Chem3208 Lectures 10–14
Electronic Correlation Methods

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The correlation energy

- HF replaces the e-e interaction by an averaged interaction

- The error in the HF method is called the correlation energy

$$\boxed{E_c = E - E_{\mathsf{HF}}}$$

- The correlation energy is small but cannot but 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

Correlation methods

1. Configuration Interaction (CID, CIS, CISD, QCISD)

2. Coupled Cluster (CCD, CCSD, CCSD[T], 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)

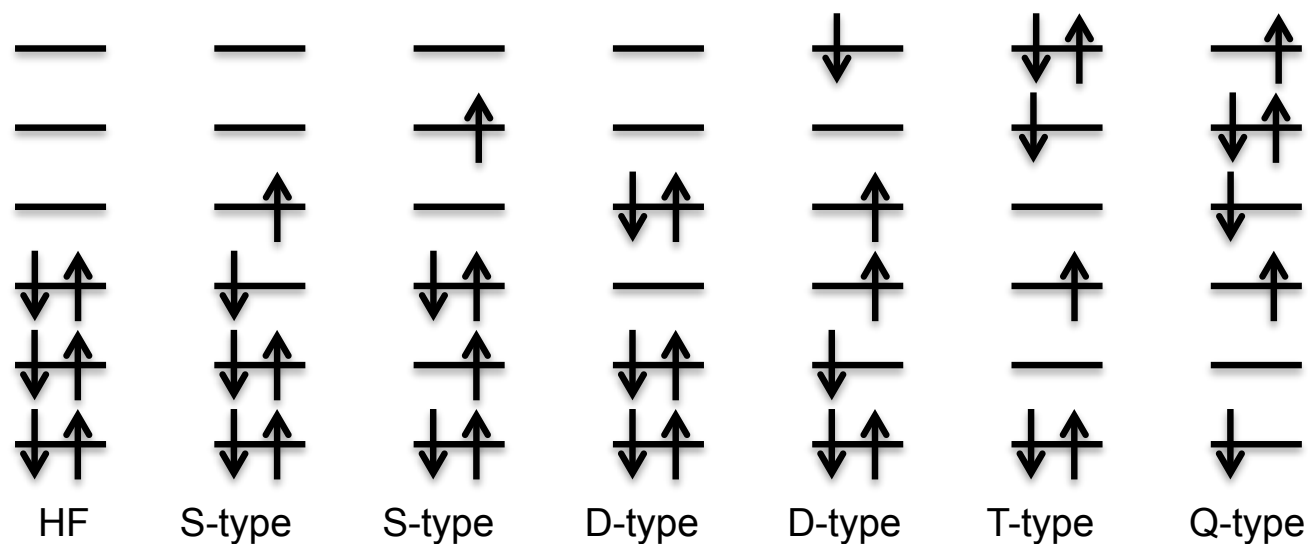7. Stochastic Quantum Monte Carlo methods (VMC, DMC, FCIQMC)

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

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{ia} c_i^a|\Psi_i^a\rangle + \sum_{\substack{i<j \\ a<b}} c_{ij}^{ab}|\Psi_{ij}^{ab}\rangle$$

$$+ \sum_{\substack{i<j<k \\ a<b<c}} c_{ijk}^{abc}|\Psi_{ijk}^{abc}\rangle + \sum_{\substack{i<j<k<l \\ a<b<c<d}} c_{ijkl}^{abcd}|\Psi_{ijkl}^{abcd}\rangle + \ldots$$

- 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

HF	S-type	S-type	D-type	D-type	T-type	Q-type

CI wave function

$$|\Phi_0\rangle = c_0|HF\rangle + c_S|S\rangle + c_D|D\rangle + c_T|T\rangle + c_Q|Q\rangle + \ldots$$

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 (cf Part IV)

- 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**

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

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**)

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

- FCI gives the exact solution of the Schrödinger equation within a given basis
- For a two-electron system, FCI = CISD
- For a three-electron system, FCI = CISDT
- FCI is becoming more and more fashionable these days (e.g. FCIQMC method)

- So, why do we care about other methods?

Full CI

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$$|\Phi_{\mathsf{FCI}}\rangle = c_0|\mathsf{HF}\rangle + c_{\mathsf{S}}|\mathsf{S}\rangle + c_{\mathsf{D}}|\mathsf{D}\rangle + c_{\mathsf{T}}|\mathsf{T}\rangle + c_{\mathsf{Q}}|\mathsf{Q}\rangle + \ldots$$

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- So, why do we care about other methods?
- Because FCI is bloody 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

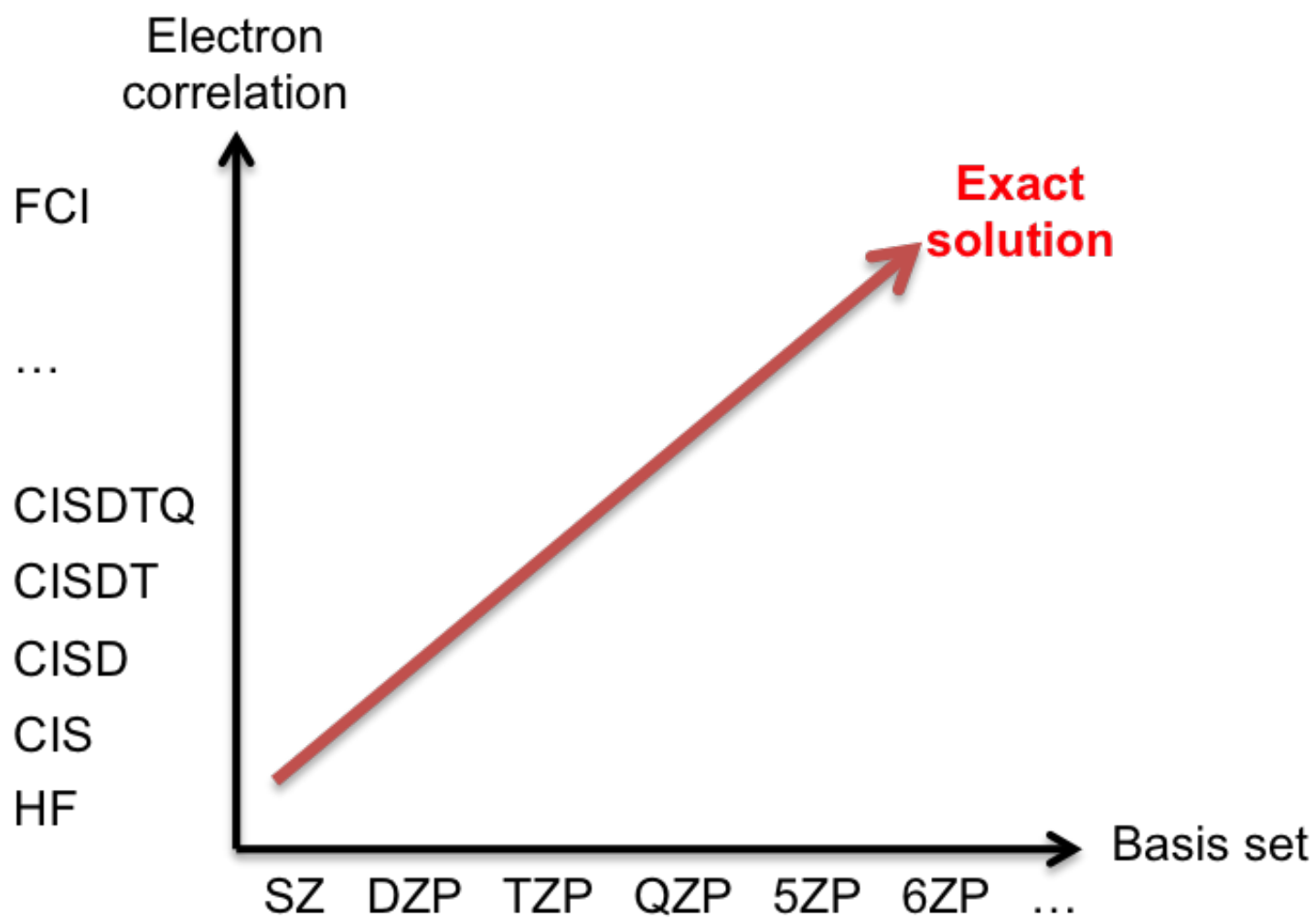- The total number of possible excited determinant is

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

- This is a lot...

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

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

How to do a CI calculation?

- Do a HF calculation to obtain occupied and virtual MOs

- Compute the CI matrix $\mathbf{H}_{CI}$ (cf next slide)

- Diagonalize $\mathbf{H}_{CI}$:

$$\boxed{\mathbf{H}_{CI}\,\mathbf{C}_{CI} = \mathbf{E}_{CI}\,\mathbf{H}_{CI}}$$

- The lowest eigenvalue corresponds to the ground state energy.

- The others correspond to excited states

- In reality, one never builds the entire $\mathbf{H}_{CI}$ because it is too big
  $\Rightarrow$ Davidson diagonalization

The FCI matrix $\mathbf{H}_{FCI}$

$$|\Phi_0\rangle = c_0|HF\rangle + c_S|S\rangle + c_D|D\rangle + c_T|T\rangle + c_Q|Q\rangle + \ldots$$

Before pruning:

	$|HF\rangle$	$|S\rangle$	$|D\rangle$	$|T\rangle$	$|Q\rangle$	$\cdots$
$\langle HF|$	$\langle HF|\mathbf{H}|HF\rangle$	$\langle HF|\mathbf{H}|S\rangle$	$\langle HF|\mathbf{H}|D\rangle$	$\langle HF|\mathbf{H}|T\rangle$	$\langle HF|\mathbf{H}|Q\rangle$	$\cdots$
$\langle S|$	$\langle S|\mathbf{H}|HF\rangle$	$\langle S|\mathbf{H}|S\rangle$	$\langle S|\mathbf{H}|D\rangle$	$\langle S|\mathbf{H}|T\rangle$	$\langle S|\mathbf{H}|Q\rangle$	$\cdots$
$\langle D|$	$\langle D|\mathbf{H}|HF\rangle$	$\langle D|\mathbf{H}|S\rangle$	$\langle D|\mathbf{H}|D\rangle$	$\langle D|\mathbf{H}|T\rangle$	$\langle D|\mathbf{H}|Q\rangle$	$\cdots$
$\langle T|$	$\langle T|\mathbf{H}|HF\rangle$	$\langle T|\mathbf{H}|S\rangle$	$\langle T|\mathbf{H}|D\rangle$	$\langle T|\mathbf{H}|T\rangle$	$\langle T|\mathbf{H}|Q\rangle$	$\cdots$
$\langle Q|$	$\langle Q|\mathbf{H}|HF\rangle$	$\langle Q|\mathbf{H}|S\rangle$	$\langle Q|\mathbf{H}|D\rangle$	$\langle Q|\mathbf{H}|T\rangle$	$\langle Q|\mathbf{H}|Q\rangle$	$\cdots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

After pruning:

	$|HF\rangle$	$|S\rangle$	$|D\rangle$	$|T\rangle$	$|Q\rangle$	$\cdots$
$\langle HF|$	$\langle HF|\mathbf{H}|HF\rangle$	0	$\langle HF|\mathbf{H}|D\rangle$	0	0	$\cdots$
$\langle S|$	0	$\langle S|\mathbf{H}|S\rangle$	$\langle S|\mathbf{H}|D\rangle$	$\langle S|\mathbf{H}|T\rangle$	0	$\cdots$
$\langle D|$	$\langle D|\mathbf{H}|HF\rangle$	$\langle D|\mathbf{H}|S\rangle$	$\langle D|\mathbf{H}|D\rangle$	$\langle D|\mathbf{H}|T\rangle$	$\langle D|\mathbf{H}|Q\rangle$	$\cdots$
$\langle T|$	0	$\langle T|\mathbf{H}|S\rangle$	$\langle T|\mathbf{H}|D\rangle$	$\langle T|\mathbf{H}|T\rangle$	$\langle T|\mathbf{H}|Q\rangle$	$\cdots$
$\langle Q|$	0	0	$\langle Q|\mathbf{H}|D\rangle$	$\langle Q|\mathbf{H}|T\rangle$	$\langle Q|\mathbf{H}|Q\rangle$	$\cdots$

Rules & Observations

1. No coupling between HF ground state $|HF\rangle$ and single excitations $|S\rangle$
   $\Rightarrow$ Brillouin theorem
   $$\langle HF|\mathbf{H}|S\rangle = 0$$

2. No coupling between $|HF\rangle$ and triples $|T\rangle$, quadruples $|Q\rangle$, etc.
   $\Rightarrow$ Slater-Condon rules
   $$\langle HF|\mathbf{H}|T\rangle = \langle HF|\mathbf{H}|Q\rangle = \ldots = 0$$
   $$\langle S|\mathbf{H}|Q\rangle = \ldots = 0$$

3. $|S\rangle$ have small effect but mix indirectly with $|D\rangle$
   $\Rightarrow$ CID $\neq$ CISD
   $$\langle HF|\mathbf{H}|S\rangle = 0 \text{ but } \langle S|\mathbf{H}|D\rangle \neq 0$$

4. $|D\rangle$ have large effect and $|Q\rangle$ more important than $|T\rangle$
   $\Rightarrow$ CID gives most of the correlation energy
   $$\langle HF|\mathbf{H}|D\rangle \gg \langle HF|\mathbf{H}|Q\rangle \gg \langle HF|\mathbf{H}|T\rangle$$

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

Size consistency and size extensivity

- Truncated CI methods are size inconsistent i.e.

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

- 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

Problem: CID for H_2

"We consider the ground state of the H_2 molecule in a minimal basis set with two spatial MOs ψ_1 and ψ_2." We give the following integrals:

$$h_1 = -1.2529 \quad h_2 = -0.4756$$

$$J_{11} = 0.6746 \quad J_{22} = 0.6975 \quad J_{12} = 0.6636 \quad K_{12} = 0.1813$$

1. Calculate the HF energy
2. Knowing that the CID matrix is

$$\mathbf{H}_{\text{CID}} = \begin{pmatrix} 2h_1 + (11|11) & (12|12) \\ (12|12) & 2h_2 + (22|22) \end{pmatrix}$$

   Calculate the ground state CID energy
3. Combining the results of the previous two questions, calculate the correlation energy