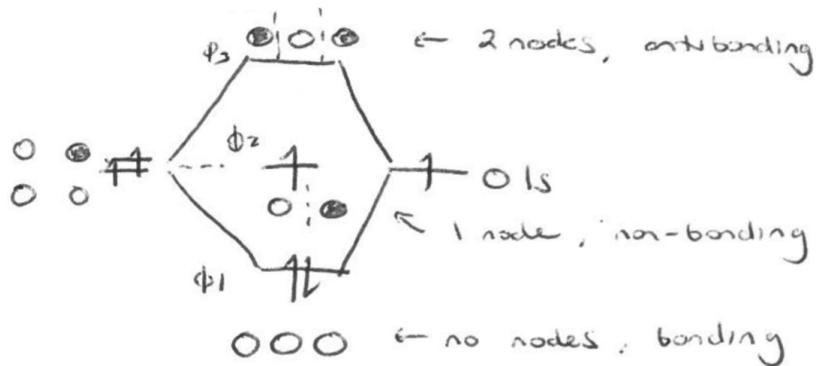
2.5 MO Diagrams for Linear Polyatomic Molecules

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.
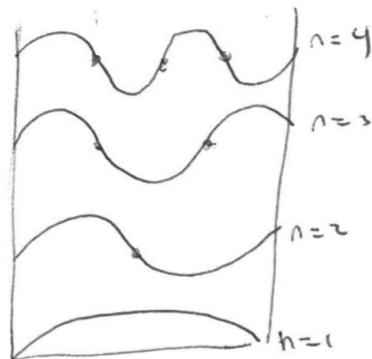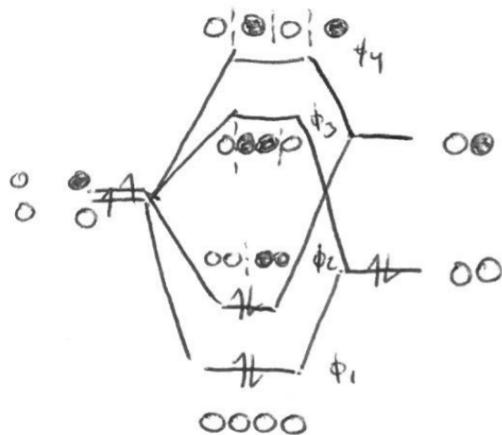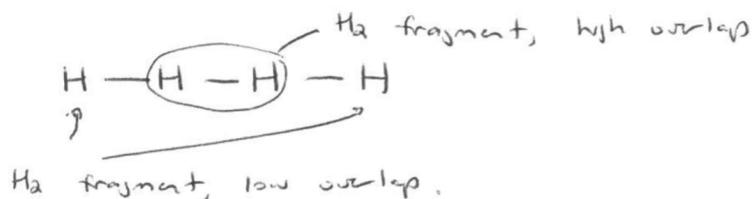
EX. Linear

Consider mixing of the σ and σ^* 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.

2.6   Symmetry Operations and Groups

Symmetry operations are transformations where the configuration of the nuclei is unchanged.

C_n: n-fold rotation (by $360°/n$) about an axis
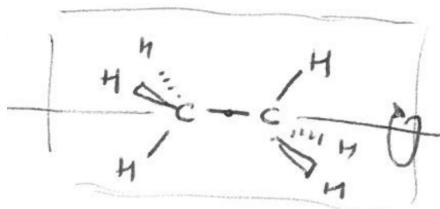
σ: reflection in a plane

S_n: n-fold improper rotation – rotation by $360°/n$, followed by reflection in the plane perpendicular to the axis of rotation

i: inversion through a centre of symmetry (i.e. $x, y, z \to -x, -y, -z$), equivalent to S_2

The highest-order C_n axis is taken as the "principal" or z-axis. Reflection planes containing this axis are σ_v (vertical) and planes perpendicular to this axis are σ_h (horizontal).

EX. ethane

C_3 rotation
σ_v reflection
S_6 improper rotation
i centre of inversion

Every molecule can be assigned to a symmetry group based on the possible symmetry operations.

1. No C_n axis

   C_1 – no symmetry elements (except the identity operation)

   C_s – a single reflection plane

   C_i – a centre of inversion symmetry only

2. A single C_n axis

   C_n – a C_n rotation axis only

   C_{nv} – a C_n axis and n vertical reflection planes (H_2O, NH_3, HF)

   C_{nh} – a C_n axis and a horizontal reflection plane (RHC=CHR)

   D_{nh} – a C_n axis, n vertical and one horizontal reflection planes (BH_3, C_6H_6)

   D_{nd} – a C_n axis with a S_{2n} axis (C_2H_6)

   Two uncommon groups are:

   D_n – a C_n axis with nC_2 axes perpendicular

   S_n – only a S_n improper rotation axis

3. Groups with many ($n > 2$) equivalent C_n axes

   T_d – regular tetrahedron (CH_4)

   O_h – regular octahedron (SF_6)

   I_h – regular icosahedron (C_{60})

MOs can also be assigned labels based on their symmetries:

   a – non-degenerate, symmetric wrt C_n rotation about principal axis

   b – non-degenerate, anti-symmetric wrt C_n rotation about principal axis

   e – doubly degenerate
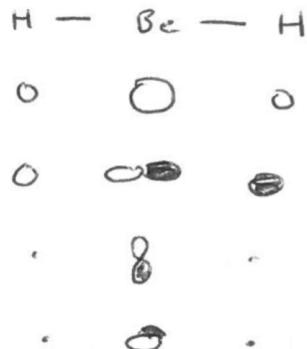
   t – triply degenerate

Subscripts of g (gerade) or u (ungerade) specify whether the MO is symmetric or anti-symmetric wrt inversion. Superscripts of $\prime$ or $\prime\prime$ specify whether the MO is symmetric or anti-symmetric wrt reflection in a horizontal plane. Subscripts of $1, 2, 3, \ldots$ distinguish between different types of a, b, e, t symmetries; there are no simple rules – use character tables.

2.7   MO Diagrams for Centro-Symmetric Molecules

Consider overlap of AOs on the central atom with those on the symmetry-equivalent terminal atoms.
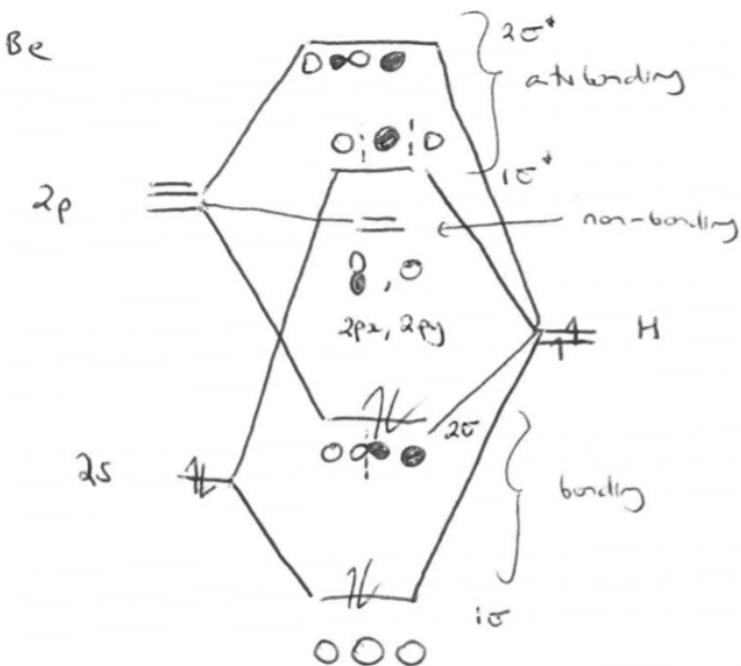
EX. BeH_2 (linear) – consider overlap of s and p orbitals of Be with the hydrogen $1s$ orbitals.
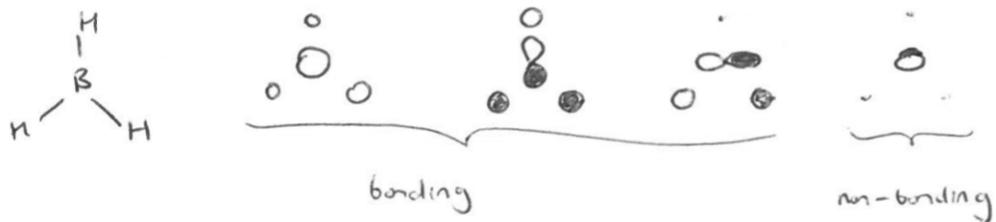
The anti-bonding MOs can be generated by changing the sign of the AO on the central atom.

Overlap between s orbitals will be greater than between s and p orbitals, giving greater stabilization.
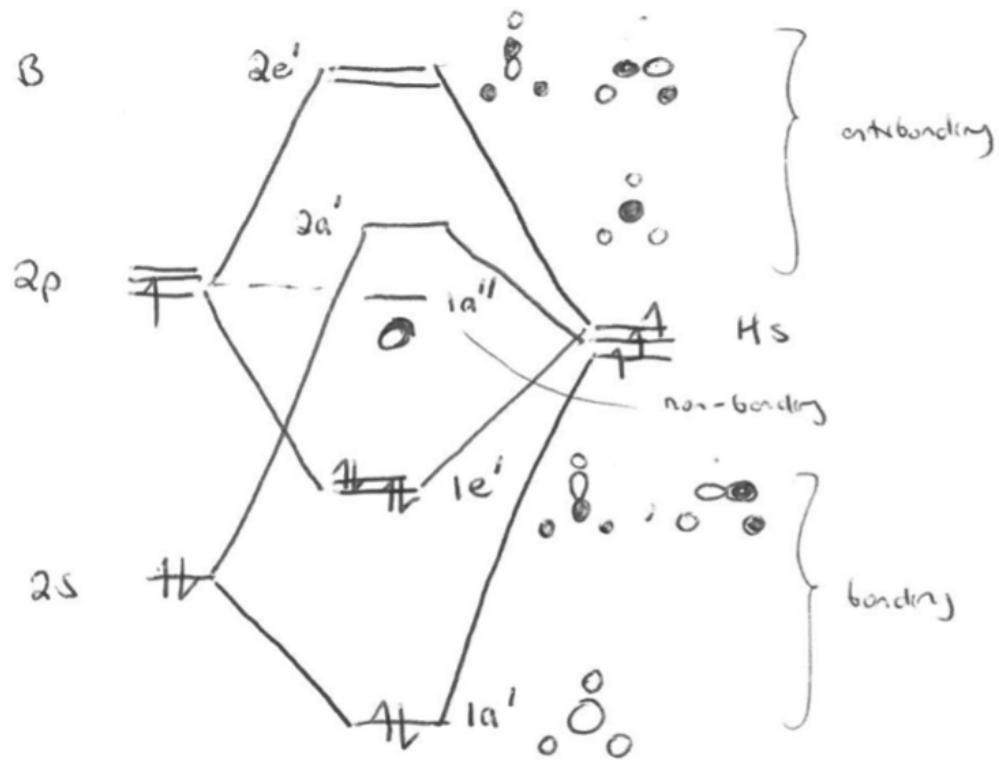
The MO diagram is:
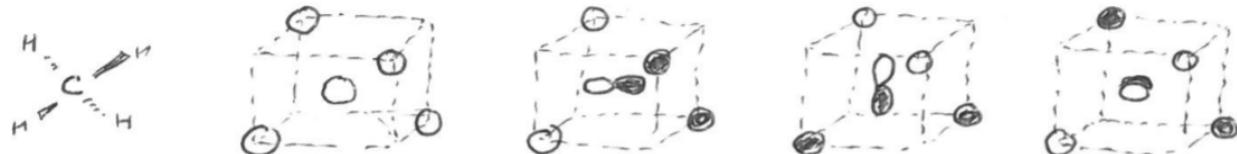
EX. BH_3 (trigonal planar) – overlap of B s and p with H $1s$ AOs.
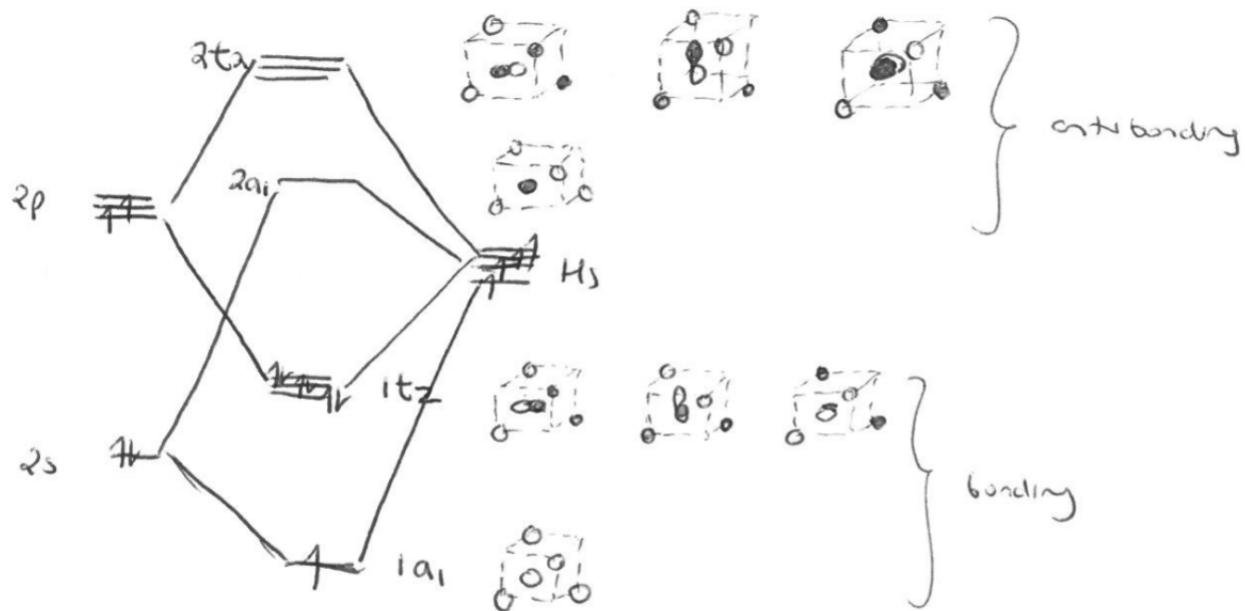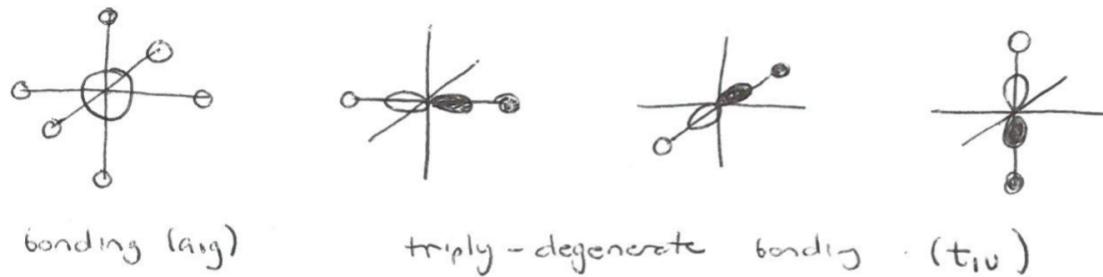
The MO diagram is:

EX. CH_4 (tetrahedral) – overlap of C s and p with H $1s$ AOs.
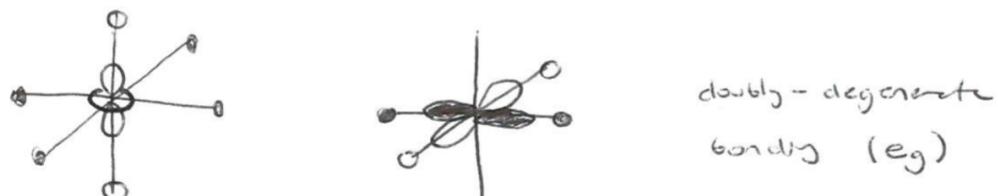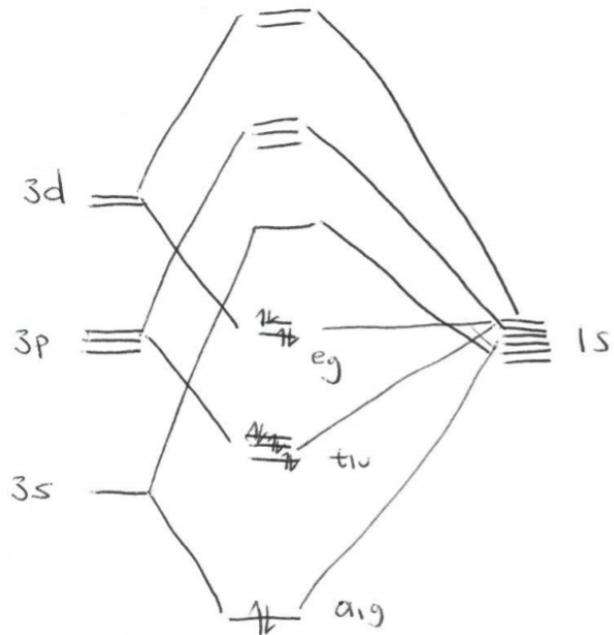
The MO diagram is:

EX. SH_6 (octahedral) – overlap of S s, p, and d with H $1s$ AOs.

bonding (a_{1g})   triply – degenerate bonding (t_{1u})
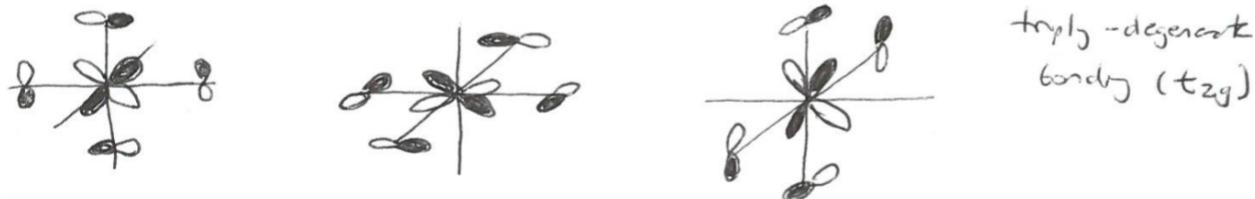
Need to involve some $3d$ orbitals to form bonds to 6 ligands – use $3d_{z^2}$ and $3d_{x^2-y^2}$ since these are equivalent in O_h symmetry.

doubly – degenerate
bonding (e_g)

The MO diagram is:
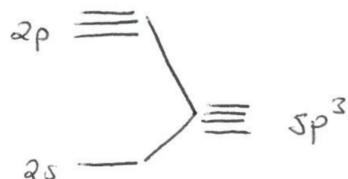
If the ligands also have p orbitals, then overlap with the d_{xy}, d_{xz}, and d_{yz} AOs on the S would generate π-bonding MOs.

triply-degenerate
bonding (t_{2g})

2.8   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.
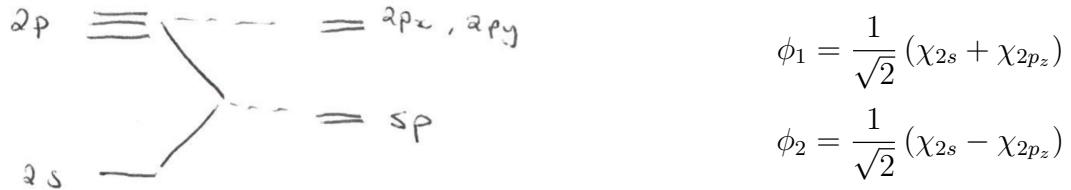
$$\phi_1 = \frac{1}{2}\left(\chi_{2s} + \chi_{2p_x} + \chi_{2p_y} + \chi_{2p_z}\right)$$

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

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

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

Similarly, for the BeH$_2$ example, we could mix the Be $2s$ and $2p_z$ AOs to give 2 equivalent sp hybrid orbitals, with each forming a bond to a H $1s$ AO.

$$\phi_1 = \frac{1}{\sqrt{2}}\left(\chi_{2s} + \chi_{2p_z}\right)$$

$$\phi_2 = \frac{1}{\sqrt{2}}\left(\chi_{2s} - \chi_{2p_z}\right)$$

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

$$\int \phi_i'\phi_j'd\tau = \delta_{ij}$$

$$\int \left(\sum_m a_{im}\phi_m\right)\left(\sum_n a_{jn}\phi_n\right)d\tau = \delta_{ij}$$

$$\sum_m\sum_n a_{im}a_{jn}\int \phi_m\phi_n d\tau = \delta_{ij}$$

$$\sum_m\sum_n a_{im}a_{jn}\delta_{mn} = \delta_{ij}$$

$$\sum_n a_{in}a_{jn} = \delta_{ij}$$

In matrix multiplication, the product **AA** 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).
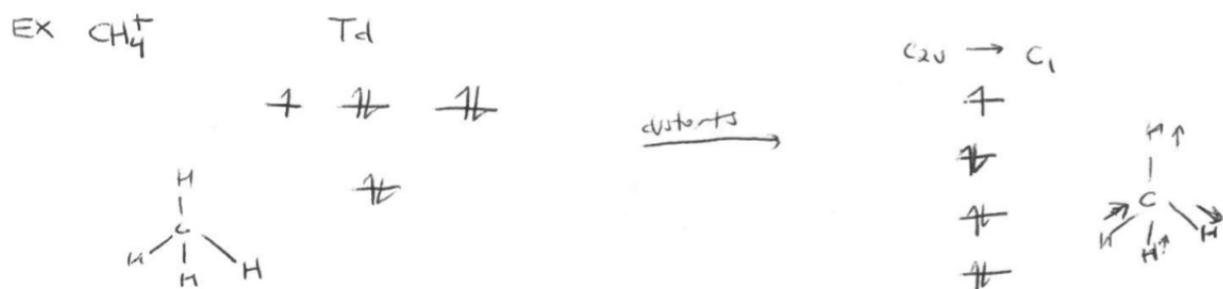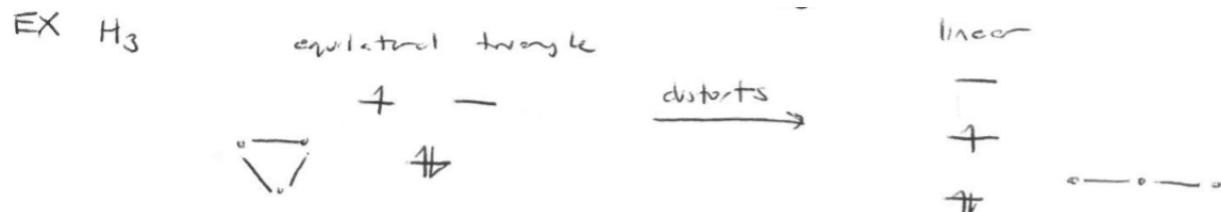
2.9   Jahn-Teller Distortions

The total electron density of a filled (or half-filled) set of degenerate orbitals has the same symmetry as the nuclear framework.

EX. the filled p-shell for a noble-gas atom has spherical symmetry

EX. 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.

EX H_3

equilateral triangle   linear

EX CH_4^+ Td

Chapter 3

Quantitative MO Theories

3.1   Hückel Theory

This applies to conjugated polyenes and arenes. Treat the π-electrons as moving in a fixed effective potential from the σ-bonding framework. π-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 β (resonance integral)

α and β are both negative. β is assigned the empirical value of -0.75 eV = -17 kcal/mol.

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

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

where χ_1 and χ_2 are the $2p_z$ orbitals of each carbon.

The secular determinant is:

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

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 $E = \alpha + \beta$,

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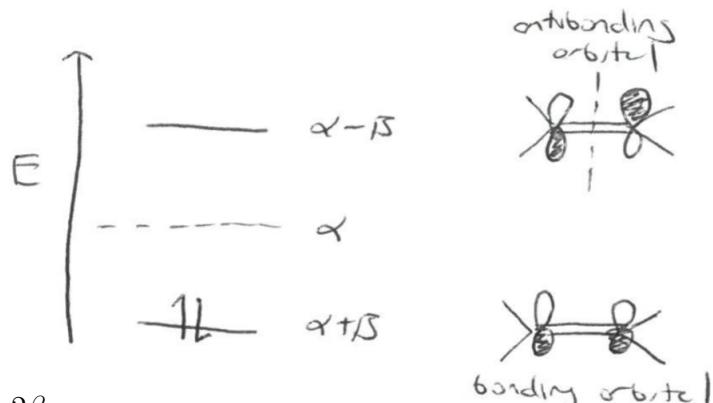
$$c_1 = c_2$$

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 π-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 β 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
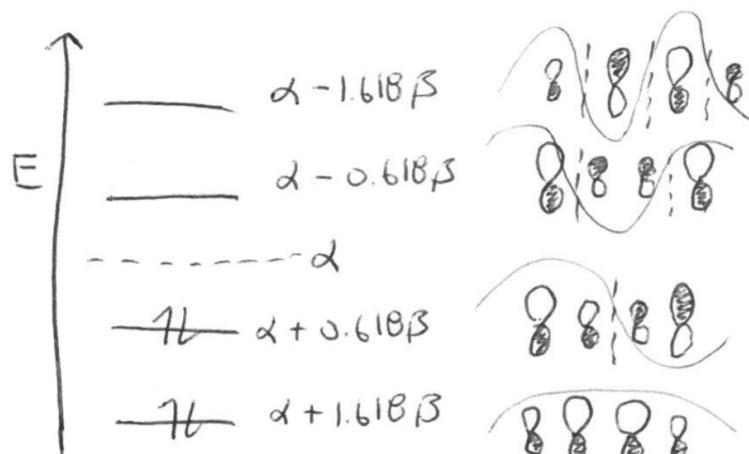
$$x^4 - 3x^2 + 1 = 0$$
$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$
$$x = \pm \left(\frac{3 \pm \sqrt{5}}{2} \right)^{1/2}$$
$$E = \alpha \pm \left(\frac{3 \pm \sqrt{5}}{2} \right)^{1/2} \beta$$

The energy-level diagram is:

$$\phi_4 = a\chi_1 - b\chi_2 + b\chi_3 - a\chi_4$$
$$\phi_3 = b\chi_1 - a\chi_2 - a\chi_3 + b\chi_4$$
$$\phi_2 = b\chi_1 + a\chi_2 - a\chi_3 - b\chi_4$$
$$\phi_1 = a\chi_1 + b\chi_2 + b\chi_3 + a\chi_4$$

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

The total π-electronic energy is $4\alpha + 2\sqrt{5}\beta$. This is lower than the sum of two unconjugated π-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 π-conjugation in butadiene.

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

$$
\phi_n = \sum_{i=1}^{6} c_{in}\chi_i
$$
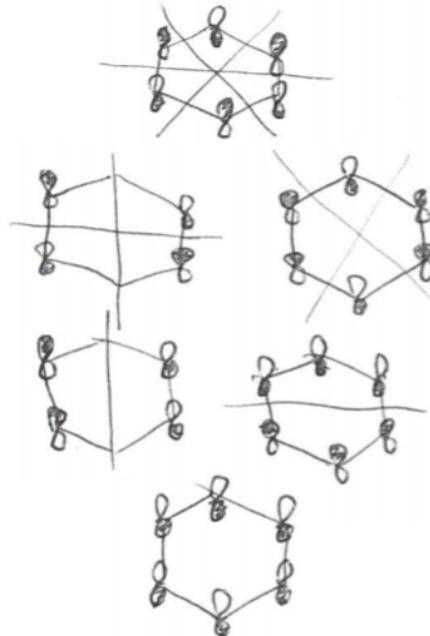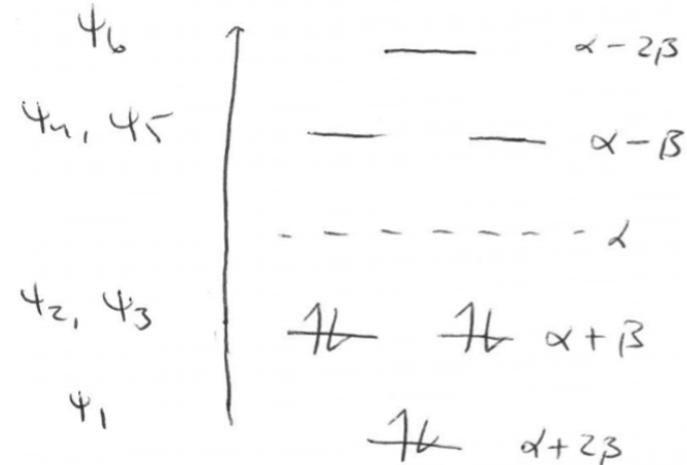
The secular determinant is

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

The six roots are

$$
\phi_1 = \frac{1}{\sqrt{6}}(\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6)
$$

$$
E_1 = \alpha + 2\beta
$$

$$
\phi_2 = \frac{1}{2}(\chi_2 + \chi_3 - \chi_5 - \chi_6)
$$

$$
E_2 = E_3 = \alpha + \beta
$$

$$
\phi_3 = \frac{1}{\sqrt{3}}\left(\chi_1 + \frac{\chi_2}{2} - \frac{\chi_3}{2} - \chi_4 - \frac{\chi_5}{2} + \frac{\chi_6}{2}\right)
$$

$$
E_4 = E_5 = \alpha - \beta
$$

$$
\phi_4 = \frac{1}{2}(\chi_2 - \chi_3 + \chi_5 - \chi_6)
$$

$$
\phi_5 = \frac{1}{\sqrt{3}}\left(\chi_1 - \frac{\chi_2}{2} - \frac{\chi_3}{2} + \chi_4 - \frac{\chi_5}{2} - \frac{\chi_6}{2}\right)
$$

$$
E_6 = \alpha - 2\beta
$$

$$
\phi_6 = \frac{1}{\sqrt{6}}(\chi_1 - \chi_2 + \chi_3 - \chi_4 + \chi_5 - \chi_6)
$$

The energy-level diagram is:

The total π-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 π-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 π-bond. The total $\sigma + \pi$ bond order for the C-C bond is 2.

EX. Benzene

$$P_{12} = 2\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + 2\,(0)\left(\frac{1}{2}\right) + 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{2\sqrt{3}}\right) = \frac{1}{3} + \frac{1}{3} = \frac{2}{3}$$
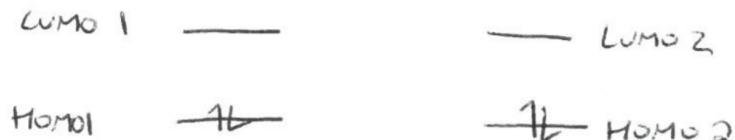
$$P_{23} = 2\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + 2\left(\frac{1}{2}\right)\left(\frac{1}{2}\right) - 2\left(\frac{1}{2\sqrt{3}}\right)\left(\frac{1}{2\sqrt{3}}\right) = \frac{1}{3} + \frac{1}{2} - \frac{1}{6} = \frac{2}{3}$$

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.
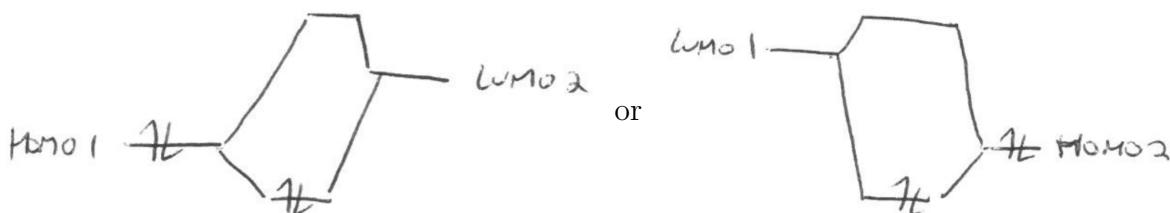
If the orbital symmetries are such that

- HOMO$_1$ overlaps HOMO$_2$, then the reaction is symmetry forbidden and has a high barrier
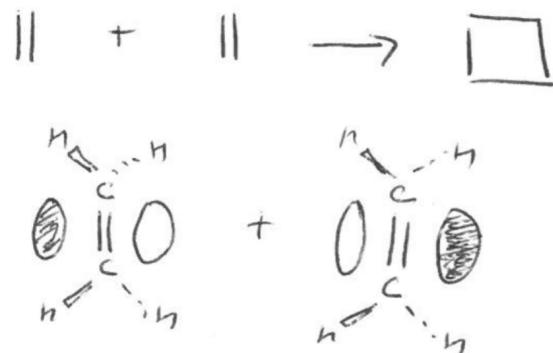
2-orbital, 4-e^- interactions are destabilizing

- HOMO$_1$ overlaps LUMO$_2$ (or vice versa), then the reactions is symmetry allowed and has a low barrier.

or
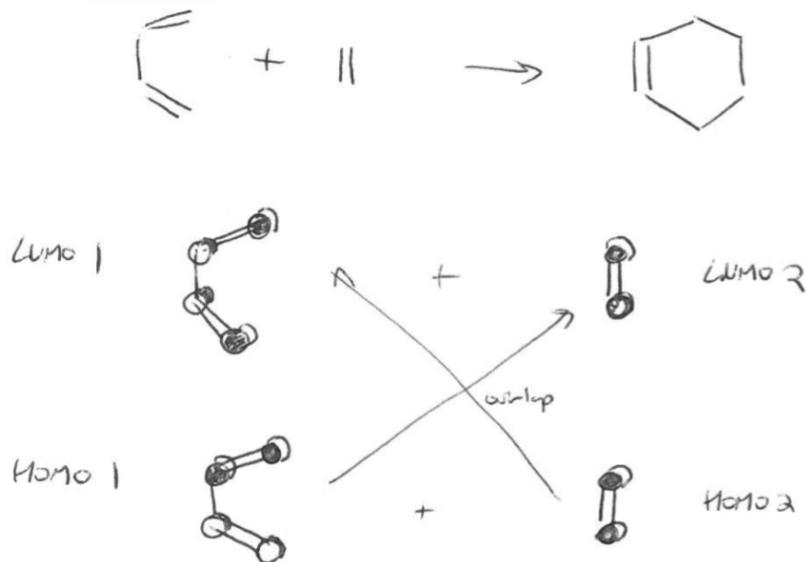
EX. Ethylene dimerization to cyclobutane

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.

3.2 Extended Hückel Theory

This methods 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 ζ (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

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

called the Wolfsberg-Helmholz-Hoffmann formula. K is a constant with empirically determined value of $K = 1.75$. This formula ensures that $H_{ij} \to 0$ as $S_{ij} \to 0$ and the atoms are non-interacting.
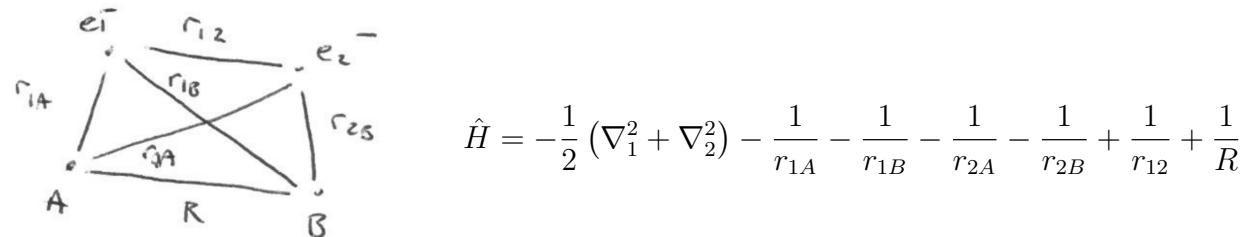
The MO energies are then evaluated computationally from the secular determinant.

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

3.3   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

$$\hat{H} = -\frac{1}{2} \left(\nabla_1^2 + \nabla_2^2 \right) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}$$

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 H$_2^+$, the bonding and anti-bonding orbitals were

$$\phi_- = \frac{1}{\sqrt{2(1-S)}} (\chi_A - \chi_B)$$

$$\phi_+ = \frac{1}{\sqrt{2(1+S)}} (\chi_A + \chi_B)$$

$$S = \int \chi_A \chi_B d\tau$$
$$= \langle \chi_A | \chi_B \rangle$$
is the overlap integral

For 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.

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

$$= \frac{1}{2(1+S)} [\chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2) + \chi_A(1)\chi_A(2) + \chi_B(1)\chi_B(2)]$$

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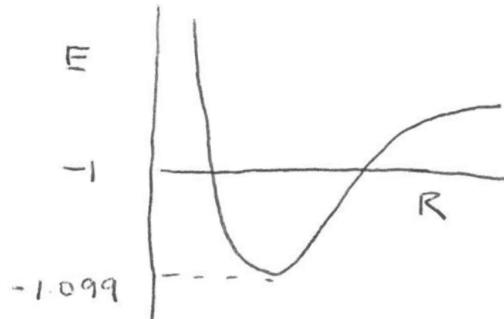
$$
\begin{aligned}
j' &= \int \frac{1}{r_B}\chi_A^2 d\mathbf{r} = \int \frac{1}{r_A}\chi_B^2 d\mathbf{r} \\
k' &= \int \frac{1}{r_A}\chi_A\chi_B d\mathbf{r} = \int \frac{1}{r_B}\chi_A\chi_B d\mathbf{r}
\end{aligned}
$$

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 ~ 2 eV)

There are two reasons for this:
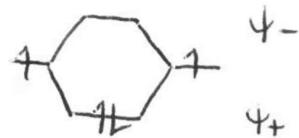
- the basis set is incomplete (only $1s$ orbital)

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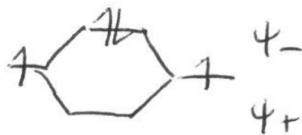
In the dissociation limit, the wavefunction should consist only of the covalent terms. This can be corrected by including more Slater determinants (or electronic configurations) in the wavefunction.

3.4 Configuration Interaction for H_2

CI is an extension of MO theory to include excited-state electronic configurations in the wavefunction. For H_2

ground electronic state, paired electrons in ϕ_+ (bonding MO)

excited electronic state, paired electrons in ϕ_- (anti-bonding MO)
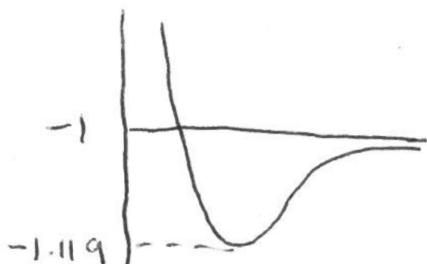
Write the wavefunction as a sum of Slater determinants with variable coefficients (the CI coefficients) to be optimized.

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

$$= [c_1\phi_+(1)\phi_+(2) + c_2\phi_-(1)\phi_-(2)] \cdot \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

Considering only the spatial part

$$\psi = \frac{c_1}{2(1+S)} [\chi_A(1) + \chi_B(1)] [\chi_A(2) + \chi_B(2)] + \frac{c_2}{2(1-S)} [\chi_A(1) - \chi_B(1)] [\chi_A(2) - \chi_B(2)]$$

$$= \frac{c_1(1-S) - c_2(1+S)}{2(1+S)(1-S)} [\chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2)] +$$

$$\frac{c_1(1-S) + c_2(1+S)}{2(1+S)(1-S)} [\chi_A(1)\chi_A(2) + \chi_B(1)\chi_B(2)]$$

$$= c_1'\psi_{\text{covalent}} + c_2'\psi_{\text{ionic}}$$

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 ~ 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   ⥮ ⥮ + ⥮ ⥮   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".
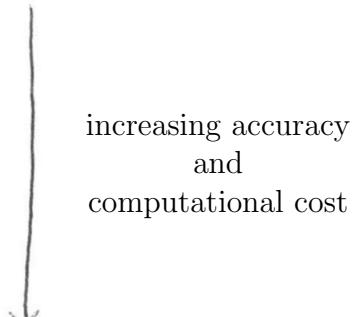
Chapter 4

Introduction to Quantum-Chemical Calculations

4.1 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, ρ, 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.

4.2 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
- 6-31G*
- 6-31+G**
- 6-311+G(2d,2p)
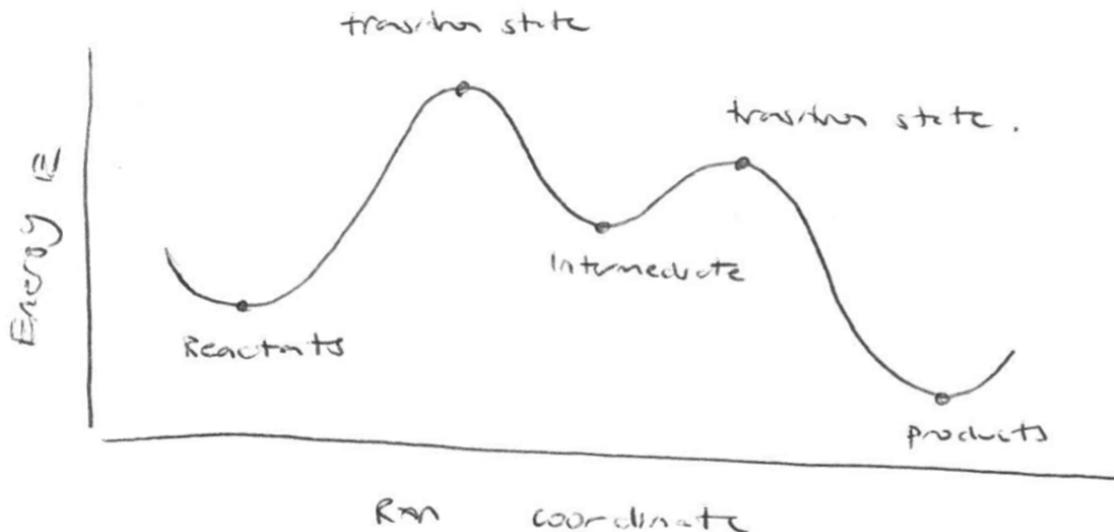
Dunning-style
- cc-pVDZ
- aug-cc-pVTZ
- aug-cc-pVQZ

increasing accuracy
and
computational cost

4.3 Potential Energy Surfaces

The Born-Oppenheimer approximation allows construction of PES.

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

$$E = E(\mathbf{q_1}, \mathbf{q_2}, \mathbf{q_3}, \ldots, \mathbf{q_N})$$

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).

4.4 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) calculated the vibrational frequencies (2nd derivatives of the energy). 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.

4.5 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.

4.6 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_2O
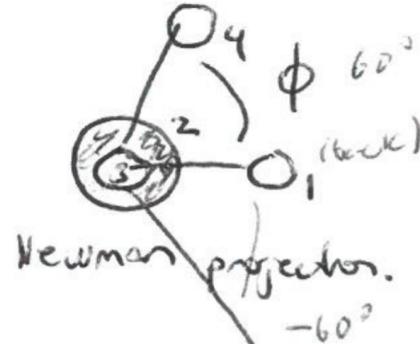
```
O
H   1   1.0
H   1   1.0   2   105.0
```

EX. NH_3

```
N
H   1   1.0
H   1   1.0   2   109.5
H   1   1.0   2   109.5   3   120.0
```

EX. CH_4

```
C
H   1   1.1
H   1   1.1   2   109.5
H   1   1.1   2   109.5   3   120.0
H   1   1.1   2   109.5   3   -120.0
```
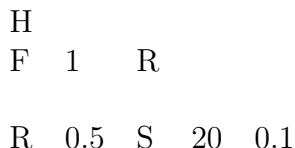
Note that angles cannot be 0° or 180°, so a dummy atom, X, is used in linear molecules.

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
```

4.7   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.
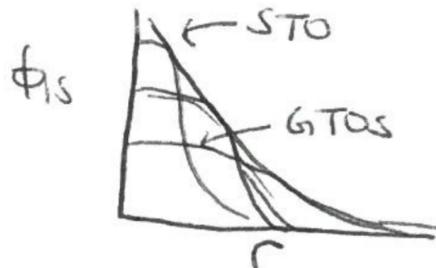
Gaussian basis functions have the form

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

where the origin of the coordinate system is the atomic nucleus. N is a normalization constant, α is a positive exponent, and i, j, k are whole numbers such that

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

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

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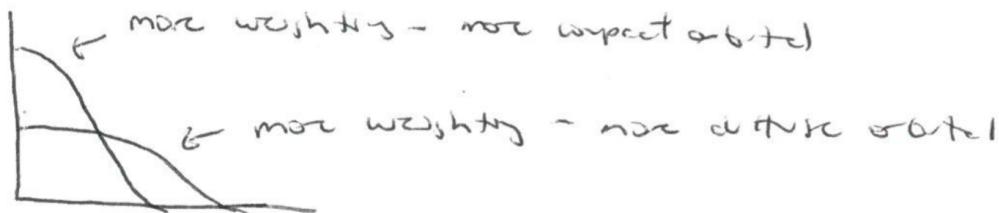
where each STO is represented by n (usually 3 or 6) Gaussians.

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

$$\text{core} \longrightarrow 6 - 31G \longleftarrow \text{valence}$$

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-ζ 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 to all elements except the s-block of the periodic table. 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-ζ 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-ζ, 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. Diffuse functions are also important for H-bonding and other intermolecular interactions.

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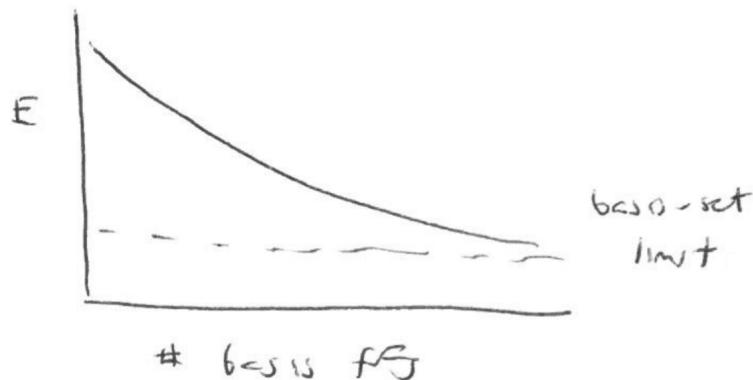
STO-3G   5 basis functions (1 per AO)
$3 \times 5 = 15$ primitive Gaussians

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.
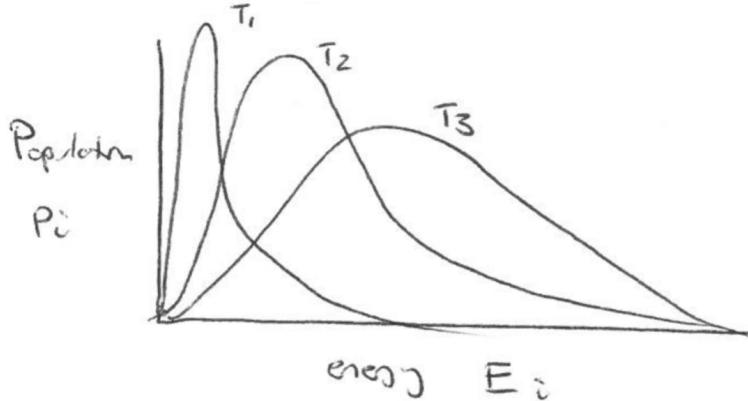
4.8   Introduction to Statistical Mechanics

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 thermo-dynamics.

At zero Kelvin, all systems will exist 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 ith 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

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

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

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

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

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

$$
\begin{aligned}
U &= E_0 + \frac{NkT^2}{Q}\left(\frac{\partial Q}{\partial T}\right) \\
&= E_0 + NkT^2 \left(\frac{h\nu}{kT^2} \frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}\right) \\
&= E_0 + \frac{Nh\nu}{e^{h\nu/kT} - 1}
\end{aligned}
$$
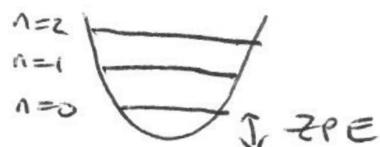
so the correction to the energy from thermal vibrations is

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

4.9   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

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

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

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 5

Electronic-Structure Methods

5.1 Hartree-Fock Theory

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

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1 & \phi_2 & \cdots & \phi_N \end{vmatrix}$$

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 $e^- \text{-} e^-$ 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:

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

which is a difference of Coulomb and exchange integrals.

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

To find the orthonormal set of spin orbitals, ϕ_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, $\hat{K}_i$ is the exchange operator, and the ε_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 orbitals (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 HF energy (and orbitals) are converged.

The HF orbital energies are

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

So the sum of orbital energies is

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

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

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

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 ϕ_i is the negative of the orbital energy, ε_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.

5.2   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 $N_\circ$ basis functions, χ_i. These can be thought of as AOs, but are usually Gaussian functions. Express each MO, ϕ_n, in terms of these basis functions

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

This expression is substituted into the Fock equations to give

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

To solve for the orbitals, ϕ_n, we need only optimize the coefficients.

Multiply through by an arbitrary basis function, χ_i, and integrate to give

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

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,

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

and this is a set of $N_\circ$ equations in $N_\circ$ 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.
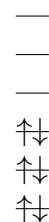
5.3 Configuration Interaction

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

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

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

$$\psi_\circ = \begin{vmatrix} \phi_1 & \phi_2 & \cdots & \phi_a & \phi_b & \cdots & \phi_n \end{vmatrix}$$

A singly-excited determinant is a wavefunction where a single electron has been excited from the occupied spin orbital ϕ_a to the virtual spin orbital ϕ_p.

$$\psi_a^p = \begin{vmatrix} \phi_1 & \phi_2 & \cdots & \phi_p & \phi_b & \cdots & \phi_n \end{vmatrix}$$

A doubly-excited determinant is a wavefunction where two electrons have been excited from occupied spin orbitals ϕ_a and ϕ_b to virtual spin orbitals ϕ_p and ϕ_q.

$$\psi_{ab}^{pq} = \begin{vmatrix} \phi_1 & \phi_2 & \cdots & \phi_p & \phi_q & \cdots & \phi_n \end{vmatrix}$$
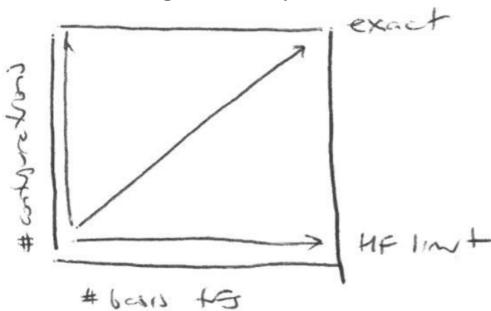
Higher excitations can be generated in the same way.

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

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

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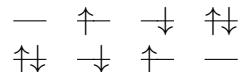
CI calculations are very computationally demanding – in practise, only a limited number of configurations, differing from $\psi_\circ$ by no more than a few spin orbitals are used. The most common is CISD (single and double excitations only).

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. He$_2$ with CISD

$$\begin{array}{cccc} \underline{\quad} & \underline{\uparrow\quad} & \underline{\quad\downarrow} & \underline{\uparrow\downarrow} \\ \underline{\uparrow\downarrow} & \underline{\quad\downarrow} & \underline{\uparrow\quad} & \underline{\quad} \end{array}$$
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 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.

5.4   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, ψ_n°. 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 λ 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

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

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

Substituting into the SE gives

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

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

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

To order λ^1: $\hat{H}^\circ \psi_n^1 + \hat{H}' \psi_n^\circ = E_n^\circ \psi_n^1 + E_n^1 \psi_n^\circ$ (∗)

To order λ^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 ψ_n° 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 ψ_ℓ° 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 ψ_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-λ^2 equation, multiply through by ψ_n° 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

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

5.5   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

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

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.

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

The ground-state energy, to first order is:

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

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 ψ_{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

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

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".

5.6   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

$$
\hat{T} = \hat{T}_{1} + \hat{T}_{2} + \hat{T}_{3} + \ldots \hat{T}_{N}
$$

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

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

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,

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

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

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

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).

5.7 Density-Functional Theory (DFT)

Given the number of electrons (N), then the external potential $V(\mathbf{r})$ (from the nuclei) generates the ground-state wavefunction, ψ, 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 $V \to \hat{H} \to \psi \to E$ (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 $V \to \psi \to \rho$. Hohenberg and Kohn showed that this mapping is one-to-one, so it is reversible and $\rho \to V \to \psi \to E$ and all properties are unique functions of the electron density.

In particular, the kinetic and potential energies are functionals of ρ:

kinetic: $$\left\langle \psi \left| -\frac{1}{2} \sum_i \nabla_i^2 \right| \psi \right\rangle = T(\rho)$$

e^--e^-: $$\left\langle \psi \left| \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \right| \psi \right\rangle = V_{ee}(\rho)$$

e^--nuc: $$\langle \psi | V | \psi \rangle = \int V \rho(\mathbf{r}) d\mathbf{r}$$

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

Consider a system of "non-interacting" electrons having the same density as the real system. The orbitals will satisfy the simple Schödinger equation

$$-\frac{1}{2} \nabla^2 \psi_i + V_\circ \psi_i = \varepsilon_\circ \psi_i$$

where $V_\circ$ is the non-interacting potential and

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

The kinetic energy of the non-interacting system

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

is likely a good approximation to the real kinetic energy.

We write the total energy as

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

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

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

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

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

where $V_{el} = \int \frac{\rho(\mathbf{r_2})}{r_{12}} d\mathbf{r_2}$ is the Coulomb potential and $\frac{\delta E_{\text{XC}}}{\delta\rho}$ 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. Density-functional methods are usually classified according to Perdew's ladder.

- LDA – the local density approximation. E_{XC} depends only on ρ

$$E_{\text{X}}^{\text{LDA}} = c_{\text{X}} \int \rho^{4/3} d\mathbf{r}$$

  There is no closed-form expression for the correlation energy. This approximation strongly overbinds chemical systems (to roughly the same extent that HF underbinds).

- GGA – generalized gradient approximation. E_{XC} depends on ρ and $\chi = |\nabla\rho|/\rho^{4/3}$ (reduced density gradient). Commonly,

$$E_{\text{X}}^{\text{GGA}} = E_{\text{X}}^{\text{LDA}} + \int F\left(\rho, \frac{|\nabla\rho|}{\rho^{4/3}}\right) d\mathbf{r}$$

  The extra term lowers the energy beyond the LDA and gives improved bond energies (errors $\sim$ 10 kcal/mol). The most common GGAs are BLYP (in chemistry) and PBE (in physics).

- meta-GGA – energies depend on ρ, $\nabla\rho$, $\nabla^2\rho$, and $\tau = \sum_i |\nabla\psi_i|^2$, which is the kinetic-energy density. These typically involve many empirical parameters and offer little advantage over GGAs. SCAN is a meta-GGA with growing popularity in physics.

- hybrid functionals – include a mixture of density-functional and Hartree-Fock exchange.

$$E_{\mathrm{X}} = cE_{\mathrm{X}}^{\mathrm{HF}} + (1-c)E_{\mathrm{X}}^{\mathrm{GGA}}$$

  Proposed in 1995 by Axel Becke, these 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).

- range-separated hybrid functionals – also include a mixture of HF and DFT, now dependent on the e^--e^- interaction range 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-wPBE (chemistry) and HSE (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.

Chapter 6

Summary and Review

To model chemical bonding using molecular-orbital theory:

- Construct molecular orbital orbitals (MOs) as linear combinations of $(s, p, d, \ldots)$ 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.

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

virtual. $\Big\{ \begin{array}{l} \underline{} \\ \underline{} \end{array}$

occupied $\Big\{ \begin{array}{ll} \text{⥮} & \leftarrow \phi_N \alpha, \\ \vdots & \phi_N \beta. \\ \text{⥮} & \leftarrow \phi_1 \alpha, \\ & \phi_1 \beta \end{array}$

- 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.

- In real calculations, Gaussian basis functions are used to construct the MOs; increasing the basis-set size increases the accuracy.

- In the simplest electronic-structure method, Hartree-Fock theory, the MO coefficients are optimized by iteratively solving the Fock equations

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

where the Fock operator is

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

Self-consistent solution is required since treatment of the $e^- \text{-} e^-$ interactions involves evaluation of Coulomb and exchange integrals that depend on all other MOs in the molecule.