

The Electron Correlation Problem

Pierre-François LOOS

Laboratoire de Chimie et Physique Quantiques (UMR 5626),
Université de Toulouse, CNRS, UPS, Toulouse, France.

ENS Lyon – Adv. Comp. Chem. 2022



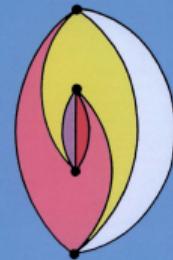
How to perform a HF calculation in practice?

The SCF algorithm (p. 146)

- ➊ Specify molecule $\{r_A\}$ and $\{Z_A\}$ and basis set $\{\phi_\mu\}$
- ➋ Calculate integrals $S_{\mu\nu}$, $H_{\mu\nu}$ and $\langle \mu\nu | \lambda\sigma \rangle$
- ➌ Diagonalize \mathbf{S} and compute $\mathbf{X} = \mathbf{S}^{-1/2}$
- ➍ Obtain **guess density matrix** for \mathbf{P}
 1. Calculate \mathbf{J} and \mathbf{K} , then $\mathbf{F} = \mathbf{H} + \mathbf{J} + \mathbf{K}$
 2. Compute $\mathbf{F}' = \mathbf{X}^\dagger \cdot \mathbf{F} \cdot \mathbf{X}$
 3. Diagonalize \mathbf{F}' to obtain \mathbf{C}' and \mathbf{E}
 4. Calculate $\mathbf{C} = \mathbf{X} \cdot \mathbf{C}'$
 5. Form a **new density matrix** $\mathbf{P} = \mathbf{C} \cdot \mathbf{C}^\dagger$
 6. **Am I converged?** If not go back to 1.
- ➎ Calculate stuff that you want, like E_{HF} for example

MODERN QUANTUM CHEMISTRY

Introduction to Advanced Electronic Structure Theory



Attila Szabo and
Neil S. Ostlund

A Slater determinant

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

- \mathcal{A} is called the **antisymmetrizer**
- $\Pi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ is a **Hartree product**
- The many-electron wave function $\Psi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ is an **antisymmetrized product of one-electron functions**

Spin and spatial orbitals

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

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

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

The spin orbitals are orthogonal

$$\langle \chi_i | \chi_j \rangle = \int \chi_i^*(\mathbf{x}) \chi_j(\mathbf{x}) d\mathbf{x} = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases}$$

The spatial orbitals are orthogonal

$$\langle \psi_i | \psi_j \rangle = \int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij} = \text{Kronecker delta}$$

The basis functions (or atomic orbitals) **are, a priori, not** orthogonal

$$\langle \phi_{\mu} | \phi_{\nu} \rangle = \int \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r} = S_{\mu\nu} = \text{Overlap matrix}$$

Comments

- $\{\phi_\mu | i = 1, \dots, K\}$ are basis functions or **atomic orbitals (AOs)**
- $\{\chi_i | i = 1, \dots, 2K\}$ are the **spin orbitals**
- $\{\psi_i | i = 1, \dots, K\}$ are the **spatial orbitals** or **molecular orbitals (MOs)**
- With K AOs, one can create K **spatial orbitals** and $2K$ **spin orbitals**
- For the ground state, the first N **spin orbitals** are occupied and the last $2K - N$ are vacant (unoccupied)
- When a system has **2 electrons in each orbital**, it is called a **closed-shell** system, otherwise it is called a **open-shell** system
- For the ground state of a closed shell, the first $N/2$ **spatial orbitals** are doubly-occupied and the last $K - N/2$ are vacant (unoccupied)
- The MOs are build by **linear combination of AOs (LCAO)**
- The coefficient $C_{\mu i}$ are determined via the **HF equations** based on **variational principle**

Ground-state Hartree-Fock determinant

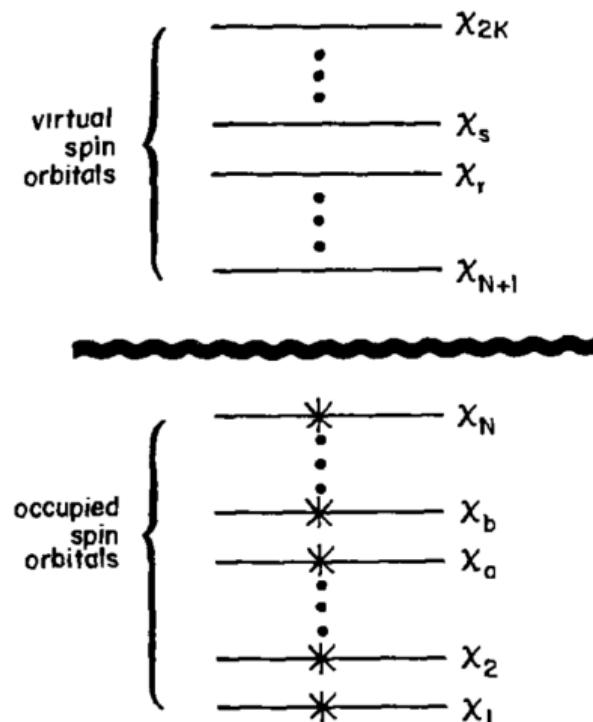


Figure 2.4 The Hartree-Fock ground state determinant, $|\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$.

Excited determinants

Reference determinant

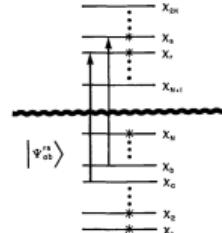
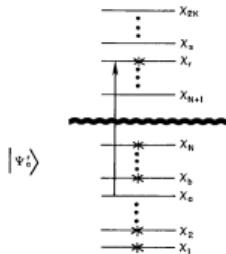
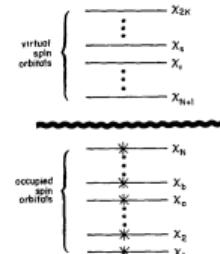
The electrons are in the N lowest orbitals (Aufbau principle): $|\Psi_0\rangle \equiv |0\rangle = |\chi_1 \dots \chi_a \chi_b \dots \chi_N\rangle$ (2)

Singly-excited determinants

Electron in a promoted in r : $|\Psi_{\text{a}}^r\rangle = |\chi_1 \dots \chi_r \chi_a \chi_b \dots \chi_N\rangle$ (3)

Doubly-excited determinants

Electrons in a and b promoted in r and s : $|\Psi_{ab}^{rs}\rangle = |\chi_1 \dots \chi_r \chi_s \chi_a \chi_b \dots \chi_N\rangle$ (4)



Physicts' notations

$$\langle i|h|j \rangle = (i|h|j) = \int \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1) d\mathbf{x}_1 \quad (5)$$

$$\langle ij|kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (6)$$

$$\langle ij||kl \rangle = \langle ij|kl \rangle - \langle ij|lk \rangle = \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} (1 - \mathcal{P}_{12}) \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (7)$$

Chemists' notations

$$(ij|kl) = (\chi_i \chi_j | \chi_k \chi_l) = \iint \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (8)$$

$$(ij||kl) = (ij|kl) - (il|kj) \quad (9)$$

Permutation symmetry

Permutation symmetry in physicists' notations

$$\langle ij|kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (10)$$

Complex-valued integrals: $\langle ij|kl \rangle = \langle ji|lk \rangle = \langle kl|ij \rangle^* = \langle lk|ji \rangle^*$ (11)

Real-valued integrals: $\langle ij|kl \rangle = \langle ji|kl \rangle = \langle ij|lk \rangle = \langle ji|lk \rangle = \langle kl|ij \rangle = \langle lk|ij \rangle = \langle kl|ji \rangle = \langle lk|ji \rangle$ (12)

Permutation symmetry in chemists' notations

$$(ij|kl) = (\chi_i \chi_j | \chi_k \chi_l) = \iint \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (13)$$

Real-valued integrals: $(ij|kl) = (ji|kl) = (ij|lk) = (ji|lk) = (kl|ij) = (lk|ij) = (kl|ji) = (lk|ji)$ (14)

Slater-Condon rules: One-electron operators

$$\mathcal{O}_1 = \sum_i^N h(i) \quad (15)$$

Case 1 = differ by zero spinorbital: $|K\rangle = |\dots mn\dots\rangle$

$$\langle K | \mathcal{O}_1 | K \rangle = \sum_m^N \langle m | h | m \rangle \quad (16)$$

Case 2 = differ by one spinorbital: $|K\rangle = |\dots mn\dots\rangle$ and $|L\rangle = |\dots pn\dots\rangle$

$$\langle K | \mathcal{O}_1 | L \rangle = \langle m | h | p \rangle \quad (17)$$

Case 3 = differ by two spinorbitals: $|K\rangle = |\dots mn\dots\rangle$ and $|L\rangle = |\dots pq\dots\rangle$

$$\langle K | \mathcal{O}_1 | L \rangle = 0 \quad (18)$$

Slater-Condon rules: Two-electron operators

$$\mathcal{O}_2 = \sum_{i < j}^N r_{ij}^{-1} \quad (19)$$

Case 1 = differ by zero spinorbital: $|K\rangle = |\dots mn\dots\rangle$

$$\langle K | \mathcal{O}_2 | K \rangle = \frac{1}{2} \sum_{mn}^N \langle mn || mn \rangle \quad (20)$$

Case 2 = differ by one spinorbital: $|K\rangle = |\dots mn\dots\rangle$ and $|L\rangle = |\dots pn\dots\rangle$

$$\langle K | \mathcal{O}_2 | L \rangle = \sum_n^N \langle mn || pn \rangle \quad (21)$$

Case 3 = differ by two spinorbitals: $|K\rangle = |\dots mn\dots\rangle$ and $|L\rangle = |\dots pq\dots\rangle$

$$\langle K | \mathcal{O}_2 | L \rangle = \langle mn || pq \rangle \quad (22)$$

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

- ① **Configuration Interaction:** CID, CIS, CISD, CISDTQ, etc.
- ② **Møller-Plesset perturbation theory:** MP2, MP3, MP4, MP5, etc.
- ③ **Coupled Cluster:** CCD, CCSD, CCSD(T), CCSDT, CCSDTQ, etc.
- ④ **Multireference methods:** MCSCF, CASSCF, RASSCF, MRCI, MRCC, CASPT2, NEVPT2, etc.
- ⑤ **Density-functional theory:** DFT, TDDFT, etc.
- ⑥ **Quantum Monte Carlo:** VMC, DMC, FCIQMC, etc.

Let's talk about notations

- Number of occupied orbitals O
- Number of vacant orbitals V
- Total number of orbitals $N = O + V$

- i, j, k, l are occupied orbitals
- a, b, c, d are vacant orbitals
- p, q, r, s are arbitrary (occupied or vacant) orbitals
- $\mu, \nu, \lambda, \sigma$ are basis function indexes

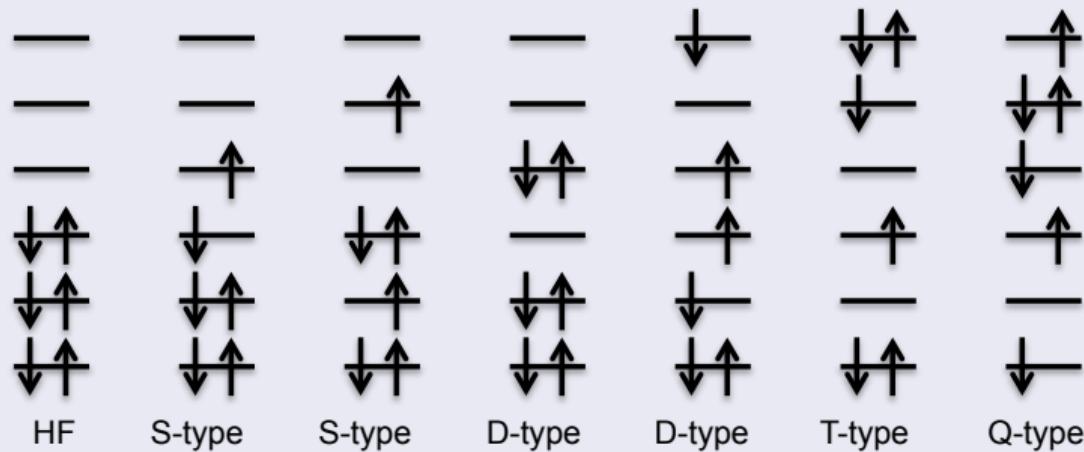
Configuration Interaction (CI)

- 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 reference (usually HF) wave function

$$|\Phi_{\text{CI}}\rangle = \underbrace{c_0 |\Psi_0\rangle}_{\text{reference}} + \underbrace{\sum_i c_i^a |\Psi_i^a\rangle}_{\substack{i \\ a \\ \text{singles}}} + \underbrace{\sum_{i < j} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle}_{\substack{i < j \\ a < b \\ \text{doubles}}} + \underbrace{\sum_{i < j < k} c_{ijk}^{abc} |\Psi_{ijk}^{abc}\rangle}_{\substack{i < j < k \\ a < b < c \\ \text{triples}}} + \underbrace{\sum_{i < j < k < l} c_{ijkl}^{abcd} |\Psi_{ijkl}^{abcd}\rangle}_{\substack{i < j < k < l \\ a < b < c < d \\ \text{quadruples}}} + \dots \quad (23)$$

CI method and Excited determinants

Excited determinants



CI wave function

$$|\Phi_{\text{CI}}\rangle = c_0 |0\rangle + c_S |S\rangle + c_D |D\rangle + c_T |T\rangle + c_Q |Q\rangle + \dots \quad (24)$$

Truncated CI

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

$$|\Phi_{\text{CIS}}\rangle = c_0 |0\rangle + c_S |S\rangle \quad (25)$$

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

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

$$|\Phi_{\text{CID}}\rangle = c_0 |0\rangle + c_D |D\rangle \quad (26)$$

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

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

$$|\Phi_{\text{CISD}}\rangle = c_0 |0\rangle + c_S |S\rangle + c_D |D\rangle \quad (27)$$

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

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

$$|\Phi_{\text{CISDT}}\rangle = c_0 |0\rangle + c_S |S\rangle + c_D |D\rangle + c_T |T\rangle \quad (28)$$

- CISDTQ**, etc.

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

$$|\Phi_{\text{FCI}}\rangle = c_0 |0\rangle + c_S |S\rangle + c_D |D\rangle + c_T |T\rangle + c_Q |Q\rangle + \dots \quad (29)$$

- 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 super computationally expensive!

Size of CI Matrix

“Assume we have 10 electrons in 38 spin MOs: 10 are occupied and 28 are empty”

- There is C_{10}^k possible ways of selecting k electrons out of the 10 occupied orbitals

$$C_n^k = \frac{n!}{k!(n-k)!}$$

- There is C_{28}^k ways of distributing them out in the 28 virtual orbitals
- For a given excitation level k , there is $C_{10}^k C_{28}^k$ excited determinants
- The total number of possible excited determinant is

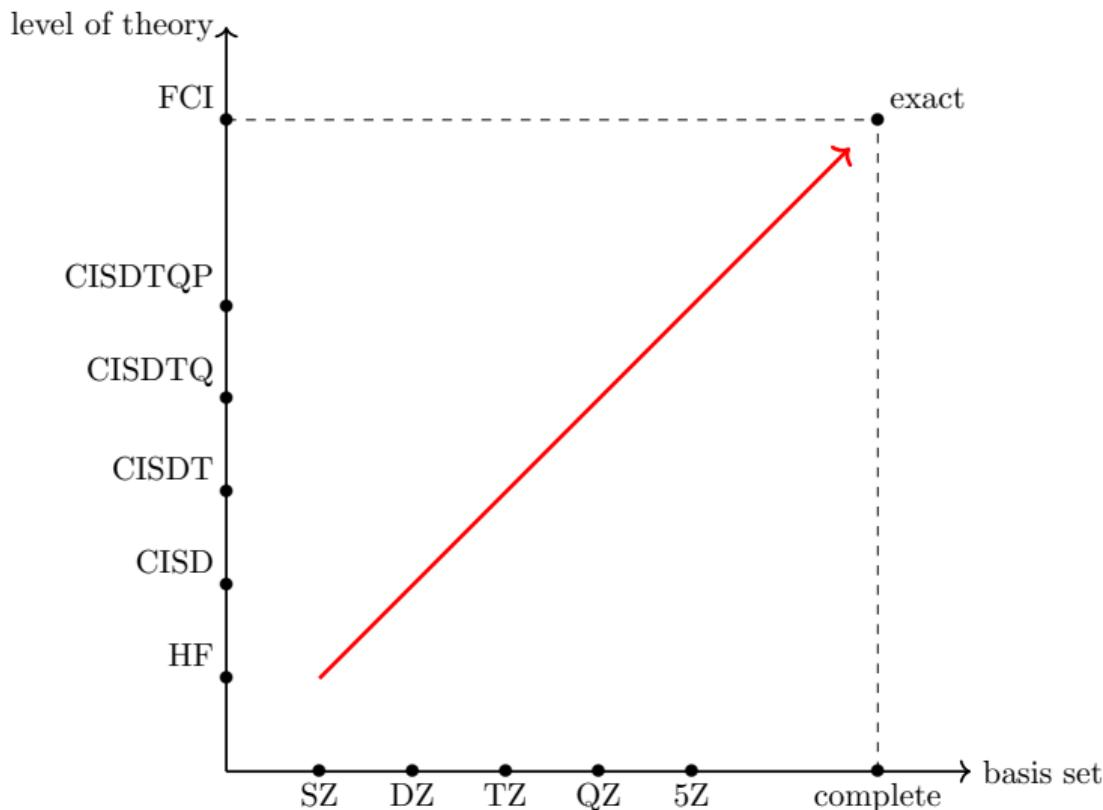
$$\sum_{k=0}^{10} C_{10}^k C_{28}^k = C_{38}^{10} = 472,733,756$$

- This is a lot...

For $n = 10$ and $N = 38$:

k	Num. of excitations
0	1
1	280
2	17,010
3	393,120
4	4,299,750
5	24,766,560
6	79,115,400
7	142,084,800
8	139,864,725
9	69,069,000
10	13,123,110
Tot.	472,733,756

Pople diagram



CI Lagrangian

The CI Lagrangian is

$$L = \langle \Phi_{\text{CI}} | \hat{H} | \Phi_{\text{CI}} \rangle - \lambda (\langle \Phi_{\text{CI}} | \Phi_{\text{CI}} \rangle - 1) \quad \text{with} \quad |\Phi_{\text{CI}}\rangle = \sum_I c_I |I\rangle \quad (30)$$

with

$$\langle \Phi_{\text{CI}} | \hat{H} | \Phi_{\text{CI}} \rangle = \sum_{IJ} c_I c_J \langle I | \hat{H} | J \rangle = \sum_I c_I^2 \underbrace{\langle I | \hat{H} | I \rangle}_{H_{II}} + \sum_{I \neq J} \underbrace{\langle I | \hat{H} | J \rangle}_{H_{IJ}} \quad (31)$$

$$\langle \Phi_{\text{CI}} | \Phi_{\text{CI}} \rangle = \sum_{IJ} c_I c_J \langle I | J \rangle = \sum_I c_I^2 \quad (32)$$

Following the variational procedure, we get

$$\frac{\partial L}{\partial c_I} = 2 \sum_J c_J H_{IJ} - 2\lambda c_I = 0 \quad \text{or} \quad \boxed{(H_{II} - \lambda)c_I + \sum_{J \neq I} H_{IJ}c_J = 0} \quad (33)$$

$$\begin{pmatrix} H_{00} - E & H_{01} & \dots & H_{0J} & \dots \\ H_{10} & H_{11} - E & \dots & H_{1J} & \dots \\ \vdots & \vdots & \ddots & \vdots & \dots \\ H_{J0} & \vdots & \dots & H_{JJ} - E & \dots \\ \vdots & \vdots & \dots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \\ \vdots \\ c_J \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ \vdots \end{pmatrix} \quad \text{or} \quad \boxed{\mathbf{H} \cdot \mathbf{c} = E\mathbf{c}} \quad (34)$$

The FCI matrix: before pruning

$$|\Phi_{\text{CI}}\rangle = c_0 |\text{HF}\rangle + c_S |\text{S}\rangle + c_D |\text{D}\rangle + c_T |\text{T}\rangle + c_Q |\text{Q}\rangle + \dots \quad (35)$$

$$\boldsymbol{H} = \begin{matrix} & | \text{HF} \rangle & | \text{S} \rangle & | \text{D} \rangle & | \text{T} \rangle & | \text{Q} \rangle & \dots \\ \langle \text{HF} | & \langle \text{HF} | \hat{H} | \text{HF} \rangle & \langle \text{HF} | \hat{H} | \text{S} \rangle & \langle \text{HF} | \hat{H} | \text{D} \rangle & \langle \text{HF} | \hat{H} | \text{T} \rangle & \langle \text{HF} | \hat{H} | \text{Q} \rangle & \dots \\ \langle \text{S} | & \langle \text{S} | \hat{H} | \text{HF} \rangle & \langle \text{S} | \hat{H} | \text{S} \rangle & \langle \text{S} | \hat{H} | \text{D} \rangle & \langle \text{S} | \hat{H} | \text{T} \rangle & \langle \text{S} | \hat{H} | \text{Q} \rangle & \dots \\ \langle \text{D} | & \langle \text{D} | \hat{H} | \text{HF} \rangle & \langle \text{D} | \hat{H} | \text{S} \rangle & \langle \text{D} | \hat{H} | \text{D} \rangle & \langle \text{D} | \hat{H} | \text{T} \rangle & \langle \text{D} | \hat{H} | \text{Q} \rangle & \dots \\ \langle \text{T} | & \langle \text{T} | \hat{H} | \text{HF} \rangle & \langle \text{T} | \hat{H} | \text{S} \rangle & \langle \text{T} | \hat{H} | \text{D} \rangle & \langle \text{T} | \hat{H} | \text{T} \rangle & \langle \text{T} | \hat{H} | \text{Q} \rangle & \dots \\ \langle \text{Q} | & \langle \text{Q} | \hat{H} | \text{HF} \rangle & \langle \text{Q} | \hat{H} | \text{S} \rangle & \langle \text{Q} | \hat{H} | \text{D} \rangle & \langle \text{Q} | \hat{H} | \text{T} \rangle & \langle \text{Q} | \hat{H} | \text{Q} \rangle & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{matrix} \quad (36)$$

The FCI matrix: after pruning

$$|\Phi_{\text{CI}}\rangle = c_0 |\text{HF}\rangle + c_S |\text{S}\rangle + c_D |\text{D}\rangle + c_T |\text{T}\rangle + c_Q |\text{Q}\rangle + \dots \quad (37)$$

$$\mathbf{H} = \begin{matrix} & | \text{HF} \rangle & | \text{S} \rangle & | \text{D} \rangle & | \text{T} \rangle & | \text{Q} \rangle & \dots \\ \langle \text{HF} | & \langle \text{HF} | \hat{H} | \text{HF} \rangle & 0 & \langle \text{HF} | \hat{H} | \text{D} \rangle & 0 & 0 & \dots \\ \langle \text{S} | & 0 & \langle \text{S} | \hat{H} | \text{S} \rangle & \langle \text{S} | \hat{H} | \text{D} \rangle & \langle \text{S} | \hat{H} | \text{T} \rangle & 0 & \dots \\ \langle \text{D} | & \langle \text{D} | \hat{H} | \text{HF} \rangle & \langle \text{D} | \hat{H} | \text{S} \rangle & \langle \text{D} | \hat{H} | \text{D} \rangle & \langle \text{D} | \hat{H} | \text{T} \rangle & \langle \text{D} | \hat{H} | \text{Q} \rangle & \dots \\ \langle \text{T} | & 0 & \langle \text{T} | \hat{H} | \text{S} \rangle & \langle \text{T} | \hat{H} | \text{D} \rangle & \langle \text{T} | \hat{H} | \text{T} \rangle & \langle \text{T} | \hat{H} | \text{Q} \rangle & \dots \\ \langle \text{Q} | & 0 & 0 & \langle \text{Q} | \hat{H} | \text{D} \rangle & \langle \text{Q} | \hat{H} | \text{T} \rangle & \langle \text{Q} | \hat{H} | \text{Q} \rangle & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{matrix} \quad (38)$$

Rules & Observations

- ① No coupling between HF ground state $|\text{HF}\rangle$ and single excitations $|S\rangle$
 \Rightarrow Brillouin's theorem

$$\langle \text{HF} | \hat{H} | S \rangle = 0 \quad (39)$$

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

$$\langle \text{HF} | \hat{H} | T \rangle = \langle \text{HF} | \hat{H} | Q \rangle = \dots = 0 \quad (40)$$

$$\langle S | \hat{H} | Q \rangle = \dots = 0 \quad (41)$$

- ③ $|S\rangle$ have small effect but mix indirectly with $|D\rangle$

$\Rightarrow \text{CID} \neq \text{CISD}$

$$\langle \text{HF} | \hat{H} | S \rangle = 0 \quad \text{but} \quad \langle S | \hat{H} | D \rangle \neq 0 \quad (42)$$

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

$$\langle \text{HF} | \hat{H} | D \rangle \gg \langle \text{HF} | \hat{H} | Q \rangle \gg \langle \text{HF} | \hat{H} | T \rangle \quad (43)$$

- ⑤ Of course, this matrix is never explicitly built in practice (Davidson algorithm)...

Example

Weights of excited configurations for Ne

Excit. level	Weight
0	9.6×10^{-1}
1	9.8×10^{-4}
2	3.4×10^{-2}
3	3.7×10^{-4}
4	4.5×10^{-4}
5	1.9×10^{-5}
6	1.7×10^{-6}
7	1.4×10^{-7}
8	1.1×10^{-9}

Correlation energy of Be and Method scaling

Method	ΔE_c	%	Scaling
HF	0	0	N^4
CIS	0	0	N^5
CISD	0.075277	96.05	N^6
CISDT	0.075465	96.29	N^8
CISDTQ	0.078372	100	N^{10}
FCI	0.078372	100	e^N

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

$$2E_c(H_2) \neq E_c(H_2 \cdots H_2)$$

- 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

Rayleigh-Schrödinger perturbation theory

Let's assume we want to find Ψ_0 and E_0 , such as

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)})\Psi_0 = E_0 \Psi_0 \quad (44)$$

and that we know

$$\boxed{\hat{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}, \quad n = 0, 1, 2, \dots, \infty} \quad (45)$$

Let's expand Ψ_0 and E_0 in term of λ :

$$E_0 = \lambda^0 E_0^{(0)} + \lambda^1 E_0^{(1)} + \lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \dots \quad (46)$$

$$\Psi_0 = \lambda^0 \Psi_0^{(0)} + \lambda^1 \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \dots \quad (47)$$

such as (intermediate normalization)

$$\left\langle \Psi_0^{(0)} \middle| \Psi_0^{(0)} \right\rangle = 1 \quad \left\langle \Psi_0^{(0)} \middle| \Psi_0^{(k)} \right\rangle = 0, \quad k = 1, 2, \dots, \infty \quad (48)$$

Rayleigh-Schrödinger perturbation theory (Part 1)

Gathering terms with respect to the power of λ :

$$\lambda^0 : \hat{H}^{(0)}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(0)} \quad (49)$$

$$\lambda^1 : \hat{H}^{(0)}\Psi_0^{(1)} + \hat{H}^{(1)}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(1)} + E_0^{(1)}\Psi_0^{(0)} \quad (50)$$

$$\lambda^2 : \hat{H}^{(0)}\Psi_0^{(2)} + \hat{H}^{(1)}\Psi_0^{(1)} = E_0^{(0)}\Psi_0^{(2)} + E_0^{(1)}\Psi_0^{(1)} + E_0^{(2)} \quad (51)$$

$$\lambda^3 : \hat{H}^{(0)}\Psi_0^{(3)} + \hat{H}^{(1)}\Psi_0^{(2)} = E_0^{(0)}\Psi_0^{(3)} + E_0^{(1)}\Psi_0^{(2)} + E_0^{(2)}\Psi_0^{(1)} + E_0^{(3)} \quad (52)$$

Using the intermediate normalization, we have

$$\lambda^0 : E_0^{(0)} = \langle \Psi_0^{(0)} | \hat{H}^{(0)} | \Psi_0^{(0)} \rangle \quad (53)$$

$$\lambda^1 : E_0^{(1)} = \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle \quad (54)$$

$$\lambda^2 : E_0^{(2)} = \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(1)} \rangle \quad \text{Wigner's (2n+1) rule!} \quad (55)$$

$$\lambda^3 : E_0^{(3)} = \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(2)} \rangle = \langle \Psi_0^{(1)} | \hat{H}^{(1)} - E_0^{(1)} | \Psi_0^{(1)} \rangle \quad (56)$$

Rayleigh-Schrödinger perturbation theory (Part 2)

Expanding $\Psi_0^{(1)}$ in the basis $\Psi_n^{(0)}$ with $n = 0, 1, 2, \dots, \infty$

$$\left| \Psi_0^{(1)} \right\rangle = \sum_n c_n^{(1)} \left| \Psi_n^{(0)} \right\rangle \Rightarrow c_n^{(1)} = \left\langle \Psi_n^{(0)} \middle| \Psi_0^{(1)} \right\rangle \quad (57)$$

Therefore,

$$\left| \Psi_0^{(1)} \right\rangle = \sum_{n \neq 0} \left| \Psi_n^{(0)} \right\rangle \left\langle \Psi_n^{(0)} \middle| \Psi_0^{(1)} \right\rangle \quad (58)$$

Using results from the previous slide, one can show that

$$E_0^{(2)} = \sum_{n \neq 0} \frac{\left\langle \Psi_0^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_n^{(0)} \right\rangle^2}{E_0^{(0)} - E_n^{(0)}} \quad (59)$$

$$E_0^{(3)} = \sum_{n,m \neq 0} \frac{\left\langle \Psi_0^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_n^{(0)} \right\rangle \left\langle \Psi_n^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_m^{(0)} \right\rangle \left\langle \Psi_m^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_0^{(0)} \right\rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})} - E_0^{(1)} \sum_{n \neq 0} \frac{\left\langle \Psi_0^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_n^{(0)} \right\rangle^2}{(E_0^{(0)} - E_n^{(0)})^2} \quad (60)$$

Møller-Plesset (MP) perturbation theory

In Møller-Plesset perturbation theory, the partition is

$$\hat{H}^{(0)} = \sum_{i=1}^N f(i) = \sum_{i=1}^N [h(i) + v^{\text{HF}}(i)], \quad \hat{H}^{(1)} = \sum_{i < j} \frac{1}{r_{ij}} - \sum_i v^{\text{HF}}(i) \quad (61)$$

Therefore,

$$E_0^{(0)} = \sum_i^{\text{occ}} \epsilon_i, \quad E_0^{(1)} = -\frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij || ij \rangle \quad \Rightarrow \quad E_{\text{HF}} = E_0^{(0)} + E_0^{(1)} \quad (62)$$

The first information about the correlation energy is given by the second-order correction

$$E_0^{(2)} = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{virt}} \frac{\langle ij || ab \rangle^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

This is the MP2 correlation energy!! (63)

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

$$\begin{aligned} E_0^{(3)} = & \frac{1}{8} \sum_{ijkl} \sum_{ab} \frac{\langle ij||ab\rangle \langle kl||ij\rangle \langle ab||kl\rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)(\epsilon_k + \epsilon_l - \epsilon_a - \epsilon_b)} \\ & + \frac{1}{8} \sum_{ij} \sum_{abcd} \frac{\langle ij||ab\rangle \langle ab||cd\rangle \langle cd||ij\rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)(\epsilon_i + \epsilon_j - \epsilon_c - \epsilon_d)} \\ & + \sum_{ijk} \sum_{abc} \frac{\langle ij||ab\rangle \langle kb||cj\rangle \langle ac||ik\rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)(\epsilon_i + \epsilon_k - \epsilon_a - \epsilon_c)} \end{aligned}$$

- MP2 and MP3 only requires only doubly excited determinants
- MP4 does need singly, doubly, triply and quadruply excited determinants!

Pople diagram

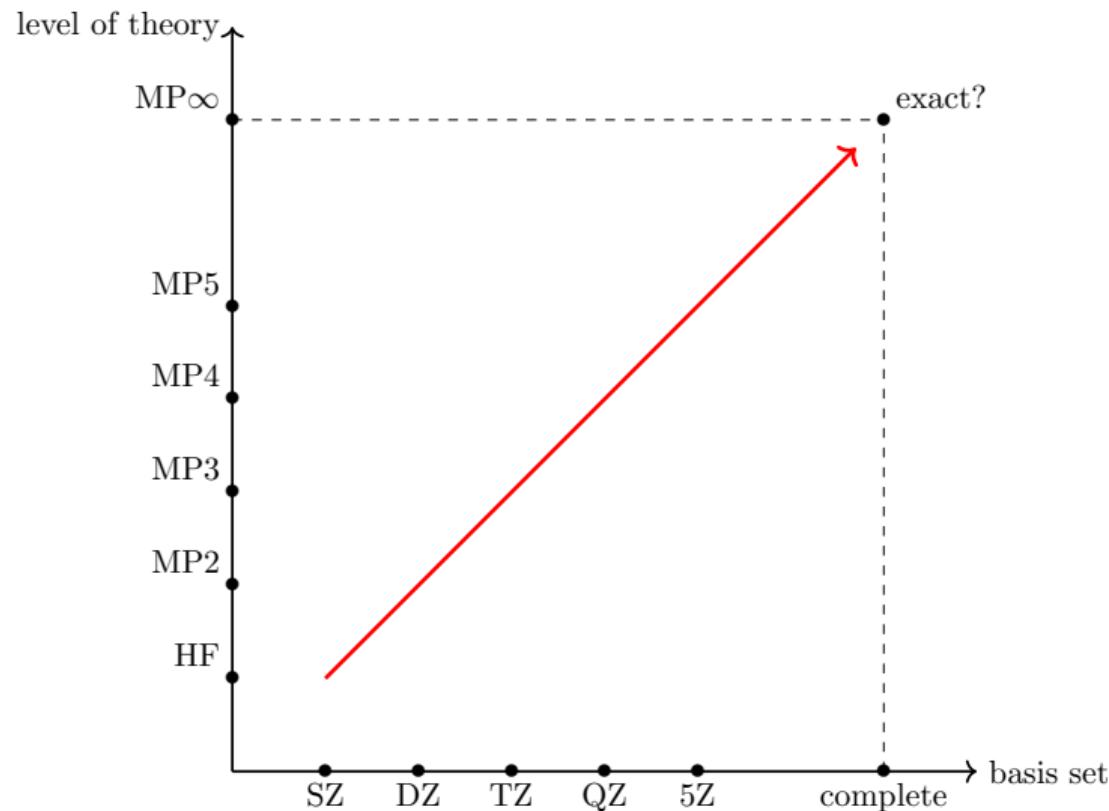


Illustration for the Be atom

Correlation energy of Be in a 4s2p basis set

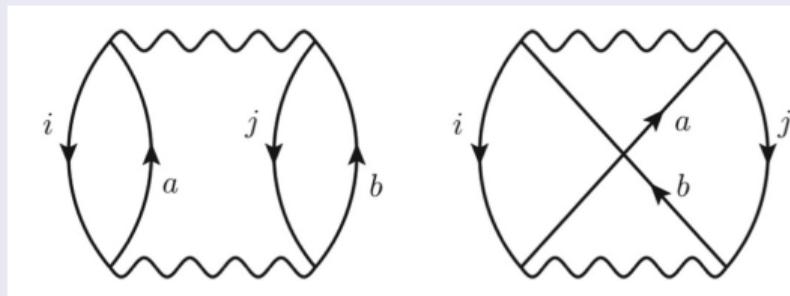
Scaling	Level	ΔE_c	%	Level	ΔE_c	%
N^5	MP2	0.053174	67.85			
N^6	MP3	0.067949	86.70	CISD	0.075277	96.05
N^7	MP4	0.074121	94.58			
N^8	MP5	0.076918	98.15	CISDT	0.075465	96.29
N^9	MP6	0.078090	99.64			
N^{10}	MP7	0.078493	100.15	CISDTQ	0.078372	100

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

MP2 correlation energy

MP2 is the simplest way of catching a good chunk of correlation:

$$\begin{aligned} E_c^{(2)} &= \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij | ab \rangle (2 \langle ij | ab \rangle - \langle ij | ba \rangle)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \\ &= \underbrace{2 \sum_{ij} \sum_{ab} \frac{\langle ij | ab \rangle^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}_{\text{direct part}} - \underbrace{\sum_{ij} \sum_{ab} \frac{\langle ij | ab \rangle \langle ij | ba \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}_{\text{exchange part}} \end{aligned} \quad (64)$$



Computing the MP2 correlation energy

How much does it cost to compute the MP2 correlation energy?

procedure MP2 CORRELATION ENERGY

```
 $E_c^{(2)} = 0$ 
for  $i = 1, O$  do
    for  $j = 1, O$  do
        for  $a = 1, V$  do
            for  $b = 1, V$  do
                 $\Delta = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$ 
                 $E_c^{(2)} = E_c^{(2)} + (2 \langle ij | ab \rangle^2 - \langle ij | ab \rangle \langle ij | ba \rangle) / \Delta$ 
            end for
        end for
    end for
end procedure
```

▷ $\mathcal{O}(N^4)$ because there are four loops!

AO to MO transformation (Take 1)

The naive way...

$$\underbrace{\langle pq | rs \rangle}_{\text{MO integrals}} = \sum_{\mu\nu\lambda\sigma} c_{\mu p} c_{\nu q} c_{\lambda r} c_{\sigma s} \underbrace{\langle \mu\nu | \lambda\sigma \rangle}_{\text{AO integrals}} \quad (65)$$

```
procedure AO-TO-MO TRANSFORMATION
    for p = 1, N do
        for q = 1, N do
            for r = 1, N do
                for s = 1, N do
                    (pq | rs) = 0
                    for μ = 1, N do
                        for ν = 1, N do
                            for λ = 1, N do
                                for σ = 1, N do
                                    (pq | rs) = (pq | rs) + cμp cνq cλr cσs ⟨ μν | λσ ⟩
                                end for
                            end for
                        end for
                    end for
                end for
            end for
        end for
    end for
end procedure
```

▷ Initialization of the array

▷ Accumulation step

▷ This is a $\mathcal{O}(N^8)$ algorithm! You won't do much quantum chemistry with this...

AO to MO transformation (Take 2)

Semi-direct algorithm...

$$\langle \textcolor{red}{pq} | \textcolor{brown}{rs} \rangle = \sum_{\mu p} c_{\mu p} \left\{ \sum_{\nu q} c_{\nu q} \left[\sum_{\lambda r} c_{\lambda r} \left(\underbrace{\sum_{\sigma s} c_{\sigma s} \langle \mu \nu | \lambda \sigma \rangle}_{\text{Step #1}} \right) \right] \right\}$$

$\overbrace{\qquad\qquad\qquad}^{\text{Step #2}}$

$\overbrace{\qquad\qquad\qquad}^{\text{Step #3}}$

$\overbrace{\qquad\qquad\qquad}^{\text{Step #4}}$

(66)

Semi-direct algorithm... Step #1

```
procedure SEMI-DIRECT ALGORITHM (STEP #1)
```

 Allocate temporary array I of size N^4

```
    for  $\mu = 1, N$  do
```

```
        for  $\nu = 1, N$  do
```

```
            for  $\lambda = 1, N$  do
```

```
                for  $\sigma = 1, N$  do
```

```
                    for  $s = 1, N$  do
```

$$I_{\mu\nu\lambda s} = I_{\mu\nu\lambda s} + c_{\sigma s} \langle \mu\nu | \lambda\sigma \rangle$$

```
                        end for
```

```
                    end for
```

```
                end for
```

```
            end for
```

```
        end for
```

```
    end for
```

▷ Step #1 costs $\mathcal{O}(N^5)$ and $\mathcal{O}(N^4)$ storage

```
end procedure
```

Semi-direct algorithm... Step #2

```
procedure SEMI-DIRECT ALGORITHM (STEP #2)
    Allocate temporary array  $J$  of size  $N^4$ 
    for  $\mu = 1, N$  do
        for  $\nu = 1, N$  do
            for  $\lambda = 1, N$  do
                for  $r = 1, N$  do
                    for  $s = 1, N$  do
                         $J_{\mu\nu rs} = J_{\mu\nu rs} + c_{\lambda r} I_{\mu\nu\lambda s}$ 
                    end for
                end for
            end for
        end for
    end for
end procedure
```

▷ Step #2 costs $\mathcal{O}(N^5)$ and $\mathcal{O}(N^4)$ storage

Semi-direct algorithm... Step #3

```
procedure SEMI-DIRECT ALGORITHM (STEP #3)
    for  $\mu$  = 1,  $N$  do
        for  $\nu$  = 1,  $N$  do
            for  $q$  = 1,  $N$  do
                for  $r$  = 1,  $N$  do
                    for  $s$  = 1,  $N$  do
                         $I_{\mu q r s} = I_{\mu q r s} + c_{v q} J_{\mu v r s}$ 
                    end for
                end for
            end for
        end for
    end for
end procedure
```

▷ Step #3 costs $\mathcal{O}(N^5)$ and no new storage

Semi-direct algorithm... Step #4

```
procedure SEMI-DIRECT ALGORITHM (STEP #4)
    for  $\mu$  = 1,  $N$  do
        for  $p$  = 1,  $N$  do
            for  $q$  = 1,  $N$  do
                for  $r$  = 1,  $N$  do
                    for  $s$  = 1,  $N$  do
                         $\langle pq | rs \rangle = \langle pq | rs \rangle + c_{\mu p} I_{\mu qrs}$ 
                    end for
                end for
            end for
        end for
    end for
end procedure
```

▷ Step #4 costs $\mathcal{O}(N^5)$ and no new storage

A few random thoughts about coupled cluster (CC)

- CC theory comes from nuclear physics
- The idea behind CC is to include all corrections of a given type to infinite order
- The CC wave function is an exponential *ansatz*
- The CC energy is size-extensive, but non-variational
- CC is considered as the gold standard for weakly correlated systems

- CC wave function

$$\Psi_{\text{CC}} = e^{\hat{T}} \Psi_0 \quad \text{where } \Psi_0 \text{ is a reference wave function} \quad (67)$$

- Excitation operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n \quad (68)$$

- Exponential *ansatz*

$$\begin{aligned}
 e^{\hat{T}} &= \hat{1} + \hat{T} + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \dots \\
 &= \hat{1} + \hat{T}_1 + \left(\underbrace{\hat{T}_2}_{\text{connected}} + \frac{1}{2} \underbrace{\hat{T}_1^2}_{\text{disconnected}} \right) + \left(\hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{1}{6} \hat{T}_1^3 \right) \\
 &\quad + \left(\underbrace{\hat{T}_4}_{\text{four electrons}} + \hat{T}_3 \hat{T}_1 + \frac{1}{2} \underbrace{\hat{T}_2^2}_{\text{two pairs of electrons}} + \frac{1}{2} \hat{T}_2 \hat{T}_1^2 + \frac{1}{24} \hat{T}_1^4 \right) + \dots
 \end{aligned} \quad (69)$$

Excitation operators

- Singles

$$\hat{T}_1 = \sum_{ia} \underbrace{t_i^a}_{\text{amplitudes}} \hat{a}_a^\dagger \hat{a}_i \Rightarrow \hat{T}_1 \Psi_0 = \sum_{ia} t_i^a \Psi_i^a \quad (70)$$

- Doubles

$$\hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \Rightarrow \hat{T}_2 \Psi_0 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \underbrace{\Psi_{ij}^{ab}}_{\text{excited determinants}} \quad (71)$$

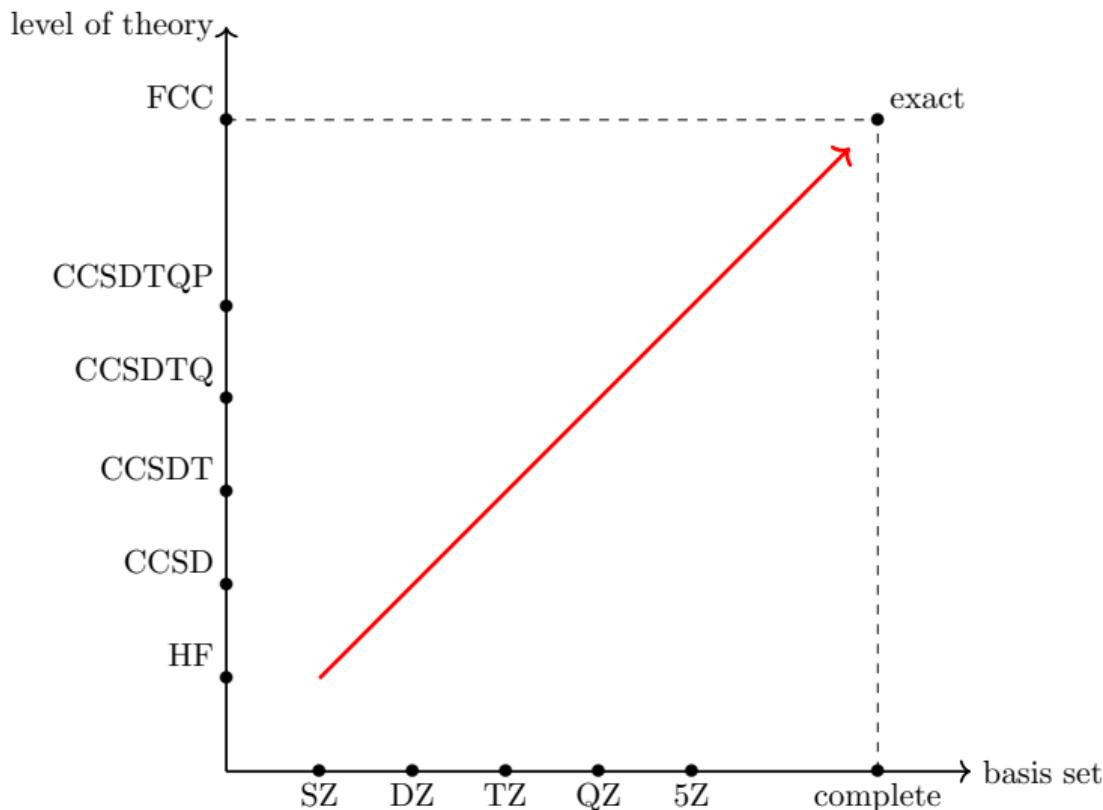
- FCI wave function

$$\Psi_{\text{FCI}} = (\hat{1} + \hat{T}) \Psi_0 = (\hat{1} + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots) \Psi_0 \quad (72)$$

- Anticommutation relation of the annihilation and creation operators

$$\hat{a}_p^\dagger \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p^\dagger = 0 \quad \hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = 0 \quad \hat{a}_p^\dagger \hat{a}_q + \hat{a}_p \hat{a}_q^\dagger = \delta_{pq} \quad (73)$$

Pople diagram



CC energies

- Schrödinger equation

$$\hat{H}|\Psi_{\text{CC}}\rangle = E|\Psi_{\text{CC}}\rangle \Rightarrow \hat{H}e^{\hat{T}}|\Psi_0\rangle = Ee^{\hat{T}}|\Psi_0\rangle \Rightarrow \underbrace{e^{-\hat{T}}\hat{H}e^{\hat{T}}}_{\text{\bar{H} = similarity transform}}|\Psi_0\rangle = E|\Psi_0\rangle \quad (74)$$

- Variational CC energy (**factorial complexity**)

$$E_{\text{VCC}} = \frac{\langle\Psi_{\text{CC}}|\hat{H}|\Psi_{\text{CC}}\rangle}{\langle\Psi_{\text{CC}}|\Psi_{\text{CC}}\rangle} = \frac{\langle\Psi_0(e^{\hat{T}})^\dagger|\hat{H}|e^{\hat{T}}\Psi_0\rangle}{\langle\Psi_0(e^{\hat{T}})^\dagger|e^{\hat{T}}\Psi_0\rangle} \geq E_{\text{exact}} \quad (75)$$

- (Traditional) projected CC energy (**polynomial complexity**)

$$E_{\text{TCC}} = \frac{\langle\Psi_0|\bar{H}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} = \frac{\langle\Psi_0 e^{-\hat{T}}|\hat{H}|e^{\hat{T}}\Psi_0\rangle}{\langle\Psi_0 e^{-\hat{T}}|e^{\hat{T}}\Psi_0\rangle} \quad (76)$$

- Unitary CC energy (**very expensive unless you have a quantum computer**)

$$E_{\text{UCC}} = \frac{\langle\Psi_0(e^{\hat{T}})^\dagger|\hat{H}|e^{\hat{T}}\Psi_0\rangle}{\langle\Psi_0(e^{\hat{T}})^\dagger|e^{\hat{T}}\Psi_0\rangle} = \frac{\langle\Psi_0 e^{-\hat{\tau}}|\hat{H}|e^{\hat{T}}\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} \quad \text{where } \hat{\tau} = \hat{T} - \hat{T}^\dagger \text{ is anti-Hermitian} \quad (77)$$

Similarity-transformed Hamiltonians & Amplitude equations

Similarity-transformed Hamiltonians

- The similarity-transformed Hamiltonian $\bar{H} = e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}}$ is **not** Hermitian:

$$(e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}})^\dagger = (e^{\hat{\tau}})^\dagger \hat{H}^\dagger (e^{-\hat{\tau}})^\dagger = e^{\hat{\tau}^\dagger} \hat{H} e^{-\hat{\tau}^\dagger} \neq e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}} \quad (78)$$

- The similarity-transformed Hamiltonian $e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}}$ is Hermitian:

$$(e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}})^\dagger = (e^{\hat{\tau}})^\dagger \hat{H}^\dagger (e^{-\hat{\tau}})^\dagger = e^{\hat{\tau}^\dagger} \hat{H} e^{-\hat{\tau}^\dagger} = e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}} \quad \text{because} \quad \hat{\tau}^\dagger = -\hat{\tau} \quad (79)$$

The two most important equations in CC theory

- The energy equation**

$$\boxed{\langle \Psi_0 | e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}} | \Psi_0 \rangle = E} \quad (80)$$

- The amplitude equation**

$$\boxed{\langle \Psi_{ij\dots}^{ab\dots} | e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}} | \Psi_0 \rangle = 0 \Rightarrow t_{ij\dots}^{ab\dots}} \quad (81)$$

Let's build the CISD and CCSD Hamiltonian matrices in the basis of $|0\rangle$, $|S\rangle$, and $|D\rangle$:

CISD Hamiltonian

$$\hat{H}_{\text{CISD}} = \begin{pmatrix} E_{\text{HF}} & 0 & H_{0D} \\ 0 & H_{SS} & H_{SD} \\ H_{D0} & H_{DS} & H_{DD} \end{pmatrix} \quad (82)$$

CCSD Hamiltonian

$$\bar{H}_{\text{CCSD}} = \begin{pmatrix} E_{\text{CC}} & \bar{H}_{0S} & \bar{H}_{0D} \\ 0 & \bar{H}_{SS} & \bar{H}_{SD} \\ 0 & \bar{H}_{DS} & \bar{H}_{DD} \end{pmatrix} \quad (83)$$

NB: This is the **equation-of-motion** (EOM) CCSD Hamiltonian!

The Hausdorff expansion

Campbell-Baker-Hausdorff formula

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!} [[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!} [[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!} [[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \dots \quad (84)$$

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \quad (85)$$

$$\left[\hat{a}_p^\dagger \hat{a}_q, \hat{a}_a^\dagger \hat{a}_i \right] = \hat{a}_p^\dagger \underbrace{\hat{a}_q \hat{a}_a^\dagger}_{\delta_{qa} - \hat{a}_a^\dagger \hat{a}_q} \hat{a}_i - \hat{a}_a^\dagger \underbrace{\hat{a}_i \hat{a}_p^\dagger}_{\delta_{ip} - \hat{a}_p^\dagger \hat{a}_i} \hat{a}_q = \hat{a}_p^\dagger \delta_{qa} \hat{a}_i - \hat{a}_a^\dagger \delta_{ip} \hat{a}_q \quad (86)$$

- At the **TCC** level, the BCH expansion **truncates naturally after the first five terms**
- At the **VCC** level, the BCH expansion **does not truncate but terminates**
- At the **UCC** level, the BCH expansion **does not terminate**

For more details about normal-ordered operators, Wick's theorem, and diagrammatic techniques, see Crawford & Schaefer, *Reviews in Computational Chemistry*, Vol. 14, Chap. 2, 2000.

Projected CC energy

Assuming that $\langle \Psi_0 | \Psi_0 \rangle = 1$, we have

$$\begin{aligned} E_{\text{CC}} &= \langle \Psi_0 | \hat{H} e^{\hat{T}} | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{H} (\hat{1} + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2) | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | \hat{H} \hat{T}_1 | \Psi_0 \rangle + \langle \Psi_0 | \hat{H} \hat{T}_2 | \Psi_0 \rangle + \frac{1}{2} \langle \Psi_0 | \hat{H} \hat{T}_1^2 | \Psi_0 \rangle \\ &= E_0 + \sum_i \sum_a t_i^a \langle \Psi_0 | \hat{H} | \Psi_i^a \rangle + \frac{1}{4} \sum_{ij} \sum_{ab} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle \Psi_0 | \hat{H} | \Psi_{ij}^{ab} \rangle \end{aligned} \tag{87}$$

HF reference wave function

- $E_0 = E_{\text{HF}}$
- $\langle \Psi_0 | \hat{H} | \Psi_i^a \rangle = \langle i | f | a \rangle = 0 \quad \Leftrightarrow \quad \text{Brillouin's theorem}$
- $\langle \Psi_0 | \hat{H} | \Psi_{ij}^{ab} \rangle = \langle ij | | ab \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle \quad \Leftrightarrow \quad \text{Two-electron integrals}$

$$E_{\text{CC}} = E_{\text{HF}} + \frac{1}{4} \sum_{ij} \sum_{ab} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle ij | | ab \rangle \quad (88)$$

CC with doubles (CCD)

- Only doubles, doubles of doubles, etc $\Rightarrow \hat{T} = \hat{T}_2$
- Still an infinite series

$$e^{\hat{T}_2} = \hat{1} + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{6} \hat{T}_2^3 + \frac{1}{24} \hat{T}_2^4 + \dots \quad (89)$$

- CCD energy

$$E_{\text{CCD}} = E_{\text{HF}} + \frac{1}{4} \sum_{ij} \sum_{ab} t_{ij}^{ab} \langle ij || ab \rangle \quad (90)$$

CCD equations

- Projection of similarity-transformed Hamiltonian onto doubles

$$\langle \Psi_{ij}^{ab} | \bar{H} | \Psi_0 \rangle = E_{\text{CC}} \langle \Psi_{ij}^{ab} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad \langle \Psi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle = 0 \quad (91)$$

- Residual equation

$$\boxed{r_{ij}^{ab} = \langle ij | ab \rangle + \Delta_{ij}^{ab} t_{ij}^{ab} + u_{ij}^{ab} + v_{ij}^{ab} = 0} \quad \Rightarrow \quad \boxed{t_{ij}^{ab} = - \frac{\langle ij | ab \rangle + u_{ij}^{ab} + v_{ij}^{ab}}{\Delta_{ij}^{ab}}} \quad (92)$$

- Energy differences

$$\Delta_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j \quad (93)$$

- Linear array

$$u_{ij}^{ab} = f(t_{ij}^{ab}) = \mathcal{O}(N^6) \quad (94)$$

- Quadratic array

$$v_{ij}^{ab} = f(t_{ij}^{ab}) = \underbrace{\mathcal{O}(N^6)}_{\text{smart}} \text{ or } \underbrace{\mathcal{O}(N^8)}_{\text{dumb}} \quad (95)$$

Each term of the linear term can be computed in $\mathcal{O}(N^6)$:

$$\begin{aligned}
 u_{ij}^{ab} = & \frac{1}{2} \sum_{cd} \underbrace{\langle ab || cd \rangle}_{VVVV} t_{ij}^{cd} + \frac{1}{2} \sum_{kl} \underbrace{\langle kl || ij \rangle}_{OOOO} t_{kl}^{ab} \\
 & + \sum_{kc} \left[-\underbrace{\langle kb || jc \rangle}_{OVOV} t_{ik}^{ac} + \langle ka || jc \rangle t_{ik}^{bc} - \langle ka || ic \rangle t_{jk}^{bc} + \langle kb || ic \rangle t_{jk}^{ac} \right]
 \end{aligned} \tag{96}$$

NB: $\text{CCD}(v_{ij}^{ab} = 0) = \text{linear CCD (LCCD)}$

Quadratic array: the **dumb** way

The quadratic term is the computational bottleneck of CCD:

$$v_{ij}^{ab} = \frac{1}{4} \sum_{klcd} \underbrace{\langle kl || cd \rangle}_{OOVV} \left[t_{ij}^{cd} t_{kl}^{ab} - 2(t_{ij}^{ac} t_{kl}^{bd} + t_{ij}^{bd} t_{kl}^{ac}) - 2(t_{ik}^{ab} t_{jl}^{cd} + t_{ik}^{cd} t_{jl}^{ab}) + 4(t_{ik}^{ac} t_{jl}^{bd} + t_{ik}^{bd} t_{jl}^{ac}) \right] \quad (97)$$

The “formal” scaling of the quadratic term is $\mathcal{O}(N^8)$

Quadratic array: the **smart** way

One can “sacrifice” storage to gain in scaling:

$$\underbrace{\langle kl|X_1|ij\rangle}_{\mathcal{O}(N^6)} = \sum_{cd} \langle kl||cd\rangle t_{ij}^{cd} \quad \underbrace{\langle b|X_2|c\rangle}_{\mathcal{O}(N^5)} = \sum_{kld} \langle kl||cd\rangle t_{kl}^{bd} \quad (98)$$

$$\underbrace{\langle k|X_3|j\rangle}_{\mathcal{O}(N^5)} = \sum_{lcd} \langle kl||cd\rangle t_{jl}^{cd} \quad \underbrace{\langle il|X_4|ad\rangle}_{\mathcal{O}(N^6)} = \sum_{kc} \langle kl||cd\rangle t_{ik}^{ac} \quad (99)$$

Now, the quadratic term can be computed in $\mathcal{O}(N^6)$

$$v_{ij}^{ab} = \frac{1}{4} \sum_{kl} \langle kl|X_1|cd\rangle t_{kl}^{ab} - \frac{1}{2} \sum_c \left[\langle b|X_2|c\rangle t_{ij}^{ac} + \langle a|X_2|c\rangle t_{ij}^{cb} \right] \\ - \frac{1}{2} \sum_k \left[\langle k|X_3|j\rangle t_{ik}^{ab} + \langle k|X_3|i\rangle t_{kj}^{ab} \right] + \sum_{kc} \left[\langle ik|X_4|ac\rangle t_{jk}^{bc} + \langle ik|X_4|bc\rangle t_{kj}^{ac} \right] \quad (100)$$

CCD algorithm

CCD subroutine

procedure ITERATIVE CCD ALGORITHM

Perform HF calculation to get ϵ_p and $\langle pq||rs \rangle$

Set $u_{ij}^{ab} = 0$, and $v_{ij}^{ab} = 0$

Compute amplitudes $t_{ij}^{ab} = -\langle ij||ab \rangle / \Delta_{ij}^{ab}$ (MP2 guess)

while $\max |r_{ij}^{ab}| > \tau$ **do**

 Form linear array u_{ij}^{ab}

 Compute intermediate arrays $\langle kl|X_1|ij \rangle$, $\langle b|X_2|c \rangle$, $\langle k|X_3|j \rangle$, and $\langle il|X_4|ad \rangle$.

 Form quadratic array v_{ij}^{ab}

 Compute residues: $r_{ij}^{ab} = \langle ij||ab \rangle + \Delta_{ij}^{ab} t_{ij}^{ab} + u_{ij}^{ab} + v_{ij}^{ab}$

 Update amplitudes: $t_{ij}^{ab} \leftarrow t_{ij}^{ab} - r_{ij}^{ab} / \Delta_{ij}^{ab}$

end while

Compute CCD energy: $E_{\text{CCD}} = E_{\text{HF}} + \frac{1}{4} \sum_{ij} \sum_{ab} t_{ij}^{ab} \langle ij||ab \rangle$

end procedure

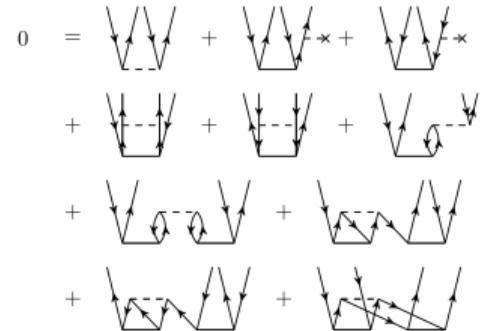


Illustration for the Be atom

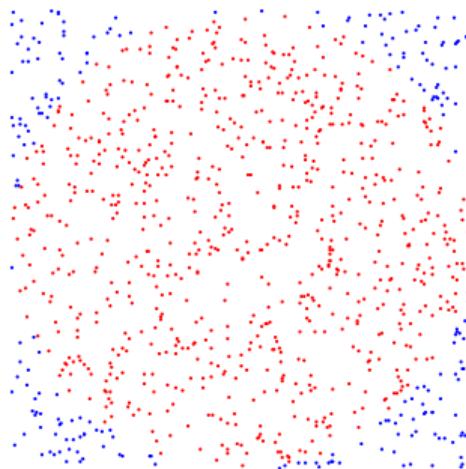
Correlation energy of Be in a 4s2p basis set

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

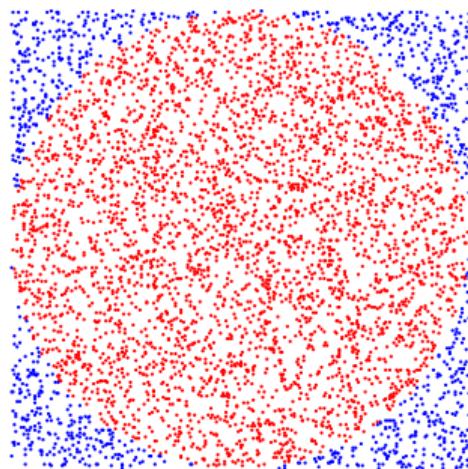
- Monte Carlo is a numerical integration method
- It is used in problems where it is too difficult or impossible to obtain analytical expressions or the dimensionality of the integral is large
- The method consists in repeating random sampling many times to obtain numerical results:
⇒ this is a non-deterministic 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

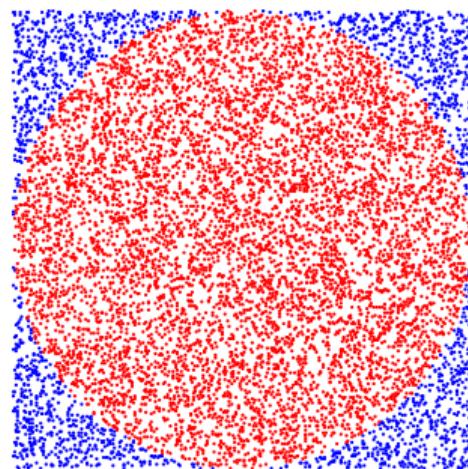
$$\int_{-1}^1 \int_{-1}^1 f(x, y) dx dy = \pi \quad \text{with} \quad f(x, y) = \begin{cases} 1, & x^2 + y^2 \leq 1, \\ 0, & \text{otherwise.} \end{cases}$$



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



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



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

- 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

$$E_{\text{VMC}} = \frac{\int \Psi_T(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R}) d\mathbf{R}}{\int \Psi_T(\mathbf{R})^2 d\mathbf{R}} = \frac{\int \frac{\hat{H}\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \Psi_T(\mathbf{R})^2 d\mathbf{R}}{\int \Psi_T(\mathbf{R})^2 d\mathbf{R}} = \frac{\int E_L(\mathbf{R}) \Psi_T(\mathbf{R})^2 d\mathbf{R}}{\int \Psi_T(\mathbf{R})^2 d\mathbf{R}} \quad (101)$$

where

$$E_L(\mathbf{R}) = \frac{\hat{H}\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \quad \text{is the local energy and } \mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) \quad (102)$$

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

$$\boxed{\frac{\partial \Phi(\mathbf{R}, \tau)}{\partial \tau} = (\hat{H} - S)\Phi(\mathbf{R}, \tau)} \quad (103)$$

- 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**
 $\rho(\mathbf{R}, \tau) = \Psi_T(\mathbf{R})\Phi(\mathbf{R}, \tau)$

$$\boxed{\frac{\partial \rho(\mathbf{R}, \tau)}{\partial \tau} = \underbrace{\frac{1}{2}\nabla^2\rho(\mathbf{R}, \tau)}_{\text{diffusion}} + \underbrace{\nabla \cdot [F(\mathbf{R})\rho(\mathbf{R}, \tau)]}_{\text{drift}} - \underbrace{[E_L(\mathbf{R}) - E_T]\rho(\mathbf{R}, \tau)}_{\text{branching}}} \quad (104)$$

where

$$F(\mathbf{R}) = \frac{\nabla \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \quad \text{is the quantum force} \quad (105)$$

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

- HF- and DFT-based methods

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

- CC-based methods

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

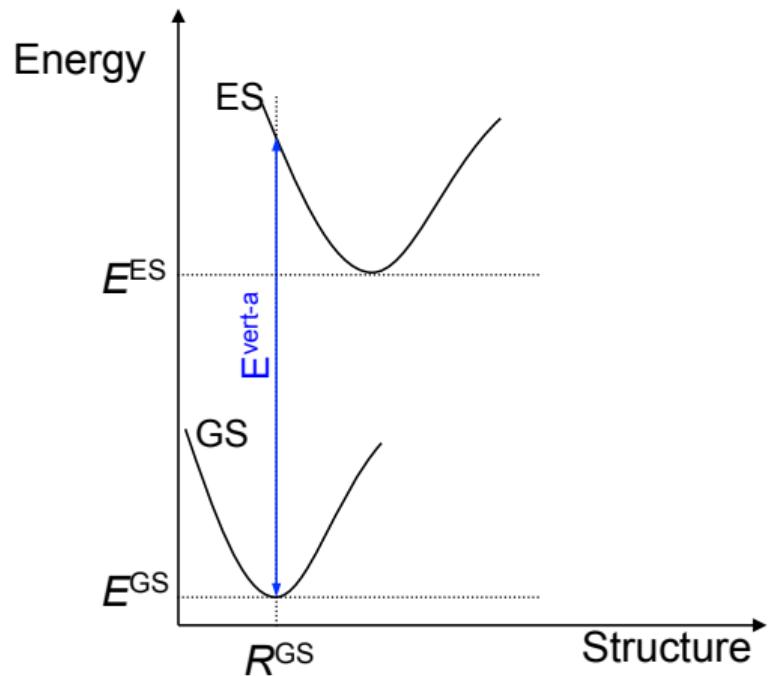
- CI-based methods

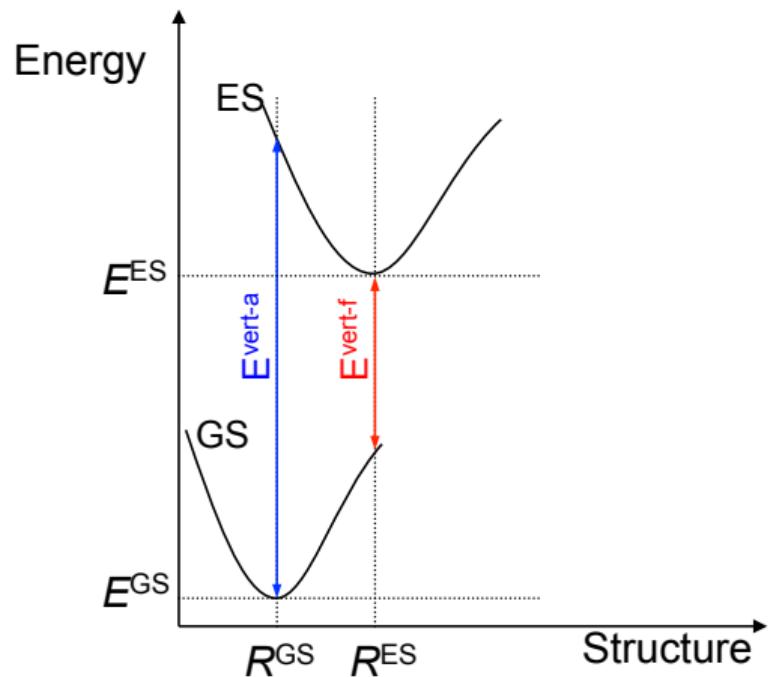
- CIS(D): perturbative approach to CIS that approximately introduces doubles
- Symmetry-adapted cluster CI (SAC-CI)

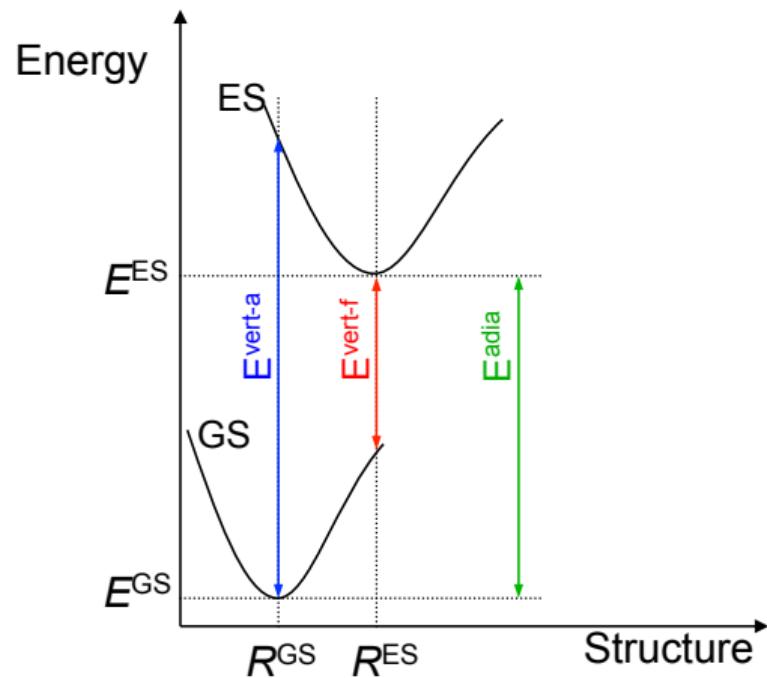
- Green's function-based methods

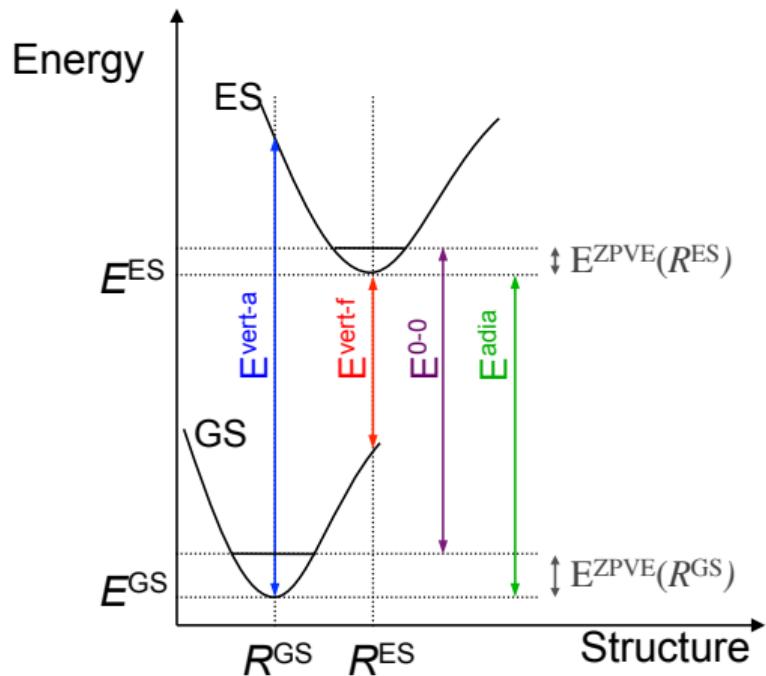
- Algebraic diagrammatic construction (ADC)
- Bethe-Salpeter equation (BSE-*GW*) formalism

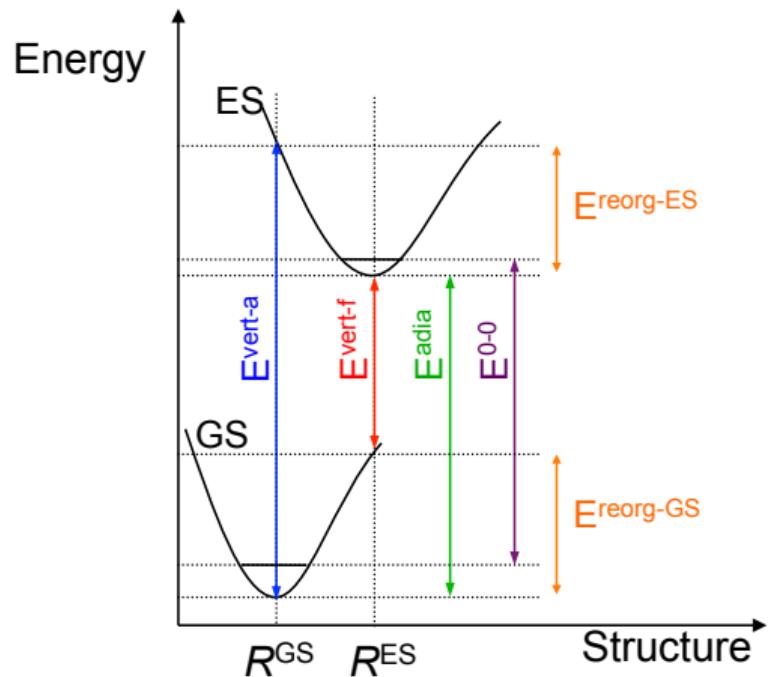
- Multiconfigurational self-consistent field (MCSCF)
 - Complete active space self-consistent field (CASSCF)
 - Complete active space perturbation theory 2nd order (CASPT2)
 - Restricted active space self-consistent field (RASSCF)
- Multireference CI (MRCI)
- Multireference CC (MRCC)

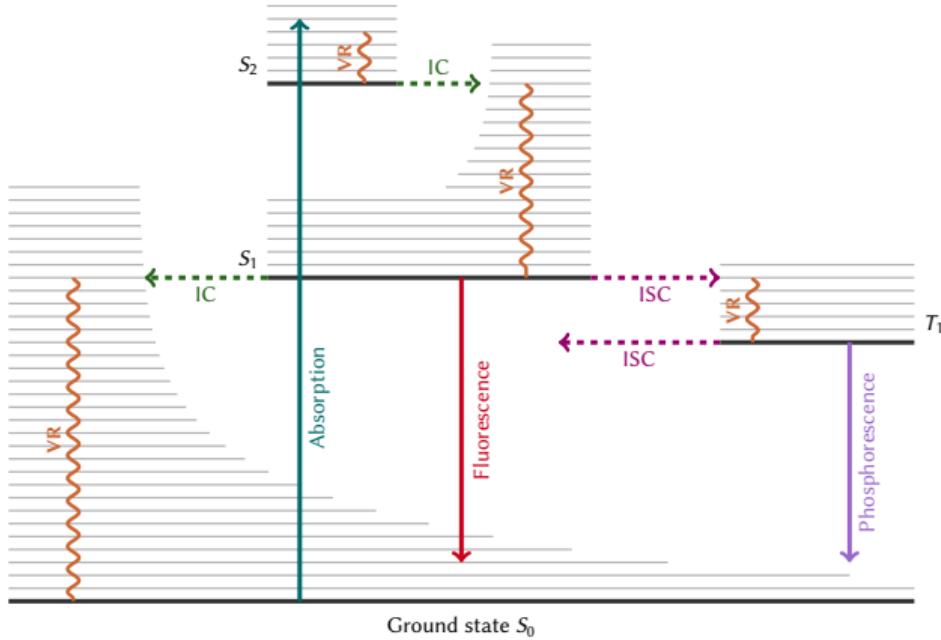












IC → Internal conversion $S_i \longrightarrow S_j$ (non radiative transition)

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

VR → Vibrational Relaxation

Equations for CIS

HF wave function

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

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \dots \chi_n(\mathbf{x}_n)\rangle$$

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

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

Solving the CIS Equations

The **Slater-Condon rules** tell us that

$$\langle \Psi_i^a | \hat{H} | \Psi_j^b \rangle = (\textcolor{red}{E_0} + \epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle ib || aj \rangle$$

with $\langle ib || aj \rangle = \langle ib | aj \rangle - \langle ib | ja \rangle$, and

$$\langle ib | aj \rangle = \iint \frac{\chi_i(\mathbf{x}_1) \chi_b(\mathbf{x}_2) \chi_a(\mathbf{x}_1) \chi_j(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{x}_1 d\mathbf{x}_2$$

Therefore,

$$\sum_{ia} [(\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle ib || aj \rangle] c_i^a = \omega_{\text{CIS}} \sum_{ia} \delta_{ij} \delta_{ab} c_i^a$$

We obtain the excitation energy ω by diagonalising \mathbf{A}

$$\boxed{\mathbf{A} \cdot \mathbf{X} = \omega \mathbf{X} \Rightarrow (\mathbf{A} - \omega \mathbf{1}) \cdot \mathbf{X} = \mathbf{0}} \quad \text{with} \quad A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle ib || aj \rangle$$

Comments, Properties, and Limitations of CIS

Comments

- ① $(\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab}$: energy difference between orbitals i and a , which are the ones from which and to which the electron is excited
- ② $\langle ib || aj \rangle$: 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 exact values)

TDHF wave function

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

$$\Psi_{\text{HF}}(\mathbf{r}_1, \dots, \mathbf{r}_n, t) \equiv \Psi_{\text{HF}}(\mathbf{R}, t) = |\chi_1(\mathbf{r}_1, t)\chi_2(\mathbf{r}_2, t)\dots\chi_n(\mathbf{r}_n, t)\rangle$$

TDHF equations

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

What physically happens?

- ① At $t = 0$, the system is in a stationary state given by $\Psi_{\text{HF}}(\mathbf{R})$
- ② A **small** TD perturbation is applied: **the orbitals 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:

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

$$\textcolor{red}{A}_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle ib | aj \rangle \quad \textcolor{blue}{B}_{ia,jb} = \langle ij | ab \rangle$$

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

Tamm-Dancoff approximation

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

Comments

- ① $(\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab}$: energy difference between orbitals i and a , which are the ones from which and to which the electron is excited
- ② $\langle ib || aj \rangle$: linear response of the Coulomb operator to the first-order changes in the one-electron orbitals
- ③ $\langle ij || ab \rangle$ 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 single “de-excitations” as well as single excitations
- ⑤ TDHF \equiv RPAX and TDHF without exchange is direct RPA (dRPA)

Properties and limitations

- ➊ TDHF is a **size-consistent method**
- ➋ One can obtain **pure singlet and triplet states** for closed-shell molecules
- ➌ TDHF has **problems with triplets (instabilities)**
- ➍ TDHF has **not** been very successful in the quantum chemistry community
- ➎ Excitation energies calculated with TDHF are slightly smaller than the ones obtained with CIS, but they are **still overestimated**
- ➏ TDHF is **not** a significative improvement over CIS and is slightly more expensive

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

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

How to solve the TDDFT equations?

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

$$\mathbf{A}_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle ib | aj \rangle + \langle ij | f_{xc} | ab \rangle$$

$$\mathbf{B}_{ia,jb} = \langle ij | ab \rangle + \langle ib | f_{xc} | aj \rangle$$

TDDFT equations

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

Tamm-Dancoff approximation

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

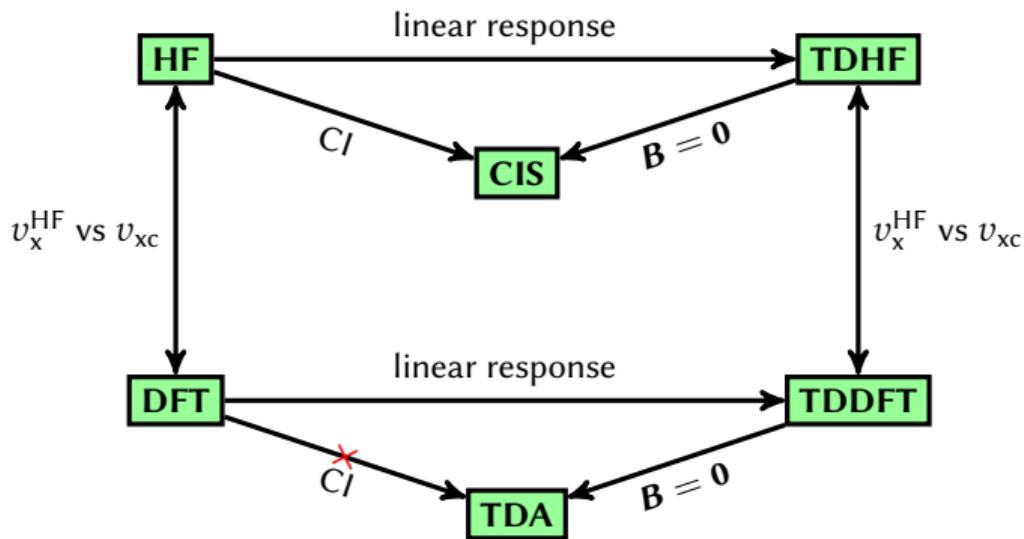
Hybrid functionals

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle ia|jb\rangle - c_{HF} \langle ij|ab\rangle + (1 - c_{HF}) \langle ia|f_{xc}|jb\rangle$$

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

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

Relationship between CIS, TDHF, DFT and TDDFT



Properties

- Although standard functionals are developed for ground states, they are also employed in TDDFT
- Results are very sensitive to the choice of the xc functional
- TDDFT is accurate for valence-excited states (error of 0.1-0.5 eV)
⇒ It can be as good as EOM-CCSD or CASPT2
- TDDFT has troubles with
 - ① Rydberg states
 - ② Valence states of molecules exhibiting extended π -systems
 - ③ Doubly excited states
 - ④ Charge-transfer (CT) excited states
 - ⑤ Core-excited states

- Rydberg states and extended π -systems:
wrong long-range behavior of standard xc functionals (faster than $1/r$)
- Doubly-excited states:
cannot be treated within linear response theory (only contains singly excited states)
- CT excited states:
excitation energies are drastically underestimated due to wrong asymptotic behavior of xc functionals.
It can be fixed using range-separated functionals (CAM-B3LYP, etc).
- In these cases, we can have errors of several eV and incorrect curvature of PES

- 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 optimize**
- 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 is 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** correlations

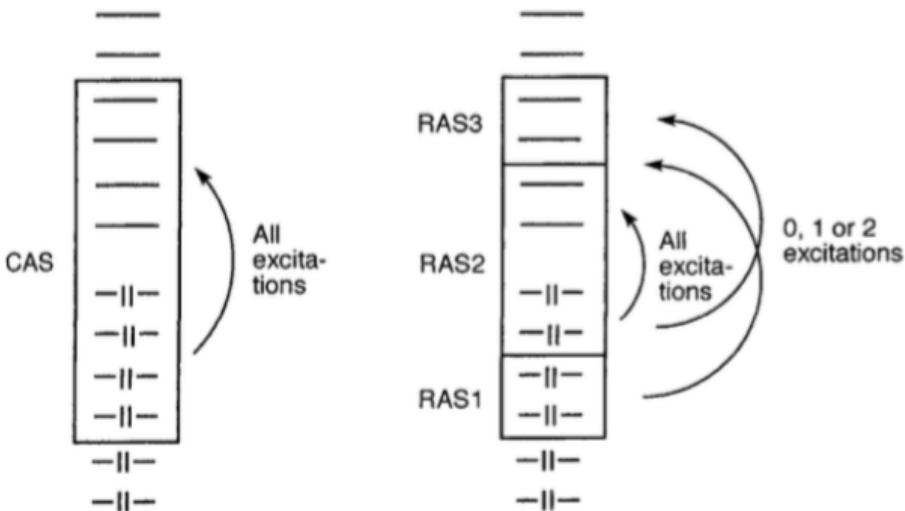
Take-home message 1

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



Number of configurations generated in an [n, n]-CASSCF wave function

<i>n</i>	Number of CSFs
2	3
4	20
6	175
8	1764
10	19404
12	226,512
14	2,760,615

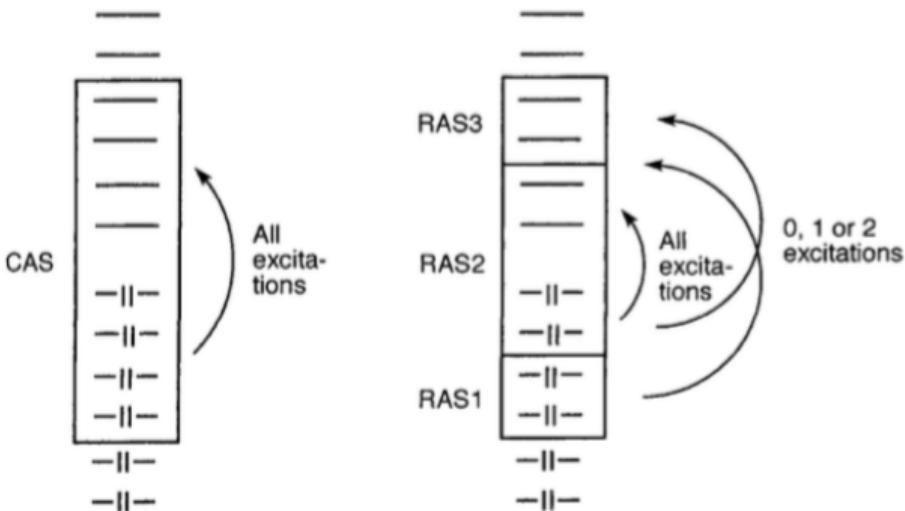
- The active MOs are divided into three spaces: **RAS1**, **RAS2** and **RAS3**
 - ① **RAS1** consists of MOs that are doubly occupied in HF reference determinant
 - ② **RAS2** is generated by FCI (analogously to CASSCF)
 - ③ **RAS3** consists of MOs that are empty in HF reference determinant
- FCI within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

Take-home message 2

MCSCF methods aren't BLACK BOX!!

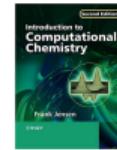
How do we choose the active space?! valence orbitals, chemical intuition, natural orbitals, automatic selection, etc.

CASSCF vs RASSCF



Good books

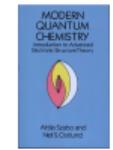
- Introduction to Computational Chemistry (Jensen)



- Essentials of Computational Chemistry (Cramer)



- Modern Quantum Chemistry (Szabo & Ostlund)



- Molecular Electronic Structure Theory (Helgaker, Jorgensen & Olsen)

