

CHEM 551: Quantum Chemistry II

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1 Born-Oppenheimer approximation

1.1 Transformation into atomic units

Recall that Schrodinger's equation is given by

$$\left(\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \right) \Psi(r) = E\Psi(r)$$

Also note that the dimension of ∇^2 is $1/\text{distance}^2$. We wish to transform Schrodinger's equation into atomic units. We will use the change of variables

$$(x, y, z) \rightarrow (\lambda x', \lambda y', \lambda z') \quad \text{and} \quad \Psi(r) \rightarrow \Psi'(r')$$

The canonical method is to choose λ such that $\frac{\hbar^2}{m_e \lambda^2} = \frac{e^2}{4\pi\epsilon_0 \lambda}$, which gives us $\lambda = \frac{\hbar^2}{m_e} \frac{4\pi\epsilon_0}{e^2} = a_0$. Also, we can write $E = E'/E_h$, where the atomic unit of energy E_h is called "1 hartree" and is equal to $\frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0}$. Now, if we remove all the primes, we can write Schrodinger's equation in atomic units:

$$\left(-\frac{1}{2} \nabla^2 - \frac{1}{r} \right) \Psi(r) = E\Psi(r)$$

We have successfully non-dimensionalized Schrodinger's equation.

1.2 The adiabatic and Born-Oppenheimer approximations

Consider that the wavefunction is a function of each electronic coordinate and each nuclear coordinate: $\Psi(r_1, \dots, r_N, R_1, \dots, R_M)$. For the benzene molecule, C_6H_6 , which contains 54 electrons plus nuclei, this means that the wavefunction is a function of 164 variables! Now consider the form of the Hamiltonian

$$\hat{H} = T_e + T_n + V_{ee} + V_{ne} + V_{nn}$$

For benzene, this Hamiltonian will be the sum of around a thousand terms. (I'll start neglecting hats on the operators that aren't \hat{H} just for convenience.) This makes direct computation very difficult. We can do some transformations:

1. Consider the ratio of proton mass to electron mass $m_p/m_e \simeq 2800$. Clearly, nuclei are much heavier; hence they move much slower than electrons. We can neglect the translation and rotation of these nuclei and transform our Hamiltonian into center of mass coordinates. This will introduce a mass polarization term $T_{mp} = \frac{1}{M} \nabla_{ei} \nabla_{ej}$, so our overall Hamiltonian is

$$\hat{H} = T_e + T_n + V_{ee} + V_{ne} + V_{nn} + T_{mp}$$

We can consider just the electronic Hamiltonian $H_e = T_e + V_{ee} + V_{ne} + V_{nn}$ which is independent of nuclear momentum.

2. Assume that

$$H_e(R, r) \psi_{ei}(R, r) = E_{ei} \psi_{ei}(R, r), \quad i = 1, 2, \dots$$

This has an infinite number of solutions. Note that H_e is Hermitian, so these electronic wavefunctions can be considered to be orthonormal. Let's expand ψ_{tot} as a linear combination of each ψ_{ei} :

$$\psi_{tot} = \sum_{i=1}^{\infty} \psi_{ei}(R, r) \psi_{ni}(R)$$

Note that the nuclear wavefunction $\psi_{ni}(R)$ acts as the linear combination coefficients. We can insert this expression into $\hat{H} \psi_{tot} = E_{tot} \psi_{tot}$ and abbreviate $T_n = \nabla_n^2$ to obtain

$$\sum_{i=1}^{\infty} (T_n + H_e + T_{mp}) \psi_{ni} \psi_{ei} = E_{tot} \sum_{i=1}^{\infty} \psi_{ni} \psi_{ei}$$

$$(\nabla_n^2 + H_e + T_{\text{mp}}) \psi_{ni} \psi_{ei} = [(\nabla_n^2 \psi_{ni}) \psi_{ei} + 2(\nabla_n \psi_{ni})(\nabla_n \psi_{ei}) + \psi_{ni}(\nabla_n^2 \psi_{ei})] + \psi_{ni} E_i \psi_{ei} + \psi_{ni} T_{\text{mp}} \psi_{ei}$$

3. Let's pre-operate on this expression with $\int d\tau_e \psi_{ej}^* = \langle \psi_{ej} |$ to obtain

$$\begin{aligned} \sum_{i=1}^{\infty} [\langle \psi_{ej} | \psi_{ei} \rangle (\nabla_n^2 \psi_{ni}) + 2(\nabla_n \psi_{ni}) \langle \psi_{ej} | \nabla_n | \psi_{ei} \rangle + \psi_{ni} \langle \psi_{ej} | \nabla_n^2 | \psi_{ei} \rangle + \psi_{ni} E_i \langle \psi_{ej} | \psi_{ei} \rangle + \psi_{ni} \langle \psi_{ej} | T_{\text{mp}} | \psi_{ei} \rangle] \\ = E_{\text{tot}} \sum_{i=1}^{\infty} \psi_{ni} \delta_{ij} = E_{\text{tot}} \psi_{nj} \\ \Rightarrow \nabla_n^2 \psi_{nj} + E_j \psi_{nj} + \sum_{i=1}^{\infty} [2(\nabla_n \psi_{ni}) \langle \psi_{ej} | \nabla_n | \psi_{ei} \rangle + \langle \psi_{ej} | \nabla_n^2 | \psi_{ei} \rangle \psi_{ni} + \langle \psi_{ej} | T_{\text{mp}} | \psi_{ei} \rangle \psi_{ni}] = E_{\text{tot}} \psi_{nj} \end{aligned}$$

Consider the terms in the summation. $2(\nabla_n \psi_{ni}) \langle \psi_{ej} | \nabla_n | \psi_{ei} \rangle$ represents 1st order adiabatic coupling, $\langle \psi_{ej} | \nabla_n^2 | \psi_{ei} \rangle \psi_{ni}$ represents 2nd order adiabatic coupling, and $\langle \psi_{ej} | T_{\text{mp}} | \psi_{ei} \rangle \psi_{ni}$ represents mass polarization. We can make certain assumptions:

- (a) Neglect the mass polarization term. It contains the nuclear mass in the denominator, so it is small.
- (b) Neglect the off-diagonal ($i \neq j$) elements in the adiabatic coupling terms.
- (c) Neglect the on-diagonal ($i = j$) elements in the adiabatic coupling terms.

The *adiabatic approximation* refers to when we neglect mass polarization and the $i \neq j$ terms. Note that the on-diagonal elements of the 1st order adiabatic coupling are zero. Apply the adiabatic approximation to obtain

$$\begin{aligned} T_n \psi_{nj} + E_j(R) \psi_{nj} + \langle \psi_{ej} | T_n | \psi_{ej} \rangle \psi_{nj} &= E_{\text{tot}} \psi_{nj} \\ \Rightarrow [T_n + E_j(R)] + \langle \psi_{ej} | T_n | \psi_{ej} \rangle \psi_{nj} &= E_{\text{tot}} \psi_{nj} \end{aligned}$$

In this, $\langle \psi_{ej} | T_n | \psi_{ej} \rangle$ is called the *diagonal correction*. In the Born-Oppenheimer approximation, we also neglect the diagonal correction. We have arrived at three rather important equations:

$$[T_n + E_j(R)] \psi_{nj} = E_{\text{tot}} \psi_{nj} \quad (\text{nuclear Schrodinger equation})$$

$$[T_e + V_{ne} + V_{ee} + V_{nn}] \psi_{ej} = E_j(R) \psi_{ej} \quad (\text{electronic Schrodinger equation})$$

$$E_j(R) = \langle \psi_{ej} | \hat{H}_e | \psi_{ej} \rangle$$

It is important to note the cases when the Born-Oppenheimer approximation fails, some of which are:

- in scattering experiments, where nuclei move quite rapidly
- when two potential energy surfaces are close, yielding an “avoided crossing”; this is related to the Jahn-Teller effect

2 Internal coordinates

Omitted.

3 Hartree-Fock

3.1 Slater determinants

Recall that a wavefunction is a *state* function. We may abbreviate a wavefunction by writing $\Psi(1, 2, \dots, N)$ where each integer represents the spatial and spin coordinates for a particular electron. Consider a wavefunction of two electrons $\Psi(1, 2)$. We can expand this in a complete orthonormal set of one-electron wavefunctions for electron 1 (since they form a complete set).

$$\Psi(1, 2) = \sum_{k_1}^{\infty} c_{k_1}(2) \psi_{k_1}(1)$$

We can do the same for c_{k_1} in terms of ψ_{k_2} as well.

$$\Psi(1, 2) = \sum_{k_2=1}^{\infty} \sum_{k_1=1}^{\infty} c_{k_1, k_2} \psi_{k_1}(1) \psi_{k_2}(2)$$

The generalized case for N electrons follows trivially. Note that the product of multiple one-electron wavefunctions $\psi_{k_1}(1) \psi_{k_2}(2) \dots \psi_{k_N}(N)$ is called a *Hartree product*. Let us define the permutation operator \hat{P}_{12} :

$$\hat{P}_{12} \Psi(1, 2) = \Psi(2, 1)$$

It switches electrons 1 and 2. Note that this allows us to describe the Pauli exclusion principle easily, which is given by

$$\Psi(2, 1) = -\Psi(1, 2)$$

A wavefunction that changes sign upon interchange of any two electrons is called *antisymmetric*, while one which retains the original sign is called *symmetric*. It turns out that we can easily write antisymmetric wavefunctions as determinants which are called *Slater determinants*. I won't go into detail as these should've been covered *ad nauseam* in previous courses. The antisymmetrization operator \hat{A} will act on a product of one-electron wavefunctions $\Pi = \psi_{k_1}(1) \dots \psi_{k_N}(N)$ to produce a determinantal wavefunction D_{k_1, \dots, k_N} . It is defined as

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_{p=1}^{N!} \chi(\hat{P}_p) \hat{P}_p$$

where $\chi(\hat{P}_p)$ is called the *character* of permutation p . It is equal to +1 if the permutation is expressed as an even number of interchanges and -1 if the permutation is expressed as an odd number of interchanges.

3.2 Hartree-Fock equations

Recall that we wish to minimize the energy $E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$ where $\Psi = \hat{A}\Pi$. Note that $\hat{A}^\dagger = \hat{A}$, $[\hat{A}, \hat{H}] = 0$, and $\hat{A}^2 = (N!/\sqrt{N!})\hat{A}$. Then we have

$$\begin{aligned} E &= \langle \Psi | \hat{H} | \Psi \rangle = \langle \hat{A}\Pi | \hat{H} | \hat{A}\Pi \rangle = \langle \Pi | \hat{A}^\dagger \hat{H} \hat{A} | \Pi \rangle = \langle \Pi | \hat{A} \hat{H} \hat{A} | \Pi \rangle = \langle \Pi | \hat{H} \hat{A} \hat{A} | \Pi \rangle = \sqrt{N!} \langle \Pi | \hat{H} | \hat{A}\Pi \rangle \\ &= \sum_{p=1}^{N!} \chi(\hat{P}_p) \langle \Pi | \hat{H} | \hat{P}_p \Pi \rangle \end{aligned}$$

To obtain an expression for \hat{H} , consider the Hamiltonian expressed in atomic units, $\hat{H} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn}$. The first two terms $\hat{T}_e + \hat{V}_{ne}$ are 1-electron operators; \hat{V}_{ee} is a 2-electron operator. Finally, \hat{V}_{nn} is a constant (a 0-electron operator). These operators are expressed as

$$\begin{aligned}
\hat{T}_e &= -\frac{1}{2} \sum_i \nabla_i^2 \\
\hat{V}_{ne} &= - \sum_i \sum_a \frac{Z_a}{|R_a - r_i|} \\
\hat{V}_{ee} &= + \sum_i \sum_{j>i} \frac{1}{|r_i - r_j|} \\
\hat{V}_{nn} &= + \sum_a \sum_{b>a} \frac{Z_a Z_b}{|R_a - R_b|}
\end{aligned}$$

In terms of a one-electron operator $\hat{h}(i)$ that includes electron kinetic energy and electron-nuclear attraction and a two-electron operator $\hat{g}(i, j)$ that represents Coulombic electron correlation, we have

$$\hat{H} = \sum_i \hat{h}(i) + \sum_i \sum_{j>i} \hat{g}(i, j) + \hat{V}_{nn}$$

Now, we have to evaluate the expression $\langle \Pi | \hat{H} | \hat{P}_p \Pi \rangle$. Let's do this part-by-part:

1. Considering the 0-electron term:

$$\langle \Psi | \hat{V}_{nn} | \Psi \rangle = V_{nn} \langle \Psi | \Psi \rangle = V_{nn} \quad (\text{constant})$$

2. Considering the 1-electron term:

- (a) Considering the case where \hat{P}_p is the identity operator:

$$\begin{aligned}
\langle \Pi | \hat{h}(i) | \Pi \rangle &= \langle \psi_1(1) \cdots \psi_i(i) \cdots \psi_N(N) | \hat{h}(i) | \psi_1(1) \cdots \psi_i(i) \cdots \psi_N(N) \rangle = \langle \psi_1(1) | \psi_1(1) \rangle \cdots \langle \psi_i(i) | \hat{h}(i) | \psi_i(i) \rangle \cdots \langle \psi_N(N) | \psi_N(N) \rangle \\
&= \langle \psi_i(i) | \hat{h}(i) | \psi_i(i) \rangle = h_i
\end{aligned}$$

where

$$h_i = \int \psi_i^*(r) \left(-\frac{1}{2} \nabla^2 - \sum_a \frac{Z_a}{|R_a - r|} \right) \psi_i(r) d\tau$$

- (b) Considering the case where \hat{P}_p is a two-element swap:

$$\begin{aligned}
\langle \Pi | \hat{h}(i) | \hat{P}_{ij} \Pi \rangle &= \langle \cdots \psi_i(i) \cdots \psi_j(j) \cdots | \hat{h}(i) | \cdots \psi_i(j) \cdots \psi_j(i) \cdots \rangle = \langle \psi_j(j) | \psi_i(j) \rangle \langle \psi_i(i) | \hat{h}(i) | \psi_j(i) \rangle \\
&= 0
\end{aligned}$$

- (c) The term is also equal to 0 for higher character permutations.

3. Considering the 2-electron term:

- (a) Considering the case where \hat{P}_p is the identity operator:

$$\langle \Pi | \hat{g}(i, j) | \Pi \rangle = \langle \psi_i(i) \psi_j(j) | \hat{g}(i, j) | \psi_i(i) \psi_j(j) \rangle$$

This quantity is known as the Coulomb integral J_{ij} , and it is evaluated as

$$\begin{aligned}
J_{ij} &= \int \int \psi_i^*(i) \psi_j^*(j) \frac{1}{|r_i - r_j|} \psi_i(i) \psi_j(j) d\tau_1 d\tau_2 \\
&= \int \int \psi_i^*(i) \psi_i(i) \frac{1}{|r_i - r_j|} \psi_j^*(j) \psi_j(j) d\tau_1 d\tau_2
\end{aligned}$$

where the two wavefunction products can be interpreted to be probability densities.

(b) Considering the case where \hat{P}_p is a two-element swap:

$$\langle \Pi | \hat{g}(i, j) | \hat{P}_{ij} \Pi \rangle = \langle \psi_i(i) \psi_j(j) | \hat{g}(i, j) | \psi_i(j) \psi_j(i) \rangle$$

This quantity is known as the exchange integral K_{ij} . It is a non-classical term.

(c) The term is equal to zero for higher character permutations.

A brief aside: From this point onwards I will use functional notation. A functional is a mapping from a vector space to its underlying scalar field; recall that the function spaces we work with are also vector spaces. Thus, a functional may map a function to a scalar, acting as a *function of a function*. For comparison, an operator is a function between vector (or function) spaces. Formally, the *bra* is a member of the *dual space* of the *ket space*, meaning that it is one of the infinitely many linear functionals that act upon kets.

Consider the energy functional:

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^N h_i + \sum_{i=1}^N \sum_{j>i}^N (J_{ij} - K_{ij}) + V_{nn} = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) + V_{nn}$$

The latter equality holds true because $J_{ii} = K_{ii}$ and $J_{ij} = J_{ji}$. In operator form, this is equivalently

$$E = \sum_{i=1}^N \langle \psi_i | \hat{h}_i | \psi_i \rangle + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \langle \psi_i | \hat{J}_j - \hat{K}_j | \psi_i \rangle + V_{nn}$$

where

$$\begin{aligned} \hat{J}_j &= \langle \psi_j(2) | \hat{g}(1, 2) | \psi_j(2) \rangle | \psi_i(1) \rangle \\ \hat{K}_j &= \langle \psi_j(2) | \hat{g}(1, 2) | \psi_i(2) \rangle | \psi_j(1) \rangle \end{aligned}$$

Note that the two expressions are subtly different.

Now, we wish to minimize $E[\Psi] = E[\psi_1, \psi_2, \dots, \psi_N]$ by varying ψ_i . We will use $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ as our constraint and construct the Lagrange functional

$$L[\psi_1, \dots, \psi_N] = E - \sum_{i,j} \lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij})$$

Suppose that we vary $\langle \psi_i | \rightarrow \langle \psi_i | + \langle \delta \psi_i |$. Then the change in energy δE is given by

$$\begin{aligned} \delta E &= \sum_{i=1}^N \langle \delta \psi_i | \hat{h} | \psi_i \rangle + \frac{1}{2} \sum_{i,j} \langle \delta \psi_i | \hat{J}_j - \hat{K}_j | \psi_i \rangle + \frac{1}{2} \sum_{i,j} \langle \delta \psi_j | \hat{J}_i - \hat{K}_i | \psi_j \rangle \\ &= \sum_{i=1}^N \langle \delta \psi_i | \hat{h} | \psi_i \rangle + \sum \langle \delta \psi_i | \hat{J}_j - \hat{K}_j | \psi_i \rangle \\ &= \sum_{i=1}^N \langle \delta \psi_i | \hat{f} | \psi_i \rangle \end{aligned}$$

where $\hat{f} = \hat{h} + \sum_j (\hat{J}_j - \hat{K}_j)$ and is called the *Fock operator*. The change in the Lagrange functional is then

$$\delta L = \delta E - \sum_{i,j} \lambda_{i,j} \langle \delta \psi_i | \psi_j \rangle = \sum_{i=1}^N \langle \delta \psi_i | \left[\hat{f} | \psi_i \rangle - \sum_{j=1}^N \lambda_{ij} | \psi_j \rangle \right] = 0$$

We can vary ψ_i independently, so the part in the brackets must be equal to 0, so

$$\hat{f} | \psi_i \rangle = \sum_{j=1}^N \lambda_{ij} | \psi_j \rangle$$

This is a set of coupled differential equations for $|\psi_i\rangle$. We may choose a unitary transform such that $\lambda_{ij} = 0$ ($i \neq j$), $\lambda_{ii} = \epsilon_i$, thereby diagonalizing \hat{f} . Thus, we arrive at the Hartree-Fock equations

$$\hat{f}|\psi_i^{\text{HF}}\rangle = \epsilon_i|\psi_i^{\text{HF}}\rangle$$

which is a set of N equations for $|\psi_i^{\text{HF}}\rangle$. Note that

$$\hat{f}(1) = \hat{h}(1) + \sum_{j=1}^N \left(\hat{J}_j - \hat{K}_j \right)$$

The sum forms an “effective potential” calculated with all of the *canonical orbital* functions. $\sum \hat{J}_j$ represents averaged electrostatic repulsion and $-\sum \hat{K}_j$ is the “exchange term”, which accounts for exchange potential due to antisymmetry requirements. This is only relevant for identical-spin electrons. ϵ_i represents the orbital energies.

3.3 Koopman’s theorem

Consider a system containing N electrons total:

$$E_N = \sum_i h_i + \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij}) + V_{\text{nn}}$$

Now suppose we remove 1 electron from orbital k and keep all the other $N - 1$ orbitals frozen. Then,

$$E_{N-1} = \sum_{i \neq k} h_i + \frac{1}{2} \sum_{i \neq k} \sum_{j \neq k} (J_{ij} - K_{ij}) + V_{\text{nn}}$$

$$\begin{aligned} E_N - E_{N-1} &= h_k + \frac{1}{2} \sum_{i=1}^N J_{ik} - \frac{1}{2} \sum_{j=1}^N K_{kj} + \frac{1}{2} \sum_{j=1}^N J_{kj} - \frac{1}{2} \sum_{i=1}^N K_{ik} \\ &= h_k + \frac{1}{2} \sum_{i=1}^N (J_{ik} - K_{ki} + J_{ki} - K_{ik}) \\ &= h_k + \frac{1}{2} \sum_{j=1}^N (J_{jk} - K_{jk}) + \frac{1}{2} \sum_{j=1}^N (J_{jk} - K_{jk}) \\ &= h_k + \sum_{j=1}^N (J_{jk} - K_{kj}) = \epsilon_k \end{aligned}$$

Thus,

$$\epsilon_k = E_N - E_{N-1} = -\text{IE}_k$$

where IE_k is the ionization energy. This is known as *Koopman’s theorem*. Note that $\sum_{k=1}^N \epsilon_k \neq E$ because repulsion is counted twice and it is missing V_{nn} :

$$E = \sum_{k=1}^N \epsilon_k - \frac{1}{2} \sum_{i,j} (J_{ij} - K_{ij}) + V_{\text{nn}}$$

3.4 Self-consistent field method

The overall process is as such:

1. Guess a set of starting functions $\{|\psi_i^{\text{HF}}\rangle\}$.
2. Construct \hat{J} , \hat{K} , \hat{f} .
3. Solve $\hat{f}|\psi_i^{\text{HF}}\rangle = \epsilon_i|\psi_i^{\text{HF}}\rangle$.
4. Take the solutions $|\psi_i^{\text{HF}}\rangle$ and go to step 2 until the energy converges.

3.5 Basis sets

Omitted.

3.6 Restricted versus unrestricted Hartree-Fock

4 Post Hartree-Fock correlation correction

4.1 Motivation

There are various types of electron correlation that are not fully accounted for through Hartree-Fock. Recall that the Hartree-Fock method uses a mean field approximation.

Fermi correlation This type of correlation *is* accounted for by Hartree-Fock but is included here for comparison. Between electrons of the same spin ($\alpha\alpha$), there is correlation resulting from the Pauli exclusion principle (exchange symmetry). The two electrons cannot be found in the same point in space. In H-F, this is fully accounted for by the electron exchange term $-\sum_j \hat{K}_j$.

Coulomb correlation Between electrons of different spin ($\alpha\beta$), there is Coulomb correlation between the spatial positions of electrons arising from classical electrostatic repulsion.

Angular and radial correlation In an s -type orbital, if the two electrons have an angle between them approximately equal to π , then the angular correlation in the s orbital is captured by a p type function. If the two electrons are collinear with the nucleus and the orbital has s symmetry, then to account for this radial correlation, a tight or diffuse s function is needed.

Dynamic and static correlation One can also divide electron correlation into dynamic vs. non-dynamic correlation. Dynamic correlation is the instantaneous correlation between movement of electrons, whereas static configuration is, well, non-dynamic. Static correlation plays a role when the ground state is well described only with more than one degenerate determinant, in which case the Hartree-Fock wavefunction is qualitatively wrong.

There are three major correlation methods: (1) configuration interaction, (2) Moller-Plesset perturbation theory, and (3) coupled cluster. In general, we use a general trial wavefunction

$$\Psi = \sum_{i=0}^{\infty} c_i D_i = c_0 \Psi^{\text{HF}} + \sum_{k_1} c_1 k_1 \Psi_{k_1}^{\text{S}} + \sum_{k_2} c_2 k_2 \Psi_{k_2}^{\text{D}} + \dots$$

That is, the trial wavefunction is a combination of a Hartree-Fock wavefunction, a “singles” wavefunction Ψ^{S} accounting for single electron excitations, a “doubles” wavefunction Ψ^{D} accounting for double electron excitations, etc. In practice, the Hartree-Fock wavefunction constitutes around 99% of the overall wavefunction. However, that does not mean the correction is trivial; the magnitude of the correction may be small, but for chemical systems, even small adjustments to energy levels can change reaction spontaneity or direction.

Note that each wavefunction is given by some determinant, and each determinant represents a *single* electron configuration. Thus, the overall wavefunction Ψ is multi-determinantal. Also note that single, double, etc. excitations refer generally to all types of electron excitations, not just HOMO to LUMO excitations.

4.2 Overall hierarchy of functions

The overall wavefunction Ψ is constructed out of many different functions. Let’s review the hierarchy of functions:

1. First, we begin with Gaussian primitives f_p .
2. We construct M basis functions χ from these Gaussians (where $M > N$). A basis function is given by

$$\chi = \sum_p d_p f_p$$

Note that these basis functions are not orthogonal.

3. We can construct M molecular orbitals ϕ from these basis functions. The first N of these are occupied MOs and the remaining $M - N$ of these are virtual MOs. These are necessarily orthonormal and are given by

$$\phi_k = \sum_i c_{ik} \chi_i$$

4. With these, we can construct the full Hartree-Fock wavefunction

$$\Psi^{\text{HF}} = \hat{A}(\phi_1, \phi_2, \dots, \phi_N)$$

5. Finally, we correct this wavefunction for correlation and arrive at our full wavefunction:

$$\Psi = \sum_i c_i \Psi_i$$

It is important to note that steps 1-3 result in one-particle functions and that steps 4-5 result in many-particle functions.

4.3 Second quantization

In the first quantization, we describe a many-particle system in the basis of single-particle states. In the second quantization, which arises primarily in quantum field theory, fields are quantized using the *number of particles occupying each state* in a complete set of single-particle states as a basis. The first and second quantizations are connected via the *creation* and *annihilation* operators. Suppose that we have four energy levels of increasing energy and two electrons; states 1 and 2 are populated. Then the electron in state 2 is excited to state 3. We can write that as

$$|\Psi^{\text{S}}\rangle = \hat{a}_3^\dagger \hat{a}_2 |\Psi^{\text{HF}}\rangle$$

The operator \hat{a} is the annihilation operator and removes an electron; the operator \hat{a}^\dagger is the creation operator and adds an electron. A state can be built up with creation operators from the *vacuum state* $| \rangle$ like so:

$$|\Psi^{\text{HF}}\rangle = \hat{a}_2^\dagger \hat{a}_1^\dagger | \rangle$$

4.4 Configuration Interaction (CI)

This is the oldest method of correlation correction. It has four basic steps:

1. Use Hartree-Fock to get Ψ^{HF} .
2. Build the excited electron configurations $\Psi = \sum_i c_i D_i$.
3. Determine the amplitudes c_i by minimizing the energy with the method of Lagrange multipliers. Our constraint is that the wavefunction must be normalized, so we minimize the quantity

$$L = \langle \Psi | \hat{H} | \Psi \rangle - \lambda [\langle \Psi | \Psi \rangle - 1]$$

Let's evaluate this expression:

$$\begin{aligned} \langle \Psi | \hat{H} | \Psi \rangle &= \sum_i \sum_j c_i c_j \langle D_i | \hat{H} | D_j \rangle = \sum_i \sum_j c_i c_j H_{ij} \\ \langle \Psi | \Psi \rangle &= \sum_i \sum_j c_i c_j \langle D_i | D_j \rangle = \sum_i c_i^2 \\ L &= \sum_i \left[\sum_j c_i c_j H_{ij} - \lambda c_i^2 + \lambda \right] \end{aligned}$$

Hence,

$$\frac{dL}{dc_i} = 0 = 2 \sum_j c_j H_{ij} - 2\lambda c_i$$

Note that the lambdas represent energies. From this, we arrive at the very important matrix equation

$$HC = EC$$

H is the CI matrix, E contains the correlation-corrected energies, and C contains the amplitudes. Consider the elements of the CI matrix. They will be zero in the following cases:

- (a) between configurations of different spatial symmetry, e.g. between *s* and *p*
- (b) between configurations of different spin multiplicity, e.g. between singlets and triplets
- (c) between the Hartree-Fock reference and singly excited configuration state functions (CSFs) (Brillouin's theorem)
- (d) between CSFs differing by more than 2 excitations

On the other hand, the non-zero elements of the CI matrix will be those corresponding to CSFs differing by at most two excitations. See: Condon-Slater rules. How many configurations will we have to calculate? Consider H₂O. Using the 6-31G(d) basis, there are 38 spin-orbitals (10 occupied, 28 virtual), and 10 electrons to place in those orbitals. Thus, we have (38 choose 10) different electron configurations, which equals 472 million!

There are different variations of CI methods.

1. Full CI (FCI) - this only works for small molecules because of computational considerations, as previously illustrated.
2. Truncated CI
 - (a) Configuration interaction singles (CIS) is limited to single excitations. It does not change the ground state energy, because electron pairs don't end up affecting each other in a new way.
 - (b) Configuration interaction singles doubles (CISD) is limited to single and double excitations. The computational complexity is $O(M^6)$ and is typically only used for small molecules, although CISD is the most common CI method.
 - (c) Configuration interaction singles doubles triples (CISDT) runs in $O(M^8)$.
3. Multi-configuration SCF is a combination of configuration interaction and the Hartree-Fock self-consistent field method. It runs H-F and determines the MO coefficients and CI coefficients all at once. Excitations must be truncated, so they are restricted to only a certain portion of the valence, e.g. the HOMO, the energy level below it, and the two energy levels above the HOMO; the other orbitals are assumed to be inactive and frozen. This is a reasonable assumption, because most chemistry only depends on those parts of the valence. CASSCF uses all excitations in the active space, and is used for getting a better wavefunction, not necessarily for getting a more accurate energy.
4. Multi-reference CI (MRCI) generates more reference functions from the original H-F reference and uses all of the references to generate excited configurations.

Note that the difference in energy $\Delta E = E - E[\Psi^{\text{HF}}]$ between the true ground-state energy and the Hartree-Fock ground-state energy is the correlation energy and it is necessarily negative. This is because the single-determinant H-F approximation does not take into account Coulomb correlation.

4.5 Moller-Plesset Perturbation Theory (MPPT)

In perturbation theory, we have

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{H}_1 + \hat{H}_2 + \dots \\ E_n &= E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots \\ |n\rangle &= N \left(|n^{(0)}\rangle + |n^{(1)}\rangle + |n^{(2)}\rangle + \dots \right)\end{aligned}$$

The corrections to the energy can be expressed as

$$\begin{aligned}E_n^{(1)} &= \langle n^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle \\ E_n^{(2)} &= \langle n^{(0)} | \hat{H}^{(1)} | n^{(1)} \rangle\end{aligned}$$

Note that in the physicists' formulation of Moller-Plesset theory, the Moller-Plesset theorem states that $E_n^{(1)} = 0$. In the chemists' formulation, the Hamiltonian is partitioned differently, so $E_n^{(1)} \neq 0$. We have $E_n^{(1)} = 2 \sum_{i=1}^{N/2} \epsilon_i$, the sum of the orbital energies, and $E_n^{(0)} + E_n^{(1)} = E_{\text{HF}}$, the Hartree-Fock energy. Thus, we must consider higher-order perturbation theory to arrive at an improvement.. Including second-order corrections is referred to as MP2, including up to fourth order is MP4, etc. The first-order state correction is given by

$$\begin{aligned}|n^{(1)}\rangle &= - \sum_{k \neq n} \frac{|k^{(0)}\rangle \langle k^{(0)} | H^{(1)} | n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}} = -\hat{Q}_n H^{(1)} | n^{(0)} \rangle, \text{ where} \\ \hat{P}_n &= \sum_{k \neq n} |k^{(0)}\rangle \langle k^{(0)}| \\ \hat{Q}_n &= \frac{\hat{P}_n}{\hat{H}^{(0)} - E_n^{(0)}}\end{aligned}$$

We can now calculate the 2nd order correction for the ground state ($n = 0$) energy. Here, we will just use 0 to refer to that state.

$$E_0^{(2)} = - \sum_{k \neq 0} \frac{\langle 0^{(0)} | H^{(1)} | k^{(0)} \rangle \langle k^{(0)} | H^{(1)} | 0^{(0)} \rangle}{E_k^{(0)} - E_0^{(0)}}$$

This quantity is always negative. For the Hamiltonian, we have

$$\begin{aligned}\hat{H}^{(0)} &= \sum_{i=1}^N \hat{f}_i = \sum_{i=1}^N \hat{h}(i) + \sum_{i=1}^N \sum_{j=1}^N \left[\hat{J}_j(i) - \hat{K}_j(i) \right] = \sum_{i=1}^N \hat{h}(i) + \sum_{i=1}^N V_{\text{eff}}(i) \\ \hat{H}^{(1)} &= \hat{H} - \hat{H}^{(0)} = \sum_{i=1}^N \sum_{j>i}^N \hat{g}_{ij} - \sum_{i=1}^N V_{\text{eff}}(i)\end{aligned}$$

Note that in the expression for $\hat{H}^{(1)}$, the first term is the correct 2-electron term. The term as a whole is the fluctuation potential. Note also that $|0^{(0)}\rangle = D_0^{(0)}$, which is the H-F wavefunction, so $E_0^{(1)} = \langle D_0^{(0)} | \hat{H}^{(1)} | D_0^{(0)} \rangle = \langle V_{\text{ee}} \rangle - 2 \langle V_{\text{ee}} \rangle = - \langle V_{\text{ee}} \rangle$, and that $E_0^{(0)} = \sum_{i=1}^N \epsilon_i$, the sum of the orbital energies. Finally, we can calculate the second-order correction to the energy

$$E_0^{(2)} = - \sum_{i<j}^{\text{occupied}} \sum_{a<b}^{\text{virtual}} \frac{|\langle D_0^{(0)} | \hat{H}^{(1)} | D_{ij}^{ab(0)} \rangle|^2}{E_{ij}^{ab(0)} - E_0^{(0)}}$$

The determinant $D_{ij}^{ab(0)}$ corresponds to a double excitation. In terms of creation and annihilation operators, it is $\hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_j \hat{a}_i$, which removes electrons i, j and adds electrons a, b . Finally, the denominator $E_{ij}^{ab(0)} - E_0^{(0)}$ is equal to $\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$.

It is important to note that this method is *not* variational and can result in an energy *lower* than the actual ground-state energy.

4.6 Coupled Cluster (CC)

Consider an excitation operator $T = T_1 + T_2 + T_3 + \dots + T_N$. The first term corresponds to single excitations, the second to doubles, etc. This operator can excite up to N electrons. Consider the singles operator operating on D_0 :

$$\hat{T}_1 D_0 = \sum_i^{\text{occupied}} \sum_a^{\text{virtual}} t_i^a D_i^a$$

In this expression, t_i^a is called the excitation amplitude. Recall the method of configuration interaction, where

$$\Psi_{\text{CI}} = (1 + \hat{T}_1 + \hat{T}_2 + \dots) D_0$$

In contrast, in coupled cluster, we will apply the exponential operator and consider $e^{\hat{T}}$; we will use the Taylor series of e and consider only the \hat{T}_1 and \hat{T}_2 terms of the resulting operator.

$$\begin{aligned} \Psi_{\text{CC}} &= e^{\hat{T}} D_0 = \left(1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \frac{1}{6} \hat{T}^3 + \dots \right) D_0 = \left(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \dots \right) D_0 \\ &= \left(1 + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right) + \left(\hat{T}_3 + \hat{T}_1 \hat{T}_2 + \frac{1}{6} \hat{T}_1^3 \right) + \dots \right) D_0 \end{aligned}$$

In the final rearrangement, the \hat{T}_1 term is a single excitation, the next grouping of terms corresponds to doubles, and then triples, and so on and so forth. Truncation using this will preserve pair excitations. The truncation scheme $\hat{T} = \hat{T}_2$ is called CCD, Coupled Cluster Doubles, and the truncation scheme $\hat{T} = \hat{T}_1 + \hat{T}_2$ is CCSD, Coupled Cluster Singles Doubles. The resulting problem is nonvariational and we must solve a series of nonlinear equations.

5 Density functional theory (DFT)

5.1 Motivation

With Hartree-Fock, we must consider a wavefunction $\Psi(\vec{r}_1, s_1, \dots, \vec{r}_N, s_N)$. This is a problem with $4N$ coordinates (in configuration space). However, suppose we consider the electron density $\rho(\vec{r})$. This is only a function of 3 coordinates - we are now in real 3D space! The electron density is defined as

$$\rho(\vec{r}) = N \int \int \dots \int \Phi^*(\vec{r}, s_1, \vec{r}_2, s_2, \dots, \vec{r}_N, s_N) \Phi(\vec{r}, s_1, \vec{r}_2, s_2, \dots, \vec{r}_N, s_N) d s_1 d \vec{r}_2 d s_2 \dots d \vec{r}_N d s_N$$

The integration is over both space and spin. The advantages of this method are that the electron density is a quantity that is intuitive, tractable, and observable. Note that N is the total number of electrons. Some properties of ρ are:

- $\rho \geq 0$ everywhere
- $\int \rho(\vec{r}) d\vec{r} = N$
- $\rho(\vec{r}) \rightarrow 0$ as $\vec{r} \rightarrow \infty$
- ρ has maxima cusps at the nuclei, and $\frac{\delta}{\delta \vec{r}} \rho(\vec{r})|_{\vec{r}=\vec{r}_A} = -2Z_A \rho(\vec{r})$. This statement is known as the *Kato theorem*.

Clearly, the use of ρ in place of Ψ is viable.

5.2 Hohenberg-Kohn theorems

Hohenberg-Kohn existence theorem This theorem states that any ground-state property is a functional of the ground-state electron density ρ . For example,

$$E = E[\rho] = T[\rho] + V_{\text{ne}}[\rho] + V_{\text{ee}}[\rho]$$

In particular, the Hohenberg-Kohn functional $F[\rho] = T[\rho] + V_{\text{ee}}[\rho]$ is guaranteed to be unique and universal. However, it is unknown.

Hohenberg-Kohn variational theorem This theorem states, in analogy to the variational theorem, that

$$E[\rho_{\text{trial}}] \geq E[\rho_0] = E$$

This suggests that we may minimize a trial electron density with Lagrange multipliers:

$$\begin{aligned} L &= E[\rho] - \lambda \left[\int \rho(\vec{r}) d\vec{r} - N \right] \\ \delta L &= \delta \left[E[\rho] - \lambda \int \rho(\vec{r}) d\vec{r} \right] \end{aligned}$$

This is indeed a variational method. However, recall that the form of the functional E is not known. We can approximate it with E_{approx} , indeed we *must* do that, but in doing so our method is no longer variational! Recall that the theorem only involves the *true* functional for the energy and not an approximate one.

5.3 Kohn-Sham theory

We can separate E into the sum of a major part and some elusive, small correction. The major part is known and can be calculated by considering a fictitious system of noninteracting particles (a reference system). We must obtain the kinetic energy of this system. However, to do so, we need the wavefunction Ψ . Thus, Kohn-Sham theory reintroduces the wavefunction into DFT. Essentially, we have

$$E[\rho] = T_{\text{ref}} + V_{\text{ne}}[\rho] + V_{\text{ec}}[\rho] + \Delta T[\rho] + \Delta V_{\text{ec}}[\rho]$$

In place of V_{ec} , the potential due to electron correlation, we will consider purely the classical electron-electron repulsion. Also, we can write $\Delta T[\rho] + \Delta V_{\text{ec}}[\rho] = E_{\text{xc}}[\rho]$, the energy of exchange correlation. All considered, we have

$$E[\rho] = T_{\text{ref}} + V_{\text{ne}}[\rho] + V_{\text{ee,classical}}[\rho] + \Delta E_{\text{xc}}[\rho]$$

Let's consider each term individually:

1. T_{ref} is the kinetic energy of the noninteracting reference. Basically, $T_{\text{ref}}[\rho] = \langle \Psi | \sum_i -\frac{1}{2} \nabla_i^2 | \Psi \rangle$, where Ψ is an antisymmetrized determinantal wavefunction formed from Kohn-Sham orbitals, i.e. $\Psi = \hat{A} [\psi_1^{\text{KS}}(1) \psi_2^{\text{KS}}(2) \dots \psi_N^{\text{KS}}(N)]$. These Kohn-Sham orbitals are numerically very similar to the Hartree-Fock orbitals - they are almost interchangeable. Substituting the latter into the former, $T_{\text{ref}}[\rho] = -\frac{1}{2} \sum_{i=1}^N \langle \psi_i^{\text{KS}} | \nabla_i^2 | \psi_i^{\text{KS}} \rangle$.
2. $V_{\text{ne}} = \int d\vec{r} \rho(\vec{r}) V_{\text{nuc}}(\vec{r}) = \int d\vec{r} \rho(\vec{r}) [-\sum_A Z_A / r_A]$.
3. $V_{\text{ee,classical}} = \iint d\vec{r}_1 d\vec{r}_2 \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}}$. This is also denoted as $J[\rho]$. *Important note:* this erroneously includes self-interaction!
4. ΔE_{xc} is difficult to calculate. In fact, it is unknown. It contains:
 - kinetic correlation energy
 - Coulombic correlation energy
 - exchange energy
 - self-interaction correction (recall that it is erroneously included by $V_{\text{ee,classical}}$)

To solve this problem, we minimize $E[\rho]$ with Lagrange multipliers. In doing so, we arrive at the Kohn-Sham equations, which are analogous to the Hartree-Fock equations. They are given by

$$\hat{h}^{\text{KS}} \psi_i^{\text{KS}} = \epsilon_i^{\text{KS}} \psi_i^{\text{KS}}$$

Note that T_{ref} necessitates the use of orbitals. Otherwise, it is impossible to calculate. The operator \hat{h}^{KS} is given by (for some arbitrary electron 1)

$$\hat{h}^{\text{KS}}(1) = -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{|\vec{r}_A - \vec{r}_1|} + \int \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}_1|} d\vec{r}' + \nu_{\text{xc}}(1)$$

In this equation, the last three terms constitute the effective potential, and $\nu_{\text{xc}}(1)$ is the exchange correlation potential, which is included here unlike in Hartree-Fock. This operator is analogous to \hat{f} , the Fock operator, and $\nu_{\text{xc}}(1)$ is analogous to $-\sum_j \hat{K}_j$. The process for solving the Kohn-Sham equations is as follows:

1. Start with a basis set; generate an overlap matrix and a density matrix $P_{rs} = \sum_{j=1}^N c_{rj} c_{sj}^*$.
2. Guess some initial electron density to get MO coefficients.
3. Form a numerical integration grid in three dimensions and compute \hat{h}^{KS} .
4. Solve $H^{\text{KS}} C = S C E$ for C .
5. From C , generate a new electron density.

6. Iterate until convergence, then from the final ρ , obtain E .

This is different from Hartree-Fock in that we *guess* the exchange correlation. Again, it is not variational, since the exchange correlation is approximated and not exact. Hence, the calculated ground state energy can be lower than the actual ground state energy.

5.4 Exchange correlation functionals

Let us first define some terminology:

$$\begin{aligned}\rho(\vec{r}) &= \rho^\alpha(\vec{r}) + \rho^\beta(\vec{r}) \quad (\text{spin densities}) \\ \zeta(\vec{r}) &= \frac{\rho^\alpha - \rho^\beta}{\rho} \quad (\text{spin polarization}) \\ r_s(\vec{r}) &= \left(\frac{4\pi\rho(\vec{r})}{3} \right)^{-1/3} \quad (\text{effective radius of one electron})\end{aligned}$$

We can make what is referred to as the *customary separation* of the exchange correlation energy:

$$E_{xc} = E_x[\rho] + E_c[\rho] = \int \rho(\vec{r})\epsilon_x(\vec{r})d\vec{r} + \int \rho(\vec{r})\epsilon_c(\vec{r})d\vec{r}$$

In this expression, ϵ_x and ϵ_c are energy densities corresponding to the exchange and correlation energies. We also have

$$\nu_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} = \epsilon_{xc}(\vec{r}) + \rho(\vec{r}) \frac{\delta \epsilon_{xc}(\vec{r})}{\delta \rho(\vec{r})}$$

We can consider the exchange and correlation energies separately:

$$\begin{aligned}E_x[\rho] &= E_x^\alpha[\rho] + E_x^\beta[\rho] \\ E_c[\rho] &= E_c^{\alpha\alpha} + E_c^{\beta\beta} + E_c^{\alpha\beta}\end{aligned}$$

There are five major groups of exchange correlation functionals we can use.

Local density approximations (LDA) We assume that $\epsilon_{xc}(\vec{r})$ depends only on $\rho(\vec{r})$. Then

$$\epsilon_x^{\text{LDA}} = -c_x \rho^{1/3}$$

This is also called the Dirac expression or the Dirac term. I have written that this is the Slater x_α method, although I'm not entirely sure what that means. We can also use the local spin density approximation (LSDA), where

$$\epsilon_x^{\text{LSDA}} = -2^{1/3} c_x \left[\rho_\alpha^{1/3} + \rho_\beta^{1/3} \right]$$

As for correlation, it's complicated, the most commonly used is ϵ_c^{VWN} where VWN stands for the authors who developed this correlation energy estimate. These can be combined by concatenating method names, e.g. SVWN for Slater exchange and VWN correlation. The latter is somehow obtained by fitting.

Generalized gradient approximation (GGA) This is a nonlocal method that improves upon LDA. Using the Perdew-Wang (1986) approximation,

$$\epsilon_x^{\text{PW86}} = e_x^{\text{LSDA}} (1 + ax^2 + bx^4 + cx^6)^{1/15}$$

where $x = \frac{|\nabla\rho|}{\rho^{4/3}}$, a scaled gradient. Some exchange functionals are PW86, B88 (B), PW91, and PBE; some correlation functionals are LYP, P86, and PBE. The combined name is just a concatenation, e.g. PW86LYP or PBEPBE.

Meta-GGA functionals These depend on ρ , $\nabla\rho$, and either $\nabla^2\rho$ or τ , which is the kinetic energy density and is related to ∇^2 . Two examples are TPSS and τ HCTH.

Hybrid functionals This method can be used in *conjunction* with any of the previously listed methods. Recall that in Hartree-Fock we are able to account for 100% of the exchange with $-\sum_j \hat{K}_j$. Thus, this method simply adds some of that H-F exchange energy to the functional for the exchange correlation and removes some of the DFT exchange energy. An example is

$$E_{\text{xc}} = (1 - a)E_{\text{x}}^{\text{DFT}} + aE_{\text{x}}^{\text{HF}} + E_{\text{c}}^{\text{DFT}}$$

The “half and half” method uses half of the LSDA exchange energy, like so:

$$E_{\text{xc}}^{\text{H\&H}} = \frac{1}{2} (E_{\text{x}}^{\text{LSDA}} + E_{\text{c}}^{\text{LSDA}}) + \frac{1}{2} E_{\text{x}}^{\text{HF}}$$

One of the most popular functionals is the Becke 3-parameter functional

$$E_{\text{xc}}^{\text{B3}} = (1 - a)E_{\text{x}}^{\text{LSDA}} + aE_{\text{x}}^{\text{HF}} + b\Delta E_{\text{x}}^{\text{GGA}} + (1 - c)E_{\text{c}}^{\text{LSDA}} + cE_{\text{c}}^{\text{GGA}}$$

The constants a, b, c were determined by fitting and are respectively equal to 0.20, 0.72, and 0.81. An extremely well-known functional is the B3LYP functional, which uses B88 exchange correction, 20% Hartree-Fock exchange, and the LYP (Lee, Yang, Parr) correlation functional. There is also B3PW91, which uses the PW91 correlation correction in place of LYP. There are also *parameter-free* hybrid functionals, where the coefficients are not fitted but rather derived from theory, such as PBE1PBE, which proposes 25% Hartree-Fock exchange.

Nonlocal methods These are the least commonly used and they include virtual orbitals.

6 Wavefunction analysis

6.1 Different types of orbitals

Recall that our wavefunctions are invariant with respect to unitary transformations of the orbitals. Thus, we can choose any set of orbitals among U -related sets. The canonical MOs (Hartree-Fock MOs) have the following properties:

- the Lagrange multipliers are diagonalized
- the orbitals are eigenfunctions of the Fock operator, \hat{f}
- these orbitals are associated with energies (Koopman's theorem)
- the symmetries of these orbitals relate to the point group of the molecule
- these orbitals are delocalized and do not align with chemical properties

They are not very useful for predicting things like molecular geometry. We can consider *localized MOs*, which are spatially confined. Some methods for finding these localized MOs are:

Boys method Minimize the spatial extent of the orbitals:

$$\sum_{i=1}^N \langle \psi_i \psi_i | |r_1 - r_2|^2 | \psi_i \psi_i \rangle$$

Edminston-Rudenberg Maximize the self-repulsion:

$$\sum_{i=1}^N \langle \psi_i \psi_i | \frac{1}{|r_1 - r_2|} | \psi_i \psi_i \rangle$$

Pipek-Mezey Maximize the partial charges:

$$\sum_{\text{atoms } A} |\rho_A|^2$$

where ρ_A is the Mulliken atomic charge.

There are also *natural MOs* (e.g. Weinhold) which diagonalize the density matrix P_{rs} . The eigenvalues are the occupation numbers (0, 1, 2) and the eigenvectors are the natural orbitals. Also, there are natural bond orbitals (NBOs) which are based on atom-by-atom partitions of P_{rs} .

6.2 Hybrid atomic orbitals

Omitted.

6.3 Partial charges and population analysis

Often we think of different atoms in a molecule as possessing partial charges. How can we use quantum chemistry to predict these charges? Here are several methods of population analysis.

Mulliken population analysis This is an old and simple method; it can be erratic. It is based on the fact that $\sum_{r,s} P_{rs} S_{rs} = N$, the number of electrons. Recall that each basis function belongs to a nucleus. The terms in this summation can be divided into two groups:

- $P_{rr} S_{rr}$, the number of electrons in atomic orbital # r
- $P_{sr} S_{sr}$ and $P_{rs} S_{rs}$ ($s \neq r$), the number of shared charges between atomic orbitals # r and # s

We can get the electron population on atom A with

$$N_A = \sum_{r \in A} \sum_{s=1}^M P_{rs} S_{rs}$$

This quantity N_A is called the *gross atom population* of atom A . Similarly, the *gross charge* on atom A is given by

$$\rho_A = Z_A - N_A$$

Lowdin population analysis This is similar to Mulliken population analysis, but instead of using PS , we use $S^{1/2}PS^{1/2}$.

Problems with population analysis Consider the water molecule, H_2O . If we use a basis set where all the basis functions are on O and none are on H, then we end up with $\rho_{\text{H}} = +1$, $\rho_{\text{O}} = -2$. However, if we use a basis set where all the basis functions are on H and none are on O, we end up with $\rho_{\text{O}} = +8$, $\rho_{\text{H}} = -4$. This looks quite ionic! The partial charges we obtain here are thus highly dependent upon our choice of basis set.

AIM: Atoms in Molecules This method considers electron densities. Between two bonded atoms, there is a saddle in electron density, that is, a surface of zero flux. We partition space into different regions using these flux surfaces and integrate over each region to gain the partial charge for the atom associated with that region. A problem: consider a single helium molecule placed in the middle of a buckyball, C_{60} . Based on the zero flux surfaces, there will be sixty bonds between He and the C atoms!

7 Time evolution of wavefunctions

7.1 Time-dependent Schrodinger equation

We represent the time evolution of the state $|\Psi(t_0)\rangle$ to $|\Psi(t)\rangle$ by applying the propagation operator: $|\Psi(t)\rangle = \hat{U}(t, t_0)|\Psi(t_0)\rangle$. Here are some properties of \hat{U} :

1. \hat{U} is unitary, meaning that $\hat{U}^\dagger = \hat{U}^{-1}$. This can be shown by considering that $\langle\Psi(t)|\Psi(t)\rangle = 1 = \langle\Psi(t_0)|\hat{U}^\dagger\hat{U}|\Psi(t_0)\rangle$.
2. The *composition* property: $\hat{U}(t_2, t_0) = \hat{U}(t_2, t_1)\hat{U}(t_1, t_0)$ for a time evolution $t_0 \rightarrow t_1 \rightarrow t_2$.
3. The *continuity* property: For an infinitesimal time step dt , $\lim_{dt \rightarrow 0} \hat{U}(t + dt, t) = I$, the identity.

All three properties are satisfied by an operator defined as such: $\hat{U}(t + dt, t) = I - i\hat{\Omega}dt$, where $\hat{\Omega}$ is a Hermitian operator and has units of inverse time (frequency). Consider that in classical mechanics, the Hamiltonian is the generator of time evolution, similar to how momentum is the generator of translation and angular momentum is the generator of rotation. We will define

$$\hat{\Omega} = \frac{\hat{H}}{\hbar}$$

Thus, the propagation operator is

$$\hat{U}(t + dt, t) = I - i\frac{\hat{H}(t)}{\hbar}dt$$

Naturally, we want to obtain equations of motion for the path $t_0 \rightarrow t \rightarrow t + dt$. Consider that

$$\begin{aligned} \hat{U}(t + dt, t_0) &= \hat{U}(t + dt, t)\hat{U}(t, t_0) = \left(I - i\frac{\hat{H}(t)}{\hbar}dt\right)\hat{U}(t, t_0) \\ \implies \hat{U}(t + dt, t_0) - \hat{U}(t, t_0) &= -i\frac{\hat{H}(t)}{\hbar}\hat{U}(t, t_0)dt \end{aligned}$$

If we divide both sides by dt and take the limit as $dt \rightarrow 0$, we arrive at

$$\frac{\delta\hat{U}(t, t_0)}{\delta t} = -i\frac{\hat{H}(t)}{\hbar}\hat{U}(t, t_0)$$

This is a 1st-order differential equation for the propagator and is known as the time-dependent Schrodinger equation for the propagator. We may operate on both sides with a state $|\Psi(t_0)\rangle$ to obtain the time-dependent Schrodinger equation for a specific state:

$$\frac{\delta|\Psi(t)\rangle}{\delta t} = -i\frac{\hat{H}(t)}{\hbar}|\Psi(t)\rangle$$

7.2 Solving the time-dependent Schrodinger equation

From the differential equations we have

$$|\Psi(t)\rangle = |\Psi(t_0)\rangle e^{-\frac{i}{\hbar}\hat{H}(t)|\Psi(t)\rangle}$$

For a time-independent $\hat{H}(t) = \hat{H}$:

$$\hat{U}(t, t_0) = e^{-\frac{i}{\hbar}\hat{H}(t-t_0)}$$

$$|\Psi(t)\rangle = U(t, t_0)|\Psi(t_0)\rangle$$

For a time-dependent $\hat{H}(t)$:

1. In the case where $[\hat{H}(t_1), \hat{H}(t_2)] = 0$:

$$\hat{U}(t, t_0) = e^{-\frac{i}{\hbar} \int_{t_0}^t \hat{H}(t') dt'}$$

This is valid for a linearly polarized field, such as light shining upon molecules.

2. In the case where $[\hat{H}(t_1), \hat{H}(t_2)] \neq 0$:

$$\hat{U}(t, t_0) = 1 + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar} \right)^n \int dt_1 \int dt_2 \cdots \int dt_n \hat{H}(t_1) \hat{H}(t_2) \cdots \hat{H}(t_n)$$

This series of integrals is known as the Dyson series. We must perform a time-ordered integration when the Hamiltonian at different times does not commute.

We can express \hat{U} in a complete energy eigenbasis of states $|a\rangle$.

$$\begin{aligned} \hat{U}(t, 0) &= e^{-\frac{i}{\hbar} \hat{H}t} = \sum_a e^{-\frac{i}{\hbar} \hat{H}t} |a\rangle \langle a| = \sum_a \left[1 - \frac{i}{\hbar} \hat{H}t + \frac{1}{2} \frac{i^2}{\hbar^2} \hat{H}^2 t^2 + \dots \right] |a\rangle \langle a| \\ &= \sum_a \left[1 - \frac{i}{\hbar} E_a t + \frac{1}{2} \frac{i^2}{\hbar^2} E_a^2 t^2 + \dots \right] |a\rangle \langle a| \\ &= \sum_a e^{-\frac{i}{\hbar} E_a t} |a\rangle \langle a| \end{aligned}$$

Consider these two cases:

1. $|\Psi\rangle$ is an eigenstate of \hat{H} : $|\Psi(0)\rangle = |n(0)\rangle$

$$|\Psi(t)\rangle = |n(t)\rangle = \sum_a e^{-\frac{i}{\hbar} E_a t} |a\rangle \langle a| n(0)\rangle = e^{-\frac{i}{\hbar} E_n t} |n(0)\rangle$$

The exponential part is a time-dependent phase component. Note that all the observables of the system are invariant with respect to time evolution:

$$\langle n(t) | \hat{B} | n(t) \rangle = \langle n(0) | e^{+\frac{i}{\hbar} E_n t} \hat{B} e^{-\frac{i}{\hbar} E_n t} | n(0) \rangle = \langle n(0) | \hat{B} | n(0) \rangle$$

Thus, the phase of the wavefunction has no physical meaning.

2. $|\Psi(0)\rangle = \sum_a |a\rangle \langle a| \Psi(0)\rangle = \sum_a c_a(0) |a\rangle$, a superposition of eigenstates:

$$|\Psi(t)\rangle = \hat{U}(t, 0) |\Psi(0)\rangle = \sum_a c_a(0) e^{-\frac{i}{\hbar} E_a t} |a\rangle$$

Note that this is a non-stationary state, because observables change in time:

$$\begin{aligned} \langle \Psi(t) | \hat{B} | \Psi(t) \rangle &= \left(\sum_{a'} \langle a' | c_{a'}^*(0) e^{+\frac{i}{\hbar} E_{a'} t} \right) \hat{B} \left(\sum_a c_a(0) e^{-\frac{i}{\hbar} E_a t} |a\rangle \right) \\ &= \sum_{a'} \sum_a \langle a' | \hat{B} | a \rangle c_{a'}^*(0) c_a(0) e^{i(E - E_a)t/\hbar} \end{aligned}$$

7.3 Schrodinger and Heisenberg pictures

$\langle \Psi(t) | \hat{B} | \Psi(t) \rangle$ can be expressed as $\left(\langle \Psi(0) | \hat{U}^\dagger \right) \hat{B} \left(\hat{U} | \Psi(0) \rangle \right)$. This is known as the Schrodinger picture, in which Ψ changes and \hat{B} stays constant. It can also be expressed as $\langle \Psi(0) | \left(\hat{U} \hat{B} \hat{U}^\dagger \right) | \Psi(0) \rangle$. This is the Heisenberg picture, in which Ψ is constant and \hat{B} changes. In the Heisenberg picture,

$$\hat{B}^{(H)} = \hat{U}^\dagger \hat{B} \hat{U} \quad \text{and} \quad \dot{\hat{B}}^{(H)} = \dot{\hat{U}}^\dagger \hat{B} \hat{U} + \hat{U}^\dagger \dot{\hat{B}} \hat{U} + \hat{U}^\dagger \hat{B} \dot{\hat{U}}$$

7.4 Interactions with external fields

We will use perturbation theory and assume that we have solved $\hat{H}^{(0)}|a\rangle = E_a|a\rangle$, where $\hat{H}(t) = \hat{H}^{(0)} + \hat{H}^{(1)}(t)$ and $\hat{H}^{(0)}$ is independent of time. Also, $|\Psi(t)\rangle = \sum_a c_a(t)e^{-\frac{i}{\hbar}E_a t}|a\rangle$, where the exponential is due to $\hat{H}^{(0)}$ and $c_a(t)$ is due to $\hat{H}^{(1)}(t)$. We wish to determine $c_a(t)$, and to do so, we consider the interaction picture. Let $|\Psi(t)\rangle_I = \hat{U}_0^\dagger |\Psi(t)\rangle$, where $\hat{U}_0 = e^{-\frac{i}{\hbar}\hat{H}^{(0)}t}$. Then,

$$\begin{aligned} \frac{d}{dt}|\Psi(t)\rangle_I &= \frac{d}{dt}[\hat{U}_0^\dagger |\Psi(t)\rangle] = \left(\frac{d}{dt}\hat{U}_0^\dagger\right)|\Psi(t)\rangle + \hat{U}_0^\dagger \left(\frac{d}{dt}|\Psi(t)\rangle\right) \\ &= \left[\frac{i}{\hbar}\hat{U}_0^\dagger \hat{H}^{(0)}\right]|\Psi(t)\rangle + \hat{U}_0^\dagger \left[-\frac{i}{\hbar}(\hat{H}^{(0)} + \hat{H}^{(1)}(t))|\Psi(t)\rangle\right] \\ &= -\frac{i}{\hbar}\hat{U}_0^\dagger \hat{H}^{(1)}(t)|\Psi(t)\rangle = -\frac{i}{\hbar}\hat{U}_0^\dagger \hat{H}^{(1)}(t)\hat{U}_0\hat{U}_0^\dagger|\Psi(t)\rangle \end{aligned}$$

Let $\hat{H}_I^{(1)} = \hat{U}_0^\dagger \hat{H}^{(1)}(t)\hat{U}_0$. Then we arrive at the time-dependent Schrodinger equations for the interaction picture,

$$\begin{aligned} \frac{d}{dt}|\Psi\rangle_I &= -\frac{i}{\hbar}\hat{H}_I^{(1)}|\Psi\rangle_I \\ \frac{d\hat{B}_I}{dt} &= -\frac{i}{\hbar}[\hat{B}_I, \hat{H}_I^{(1)}] \end{aligned}$$

To review the different “pictures” considered so far:

time – dependence	Schrodinger	Heisenberg	Interaction
state	$\hat{H}^{(0)} + \hat{H}^{(1)}$	0	$\hat{H}^{(0)}$
operator	0	$\hat{H}^{(0)} + \hat{H}^{(1)}$	$\hat{H}^{(1)}$

If we left-multiply the TDSE for $|\Psi\rangle_I$ by an eigenstate $\langle k|$ of $\hat{H}^{(0)}$, we obtain

$$\frac{i}{\hbar} \frac{d}{dt} \langle k|\Psi\rangle_I = \sum_q \langle k|\hat{H}_I^{(1)}|q\rangle \langle q|\Psi\rangle_I$$

Note that

$$\langle k|\hat{H}_I^{(1)}|q\rangle = \langle k|\hat{U}_0^\dagger \hat{H}^{(1)}\hat{U}_0|q\rangle = \langle k|\hat{H}^{(1)}|q\rangle e^{+i(E_k - E_q)t/\hbar}$$

We will use the notation $\omega_{kq}t = (E_k - E_q)t/\hbar$. Then,

$$i\hbar\dot{c}_k = \sum_q \hat{H}_{kq}^{(1)} e^{+i\omega_{kq}t}$$

ASDASDAS