

Introduction to Computational Quantum Chemistry: Theory

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3108 Course Lectures 2007



Lectures

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 Configuration Interaction

- The correlation energy
- Configuration expansion of the wavefunction

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Correlated Methods

- Configuration interaction
- Coupled-cluster theory
- Perturbation theory
- Computational Cost

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Basis Sets

- Basis functions
- Additional types of functions

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Density Functional Theory

- Density functionals
- The Hohenberg–Kohn theorems
- DFT models

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- 7 Model Chemistries**
 - Model chemistries

Lecture

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Computational chemistry

- **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.

Nobel recognition



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

Theoretical model

- The theoretical foundation for computational chemistry is the time-independent **Schrödinger wave equation**:

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

- Ψ 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:

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

$$\hat{T}_e = -\frac{1}{2} \sum_i \nabla_i^2 \quad \hat{T}_n = -\frac{1}{2M_A} \sum_A \nabla_A^2$$

- ∇^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:

$$\hat{V}_{nn} = \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}$$

- \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:

$$\hat{V}_{ee} = \sum_{i < j} \frac{1}{r_{ij}}$$

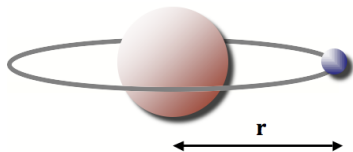
Atomic units

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** ($a_0 = 5.29 \times 10^{-11} \text{m}$)
- 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 -0.5 hartree. In more familiar units this is $-1,313 \text{ kJ/mol}$

The hydrogen atom



- We will use the nucleus as the centre of our coordinates.
- The Hamiltonian is then given by:

$$\begin{aligned}\hat{H} &= \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \\ &= -\frac{1}{2}\nabla_r^2 - \frac{1}{r}\end{aligned}$$

- And the wavefunction is simply a function of \mathbf{r} : $\Psi(\mathbf{r})$

The Born-Oppenheimer approximation

- Nuclei are much heavier than electrons (the mass of a proton ≈ 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:

$$\Psi(\mathbf{R}, \mathbf{r}) = \Psi_n(\mathbf{R})\Psi_e(\mathbf{r}; \mathbf{R})$$

where the ‘;’ notation indicates a parametric dependence.

- The **potential energy surface** is a direct consequence of the BO approximation.

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.*)
 - 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.

Computable properties

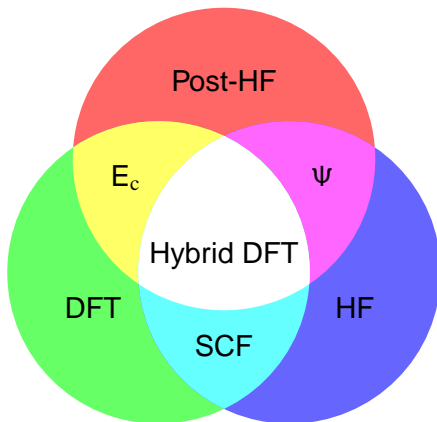
Many molecular properties can be computed, these include

- 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

Statement of the problem

- 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.

Classification of methods



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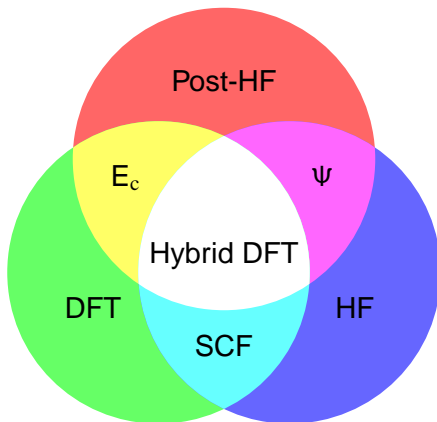
Previously on 3108

- 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

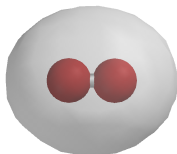


Hartree-Fock theory

- 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.

Hartree-Fock theory

Consider the H_2 molecule:



- The total wavefunction involves 4 coordinates:

$$\Psi = \Psi(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}_1, \mathbf{r}_2)$$
- We invoke the Born-Oppenheimer approximation:

$$\Psi = \Psi_n(\mathbf{R}_1, \mathbf{R}_2) \psi_e(\mathbf{r}_1, \mathbf{r}_2).$$
- How do we model $\Psi_e(\mathbf{r}_1, \mathbf{r}_2)$?

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, ψ_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 is sometimes called the **independent electron 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:

$$\Psi(\mathbf{r}_2, \mathbf{r}_1) = \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) \neq -\Psi(\mathbf{r}_1, \mathbf{r}_2)$$

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

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)]$$

The Hartree-Fock wavefunction

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

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \cdots & \psi_N(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_N) & \psi_2(\mathbf{r}_N) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix}$$

- This ensures the electrons are **indistinguishable** and are therefore associated with every orbital!
- A Slater determinant is often written as $|\psi_1, \psi_2, \dots, \psi_N\rangle$

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**:

$$\psi_i(\mathbf{r}_i) = \sum_{\mu} C_{\mu i} \chi_{\mu}(\mathbf{r}_i)$$

- The χ_{μ} are **atomic orbitals** or **basis functions**.
- The $C_{\mu i}$ are **MO coefficients**.

An example

The diagram illustrates the formation of molecular orbitals from two hydrogen 1s atomic orbitals. On the left and right are two black circles representing the $1s$ atomic orbitals, each labeled χ_{1s} and H_A and H_B respectively. In the center, a dashed hexagon represents the interaction region. Inside this hexagon, two arrows point towards each other, labeled σ , representing the bonding molecular orbital. Above the hexagon, two arrows point away from each other, labeled σ^* , representing the antibonding molecular orbital. At the top and bottom of the diagram are two pairs of circles: a black and a white circle at the top, and two black circles at the bottom, representing the atomic orbitals in the bonding and antibonding states.

$$\begin{aligned}\psi_1 &= \sigma = \frac{1}{\sqrt{2}} (\chi_{1s}^A + \chi_{1s}^B) \\ \psi_2 &= \sigma^* = \frac{1}{\sqrt{2}} (\chi_{1s}^A - \chi_{1s}^B)\end{aligned}$$

- For H_2 the MO coefficients, $C_{\mu i}$, are $\pm \frac{1}{\sqrt{2}}$

The HF energy

- 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:

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

- 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 HF energy

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

$$\psi_i(\mathbf{r}_i) = \sum_{\mu} c_{\mu i} \chi_{\mu}(\mathbf{r}_i)$$

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

$$\begin{aligned} H_i &= \langle \psi_i | \hat{h} | \psi_i \rangle \\ &= \sum_{\mu\nu} c_{\mu i} c_{\nu i} \langle \chi_{\mu} | \hat{h} | \chi_{\nu} \rangle \end{aligned}$$

- The J_{ij} and K_{ij} matrices can also be written in terms of the MO coefficients, $c_{\mu i}$.

The variational principle

- 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**.

The self-consistent field method

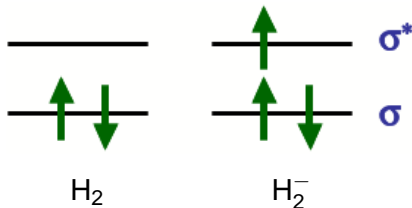
- Thus, computing the **HF energy** implies computing the $C_{\mu i}$.
- To compute the $C_{\mu i}$ we must minimise the **HF energy** according to the variational principle.
- Which comes first: the **HF energy** or the $C_{\mu i}$?

The SCF Process

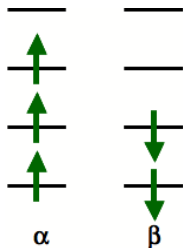
- 1 Guess a set of MOs, $C_{\mu i}$
- 2 Use MOs to compute H_i , J_{ij} and K_{ij}
- 3 Solve the HF equations for the energy and new MOs
- 4 Are the new MOs different? Yes \rightarrow (2) : No \rightarrow (5)
- 5 Self-consistent field converged

Electron Spin

- So far for simplicity we have ignored the **spin variable**, ω .
- Each MO actually contains a **spatial** part and a **spin** part.
- For each spatial orbital, there are two spin orbitals:
 $\chi_i^\alpha(\mathbf{r}, \omega) = \phi_i(\mathbf{r})\alpha(\omega)$ and $\chi_i^\beta(\mathbf{r}, \omega) = \phi_i(\mathbf{r})\beta(\omega)$.
- This is reasonable for **closed-shell** systems, but not for **open-shell** systems.



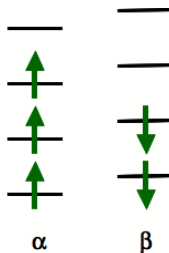
Restricted and unrestricted HF theory



RHF

The spatial part of the spin orbitals are the **same**:

$$\phi_i^\alpha = \phi_i^\beta$$



UHF

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).

Previously on 3108

- The MO approximation and the Hartree wavefunction:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$$

- Antisymmetry and the Hartree-Fock wavefunction:

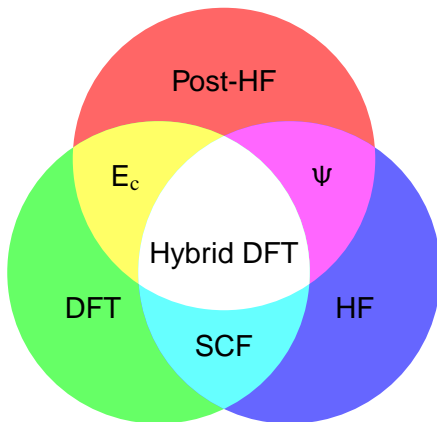
$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)]$$

- The LCAO approximation

$$\psi_i(\mathbf{r}_i) = \sum_{\mu} C_{\mu i} \chi_{\mu}(\mathbf{r}_i)$$

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

Classification of methods



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Energy decomposition

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

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

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

$$E_{el} = \underbrace{E_T + E_V}_{\hat{T}_e + \hat{V}_{ne}} + \underbrace{E_J + E_K + E_C}_{\hat{V}_{ee}}$$

- 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.

Electronic energy decomposition

$$E = E_T + E_V + E_J + E_K + E_C$$

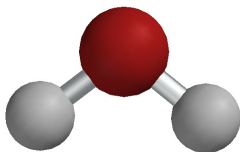
- For the Ne atom, the above energy terms are:

$$\begin{aligned} E_T &= +129 E_h \\ E_V &= -312 E_h \\ E_J &= +66 E_h \\ E_K &= -12 E_h \quad 9.3\% \\ E_C &= -0.4 E_h \quad 0.3\% \end{aligned}$$

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

The importance of E_C

Consider the atomisation energy of the water molecule:



Energy	H ₂ O	2 H + O	ΔE
E_{HF}	-76.057770	-75.811376	0.246393
E_{CCSD}	-76.337522	-75.981555	0.355967

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

Modelling the correlation energy

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.

Configuration interaction

- Recall the HF wavefunction is a single determinant made up of the product of occupied molecular orbitals ψ_i :

$$\Psi_0 = |\psi_1, \psi_2, \dots \psi_N\rangle$$

$$\psi_i = \sum_{\mu} C_{\mu i} \chi_{\mu}$$

- 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 interaction

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

$$\Psi_0 = |\psi_1, \psi_2, \dots \psi_i \psi_j \dots \psi_N\rangle$$

$$\Psi_i^a = |\psi_1, \psi_2, \dots \psi_a \psi_j \dots \psi_N\rangle$$

$$\Psi_{ij}^{ab} = |\psi_1, \psi_2, \dots \psi_a \psi_b \dots \psi_N\rangle$$

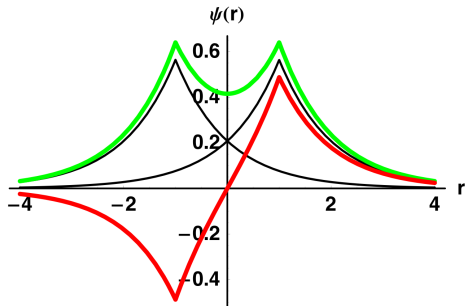
- These **configurations** can be mixed together to obtain a better approximation to the wavefunction:

$$\Psi_{\text{CI}} = c_0 \Psi_0 + \sum_i c_i^a \Psi_i^a + \sum_{ij} c_{ij}^{ab} \Psi_{ij}^{ab} + \dots$$

- The CI coefficients, $c_i^a, c_{ij}^{ab} \dots$ can be found via the **variational method**

How does this help?

Consider a minimal H_2 system with two MOs:



$$\psi_1 = \sigma = \frac{1}{\sqrt{2}} (\chi_{1s}^A + \chi_{1s}^B)$$

$$\psi_2 = \sigma^* = \frac{1}{\sqrt{2}} (\chi_{1s}^A - \chi_{1s}^B)$$

The anti-bonding orbital, σ^* , 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

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- Additional types of functions

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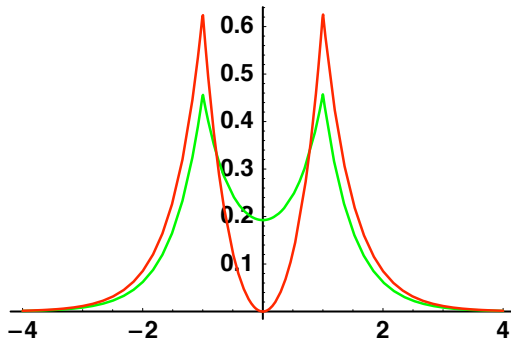
- The **origins** of the electronic correlation energy
- The **importance** of the electronic correlation energy
- The idea of a **configuration** (determinant):

$$\begin{aligned}\Psi_0 &= |\psi_1, \psi_2, \dots \psi_i \psi_j \dots \psi_N\rangle \\ \Psi_i^a &= |\psi_1, \psi_2, \dots \psi_a \psi_j \dots \psi_N\rangle \\ \Psi_{ij}^{ab} &= |\psi_1, \psi_2, \dots \psi_a \psi_b \dots \psi_N\rangle\end{aligned}$$

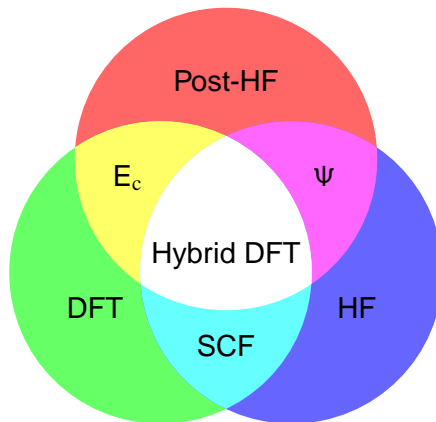
- The **configuration interaction** wavefunction

$$\Psi_{\text{CI}} = c_0 \Psi_0 + \sum_i^{\text{occ}} \sum_a^{\text{vir}} c_i^a \Psi_i^a + \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} c_{ij}^{ab} \Psi_{ij}^{ab} + \dots$$

Orbital densities



Classification of 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 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

Size consistency

- 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:

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

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

- The CCD wavefunction can then be written as :

$$\begin{aligned} \Psi_{\text{CCD}} &= \exp(T_2)\Psi_0 \\ &= \left[1 + T_2 + \frac{T_2^2}{2!} + \frac{T_2^3}{3!} + \dots \right] \Psi_0 \end{aligned}$$

- T_2^2 gives some quadruple excitations and leads to **size-consistency**

The HF Hamiltonian

- 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:

$$\hat{H}_0 = \sum_i f(\mathbf{r}_i)$$

$$f(\mathbf{r}_i) = \hat{T}(\mathbf{r}_i) + \hat{V}_{\text{ne}}(\mathbf{r}_i) + \hat{v}^{\text{HF}}(\mathbf{r}_i)$$

- 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 λ (which is later set to unity)

$$\psi_\lambda = \psi_0 + \lambda \psi_1 + \lambda^2 \psi_2 + \dots$$

$$E_\lambda = E_0 + \lambda E_1 + \lambda^2 E_2 + \dots$$

- ψ_0 and E_0 are the HF wavefunction and energy

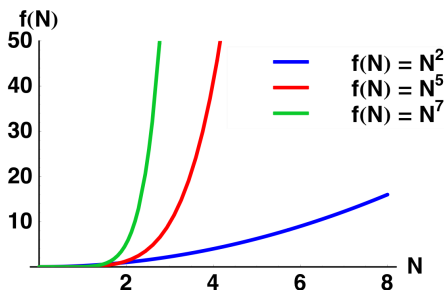
Møller-Plesset perturbation theory

- **MP n** is obtained by truncating the expansion at order λ^n
- The **MP1** energy is the same as the HF energy
- The **MP2** energy is given by:

$$E_{\text{MP2}} = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} \frac{|\langle \Psi_0 | \hat{V} | \Psi_{ij}^{ab} \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

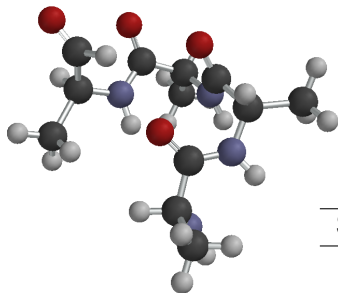
- The cost of calculating the **MP2** energy scales as $\mathcal{O}(N^5)$ and typically recovers $\sim 80\text{-}90\%$ of the correlation energy
- The **MP n** energy is **size-consistent** but not **variational**
- The **MP series** may **diverge** for large orders

Scaling



- HF formally scales as $\mathcal{O}(N^4)$, practically as $\mathcal{O}(N^2)$
- MP_n scales as $\mathcal{O}(N^{n+3})$
- CCSD and CISD scale as $\mathcal{O}(N^6)$
- CCSD(T) scales as $\mathcal{O}(N^7)$
- CCSDT scales as $\mathcal{O}(N^8)$

An example



System	t_{HF}	t_{MP2}	t_{CCSD}
Ala ₁	2.6 s	40 s	58 m
Ala ₂	47 s	6 m 30 s	
Ala ₃	3m 20 s	30 m 50 s	
Ala ₄	8m 20 s		

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

Previously on 3108

- Correlated wavefunction methods:

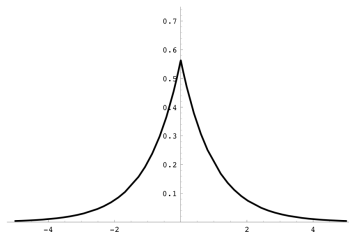
Theory	Ψ	Variational	Size-Consistent
CI	$(1 + T_1 + T_2 + \dots)\Psi_0$	✓	✗
CC	$\exp(T_1 + T_2 + \dots)\Psi_0$	✗	✓
MP	$\Psi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \dots$	✗	✓

- 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**

Basis functions

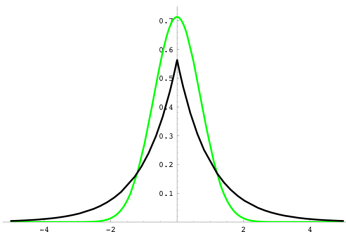
- The atom-centred functions used to describe the **atomic orbitals** are known as **basis functions** and collectively form a **basis set**
- Larger basis sets give a **better approximation** to the atomic orbitals as they place fewer restrictions on the wavefunction
- Larger basis sets attract a **higher computational cost**
- Basis sets are carefully designed to give the best description for the lowest cost

Gaussian basis representations



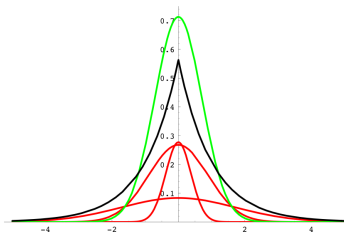
- The 1s orbital of the H atom is an exponential $e^{-\alpha|\mathbf{r}-\mathbf{A}|}$ which gives rise to difficult integrals
- **Primitive** Gaussians, $e^{-\beta|\mathbf{r}-\mathbf{A}|^2}$ yield easier integrals but do not have the correct behaviour
- If we take fixed combinations of Gaussians $\{D_i e^{-\beta_i|\mathbf{r}-\mathbf{A}|^2}\}$
- ...we get the best of both worlds $\sum_i D_i e^{-\beta_i|\mathbf{r}-\mathbf{A}|^2}$

Gaussian basis representations

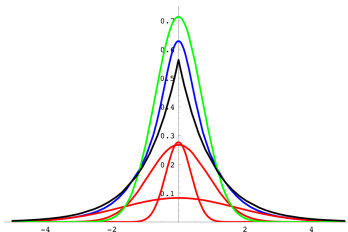


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Gaussian basis functions

- 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 χ
- K is the degree of **contraction** of χ
- D_i are the **contraction coefficients** of χ
- α_i are the **exponents** of χ
- These types of basis functions are sometimes referred to as **GTOs**

Minimal basis sets

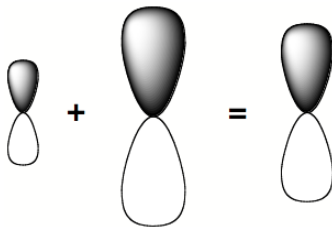
- The simplest possible atomic orbital representation is called a **minimal basis set**
- Minimal basis sets contain the minimum number of basis functions to accommodate all of the electrons in the atom
- For example:
 - H & He** a single function (1s)
 - 1st row** 5 functions, (1s, 2s, 2p_x, 2p_y, 2p_z)
 - 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**

Minimal basis sets

- The **STO-3G** basis set is a minimal basis set where each atomic orbital is made up of **3** Gaussians. STO-*n*G 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

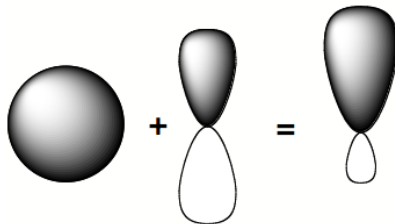
- Split-valence basis sets model each valence orbital by two or more basis functions that have different exponents
- They allow for size variations that occur in bonding



- Examples include the **double split valence** basis sets, 3-21G and 6-31G, and **triple split valence** basis sets such as 6-311G

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.

Mix and match

- 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

Examples

Basis set	Description	No. functions			
		H	C,O	H ₂ O	C ₆ H ₆
STO-3G	Minimal	1	5	7	36
3-21G	Double split-valence	2	9	13	66
6-31G(<i>d</i>)	Double split-valence with polarisation	2	15	19	102
6-31G(<i>d</i> , <i>p</i>)	Ditto, with <i>p</i> functions on H	5	15	25	120
6-311+G(<i>d</i> , <i>p</i>)	Triple split-valence with polarisation, <i>p</i> functions on H and diffuse functions on heavy atoms	6	22	34	168

Accuracy

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:

Basis set	Bond Length (Å)	D_0 (kJ/mol)
6-31G(<i>d</i>)	0.9337	491
6-31G(<i>d</i> , <i>p</i>)	0.9213	523
6-31+G(<i>d</i>)	0.9408	515
6-311G(<i>d</i>)	0.9175	484
6-311+G(<i>d</i> , <i>p</i>)	0.9166	551
Expt.	0.917	566

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

Lecture

4

Correlated Methods

- Configuration interaction
- Coupled-cluster theory
- Perturbation theory
- Computational Cost

5

Basis Sets

- Basis functions
- Additional types of functions

6

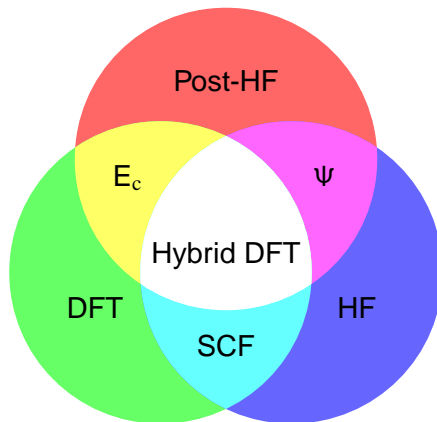
Density Functional Theory

- Density functionals
- The Hohenberg–Kohn theorems
- DFT models

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



What is the density?

- The electron density is a fundamental quantity in quantum chemistry

$$\rho(\mathbf{r}_1) = \int \cdots \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N$$

- $\rho(\mathbf{r})d\mathbf{r}$ gives the **probability** of finding an electron in the volume element **$d\mathbf{r}$**
- 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:

$$f(x) = x^2 - 1 \quad f(3) = 8$$

- 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:

$$N[\rho] = \int \rho(\mathbf{r}) d\mathbf{r}$$

simply gives the number of electrons in the molecule

- Density functional theory (DFT) focusses 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:

$$E_J = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$E_V = - \sum_A \int \frac{Z_A \rho(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|} d\mathbf{r}$$

- What about E_T , E_K and E_C ?

Orbital functionals

- In Hartree-Fock theory, E_T , E_K and E_C , are all **orbital functionals**, eg:

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

- No (known) exact expression for the kinetic energy in terms of ρ 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 $\rho(\mathbf{r})$ 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 $\nu(\mathbf{r})$, 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 Hohenberg–Kohn theorems

- 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

- 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:

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

- Much later, Vosko, Wilk and Nusair parameterised a correlation functional based on the UEG, its form is more complicated and it is inexact

Local density approximation

- 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_α theory**

Gradient corrected functionals

- Gradient corrected functions depend on $\nabla\rho$ as well as ρ
- 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:

$$E^{B3LYP} = (1 - c_1)E_X^{D30} + c_1 E_K^{Fock} + c_2 E_X^{B88} + (1 - c_3)E_C^{VWN} + c_3 E_C^{LYP}$$

- B3LYP is **the** most popular density functional that is used and yields very good structural and thermochemical properties

Strengths and weaknesses

Advantages of DFT methods include:

- Low computational cost
- Good accuracy for structures and thermochemistry
- The density is conceptually more simple than Ψ

Disadvantages of DFT methods include:

- Can fail spectacularly and unexpectedly
- No systematic way of improving the results
- Integrals require numerical quadrature grids

Lecture

7

Model Chemistries

- Model chemistries

Levels of theory

- 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

	HF	MP2	MP3	MP4	CCSD(T)	...	Full CI
Minimal	Low-level	Unbalanced
Split-Valence					
Polarised							
Diffuse	...						
Polarised + Diffuse							
⋮						⋮	
Infinite	Unbalanced						Exact!

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

Performance

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

Bond-length	HF	MP2	LDA	GGA	Hybrid
Deviation Å	0.021	0.014	0.016	0.017	0.011

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

AE	HF	MP2	LDA	GGA	Hybrid
Deviation kcal/mol	119.2	22.0	52.2	7.0	6.8

Performance

Calculated electron affinity (eV) for Fluorine:

	HF	MP2	B3LYP
STO-3G	-10.16	-10.16	-9.01
3-21G	-1.98	-1.22	-0.86
6-31G(<i>d</i>)	-0.39	+1.07	+1.05
6-311+G(2 <i>df</i> , <i>p</i>)	+1.20	+3.44	+3.46
6-311+G(3 <i>df</i> ,2 <i>p</i>)	+1.19	+3.54	+3.46
Experiment	+3.48		