Introduction to Computational Chemistry: Theory

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3023 Course Lectures
Lecture 1

1. **Introduction**
   - Background
   - The Wave Equation
   - Computing Chemistry

2. **Hartree–Fock Theory**
   - The molecular orbital approximation
   - The self-consistent field
   - Restricted and unrestricted HF theory

3. **Basis Sets**
   - Basis functions
   - Additional types of functions
   - Computational Aspects
Computational chemistry

- **Computational Chemistry** is the modeling of chemical phenomenon using computers rather than chemicals.
- The models used vary in their sophistication:
  - Cheminformatics
  - Molecular mechanics
  - Semi-empirical methods
  - *Ab initio* quantum chemistry
- All these methods, except the last, rely on empirical information (parameters, energy levels *etc.*).
- In this course we will focus on *ab initio* quantum chemistry.
Ab initio quantum chemistry

- **Ab initio** means “from the beginning” or “from first principles”, *i.e.* quantum mechanics.

> “The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.”

> P.A.M. Dirac

- Over the last four decades powerful molecular modelling tools have been developed which are capable of accurately predicting properties of molecules.
- These developments have come about largely due to:
  - The dramatic increase in **computer speed**.
  - The design of efficient quantum chemical **algorithms**.
Advantages

Calculations are

- **safe**: many experiments have an intrinsic danger associated with them.
- **clean**: there are no waste chemicals produced.
- **cost effective**: compared to performing experiments.
- **easy**: many experiments can be difficult to perform.

Calculations may also be to give **greater insight** into the chemistry by providing more information about the system.
Introduction

Plastics in Packaging

GET A GRIP
How new technology can do away with the need for handles

Hartree–Fock Theory

Background

Example

Plastics in Packaging © 2011 SENV Publishing / Cepag - February

Basis Sets

Quantum leap

Supercomputers and quantum chemistry could be behind the development of more robust plastics. Steven Pavicitch talks to the scientist behind the research.
Disadvantages

Calculations can also be

- **applied uncritically**: just because you can do something doesn’t mean you should.
- **wrong**: there may be approximations in the models used, or bugs in the code.
- **a black box**: software packages insulate chemists from the underlying theory.

Computational chemistry is **not a replacement** for experimental studies, but plays an important role in enabling chemists to:

- **Explain** and rationalise known chemistry
- **Explore** new or unknown chemistry
The theoretical foundation for quantum chemistry is the time-independent Schrödinger wave equation:

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

- $\psi$ is the Wavefunction. It is a function of the positions of all the fundamental particles (electrons and nuclei) in the system.
- $\hat{H}$ is the Hamiltonian operator. It is the operator associated with the observable energy.
- $E$ is the Total Energy of the system. It is a scalar (number).
- Relativistic effects are usually small and will be ignored.
The Hamiltonian

The Hamiltonian, $\hat{H}$, is an operator. It contains all the terms that contribute to the energy of a system:

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

$\hat{T}$ is the kinetic energy operator:

$$\hat{T} = \hat{T}_e + \hat{T}_n$$

$$\hat{T}_e = -\frac{1}{2} \sum_i \nabla^2_i$$

$$\hat{T}_n = -\frac{1}{2M_A} \sum_A \nabla^2_A$$

$\nabla^2$ is the Laplacian given by:

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

- $\hat{V}$ is the potential energy operator:
  
  \[ \hat{V} = \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \]

- $\hat{V}_{nn}$ is the nuclear-nuclear repulsion term:
  
  \[ \hat{V}_{nn} = \sum_{A < B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \]

- $\hat{V}_{ne}$ is the nuclear-electron attraction term:
  
  \[ \hat{V}_{ne} = -\sum_{iA} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|} \]

- $\hat{V}_{ee}$ is the electron-electron repulsion term:
  
  \[ \hat{V}_{ee} = \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \]
All quantum chemical calculations use a special system of units which, while not part of the SI, are very natural and greatly simplify expressions for various quantities.

- The length unit is the bohr \((a_0 = 5.29 \times 10^{-11}\text{m})\)
- The mass unit is the electron mass \((m_e = 9.11 \times 10^{-31}\text{kg})\)
- The charge unit is the electron charge \((e = 1.60 \times 10^{-19}\text{C})\)
- The energy unit is the hartree \((E_h = 4.36 \times 10^{-18}\text{J})\)

For example, the energy of the H atom is \(-\frac{1}{2}\) hartree (exactly). In more familiar units this is \(-1,313\) kJ/mol.
We will use the nucleus as the centre of our coordinates. The Hamiltonian is then given by:

\[
\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} = -\frac{1}{2} \nabla^2 r - \frac{1}{r}
\]

The ground-state wavefunction is simply a function of \( r \).
The chemical connection

- So far we have focused mainly on obtaining the total energy of our system.
- Many chemical properties can be obtained from derivatives of the energy with respect to some external parameter.
- Examples of external parameters include:
  - Geometric parameters (bond lengths, angles etc.).
  - Applied electric fields (e.g. from a solvent)
  - Magnetic field (in NMR experiments).
- 1\textsuperscript{st} and 2\textsuperscript{nd} derivatives are commonly available and used.
- Higher derivatives are required for some properties, but are expensive (and difficult!) to compute.
Computational quantum chemistry have been successfully applied to both organic and inorganic problems. However, inorganic systems are typically harder to deal with because:

- heavy atoms contain many more electrons
- relativistic effects become important
- higher density of electronic states (esp. transition metals)
- smaller HOMO-LUMO gaps
- fewer methods available (e.g. basis sets)

That said, the theory remains the same for all systems.
Different **models** for chemistry:
- Cheminformatics (functional groups)
- Molecular mechanics (atoms)
- Semi-empirical models (approximate QM)
- Quantum chemistry (fundamental particles)

The Schrödinger wave equation: $\hat{H}\psi = E\psi$

The **Hamiltonian** is made up of energy terms:

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}$$

The **wavefunction** gives a complete description of the system.

Chemical properties are obtained from **derivatives** of the energy with respect to **external parameters**.
Lecture 2

1 Introduction
   - Background
   - The Wave Equation
   - Computing Chemistry

2 Hartree–Fock Theory
   - The molecular orbital approximation
   - The self-consistent field
   - Restricted and unrestricted HF theory

3 Basis Sets
   - Basis functions
   - Additional types of functions
   - Computational Aspects
Hartree-Fock theory

- HF theory is the simplest wavefunction-based method.
- It relies on the following approximations:
  - The **Born-Oppenheimer** approximation
  - The **independent electron** approximation
  - The **linear combination of atomic orbitals** approximation
- The Hartree-Fock model introduces an intrinsic error called the **correlation energy**.
- It forms the foundation for more elaborate electronic structure methods.
The Born-Oppenheimer approximation

- Nuclei are much heavier than electrons (the mass of a proton $\approx 2000$ times that of an electron) and therefore travel much more slowly.
- We assume the electrons can react *instantaneously* to any motion of the nuclei (think of a fly around a rhinoceros).
- This means the nuclei are stationary w.r.t. the electrons.
- This assumption allows us to factorise the wave equation:

  $$\Psi(R, r) = \psi_n(R)\psi_e(r; R)$$

  where the ‘;’ notation indicates a parametric dependence.
- The potential energy surface is a direct consequence of the BO approximation.
The molecular orbital approximation

The independent electron approximation

Consider the $\text{H}_2$ molecule:

- The total wavefunction involves 4x3 spatial coordinates:
  \[ \Psi = \Psi(R_1, R_2, r_1, r_2) \]

- We invoke the Born-Oppenheimer approximation:
  \[ \Psi = \Psi_n(R_1, R_2)\Psi_e(r_1, r_2) \]

- How do we model $\Psi_e(r_1, r_2)$?
The molecular orbital approximation

The Hartree wavefunction

- We assume the wavefunction can be written as a **Hartree product**: $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$
- The individual one-electron wavefunctions, $\psi_i$ are called molecular orbitals.
- This form of the wavefunction does not allow for instantaneous interactions of the electrons.
- Instead, the electrons feel the **average** field of all the other electrons in the system.
- The Hartree form of the wavefunction is is sometimes called the **independent electron approximation**.
One of the postulates of quantum mechanics is that the total wavefunction must be \textit{antisymmetric} with respect to the interchange of electron coordinates.

Antisymmetry is a consequence of the \textbf{Pauli Principle}.

The Hartree wavefunction is not antisymmetric:

\[
\Psi(r_2, r_1) = \psi_1(r_2)\psi_2(r_1) \neq -\Psi(r_1, r_2)
\]

We can make the wavefunction antisymmetric by adding all signed permutations:

\[
\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \left[ \psi_1(r_1)\psi_2(r_2) - \psi_1(r_2)\psi_2(r_1) \right]
\]
The molecular orbital approximation

The Hartree-Fock wavefunction

- The antisymmetrised Hartree wavefunction is called the Hartree-Fock wavefunction.
- It can be written as a Slater determinant:

\[
\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_N(r_1) \\
\psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_N(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(r_N) & \psi_2(r_N) & \cdots & \psi_N(r_N)
\end{vmatrix}
\]

- This ensures the electrons are indistinguishable and are therefore associated with every orbital!
- A Slater determinant is often written as \( |\psi_1, \psi_2, \cdots, \psi_N \rangle \)
The molecular orbital approximation

The LCAO approximation

- The HF wavefunction is **antisymmetric** and written in terms of the one-electron molecular orbitals (MOs).
- What do the MOs look like?
- We write them as a **linear combination of atomic orbitals**: 

\[ \psi_i(r_i) = \sum_{\mu} C_{\mu i} \chi_{\mu}(r_i) \]

- The \( \chi_\mu \) are **atomic orbitals or basis functions**.
- The \( C_{\mu i} \) are **MO coefficients**.
An example

The H$_2$ molecule:

For H$_2$ the MO coefficients, $C_{\mu i}$, are $\pm \frac{1}{\sqrt{2}}$.
The molecular orbital approximation

The HF energy

- If $\psi$ is normalised, the expectation value of the energy is given by: $E = \langle \psi | \hat{H} | \psi \rangle$
- For the HF wavefunction, this can be written:

$$E_{HF} = \sum_i H_i + \frac{1}{2} \sum_{ij} (J_{ij} - K_{ij})$$

- $H_i$ involves one-electron terms arising from the kinetic energy of the electrons and the nuclear attraction energy.
- $J_{ij}$ involves two-electron terms associated with the coulomb repulsion between the electrons.
- $K_{ij}$ involves two-electron terms associated with the exchange of electronic coordinates.
The molecular orbital approximation

The HF energy

- Remember that our wavefunction is given in terms of a determinant: $|\psi_1, \psi_2, \ldots \psi_N\rangle$
- And our MOs are written as a LCAO:

$$\psi_i(r_i) = \sum_{\mu} C_{\mu i} \chi_{\mu}(r_i)$$

- We can write the one-electron parts of the energy as:

$$H_i = \langle \psi_i | \hat{h} | \psi_i \rangle = \sum_{\mu \nu} C_{\mu i} C_{\nu i} \langle \chi_{\mu} | \hat{h} | \chi_{\nu} \rangle$$

- The $J_{ij}$ and $K_{ij}$ matrices can also be written in terms of the MO coefficients, $C_{\mu i}$. 
The MO coefficients, $C_{\mu i}$, can be determined using the variational theorem:

**Variational Theorem**

The energy determined from any approximate wavefunction will always be greater than the energy for the exact wavefunction.

- The energy of the exact wavefunction serves as a *lower bound* on the calculated energy and therefore the $C_{\mu i}$ can be simply adjusted until the total energy of the system is minimised. This is the *variational method*.
The self-consistent field method

- Consider a 2-electron system with MOs \( \psi_1(r_1) \) and \( \psi_2(r_2) \).
- Electron 1 feels the nuclei and the field of \( \psi_2(r_2) \).
- Electron 2 feels the nuclei and the field of \( \psi_1(r_1) \).
- This creates a chicken and egg situation: we need \( \psi_2 \) to solve for \( \psi_1 \), but we need \( \psi_1 \) to solve for \( \psi_2 \).

The SCF Process

1. Guess a set of MOs, \( C_{\mu i} \)
2. Use MOs to compute \( H_i, J_{ij} \) and \( K_{ij} \)
3. Solve the HF equations to obtain a new set of MOs
4. Are the new MOs different? Yes → (2) : No → (5)
5. Self-consistent field converged
So far for simplicity we have ignored the spin variable, $\omega$.
Each MO actually contains a spatial part and a spin part.
For each spatial orbital, there are two spin orbitals:
$$\chi_i^\alpha(r, \omega) = \psi_i(r)\alpha(\omega) \quad \text{and} \quad \chi_i^\beta(r, \omega) = \psi_i(r)\beta(\omega).$$
This is reasonable for closed-shell systems, but not for open-shell systems.
Restricted and unrestricted HF theory

The spatial part of the spin orbitals are the same:

\[ \phi_i^\alpha = \phi_i^\beta \]

The spatial part of the spin orbitals are different:

\[ \phi_i^\alpha \neq \phi_i^\beta \]
Advantages of the UHF method:

- The UHF wavefunction has more flexibility and can give a lower energy (variationally better).
- Provides a qualitatively correct description of bond-breaking.
- Provides a better model for systems with unpaired electrons.

Disadvantages of the UHF method:

- Calculations take slightly longer to perform than for RHF.
- Can lead to spin-contamination which means the wavefunction is no longer a spin-eigenfunction (as it should be).
The Born-Oppenheimer approximation clamps the nuclei and implies $\hat{T}_n = 0$ and $\hat{V}_{nn}$ is constant.

The P.E.S. is a consequence of the B.O.

The independent electron (Hartree) wavefunction:

$$\Psi(r_1, r_2) = \psi_1(r_1)\psi_2(r_2)$$

Antisymmetry and the Hartree-Fock wavefunction:

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} [\psi_1(r_1)\psi_2(r_2) - \psi_1(r_2)\psi_2(r_1)]$$

The LCAO approximation

$$\psi_i(r_i) = \sum_{\mu} C_{\mu i} \chi_{\mu}(r_i)$$

The variational method and self-consistent field calculation
Lecture 3

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3 Basis Sets
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Basis functions

- The atom-centred functions used to describe the atomic orbitals are known as basis functions and collectively form a basis set.
- Larger basis sets give a better approximation to the atomic orbitals as they place fewer restrictions on the wavefunction.
- Larger basis sets attract a higher computational cost.
- Standard basis sets are carefully designed to give the best description for the lowest cost.
The 1s orbital of the H atom is an exponential $e^{-\alpha |r-A|}$ which gives rise to difficult integrals.

Primitive Gaussians, $e^{-\beta |r-A|^2}$ yield easier integrals but do not have the correct behaviour.

If we take fixed combinations of Gaussians $\{D_i e^{-\beta_i |r-A|^2}\}$...

...we get the best of both worlds: $\sum_i D_i e^{-\beta_i |r-A|^2}$
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Basis functions

\section*{Gaussian basis functions}

A Cartesian Gaussian basis function can be written:

\[ \chi(x, y, z) = x^a y^b z^c \sum_{i=1}^{K} D_i e^{-\alpha_i(x^2+y^2+z^2)} \]

- \( a + b + c \) is the angular momentum of \( \chi \)
- \( K \) is the degree of contraction of \( \chi \)
- \( D_i \) are the contraction coefficients of \( \chi \)
- \( \alpha_i \) are the exponents of \( \chi \)
- These types of basis functions are sometimes referred to as Gaussian type orbitals (GTOs).
The simplest possible atomic orbital representation is called a **minimal basis set**.

Minimal basis sets contain one basis functions for each occupied atomic orbital.

For example:
- H & He: 1 function (1s)
- 1\textsuperscript{st} row: 5 functions, (1s, 2s, 2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z})
- 2\textsuperscript{nd} row: 9 functions, (1s, 2s, 2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z}, 3s, 3p\textsubscript{x}, 3p\textsubscript{y}, 3p\textsubscript{z})

Functions are always added in **shells**, e.g. a p shell consists of three functions.
The **STO-3G** basis set is a minimal basis set where each atomic orbital is made up of 3 Gaussians.

The **STO-6G** basis set is a minimal basis set where each atomic orbital is made up of 6 Gaussians.

Minimal basis sets are not well suited to model the anisotropic effects of bonding.

Basis function exponents do not vary and therefore the orbitals have a fixed size and cannot expand or contract.
Split-valence basis sets model each valence orbital by two or more basis functions that have different exponents. They allow for size variations that occur in bonding:

- **Double split valence** basis sets: 3-21G, 6-31G and VDZ
- **Triple split valence** basis sets: 6-311G and VTZ
Polarisation functions

- Polarisation functions have **higher angular momentum** than the occupied AOs.
- They allow for **anisotropic variations** that occur in bonding.

6-31G(\(d\)) or 6-31G* include \(d\) functions on the **heavy** atoms (non-hydrogen).

6-31G(\(d, p\)) or 6-31G** include \(d\) functions on heavy atoms and \(p\) functions on hydrogen atoms.
Diffuse functions

Diffuse basis functions are additional functions with small exponents, and are therefore have large spatial extent. They allow for accurate modelling of systems with weakly bound electrons, such as:

- Anions
- Excited states

A set of diffuse functions usually includes a diffuse $s$ orbital and a set of diffuse $p$ orbitals with the same exponent.

Examples include 6-31+G which has diffuse functions on the heavy atoms and 6-31++G which has diffuse functions on hydrogen atoms as well.
Larger basis sets can be built up from these components, for example 6-311++G(2df,2pd).

Dunning basis sets also exist, for example pVDZ and pVTZ (polarised double split valence and triple split valence, respectively).

Some basis sets work better for HF and DFT calculations (e.g. Pople basis sets and Jensen’s pc-n bases).

Others are best for correlated calculations (e.g. cc-pV*Z).

Carefully designed sequences of basis sets can be used to extrapolate to the basis set limit. For example cc-pVDZ, cc-pVTZ, cc-pVQZ. . .
Effective core potentials

- **Effective Core Potentials** replace core electrons with an effective potential which is added to the Hamiltonian.
- ECPs have two main advantages:
  - They reduce the number of electrons (cheaper).
  - They can be parameterised to take account of relativity.
- Non-relativistic ECPs include **HWMB** (STO-3G) and **LANL2DZ** (6-31G).
- Relativistic ECPs include **SRSC** (6-311G*) and **SRLC** (6-31G).
- The size of the core can vary, for example:
  - **SRLC (large core)**: K = \([\text{Ar}] + 3s, 2p\)
  - **SRSC (small core)**: K = \([\text{Ne}] + 5s, 4p\)
- ECPs are particularly useful for transition metals.
Counting basis functions

It is important to have an idea of how many basis functions are in your molecule as this will determine the cost of the calculation.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Description</th>
<th>No. functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>Minimal</td>
<td>1 H, 5 C,O, 7 H$_2$O, 36 C$_6$H$_6$</td>
</tr>
<tr>
<td>3-21G</td>
<td>Double split-valence</td>
<td>2 H, 9 C,O, 13 H$_2$O, 66 C$_6$H$_6$</td>
</tr>
<tr>
<td>6-31G($d$)</td>
<td>Double split-valence with polarisation</td>
<td>2 H, 15 C,O, 19 H$_2$O, 102 C$_6$H$_6$</td>
</tr>
<tr>
<td>6-31G($d$, $p$)</td>
<td>Ditto, with $p$ functions on H</td>
<td>5 H, 15 C,O, 25 H$_2$O, 120 C$_6$H$_6$</td>
</tr>
<tr>
<td>6-311+G($d$, $p$)</td>
<td>Triple split-valence with polarisation, $p$ functions on H and diffuse</td>
<td>6 H, 22 C,O, 34 H$_2$O, 168 C$_6$H$_6$</td>
</tr>
</tbody>
</table>
The accuracy of the computed properties is sensitive to the quality of the basis set. Consider the bond length and dissociation energy of the hydrogen fluoride molecule:

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Bond Length (Å)</th>
<th>D₀ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G(d)</td>
<td>0.9337</td>
<td>491</td>
</tr>
<tr>
<td>6-31G(d, p)</td>
<td>0.9213</td>
<td>523</td>
</tr>
<tr>
<td>6-31+G(d)</td>
<td>0.9408</td>
<td>515</td>
</tr>
<tr>
<td>6-311G(d)</td>
<td>0.9175</td>
<td>484</td>
</tr>
<tr>
<td>6-311+G(d, p)</td>
<td>0.9166</td>
<td>551</td>
</tr>
<tr>
<td>Expt.</td>
<td>0.917</td>
<td>566</td>
</tr>
</tbody>
</table>

ZPVE = 25 kJ/mol  MP2/6-311+G(d, p)
Lecture 3 summary

- Gaussian basis functions
  - Primitive functions
  - Contracted basis functions
- Minimal basis sets
- Additional types of functions
  - Split valence
  - Polarisation functions
  - Diffuse functions
- Effective Core Potentials (ECPs)
Lecture 4

4 The Correlation Energy
- The correlation energy
- Configuration expansion of the wavefunction

5 Correlated Methods
- Configuration expansion of the wavefunction
- Post HF methods

6 Density Functional Theory
- Density functionals
- The Hohenberg–Kohn theorems
- DFT models
The Correlation Energy
Correlated Methods
Density Functional Theory

The correlation energy

The story so far

- The Hartree wavefunction is based on molecular orbitals:
\[ \psi_H(r_1, r_2) = \psi_1(r_1)\psi_2(r_2) \]

and models \( E_T, E_V \) and \( E_J \), but is not antisymmetric.

- The Hartree-Fock wavefunction is antisymmetric and can therefore model the exchange energy, \( E_K \)
\[ \psi_{HF}(r_1, r_2) = \frac{1}{\sqrt{2}} [\psi_1(r_1)\psi_2(r_2) - \psi_1(r_2)\psi_2(r_1)] \]

- Hartree-Fock theory has an intrinsic error. We call this the correlation energy and is defined by:
\[ E_C = E - E_{HF} \]
The correlation energy

Classification of methods

- Post-HF
- Hybrid DFT
- DFT
- SCF
- HF
- $E_c$
- $\Psi$
The electronic Hamiltonian (energy operator) has several terms:

\[ \hat{H}_e = \hat{T}_e(r) + \hat{V}_{ne}(r; R) + \hat{V}_{ee}(r) \]

This operator is linear, thus the electronic energy can also be written as a sum of several terms:

\[ E_e = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} \]

The electron-electron repulsion term has been broken into three terms: \( E_J + E_K + E_C \)
Electronic energy decomposition

- $E_J$ is the **coulomb repulsion** energy. This energy arises from the classical electrostatic repulsion between the charge clouds of the electrons and is correctly accounted for in the Hartree wavefunction.

- $E_K$ is the **exchange** energy. This energy directly arises from making the wavefunction antisymmetric with respect to the interchange of electronic coordinates, and is correctly accounted for in the Hartree-Fock wavefunction.

- $E_C$ is the **correlation** energy. This is the error associated with the mean-field approximation which neglects the **instantaneous interactions** of the electrons. So far we do not have wavefunction which models this part of the energy.
Electronic energy decomposition

The total electronic energy can be decomposed as follows:

\[ E = E_T + E_V + E_J + E_K + E_C \]

- For the Ne atom, the above energy terms are:
  \[ E_T = +129 \text{ } E_h \]
  \[ E_V = -312 \text{ } E_h \]
  \[ E_J = +66 \text{ } E_h \]
  \[ E_K = -12 \text{ } E_h \quad 9.3\% \]
  \[ E_C = -0.4 \text{ } E_h \quad 0.3\% \]

- The HF energy accounts for more than 99% of the energy.
- If the correlation energy is so small, can we neglect it?
The correlation energy

The importance of $E_C$

Consider the atomisation energy of the water molecule:

<table>
<thead>
<tr>
<th>Energy</th>
<th>$\text{H}_2\text{O}$</th>
<th>$2\text{ H + O}$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{HF}}$</td>
<td>-76.057770</td>
<td>-75.811376</td>
<td>0.246393</td>
</tr>
<tr>
<td>$E_{\text{CCSD}}$</td>
<td>-76.337522</td>
<td>-75.981555</td>
<td>0.355967</td>
</tr>
</tbody>
</table>

If we neglect the correlation energy in the atomisation of water we make a 30% error!
The electron correlation energy

- The correlation energy is sensitive to changes in the number of electron pairs.
- The correlation energy is always negative.
- There are two components to the correlation energy:
  - **Dynamic correlation** is the energy associated with the dance of the electrons as they try to avoid one another. This is important in bond breaking processes.
  - **Static correlation** arises from deficiencies in the single determinant wavefunction and is important in systems with stretched bonds and low-lying excited states.
- Electron correlation gives rise to the inter-electronic cusp.
- Computing the correlation energy is the single most important problem in quantum chemistry.
There exists a plethora of methods to compute the correlation energy, each with their own strengths and weaknesses:

- Configuration interaction (CISD, CISD(T))
- Møller-Plesset perturbation theory (MP2, MP3 . . . )
- Quadratic configuration interaction (QCISD)
- Coupled-cluster theory (CCD, CCSD, CCSDT)
- Multi-configuration self-consistent field theory (MCSCF)
- Density functional theory (DFT)

In practice, none of these methods are exact, but they all (except for DFT) provide a well-defined route to exactitude.
Recall the HF wavefunction is a single determinant made up of the product of occupied molecular orbitals \( \psi_i \):

\[
\Psi_0 = |\psi_1, \psi_2, \ldots \psi_N\rangle
\]

\[
\psi_i = \sum_{\mu} C_{\mu i} \chi_{\mu}
\]

This is referred to as a single configuration treatment.

If we have \( M \) atomic orbitals, the HF method gives us \( M \) molecular orbitals, but only the lowest \( N \) are occupied.

The remaining \( M - N \) orbitals are called virtual orbitals.
Configuration expansion of the wavefunction

Configuration interaction

- We can create different configurations by “exciting” one or more electrons from occupied to virtual orbitals:

\[ \psi_0 = |\psi_1, \psi_2, \ldots \psi_i, \psi_j, \ldots \psi_N\rangle \]

\[ \psi^a_i = |\psi_1, \psi_2, \ldots \psi_a, \psi_j, \ldots \psi_N\rangle \]

\[ \psi^{ab}_{ij} = |\psi_1, \psi_2, \ldots \psi_a, \psi_b, \ldots \psi_N\rangle \]

- These configurations can be mixed together to obtain a better approximation to the wavefunction:

\[ \psi_{CI} = c_0 \psi_0 + \sum_{i}^{occ} \sum_{a}^{vir} c^a_i \psi^a_i + \sum_{ij}^{occ} \sum_{ab}^{vir} c^{ab}_{ij} \psi^{ab}_{ij} + \ldots \]

- The CI coefficients, \( c^a_i \), \( c^{ab}_{ij} \) \ldots can be found via the variational theorem.
Lecture 5

4 The Correlation Energy
- The correlation energy
- Configuration expansion of the wavefunction

5 Correlated Methods
- Configuration expansion of the wavefunction
- Post HF methods

6 Density Functional Theory
- Density functionals
- The Hohenberg–Kohn theorems
- DFT models
To improve on the HF wavefunction, we need to consider excited configurations:

\[ \Psi_{CI} = c_0 \Psi_0 + \sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} c_i^a \Psi_i^a + \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} c_{ij}^{ab} \Psi_{ij}^{ab} + \ldots \]
The Correlation Energy

Correlated Methods

Density Functional Theory

How does this help?

Consider a minimal $H_2$ system with two MOs:

$$
\psi_1 = \sigma = \frac{1}{\sqrt{2}} (\chi_A^{1s} + \chi_B^{1s})
$$

$$
\psi_2 = \sigma^* = \frac{1}{\sqrt{2}} (\chi_A^{1s} - \chi_B^{1s})
$$

$\Psi_{CI} = C_0 \chi_1 + C_1 \chi_1^* + C_2 \chi_1 + C_3 \chi_1$

The node in the $\sigma^*$ orbital allows the electrons to spend more time apart, thus lowering the electron repulsion energy.
Orbital densities

The picture can be made clearer by considering density plots of the two orbitals:

\[ \Psi_{ci} = C_0 \underbrace{1}_{\text{orbital } i} + C_1 \underbrace{1}_{\text{orbital } i} + C_2 \underbrace{1}_{\text{orbital } i} + C_3 \underbrace{1}_{\text{orbital } i} \]

- This mixing is a compromise as \( E_T \) and \( E_V \) also change.
- This can be viewed as a dynamic correlation effect.
How else does this help?

- Adding in configurations also helps modelling stretched bonds.

\[ \Psi_{\text{CI}} = C_0 \begin{array}{cccc} & 1 & & \\ & & 1 & \\ & & & 1 \end{array} + C_1 \begin{array}{cccc} 1 & & & \\ & & 1 & \\ & & & 1 \end{array} + C_2 \begin{array}{cccc} & & 1 & \\ & & & 1 \end{array} + C_3 \begin{array}{cccc} & & & 1 \\ & & & 1 \end{array} \]

- This can be viewed as a static correlation effect.

\[
\begin{align*}
C_0 & \approx 1 \\
C_1 & \approx 0 \\
C_0 & \approx 0 \\
C_1 & \approx 1
\end{align*}
\]
Post HF methods

**Configuration interaction**

- If we allow all possible configurations to mix in then we obtain the Full-CI wavefunction. This is the most complete treatment possible for a given set of basis functions.
- **Complete-CI** is Full-CI in an infinite basis set and yields the exact non-relativistic energy.
- The cost of full-CI scales exponentially and is therefore only feasible for molecules with around 12 electrons and modest basis sets.
- **Truncated CI** methods limit the types of excitations:
  - CIS adds only single excitations (same as HF!)
  - CID adds only double excitations
  - CISD adds single and double excitations, $O(N^6)$
  - CISDT adds single, double and triple excitations, $O(N^8)$
A method is size-consistent if it yields $M$ times the energy of a single monomer when applied to $M$ non-interacting monomers.

HF and Full-CI theories are size consistent, but truncated CI approaches are not.

A method that is not size-consistent:
- Yields poor dissociation energies.
- Treats large systems poorly.

Coupled-cluster wavefunctions are like CI wavefunctions, but include terms to maintain size-consistency.
- CCSD includes all single and double excitations, but also includes some quadruple excitations.

Coupled-cluster wavefunctions are not variational.
The CISD wavefunctions for two separate two-electron systems includes double excitations on both:

\[ \text{He}_1 \quad \text{He}_2 \]

When considered as a single system, however, these lead to quadruple excitations, which are not included in CISD.

CCSD includes these types of excitation, making it size-consistent.
Møller-Plesset perturbation theory

In Møller-Plesset Perturbation Theory the Hamiltonian is divided into two parts:

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

\( \hat{H}_0 \) is the Hartree-Fock Hamiltonian.
\( \lambda \hat{V} \) is a perturbation, which is assumed to be small.

The wavefunction and energy are then expanded as a power series in \( \lambda \) (which is later set to 1):

\[ \psi_\lambda = \psi_0 + \lambda \psi_1 + \lambda^2 \psi_2 + \ldots \]

\[ E_\lambda = E_0 + \lambda E_1 + \lambda^2 E_2 + \ldots \]

\( \psi_0 \) and \( E_0 \) are the HF wavefunction and energy.
Post HF methods

Møller-Plesset perturbation theory

- MP\( n \) is obtained by truncating the expansion at order \( \lambda^n \).
- The MP1 energy is the same as the HF energy.
- The MP2 energy is given by:

\[
E_{\text{MP}2} = \sum_{i<j} \sum_{a<b} \frac{\langle \Psi_0 | \hat{V} | \Psi_{ij}^{ab} \rangle^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}
\]

- The cost of calculating the MP2 energy scales as \( O(N^5) \) and typically recovers \( \sim 80-90\% \) of the correlation energy.
- The MP\( n \) energy is size-consistent but not variational.
- The MP series may diverge for large orders.
The number of basis functions $N$ can be used as a measure of the size of the system. The cost of different methods scales differently:

- HF formally scales as $O(N^4)$, practically as $O(N^2)$
- $\text{MP}n$ scales as $O(N^{n+3})$
- CCSD and CISD are $O(N^6)$
- CCSD(T) scales as $O(N^7)$
- CCSDT scales as $O(N^8)$
## Post HF methods

### An example

<table>
<thead>
<tr>
<th>System</th>
<th>$t_{HF}$</th>
<th>$t_{MP2}$</th>
<th>$t_{CCSD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ala$_1$</td>
<td>2.6 s</td>
<td>40 s</td>
<td>58 m</td>
</tr>
<tr>
<td>Ala$_2$</td>
<td>47 s</td>
<td>7 m</td>
<td></td>
</tr>
<tr>
<td>Ala$_3$</td>
<td>200 s</td>
<td>31 m</td>
<td></td>
</tr>
<tr>
<td>Ala$_4$</td>
<td>8 m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Summary of post-HF methods

Correlated wavefunction methods:

<table>
<thead>
<tr>
<th>Theory</th>
<th>Finite Expansion</th>
<th>Variational</th>
<th>Size-Consistent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI</td>
<td>✓</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>CC</td>
<td>✓</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>MP</td>
<td>✗</td>
<td>✗</td>
<td>✓</td>
</tr>
</tbody>
</table>

Each of these methods gives a hierarchy to exactitude.

- Full-CI gives the exact energy (within the given basis set).
- The concepts of variational and size-consistent methods.
- Coupled-cluster methods are currently the most accurate generally applicable methods in quantum chemistry.
- CCSD(T) has been called the “gold standard” and is capable of yielding chemical accuracy (< 1 kcal/mol error).
Lecture 6

4 The Correlation Energy
- The correlation energy
- Configuration expansion of the wavefunction

5 Correlated Methods
- Configuration expansion of the wavefunction
- Post HF methods

6 Density Functional Theory
- Density functionals
- The Hohenberg–Kohn theorems
- DFT models
Classification of methods
What is the density?

- The electron density is a fundamental quantity in quantum chemistry:

\[ \rho(r_1) = N \int \cdots \int \psi^*(r_1, r_2, \ldots, r_N)\psi(r_1, r_2, \ldots, r_N) dr_2 \cdots dr_N \]

- \( \rho(r) dr \) gives a measure of the probability of finding an electron in the volume element \( dr \).
- It is a function of three variables \((x, y, z)\) and is therefore (relatively) easy to visualise.
What is a functional?

- A function takes a number and returns another number:
  \[ f(x) = x^2 - 1 \quad \text{and} \quad f(3) = 8 \]

- An operator takes a function and returns another function:
  \[ \hat{D}(f) = \frac{df}{dx} \quad \hat{D}(x^2 - 1) = 2x \]

- A functional takes a function and returns a number:
  \[ F[f] = \int_0^1 f(x) \, dx \quad F[x^2 - 1] = -2/3 \]
A density functional takes the electron density and returns a number, for example:

\[ N[\rho] = \int \rho(r) \, dr \]

simply gives the number of electrons in the molecule.

Density functional theory (DFT) focuses on functionals that return the energy of the system.
What is a density functional?

The total energy can be decomposed into the following parts:

\[ E = E_T + E_V + E_J + E_K + E_C \]

- The classical potential energy terms of the total energy can be expressed exactly in terms of the density:
  \[ E_J = \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 \]
  \[ E_V = - \sum_A \int \frac{Z_A \rho(r)}{|R_A - r|} dr \]

- What about \( E_T, E_K \) and \( E_C \)?
In Hartree-Fock theory, $E_T$, $E_K$ and $E_C$, are all orbital functionals, eg:

$$E_T = -\frac{1}{2} \sum_i \int \psi_i(r) \nabla^2 \psi_i(r) dr$$

No (known) exact expression for the kinetic energy in terms of $\rho$ exists.

The exchange energy is non-classical, so should we expect there to be an expression for the exchange energy in terms of the classical density?
The Hohenberg–Kohn theorems

The First Hohenberg-Kohn Theorem

The electron density $\rho$ determines the external potential $\nu$.

- This theorem shows a one-to-one correspondence between $\rho$ and $\nu$ and therefore (via the S.W.E.) $\psi$.
- It also shows that there exists a universal and unique energy functional of the density.

The Second Hohenberg-Kohn Theorem

For any valid trial density, $\tilde{\rho}$: $E_\nu \leq E_\nu[\tilde{\rho}]$

- The second HK theorem establishes a variational principle for ground-state DFT.
The Hohenberg–Kohn theorems

Density functional theory

- The HK theorems are non-constructive, so we don’t know what the form of the universal functional is.
- Research in DFT largely focusses on the development of approximate functionals that model experimental data.
- Kinetic energy functionals are particularly problematic as $E_T$ is so large and even a small relative error gives large absolute errors.
- Almost all DFT calculations rely on the Kohn-Sham approximation, which avoids the need for a kinetic energy density functional.
- Different DFT methods differ in the way they represent $E_X$ and $E_C$. 
The uniform electron gas is a model system with a constant density of electrons.

In 1930 Dirac showed that the exact exchange energy for this system is given by:

$$E_X = -C_x \int \rho^{4/3}(r) dr$$

Much later, Vosko, Wilk and Nusair parameterised a correlation functional (VWN) based on the UEG, its form is more complicated and it is inexact.
Applying the UEG functionals to molecular system is called the **local (spin) density approximation (LDA)**.

Combining the Dirac and VWN expressions gives the **S-VWN** functional.

The LDA functional for $E_X$ underestimates the true exchange energy by about 10% whereas the VWN functional overestimates $E_C$ by as much as 100%.

Together they **overbind** molecular systems.

The constant $C_X$ is sometimes scaled to account for the over-binding, this gives $X_\alpha$ theory.
Gradient corrected functionals depend on $\nabla \rho$ as well as $\rho$.
The gradient helps to account for deviations from uniformity in molecular systems.
The generalised gradient approximation exchange functionals have the form

$$E_X = \int \rho^{4/3}(r)g(x)dr$$

where $x$ is the reduced gradient.

Different GGAs, such as Perdew ’86 and Becke ’88 are defined by different $g(x)$ functions.
GGA correlation functionals

- There are also GGA correlation functionals such as Lee-Yang-Parr (LYP) and Perdew ’86.
- $E_X$ and $E_C$ can be mixed and matched, although certain combinations such as BLYP work particularly well.
- Combining a correlation functional with Hartree-Fock exchange does not work well, but hybrid functionals do:

$$E^{B3LYP} = (1 - c_1 - c_2)E^{D30}_X + c_1 E^{Fock}_K + c_2 E^{B88}_X + (1 - c_3)E^{VWN}_C + c_3 E^{LYP}_C$$ (1)

- B3LYP is the most popular density functional that is used and yields very good structural and thermochemical properties.
Advantages of DFT methods include:

- Low computational cost
- Good accuracy for structures and thermochemistry
- The density is conceptually simpler than $\Psi$

Disadvantages of DFT methods include:

- Can fail spectacularly and unexpectedly
- No systematic way of improving the results
- Integrals require numerical quadrature grids
A functional takes in a function and returns a number.
The density, $\rho(r)$, contains all the information necessary, as shown by the Hohenberg-Kohn theorems.
Density functionals can be used to compute the difficult exchange and correlation energies cheaply.
LDA functionals, e.g. S-VWN, are based on the UEG, they overbind.
GGA functionals, e.g. B-LYP, incorporate the reduced density gradient and are much more accurate.
Hybrid functionals, e.g. B3LYP, incorporate Fock exchange and are the most accurate.
Model Chemistries

- Model chemistries
- Performance
Many molecular properties can be computed, these include:

- Bond energies and reaction energies
- Structures of ground-, excited- and transition-states
- Atomic charges and electrostatic potentials
- Dipole moments and multipole moments
- Vibrational frequencies (IR and Raman)
- Transition energies and intensities for UV and IR spectra
- NMR chemical shifts coupling constants and shielding tensors
- Polarisabilities and hyperpolarisabilities
- Reaction pathways and mechanisms
Quantum chemistry abounds with many levels of theory that represent a trade-off between cost and accuracy.

- Small basis sets and treating correlation at a low-level of theory gives low-cost methods.
- Using large basis sets and treating correlation at a high-level of theory gives high accuracy methods.

Both the cost and accuracy also depend on the property being calculated:

- Energies are cheapest to compute.
- Geometries are relatively cheap (1st derivatives).
- Harmonic frequencies more expensive (2nd derivatives).
- Anharmonic corrections are very expensive (3rd & 4th derivatives).

Computer memory may also be a limitation.
A minimal basis Hartree-Fock calculation forms our baseline, other levels of theory distinguish themselves by their treatment of the correlation energy (left to right) and the size of the basis (top to bottom).

<table>
<thead>
<tr>
<th>Model Chemistries</th>
<th>HF</th>
<th>MP2</th>
<th>MP3</th>
<th>MP4</th>
<th>CCSD(T)</th>
<th>…</th>
<th>Full CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Split-Valence</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarised</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffuse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarised +</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffuse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Infinite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Infinite

Unbalanced

Exact!
Experimental data forms a valuable means of establishing the reliability of a particular level of theory.

Data sets such as the G2 and G3 sets are made up of accurate values with experimental uncertainties of less than 1 kcal/mol (chemical accuracy).

The G2 set consists of thermochemical data including atomisation energies, ionisation potentials, electron affinities and proton affinities for a range of small molecules.

These data set can be used to benchmark a level of theory.

What if we want to apply our method to an unknown system?
If we wish to apply a level of theory to a system that has no experimental data available, we need to converge the level of theory to have confidence in our results.

We start near the top left-hand (cheap) corner of the Pople diagram and move along the diagonal towards the bottom right-hand (expensive) corner carrying out several calculations.

When we see no significant improvement in the result, then we conclude that we have the correct answer.

Note that we cannot apply this approach to DFT methods (although we can converge the basis set).
Specifying the level of theory

- **Geometric properties** converge faster (with respect to the level of theory) than the energy (they are less sensitive to correlation).
- It is common to optimise the geometry at a **low-level** of theory, and then compute the energy at a **higher level** of theory.
- The notation for this is: `energy-method / basis-set // geometry-method / basis-set`.
- The `//` can be read as ‘optimised at’.
- For example: `CCSD(T) / 6-311G(2d,p) // HF / 6-31G`
Performance

Average deviation from experiment for bond-lengths of 108 main-group molecules using 6-31G(d,p)

<table>
<thead>
<tr>
<th>Bond-length</th>
<th>HF</th>
<th>MP2</th>
<th>LDA</th>
<th>GGA</th>
<th>Hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deviation Å</td>
<td>0.021</td>
<td>0.014</td>
<td>0.016</td>
<td>0.017</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Average deviation from experiment for atomisation energies of 108 main-group molecules using 6-31G(d,p)

<table>
<thead>
<tr>
<th>AE</th>
<th>HF</th>
<th>MP2</th>
<th>LDA</th>
<th>GGA</th>
<th>Hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deviation kcal/mol</td>
<td>119.2</td>
<td>22.0</td>
<td>52.2</td>
<td>7.0</td>
<td>6.8</td>
</tr>
</tbody>
</table>
Calculated electron affinity (eV) for Fluorine:

\[ \text{F + e}^- \rightarrow \text{F}^- \]

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>MP2</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>-10.16</td>
<td>-10.16</td>
<td>-9.01</td>
</tr>
<tr>
<td>3-21G</td>
<td>-1.98</td>
<td>-1.22</td>
<td>-0.86</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>-0.39</td>
<td>+1.07</td>
<td>+1.05</td>
</tr>
<tr>
<td>6-311+G(2df,p)</td>
<td>+1.20</td>
<td>+3.44</td>
<td>+3.46</td>
</tr>
<tr>
<td>6-311+G(3df,2p)</td>
<td>+1.19</td>
<td>+3.54</td>
<td>+3.46</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td></td>
<td>+3.48</td>
</tr>
</tbody>
</table>
Convergence of MP methods relative to Full-CI using the STO-3G basis.

<table>
<thead>
<tr>
<th>Method</th>
<th>HCN</th>
<th>CN−</th>
<th>CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2</td>
<td>-91.82033</td>
<td>-91.07143</td>
<td>-91.11411</td>
</tr>
<tr>
<td>MP3</td>
<td>-91.82242</td>
<td>-91.06862</td>
<td>-91.12203</td>
</tr>
<tr>
<td>MP4</td>
<td>-91.82846</td>
<td>-91.07603</td>
<td>-91.13538</td>
</tr>
<tr>
<td>MP5</td>
<td>-91.83129</td>
<td>-91.07539</td>
<td>-91.14221</td>
</tr>
<tr>
<td>MP6</td>
<td>-91.83233</td>
<td>-91.07694</td>
<td>-91.14855</td>
</tr>
<tr>
<td>MP7</td>
<td>-91.83264</td>
<td>-91.07678</td>
<td>-91.15276</td>
</tr>
<tr>
<td>MP8</td>
<td>-91.83289</td>
<td>-91.07699</td>
<td>-91.15666</td>
</tr>
<tr>
<td>Full-CI</td>
<td>-91.83317</td>
<td>-91.07706</td>
<td>-91.17006</td>
</tr>
</tbody>
</table>

$\Delta E < 0.001$

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MP6</td>
<td>MP6</td>
<td>MP19</td>
<td></td>
</tr>
</tbody>
</table>
In general, the use of moderately large basis sets such as 6-311G(d,p) combined with the MP2 treatment of electron correlation leads to calculated structures very close to experiment.

For difficult systems, the Coupled Cluster (CC) methods correspond to an electron correlation treatment better than MP4 and thus greater accuracy is achieved, e.g. ozone:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MP2</th>
<th>CCSD</th>
<th>CCSD(T)</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–O bond (Å)</td>
<td>1.307</td>
<td>1.311</td>
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<td>1.272</td>
</tr>
<tr>
<td>∠OOO (°)</td>
<td>113.2</td>
<td>114.6</td>
<td>116.7</td>
<td>116.8</td>
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