

Panorama of the methods in quantum chemistry

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Workshop on wave-function methods in quantum chemistry and nuclear physics



“Chemical” assumptions for this afternoon...

- **Chemistry is about energy differences!**
- We consider the **time-independent** Schrödinger equation
- We don't care about **relativistic effects**
- We decouple nuclei and electrons \Rightarrow **Born-Oppenheimer approximation**
- Electronic part is solved with the nuclear positions as parameters \Rightarrow **potential energy surface (PES)**
- We are interested by **electrons** which are **fermions** \Rightarrow **Pauli exclusion principle**
 $|\alpha\rangle =$ **spin-up** electron and $|\beta\rangle =$ **spin-down** electron

$$\langle \alpha | \beta \rangle = 0 \quad \langle \alpha | \alpha \rangle = 1 \quad \langle \beta | \beta \rangle = 1$$

The Hamiltonian in Chemistry

In the Schrödinger equation

$$H\Phi(r, R) = E\Phi(r, R)$$

The total Hamiltonian is

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

What are all these terms?

- T_n is the kinetic energy of the nuclei
- T_e is the kinetic energy of the electrons
- V_{ne} is the Coulomb attraction between nuclei and electrons
- V_{ee} is the Coulomb repulsion between electrons
- V_{nn} is the Coulomb repulsion between nuclei

The Hamiltonian in Chemistry (Take 2)

In atomic units
($m = e = \hbar = 1$)

$$T_n = - \sum_{A=1}^{N_{\text{nuc}}} \frac{\nabla_A^2}{2M_A}$$

$$T_e = - \sum_{i=1}^N \frac{\nabla_i^2}{2}$$

$$V_{ne} = - \sum_{A=1}^{N_{\text{nuc}}} \sum_{i=1}^N \frac{Z_A}{r_{iA}}$$

$$V_{ee} = \sum_{i < j}^N \frac{1}{r_{ij}}$$

$$V_{nn} = \sum_{A < B}^{N_{\text{nuc}}} \frac{Z_A Z_B}{R_{AB}}$$

- ∇^2 is the **Laplace operator** (or Laplacian)
- M_A is the **mass** of nucleus A
- Z_A is the **charge** of nucleus A
- r_{iA} is the **distance** between electron i and nucleus A
- r_{ij} is the **distance** between electrons i and j
- R_{AB} is the **distance** between nuclei A and B

Electronic Hamiltonian

The **electronic Hamiltonian** is

$$H_e = T_e + V_{ne} + V_{ee} + V_{nn}$$

Because $M_A \gg 1$, the nuclear coordinates are “parameters”:

$$\Phi(\mathbf{r}, \mathbf{R}) = \Xi(\mathbf{R})\Psi(\mathbf{r}, \{\mathbf{R}\})$$

The Hartree-Fock Wave Function

The Hartree-Fock Approximation is...

- an independent-particle model \Rightarrow interactions are taken into account in an average fashion
- the starting point of pretty much anything in quantum chemistry!

A Slater Determinant

$$\mathbf{x} = (\omega, \mathbf{r}) \quad \Psi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

- The variable \mathbf{x} combines spin (ω) and spatial (\mathbf{r}) coordinates
- Ψ_{HF} is an antisymmetrized product of one-electron functions known as orbitals

The Hartree-Fock Wave Function (Take 2)

Molecular orbitals (MO)

$$\chi_i(\mathbf{x}) = \sigma(\omega)\psi_i(\mathbf{r}) = \begin{cases} \alpha(\omega)\psi_i(\mathbf{r}) \\ \beta(\omega)\psi_i(\mathbf{r}) \end{cases}$$

$$\psi_i(\mathbf{r}) = \sum_{\mu}^K C_{\mu i} \phi_{\mu}(\mathbf{r})$$

These are **restricted spin orbitals** \Rightarrow **Restricted Hartree-Fock = RHF**

The spin orbitals are orthogonal

The spatial orbitals are orthogonal

$$\langle \chi_i | \chi_j \rangle = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases}$$

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} = \text{Kronecker delta}$$

The atomic orbitals **are not** orthogonal

$$\langle \phi_{\mu} | \phi_{\nu} \rangle = S_{\mu\nu} = \text{Overlap matrix}$$

The Hartree-Fock energy

We know that

$$H_e = T_e + V_{ne} + V_{ee} + V_{nn}$$

We define a few quantities:

- the **one-electron Hamiltonian** (or core Hamiltonian) = nice guy!

$$O_1 = T_e + V_{ne} = \sum_{i=1}^N h(i) \quad \text{where} \quad h(i) = -\frac{\nabla_i^2}{2} - \sum_{A=1}^{N_{\text{nuc}}} \frac{Z_A}{r_{iA}}$$

- the **two-electron Hamiltonian** (electron-electron repulsion) = nasty guy!

$$O_2 = V_{ee} = \sum_{i < j}^N \frac{1}{r_{ij}}$$

Therefore, we have

$$H_e = \sum_{i=1}^N h(i) + \sum_{i < j}^N \frac{1}{r_{ij}} + V_{nn}$$

The Hartree-Fock energy (Take 2)

- **Nuclear repulsion:** $\langle \Psi_{\text{HF}} | V_{\text{nn}} | \Psi_{\text{HF}} \rangle = V_{\text{nn}} \langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle = V_{\text{nn}}$

- **Core Hamiltonian:**

$$\langle \Psi_{\text{HF}} | O_1 | \Psi_{\text{HF}} \rangle = \sum_{i=1}^N \langle \chi_i(1) | h(1) | \chi_i(1) \rangle = \sum_{i=1}^N h_i$$

- **Two-electron Hamiltonian:**

$$\begin{aligned} \langle \Psi_{\text{HF}} | O_2 | \Psi_{\text{HF}} \rangle &= \sum_{i < j}^N \left[\langle \chi_i(1) \chi_j(2) | r_{12}^{-1} | \chi_i(1) \chi_j(2) \rangle - \langle \chi_i(1) \chi_j(2) | r_{12}^{-1} | \chi_j(1) \chi_i(2) \rangle \right] \\ &= \sum_{i < j}^N (\mathcal{J}_{ij} - \mathcal{K}_{ij}) = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (\mathcal{J}_{ij} - \mathcal{K}_{ij}) \quad \text{because } \boxed{\mathcal{J}_{ii} = \mathcal{K}_{ii}} \end{aligned}$$

$$E_{\text{HF}} = \sum_{i=1}^N h_i + \sum_{i < j}^N (\mathcal{J}_{ij} - \mathcal{K}_{ij})$$

Coulomb operator $\mathcal{J}_i(1) | \chi_j(2) \rangle = \langle \chi_i(2) | r_{12}^{-1} | \chi_i(2) \rangle | \chi_j(1) \rangle$

Exchange operator $\mathcal{K}_i(1) | \chi_j(2) \rangle = \langle \chi_i(2) | r_{12}^{-1} | \chi_j(2) \rangle | \chi_i(1) \rangle$

The Fock matrix

Using the **variational principle**, one can show that, to minimise the energy, the MOs need to **diagonalise the Fock operator**

$$f(1) = h(1) + \sum_j^{\text{occ}} [\mathcal{J}_j(1) - \mathcal{K}_j(1)]$$

For a **closed-shell system** (i.e. two electrons in each orbital)

$$f(1) = h(1) + \sum_j^{N/2} [2J_j(1) - K_j(1)] \quad (\text{closed shell})$$

These orbitals are called **canonical molecular orbitals** (= eigenvectors):

$$f(1) \chi_i(1) = \varepsilon_i(1) \chi_i(1)$$

and ε_i are called the **MO energies** (= eigenvalues)

Introduction of a basis

Expansion in a basis

$$\psi_i(\mathbf{r}) = \sum_{\mu}^K C_{\mu i} \phi_{\mu}(\mathbf{r}) \quad \equiv \quad |i\rangle = \sum_{\mu}^K C_{\mu i} |\mu\rangle$$

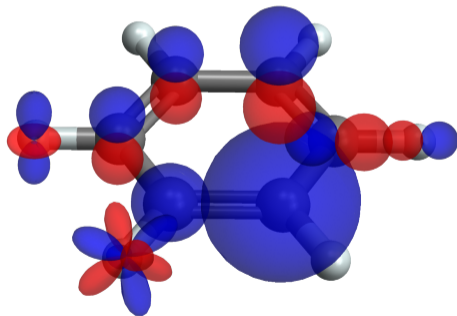
K AOs gives K MOs: $N/2$ are doubly-occupied MOs and $K - N/2$ are vacant/virtual MOs

Roothaan-Hall equations

$$\begin{aligned}
 f|i\rangle = \varepsilon_i|i\rangle &\Rightarrow f \sum_{\nu} C_{\nu i} |\nu\rangle = \varepsilon_i \sum_{\nu} C_{\nu i} |\nu\rangle \\
 \Rightarrow \langle \mu | f \sum_{\nu} C_{\nu i} |\nu\rangle &= \varepsilon_i \langle \mu | \sum_{\nu} C_{\nu i} |\nu\rangle \\
 \Rightarrow \sum_{\nu} C_{\nu i} \langle \mu | f | \nu \rangle &= \sum_{\nu} C_{\nu i} \varepsilon_i \langle \mu | \nu \rangle \Rightarrow \boxed{\sum_{\nu} F_{\mu\nu} C_{\nu i} = \sum_{\nu} S_{\mu\nu} C_{\nu i} \varepsilon_i}
 \end{aligned}$$

Atom-centered Gaussian basis sets (cf Emmanuel Giner's Talk)

$$\phi_{\mu}(\mathbf{r}) = (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} \exp(-\alpha|\mathbf{r} - \mathbf{A}|^2) \quad \mathbf{A} = (A_x, A_y, A_z) \quad \mathbf{a} = (a_x, a_y, a_z)$$



Chemists vs Physicists or Mulliken vs Dirac (cf Emmanuel Giner's Talk)

HF energy in the AO basis (closed-shell system)

$$E_{\text{HF}} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^c + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\sigma|\lambda\nu) \right] P_{\lambda\sigma} \quad P_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{\mu i} C_{\nu i}$$

Chemist's notation for two-electron integrals

$$(\mu\nu|\lambda\sigma) = \iint \phi_{\mu}(\mathbf{1})\phi_{\nu}(\mathbf{1}) \frac{1}{r_{12}} \phi_{\lambda}(\mathbf{2})\phi_{\sigma}(\mathbf{2}) d\mathbf{r}_1 d\mathbf{r}_2$$

$$(\mu\nu||\lambda\sigma) = (\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)$$

Physicist's notation for two-electron integrals

$$\langle \mu\nu|\lambda\sigma \rangle = \iint \phi_{\mu}(\mathbf{1})\phi_{\nu}(\mathbf{2}) \frac{1}{r_{12}} \phi_{\lambda}(\mathbf{1})\phi_{\sigma}(\mathbf{2}) d\mathbf{r}_1 d\mathbf{r}_2$$

$$\langle \mu\nu||\lambda\sigma \rangle = \langle \mu\nu|\lambda\sigma \rangle - \langle \mu\nu|\sigma\lambda \rangle$$

Unrestricted HF (UHF)

How to model open-shell systems?

- RHF is made to describe **closed-shell systems** and we have used **restricted spin orbitals**:

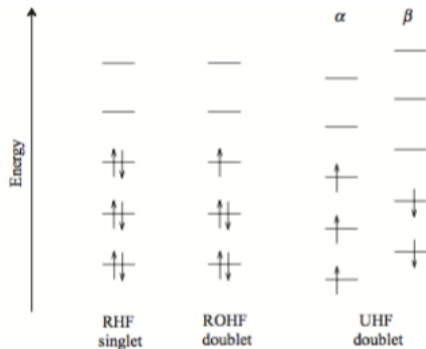
$$\chi_i^{\text{RHF}}(\mathbf{x}) = \begin{cases} \alpha(\omega) \psi_i(\mathbf{r}) \\ \beta(\omega) \psi_i(\mathbf{r}) \end{cases}$$

- It does **not** describe **open-shell systems**
- For open-shell systems we can use **unrestricted spin orbitals**

$$\chi_i^{\text{UHF}}(\mathbf{x}) = \begin{cases} \alpha(\omega) \psi_i^\alpha(\mathbf{r}) \\ \beta(\omega) \psi_i^\beta(\mathbf{r}) \end{cases}$$

- RHF = **Restricted** Hartree-Fock \leftrightarrow **Roothaan-Hall equations**
- UHF = **Unrestricted** Hartree-Fock \leftrightarrow **Pople-Nesbet equations**
- **Restricted Open-shell Hartree-Fock (ROHF)** do exist but we won't talk about it

RHF, ROHF and UHF



- RHF = **R**estricted Hartree-Fock
- UHF = **U**nrestricted Hartree-Fock
- ROHF = **R**estricted **O**pen-shell Hartree-Fock

Unrestricted Hartree-Fock Equations

UHF equations for unrestricted spin orbitals

To minimize the UHF energy, the unrestricted spin orbitals must be eigenvalues of the α and β Fock operators:

$$f^\alpha(1) \psi_j^\alpha(1) = \varepsilon_j^\alpha \psi_j^\alpha(1)$$

$$f^\beta(1) \psi_j^\beta(1) = \varepsilon_j^\beta \psi_j^\beta(1)$$

where

$$f^\alpha(1) = h(1) + \sum_i^{N^\alpha} [J_i^\alpha(1) - K_i^\alpha(1)] + \sum_i^{N^\beta} J_i^\beta(1)$$

The Coulomb and Exchange operators are

$$J_i^\alpha(1) = \int \psi_i^\alpha(2) r_{12}^{-1} \psi_i^\alpha(2) dr_2$$

$$K_i^\alpha(1) \psi_j^\alpha(1) = \left[\int \psi_i^\alpha(2) r_{12}^{-1} \psi_j^\alpha(2) dr_2 \right] \psi_i^\alpha(1)$$

The correlation energy

- HF replaces the e-e interaction by an **averaged interaction**
- The error in the HF method is called the **correlation energy**

$$E_c = E - E_{\text{HF}}$$

- The correlation energy is small **but cannot be neglected!**
- HF energy **roughly 99%** of total but **chemistry very sensitive to remaining 1%**
- The correlation energy is **always negative**
- Computing E_c is one of the **central problem of quantum chemistry**
- In quantum chemistry, we usually **“freeze” the core electrons** for correlated calculations

Correlation methods

- 1 **Configuration Interaction** (CID, CIS, CISD, QCISD)
- 2 **Coupled Cluster** (CCD, CCSD, CCSD(T), CCSDT)
- 3 **Møller-Plesset perturbation theory** (MP2, MP3, MP4)
- 4 **Multireference methods** (MCSCF, CASSCF, RASSCF, MRCC, CASPT2)
- 5 **Explicitly correlated F12 methods** (MP2-F12, CCSD-F12, CAS-F12)
- 6 **Density-functional theory** (DFT, TDDFT)
- 7 **Stochastic Quantum Monte Carlo methods** (VMC, DMC, FCIQMC)

Configuration Interaction (CI)

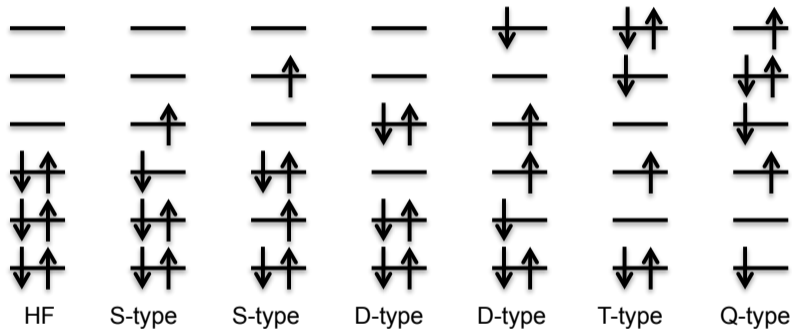
- This is the **oldest** and perhaps the **easiest method to understand**
- CI is based on the **variational principle** (like HF)
- The CI wave function is a **linear combination of determinants**
- CI methods use **excited determinants** to “improve” the HF wave function

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{ia} c_i^a |\Psi_i^a\rangle + \sum_{\substack{i<j \\ a<b}} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \sum_{\substack{i<j<k \\ a<b<c}} c_{ijk}^{abc} |\Psi_{ijk}^{abc}\rangle + \sum_{\substack{i<j<k<l \\ a<b<c<d}} c_{ijkl}^{abcd} |\Psi_{ijkl}^{abcd}\rangle + \dots$$

- In Ψ_{ij}^{ab} , the electrons in **occupied spinorbital i and j** have been promoted to the **virtual spinorbitals a and b**

CI method and Excited determinants

Excited determinants



CI wave function

$$|\Phi_0\rangle = c_0|\text{HF}\rangle + c_S|\text{S}\rangle + c_D|\text{D}\rangle + c_T|\text{T}\rangle + c_Q|\text{Q}\rangle + \dots$$

Truncated CI

- When $|S\rangle$ (**singles**) are taken into account: **CIS**

$$|\Phi_{\text{CIS}}\rangle = c_0|\text{HF}\rangle + c_S|S\rangle$$

NB: CIS is an **excited state method**

- When $|D\rangle$ (**doubles**) are taken into account: **CID**

$$|\Phi_{\text{CID}}\rangle = c_0|\text{HF}\rangle + c_D|D\rangle$$

NB: CID is the **cheapest CI method**

- When $|S\rangle$ and $|D\rangle$ are taken into account: **CISD**

$$|\Phi_{\text{CISD}}\rangle = c_0|\text{HF}\rangle + c_S|S\rangle + c_D|D\rangle$$

NB: CISD is the **most commonly-used** CI method

- When $|S\rangle$, $|D\rangle$ and $|T\rangle$ (**triples**) are taken into account: **CISDT**

$$|\Phi_{\text{CISDT}}\rangle = c_0|\text{HF}\rangle + c_S|S\rangle + c_D|D\rangle + c_T|T\rangle$$

- **CISDTQ**, etc.

Full CI

- When all possible excitations are taken into account
this is called a Full CI calculation (**FCI**)

$$|\Phi_{\text{FCI}}\rangle = c_0|\text{HF}\rangle + c_S|\text{S}\rangle + c_D|\text{D}\rangle + c_T|\text{T}\rangle + c_Q|\text{Q}\rangle + \dots$$

- FCI gives the exact solution of the Schrödinger equation within a given basis
- FCI is becoming more and more fashionable these days (e.g. FCIQMC and SCI methods)
- So, why do we care about other methods?
- Because FCI is bloody computationally expensive!
- Selected CI (SCI) methods have recently resurrected!! Cf Sandeep Sharma's talk

The FCI matrix

$$|\Phi_0\rangle = c_0|\text{HF}\rangle + c_S|\text{S}\rangle + c_D|\text{D}\rangle + c_T|\text{T}\rangle + c_Q|\text{Q}\rangle + \dots$$

Before pruning:

	$ \text{HF}\rangle$	$ \text{S}\rangle$	$ \text{D}\rangle$	$ \text{T}\rangle$	$ \text{Q}\rangle$	\dots
$\langle\text{HF} $	$\langle\text{HF} \text{H} \text{HF}\rangle$	$\langle\text{HF} \text{H} \text{S}\rangle$	$\langle\text{HF} \text{H} \text{D}\rangle$	$\langle\text{HF} \text{H} \text{T}\rangle$	$\langle\text{HF} \text{H} \text{Q}\rangle$	\dots
$\langle\text{S} $	$\langle\text{S} \text{H} \text{HF}\rangle$	$\langle\text{S} \text{H} \text{S}\rangle$	$\langle\text{S} \text{H} \text{D}\rangle$	$\langle\text{S} \text{H} \text{T}\rangle$	$\langle\text{S} \text{H} \text{Q}\rangle$	\dots
$\langle\text{D} $	$\langle\text{D} \text{H} \text{HF}\rangle$	$\langle\text{D} \text{H} \text{S}\rangle$	$\langle\text{D} \text{H} \text{D}\rangle$	$\langle\text{D} \text{H} \text{T}\rangle$	$\langle\text{D} \text{H} \text{Q}\rangle$	\dots
$\langle\text{T} $	$\langle\text{T} \text{H} \text{HF}\rangle$	$\langle\text{T} \text{H} \text{S}\rangle$	$\langle\text{T} \text{H} \text{D}\rangle$	$\langle\text{T} \text{H} \text{T}\rangle$	$\langle\text{T} \text{H} \text{Q}\rangle$	\dots
$\langle\text{Q} $	$\langle\text{Q} \text{H} \text{HF}\rangle$	$\langle\text{Q} \text{H} \text{S}\rangle$	$\langle\text{Q} \text{H} \text{D}\rangle$	$\langle\text{Q} \text{H} \text{T}\rangle$	$\langle\text{Q} \text{H} \text{Q}\rangle$	\dots
\vdots	\vdots	\vdots	\vdots	\vdots	\vdots	\vdots

After pruning:

	$ \text{HF}\rangle$	$ \text{S}\rangle$	$ \text{D}\rangle$	$ \text{T}\rangle$	$ \text{Q}\rangle$	\dots
$\langle\text{HF} $	$\langle\text{HF} \text{H} \text{HF}\rangle$	0	$\langle\text{HF} \text{H} \text{D}\rangle$	0	0	\dots
$\langle\text{S} $	0	$\langle\text{S} \text{H} \text{S}\rangle$	$\langle\text{S} \text{H} \text{D}\rangle$	$\langle\text{S} \text{H} \text{T}\rangle$	0	\dots
$\langle\text{D} $	$\langle\text{D} \text{H} \text{HF}\rangle$	$\langle\text{D} \text{H} \text{S}\rangle$	$\langle\text{D} \text{H} \text{D}\rangle$	$\langle\text{D} \text{H} \text{T}\rangle$	$\langle\text{D} \text{H} \text{Q}\rangle$	\dots
$\langle\text{T} $	0	$\langle\text{T} \text{H} \text{S}\rangle$	$\langle\text{T} \text{H} \text{D}\rangle$	$\langle\text{T} \text{H} \text{T}\rangle$	$\langle\text{T} \text{H} \text{Q}\rangle$	\dots
$\langle\text{Q} $	0	0	$\langle\text{Q} \text{H} \text{D}\rangle$	$\langle\text{Q} \text{H} \text{T}\rangle$	$\langle\text{Q} \text{H} \text{Q}\rangle$	\dots
\vdots	\vdots	\vdots	\vdots	\vdots	\vdots	\vdots

Rules & Observations

- ① No coupling between HF ground state $|HF\rangle$ and single excitations $|S\rangle$
 \Rightarrow Brillouin theorem

$$\langle HF|H|S\rangle = 0$$

- ② No coupling between $|HF\rangle$ and triples $|T\rangle$, quadruples $|Q\rangle$, etc.
 \Rightarrow Slater-Condon rules

$$\langle HF|H|T\rangle = \langle HF|H|Q\rangle = \dots = 0$$

$$\langle S|H|Q\rangle = \dots = 0$$

- ③ $|S\rangle$ have small effect but mix indirectly with $|D\rangle$
 \Rightarrow CID \neq CISD

$$\langle HF|H|S\rangle = 0 \text{ but } \langle S|H|D\rangle \neq 0$$

- ④ $|D\rangle$ have large effect and $|Q\rangle$ more important than $|T\rangle$
 \Rightarrow CID gives most of the correlation energy

$$\langle HF|H|D\rangle \gg \langle HF|H|Q\rangle \gg \langle HF|H|T\rangle$$

Size consistency and size extensivity

- Truncated CI methods are **size inconsistent** i.e.

$$2E_c(\text{H}_2) \neq E_c(\text{H}_2 \cdots \text{H}_2)$$

- Size consistent defines for **non-interacting fragment**
- **Size extensivity** refers to the scaling of E_c with the number of electrons
- **NB:** FCI is size consistent and size extensive

Møller-Plesset (MP) perturbation theory

In **Møller-Plesset perturbation theory**, the partition is

$$H^{(0)} = \sum_{i=1}^N f(i) = \sum_{i=1}^N [h(i) + v^{\text{HF}}(i)], \quad H^{(1)} = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i v^{\text{HF}}(i)$$

Therefore,

$$E_0^{(0)} = \sum_i^{\text{occ}} \varepsilon_i, \quad E_0^{(1)} = -\frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij || ij \rangle \Rightarrow \boxed{E_{\text{HF}} = E_0^{(0)} + E_0^{(1)}}$$

The first information about the correlation energy is given by the 2nd-order energy

$$\boxed{E_0^{(2)} = \sum_{i<j}^{\text{occ}} \sum_{a<b}^{\text{virt}} \frac{\langle ij || ab \rangle^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}}$$

This is the MP2 energy!!

There's a similar expression for the MP3 energy, but I was too lazy to type it.

MP3 energy

The third-order correction is a bit ugly...

$$\begin{aligned}
 E_0^{(3)} = & \frac{1}{8} \sum_{ijkl} \sum_{ab} \frac{\langle ij||ab \rangle \langle kl||ij \rangle \langle ab||kl \rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k + \varepsilon_l - \varepsilon_a - \varepsilon_b)} \\
 & + \frac{1}{8} \sum_{ij} \sum_{abcd} \frac{\langle ij||ab \rangle \langle ab||cd \rangle \langle cd||ij \rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_c - \varepsilon_d)} \\
 & + \sum_{ijk} \sum_{abc} \frac{\langle ij||ab \rangle \langle kb||cj \rangle \langle ac||ik \rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_c)}
 \end{aligned}$$

NB:

MP2 and MP3 only requires only doubly excited determinants

MP4 does need singly, doubly, triply and quadruply excited determinant!

Illustration for the Be atom

Correlation energy of Be in a 4s2p basis set

Scaling	Level	ΔE_c	%	Level	ΔE_c	%
K^5	MP2	0.053174	67.85			
K^6	MP3	0.067949	86.70	CISD	0.075277	96.05
K^7	MP4	0.074121	94.58			
K^8	MP5	0.076918	98.15	CISDT	0.075465	96.29
K^9	MP6	0.078090	99.64			
K^{10}	MP7	0.078493	100.15	CISDTQ	0.078372	100

- **MPn is not a variational method**, i.e. you can get **an energy lower than the true ground state energy!**
- MPn **fails** for systems with **small HOMO-LUMO gap**
- The MPn series **can oscillate** around the exact energy
- **MPn is size-consistent!**

Coupled Cluster wave function

- Idea behind CC

"Perturbation methods add all types of corrections (S, D, T, Q, etc.) to the reference wave function to a given order (2, 3, 4, etc.). The idea in CC methods is to include all corrections of a given type to infinite order.

- Excitation operator

$$T = T_1 + T_2 + T_3 + T_4 + \dots$$

- Action on the HF wave function

$$T_1 \Psi_0 = \sum_{ia} t_i^a \Psi_i^a \quad T_2 \Psi_0 = \sum_{\substack{i < j \\ a < b}} t_{ij}^{ab} \Psi_{ij}^{ab}$$

- CI wave function

$$\Psi_{CI} = (1 + T) \Psi_0$$

- CC wave function

$$\boxed{\Psi_{CC} = e^T \Psi_0} \quad e^T = 1 + T + \frac{T^2}{2} + \frac{T^3}{6} + \dots = \sum_{k=0}^{\infty} \frac{T^k}{k!}$$

Coupled Cluster wave function

$$e^T = 1 + T_1 + \left(T_2 + \frac{T_1^2}{2} \right) + \left(T_3 + T_2 T_1 + \frac{T_1^3}{6} \right) \\ + \left(T_4 + T_3 T_1 + \frac{T_2^2}{2} + \frac{T_2 T_1^2}{2} + \frac{T_1^4}{24} \right) + \dots$$

- singles = T_1
- doubles = **connected doubles** T_2 + **disconnected doubles** T_1^2
- T_4 = four electrons interacting simultaneously
- T_2^2 = two non-interacting pairs of interacting electrons
- Compared to CI, CC contains additional terms arising from products of excitations at each excitation level
 \Rightarrow **CC is size consistent!!** but **not variational!!**
- CISD lacks $T_2^2 \Rightarrow$ **not size consistent**

Connections between CI, CC and MP

$$e^T = 1 + T_1 + \left(T_2 + \frac{T_1^2}{2} \right) + \left(T_3 + T_2 T_1 + \frac{T_1^3}{6} \right) + \left(T_4 + T_3 T_1 + \frac{T_2^2}{2} + \frac{T_2 T_1^2}{2} + \frac{T_1^4}{24} \right) + \dots$$

- MP2 and MP3 uses **only doubles**
- MP4 uses singles, doubles, triples (T_3) and quadruples (T_4)
- CCD \approx MP4(DQ) and CCSD \approx MP4(SDQ)
- MP2, MP3 and MP4(SDQ) can be obtained in 1st CCSD iteration
- **CCSD lacks connected triples T_3**
 - 1 CCSDT but very expensive!
 - 2 CCSD(T) where **triples comes from MP4 (non-iterative)**
 - 3 CCSD(T) = **Gold Standard Of Quantum Chemistry** (for ground state AND weakly correlated systems)

Illustration for the Be atom

Correlation energy of Be in a 4s2p basis set

Scaling	Level	ΔE_c	%	Level	ΔE_c	%	Level	ΔE_c	%
K^5	MP2	0.053174	67.85						
K^6	MP3	0.067949	86.70	CISD	0.075277	96.05	CCSD	0.078176	99.75
K^7	MP4	0.074121	94.58				CCSD(T)	0.078361	99.99
K^8	MP5	0.076918	98.15	CISDT	0.075465	96.29	CCSDT	0.078364	99.99
K^9	MP6	0.078090	99.64						
K^{10}	MP7	0.078493	100.15	CISDTQ	0.078372	100	CCSDTQ	0.078372	100

As a rule of thumb:

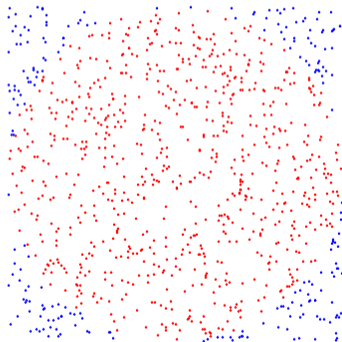
HF \ll MP2 < CISD < MP4(SDQ) \sim CCSD < MP4 < CCSD(T)

Monte Carlo (MC) method

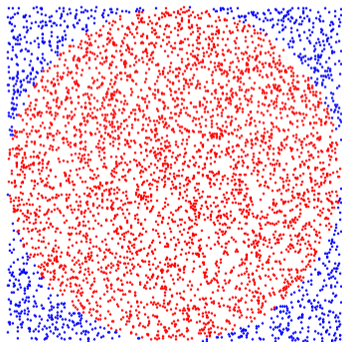
- Monte Carlo is a **numerical integration method**
- It is used in problems where it is **too difficult or impossible to obtain analytical expressions or the dimensionality of the integral is large**
- The method consists in **repeating random sampling many times** to obtain numerical results:
⇒ this is a **non-deterministic** or **stochastic** method.
- **MC converges as $N^{-1/2}$** where N is the number of MC step
- In 1946, **Stanislaw Ulam** was the first mathematician to dignify this approach with a name, in honor of his uncle having a little issue with gambling
- **Nicolas Metropolis** also made important contributions (**Metropolis algorithm**)

Monte Carlo computation of π

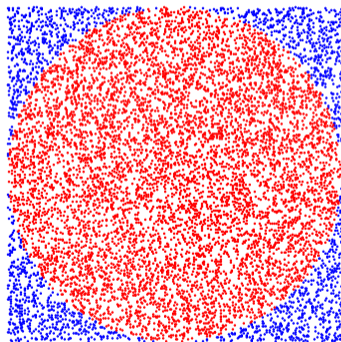
$$\int_{-1}^1 \int_{-1}^1 f(x, y) dx dy = \pi \quad \text{with} \quad f(x, y) = \begin{cases} 1, & x^2 + y^2 \leq 1, \\ 0, & \text{otherwise.} \end{cases}$$



$$\pi \approx \frac{774}{1000} = 3.096$$



$$\pi \approx \frac{3962}{5000} = 3.1696$$



$$\pi \approx \frac{7948}{10000} = 3.1792$$

Variational Monte Carlo (VMC) — cf Claudia Filippi's talk

- Within quantum chemistry, **VMC** is used to obtain expectation values (mainly energies)
- In VMC, the expectation value of the Hamiltonian with respect to a **trial wave function** Ψ_T is obtained using a **stochastic integration technique**
- The **VMC energy is an upper bound to the exact ground state energy**

$$E_{\text{VMC}} = \frac{\int \Psi_T(\mathbf{R}) H \Psi_T(\mathbf{R}) d\mathbf{R}}{\int \Psi_T(\mathbf{R})^2 d\mathbf{R}} = \frac{\int \frac{H \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \Psi_T(\mathbf{R})^2 d\mathbf{R}}{\int \Psi_T(\mathbf{R})^2 d\mathbf{R}} = \frac{\int E_L(\mathbf{R}) \Psi_T(\mathbf{R})^2 d\mathbf{R}}{\int \Psi_T(\mathbf{R})^2 d\mathbf{R}}$$

where

$$E_L(\mathbf{R}) = \frac{\hat{H} \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \text{ is the local energy and } \mathbf{R} = (r_1, r_2, \dots, r_n)$$

Diffusion Monte Carlo (DMC) — cf Claudia Filippi's talk

Time-dependent Schrödinger equation **written in imaginary time**:

$$\frac{\partial \Phi(\mathbf{R}, \tau)}{\partial \tau} = (H - S)\Phi(\mathbf{R}, \tau)$$

- For $\tau \rightarrow \infty$, the solution is the **exact ground state wave function** $\Phi(\mathbf{R})$
- DMC generates **configurations** (or **walkers**) distributed according to the **density** $\rho(\mathbf{R}, \tau) = \Psi_T(\mathbf{R}) \Phi(\mathbf{R}, \tau)$

$$\frac{\partial \rho(\mathbf{R}, \tau)}{\partial \tau} = \underbrace{\frac{1}{2} \nabla^2 \rho(\mathbf{R}, \tau)}_{\text{diffusion}} + \underbrace{\nabla \cdot [F(\mathbf{R}) \rho(\mathbf{R}, \tau)]}_{\text{drift}} - \underbrace{[E_L(\mathbf{R}) - E_T] \rho(\mathbf{R}, \tau)}_{\text{branching}}$$

where

$$F(\mathbf{R}) = \frac{\nabla \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \text{ is the quantum force}$$

If $\Psi_T(\mathbf{R})$ has **exact nodes**, DMC energy = **exact energy** (fixed-node error)

Excited state methods: single-reference methods

• HF- and DFT-based methods

- Configuration interaction single (CIS)
- Time-dependent HF (TDHF)
- Time-dependent DFT (TDDFT)
- Excited-state HF and KS solutions (MOM)

• CC-based methods

- Equation-of-motion CC (EOM-CCSD, EOM-CCSDT, etc)
- CC2 and CC3 (approximation of CCSD and CCSDT with linear response)

• CI-based methods

- CIS(D): perturbative approach to CIS that approximately introduces doubles
- Symmetry-adapted cluster CI (SAC-CI)

• Green's function-based methods

- Algebraic diagrammatic construction (ADC)
- Bethe-Salpeter equation (BSE-GW) formalism

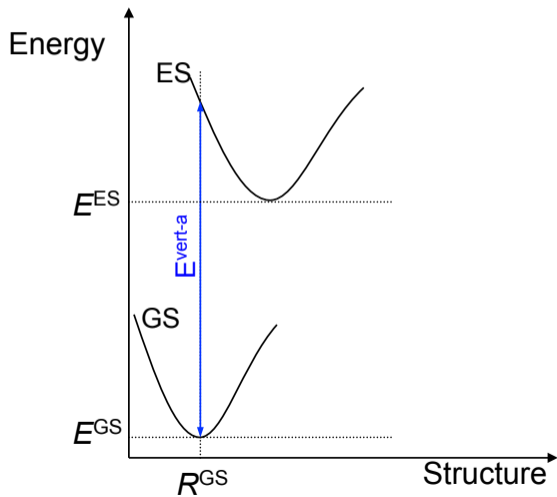
Excited state methods: multi-reference methods

- **Multiconfigurational self-consistent field (MCSCF)**
 - Complete active space self-consistent field (CASSCF)
 - Complete active space perturbation theory 2nd order (CASPT2)
 - Restricted active space self-consistent field (RASSCF)

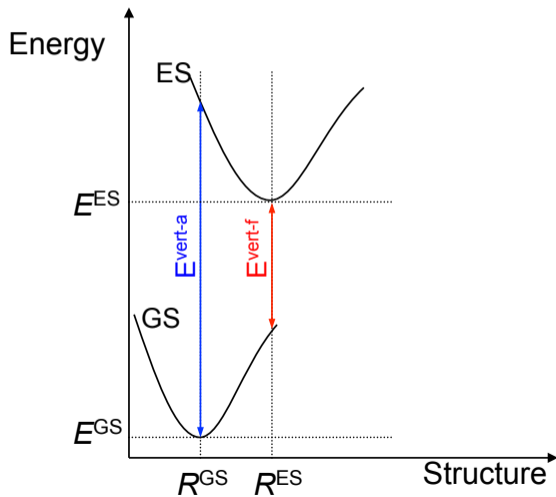
- **Multireference CI (MRCI)**

- **Multireference CC (MRCC)**

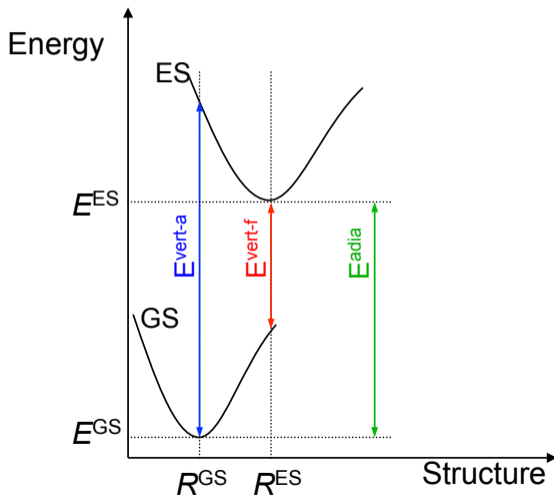
Photochemistry



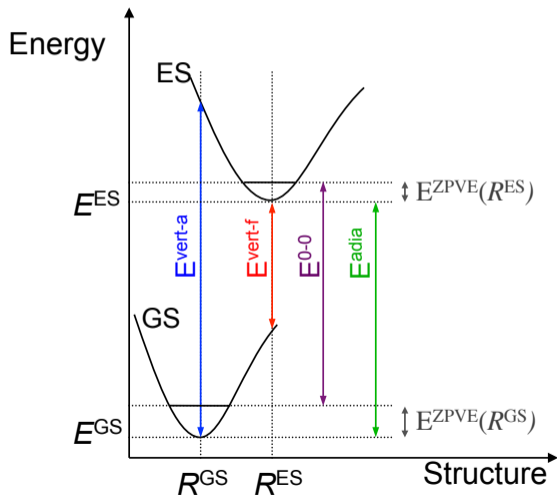
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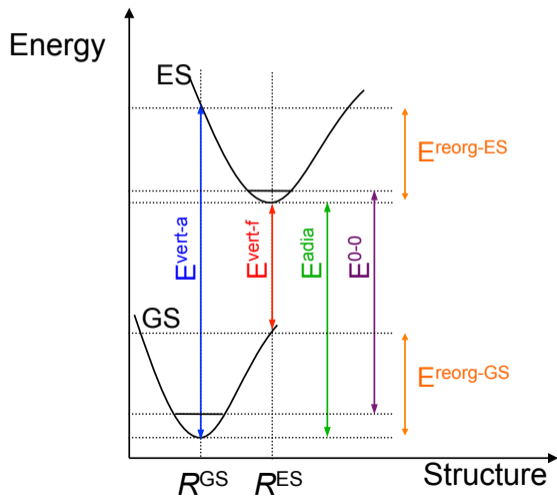
Photochemistry

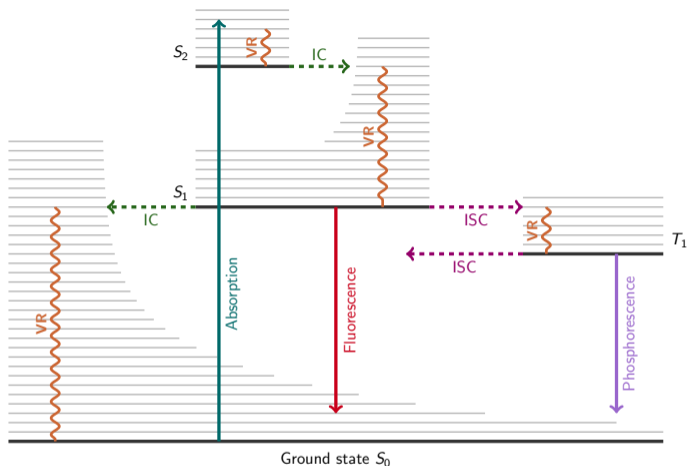


Photochemistry



Photochemistry





- - - IC → Internal conversion $S_i \rightarrow S_j$ (non radiative transition)

- - - ISC → Intersystem crossing $S_i \rightarrow T_j$ (non radiative transition)

VR → Vibrational Relaxation

Equations for CIS

HF wave function

The HF ground-state wave function is taken as a **reference**

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) \equiv \Psi_0(\mathbf{R}) = |\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \dots \phi_n(\mathbf{r}_n)\rangle$$

CIS wave function

$$|\Psi_{\text{CIS}}\rangle = \sum_i^{\text{occ}} \sum_a^{\text{virt}} c_i^a |\Psi_i^a\rangle \quad \text{where } |\Psi_i^a\rangle \text{ are singly-excited determinants}$$

CIS energy

$$\begin{aligned} \boxed{\mathbf{H}|\Psi_{\text{CIS}}\rangle = E_{\text{CIS}}|\Psi_{\text{CIS}}\rangle} &\Rightarrow \sum_{ia} c_i^a \mathbf{H}|\Psi_i^a\rangle = E_{\text{CIS}} \sum_{ia} c_i^a |\Psi_i^a\rangle \\ &\Rightarrow \sum_{ia} c_i^a \langle \Psi_j^b | \mathbf{H} | \Psi_i^a \rangle = E_{\text{CIS}} \sum_{ia} c_i^a \delta_{ij} \delta_{ab} \end{aligned}$$

Solving the CIS equations

The Slater-Condon rules tell us that

$$\langle \Psi_j^b | H | \Psi_i^a \rangle = (E_0 + \varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + (ia||jb)$$

with $(ia||jb) = (ia|jb) - (ij|ab)$, and

$$(ia|jb) = \iint \frac{\phi_i(\mathbf{r}_1) \phi_a(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \phi_b(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Therefore,

$$\sum_{ia} [(\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + (ia||jb)] c_i^a = \omega_{\text{CIS}} \sum_{ia} \delta_{ij} \delta_{ab} c_i^a$$

We obtain ω by diagonalising A

$$AX = \omega X \quad \Rightarrow \quad (A - \omega)X = 0$$

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + (ia||jb)$$

Comments, properties and limitations of CIS

Comments

- 1 $(\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}$: energy difference between orbitals i and a , which are the ones from which and to which the electron is excited
- 2 $(ia||jb)$: **linear response** of the Coulomb operator to the first-order changes in the one-electron orbitals

Properties and limitations

- 1 All excited-state total energies are **true upper bounds** to their exact values
- 2 CIS is **size-consistent**
- 3 One can obtain **pure singlet and triplet states** (no spin contamination)
- 4 CIS excitation energies are usually **overestimated**
(too large by about 0.5-2 eV compared to experimental values)

Time-dependent Hartree-Fock (TDHF)

TDHF wave function

The reference wave function is a **time-dependent HF wave function**:

$$\Psi_{\text{HF}}(\mathbf{r}_1, \dots, \mathbf{r}_n, t) \equiv \Psi_{\text{HF}}(\mathbf{R}, t) = |\phi_1(\mathbf{r}_1, t)\phi_2(\mathbf{r}_2, t) \dots \phi_n(\mathbf{r}_n, t)\rangle$$

TDHF equations

$$F(\mathbf{R}, t)\Psi_{\text{HF}}(\mathbf{R}, t) = i\frac{\partial}{\partial t}\Psi_{\text{HF}}(\mathbf{R}, t) \quad F(\mathbf{R}, t) = F(\mathbf{R}) + V(\mathbf{R}, t) = F(\mathbf{R}) + \sum_i^n v_i(\mathbf{r}_i, t)$$

What physically happens?

- ① At $t = 0$, the system is in a stationary state given by $\Psi_0(\mathbf{R})$
- ② A **small** TD perturbation is applied: $\phi_i(\mathbf{r})$'s respond only slightly
- ③ **Linear response**: we use 1st-order TD perturbation theory to find this response

Time-dependent Hartree-Fock (TDHF)

How to solve the TDHF equations?

We have a **non-Hermitian problem**:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_m \\ \mathbf{Y}_m \end{pmatrix} = \omega_m \begin{pmatrix} \mathbf{X}_m \\ \mathbf{Y}_m \end{pmatrix}$$

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia||jb) \quad B_{ia,jb} = (ia||bj)$$

which can be reduced in a **Hermitian eigenvalue equation**

Tamm-Dancoff approximation

- ① CIS is equivalent to TDHF with $\mathbf{B} = 0$
- ② This is the **Tamm-Dancoff approximation (TDA)**

Comments on TDHF

Comments

- ① $(\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}$: energy difference between orbitals i and a , which are the ones from which and to which the electron is excited
- ② $(ia||jb)$: **linear response** of the **Coulomb operator** to the first-order changes in the one-electron orbitals
- ③ $(ia||bj)$ **linear response** of the **exchange operator** to the first-order changes in the one-electron orbitals
- ④ **TDHF is an extension of CIS:**
It includes “**singly de-excited**” states as well as “**singly excited**” states
- ⑤ **TDHF \equiv RPax** and **TDHF without exchange** is direct RPA (dRPA)

Properties and limitations of TDHF

Properties and limitations

- 1 TDHF is a **size-consistent method**
- 2 One can obtain **pure singlet and triplet states** for closed-shell molecules
- 3 TDHF has **problems with triplets (instabilities)**
- 4 TDHF has **not** been very successful in the quantum chemistry community
- 5 Excitation energies calculated with TDHF are slightly smaller than the ones obtained with CIS, but they are **still overestimated**
- 6 TDHF is **not** a significant improvement over CIS and is slightly more expensive

Time-dependent density-functional theory (TDDFT)

The Runge-Gross theorem

The **Runge-Gross theorem** can be seen as the **time-dependent analogue of the first Hohenberg-Kohn theorem** and constitutes the cornerstone of the formal foundation of the **time-dependent Kohn-Sham (KS) formalism**

TDDFT equations

$$F_{\text{KS}}(\mathbf{R}, t)\Psi_{\text{KS}}(\mathbf{R}, t) = i\frac{\partial}{\partial t}\Psi_{\text{KS}}(\mathbf{R}, t)$$

How to solve the TDDFT equations?

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_m \\ \mathbf{Y}_m \end{pmatrix} = \omega_m \begin{pmatrix} \mathbf{X}_m \\ \mathbf{Y}_m \end{pmatrix}$$

$$\mathbf{A}_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia|jb) + (ib|f_{\text{xc}}|ja)$$

$$\mathbf{B}_{ia,jb} = (ia|bj) + (ij|f_{\text{xc}}|ab)$$

TDDFT equations

$$(ia|f_{xc}|jb) = \iint \phi_i(\mathbf{r}_1)\phi_a(\mathbf{r}_1) \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} \phi_j(\mathbf{r}_2)\phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Tamm-Dancoff approximation

- 1 In the **Tamm-Dancoff approximation (TDA)**, we set $B = 0$:
 \Rightarrow **TDA/TDDFT**
- 2 It's a very good approximation & it makes the problem Hermitian

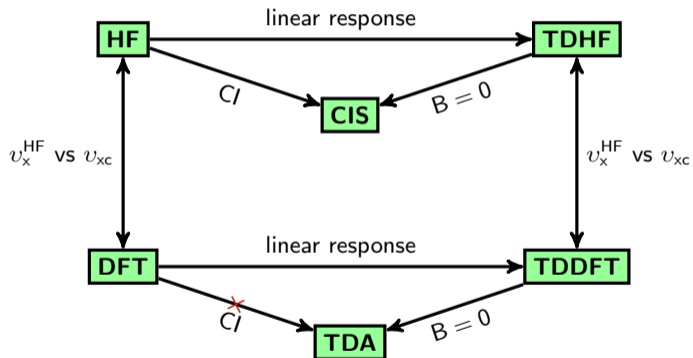
Hybrid functionals

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia|jb) - c_{HF}(ij|ab) + (1 - c_{HF})(ia|f_{xc}|jb)$$

$$B_{ia,jb} = (ia|bj) - c_{HF}(ib|aj) + (1 - c_{HF})(ia|f_{xc}|bj)$$

where c_{HF} is the fraction of HF exchange in the hybrid functional

Relationship between CIS, TDHF, DFT and TDDFT



Multiconfigurational self-consistent field (MCSCF) — cf Stefan Knecht's talk

- MCSCF is a **CI on steroids**:
both the **coefficients in front of the determinants** and the **MOs used for constructing the determinants** are optimised
- MCSCF optimisation is **iterative** like the SCF procedure in HF or KS
- MCSCF are **much harder to converge and prone to converge on solutions that are not minima** (2nd-order SCF procedure)
- MCSCF wave function is usually smaller than CI because **harder to optimise**
- MCSCF (**orbital relaxation**) do not recover a large fraction of the correlation energy: **static correlation**
- CI recovers a large fraction of the correlation energy: **dynamic correlation**

The two faces of correlation energy

Static correlation energy

Energy lowering introduced by adding enough **flexibility in the wave function to be able to qualitatively describe the system**. This is essentially the effect of allowing orbitals to become (partly) singly-occupied instead of forcing double occupation, i.e. describing near-degeneracy effects (two or more configurations having almost the same energy)

Dynamic correlation energy

The remaining energy lowering by correlating the **motion of the electrons** and the **electronic cusp**. The problem is that there is no rigorous way of separating **dynamic** and **static** correlation

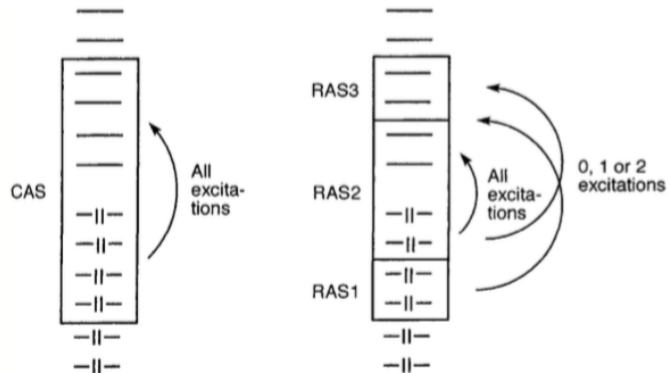
Take-home message 1

MCSCF methods are mainly used for generating a qualitatively correct wave function, i.e. recovering the “static” part of the correlation

Complete active space self-consistent field (CASSCF)

- In CASSCF, the selection of configurations is done by partitioning the MOs into **active** and **inactive** spaces
- The **active MOs** will typically be some of the **highest occupied** and some of the **lowest unoccupied MOs** from HF calculation
- The **inactive MOs** have **either 2 or 0 electrons**, i.e. always either doubly occupied or empty
- **$[n, m]$ -CASSCF**: n electrons are distributed in all possible ways in m orbitals
- CASSCF gets the **"static"** part of the correlation energy
⇒ **CASPT2** is used to get the **"dynamical"** part

CASSCF vs RASSCF



Restricted active space self-consistent field (RASSCF)

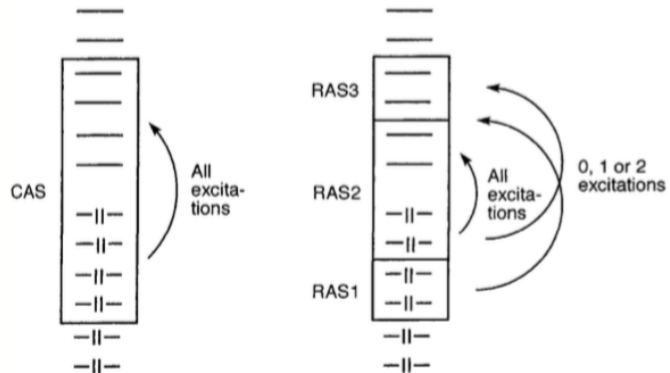
- The active MOs are divided into three spaces: **RAS1**, **RAS2** and **RAS3**
 - 1 **RAS1** consists of MOs that are doubly occupied in HF reference determinant
 - 2 **RAS2** is generated by a FCI (analogously to CASSCF)
 - 3 **RAS3** consists of MOs that are empty in HF reference determinant
- FCI within **RAS2**
- CISD from **RAS1** to **RAS3** and from **RAS2** to **RAS3**
- This procedure can be customised if required

Take-home message 2

MCSCF methods aren't BLACK BOX!!

How do we choose the active space?! valence orbitals, chemical intuition, natural orbitals, automatic selection, etc.

CASSCF vs RASSCF



Good books

- Introduction to Computational Chemistry (Jensen)
- Essentials of Computational Chemistry (Cramer)
- Modern Quantum Chemistry (Szabo & Ostlund)
- Molecular Electronic Structure Theory (Helgaker, Jorgensen & Olsen)

