

# CHM 673

## Lecture 10: Electron correlation. Configuration interaction

---

Suggested reading:

Chapter 2.2.6-2.2.7, 4.1, 4.2, 4.6 from S&O

Chapter 4.1, 4.2, 4.5 from Jensen

<http://vergil.chemistry.gatech.edu/courses/chem6485/pdf/intro-e-correlation.pdf>

<http://vergil.chemistry.gatech.edu/notes/ci.pdf>

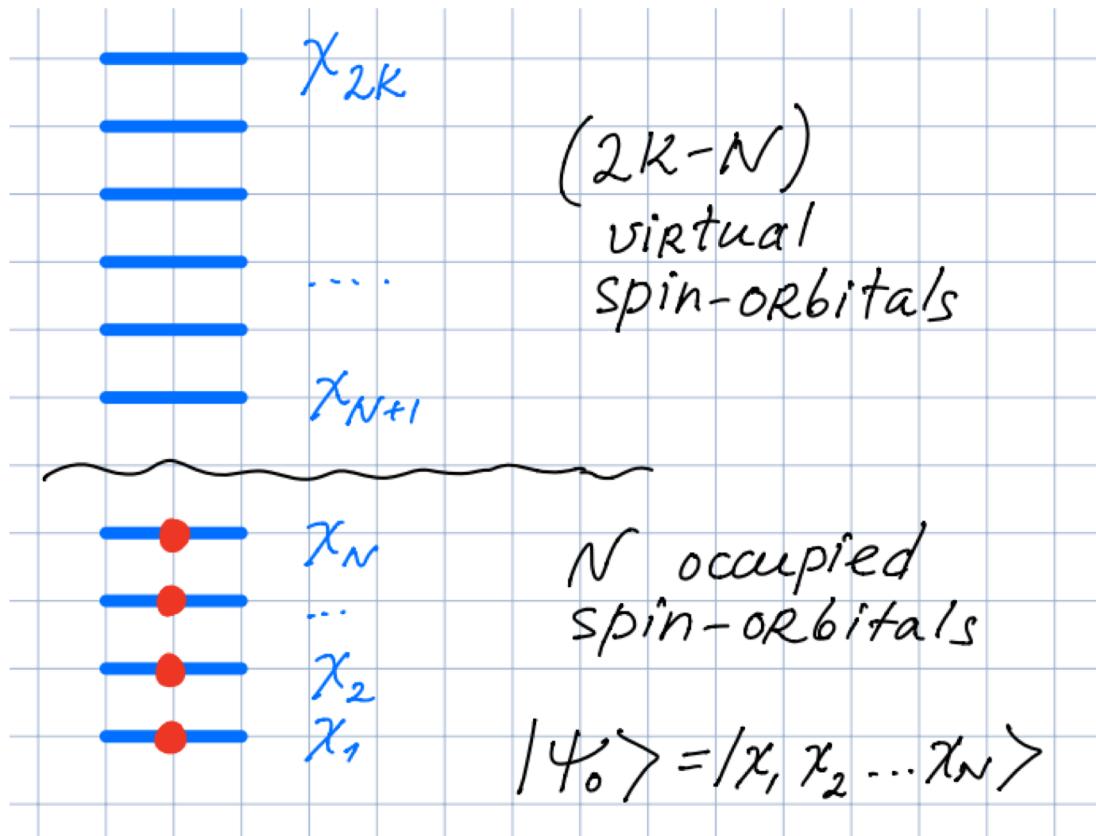
# Hartree-Fock model

After solving 2K HF eq-ns:

$$\hat{f}_i |\chi_i\rangle = \varepsilon_i |\chi_i\rangle$$

K – the total number of spatial orbitals, which is determined by the total number of basis functions – stay tuned  
2K - the total number of spin-orbitals

2K orthonormal spin-orbitals  $\{\chi_i\}$  with orbital energies  $\{\varepsilon_i\}$  is produced



The Slater determinant formed from the N lowest occupied spin-orbitals

$|\Phi_0\rangle = |\chi_1, \chi_2, \dots, \chi_N\rangle$  is the Hartree-Fock ground state wave function.

It is the best variational approximation to the ground state of the system in the single determinantal form.

# Hartree-Fock solutions

---

$\hat{f}_i|\chi_i\rangle = \varepsilon_i|\chi_i\rangle$       2K orthonormal spin-orbitals  $\{\chi_i\}$  with orbital energies  $\{\varepsilon_i\}$  is produced

**Q:** Is the Hartree-Fock ground state wave function the exact solution to the system?

**Q:** How to improve it?

# The exact solution to N-electron problem

Given N electrons and 2K spin orbitals

The best solution is to combine together **all possible valid determinants**  $\Psi = \sum_i c_i \Phi_i$  and use the variational principle to minimize the ground state energy.

This model is called **Full Configuration Interaction (FCI)**

**FCI is the exact solution of electronic SE in a given spin-orbital basis (with given K)**

How big is a FCI wave function? The number of possible SDs is given as the number of times we can draw N spin-orbitals from a pool of 2K:

$$\# \text{configurations} = C_{2K}^N = \frac{(2K)!}{N! (2K - N)!} \approx 10^N$$

Today largest computations can deal with  $\sim 10^9$  configurations

$N$	$2K$	$C_{2K}^N$
2	10	45
4	20	4845
6	30	593775
8	40	$7.7 \cdot 10^7$
10	50	$1.0 \cdot 10^{10}$
20	100	$5.4 \cdot 10^{20}$

# Electron correlation

---

Hartree-Fock model (aka mean-field theory):

- electronic interactions are averaged out, or
- electrons feel averaged in time positions of other electrons
- however, same-spin electrons are correlated (exchange correlation)

Correlation energy:  $E_{corr} = E_{exact} - E_{RHF} = E_{FCI} - E_{RHF}$

Correlation energy:

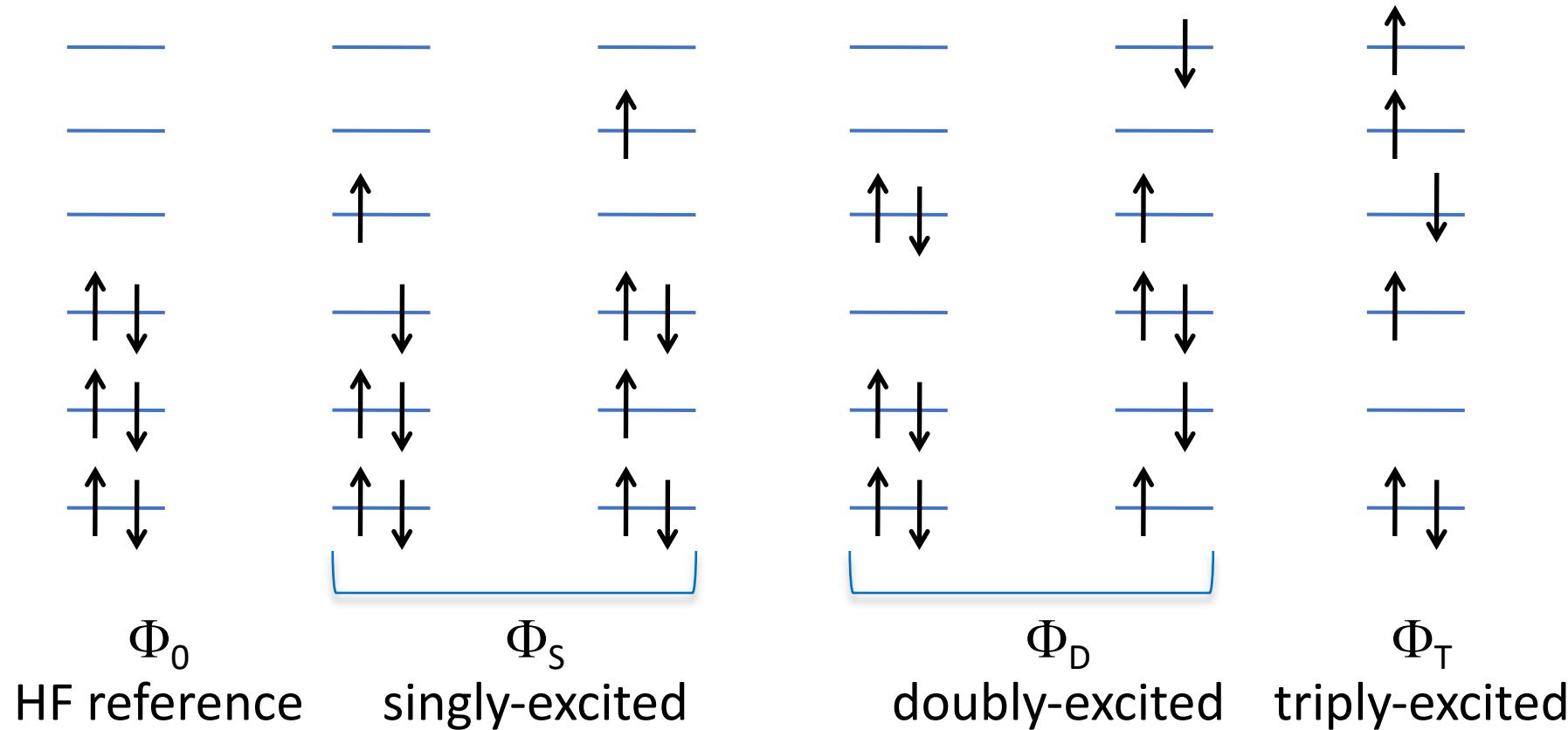
- ~0.5-1.0 eV per electron pair
- scales with the size of the molecule
- can change in chemical reaction (e.g., H<sub>2</sub> dissociation)

Chemical consequences of lacking electron correlation in the HF model:

Increased ionicity, dipole moments ~20% too big, vibrational frequencies ~10% too big, chemical bonds too rigid

# Excited Slater determinants

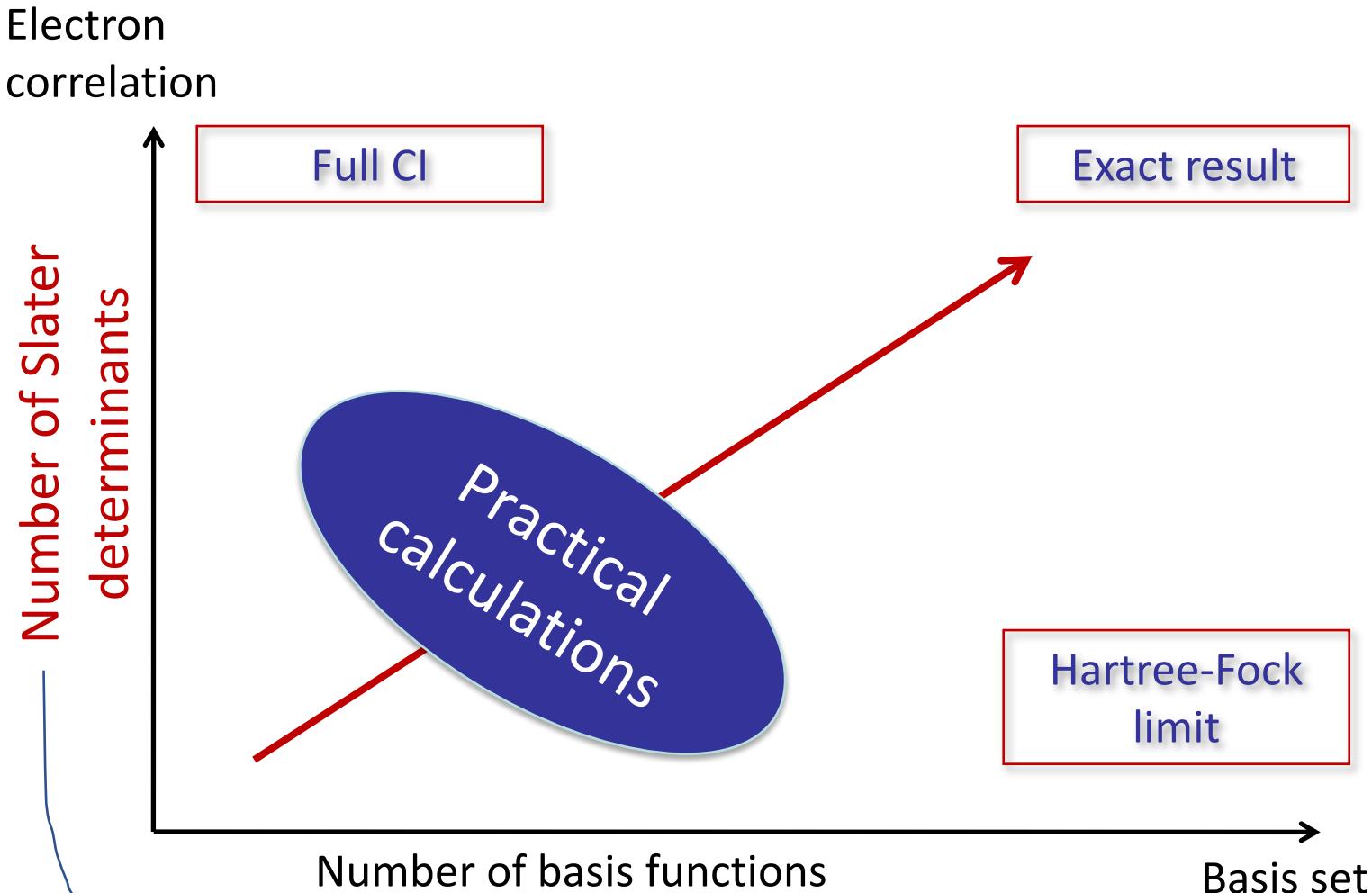
Electron correlation can be described with partial occupation of antibonding orbitals, i.e., by including excited SDs into the wave function



$$|\Psi\rangle = a_0 |\Phi_0\rangle + \sum_S a_S |\Phi_S\rangle + \sum_D a_D |\Phi_D\rangle + \sum_T a_T |\Phi_T\rangle + \dots$$

exact (FCI) wave function

# Theoretical model chemistries (John Pople)



$$|\Psi\rangle = a_0 |\Phi_0\rangle + \sum_S a_S |\Phi_S\rangle + \sum_D a_D |\Phi_D\rangle + \sum_T a_T |\Phi_T\rangle + \dots$$

# Electron correlation: methodology

---

Electron correlation can be recovered in post-Hartree-Fock calculations employing:

- Variational principle: Configuration Interaction methods (FCI, CISD, QCISD(T), etc)
- Perturbation theory: Moller-Plesset perturbation theory (MP2, MP4, etc)
- Coupled-cluster ansatz (CCSD, CCSD(T), CCSDT etc)
- Density Matrix Renormalization Group (DMRG) theory
- Quantum Monte-Carlo (QMC)
- ...

or using Kohn-Sham Density Functional Theory (DFT)

# Types of electron correlation

Recall Heisenberg uncertainty principle       $\Delta p \Delta x \geq \frac{\hbar}{2}$

Since  $\Delta p \sim \Delta E_{kin} \rightarrow$

- a spatially localized electron has large uncertainty in its kinetic energy
- an electron with well-defined energy should be delocalized in space

Electron correlation:

- **dynamical**  
correlation local in space: small  $\Delta x$ ,  $E_{kin}$  is undefined
- **static or non-dynamical**  
degenerate energy (small spread of  $E_{kin}$ ), electron position is undefined (large  $\Delta x$ )
- **long-range ( dispersion )**

**Hartree-Fock misses both dynamical, non-dynamical and long-range correlation!**

# Types of electron correlation

Recall Heisenberg uncertainty principle

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

Since  $\Delta p \sim \Delta E_{kin} \rightarrow$

- a spatially localized electron has large uncertainty in its kinetic energy
  - an electron with well-defined energy should be delocalized in space
- 

## Dynamical correlation:

- correlation local in space: small  $\Delta x$ ,  $E_{kin}$  is undefined
- physical meaning: electrons avoid each other at short range
- typically observed as many small contributions to the wave function (many excited SDs with small weights)
- present in majority of chemical systems

# Types of electron correlation

Recall Heisenberg uncertainty principle

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

Since  $\Delta p \sim \Delta E_{kin} \rightarrow$

- a spatially localized electron has large uncertainty in its kinetic energy
  - an electron with well-defined energy should be delocalized in space
- 

## Static or non-dynamical correlation:

- degenerate energy (small spread of  $E_{kin}$ ), electron position is undefined (large  $\Delta x$ )
- mixing of states with almost degenerate energies results in low-frequency oscillations  $\rightarrow$  slow electrons  $\rightarrow$  mean-field works worse than for fast electrons (averaging of electron position leads to larger errors)
- observed as a few significant contributions to the wave function (several excited SDs with large weights)
- typically present in bond-dissociation, anions, molecules with several Lewis structures, radicals, diradicals, etc.

# Types of electron correlation

Recall Heisenberg uncertainty principle

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

Since  $\Delta p \sim \Delta E_{kin} \rightarrow$

- a spatially localized electron has large uncertainty in its kinetic energy
  - an electron with well-defined energy should be delocalized in space
- 

## Long-range electron correlation or dispersion:

- think of  $\text{He}_2$  dimer. It is very weakly bound (He becomes liquid at  $\sim 4$  K). Why? Long-range correlation!
- interaction of instantaneously moving electrons belonging to different molecules (can be modeled as interaction of instantaneous dipole moments) is always attractive, decays as  $(-1/R^6)$  with the distance
- this is a physical origin of attractive part of van der Waals interactions

# Configuration Interaction (CI) methods

---

Trial wave function – a linear combination of Slater determinants:

$$\Psi_{CI} = a_0 \Phi_{HF} + \sum_S a_S \Phi_S + \sum_D a_D \Phi_D + \sum_T a_T \Phi_T + \dots = \sum_{i=0} a_i \Phi_i$$

- Expansion coefficients are determined by requiring that the energy should be a minimum → variational principle is used
- Spin orbitals are from HF calculation – held fixed!
- The energy is minimized under the constraint that the CI wave function is normalized

# Variational principle for CI

$|\Phi_i\rangle$  - Slater determinants built on HF orbitals

$$|\Psi_{CI}\rangle = \sum_i c_i |\Phi_i\rangle \quad \text{want to determine } c_i \text{ that minimize total energy}$$

$$L = \langle \Psi_{CI} | \hat{H} | \Psi_{CI} \rangle - E (\langle \Psi_{CI} | \Psi_{CI} \rangle - 1) \quad \text{Lagrangian, takes care of normalization of CI wf}$$

$$\langle \Psi_{CI} | \hat{H} | \Psi_{CI} \rangle = \sum_{ij} c_i^* c_j \langle \Phi_i | \hat{H} | \Phi_j \rangle = \sum_{ij} c_i^* c_j H_{ij}$$

$$\langle \Psi_{CI} | \Psi_{CI} \rangle = \sum_{ij} c_i^* c_j \langle \Phi_i | \Phi_j \rangle = \sum_i |c_i|^2 \quad \text{different SDs are orthogonal!}$$

$$L = \sum_{ij} c_i^* c_j H_{ij} - E(\sum_i |c_i|^2 - 1)$$

$$\delta L = \sum_{ij} \delta c_i^* c_j H_{ij} - E \sum_i \delta c_i^* c_i + c.c. = 0$$

$$\sum_j c_j H_{ij} - E \sum_i c_i = 0 \quad \rightarrow \quad \text{Eigenvalue problem: } \mathbf{H}\mathbf{c} = E\mathbf{c}$$

$\mathbf{c}$  – column-vector representing  $|\Psi_{CI}\rangle$  in basis of SDs  $|\Phi_i\rangle$

# CI Hamiltonian matrix elements

Brillouin  
theorem

$$H_{ij} \left( \Phi_{HF} \Phi_S \Phi_D \Phi_T \Phi_Q \dots \right)$$
$$\begin{pmatrix} \Phi_{HF} \\ \Phi_S \\ \Phi_D \\ \Phi_T \\ \Phi_Q \\ \vdots \end{pmatrix} \begin{matrix} E_{HF} & 0 & x & 0 & 0 & 0 \\ 0 & E_S & x & x & 0 & 0 \\ x & x & E_D & x & x & 0 \\ 0 & x & x & E_T & x & x \\ 0 & 0 & x & x & E_Q & x \\ 0 & 0 & 0 & x & x & \ddots \end{matrix}$$

Slater-Condon  
rules

Some other elements of CI matrix may become 0:

- spin-symmetry (Slater determinants of different spin do not interact through Hamiltonian)
- spatial symmetry

# How many determinants are in CI wavefunction?

N electrons, K orbitals, n-tuple excitation →  
number of n-tuply excited determinants: 
$$\binom{2N}{n} \binom{2K - N}{n}$$

Number of singlet symmetry-adapted configurations (SAC)  
for H<sub>2</sub>O in 6-31G(d)

Excitation level	# of excited SAC	Total # of SAC
1	71	71
2	2485	2556
3	40040	42596
4	348530	391126
5	1723540	2114666
6	5033210	7147876
7	8688680	15836556

dimensionality of  $H_{ij}$  !!!

# CI correlation energy

It is convenient to introduce intermediate normalization

Rewrite FCI wf as

$$\Psi_{CI} = \sum_i c_i \Phi_i = \Phi_0 + \sum_{i \neq 0} c_i \Phi_i$$

$$\langle \Psi_{CI} | \Psi_{CI} \rangle = 1 + \sum (c_i^a)^2 + \sum (c_{ij}^{ab})^2 + \dots \neq 1$$

$$\langle \Phi_0 | \Psi_{CI} \rangle = 1$$

HF wavefunction

But  $\langle \Phi_0 | \Psi_{CI} \rangle = 1 + \langle \Phi_0 | \sum c_i^a \Phi_i^a + \sum c_{ij}^{ab} \Phi_{ij}^{ab} + \dots \rangle = 1$

orthogonality of different SDs!

From the variational principle:

$$\hat{H} | \Psi_{CI} \rangle = E | \Psi_{CI} \rangle$$

Subtract Hartree-Fock energy  $E_0 \rightarrow (\hat{H} - E_0) | \Psi_{CI} \rangle = (E - E_0) | \Psi_{CI} \rangle = E_{corr} | \Psi_{CI} \rangle$

$$\langle \Phi_0 | \hat{H} - E_0 | \Psi_{CI} \rangle = E_{corr} \langle \Phi_0 | \Psi_{CI} \rangle = E_{corr}$$

# CI correlation energy

$$E_{corr} = \langle \Phi_0 | \hat{H} - E_0 | \Psi_{CI} \rangle$$

C – excitation operators

$$\Psi_{CI} = \Phi_0 + \sum_{i \neq 0} c_i \Phi_i = (1 + \hat{C}_1 + \hat{C}_2 + \dots + \hat{C}_N) \Phi_0$$

Single excitation operator

$$\hat{C}_1 = \sum_i^{\text{occ}} \sum_a^{\text{vir}} \hat{a}_a^\dagger \hat{a}_i$$

Double excitation operator

$$\hat{C}_2 = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j$$

$$E_{corr} = \langle \Phi_0 | \hat{H} - E_0 | (1 + \hat{C}_1 + \hat{C}_2 + \dots + \hat{C}_N) \Phi_0 \rangle$$

$$\langle \Phi_0 | \hat{H} | \hat{C}_1 \Phi_0 \rangle = 0 \quad \text{Brillouin's theorem}$$

$$\langle \Phi_0 | \hat{H} | \hat{C}_3 \Phi_0 \rangle = 0 \quad \text{SDs different by more than two orbitals do not interact}$$

$$E_{corr} = \langle \Phi_0 | \hat{H} | \hat{C}_2 \Phi_0 \rangle = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} c_{ij}^{ab} \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle$$

correlation is associated with population of antibonding orbitals

# CI Hamiltonian matrix elements

Brillouin  
theorem

$$H_{ij} \left( \Phi_{HF} \Phi_S \Phi_D \Phi_T \Phi_Q \dots \right)$$
$$\begin{pmatrix} \Phi_{HF} \\ \Phi_S \\ \Phi_D \\ \Phi_T \\ \Phi_Q \\ \vdots \end{pmatrix} \begin{matrix} E_{HF} & 0 & x & 0 & 0 & 0 \\ 0 & E_S & x & x & 0 & 0 \\ x & x & E_D & x & x & 0 \\ 0 & x & x & E_T & x & x \\ 0 & 0 & x & x & E_Q & x \\ 0 & 0 & 0 & x & x & \ddots \end{matrix}$$

Slater-Condon  
rules

Some other elements of CI matrix may become 0:

- spin-symmetry (Slater determinants of different spin do not interact through Hamiltonian)
- spatial symmetry

# How to diagonalize the Hamiltonian matrix?

---

We need to extract **one or a few** of the **lowest** eigenvalues and eigenvectors of sparse Hamiltonian matrix →  
**iterative diagonalization techniques**

**Davidson iterative diagonalization procedure:**

finds the lowest solutions to the H matrix by approximating them with solutions of a smaller matrix

# Davidson iterative diagonalization procedure

$$L \begin{bmatrix} b \\ \vdots \\ b \end{bmatrix} * H \begin{bmatrix} b \\ \vdots \\ b \end{bmatrix} N = G \begin{bmatrix} L \\ \vdots \\ L \end{bmatrix}$$

- $\{b_i\}$  – guess vectors,  $i=1, L$ ,  $L \geq M$  – number of solutions (ex. states)
- form  $G_{ij} = (b_i, H_{ij} b_j) = (b_i, \sigma_j)$
- diagonalize  $G_{ij}$ :  $G \alpha^k = \rho^k \alpha^k$ ,  $k = 1, M$  – number of solutions required

- form the correction vector

$$\delta^k = -\frac{\sum_{i=1}^L \alpha^k (H - \rho^k) b_i}{H_{diag} - \rho^k}$$

- normalize  $\{\delta^k\}$
- orthonormalize  $\{\delta^k\}$  against  $\{b_i\}$  and add them to  $\{b_i\}$  set

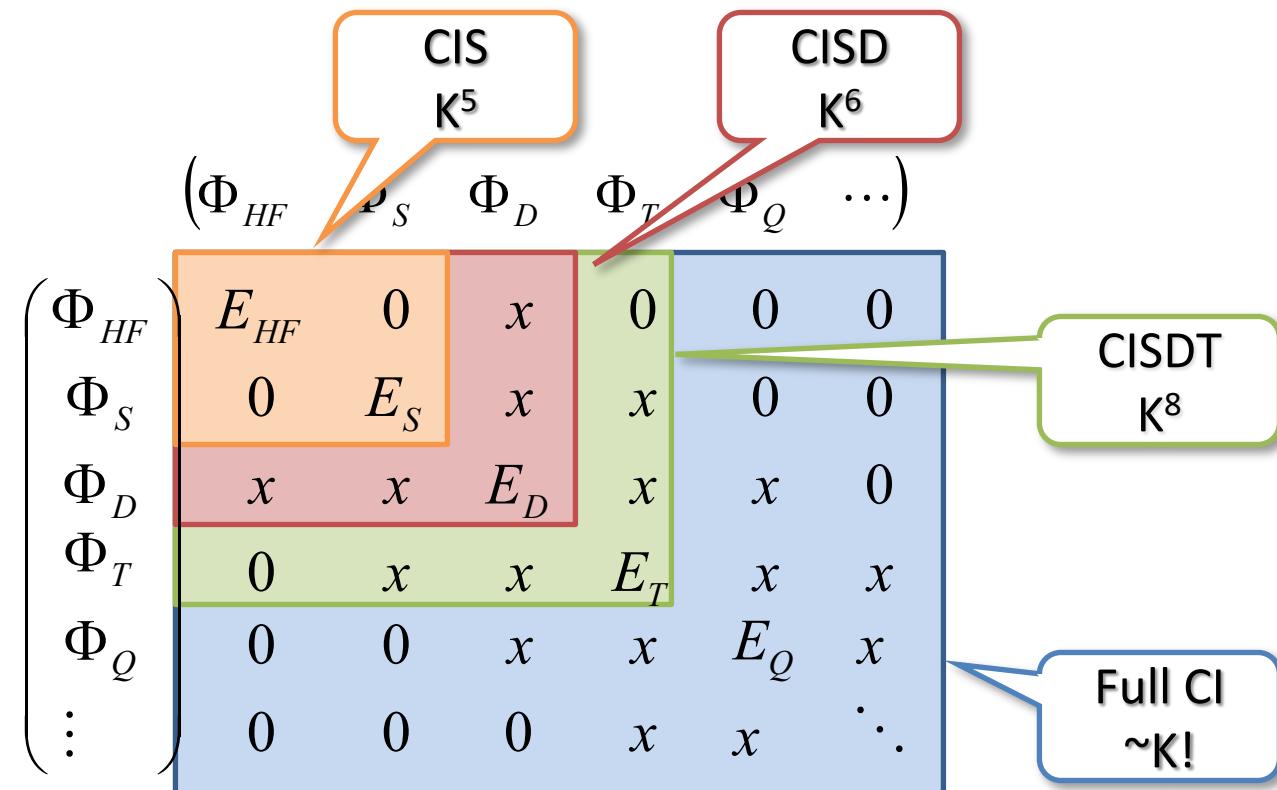
# Truncated CI

Is it possible to simplify the Hamiltonian matrix?  
Are all excited determinants equally important?

## Truncated configuration interaction

methods:

- configuration interaction singles (CIS)
- configuration interaction singles and doubles (CISD)
- configuration interaction singles, doubles and triples (CISDT)
- ...



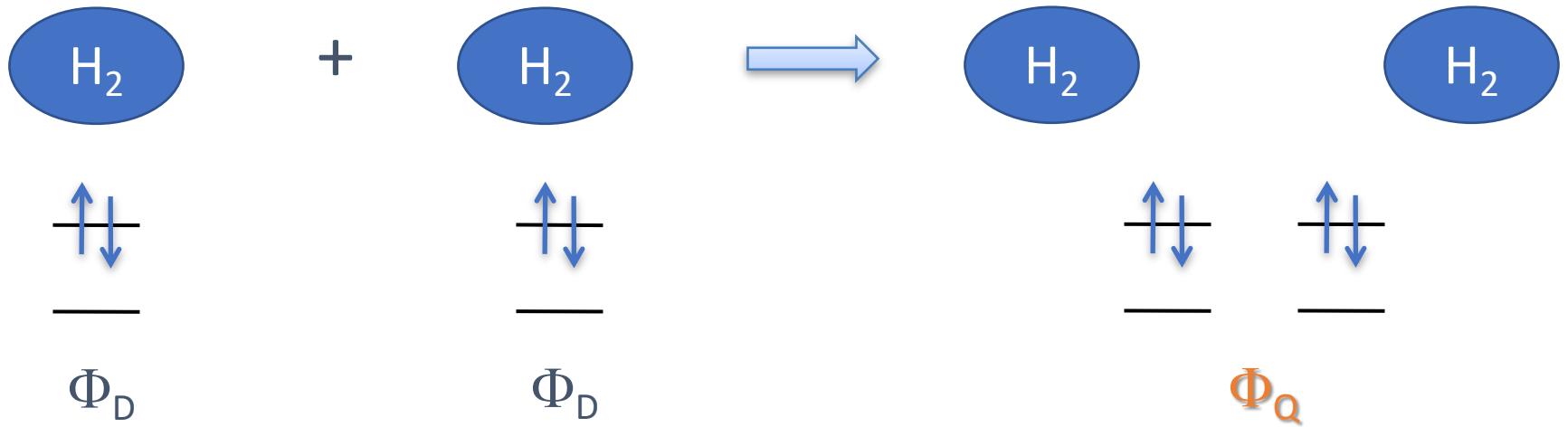
# Truncated CI: size consistency problem



For non-interacting systems A and B

**Size consistency:**  $E(A) + E(B) = E(A+B)$

Consider a pair of far-separated  $H_2$  molecules and try to describe them with CISD



**Truncated CI methods (except of CIS) are not size consistent!**

The accuracy of truncated CI methods (CISD, CISDT, etc) deteriorates quickly with molecular size. These methods are unreliable and rarely used

# Configuration interaction: summary

---

- Configuration Interaction – variational method, CI energy is an upper bound to the exact solution of the Schrodinger equation
- Full CI represents the exact wave function as a linear combination of N-electron functions (Slater determinants)
- In the complete N-electron function set, Full CI provides the exact solution in a given basis set. However, computational cost of Full CI is factorial
- Truncated CI (CISD, CISDT, etc) are size inconsistent; their accuracy deteriorates with increase of the system size
- The most important contribution to the correlation energy is due to double excitations