Introduction to Computational Quantum Chemistry: Theory

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3108 Course Lectures 2007
Lectures

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   - The wave equation
   - Computing chemistry

2 Hartree–Fock Theory
   - The molecular orbital approximation
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3. **Configuration Interaction**
   - The correlation energy
   - Configuration expansion of the wavefunction
Computational chemistry can be described as chemistry performed using computers rather than chemicals. It covers a broad range of topics including:

- Cheminformatics
- Statistical mechanics
- 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 the last of these methods.
Ab initio quantum chemistry

- *Ab initio* means “from the beginning” or “from first principles”.

- *Ab initio* quantum chemistry distinguishes itself from other computational methods in that it is based solely on established laws of nature: quantum mechanics.

- Over the last two decades powerful molecular modelling tools have been developed which are capable of accurately predicting structures, energetics, reactivities and other properties of molecules.

- These developments have come about largely due to:
  - The dramatic increase in computer speed.
  - The design of efficient quantum chemical algorithms.
The 1998 Nobel Prize in Chemistry was awarded to Walter Kohn “for his development of the density functional theory” and John Pople “for his development of computational methods in quantum chemistry”.
Advantages

- Calculations are easy to perform, whereas experiments are often difficult.
- Calculations are becoming less costly, whereas experiments are becoming more expensive.
- Calculations can be performed on any system, even those that don’t exist, whereas many experiments are limited to relatively stable molecules.
- Calculations are safe, whereas many experiments have an intrinsic danger associated with them.
Disadvantages

- Calculations are too easy to perform, many black-box programs are available to the uninitiated.
- Calculations can be very expensive in terms of the amount of time required.
- Calculations can be performed on any system, even those that don’t exist!

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 computational 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).
- The wave equation is a postulate of quantum mechanics.
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:

\[
\hat{T} = \hat{T}_e + \hat{T}_n
\]

\[
\hat{T}_e = -\frac{1}{2} \sum_i \nabla_i^2
\]

\[
\hat{T}_n = -\frac{1}{2M} \sum_A \nabla_A^2
\]

- \( \nabla^2 \) 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:

\[
\hat{V}_{nn} = \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}}
\]

- \( \hat{V}_{ne} \) is the nuclear-electron attraction term:

\[
\hat{V}_{ne} = -\sum_{iA} \frac{Z_A}{R_{iA}}
\]

- \( \hat{V}_{ee} \) is the electron-electron repulsion term:

\[
\hat{V}_{ee} = \sum_{i < j} \frac{1}{r_{ij}}
\]
Atomic units

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

For example, the energy of the H atom is -0.5 hartree. 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:

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

\[ = -\frac{1}{2} \nabla^2 - \frac{1}{r} \]

And the wavefunction is simply a function of \( r \): \( \psi(r) \)
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 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.
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.)
- External electric field (for example from a solvent or other molecule in the system)
- External magnetic field (NMR experiments)

1st and 2nd derivatives are commonly available and used.

Higher derivatives are required for some properties, but are expensive (and difficult!) to compute.

Some derivatives must be computed numerically.
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
- Vibrational frequencies (IR and Raman)
- Transition energies and intensities for UV and IR spectra
- NMR chemical shifts
- Dipole moments, polarisabilities and hyperpolarisabilities
- Reaction pathways and mechanisms
The SWE is a second-order linear differential equation.

Exact solutions exist for only a small number of systems:
- The rigid rotor
- The harmonic oscillator
- A particle in a box
- The hydrogenic ions (H, He$^+$, Li$^{2+}$, ...)

Approximations must be used:
- Hartree-Fock theory a wavefunction-based approach that relies on the mean-field approximation.
- Density Functional Theory whose methods obtain the energy from the electron density rather than the (more complicated) wavefunction.

Relativity is usually ignored.
Computing chemistry

Classification of methods

- Post-HF
- Hybrid DFT
- DFT
- SCF
- HF

\[ \Psi \]

\[ E_c \]
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   - The correlation energy
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Previously on 3108

- 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 Born-Oppenheimer approximation clamps the nuclei and implies \( \hat{T}_n = 0 \) and \( \hat{V}_{nn} \) is constant.
- Atomic units (bohr, hartree, etc.)
- Chemical properties are obtained from derivatives of the energy with respect to external parameters, (e.g. first derivatives of the energy w.r.t. nuclear coordinates can be used to find transition structures and equilibrium geometries.)
Classification of methods

- Post-HF
- Hybrid DFT
- DFT
- SCF
- HF
- \( E_c \)
- \( \Psi \)
Hartree-Fock theory

- HF theory is the simplest wavefunction-based method.
- It forms the foundation for more elaborate electronic structure methods.
- It is synonymous with the Molecular Orbital Approximation.
- It relies on the following approximations:
  - The Born-Oppenheimer approximation
  - The independent electron approximation
  - The linear combination of atomic orbitals approximation
- It does not model the correlation energy, by definition.
Consider the $H_2$ molecule:

- The total wavefunction involves 4 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: \( \Psi(r_1, r_2) = \psi_1(r_1)\psi_2(r_2) \)
- 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 averaged field of all the other electrons in the system.
- The Hartree form of the wavefunction is sometimes called the independent electron approximation.
The molecular orbital approximation

The Pauli principle

- One of the postulates of quantum mechanics is that the total wavefunction must be **antisymmetric** with respect to the interchange of electron coordinates.
- The **Pauli Principle** is a consequence of antisymmetry.
- 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 antisymmetrized wavefunction is called the Hartree-Fock wavefunction.
- It can be written as a Slater determinant:

\[
\Psi = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc}
\psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_N(r_1) \\
\psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_N(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(r_N) & \psi_2(r_N) & \cdots & \psi_N(r_N)
\end{array} \right|
\]

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

The LCAO approximation

- The HF wavefunction is an antisymmetric wavefunction written in terms of the one-electron 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.
The H$_2$ molecule:

\[
\psi_1 = \sigma = \frac{1}{\sqrt{2}} (\chi_A^{1s} + \chi_B^{1s})
\]
\[
\psi_2 = \sigma^* = \frac{1}{\sqrt{2}} (\chi_A^{1s} - \chi_B^{1s})
\]

For H$_2$ the MO coefficients, $C_{\mu i}$, are $\pm \frac{1}{\sqrt{2}}$
If the wavefunction is normalized, 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.
Thus, computing the HF energy implies computing the $C_{\mu i}$.

To compute the $C_{\mu i}$ we must minimise the HF energy according to the variational principle.

Which comes first: the HF energy or the $C_{\mu i}$?

### 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 for the energy and new 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:

\[
\chi_i^\alpha(\mathbf{r}, \omega) = \phi_i(\mathbf{r}) \alpha(\omega) \quad \text{and} \quad \chi_i^\beta(\mathbf{r}, \omega) = \phi_i(\mathbf{r}) \beta(\omega).
\]

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:

\[ \phi_i^\alpha \neq \phi_i^\beta \]
Pros and cons

Advantages of the Unrestricted Hartree-Fock method:

- Accounts for **spin-polarisation**, the process by which unpaired electrons perturb paired electrons, and therefore gives realistic spin densities.
- 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 MO approximation and the Hartree wavefunction:

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

Antisymmetry and the Hartree-Fock wavefunction:

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

The LCAO approximation

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

The variational method and self-consistent field calculation

Restricted and unrestricted Hartree-Fock theory
Classification of methods

- Post-HF
- Hybrid DFT
- DFT
- SCF
- HF
- $E_c$
- $\Psi$
Lecture

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The correlation energy

**Energy decomposition**

- The electronic Hamiltonian (energy operator) has several terms:

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

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

\[
E_{el} = E_T + E_V + E_J + E_K + E_C
\]

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

- Where we have broken down the electron-electron repulsion energy 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.
The correlation energy

Electronic energy decomposition

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

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

- 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>H$_2$O</th>
<th>2 H + O</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{HF}$</td>
<td>-76.057770</td>
<td>-75.811376</td>
<td>0.246393</td>
</tr>
<tr>
<td>$E_{CCSD}$</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 correlation energy

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

\[ \Psi_0 = |\psi_1, \psi_2, \ldots \psi_i \psi_j \ldots \psi_N\rangle \]
\[ \Psi_i^a = |\psi_1, \psi_2, \ldots \psi_a \psi_j \ldots \psi_N\rangle \]
\[ \Psi_{ij}^{ab} = |\psi_1, \psi_2, \ldots \psi_a \psi_b \ldots \psi_N\rangle \]

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

\[ \Psi_{\text{CI}} = c_0 \Psi_0 + \sum_i c_i^a \Psi_i^a + \sum_{ij} c_{ij}^{ab} \Psi_{ij}^{ab} + \ldots \]

The CI coefficients, \( c_i^a, c_{ij}^{ab} \ldots \) can be found via the variational method.
Consider a minimal $\text{H}_2$ system with two MOs:

\[ \psi_1 = \sigma = \frac{1}{\sqrt{2}} (\chi^A_{1s} + \chi^B_{1s}) \]

\[ \psi_2 = \sigma^* = \frac{1}{\sqrt{2}} (\chi^A_{1s} - \chi^B_{1s}) \]

The anti-bonding orbital, $\sigma^*$, has a node at the origin. By allowing this orbital to mix in the electrons can spend more time apart on average, thus lowering the repulsion energy.
Lecture

4 Correlated Methods
- Configuration interaction
- Coupled-cluster theory
- Perturbation theory
- Computational Cost

5 Basis Sets
- Basis functions
- Additional types of functions

6 Density Functional Theory
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Previously on 3108

- The MO approximation and the Hartree wavefunction:
  \[ \Psi(r_1, r_2) = \psi_1(r_1)\psi_2(r_2) \]

- Antisymmetry and the Hartree-Fock wavefunction:
  \[ \Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \left[ \psi_1(r_1)\psi_2(r_2) - \psi_1(r_2)\psi_2(r_1) \right] \]

- The LCAO approximation
  \[ \psi_i(r_i) = \sum_{\mu} C_{\mu i} \chi_\mu(r_i) \]

- The variational method and self-consistent field calculation
- Restricted and unrestricted Hartree-Fock theory
Previously on 3108

- The origins of the electronic correlation energy
- The importance of the electronic correlation energy
- The idea of a configuration (determinant):

\[
\Psi_0 = |\psi_1, \psi_2, \ldots \psi_i \psi_j \ldots \psi_N\rangle \\
\Psi_i^a = |\psi_1, \psi_2, \ldots \psi_a \psi_j \ldots \psi_N\rangle \\
\Psi_{ij}^{ab} = |\psi_1, \psi_2, \ldots \psi_a \psi_b \ldots \psi_N\rangle
\]

- The configuration interaction wavefunction

\[
\Psi_{CI} = c_0 \Psi_0 + \sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} c_i^a \Psi_i^a + \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} c_{ij}^{ab} \Psi_{ij}^{ab} + \ldots
\]
Orbital densities
Classification of methods

- Post-HF
- Hybrid DFT
- DFT
- SCF
- HF
- $E_c$
- $\Psi$
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 that can occur:

- CIS adds only single excitations (same as HF!)
- CID adds only double excitations
- CISD adds single and double excitations
- CISDT adds single, double and triple excitations
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 because the correlation energy per monomer tends to zero as the number of monomers increases.
**Coupled-cluster theories**

- The CID wavefunction can be written as $\psi_{\text{CID}} = (1 + T_2)\psi_0$ where:

  $$T_2 = \frac{1}{4} \sum_i^{\text{occ}} \sum_j^{\text{occ}} \sum_a^{\text{virt}} \sum_b^{\text{virt}} c_{ij}^{ab} \hat{a}_a \hat{a}_b \hat{a}_j^* \hat{a}_j^*$$

  The $\hat{a}$ and $\hat{a}^*$ are creation and annihilation operators.

- The CCD wavefunction can then be written as:

  $$\psi_{\text{CCD}} = \exp(T_2)\psi_0$$

  $$= \left[ 1 + T_2 + \frac{T_2^2}{2!} + \frac{T_2^3}{3!} + \ldots \right] \psi_0$$

- $T_2^2$ gives some quadruple excitations and leads to size-consistency.
The Hartree-Fock wavefunction is **not** an eigenfunction of the Hamiltonian $\hat{H}\psi_0 \neq E_{\text{HF}}\psi_0$

However, it can be considered as an eigenfunction of the Hartree–Fock Hamiltonian:

$$\hat{H}_0 = \sum_i f(r_i)$$

$$f(r_i) = \hat{T}(r_i) + \hat{V}_{\text{ne}}(r_i) + \hat{\nu}_{\text{HF}}(r_i)$$

The difference between these operators, $\hat{H} - \hat{H}_0$ gives the correlation energy.
Møller-Plesset perturbation theory

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

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

- The perturbation, \( \lambda \hat{V} \), is assumed to be small
- The wavefunction and energy are then expanded as a power series in \( \lambda \) (which is later set to unity)

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

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

- \( \psi_0 \) and \( E_0 \) are the HF wavefunction and energy
Møller-Plesset perturbation theory

- $\text{MP}^n$ is obtained by truncating the expansion at order $\lambda^n$
- The $\text{MP}1$ energy is the same as the HF energy
- The $\text{MP}2$ energy is given by:

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

- The cost of calculating the $\text{MP}2$ energy scales as $O(N^5)$ and typically recovers $\sim 80-90\%$ of the correlation energy
- The $\text{MP}^n$ energy is size-consistent but not variational
- The $\text{MP}$ series may diverge for large orders
HF formally scales as $O(N^4)$, practically as $O(N^2)$

MP$_n$ scales as $O(N^{n+3})$

CCSD and CISD scale as $O(N^6)$

CCSD(T) scales as $O(N^7)$

CCSDT scales as $O(N^8)$
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>6 m 30 s</td>
<td></td>
</tr>
<tr>
<td>Ala$_3$</td>
<td>3m 20 s</td>
<td>30 m 50 s</td>
<td></td>
</tr>
<tr>
<td>Ala$_4$</td>
<td>8m 20 s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Lecture

4 Correlated Methods
- Configuration interaction
- Coupled-cluster theory
- Perturbation theory
- Computational Cost

5 Basis Sets
- Basis functions
- Additional types of functions

6 Density Functional Theory
- Density functionals
- The Hohenberg–Kohn theorems
- DFT models
Correlated wavefunction methods:

<table>
<thead>
<tr>
<th>Theory</th>
<th>$\psi$</th>
<th>Variational</th>
<th>Size-Consistent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI</td>
<td>$(1 + T_1 + T_2 + \ldots)\psi_0$</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>CC</td>
<td>$\exp(T_1 + T_2 + \ldots)\psi_0$</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>MP</td>
<td>$\psi_0 + \lambda \psi_1 + \lambda^2 \psi_2 + \ldots$</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.
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 the place fewer restrictions on the wavefunction.

Larger basis sets attract a higher computational cost.

Basis sets are carefully designed to give the best description for the lowest cost.
Basis functions

**Gaussian basis representations**

- 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 $\sum_i D_i e^{-\beta_i |r-A|^2}$
Basis functions

Gaussian basis representations

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...we get the best of both worlds $\sum_i D_i e^{-\beta_i |r-A|^2}$
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 GTOs
The simplest possible atomic orbital representation is called a **minimal basis set**.

Minimal basis sets contain the minimum number of basis functions to accommodate all of the electrons in the atom.

For example:
- **H & He** a single function \((1s)\)
- **1st row** 5 functions, \((1s, 2s, 2p_x, 2p_y, 2p_z)\)
- **2nd row** 9 functions, \((1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z)\)

Functions are always added in **shells**.
The STO-3G basis set is a minimal basis set where each atomic orbital is made up of 3 Gaussians. STO-nG also exist.

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

Because the exponents do not vary, the orbitals have a fixed size and therefore cannot expand or contract
Split valence functions

- 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.

Examples include the double split valence basis sets, 3-21G and 6-31G, and triple split valence basis sets such as 6-311G.
Correlated Methods  
Basis Sets  
Density Functional Theory

Additional types of functions

**Polarisation functions**

- Polarisation functions have higher angular momentum.
- They allow for anisotropic variations that occur in bonding and help model the *inter-electronic cusp*

Examples include 6-31G(\(d\)) or 6-31G* which include \(d\) functions on the heavy atoms 6-31G(\(d, p\)) or 6-31G** which 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 large.
- 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 $6-311++G(2df,2dp)$.

Dunning basis sets also exist, for example pVDZ and pVTZ.

For larger atoms Effective Core Potentials (ECPs) are often used. These replace the core electrons with an effective potential and have two main advantages:

- They reduce the number of electrons (cheaper)
- They can be parameterized to take account of relativity

The valence electrons are still modelled using GTOs.
### Additional types of functions

#### Examples

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Description</th>
<th>No. functions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H</td>
</tr>
<tr>
<td>STO-3G</td>
<td>Minimal</td>
<td>1</td>
</tr>
<tr>
<td>3-21G</td>
<td>Double split-valence</td>
<td>2</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>Double split-valence with polarisation</td>
<td>2</td>
</tr>
<tr>
<td>6-31G(d, p)</td>
<td>Ditto, with p functions on H</td>
<td>5</td>
</tr>
<tr>
<td>6-311+G(d, p)</td>
<td>Triple split-valence with polarisation, p functions on H and diffuse functions on heavy atoms</td>
<td>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

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- Density functionals
- The Hohenberg–Kohn theorems
- DFT models
Previously on 3108

- 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)
Classification of methods

- Post-HF
- Hybrid DFT
- DFT
- SCF
- HF
- $\Psi$
- $E_c$
The electron density is a fundamental quantity in quantum chemistry

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

\( \rho(r) dr \) gives 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
Density functionals

What is a functional?

- A function takes a number and returns another number:
  \[ f(x) = x^2 - 1 \quad f(3) = 8 \]
- 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:
  \[ F[f] = \int_{0}^{1} f(x) dx \quad F[x^2 - 1] = -2/3 \]
What is a density functional?

- 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?**

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

- 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 $\rho(r)$ determines the external potential

- This theorem establishes the existence of a (universal and unique) energy functional of the density

**The Second Hohenberg-Kohn Theorem**

Any approximate density $\tilde{\rho}$ which provides the external potential $\nu(r)$, determines its own wavefunction.

- The second HK theorem can be used to establish a variational principle for DFT, although it restricts the theory to ground states
The HK theorems are non-constructive, so we don’t know what the form of the universal functional is.

Research in the DFT largely falls down to 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 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 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

- Gradient corrected functions 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

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

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:

$$E_{B3LYP} = (1 - c_1)E_X^{D30} + c_1 E_{K}^{\text{Fock}} + c_2 E_X^{B88} + (1 - c_3) E_C^{\text{VWN}} + c_3 E_{C}^{LYP}$$

- 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 more simple than $\Psi$

Disadvantages of DFT methods include:
- Can fail spectacularly and unexpectedly
- No systematic way of improving the results
- Integrals require numerical quadrature grids
Model Chemistries

Model chemistries
Quantum chemistry abounds with many levels of theory that represent a trade-off between computational cost and accuracy.

A minimal basis Hartree-Fock calculation forms our baseline, other level of theory distinguish themselves by their treatment of the correlation energy and the size of the basis.

- **Cost** favours small basis sets and a low-level treatment of correlation.
- **Accuracy** favours large basis sets and a high-level treatment of correlation.
## The Pople Diagram

<table>
<thead>
<tr>
<th>Model Chemistry</th>
<th>HF</th>
<th>MP2</th>
<th>MP3</th>
<th>MP4</th>
<th>CCSD(T)</th>
<th>\ldots</th>
<th>Full CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimal Split-Valence</td>
<td>Low-level</td>
<td>\ldots</td>
<td>\ldots</td>
<td>\ldots</td>
<td>\ldots</td>
<td>Unbalanced</td>
<td></td>
</tr>
<tr>
<td>Polarised Diffuse</td>
<td>\ldots</td>
<td>\ldots</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarised + Diffuse</td>
<td>\ldots</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Infiinite</td>
<td>Unbalanced</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Exact!</td>
</tr>
</tbody>
</table>
Establishing the reliability of a method

- **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 experimental values with 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 (1 or 2 heavy atoms).
- These data set can be used to **benchmark** a level of theory.
- What if we want to apply our method to an unknown system?
Establishing the reliability of a method

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 towards the bottom right-hand (expensive) corner carrying out several calculations.

When we see no 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`.

- For example: `CCSD(T)/6-311G(2d,p)//HF/6-31G`
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:

<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>