Hartree-Fock Method and Beyond

Daniele Toffoli

Department of Chemistry, Middle East Technical University, Ankara, Turkey.

August 19, 2009
Outline

1. Configuration Interaction Theory
   - Correlation Energy
   - The algebraic approximation
   - A simple example: the H₂ molecule
   - Size Extensivity

2. Möller-Plesset Perturbation Theory
   - Non-degenerate Rayleigh-Schrödinger Perturbation Theory
   - Perturbative Expansion of the correlation energy
   - Size extensivity of MPn methods

3. Overview of Coupled-Cluster Theory

4. Tutorial
   - Overview of GAMESS-US
   - Gaussian basis sets: an overview
1 Configuration Interaction Theory
   - Correlation Energy
   - The algebraic approximation
   - A simple example: the H\textsubscript{2} molecule
   - Size Extensivity

2 Möller-Plesset Perturbation Theory
   - Non-degenerate Rayleigh-Schrödinger Perturbation Theory
   - Perturbative Expansion of the correlation energy
   - Size extensivity of MP\textit{n} methods

3 Overview of Coupled-Cluster Theory

4 Tutorial
   - Overview of GAMESS-US
   - Gaussian basis sets: an overview
SCF Method: drawbacks

- A restricted closed shell HF solution is unable to properly describe molecular dissociation (H₂ dissociates in closed shell fragments, i.e. H⁺ and H⁻)
- UHF is sometimes used for open-shell systems.
- Lack of correlation in the electronic motion.
SCF Method: drawbacks

Figure 4.3 6-31G** potential energy curves for H₂.
**Correlation Energy**

\[ E_C = E_{\text{Exact}}^{\text{NR}} - E_{HF} \]

**Correlation energy**: energy difference between the energy of the exact solution and the energy of the Hartree-Fock solution.

The **correlated** electron motion can be described in terms of virtual excitations, or equivalently through mixing of electronic configurations (Slater determinants).
Correlation Energy

\[ E_C = E_{\text{Exact}}^{\text{NR}} - E_{\text{HF}} \]

**correlation energy**: energy difference between the energy of the exact solution and the energy of the Hartree-Fock solution.

The correlated electron motion can be described in terms of virtual excitations, or equivalently through mixing of electronic configurations (Slater determinants).
Correlation Energy

\[ E_C = E_{\text{Exact}}^{\text{NR}} - E_{HF} \]

correlation energy: energy difference between the energy of the exact solution and the energy of the Hartree-Fock solution.

The correlated electron motion can be described in terms of virtual excitations, or equivalently through mixing of electronic configurations (Slater determinants).
Upon solution of the SCF equations in a finite basis of 2K functions:

\[ \hat{f}_i \chi_i = \epsilon_i \chi_i \]

We get \( \binom{2K}{N} \) Slater determinants, of which the Hartree-Fock one has the lowest energy.

This set of Slater determinants constitutes our \( N \) electron basis.
Upon solution of the SCF equations in a finite basis of $2K$ functions:

$$\hat{f} \chi_i = \epsilon_i \chi_i$$

We get $\binom{2K}{N}$ Slater determinants, of which the Hartree-Fock one has the lowest energy.

This set of Slater determinants constitutes our $N$ electron basis.
Upon solution of the SCF equations in a finite basis of 2K functions:

\[ \hat{f}_i \chi_i = \epsilon_i \chi_i \]

We get \( \binom{2K}{N} \) Slater determinants, of which the Hartree-Fock one has the lowest energy.

This set of Slater determinants constitutes our \( N \) electron basis.
All \( \binom{2K}{N} \) Slater determinants can be classified based on the orbital differences with respect to the HF reference state:

\[
\begin{align*}
|\psi_0\rangle &= |\chi_i\chi_j \cdots \chi_a \cdots \chi_b \cdots \chi_c \cdots \chi_k\rangle \\
|\psi^r_a\rangle &= |\chi_i\chi_j \cdots \chi_r \cdots \chi_b \cdots \chi_c \cdots \chi_k\rangle \\
|\psi^{rs}_{ab}\rangle &= |\chi_i\chi_j \cdots \chi_r \cdots \chi_s \cdots \chi_c \cdots \chi_k\rangle \\
&\vdots
\end{align*}
\]

SCF state
singly excited
doubly excited

\[
|\Phi\rangle = c_0|\psi_0\rangle + \sum_{ar} c^r_a|\psi^r_a\rangle + \left(\frac{1}{2!}\right)^2 \sum_{ab} c^{rs}_{ab}|\psi^{rs}_{ab}\rangle + \ldots
\]
The algebraic approximation

All \( \binom{2K}{N} \) Slater determinants can be classified based on the orbital differences with respect to the HF reference state:

\[
|\psi_0\rangle = |\chi_i\chi_j \cdots \chi_a \cdots \chi_b \cdots \chi_c \cdots \chi_k\rangle
\]

- **SCF state**

\[
|\psi_r\rangle = |\chi_i\chi_j \cdots \chi_r \cdots \chi_b \cdots \chi_c \cdots \chi_k\rangle
\]

- **singly excited**

\[
|\psi_{rs}^{ab}\rangle = |\chi_i\chi_j \cdots \chi_r \cdots \chi_s \cdots \chi_c \cdots \chi_k\rangle
\]

- **doubly excited**

\[
|\Phi\rangle = c_0|\psi_0\rangle + \sum_{ar} c'_a|\psi_r^a\rangle + \left(\frac{1}{2!}\right)^2 \sum_{ab} c_{ab}^{rs} |\psi_{rs}^{ab}\rangle + \ldots
\]

Daniele Toffoli
Hartree-Fock Method and Beyond
The variational principle is invoked. We need to solve a matrix eigenvalue problem:

\[ HC = EC \]

The dimensionality of the CI matrix is equal to the number of Slater determinants included in the CI expansion, i.e.

\( \binom{2K}{N} \)

The dimension is prohibitively large even for the smallest systems (\( \sim 30 \times 10^6 \) for \( N_{el} = 10 \) and \( N_b = 19 \)). Iterative diagonalization techniques.
Sparsity of the CI matrix

\[ |\Phi\rangle = c_0 |\Psi_0\rangle + c_S |S\rangle + c_D |D\rangle + c_T |T\rangle + \ldots \]

- \( \langle \Psi_0 | \hat{H} | S \rangle = 0 \) in virtue of the Brillouin Theorem.
- \( \langle S | \hat{H} | Q \rangle = \langle \Psi_0 | \hat{H} | T \rangle = 0 \) and so on
- \( \langle D | \hat{H} | Q \rangle = \langle \psi_{rs}^{ab} | \hat{H} | \psi_{cdef}^{tuvw} \rangle \neq 0 \) only if \( ab \in cdef \) and \( rs \in tuvw \)
- The CI matrix is sparse.
Sparsity of the CI matrix

Further reduction of computational complexity is due to:

- **Molecular symmetry**: the Hamiltonian matrix will be block diagonal in a symmetry adapted basis set, and the matrix dimension is reduced compared to complete neglect of symmetry.

- **Spin properties**: Spin-adapted basis set (Configuration State Functions, CSFs) instead of simple determinants. For singlet states, we discard determinants for which $N_\alpha \neq N_\beta$.

- **Use of optimal one electron basis**: natural spin orbitals.
One electron reduced density matrices

\[ \gamma_1(x_1, x'_1) = N \int \psi(x_1, x_2, \ldots, x_N) \psi^*(x'_1, x_2, \ldots, x_N) \, dx_2, \ldots, dx_N \]

- The electron density, \( \rho(x_1) \) is simply the diagonal element of the one-electron reduced density matrix:
  - \( \text{Tr} \gamma_1(x_1, x'_1) = N \)
  - \( \gamma_1 \) is hermitean, i.e. \( \gamma_1^\dagger = \gamma_1 \).
  - \( \langle \psi | \hat{O}_1 | \psi \rangle = tr(\hat{h}_1) \).
One electron reduced density matrices

Density matrix in HF theory

$$\gamma_1(x_1, x'_1) = \sum_i \sum_j \chi_i(x_1) \gamma_{ij} \chi_j^*(x'_1)$$

from which we have:

- \(\gamma_{ab} = \delta_{ab}\) for **occupied** orbitals
- \(\gamma_{rs} = 0\) for **virtual** orbitals

The diagonal elements can be interpreted as orbital occupation numbers.
One electron reduced density matrices

Density matrix for a CI wave function

$$\gamma_1(x_1, x'_1) = \sum_i \sum_j \chi_i(x_1) \gamma_{ij} \chi_j^*(x'_1)$$

- $\gamma$ is not diagonal.
- $\gamma^\dagger = \gamma$ i.e. can be diagonalised by a unitary change of basis: natural spin-orbitals

$$\chi'_i = \sum_j \chi_j U_{ij}$$
Density matrix for a CI wave function

- In the natural spin-orbital basis:

\[ \gamma_1(x_1, x'_1) = \sum_k \chi'_k(x_1) \lambda_k \chi'^*_k(x'_1) \]

- \( \lambda_k \) are occupation numbers: \( 0 \leq \lambda_k \leq 1 \)

In the basis of the natural orbitals the CI expansion is more compact.
FCI in minimal basis for the H\textsubscript{2} molecule

The Hartree-Fock solution in minimal basis is determined solely by symmetry considerations:

\[
\psi_1 \equiv 1 = \frac{1}{\sqrt{2(1 + S)}} (\phi_1 + \phi_2)
\]

\[
\psi_2 \equiv 2 = \frac{1}{\sqrt{2(1 - S)}} (\phi_1 - \phi_2)
\]

- \(\phi_1\) and \(\phi_1\) are 1s orbitals centered on the two nuclei.
- \(S_{12}\): extra-diagonal overlap matrix element.
- \(\psi_1\) is totally symmetric: doubly occupied in the HF ground state.
Only two closed shell determinants mix in the FCI ground state (intermediate normalization):

$$|\psi\rangle = 1|1\bar{1}\rangle + c|2\bar{2}\rangle$$

**FCI matrix elements**

- $$\langle 1\bar{1}|H|1\bar{1}\rangle = E_{HF} = 2\epsilon_1 - J_{11}$$
- $$\langle 1\bar{1}|H|2\bar{2}\rangle = \langle 1\bar{1}|2\bar{2}\rangle = K_{12} = \langle 2\bar{2}|H|1\bar{1}\rangle$$
- $$\langle 2\bar{2}|H|2\bar{2}\rangle = \epsilon_2 - 4J_{12} + J_{22} + 2K_{12}$$
FCI in minimal basis for the $\text{H}_2$ molecule

**FCI eigenvalue problem**

\[
\begin{pmatrix}
2\epsilon_1 - J_{11} & K_{12} \\
K_{12} & 2\epsilon_2 - 4J_{12} + J_{22} + 2K_{12}
\end{pmatrix}
\begin{pmatrix}
1 \\
c
\end{pmatrix}
= \epsilon
\begin{pmatrix}
1 \\
c
\end{pmatrix}
\]

We now subtract from both sides the Hartree-Fock energy:

\[
\begin{pmatrix}
2\epsilon_1 - J_{11} & 0 \\
0 & 2\epsilon_1 - J_{11}
\end{pmatrix}
\]
FCI in minimal basis for the $H_2$ molecule

CI eigenvalue problem

$$
\begin{pmatrix}
0 & K_{12} \\
K_{12} & 2\Delta
\end{pmatrix}
\begin{pmatrix}
1 \\
c
\end{pmatrix}
= E_c
\begin{pmatrix}
1 \\
c
\end{pmatrix}
$$

Correlation energy in FCI

$$
E_c = \Delta - \sqrt{\Delta^2 + K_{12}^2}
$$

where $2\Delta = 2(\epsilon_2 - \epsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}$. 
Size extensivity: For $N$ weakly interacting molecules, the energy of the super system should be proportional to the number of molecules. In the limit where the separation between the molecules is infinite, the energy of the super-system is exactly $N$ times the energy of a single molecule.

An electronic structure method is size-extensive if the energy of the super system is predicted to be exactly $N$ times the energy of a single molecule. Otherwise, the method is not size-extensive.
**Size Extensivity of the FCI parameterization**

**FCI wave function of two non-interacting H$_2$ molecules**

Only four determinants mix in the FCI wave function, due to spatial and spin symmetry:

\[
|\Phi_0\rangle = |\psi_0\rangle + c_1 |\tilde{1}_1 1_2 \tilde{2}_2 \rangle + c_2 |2_1 \tilde{2}_1 1_2 \tilde{1}_2 \rangle + c_3 |2_1 \tilde{2}_1 2_2 \tilde{2}_2 \rangle
\]

**FCI eigenvalue problem**

\[
\begin{pmatrix}
0 & K_{12} & K_{12} & 0 \\
K_{12} & 2\Delta & 0 & K_{12} \\
K_{12} & 0 & 2\Delta & K_{12} \\
0 & K_{12} & K_{12} & 4\Delta
\end{pmatrix}
\begin{pmatrix}
1 \\
c_1 \\
c_2 \\
c_3
\end{pmatrix}
= E_c
\begin{pmatrix}
1 \\
c_1 \\
c_2 \\
c_3
\end{pmatrix}
\]
Size Extensivity of the FCI parameterization

FCI correlation energy

Solving the linear system of equations we obtain:

- $c_1 = c_2 = \frac{2K_{12}}{E_c - 4\Delta}$
- $c_3 = c_1^2$

from which:

$$E_c = 2(\Delta - \sqrt{\Delta^2 + K_{12}^2})$$

which must be compared with the correlation energy for a single H₂ molecule: $E_c = \Delta - \sqrt{\Delta^2 + K_{12}^2}$. It therefore follows that FCI is indeed **size consistent**.
The condition $c_3 = c_1^2$ is only valid in the limit of non interacting systems. One could hope that this could represent a good first order approximation. This approximation is at the basis of the superior accuracy of Coupled-Cluster methods (the so called disconnected amplitudes).
DCI wave function of two non-interacting $H_2$ molecules:

$$|\Phi_0\rangle = |\Psi_0\rangle + c_1 |1_1 \bar{1}_2 2_2 \bar{2}_2\rangle + c_2 |2_1 \bar{2}_1 1_2 \bar{1}_2\rangle$$

DCI eigenvalue problem:

$$\begin{pmatrix} 0 & K_{12} & K_{12} \\ K_{12} & 2\Delta & 0 \\ K_{12} & 0 & 2\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \end{pmatrix} = E_c \begin{pmatrix} 1 \\ c_1 \\ c_2 \end{pmatrix}$$
Size Extensivity of the DCI parameterization

DCI correlation energy

Solving the linear system of equations we obtain:

\[ c_1 = c_2 = \frac{2K_{12}}{(E_c - 4\Delta)} \]

\[ E_c = \Delta - \sqrt{\Delta^2 + 2K_{12}^2} \]

which is clearly not size consistent.
For $N$ non interacting molecules we need to solve:

\[
\begin{pmatrix}
  0 & K_{12} & K_{12} & \ldots & \ldots \\
  K_{12} & 2\Delta & 0 & 0 & \ldots \\
  K_{12} & 0 & 2\Delta & 0 & \ldots \\
  K_{12} & 0 & 0 & 2\Delta & \ldots \\
  \ldots & \ldots & \ldots & \ldots & \ldots 
\end{pmatrix}
\begin{pmatrix}
  1 \\
  c_1 \\
  c_2 \\
  c_3 \\
  \ldots
\end{pmatrix}
= E_c
\begin{pmatrix}
  1 \\
  c_1 \\
  c_2 \\
  c_3 \\
  \ldots
\end{pmatrix}
\]

to obtain:

\[c_1 = c_2 = c_3 = \ldots = \frac{K_{12}}{E_c - 2\Delta}\]

and the correlation energy will be given by:

\[E_c = NK_{12}c_1 = \Delta - \sqrt{\Delta^2 + NK_{12}^2}\]
Size Extensivity of the DCI parameterization

\[ E_c \sim \sqrt{N} \text{ for } N \to \infty. \]  
DCI is therefore unable to recover any fraction of the correlation energy for large \( N \), since \( \frac{E_c}{N} \to 0 \). Every truncated CI method is not size consistent.
It is easy to demonstrate that the coefficient of the HF determinant in the DCI wave function is given by:

\[
c_0 = \frac{1}{\sqrt{1 + Nc_1^2}}
\]

In the limit of large \(N\), the coefficient of the HF solution goes to zero, i.e.

\[
c_0 = \frac{1}{\sqrt{1 + Nc_1^2}} \longrightarrow 0 \quad \text{for} \quad N \longrightarrow \infty.
\]
Multiconfigurational Self-Consistent Field Theory (MCSCF)

MCSCF ansatz

\[ |\psi^{MCSCF}\rangle = c_1 |\psi_1\rangle + c_2 |\psi_2\rangle + \ldots + c_N |\psi_N\rangle \]

- combine the variational optimization of the CI coefficients together with the variational optimization of the one-particle spin orbitals.
- The MCSCF wave function is very flexible: a large portion of the molecular PES can be explored, away from the equilibrium geometry.
- Too few, even if carefully selected, determinants (active and inactive space selections).
An MCSCF wave function is chosen as a reference: enhanced accuracy into a larger configurational space.

The number of configurations is increased by a factor equal to the number of configurations in the MCSCF wave function.

Computationally very expensive: single and double excitations.
1. Configuration Interaction Theory
   - Correlation Energy
   - The algebraic approximation
   - A simple example: the H\textsubscript{2} molecule
   - Size Extensivity

2. Möller-Plesset Perturbation Theory
   - Non-degenerate Rayleigh-Schrödinger Perturbation Theory
   - Perturbative Expansion of the correlation energy
   - Size extensivity of MPn methods

3. Overview of Coupled-Cluster Theory

4. Tutorial
   - Overview of GAMESS-US
   - Gaussian basis sets: an overview
Assume our Hamiltonian can be written as:

\[ \hat{H} = \hat{H}_0 + \hat{V} \]

- \( \hat{H}_0 \) is an Hamiltonian for a problem for which the exact eigenfuntions and eigenvalues can be computed:

\[ \hat{H}_0 | \psi_n^{(0)} \rangle = E_n^{(0)} | \psi_n^{(0)} \rangle \]

- \( \hat{V} \): (small) perturbation operator.
- Example: Anharmonic part of PESs, correlation energy.
Assume our Hamiltonian can be written as:

\[ \hat{H} = \hat{H}_0 + \hat{V} \]

- \( \hat{H}_0 \) is an Hamiltonian for a problem for which the exact eigenfunctions and eigenvalues can be computed:

\[ \hat{H}_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle \]

- \( \hat{V} \): (small) perturbation operator.

Example: Anharmonic part of PESs, correlation energy.
PT Equations

Assume our Hamiltonian can be written as:

$$\hat{H} = \hat{H}_0 + \hat{V}$$

- $\hat{H}_0$ is an Hamiltonian for a problem for which the exact eigenfunctions and eigenvalues can be computed:

$$\hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$$

- $\hat{V}$: (small) *perturbation* operator.

- Example: Anharmonic part of PESs, correlation energy.
PT Equations

We expand both the energy, $E_i$, and the wave function, $|\Phi_i\rangle$ for the $i$-th level in Taylor series of the order perturbation:

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \lambda^3 E_i^{(3)} + \ldots,$$

and

$$|\Phi_i\rangle = |i\rangle + \lambda |\psi_i^{(1)}\rangle + \lambda^2 |\psi_i^{(2)}\rangle + \lambda^3 |\psi_i^{(3)}\rangle + \ldots,$$

- $E_i^{(1)}$ and $|\psi_i^{(1)}\rangle$: first-order corrections for the $i$-th level.
- $E_i^{(2)}$ and $|\psi_i^{(2)}\rangle$: second-order corrections for the $i$-th level.
Imposing the condition $\langle i | \Phi_i \rangle = 1$ to the wave function:

$$|\Phi_i\rangle = |i\rangle + \lambda |\psi_i^{(1)}\rangle + \lambda^2 |\psi_i^{(2)}\rangle + \lambda^3 |\psi_i^{(3)}\rangle + \ldots,$$

we obtain:

$$\langle i | \psi_i^{(n)} \rangle = 0$$

valid at each order in the perturbation.
PT Equations

Insert the perturbation expansion for the energy and wave function in the Schrödinger Equation:

\[
(\hat{H}_0 + \lambda \hat{V})(|i\rangle + \lambda |\psi_i^{(1)}\rangle + \lambda^2 |\psi_i^{(2)}\rangle + \ldots) = \\
(E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \ldots)(|i\rangle + \lambda |\psi_i^{(1)}\rangle + \lambda^2 |\psi_i^{(2)}\rangle + \ldots)
\]
Group terms of the same order in the perturbation:

\[
\hat{H}_0 | \hat{i} \rangle = E_i^{(0)} | i \rangle \\
(\hat{H}_0 - E_i^{(0)}) | \psi_i^{(1)} \rangle = (E_i^{(1)} - \hat{V}) | i \rangle \\
(\hat{H}_0 - E_i^{(0)}) | \psi_i^{(2)} \rangle = (E_i^{(1)} - \hat{V}) | \psi_i^{(1)} \rangle + E_i^{(2)} | i \rangle \\
(\hat{H}_0 - E_i^{(0)}) | \psi_i^{(3)} \rangle = (E_i^{(1)} - \hat{V}) | \psi_i^{(2)} \rangle + E_i^{(2)} | \psi_i^{(1)} \rangle + E_i^{(3)} | i \rangle
\]
PT Equations

If now we multiply each member of the set on the left by $\langle i |$, we obtain the following equations:

\[ E_i^{(0)} = \langle i | \hat{H}_0 | i \rangle \]
\[ E_i^{(1)} = \langle i | \hat{V} | i \rangle \]
\[ E_i^{(2)} = \langle i | \hat{V} | \psi_i^{(1)} \rangle \]
\[ E_i^{(3)} = \langle i | \hat{V} | \psi_i^{(2)} \rangle \]
\[ \vdots \]
\[ E_i^{(n)} = \langle i | \hat{V} | \psi_i^{(n-1)} \rangle \]
\[ \vdots \]
We can rearrange the first order equations to obtain:

\[(E_i^{(0)} - \hat{H}_0)|\psi_i^{(1)}\rangle = (\hat{V} - \langle i | \hat{V} | i \rangle) |i\rangle\]

\[|\psi_i^{(1)}\rangle \text{ is expanded in the basis of the eigenvectors of } \hat{H}_0\]

\[|\psi_i^{(1)}\rangle = \sum_j c_j |j\rangle\]
PT Equations

First order correction to the wave function

\[ |\psi_{i}^{(1)}\rangle = \sum_j \langle j | \psi_{i}^{(1)} \rangle |j\rangle \]

\[ = \sum_j \langle j | \hat{V} |i\rangle |j\rangle \frac{\langle j | |i\rangle}{(E_{i}^{(0)} - E_{j}^{0})}. \]

First order correction to the energy

\[ E_{i}^{(1)} = \langle i | \hat{V} |i\rangle \]
PT Equations

Second-order correction to the energy

\[ E_i^{(2)} = \sum_j \frac{\langle i | \hat{V} | j \rangle \langle j | \hat{V} | i \rangle}{(E_i^{(0)} - E_j^{(0)})} \]

Second-order correction to the wave function

\[ |\psi_i^{(2)}\rangle = \sum_j' \sum_k' \frac{\langle j | \hat{V} | k \rangle \langle k | \hat{V} | i \rangle}{(E_i^{(0)} - E_j^{0})(E_i^{(0)} - E_k^{0})} |j\rangle \\
- E_i^{(1)} \sum_j' \frac{\langle j | \hat{V} | i \rangle}{(E_i^{(0)} - E_j^{(0)})^2} |j\rangle \]
Third-order correction to the energy

\[ E_i^{(3)} = \sum_j' \sum_k' \frac{\langle i | \hat{V} | j \rangle \langle j | \hat{V} | k \rangle \langle k | \hat{V} | i \rangle}{(E_i^{(0)} - E_j^{(0)})(E_i^{(0)} - E_k^{(0)})} \]

\[ - E_i^{(1)} \sum_j' \frac{|\langle j | \hat{V} | i \rangle|^2}{(E_i^{(0)} - E_j^{(0)})^2}. \]

or:

\[ E_0^{(3)} = A_0^{(3)} + B_0^{(3)} \]
The fluctuation potential

The electrostatic Hamiltonian is partitioned as follows:

\[ \hat{H} = \hat{H}_0 + \hat{V} \]

with

- \( \hat{H}_0 = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i^2 + \hat{v}_{HF}(i) \right) \) (Fockian)
- \( \hat{V} = \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \hat{v}_{HF}(i) \) (fluctuation potential).
Any Slater determinant built from HF spin orbitals is an eigenstate of $\hat{H}_0$:

$$\hat{H}_0 |n\rangle = \sum_{i=1}^{N} \epsilon_i |n\rangle$$

with:

$$|\psi_n^{(0)}\rangle \equiv |n\rangle = |\chi_i \chi_j \ldots \chi_k\rangle$$

We can construct a perturbative expansion of the correlation energy.
By using the Slater-Condon rules one obtains:

**MP1 Equations**

\[
E_0^{(1)} = \langle \psi_0^{(0)} \rvert \hat{V} \rvert \psi_0^{(0)} \rangle \\
= \langle \psi_0^{(0)} \rvert \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \hat{V}_{HF}(i) \rvert \psi_0^{(0)} \rangle \\
= -\frac{1}{2} \sum_{ab} \langle ab \rvert \rvert ab \rangle
\]
A perturbative expansion of the correlation energy must begin with the second order correction.
**MP2 Equations**

\[
E^{(2)}_0 = \langle 0 | \hat{V} | \psi^{(1)}_0 \rangle \\
= \sum_n \frac{\langle 0 | \hat{V} | n \rangle \langle n | \hat{V} | 0 \rangle}{(E^{(0)}_0 - E^{(0)}_n)}.
\]

- \( |n\rangle \) denotes an excited determinant.
- The sum spans all the excited states.
- Only doubly excited Slater determinants can contribute (Brillouin theorem).
**MPn Equations**

**MP2 Equations**

\[
E_0^{(2)} = \frac{1}{4} \sum_{abrs} \frac{\langle ab || rs \rangle \langle rs || ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}
\]

\[
= \frac{1}{4} \sum_{ab} \sum_{rs} \frac{\left| \langle ab || rs \rangle \right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}.
\]
MPn Equations

MP3 Equations

\[
E_{0}^{(3)} = \sum_{m \neq 0} \sum_{n \neq 0} \frac{\langle 0 | \hat{V} | m \rangle \langle m | \hat{V} | n \rangle \langle n | \hat{V} | 0 \rangle}{(E_{0}^{(0)} - E_{m}^{(0)})(E_{0}^{(0)} - E_{n}^{(0)})} 
- E_{0}^{(1)} \sum_{n \neq 0} \frac{|\langle n | \hat{V} | 0 \rangle|^{2}}{(E_{0}^{(0)} - E_{n}^{(0)})^{2}}.
\]
Consider the special case of $N$ non interacting $H_2$ molecules in a minimal basis set:

Hartree-Fock solution

$$|HF\rangle = |1_1 \bar{1}_1 1_2 \bar{1}_2 1_3 \bar{1}_3 \ldots 1_N \bar{1}_N\rangle$$

- 1 and 2 denotes the HOMO (bonding orbital $\sigma_g$) and LUMO (anti-bonding orbital $\sigma_u^*$) orbitals.
- Subscripts refer to a particular molecule, from 1 to $N$.
- Overbars denote spatial orbitals occupied by electrons with $\beta$ spin.
Size-consistency of Hartree-Fock

Size consistency of $E_0^{(0)}$

\[
E_0^{(0)} = \langle HF|\hat{H}_0|HF\rangle = \langle HF|\sum_{k=1}^{2N} \hat{f}(k)|HF\rangle
\]

\[
= 2 \sum_{i=1}^{N} \langle 1_i|\hat{f}|1_i\rangle
\]

\[
= 2N\epsilon_1
\]
Size-consistency of $E_0^{(1)}$

\[
E_0^{(1)} = \langle HF|\hat{V}|HF\rangle = \langle HF|\sum_{k<l} \frac{1}{r_{kl}}|HF\rangle - \langle HF|\sum_{k=1}^{2N} \hat{v}_{HF}(k)|HF\rangle
\]
Size-consistency of Hartree-Fock

**NOTE**

We need to calculate integrals of the type:

$$\langle ab | ab \rangle = \int \int \phi_a(r_1)\phi_b(r_2) \frac{1}{r_{12}} \phi_a(r_1)\phi_b(r_2) \, dr_1 \, dr_2$$

- The only bi-electronic integrals which are different from zero must involve spatial orbitals of the same molecule.
Size-consistency of $E_0^{(1)}$; Part I

\[
\langle HF | \sum_{k<l} \frac{1}{r_{kl}} | HF \rangle = \frac{1}{2} \sum_{i=1}^{N} \left\{ \langle 1_i 1_i | 1_i 1_i \rangle + \langle 1_i \bar{1}_i | 1_i \bar{1}_i \rangle \right. \\
+ \langle \bar{1}_i 1_i | \bar{1}_i 1_i \rangle + \langle \bar{1}_i \bar{1}_i | \bar{1}_i \bar{1}_i \rangle \}
\]

\[
= \frac{1}{2} \sum_{i=1}^{N} \left\{ \langle 1_i \bar{1}_i | 1_i \bar{1}_i \rangle + \langle \bar{1}_i 1_i | \bar{1}_i 1_i \rangle \right. \\
+ \langle \bar{1}_i 1_i | \bar{1}_i 1_i \rangle + \langle \bar{1}_i \bar{1}_i | \bar{1}_i \bar{1}_i \rangle \}
\]

\[
= \frac{1}{2} \sum_{i=1}^{N} \left\{ 2 \langle 1_i 1_i | 1_i 1_i \rangle \right. \\
= NJ_{11}.
\]
Size-consistency of $E_0^{(1)}$; Part II

$$
\langle HF | \sum_{k=1}^{2N} \hat{v}_{HF}(k) | HF \rangle = \sum_{i=1}^{N} \{ \langle 1 | \hat{v}_{HF} | 1 \rangle + \langle \bar{1} | \hat{v}_{HF} | \bar{1} \rangle \}
$$

$$
= \sum_{i=1}^{N} \{ \langle 1 | \hat{J}_1 + \hat{J}_{\bar{1}} - \hat{K}_1 - \hat{K}_{\bar{1}} | 1 \rangle \\
+ \langle \bar{1} | \hat{J}_1 + \hat{J}_{\bar{1}} - \hat{K}_1 - \hat{K}_{\bar{1}} | \bar{1} \rangle \}
$$

$$
= 2NJ_{11}
$$
Size-consistency of Hartree-Fock

\[ E_{HF} = E_0^{(0)} + E_0^{(1)} = 2N\epsilon_1 - NJ_{11} = N(2\epsilon_1 - J_{11}) \]

- The HF energy is indeed size-consistent.
- HF and DFT are size-consistent EE methods. They retain their accuracy with increasing system size.
$$\langle 1_i \bar{1}_i | \hat{V} | 2_i \bar{2}_i \rangle = \langle 1_i \bar{1}_i | \sum_{k<l} \frac{1}{r_{kl}} | 2_i \bar{2}_i \rangle - \langle 1_i \bar{1}_i | \sum_{k=1}^{2N} \hat{V}_{HF}(k) | 2_i \bar{2}_i \rangle$$

$$= \langle 1_i \bar{1}_i | \sum_{k<l} \frac{1}{r_{kl}} | 2_i \bar{2}_i \rangle$$

$$= \langle 1_i \bar{1}_i | 2_i \bar{2}_i \rangle - \langle 1_i \bar{1}_i | \bar{2}_i 2_i \rangle$$

$$= \langle 1_i \bar{1}_i | 2_i \bar{2}_i \rangle$$

$$= \langle 12 | 12 \rangle$$

$$= K_{12}$$
The MP2 energy is size-consistent as well.
Size-consistency of MP3

MP3 Energy

\[ E_0^{(3)} = A_0^{(3)} + B_0^{(3)} \]

Let consider the two terms separately.
The $B_0^{(3)}$ contribution is NOT size consistent!
Size-consistency of MP3

\[ A_0^{(3)} \text{ contribution} \]

\[
A_0^{(3)} = \sum_{m \neq 0} \sum_{n \neq 0} \frac{\langle 0 | \hat{V} | n \rangle \langle n | \hat{V} | m \rangle \langle m | \hat{V} | 0 \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})}
\]

\[
= \sum_{i=1}^{N} \frac{K_{12}^2}{4(\epsilon_2 - \epsilon_1)^2} \left\{ -NJ_{11} + J_{11} + J_{22} - 4J_{12} + 2K_{12} \right\}
\]

\[
= - \frac{N^2 K_{12}^2 J_{11}}{4(\epsilon_2 - \epsilon_1)^2}
\]

\[
+ \frac{NK_{12}^2}{4(\epsilon_2 - \epsilon_1)^2} (J_{11} + J_{22} - 4J_{12} + 2K_{12}).
\]
Size-consistency of MP3

MP3 Energy

\[ E_0^{(3)} = A_0^{(3)} + B_0^{(3)} \]

\[ = \frac{NK_{12}^2}{4(\epsilon_2 - \epsilon_1)^2} (J_{11} + J_{22} - 4J_{12} + 2K_{12}) \]

- The MP3 energy is size-consistent as well.
- For higher orders the situation is similar. The MPn expansion is size-extensive order by order.
1. Configuration Interaction Theory
   - Correlation Energy
   - The algebraic approximation
   - A simple example: the H\textsubscript{2} molecule
   - Size Extensivity

2. Möller-Plesset Perturbation Theory
   - Non-degenerate Rayleigh-Schrödinger Perturbation Theory
   - Perturbative Expansion of the correlation energy
   - Size extensivity of MP\textsubscript{n} methods

3. Overview of Coupled-Cluster Theory

4. Tutorial
   - Overview of GAMESS-US
   - Gaussian basis sets: an overview
The exponential ansatz

Nowadays CC is the method of choice when calculating ground-state molecular properties in the vicinity of the molecular equilibrium geometry.

It is based on the exponential ansatz for the $N$-electron wave function:

$$|\psi\rangle = e^{\hat{T}}|HF\rangle$$

$|HF\rangle$ is the HF solution.

$\hat{T}$ is a multi-electron operator, called cluster operator.
The Cluster operator

- It can be written as a sum of strings of creation-annihilation operators:
- The expansion of $\hat{T}$ contains a finite number of terms.

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots + \hat{T}_N$$
The Cluster operator

Cluster operator in second quantization

\[ \hat{T}_1 = \sum_{ar} t^r_{ar} \hat{a}^\dagger_r \hat{a}_a \]

\[ \hat{T}_2 = \sum_{a<b} \sum_{r<s} t^{rs}_{ab} \hat{a}^\dagger_s \hat{a}^\dagger_r \hat{a}_b \hat{a}_a \]

\[ \hat{T}_3 = \sum_{a<b<c} \sum_{r<s<t} t^{rst}_{abc} \hat{a}^\dagger_t \hat{a}^\dagger_s \hat{a}^\dagger_r \hat{a}_c \hat{a}_b \hat{a}_a \]

- \( t^r_{ar}, t^{rs}_{ab}, t^{rst}_{abc}, \ldots \): cluster amplitudes. The parameters of the CC wave function.
Exponential vs linear ansatz

<table>
<thead>
<tr>
<th>CI ansatz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CC ansatz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
</tr>
</tbody>
</table>

- The exponential ansatz is at the basis of the CC size-extensivity
- For a non-truncated $\hat{T}$ operator the Full-CI wave function is recovered.
The CC equations

- Insert the exponential ansatz in the Schrödinger Equation:

\[ \hat{H}e^{\hat{T}} |HF\rangle = E e^{\hat{T}} |HF\rangle. \]

- Multiply in turn both sides by the HF reference state, \( \langle HF | \), and a determinant in the excitation manifold, \( \psi_{rst...}^{abc...} \):

\[ \langle HF | \hat{H} e^{\hat{T}} |HF\rangle = E \]
\[ \langle \psi_{abc...}^{rst...} | \hat{H} e^{\hat{T}} |HF\rangle = E \langle \psi_{abc...}^{rst...} | e^{\hat{T}} |HF\rangle \]

- The resulting non-linear system must be (iteratively) solved for the cluster amplitudes.
The CCD wave function contains also quadruple, sextuple \ldots excitation.

The former enter as products of amplitudes corresponding to pair-excitations (disconnected excitations).
CC Theory is NOT variational

- The CI coefficients are variationally optimized.
- The CC amplitudes are obtained by projection of the Schrödinger equation on the excitation manifold.
- The accuracy is high enough for the loss of variational property to be of no practical concern.
- It is assumed that the system can be (reasonably) well described by a single determinant.
- It is not possible to explore large portions of the PES.
- A multireference generalization is being developed.
- New developments also in vibrational structure theory, VCC.
1. Configuration Interaction Theory
   - Correlation Energy
   - The algebraic approximation
   - A simple example: the H₂ molecule
   - Size Extensivity

2. Möller-Plesset Perturbation Theory
   - Non-degenerate Rayleigh-Schrödinger Perturbation Theory
   - Perturbative Expansion of the correlation energy
   - Size extensivity of MPn methods

3. Overview of Coupled-Cluster Theory

4. Tutorial
   - Overview of GAMESS-US
   - Gaussian basis sets: an overview
Gamess QCP

Developed in the group of Mark S. Gordon at Ames Laboratory/Iowa State University:
http://www.msg.chem.iastate.edu

- Free for academic purposes.
- Large selection of wave function parameterizations.
- Explicit vibrational wave function methods.
Gamess QCP

Capabilities

- RHF, UHF, MCSCF.
- DFT, MPn, CI, CC, EOM-CC.
- VSCF and post-VSCF methods.
- Calculation of static and dynamic molecular properties (pol. hyper-pol.).
- Scalar and spin-orbit relativistic effects.
- Solvent effects.
- Good selection of plug-ins for different types of calculations.
### Choice of the one-electron basis

#### Requirements

- The basis set should be complete.
- The basis elements should approximate at best the atomic orbitals.
- The integral evaluation must be fast.
Choice of the one-electron basis

![Graph showing the comparison between Gaussian and Slater type basis functions.](image)
### (nodeless) Gaussians vs Slater type functions

- GTOs display a wrong behaviour at the nucleus (cusp condition).
- GTOs decay too fast at large distances.
- STOs: numerical integral evaluation, feasible but costly (ADF).
- GTOs: the integration is analytical.
- **GTOs are usually preferred over STOs.**
Classification of basis sets

split-valence basis set

The core electrons do not participate in the chemical bonding. The main focus is in the description of the valence orbitals (anisotropy in the electron distribution).

- **STO-nG**: n Gaussian are fitted to a Slater type orbital: Minimal basis.
- **DZV**: two basis functions for each valence orbital.
- **TZV**: three basis functions for each valence orbital.
- **nZV**: n basis functions for each valence orbital.
Polarization functions

- **Polarization functions**: functions with higher angular momentum, $l + 1, l + 2, \ldots$. Used to describe the directionality of the chemical bond.
- Essential in correlated calculations (angular correlation: two electrons are on the opposite side of the nucleus)
- Denoted with a P in their name: DZP, TZP etc.
Diffuse functions

- Used for describing situations of diffuse electron distributions (e.g. attachment processes).
- Essential for the calculation of excited states.
- Essential for properties depending on the "tail" of the wave function.
Contracted basis sets, CGTOs

Basis functions are expressed as (fixed) linear combinations of primitive gaussian functions (PGTOs). The number of parameters to be determined variationally is lower.

- Convenient for core electrons.
- The integral evaluation over molecular orbitals is more efficient.

Types of contractions

- **general**: each primitive enters in all of the CGTOs. Used for correlated calculations.
- **segmented**: each primitive is used in only one CGTO. Contractions are optimized in molecular HF calculations.
Common basis sets

### Pople style basis sets

Optimized in atomic Hartree-Fock calculations. Mainly used for SCF calculations (DFT and HF).

- **3-21G**: split-valence basis. 3 PGTOs for the core orbitals. 2 PGTOs for the inner part of the valence, 1 PGTO for the outer part. (Es: for C (6s3p) → [3s2p])
- **6-311G**: Triple split-valence basis.
- polarization and diffuse (+) functions can be added.
Correlation-consistent basis sets

- Correlating (virtual) atomic orbitals are represented by basis functions optimized at the CISD level.
- Functions that contribute to similar amounts of correlation energy are included at the same stage.
- General contractions.
- Standard nomenclature: (aug-)cc-pVXZ for valence correlation (X=D,T,Q,5 ...).
One- and N-electron requirements

Approximation to exact solution of many-particle problem

# spatial functions

# Slater determinants

Full CI

HF limit

exact solution
References

- Frank Jensen, "Introduction to Computational Chemistry".
- Poul Jorgensen, Jeppe Olsen, Trygve Helgaker, "Molecular Electronic-Structure Theory".