Electron Correlation:
Single-Reference Methods

Jürgen Gauss

JOHANNES GUTENBERG
UNIVERSITÄT MAINZ

I.

What is Electron Correlation?

Correlation in Probability Theory

two variables *x* and *y* and probability densities *P(x), P(y), P(x,y)*

variables *x* and *y* independent if

$$P(x,y) \;=\; P(x)P(y)$$

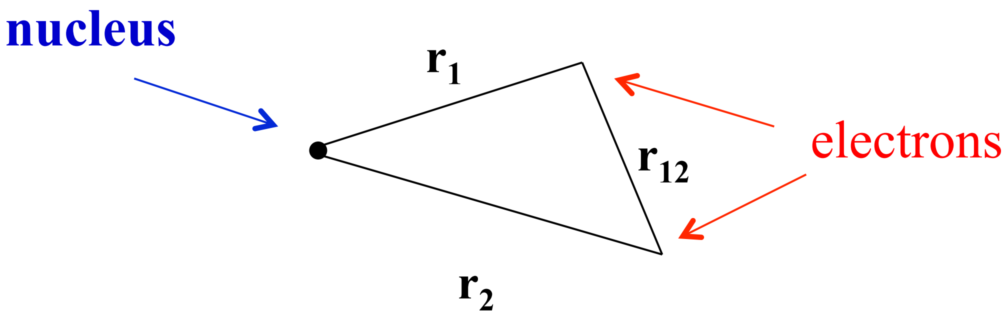
otherwise

$$P(x,y) \;\neq\; P(x)P(y)$$

the variables are correlated

Electron Correlation: the Helium Atom

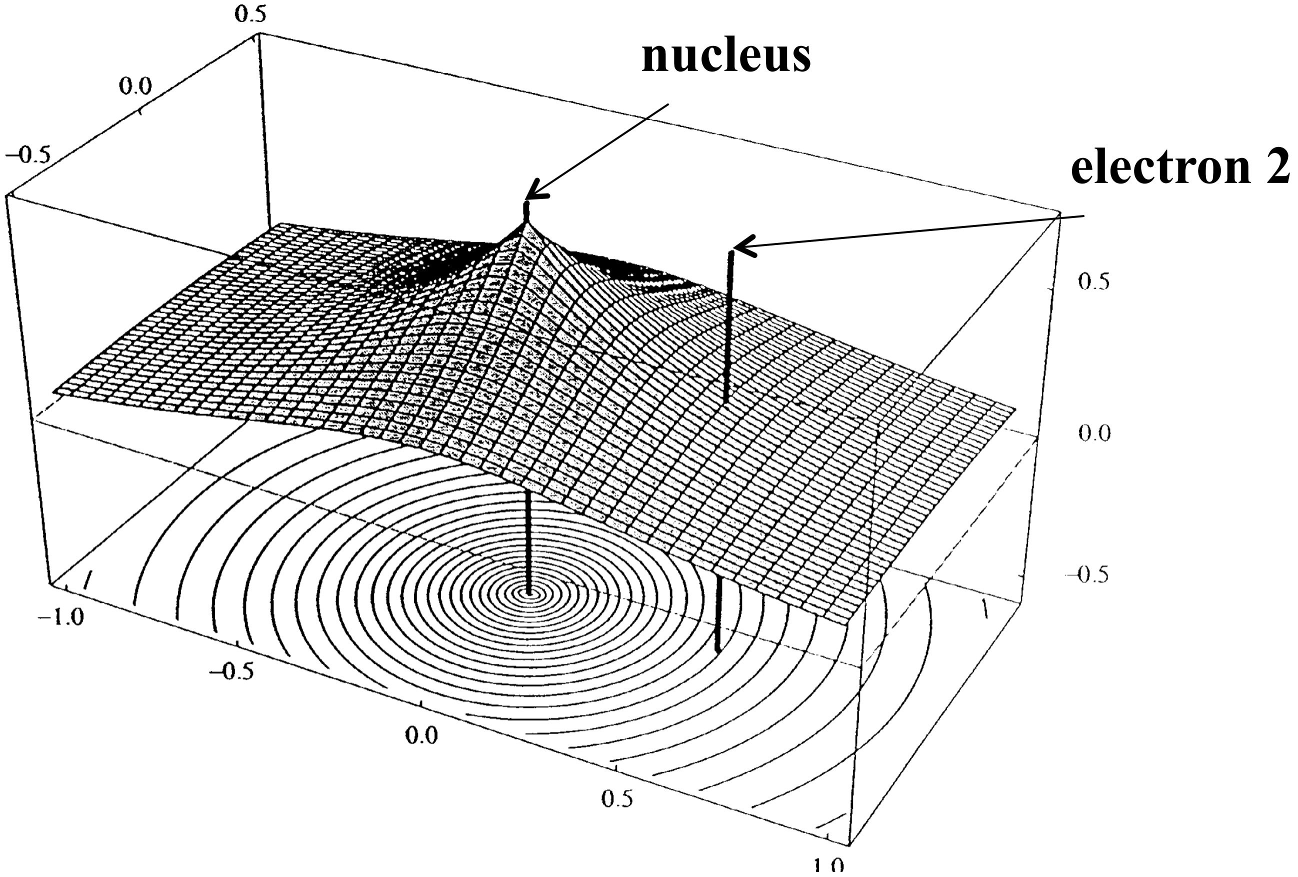
helium atom:



electron density $\rho(\mathbf{r})$

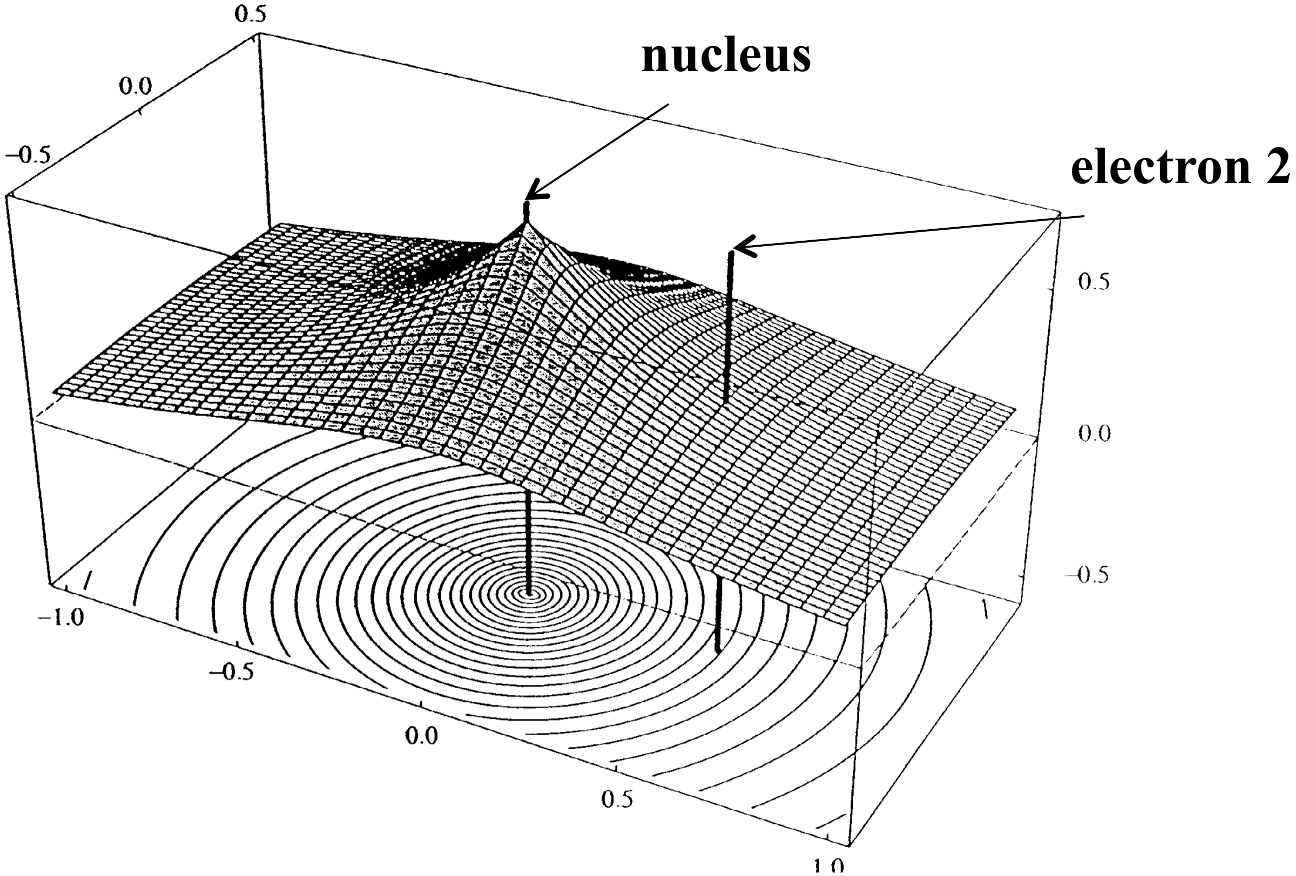
pair density $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$

Electron Correlation: the Helium Atom



wave function $\Psi_{HF}(r_1,r_2)$ *as function of* r_1

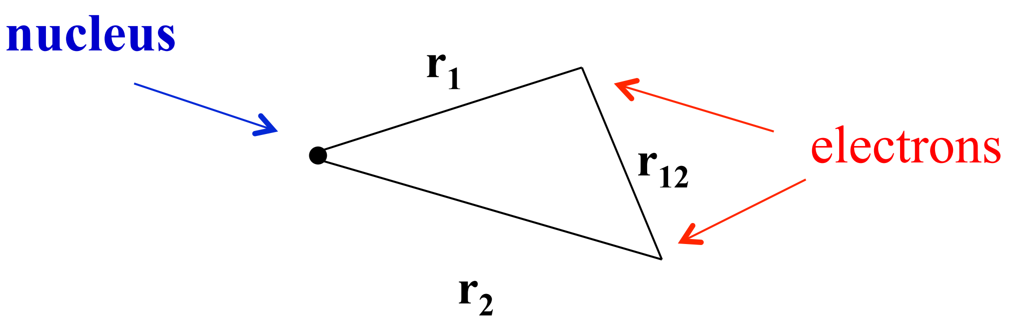
Electron Correlation: the Helium Atom



HF description: independent motion

Electron Correlation: the Helium Atom

helium atom:

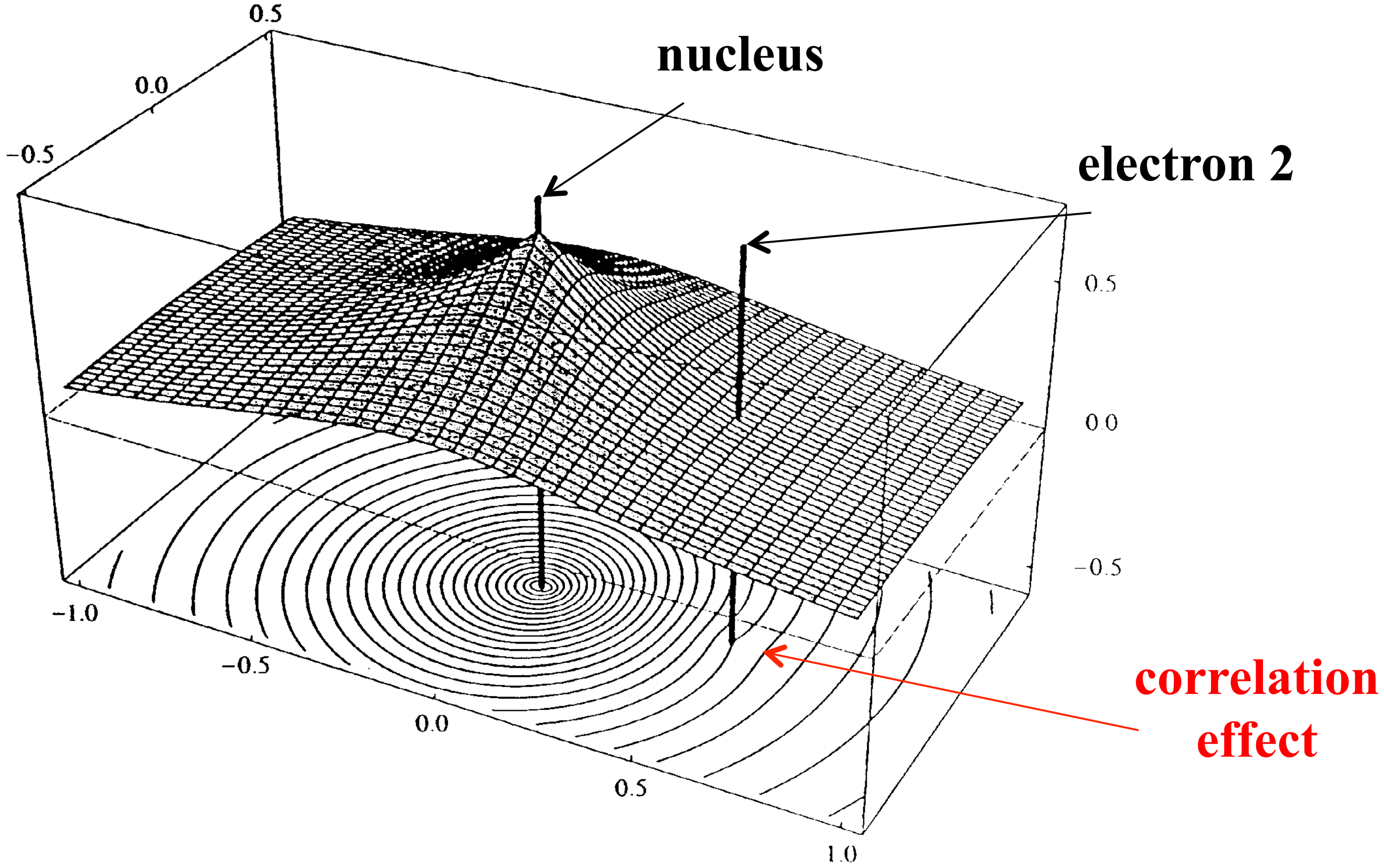


electron density $\rho(\mathbf{r})$

pair density $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$

HF pair density $\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4}\,\rho(\mathbf{r}_1)\,\rho(\mathbf{r}_2)$

Electron Correlation: the Helium Atom



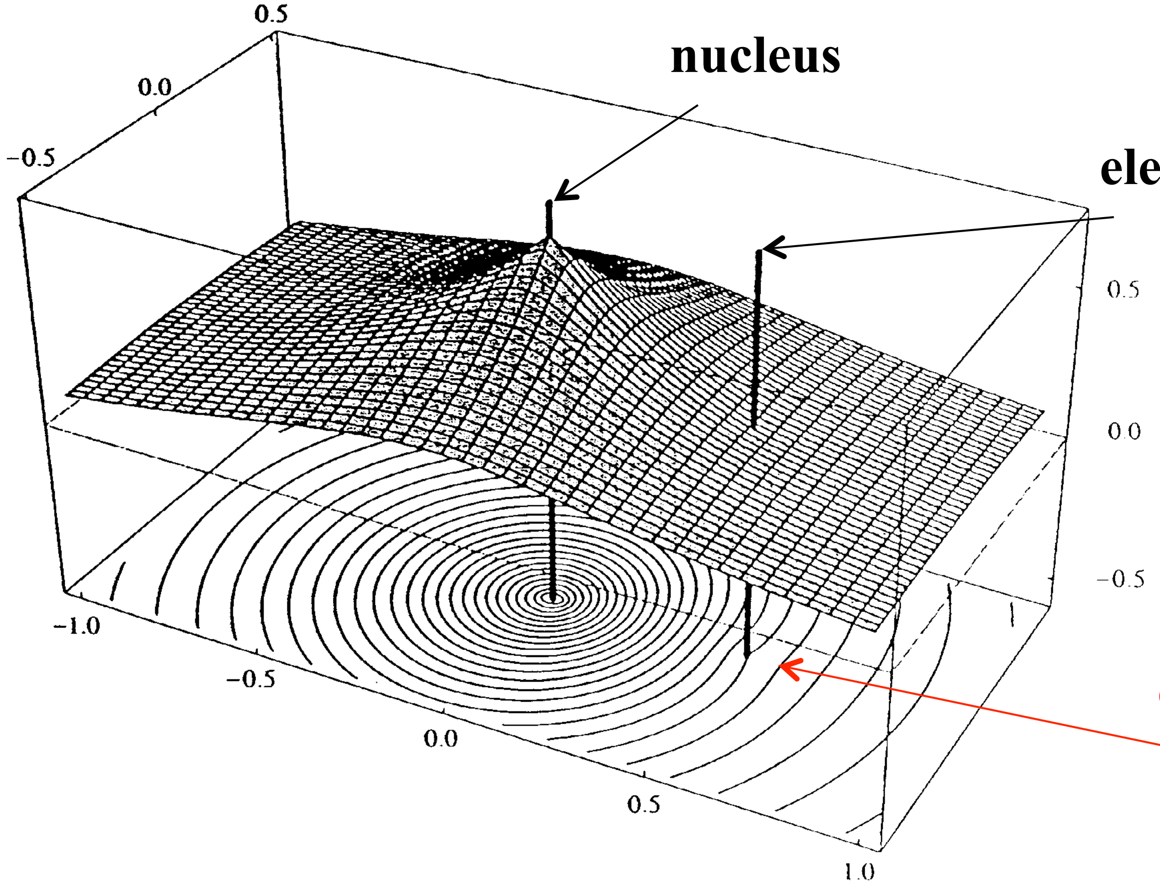
nucleus

electron 2

correlation effect

wave function $\Psi_{exact}(r_1,r_2)$ as function of r_1

Electron Correlation: the Helium Atom



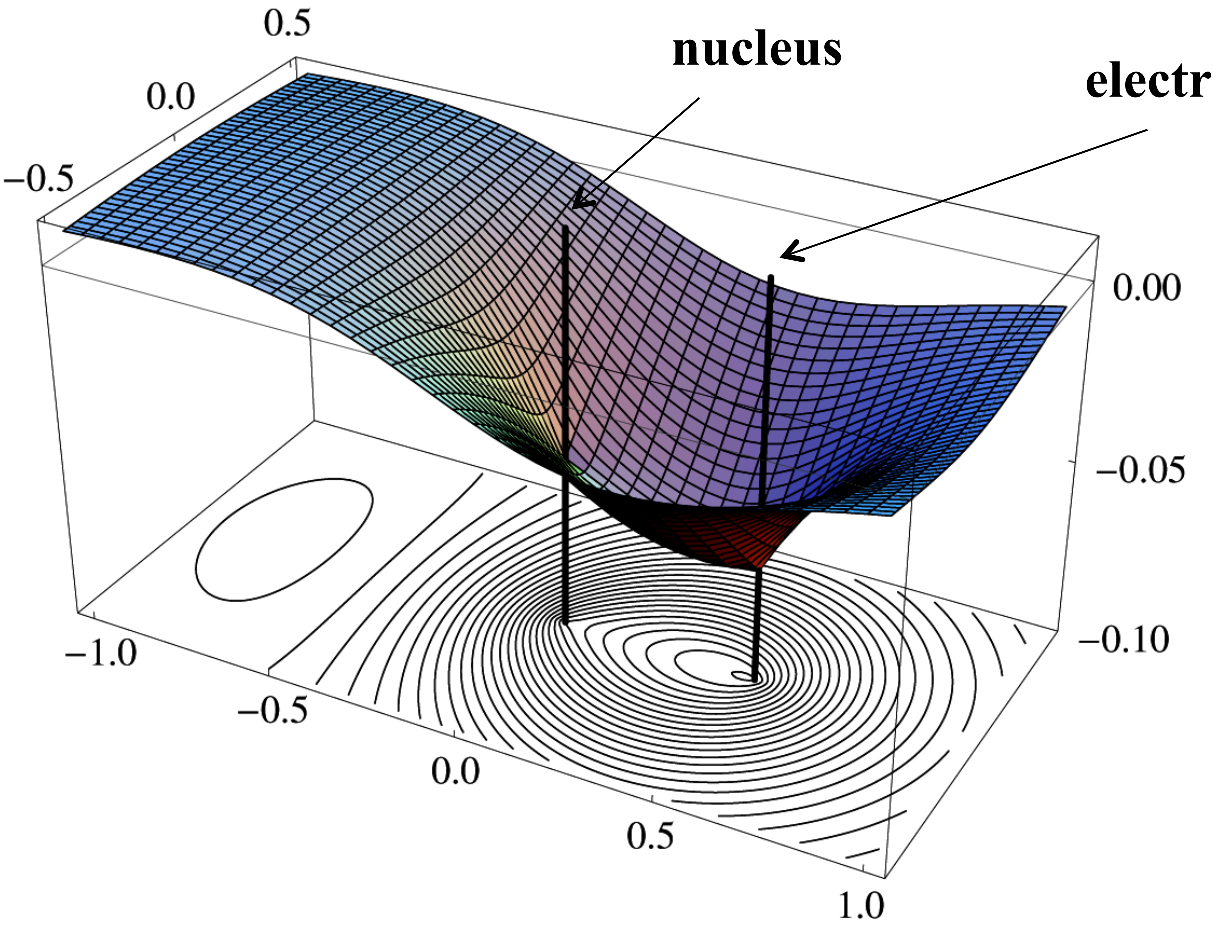
nucleus

electron 2

correlation effect

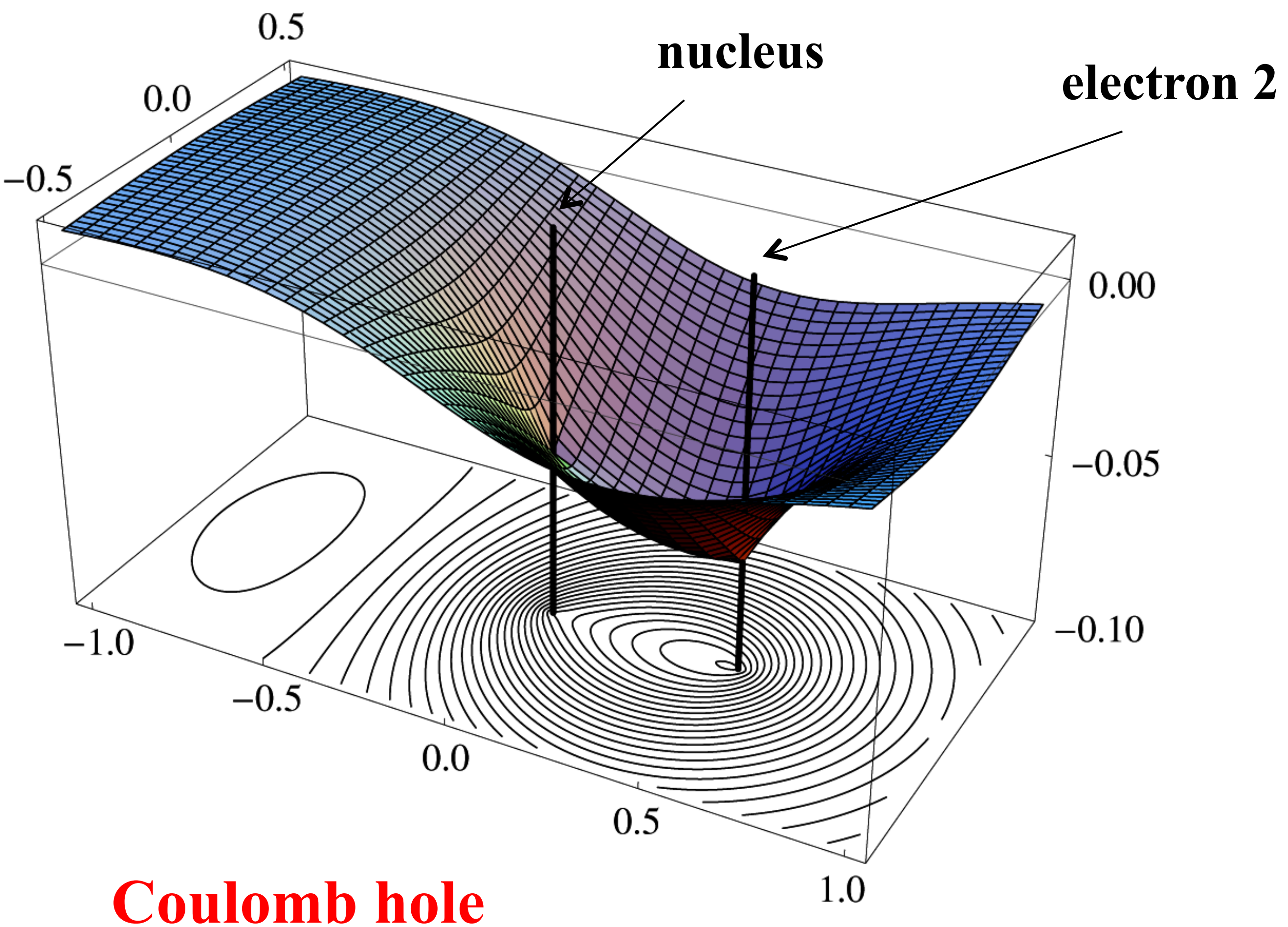
correlated motion

Electron Correlation: the Helium Atom



$\Psi_{exact}(r_1,r_2)$ - $\Psi_{HF}(r_1,r_2)$, as function of r_1

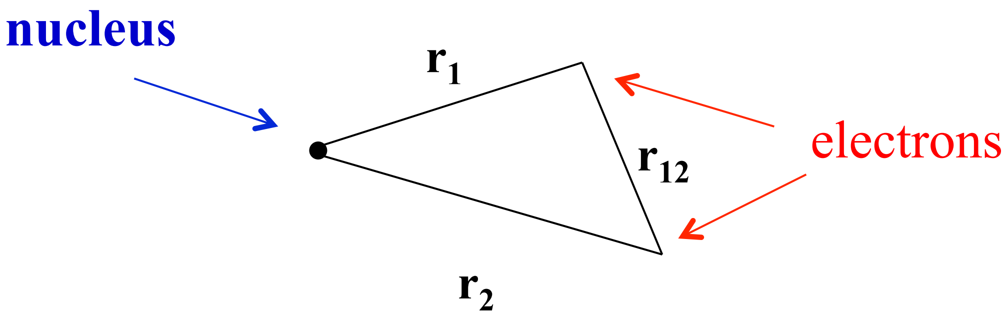
Electron Correlation: the Helium Atom



Coulomb hole

Electron Correlation: the Helium Atom

helium atom:

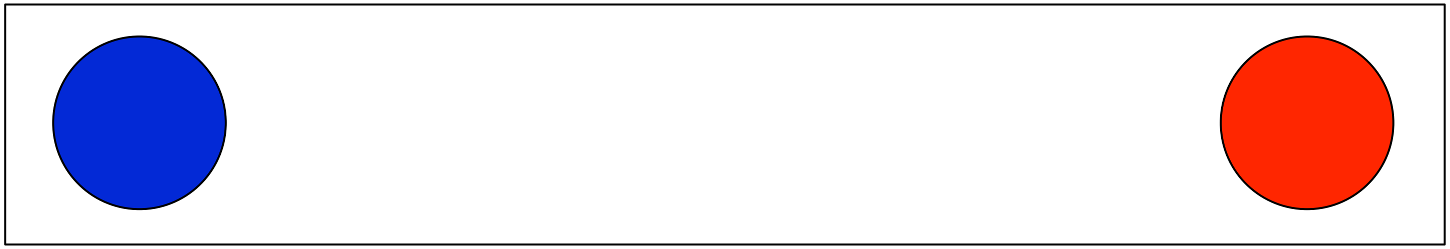


electron density $\rho(\mathbf{r})$

pair density $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$

exact pair density $\rho_2(\mathbf{r}_1, \mathbf{r}_2) \neq \frac{1}{4}\, \rho(\mathbf{r}_1)\, \rho(\mathbf{r}_2)$

Electron Correlation: the Extreme Case



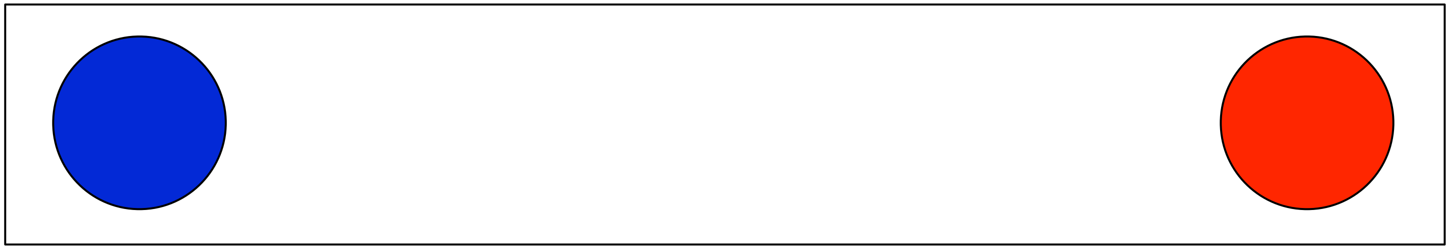
two interacting electrons

two possible sites 🔴 🔵

probabilities:

one electron at 🔵	50 %
one electron at 🔴	50 %

Electron Correlation: the Extreme Case



two interacting electrons

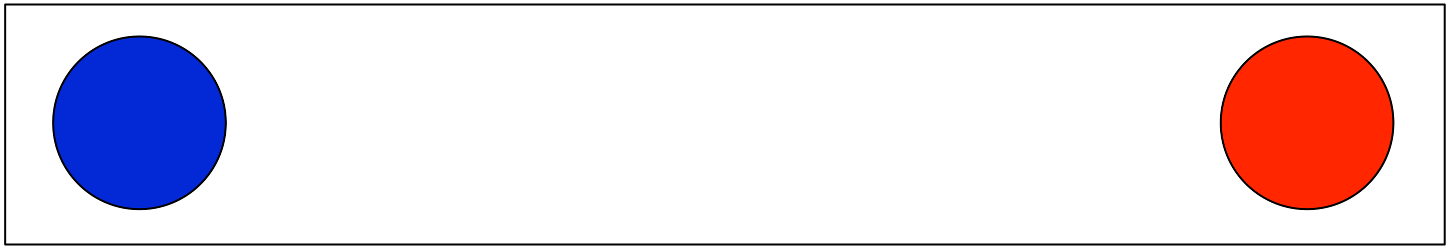
two possible sites 🔴 🔵

mean-field (HF) description

not favorable!

both electrons at 🔵	25 %
both electrons at 🔴	25 %
one electron at 🔴 and one at 🔵	50 %

Electron Correlation: the Extreme Case



two interacting electrons

two possible sites 🔴 🔵

avoids unfavorable combinations

correlated description

both electrons at 🔵	0 %
both electrons at 🔴	0 %
one electron at 🔴 and one at 🔵	100 %

Different Types of Electron Correlation

- **Fermi correlation (exchange)**

electrons of same spin avoid each other due to the antisymmetry requirement (→ Fermi hole)

already treated at HF level

independent of Coulomb interactions

- **Coulomb correlation**

electrons (independent of spin) avoid each other due to the repulsive Coulomb interactions (→ Coulomb hole)

not treated at HF level, requires post-HF methods

Electron-Correlation Energy

usual definition (Löwdin, 1955):

$$\Delta E_{corr} \;=\; E_{nrl} \;-\; E_{HF}$$

- **focus on Coulomb correlation**

- **Fermi correlation in E_{HF} already included**

- **HF for electron correlation reference point**

Different Types of Electron Correlation

- **dynamical correlation**

  electrons (independent of spin) avoid each other due to the repulsive Coulomb interactions (→ Coulomb hole)

- **static (non-dynamical) correlation**

  (quasi-)degeneracy of Slater determinants/configurations

$E(\Phi_1) \approx E(\Phi_2)$ → $\Psi \approx c_1\Phi_1 + c_2\Phi_2$

Single- and Multireference Methods

no static correlation

HF quality correct → good starting point for correlation treatment

one Slater determinants dominates

**applies for many/most molecules in and
close to their equilibrium configuration**

→ single-reference treatment

static correlation

multi-reference treatment required

II.

Importance of Electron Correlation

Magnitude of Correlation Energies

	H_2O	HCN
E_{HF}	-76.068	-92.916
ΔE_{corr}	-0.372	-0.518
ΔE_{rel}	-0.052	-0.044

correlation energies typically < 1% of the total energies

Chemical Relevance of Electron Correlation

0.001 Hartree $\hat{=}$ 2.6255 kJ/mol

correlation energies strongly dependent on valence electrons

correlation effects always important when bonds are broken

Chemical Relevance of Electron Correlation

example: $CO \rightarrow C(^3P) + O(^3P)$

dissocation energy (D_e) of CO

	C	O	CO	D_e in a.u.
E(HF)	-37.693774	-74.819232	-112.790997	.277991
E(corr)	-.151537	-.248978	-.536591	.136076
E(total)	-37.845307	-75.068210	-113.327588	.414071

Chemical Relevance of Electron Correlation

example: $CO \rightarrow C(^3P) + O(^3P)$

dissocation energy (D_e) **of CO**

	C	O	CO	D_e in kJ/mol
E(HF)	-37.693774	-74.819232	-112.790997	729.9
E(corr)	-.151537	-.248978	-.536591	357.3
E(total)	-37.845307	-75.068210	-113.327588	1087.2

electron-correlation effects are significant

III.

Perturbative Treatment of Electron Correlation:

Møller-Plesset Perturbation Theory

Hamilton Operator for Many-Electron Systems

non-relativistic Hamiltonian for atoms and molecules

$$\hat{H} \;=\; \sum_{\alpha} \hat{h}(\alpha) \;+\; \sum_{\alpha<\beta} \frac{1}{r_{\alpha\beta}}$$

one-electron terms

two-electron terms

prohibits exact solution
→ electron correlation

Møller-Plesset Perturbation Theory

electron correlation small effect

→ treatment via perturbation theory on top of HF

perturbation theory:

zeroth-order → HF theory $\Psi^{(0)} = \Psi_{HF}$

$$\hat{H}^{(0)} = \sum_{\alpha} \hat{F}(\alpha) \qquad E^{(0)} = \sum_{i} \varepsilon_i$$

Møller-Plesset ansatz

$$\begin{aligned} E_{HF} &= \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle \\ &= \langle \Psi_{HF} | \hat{H}^{(0)} + \hat{H}' | \Psi_{HF} \rangle \\ &= E^{(0)} + E^{(1)} \end{aligned}$$

electron correlation in second order

MP2 Perturbation Theory

second-order perturbation theory

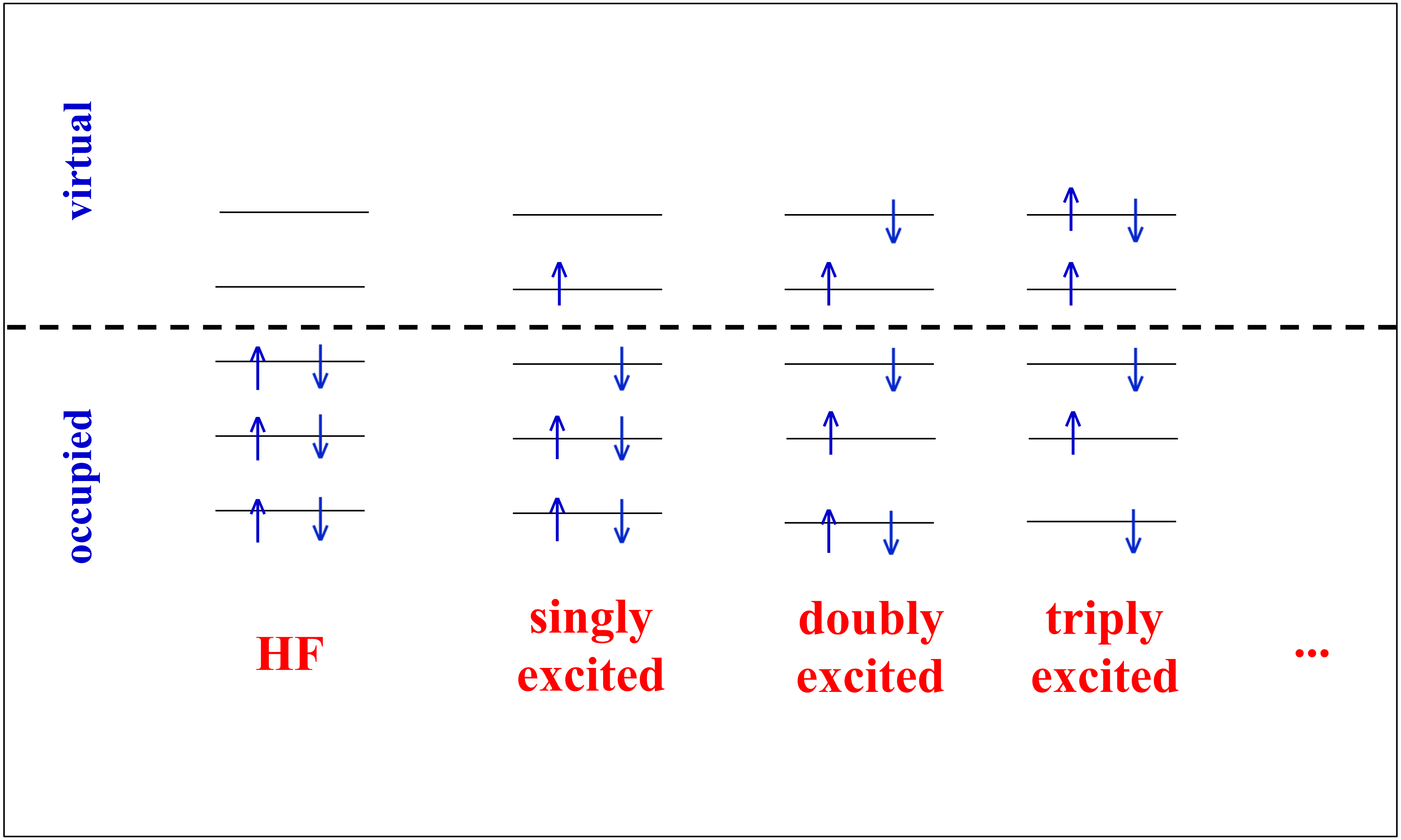
$$E^{(2)} = \sum_{I\neq 0} \frac{\langle\Phi_0^{(0)}|\hat{H}|\Phi_I^{(0)}\rangle\langle\Phi_I^{(0)}|\hat{H}|\Phi_0^{(0)}\rangle}{E_0^{(0)} - E_I^{(0)}}$$

HF wavefunction

other eigenfunctions to $H^{(0)}$

eigenfunctions to $H^{(0)}$: **all Slater determinants constructed from occupied and virtual canonical HF orbitals**

Excitation Level of Slater Determinants



virtual

occupied

HF

singly excited

doubly excited

triply excited

...

Slater-Condon Rules and Brillouin Theorem

Slater-Condon rules

rules for matrix elements involving two different Slater determinants

for H containing one- and two-electron operators

$$\langle \Phi_I | \hat{H} | \Phi_J \rangle \neq 0$$

only if Φ_I and Φ_J differ at most by a double excitation

Brillouin theorem

$$\langle \Phi_{HF} | \hat{H} | \Phi_i^a \rangle = 0$$

singly excited determinant

MP2 Perturbation Theory

second-order perturbation theory

$$E^{(2)} = \sum_{I \neq 0} \frac{\langle \Phi_0^{(0)} | \hat{H} | \Phi_I^{(0)} \rangle \langle \Phi_I^{(0)} | \hat{H} | \Phi_0^{(0)} \rangle}{E_0^{(0)} - E_I^{(0)}}$$

leads to

$$E_{MP2} = \sum_{i<j} \sum_{a<b} \frac{|\langle ab||ij \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

antisymmetrized two-electron integral

indices of occupied spin orbitals

indices of virtual spin orbitals

orbital energy denominator

Importance of Double Excitations

	increment	total
$\Delta E(MP2)$	-0.2040	-0.2040
$\Delta E(MP3)$	-0.0068	-0.2108
$\Delta E(MP4)$	-0.0052	-0.2160
ΔE_{corr}	-0.2170	-0.2170

H_2O, cc-pVDZ basis

MP2 recovers typically more than 95 % of electron correlation

MP3 involves only doubles, singles and triples only at MP4

IV.

Exact Solution of the Correlation Problem:

Full Configuration Interaction

Exact Solution of Electron-Correlation Problem

define effective (zeroth-order) Hamiltonian

$$\hat{H}_0 = \sum_{\alpha} \hat{F}(\alpha)$$

↘

solve one-electron problem
(e.g., HF equations)

$$\hat{F}\, \varphi_p = \epsilon_p\, \varphi_p$$

↓

„complete“ one-electron basis
(spin orbitals)

$$\{\varphi_p, p = 1, \ldots\}$$

within given AO basis

↙

Slater determinants
(take care of antisymmetry)

$$\Phi_I = \frac{1}{\sqrt{N!}} \left| \varphi_{I1}\, \varphi_{I2} \,\cdots\, \varphi_{IN} \right|$$

↓

$$\{\Phi_I, I = 1, \ldots\}$$

complete many-electron basis

Exact Solution of Electron-Correlation Problem

expansion in a complete set of Slater determinants

$$\Psi = \sum_I c_I \, \Phi_I = c_0 \, \Phi_{HF} + \sum_{I \neq 0} c_I \, \Phi_I$$

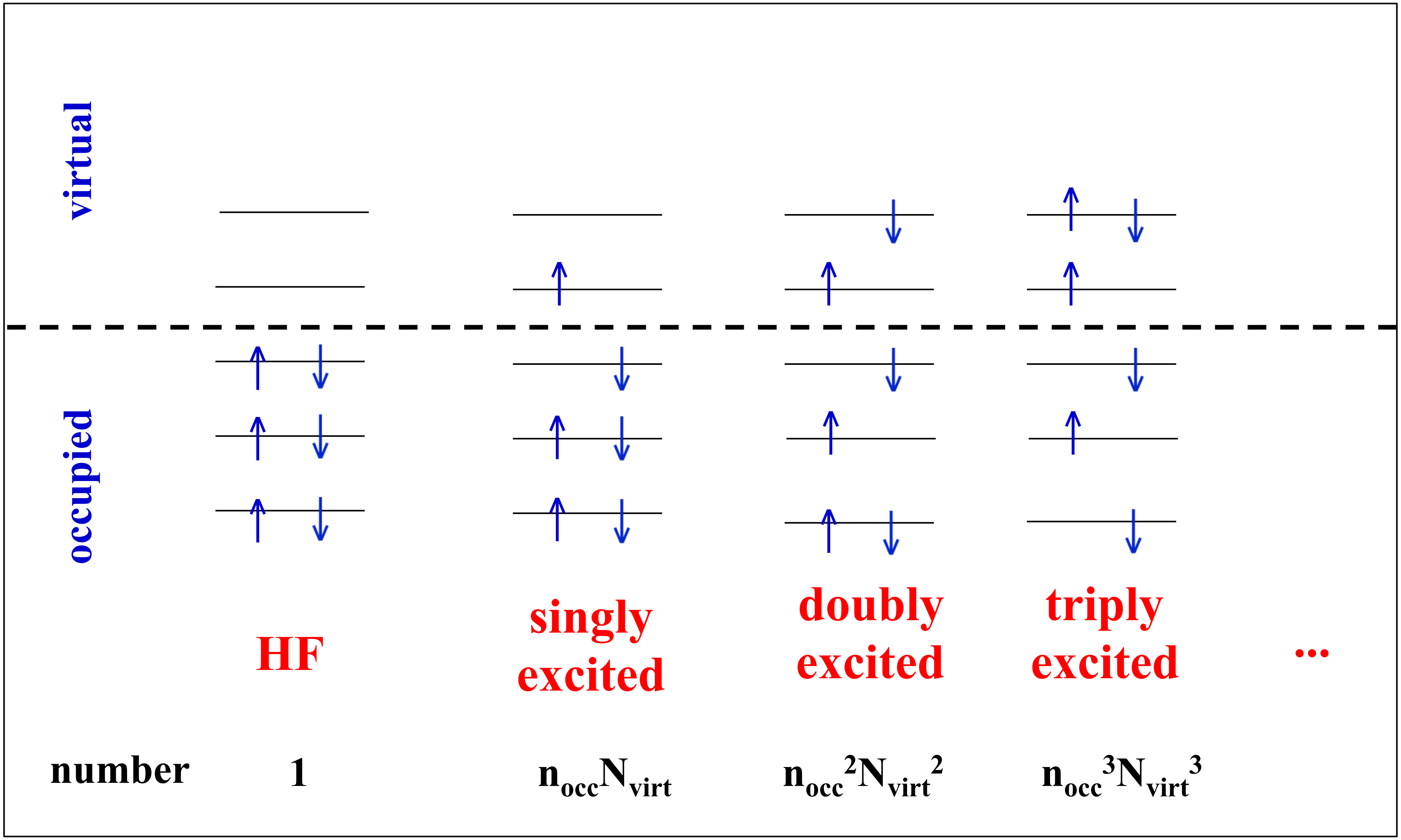
excited determinants

together with variational principle

$$\sum_J H_{IJ} \, c_J = E \, c_I \qquad H_{IJ} = \langle \Phi_I | \hat{H} | \Phi_J \rangle$$

⇒ Full Configuration Interaction (FCI)

Excitation Level of Slater Determinants



	HF	singly excited	doubly excited	triply excited	...
number	1	$n_{occ}N_{virt}$	$n_{occ}^2N_{virt}^2$	$n_{occ}^3N_{virt}^3$	

Full CI Approach

Full CI:

- factorial growth of cost
- not practial, only for benchmarking

small molecules and basis (e.g., H_2O, DZP)

benzene, DZP: ≈ 10^{42} determinants

typical examples:

	E(FCI), in a.u.
BH, TZP+	-25.243140
H_2O, cc-pVDZ	-76.243773
CO, cc-pVDZ	-113.055853

V.

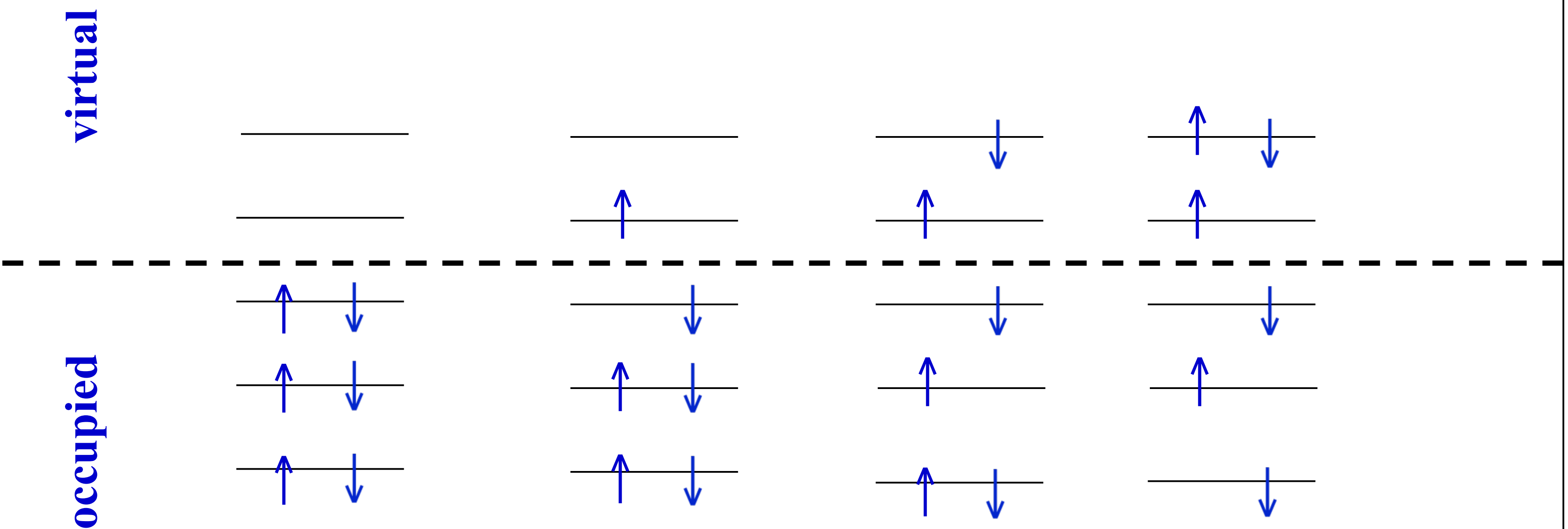
Truncated Configuration-Interaction Schemes

Full and Truncated CI Methods

Full CI:
- factorial growth of cost
- not practial, only for benchmarking

=> truncate determinantal basis (approximation)

Excited Slater Determinants



	HF	singly excited	doubly excited	triply excited	…
number	1	$n_{occ}N_{virt}$	$n_{occ}^2N_{virt}^2$	$n_{occ}^3N_{virt}^3$	

Truncated CI Methods

truncate determinantal basis (approximation)

chose determinants according to excitation level

double excitations are most important

=> truncated CI methods such as CISD

$$\Psi_{CISD} \quad = \quad c_0 \; \Phi_0 \; + \sum_{I \in S,D} \; c_I \; \Phi_I$$

excited determinants restricted to single + double excitations

Solution of the CI Problem

CI problem:

$$\mathbf{H}\,\mathbf{c} = E\,\mathbf{c}$$

eigenvalue problem for matrix H

no direct diagonalization of H (too expensive)

Davidson scheme:

- **diagonalize H in a (small) iterative subspace**
- **expand subspace until convergence**
- **computational cost due to product** $\mathbf{H}\cdot\mathbf{c}$

Convergence to FCI

example: H_2O, cc-pVDZ

CI method	Energy [a.u.]
CISD	-76.231972
CISDT	-76.234926
CISDTQ	-76.243457
CI(5)	-76.243640
CI(6)	-76.243770
CI(7)	-76.243772
CI(8)	-76.243773
CI(9)	-76.243773
FCI	-76.243773

Computational Cost

approximation	cost
CISD	N^6
CISDT	N^8
CISDTQ	N^{10}
CI(5)	N^{12}
…	…
FCI	

VI.

Size Consistency and Size Extensivity

Separability for Non-Interacting Systems

non-interacting systems A and B

$$r_{AB} \rightarrow \infty$$

$$\boxed{E_{AB} = E_A + E_B}$$

- additivity of energy
- multiplicative separability of wavefunction

Size Consistency

$$r_{AB} \to \infty$$

A method is termed size consistent if the sum of energies computed for two non-interacting subsystems A and B is equal to the energy obtained for the supersystem consisting of both A and B

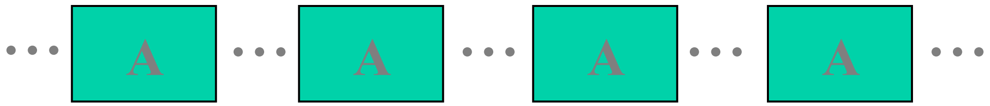
Pople, Binkley, Seeger (1976)

a) individual quantum-chemical calculations for A and B → $E_A + E_B$

b) one quantum-chemical calculation for A+B → E_{AB}

size consistency: $E_{AB} = E_A + E_B$

Size Extensivity



=> $$E = n \cdot E_A$$

A size-extensive method provides results that scale linearly with the size of the system

Bartlett, Purvis (1978)

- **formal definition**, independent of non-interacting reference systems
- exploits full power in the context of **diagrammatic techniques**
- **size extensivity implies size consistency**, the reverse is not true
- ensures quality of results **independent of size of systems**

Size-Consistency Problem of Truncated CI

CISD approximation:

$HF \cdots HF$

	$2 \times E_{HF}$	$E_{HF\cdots HF}$	Δ
HF-SCF	-200.558	-200.558	0.000
CISD	-200.576	-200.559	-0.017 ≈11 kcal/mol

calculations with tzp basis set

truncated CI methods are not size consistent

Empirical Size-Consistency Corrections

Davidson correction:

$$\Delta E_{Davidson} = \Delta E_{corr} \, (1 - c_0^2)$$

to be added to the CISD energy, approximately size consistent

Coupled-Pair Functional Methods:

restore approximate size consistency
by modifying the denominator in the energy expression to be minimized

CPF, ACPF, AQCC, ...   due to Ahlrichs, Gdanitz, Szalay, Bartlett, ...

VII.

Exponential Ansatz for Wavefunction

Multiplicative Separability of the Wavefunction

non-interacting systems A and B

$$\hat{H}_{AB} \quad = \quad \hat{H}_A \quad + \quad \hat{H}_B$$

=> separation ansatz

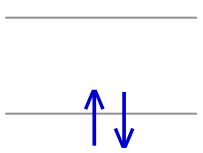
$$E_{AB} \quad = \quad E_A \quad + \quad E_B$$ **additive**

$$\Psi_{AB} \quad = \quad \underset{\nearrow}{\hat{\mathcal{A}}} \;\; \Psi_A \;\; \Psi_B$$ **multiplicative**

antisymmetrizer

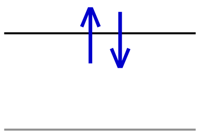
Multiplicative Separability of the Wavefunction

H_2 molecule, minimal basis



$$\Phi_{HF}$$

HF determinant



$$\Phi_D$$

double excitation

$$\Psi_{CID} = \Phi_{HF} + c\,\Phi_D$$

(not normalized)

$$= (1 + \hat{\tau}_D)\,\Phi_{HF}$$

operator, generates a by *c* weighted double excitations

H_2: CID = FCI = exact solution

Multiplicative Separability of the Wavefunction

two H_2 molecules, minimal basis

H_2(A) + H_2(B)

CID wavefunction

$$\Psi_{CID} = (1 + \hat{\tau}_{D,A} + \hat{\tau}_{D,B})\, \Phi_{HF}$$

but

$$\begin{aligned}
\hat{\mathcal{A}}\, \Psi_{CID,A}\, \Psi_{CID,B} &= \hat{\mathcal{A}}\, \{(1 + \hat{\tau}_{D,A})\, \Phi_{HF,A}\}\, \{(1 + \hat{\tau}_{D,B})\, \Phi_{HF,B}\} \\
&= \hat{\mathcal{A}}\, (1 + \hat{\tau}_{D,A})\, (1 + \hat{\tau}_{D,B})\, \Phi_{HF,A}\, \Phi_{HF,B} \\
&= (1 + \hat{\tau}_{D,A})\, (1 + \hat{\tau}_{D,B})\, \Phi_{HF} \\
&= (1 + \hat{\tau}_{D,A} + \hat{\tau}_{D,B} + \hat{\tau}_{D,A}\, \hat{\tau}_{D,B})\, \Phi_{HF}
\end{aligned}$$

quadruple excitation, missing in CID => problem

Multiplicative Separability of the Wavefunction

problem of CI:

excitations are additive

$$\sum_{i=A,B,\ldots} \hat{\tau}_{D,i}$$

contradiction !?!

required is a product

$$\prod_{i=A,B,\ldots} \cdots$$

Multiplicative Separability of the Wavefunction

one, two, three, ... H_2 molecules

$$\Psi_1 = (1 + \hat{\tau}_{D,A})\,\Phi_{HF}$$

$$\Psi_2 = (1 + \hat{\tau}_{D,A})\,(1 + \hat{\tau}_{D,B})\,\Phi_{HF}$$

$$\Psi_3 = (1 + \hat{\tau}_{D,A})\,(1 + \hat{\tau}_{D,B})\,(1 + \hat{\tau}_{D,C})\,\Phi_{HF}$$

$$\cdots$$

$$\Psi = \prod_{i=A,B,\ldots} (1 + \hat{\tau}_{D,i})\,\Phi_{HF}$$

Exponential Form for the Wavefunction

proper form of wavefunction

$$\Psi = \prod_{i=A,B,\ldots} (1 + \hat{\tau}_{D,i})\, \Phi_{HF}$$

rewrite in exponential form

$$\prod_{i=A,B,\ldots} (1 + \hat{\tau}_{D,i})\, \Phi_{HF} \equiv \exp\Big(\sum_{i=A,B,\ldots} \hat{\tau}_{D,i}\Big)\, \Phi_{HF}$$

multiplicative separability via additivity in exponent

Exponential of Operators

definition via a power series

$$\exp(\hat{A}) \;=\; 1 \;+\; \hat{A} \;+\; \frac{1}{2!}\hat{A}^2 \;+\; \frac{1}{3!}\hat{A}^3 \;+\; \ldots \;+\; \frac{1}{n!}\hat{A}^n \;+\; \ldots$$

exponential of a number → **non-terminating power series**

exponential of an operator → **power series can terminate**

depending on operator

Exponential Form for the Wavefunction

$$\prod_{i=A,B,\ldots} (1 + \hat{\tau}_{D,i})\ \Phi_{HF} \equiv \exp(\sum_{i=A,B,\ldots} \hat{\tau}_{D,i})\ \Phi_{HF}$$

proper counting

$$\frac{1}{2}\left(\sum_i \hat{\tau}_{D,i}\right)^2 \Rightarrow \frac{1}{2}\,\hat{\tau}_{D,A}\,\hat{\tau}_{D,B} + \frac{1}{2}\,\hat{\tau}_{D,B}\,\hat{\tau}_{D,A} + \ldots$$

$$\Rightarrow \hat{\tau}_{D,A}\,\hat{\tau}_{D,B} + \ldots$$

same excitation cannot be applied twice

$$\hat{\tau}_{D,A}\,\hat{\tau}_{D,A} = 0$$

Exponential Form for the Wavefunction

exponential ansatz

$$\Psi \quad = \quad \exp(\hat{T})\ \Psi_0$$

excitations
represented via an operator

reference determinant

proper multiplicative behaviour => size extensivity

Historical Remarks

- statistical physics
  - power expansion of partition function for interacting gases

Ursell (1927), Mayer (1941)

- nuclear physics
  - first use of exponential ansatz in quantum-mechanical context
  - quantum-mechanical description of nuclear matter

F. Coester, H. Kümmel (1958, 1960)

- electronic-structure theory
  - application to the electron-correlation problem

=> coupled-cluster theory J. Čížek (1966)

  - see also earlier work by Hubbard (1957) and Sinanoğlu (1962)

Connected and Disconnected Excitations

$$\Psi \;=\; \prod_{i=A,B,\ldots} (1 \;+\; \hat{\tau}_{D,i})\; \Phi_{HF}$$

$$\Psi \;=\; \Phi_{HF} \;+\; \hat{\tau}_{D,A}\, \Phi_{HF} \;+\; \ldots \;+\; \hat{\tau}_{D,A}\hat{\tau}_{D,B}\, \Phi_{HF} \;+\; \ldots$$

connected excitations

disconnected excitations

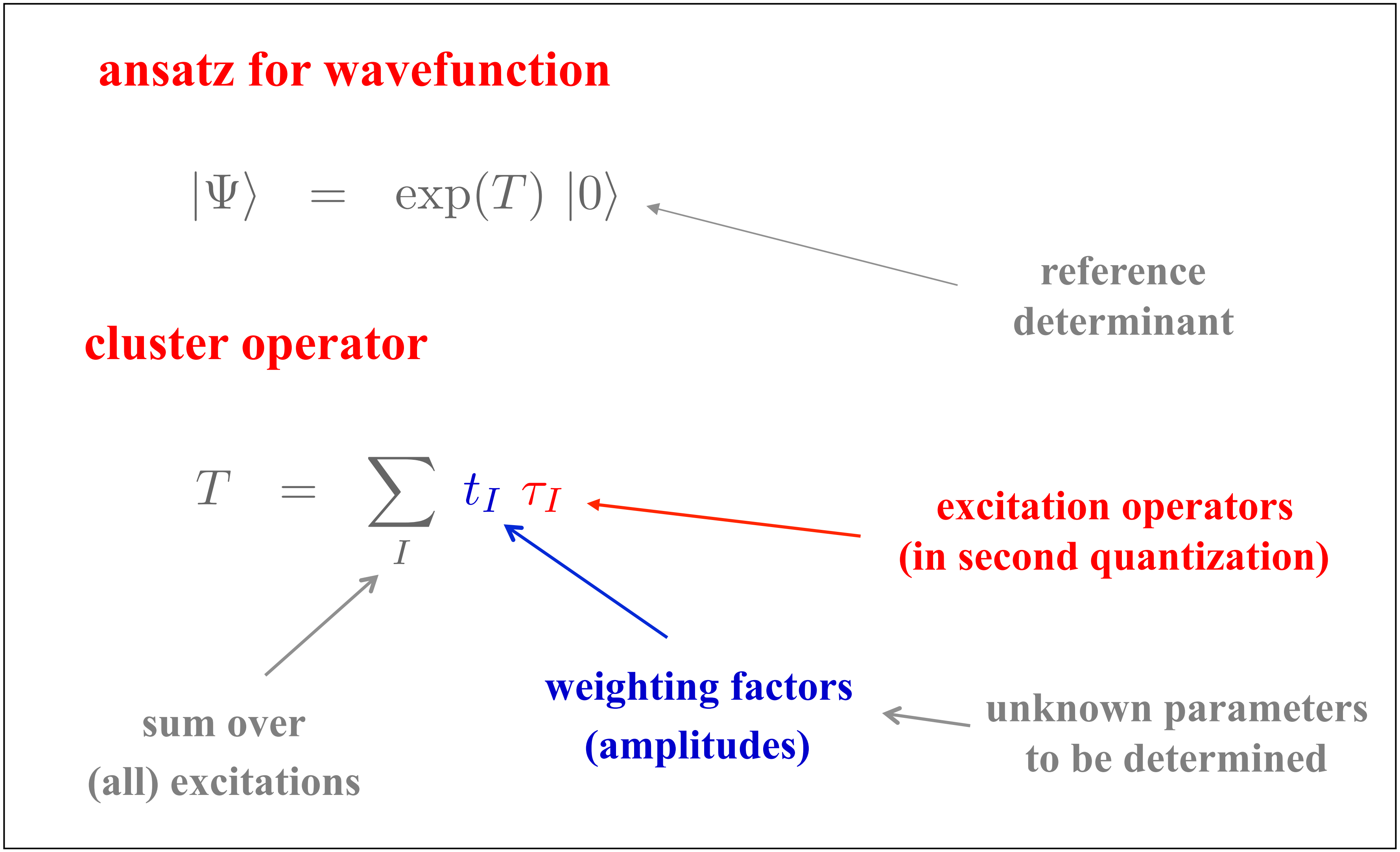
(products of connected excitations)

CI does not differ between connected and disconnected excitations

VIII.

Coupled-Cluster Theory

Coupled-Cluster Ansatz for Wavefunction



ansatz for wavefunction

$$|\Psi\rangle \quad = \quad \exp(T)\ |0\rangle$$

reference determinant

cluster operator

$$T \quad = \quad \sum_I t_I \ \tau_I$$

excitation operators (in second quantization)

sum over (all) excitations

weighting factors (amplitudes)

unknown parameters to be determined

Cluster Operator

classification of excitation $$T = T_1 + T_2 + T_3 + \ldots$$

$$T_1 = \sum_a \sum_i t_i^a \; a_a^\dagger a_i$$

single excitations

$$T_2 = \frac{1}{4} \sum_{a,b} \sum_{i,j} t_{ij}^{ab} \; a_a^\dagger a_i a_b^\dagger a_j$$

double excitations

$$\ldots$$

all possible excitations $$T = T_1 + T_2 + T_3 + \ldots + T_N$$

truncated schemes, e.g. $$T = T_1 + T_2$$

Equivalence of CC and FCI parameterization

CC wavefunction		**CI wavefunction**
$\vert\Psi\rangle \;=\; \exp(T)\;\vert 0\rangle$		$\vert\Psi\rangle \;=\; C\;\vert 0\rangle$
$T_1\;\vert 0\rangle$	**singly excited**	$C_1\;\vert 0\rangle$
$(T_2 + \frac{1}{2!}T_1^2)\;\vert 0\rangle$	**doubly excited**	$C_2\;\vert 0\rangle$
$(T_3 + T_2T_1 + \frac{1}{3!}T_1^3)\;\vert 0\rangle$	**triply excited**	$C_3\;\vert 0\rangle$
$(T_4 + T_3T_1 + \frac{1}{2!}T_2^2$	**quadruply excited**	$C_4\;\vert 0\rangle$
$+ \frac{1}{2!}T_1^2T_2 + \frac{1}{4!}T_1^4)\;\vert 0\rangle$	$\ldots$	

matching number of parameters

=> CC ansatz parameterizes the exact wavefunction

Truncated Coupled-Cluster Wavefunctions

$$T = T_2$$

truncation in the cluster operator

CCD = CC doubles

$$|\Psi_{CCD}\rangle = |0\rangle + T_2\,|0\rangle + \frac{1}{2!}T_2^2\,|0\rangle + \frac{1}{3!}T_2^3\,|0\rangle + \ldots$$

connected
double excitations

disconnected
quadruple, sextuple, ... excitations

Coupled-Cluster Ansatz

- **ansatz for many-electron wavefunction**
  - able to parameterize **exact solution**
  - multiplicatively separable → **size consistency and extensivity**
  - unknown parameters: **amplitudes** in cluster operator
- **determination of actual CC wavefunction**
  - determine **amplitudes** in cluster operator
  - solve **Schrödinger equation** with CC ansatz

what is a suitable procedure and what to do in the case of approximations?

Variational Coupled-Cluster Theory

determination of amplitudes via variation principle

minimization of

$$\tilde{E} = \frac{\langle 0|\exp(T^\dagger)H\exp(T)|0\rangle}{\langle 0|\exp(T^\dagger)\exp(T)|0\rangle}$$

CC wavefunction
not normalized

adjoint of CC wavefunction

non-truncating operator

$$\exp(T^\dagger)H\exp(T) = H + T^\dagger H + HT + \frac{1}{2!}{T^\dagger}^2 H + T^\dagger HT + \frac{1}{2!}HT^2 + \ldots$$

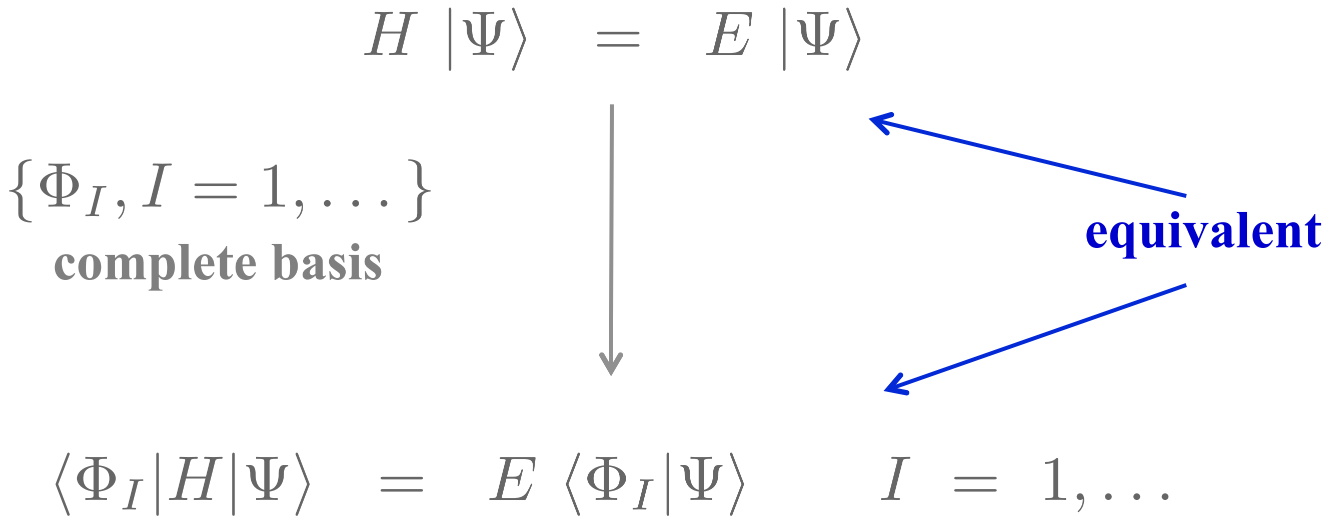
cost independent of choice of *T* always similar to FCI

=> not feasible for practical schemes

see work by Van Voorhis, Head-Gordon (2000),
recent work on quasi-variational CC by Knowles and co-workers (2010),
and work on XCC by Bartlett and Noga (1988)

Algebraic Equations via Projection

transform an operator equation into a set of algebraic equations



$$H\,|\Psi\rangle \quad = \quad E\,|\Psi\rangle$$

$$\{\Phi_I, I = 1, \ldots\}$$

complete basis

equivalent

$$\langle\Phi_I|H|\Psi\rangle \quad = \quad E\,\langle\Phi_I|\Psi\rangle \qquad I \;=\; 1, \ldots$$

matching number of equations and wavefunction parameters (amplitudes)

Coupled-Cluster Theory

- **insertion into Schrödinger equation**

$$H \;\exp(T)\;|0\rangle \;=\; E\;\exp(T)\;|0\rangle$$

- **multiplication from the left with exp(-*T*)**

$$\exp(-T)\;H\;\exp(T)\;|0\rangle \;=\; E\;|0\rangle$$

- **projection onto reference determinant**

→ **CC energy** $$E \;=\; \langle 0|\;\exp(-T)\;H\;\exp(T)\;|0\rangle$$

- **projection onto excited determinants**

→ **CC equations** $$0 \;=\; \langle \Phi_P|\;\exp(-T)\;H\;\exp(T)\;|0\rangle$$

non-linear equations for amplitudes

Standard CC Theory

- untruncated CC approaches

  matching number of equations and parameters (amplitudes)
  - projection on all excited determinants
  - same number of excitations as in many-electron basis

- truncated CC approaches
  - projection on all excited determinants → unsolvable problem
  - project only on those determinants for which excitations are in *T*

$\mathbf{T} = \mathbf{T_2}$ → project onto $\boldsymbol{\Phi}_{\mathbf{D}}$

$\mathbf{T} = \mathbf{T_1} + \mathbf{T_2}$ → project onto $\boldsymbol{\Phi}_{\mathbf{S}}, \boldsymbol{\Phi}_{\mathbf{D}}$

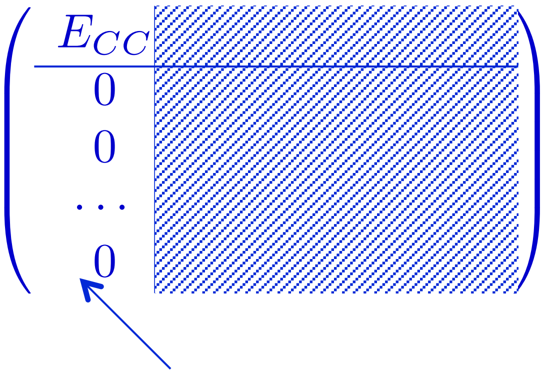
Schrödinger equation can no longer be solved in an exact manner

Incomplete Projection

solving CC equations $0 \;=\; \langle\Phi_P|\;\exp(-T)\;H\;\exp(T)\;|0\rangle$

analysis of matrix $\bar{H}_{PQ} = \langle\Phi_P|\;\exp(-T)\;H\;\exp(T)\;|\Phi_Q\rangle$

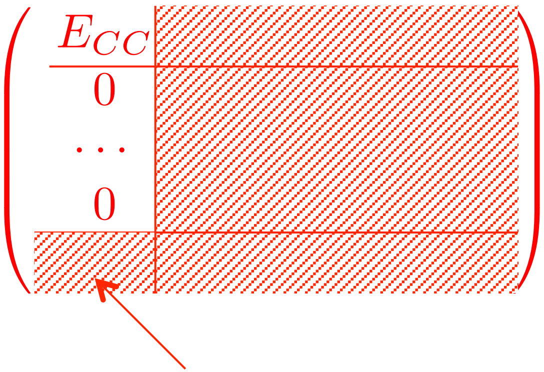
full CC



all entries zero

=> equivalent to FCI

truncated CC



block not zero !!

=> approximate solution

Coupled-Cluster Equations

$$E = \langle 0| \; \exp(-T) \; H \; \exp(T) \; |0\rangle$$

$$0 = \langle \Phi_P| \; \exp(-T) \; H \; \exp(T) \; |0\rangle \qquad P = 1, \ldots$$

How do we continue from here?

Coupled-Cluster Equations

„Simplifications“

Baker-Campbell-Hausdorff expansion

$$\exp(-T)\ H\ \exp(T) \ = \ H \ + \ [H,T] \ + \ \frac{1}{2!}[[H,T],T] \ + \ \ldots$$

expansion in terms of commutators

Normal Ordering

in the **normal-ordered product form** of an operator, N(A), all annihilation operators are to the **right** of the creation operators

$$N(\hat{a}_p\hat{a}_q^\dagger\hat{a}_r) \quad = \quad -\hat{a}_q^\dagger\hat{a}_p\hat{a}_r$$

sign: $(-1)^p$ with p as number of required transpositions to reach normal ordering

advantage of normal ordering

$$\langle \mathrm{VAC}|N(\ldots\hat{a}_p^\dagger\hat{a}_q\ldots)|\mathrm{VAC}\rangle \quad = \quad 0$$

except *N(…)* = number

expectation values of normal-ordered operators are simple **to evaluate!**

Normal Ordering via Commutators

$$
\begin{aligned}
\hat{a}_p\hat{a}_q\hat{a}_r^\dagger\hat{a}_s^\dagger &= \hat{a}_p[\hat{a}_q,\hat{a}_r^\dagger]_+\hat{a}_s^\dagger \; - \; \hat{a}_p\hat{a}_r^\dagger\hat{a}_q\hat{a}_s^\dagger \\
&= \delta_{qr}[\hat{a}_p,\hat{a}_s^\dagger]_+ \; - \; \delta_{qr}\hat{a}_s^\dagger\hat{a}_p \; + \; [\hat{a}_p,\hat{a}_r^\dagger]_+\hat{a}_q\hat{a}_s^\dagger \; + \; \hat{a}_r^\dagger\hat{a}_p\hat{a}_q\hat{a}_s^\dagger \\
& \qquad \cdots \\
&= \delta_{qr}\delta_{ps} \; - \; \delta_{pr}\delta_{qs} \; - \; \delta_{qr}\hat{a}_s^\dagger\hat{a}_p \; + \; \delta_{pr}\hat{a}_s^\dagger\hat{a}_q \; + \\
& \qquad \delta_{qs}\hat{a}_r^\dagger\hat{a}_p \; - \delta_{ps}\hat{a}_r^\dagger\hat{a}_q \; + \; \hat{a}_r^\dagger\hat{a}_s^\dagger\hat{a}_p\hat{a}_q
\end{aligned}
$$

Contractions

contraction of a pair of operators

general definition

$$\wick{\c{\hat{b}}\,\c{\hat{c}}} = \hat{b}\,\hat{c} - N(\hat{b}\hat{c})$$

specific cases

$$\wick{\c{\hat{a}}_p\,\c{\hat{a}}_q} = 0 \qquad \wick{\c{\hat{a}}_p^\dagger\,\c{\hat{a}}_q^\dagger} = 0 \qquad \wick{\c{\hat{a}}_p^\dagger\,\c{\hat{a}}_q} = 0$$

$$\begin{aligned} \wick{\c{\hat{a}}_p\,\c{\hat{a}}_q^{+}} &= \hat{a}_p\,\hat{a}_q^\dagger - N(\hat{a}_p\hat{a}_q^\dagger) \\ &= \delta_{pq} \end{aligned}$$

$\neq 0$ only, if operators are **not** in normal order

Wick's Theorem

an arbitrary product of creation and annihilation operators

$$\hat{X} \quad = \quad \ldots \hat{a}_p^\dagger \hat{a}_q \hat{a}_r^\dagger \hat{a}_s \ldots$$

is equal to the normal-ordered product, *N(X)*, plus all normal-ordered products of *X* that contain one, two, three, … contractions of two operators

$$\hat{X} = N(\hat{X}) + \sum N(\overset{\sqcap}{\hat{X}}) + \sum N(\overset{\sqcap}{\overset{\sqcap}{\hat{X}}}) + \ldots$$

Wick's Theorem: Example

$$
\begin{aligned}
\hat{a}_p\hat{a}_q\hat{a}_r^\dagger\hat{a}_s^\dagger &= N(\hat{a}_p\hat{a}_q\hat{a}_r^\dagger\hat{a}_s^\dagger) && = \hat{a}_r^\dagger\hat{a}_s^\dagger\hat{a}_p\hat{a}_q \\
&+N(\wick{\c1{\hat{a}}_p \c1{\hat{a}}_q}\hat{a}_r^\dagger\hat{a}_s^\dagger) && +\ 0 \\
&+N(\wick{\c1{\hat{a}}_p\hat{a}_q \c1{\hat{a}}_r^\dagger}\hat{a}_s^\dagger) && +\ \delta_{pr}\hat{a}_s^\dagger\hat{a}_q \\
&+N(\wick{\c1{\hat{a}}_p\hat{a}_q\hat{a}_r^\dagger \c1{\hat{a}}_s^\dagger}) && -\ \delta_{ps}\hat{a}_r^\dagger\hat{a}_q \\
&+N(\wick{\hat{a}_p \c1{\hat{a}}_q \c1{\hat{a}}_r^\dagger}\hat{a}_s^\dagger) && -\ \delta_{qr}\hat{a}_s^\dagger\hat{a}_p \\
&+N(\wick{\hat{a}_p \c1{\hat{a}}_q\hat{a}_r^\dagger \c1{\hat{a}}_s^\dagger}) && +\ \delta_{qs}\hat{a}_r^\dagger\hat{a}_p \\
&+N(\wick{\hat{a}_p\hat{a}_q \c1{\hat{a}}_r^\dagger \c1{\hat{a}}_s^\dagger}) && +\ 0 \\
&+N(\wick{\c1{\hat{a}}_p \c1{\hat{a}}_q \c2{\hat{a}}_r^\dagger \c2{\hat{a}}_s^\dagger}) && +\ 0 \\
&+N(\wick{\c1{\hat{a}}_p \c2{\hat{a}}_q \c2{\hat{a}}_r^\dagger \c1{\hat{a}}_s^\dagger}) && +\delta_{ps}\delta_{qr} \\
&+N(\wick{\c1{\hat{a}}_p \c2{\hat{a}}_q \c1{\hat{a}}_r^\dagger \c2{\hat{a}}_s^\dagger}) && -\delta_{qs}\delta_{pr}
\end{aligned}
$$

Quasi-Particle Formalism

$|\mathrm{VAC}\rangle$

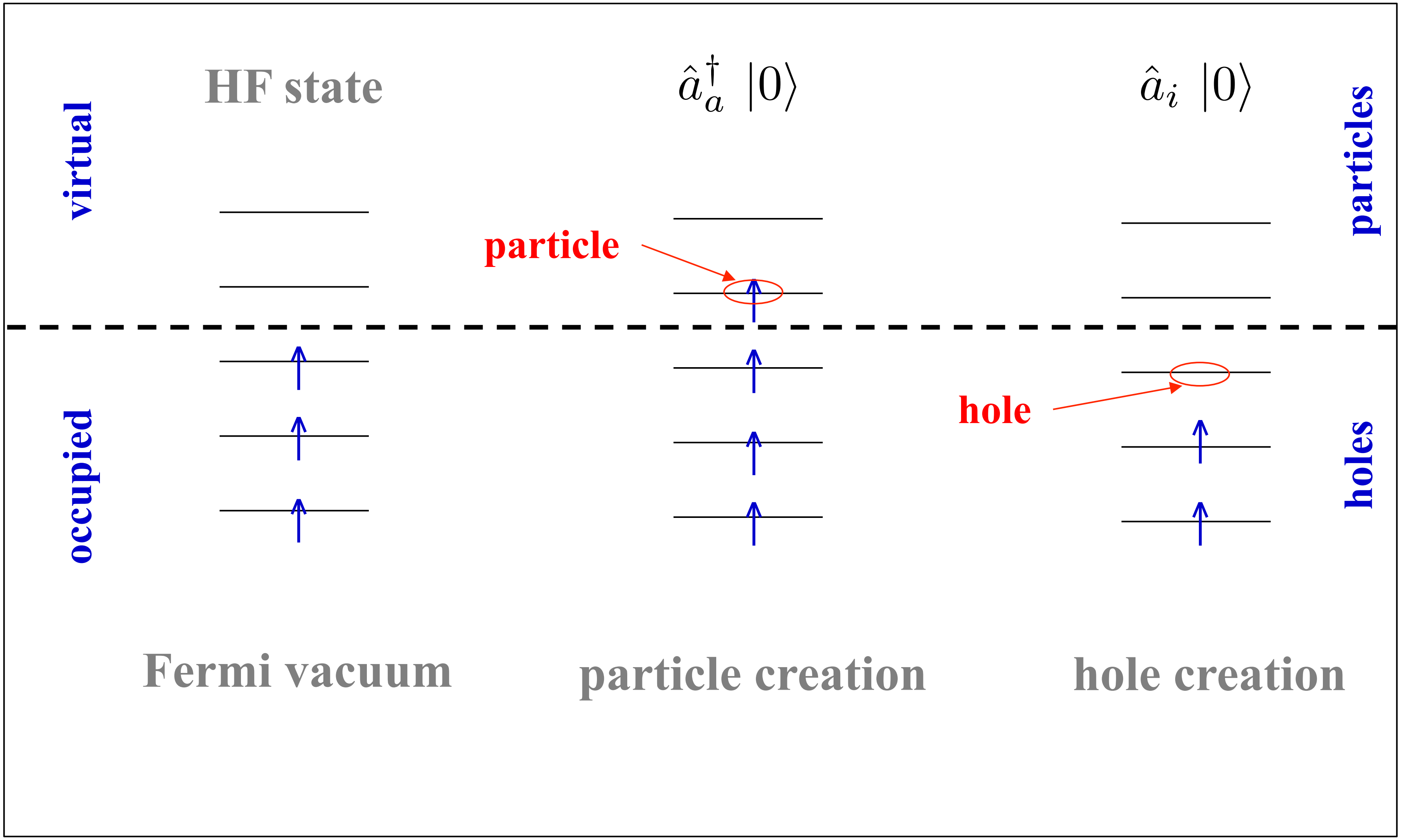
as reference for
N-electron systems
not useful

$|HF\rangle \quad \equiv \quad |0\rangle$

useful for N-electron systems,
as only **changes wrt**
HF reference are considered

=> particle-hole formalism

Quasi-Particle Formalism



Quasi-Particle Formalism

new definition of creation and annihilation operators

$$\hat{b}_i^\dagger := \hat{a}_i \qquad \hat{b}_i := \hat{a}_i^\dagger$$

hole creation and annihilation

$$\hat{b}_a^\dagger := \hat{a}_a^\dagger \qquad \hat{b}_a := \hat{a}_a$$

particle creation and annihilation

unchanged anti-commutator relations

usual convention:

indices *i,j,k*, … occupied; *a,b,c*, … virtual; *p,q,r*, … generic

Hamilton Operator in Normal-Ordered Form

$$H = E_{HF} + \sum_{p,q} f_{pq}\{p^\dagger q\} + \frac{1}{4}\sum_{p,q,r,s} \langle pq||rs\rangle\{p^\dagger q^\dagger s r\}$$

$$\sum_{i,j} h_{ij}\{\contraction{}{i^\dagger}{}{j} i^\dagger j\} \longrightarrow \sum_{i} h_{ii}$$

$$\frac{1}{4}\sum_{i,j,k,l} \langle ij||kl\rangle\{\contraction[2ex]{}{i^\dagger}{j^\dagger}{l}\contraction{i^\dagger}{j^\dagger}{l}{k} i^\dagger j^\dagger l k\} \searrow$$

$$\frac{1}{2}\sum_{i,j} \langle ij||ij\rangle$$

$$\frac{1}{4}\sum_{i,j,k,l} \langle ij||kl\rangle\{\contraction[2ex]{}{i^\dagger}{j^\dagger l}{k}\contraction{i^\dagger}{j^\dagger}{}{l} i^\dagger j^\dagger l\, k\} \nearrow$$

$$4 \times \frac{1}{4}\sum_{p,q} \langle pi||qj\rangle\{p^\dagger\, \contraction{}{i^\dagger}{q}{j} i^\dagger q j\}$$

$$\longrightarrow \sum_{p,q} \langle pi||qi\rangle\ \{p^\dagger q\}$$

Fock matrix

$$f_{pq} = h_{pq} + \sum_{i} \langle pi||qi\rangle$$

Hamilton Operator in Normal-Ordered Form

$$
\begin{aligned}
H \;=\; & E_{HF} \\
& + \sum_{i,j} f_{ij}\{i^\dagger j\} + \sum_{i,a} f_{ia}\{i^\dagger a\} \\
& + \sum_{a,i} f_{ai}\{a^\dagger i\} + \sum_{a,b} f_{ab}\{a^\dagger b\} \\
& + \frac{1}{4}\sum_{i,j,k,l}\langle ij||kl\rangle\{i^\dagger j^\dagger lk\} + \frac{1}{2}\sum_{i,j,k,a}\langle ij||ka\rangle\{i^\dagger j^\dagger ak\} \\
& + \frac{1}{2}\sum_{i,j,k,a}\langle ia||jk\rangle\{i^\dagger a^\dagger kj\} + \frac{1}{4}\sum_{i,j,a,b}\langle ij||ab\rangle\{i^\dagger j^\dagger ba\} \\
& + \frac{1}{4}\sum_{i,j,a,b}\langle ab||ij\rangle\{a^\dagger b^\dagger ji\} + \sum_{i,j,a,b}\langle ai||bj\rangle\{a^\dagger i^\dagger jb\} \\
& + \frac{1}{2}\sum_{i,a,b,c}\langle ai||bc\rangle\{a^\dagger i^\dagger cb\} + \frac{1}{2}\sum_{i,a,b,c}\langle ab||ci\rangle\{a^\dagger b^\dagger ic\} \\
& + \frac{1}{4}\sum_{a,b,c,d}\langle ab||cd\rangle\{a^\dagger b^\dagger dc\}
\end{aligned}
$$

Hamilton Operator in Normal-Ordered Form

$$H = E_{HF} + f_N + W_N$$

HF energy

one-body operator

two-body operator

$$\begin{aligned} H_N &= H - \langle 0|H|0\rangle \\ &= f_N + W_N \end{aligned}$$

Coupled-Cluster Equations

„Simplifications“

- **normal-ordered representation of commutators**

$$\begin{aligned}[A,B] &= AB - BA \\ &= \underbrace{\{AB\} - \{BA\}}_{=\ 0} + \{\overbracket{AB}\} - \{\overbracket{BA}\}\end{aligned}$$

Coupled-Cluster Equations

„Simplifications“

- ***T*** **only consists of quasi-particle creation operators**

$$\{\overbracket{T H}\} \; = \; 0, \qquad \textbf{etc.}$$

$$\longrightarrow \qquad [H,T] \; = \; \underbrace{\{\overbracket{H T}\} \; + \; \{\overbracket{\overbracket{H T}}\} \; + \; \ldots}_{\equiv \; (H \; T)_c}$$

$$\exp(-T) \; H \exp(T) \; = \; \underbrace{H \; + \; (H \; T)_c \; + \; \frac{1}{2!}((H \; T)_c \; T)_c \; + \; \ldots}_{\equiv \; (H \; \exp(T))_c}$$

CCD Equations

$$E = \langle 0 | \; (H \;\; \exp(T))_c \; | 0 \rangle$$

$$0 = \langle \Phi_P | \; (H \;\; \exp(T))_c \; | 0 \rangle$$

with

$$H = E_{HF} + f_N + W_N \qquad\qquad T = T_2$$

normal-ordered Hamiltonian **only double excitations**

and projection on doubly excited determinants $\boldsymbol{\Phi_{\mathrm{D}} \equiv \Phi_{\mathrm{ij}}^{\mathrm{ab}}}$

Excitation Rank

count excitation levels

- **projection on Φ_P defines overall excitation levels**
- **T_n corresponds to an n-tuple excitation**
- **f_N corresponds to excitation by -1, 0 , 1**
- **W_N corresponds to excitation by -2, -1, 0 , 1, 2**

example

$$W_N T_2 T_2$$

→ **corresponds to 2+2+(-2,-1,0,1,2) → (2,3,4,5,6) excitations**

no contribution to projection on Φ_S, but for those on Φ_D, Φ_T, ...

CCD Approximation

$$H \; = \; E_{HF} \; + \; f_N \; + \; W_N \qquad\qquad T \; = \; T_2$$

CCD energy

$$E \; = \; \langle 0| \; (H \;\; \exp(T))_c \; |0\rangle$$

=> $$E \; = \; \langle 0| \; H \; + \; (HT_2)_c \; + \; \frac{1}{2!}((HT_2)_c T_2)_c \; + \; \ldots \; |0\rangle$$

=> $$E \; = \; E_{HF} \; + \; \langle 0|(W_N T_2)_c|0\rangle$$

CCD Approximation

$$H \quad = \quad E_{HF} \; + \; f_N \; + \; W_N \qquad\qquad T \quad = \quad T_2$$

amplitude equations

projection on doubly excited determinants

$$0 \quad = \quad \langle \Phi_D | \; (H \;\; \exp(T))_c \; |0\rangle$$

$$=> \quad 0 \quad = \quad \langle \Phi_D | \; H \; + \; (HT_2)_c \; + \; \frac{1}{2!}((HT_2)_c T_2)_c \; + \; \cdots \quad |0\rangle$$

$$=> \quad 0 \quad = \quad \langle \Phi_D | W_N \; + \; (f_N T_2)_c \; + \; (W_N T_2)_c$$

$$+ \; \frac{1}{2!}((W_N T_2)_c) T_2)_c |0\rangle$$

Connectedness

consider connectedness of terms

at most two connections for f_N

at most four connections for W_N

		possible excitation
f_N:	no connection	(-1,0,1)
	one connection	(-1,0)
	two connections	(-1)
W_N	no connection	(-2,-1,0,1,2)
	one connection	(-2,-1,0,1)
	two connections	(-2-1,0)
	three connections	(-2,-1)
	four connections	(-2)

CCSD Equations

$$H = E_{HF} + f_N + W_N \qquad T = T_1 + T_2$$

$$E = E_{HF} + \langle 0 | (f_N T_1)_c + (W_N T_2)_c + \frac{1}{2!}((W_N T_1)_c) T_1)_c \, |0\rangle$$

projection on singly excited determinants

$$\begin{aligned} 0 = \langle \Phi_S | \, & f_N \\ & + (f_N T_1)_c + (W_N T_1)_c + (f_N T_2)_c + (W_N T_2)_c \\ & + \frac{1}{2!}((f_N T_1)_c T_1)_c + \frac{1}{2!}((W_N T_1)_c T_1)_c \\ & + ((W_N T_2)_c T_1)_c + \frac{1}{3!}(((W_N T_1)_c T_1)_c) T_1)_c \, |0\rangle \end{aligned}$$

singly excited determinants

CCSD Equations

$$H = E_{HF} + f_N + W_N \qquad\qquad T = T_1 + T_2$$

projection on doubly excited determinants

$$\begin{aligned} 0 \;=\; \langle \Phi_D | \; & W_N + (W_N T_1)_c + (f_N T_2)_c + (W_N T_2)_c \\ & + \frac{1}{2!}((W_N T_1)_c T_1)_c + ((f_N T_2)_c T_1)_c + ((W_N T_2)_c T_1)_c \\ & + \frac{1}{2!}((W_N T_2)_c T_2)_c \\ & + \frac{1}{2!}(((W_N T_2)_c T_1)_c) T_1)_c + \frac{1}{3!}(((W_N T_1)_c T_1)_c) T_1)_c \\ & + \frac{1}{4!}((((W_N T_1)_c T_1)_c) T_1)_c) T_1)_c \; |0\rangle \end{aligned}$$

doubly excited determinants

$f_N T_1$ and $(((f_N T_1)_c T_1)_c T_1)_c$ cannot contribute due to the connectness requirement

Why do the CC Equations Terminate?

each T must be „connected“ to H

H only contains up to two-body operators

→ **at most 4 quasi-particle annihilation operators available for contractions**

→ **at most 4 T operators can be „connected“ with H**

=> $(H \exp(T))_c$ contains at most quartic terms!

Size Extensivity

CC equations contain only „connected“ terms

=> size extensivity

correct (linear) scaling with
size of systems/number of electrons

ensures that quality of results is independent of size

connected terms	linear scaling
disconnected terms	quadratic, cubic, ... (unphysical) scaling

Size Extensivity

disconnected term $(WT)_d$	**connected term $(WT)_c$**
system A	
one contribution (W from A, T from A)	one contribution (W from A, T from A)
system A+B	
four contribution (W from A, T from A W from A, T from B, W from B, T from A W from B. T from B)	two contribution (W from A, T from A W from B, T from B)
quadratic scaling (wrong!)	**linear scaling**

Detailed Expressions for the CC Equations

- **algebraic analysis via Wick's theorem**
  - tedious, **not recommended**
  - suitable for **computer algebra**

- **analysis by means of diagrammatic techniques**
  - simple access via **graphical** representations
  - automatic elimination of **non-contributing** term
  - (better) suitable for **computer algebra**

IX.

Diagrammatic Techniques in CC Theory

Diagrammatic Representation: Operators

operators

$$f_{pq}\{a_p^\dagger a_q\} \longrightarrow f_N$$

$$\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} \longrightarrow W_N$$

$$t_{ij}^{ab}\{a_a^\dagger a_b^\dagger a_j a_i\} \longrightarrow T$$

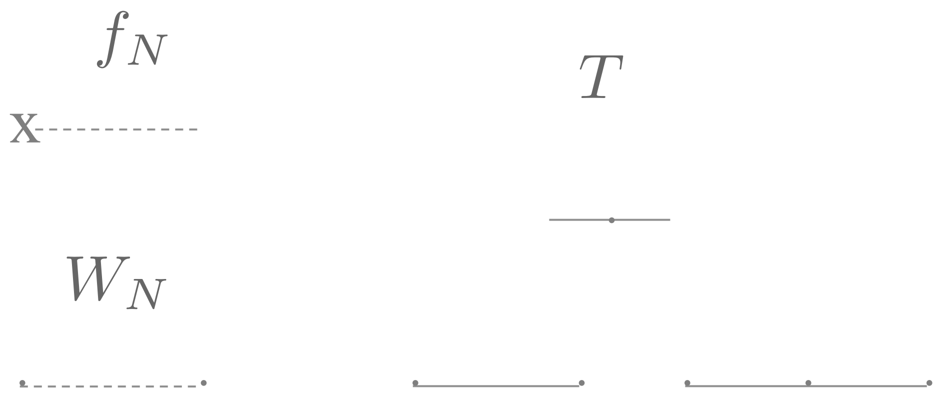
matrix element

product of creation and annihilation operators

graphical representation

symbol with vertices

number of vertices = number of p^+q pairs

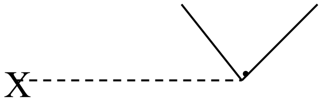


Diagrammatic Representation: Operators

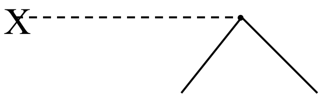
QP-creation/annihilation operators → **lines**

QP-creation operators (QPC) → lines **above** vertex

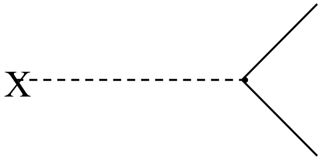
QP-annihilation operators (QPA) → lines **below** vertex



2 QPC



2 QPA



1 QPC and QPA

arrow direction

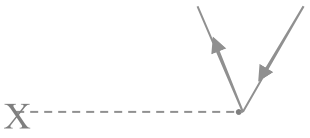
particles (**virtual** orbitals) ↑ **upwards**

holes (**occupied** orbitals) ↓ **downwards**

Diagrammatic Representation: Operators

at each vertex there is **one incoming** and **one outgoing** line
(conservation of particle number)

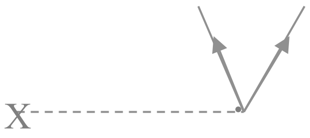
$a_a^\dagger a_i$



correct

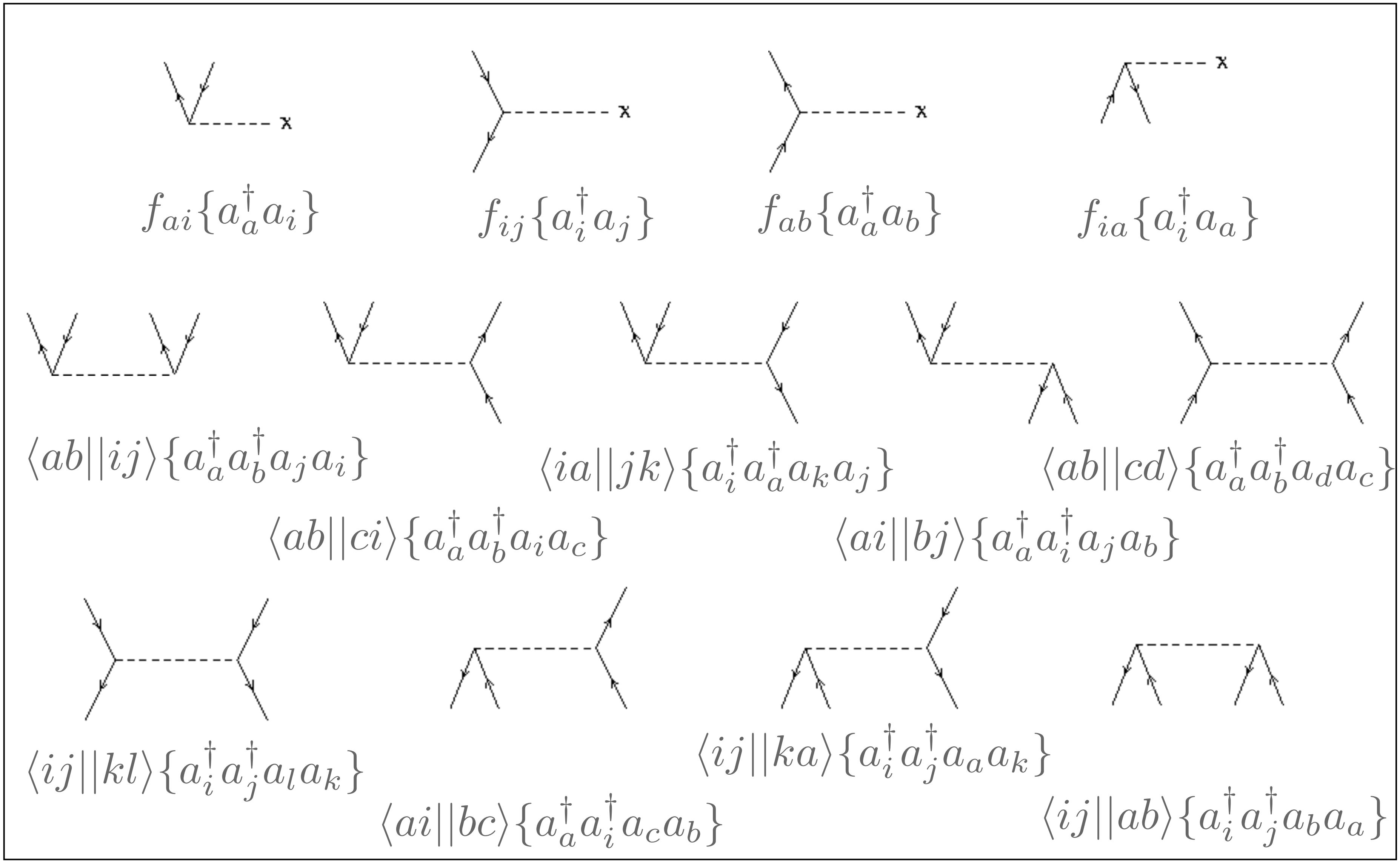
$a_a^\dagger a_b^\dagger$

(non existing)



wrong

Diagrammatic Representation of the Hamilton Operator



$$f_{ai}\{a_a^\dagger a_i\}$$

$$f_{ij}\{a_i^\dagger a_j\}$$

$$f_{ab}\{a_a^\dagger a_b\}$$

$$f_{ia}\{a_i^\dagger a_a\}$$

$$\langle ab||ij\rangle\{a_a^\dagger a_b^\dagger a_j a_i\}$$

$$\langle ab||ci\rangle\{a_a^\dagger a_b^\dagger a_i a_c\}$$

$$\langle ia||jk\rangle\{a_i^\dagger a_a^\dagger a_k a_j\}$$

$$\langle ai||bj\rangle\{a_a^\dagger a_i^\dagger a_j a_b\}$$

$$\langle ab||cd\rangle\{a_a^\dagger a_b^\dagger a_d a_c\}$$

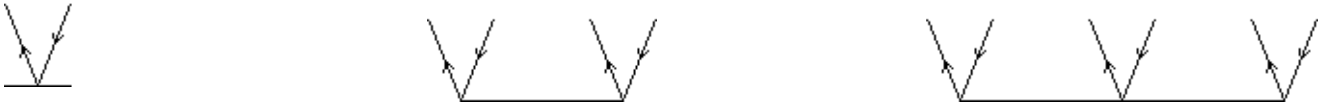
$$\langle ij||kl\rangle\{a_i^\dagger a_j^\dagger a_l a_k\}$$

$$\langle ai||bc\rangle\{a_a^\dagger a_i^\dagger a_c a_b\}$$

$$\langle ij||ka\rangle\{a_i^\dagger a_j^\dagger a_a a_k\}$$

$$\langle ij||ab\rangle\{a_i^\dagger a_j^\dagger a_b a_a\}$$

Diagrammatic Representation of the Cluster Operator



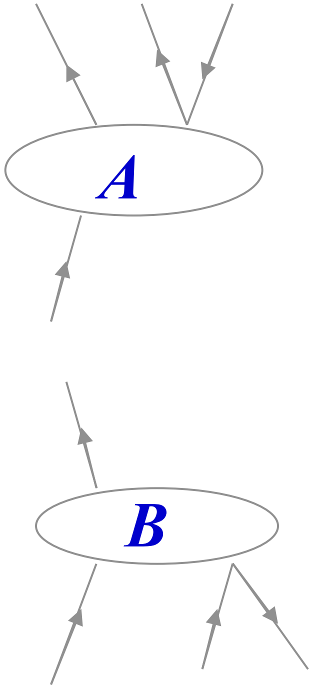
etc.

$t_i^a \ \{a_a^\dagger a_i\}$ $\quad$ $t_{ij}^{ab} \ \{a_a^\dagger a_b^\dagger a_j a_i\}$ $\quad$ $t_{ijk}^{abc} \ \{a_a^\dagger a_b^\dagger a_c^\dagger a_k a_j a_i\}$

Diagrammatic Representation: Contractions

product of two operators A and B

$A\,B \longrightarrow$



left operator (A) **above** right operator (B)

Diagrammatic Representation: Contractions

normal-ordered product form according to **Wick’s theorem**

all „diagrams“, in which the two operators are
connected via none, one, two, … lines

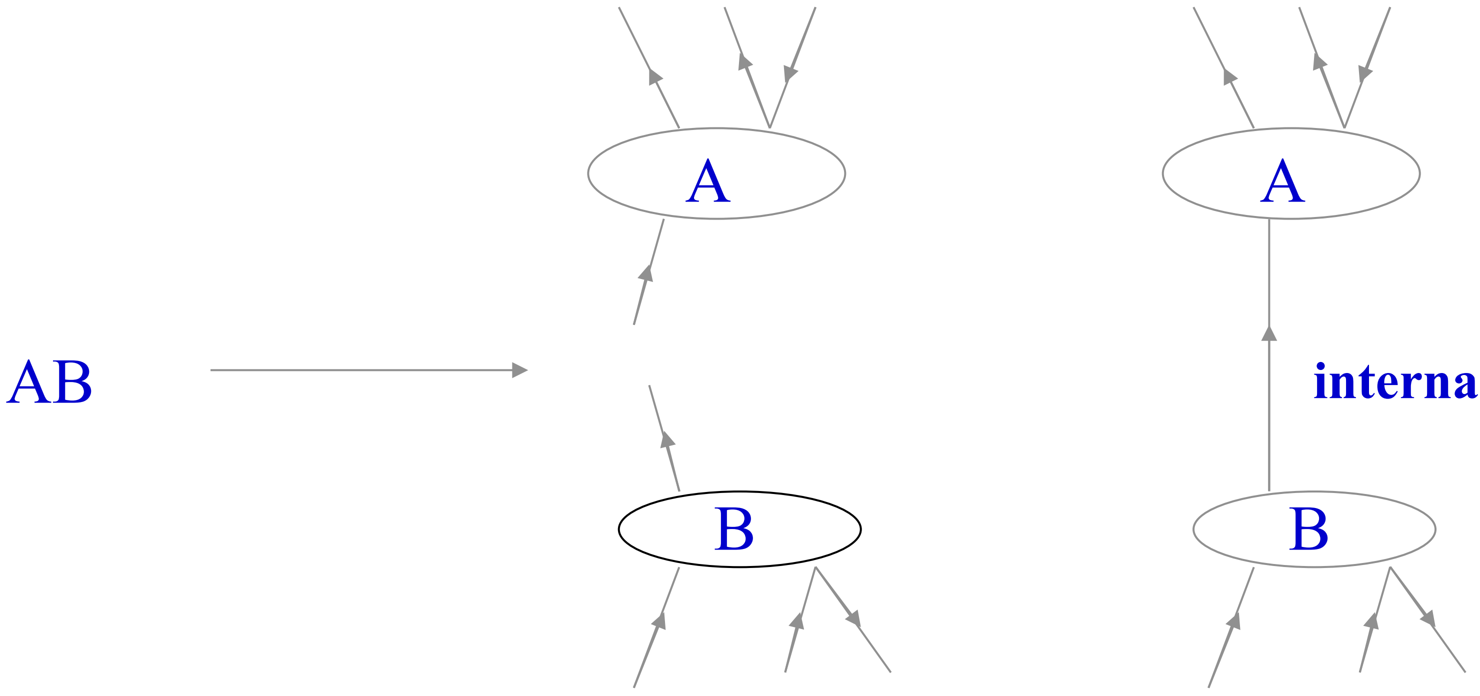
connection = contraction

connection only possible in the case of **same** directions of arrows

connections only between **QPC in *B*** and **QPA in *A***

Diagrammatic Representation: Contractions

example



open lines

(remaining QPC and QPA)

internal line

no contraction

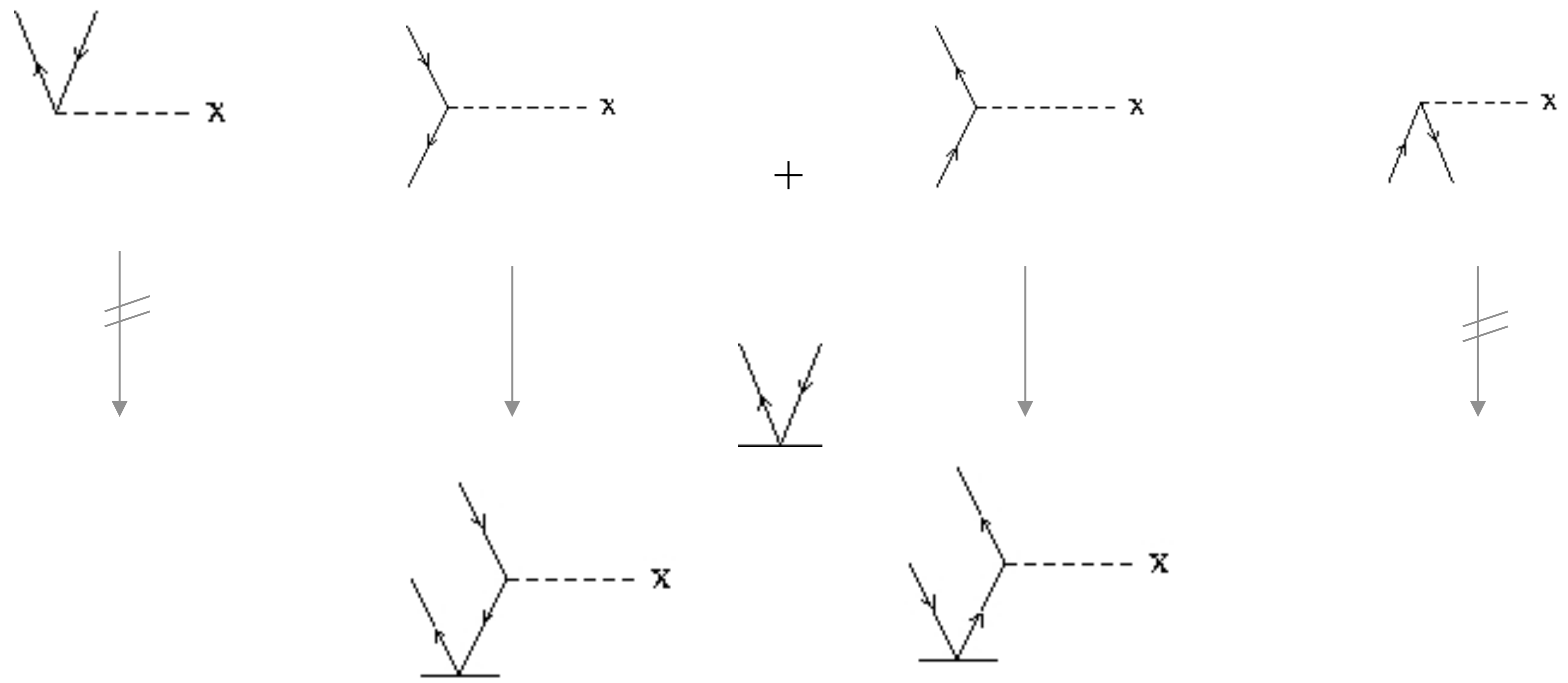
one contraction

Diagrammatic Representation: Contractions

example

$$\langle \Phi_i^a | \; (f_N \; T_1)_c | 0 \rangle$$

2 open lines

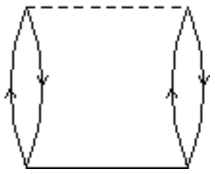


Connected, Disconnected, Linked, Unlinked

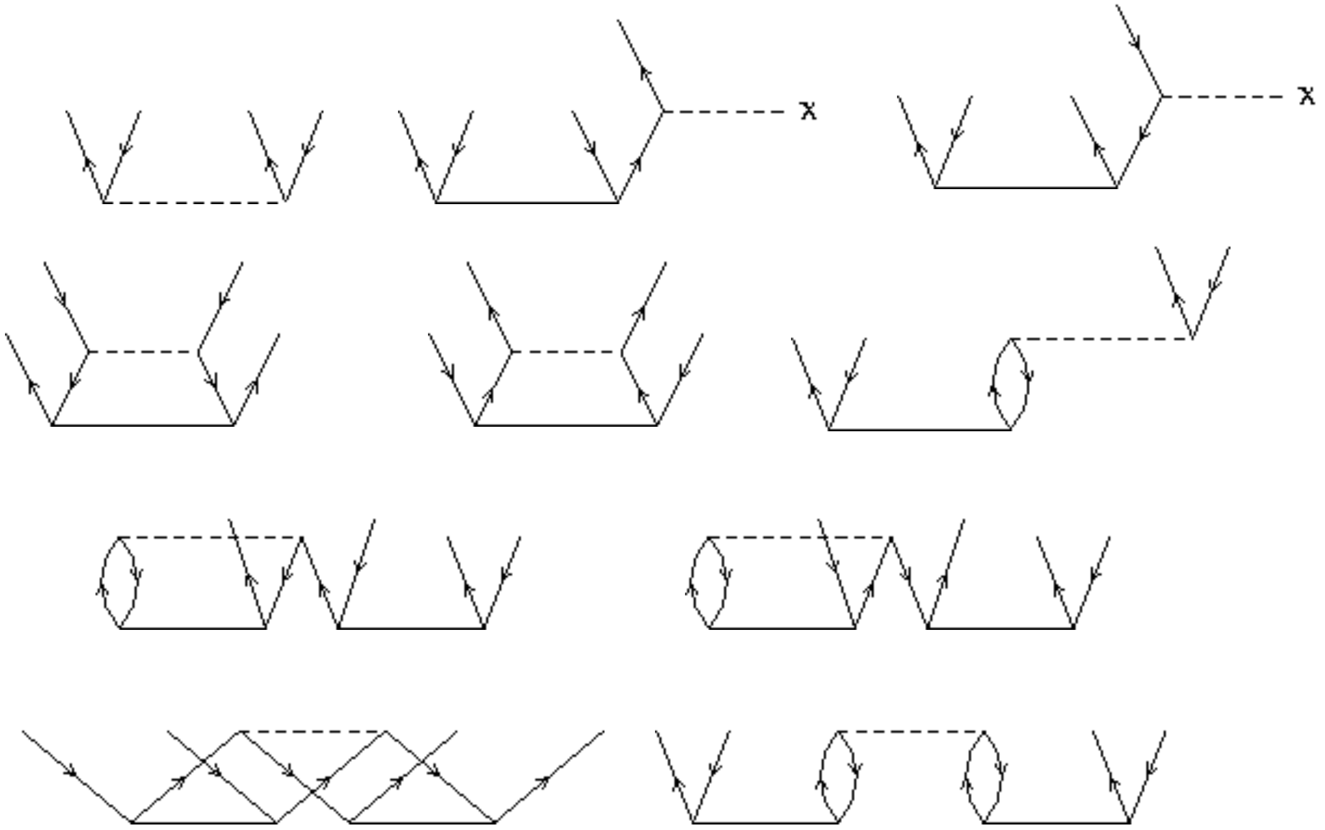
open	with open lines
closed	no open lines
connected	all parts of the diagram are connected via lines
disconnected	not all parts of the diagram are connected via lines
linked	closed and „connected“
unlinked	closed and „disconnected“

Diagrammatic Representation of the CCD Model

CC energy:

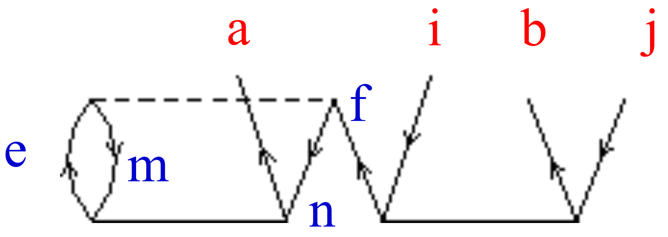


CC equations:



Algebraic Analysis of Diagrams

Each line of the diagram corresponds to an index. The indices of the open lines correspond to the „target“indices (i, j, k, … in the case of holes and a, b, c, … in the case of particles), the indices of the internal lines correspond to the „summation“ indices (m, n, o, … in the case of holes and e, f, g, …in the case of particles)

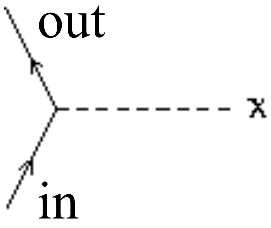


target indices

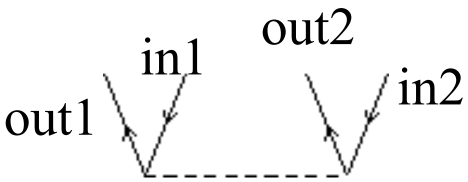
summation indices

Algebraic Analysis of Diagrams

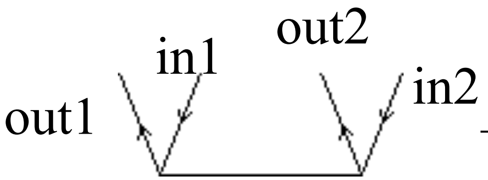
The **symbols for the operators** are replaced by the corresponding **matrix elements**.



$$\longrightarrow \quad f(out, in)$$



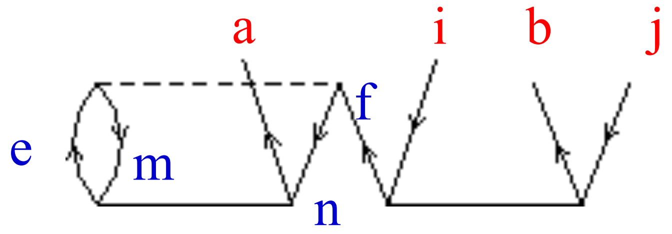
$$\longrightarrow \quad \langle out1\ out2 \,||\, in1\ in2 \rangle$$



$$\longrightarrow \quad t^{out1\ \ out2}_{in1\ \ in2}$$

Algebraic Analysis of Diagrams

sum over all indices of the **internal** lines



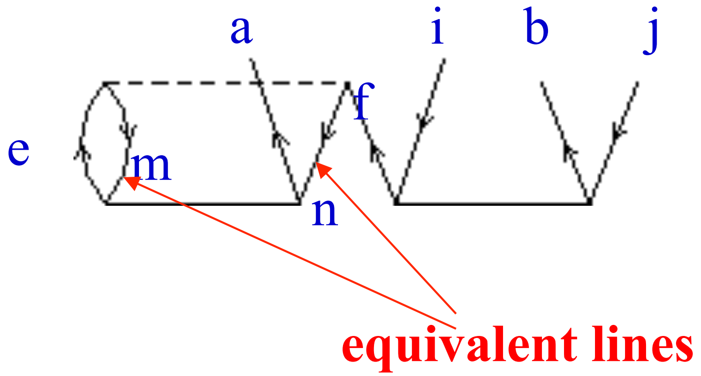
target indices

summation indices

=> $$\sum_{m,n}\sum_{e,f} t_{mn}^{ea}\; t_{ij}^{fb}\; \langle mn||ef\rangle$$

Algebraic Analysis of Diagrams

n **equivalent** lines (same arrow direction, connection to same operator symbols) yield a **factor** of 1/n!



target indices

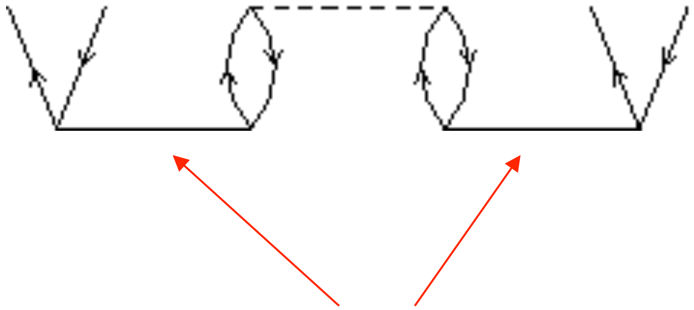
summation indices

→ factor 1/2

=> $$\frac{1}{2}\sum_{m,n}\sum_{e,f} t_{mn}^{ea}\; t_{ij}^{fb}\; \langle mn||ef\rangle$$

Algebraic Analysis of Diagrams

n **equivalent** operators (connected to the same operator(s) via lines of the same arrow direction) yield a **factor** of 1/n!

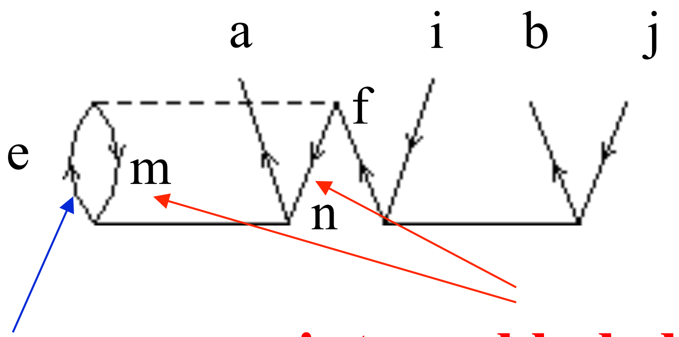


equivalent T_2 operators

=> **factor 1/2**

Algebraic Analysis of Diagrams

the sign of a diagram is given as $(-1)^{h+l}$ with h as the number of **„internal hole lines“** and l as the number of **„loops“**



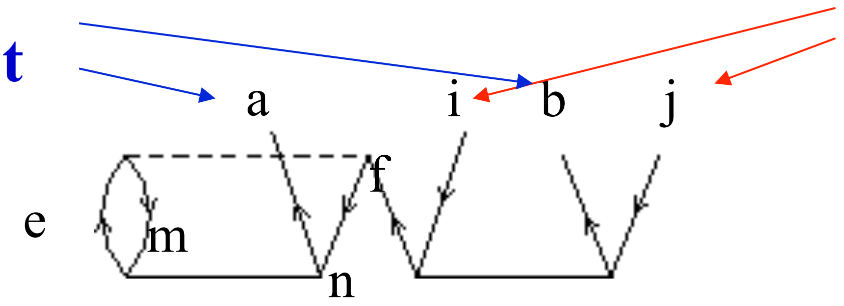
loop

internal hole lines

=> negative sign

Algebraic Analysis of Diagrams

sum over all **non-equivalent permutations** of the indices of the **open hole** and **particle** lines, respectively



non equivalent

equivalent

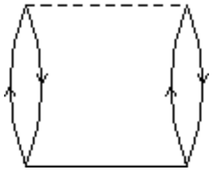
$$-\frac{1}{2}P_-(ab)\sum_{m,n}\sum_{e,f}\ t_{mn}^{ea}\ t_{ij}^{fb}\ \langle mn||ef\rangle$$

sign: (-1)^p with *p* as the parity of permutation

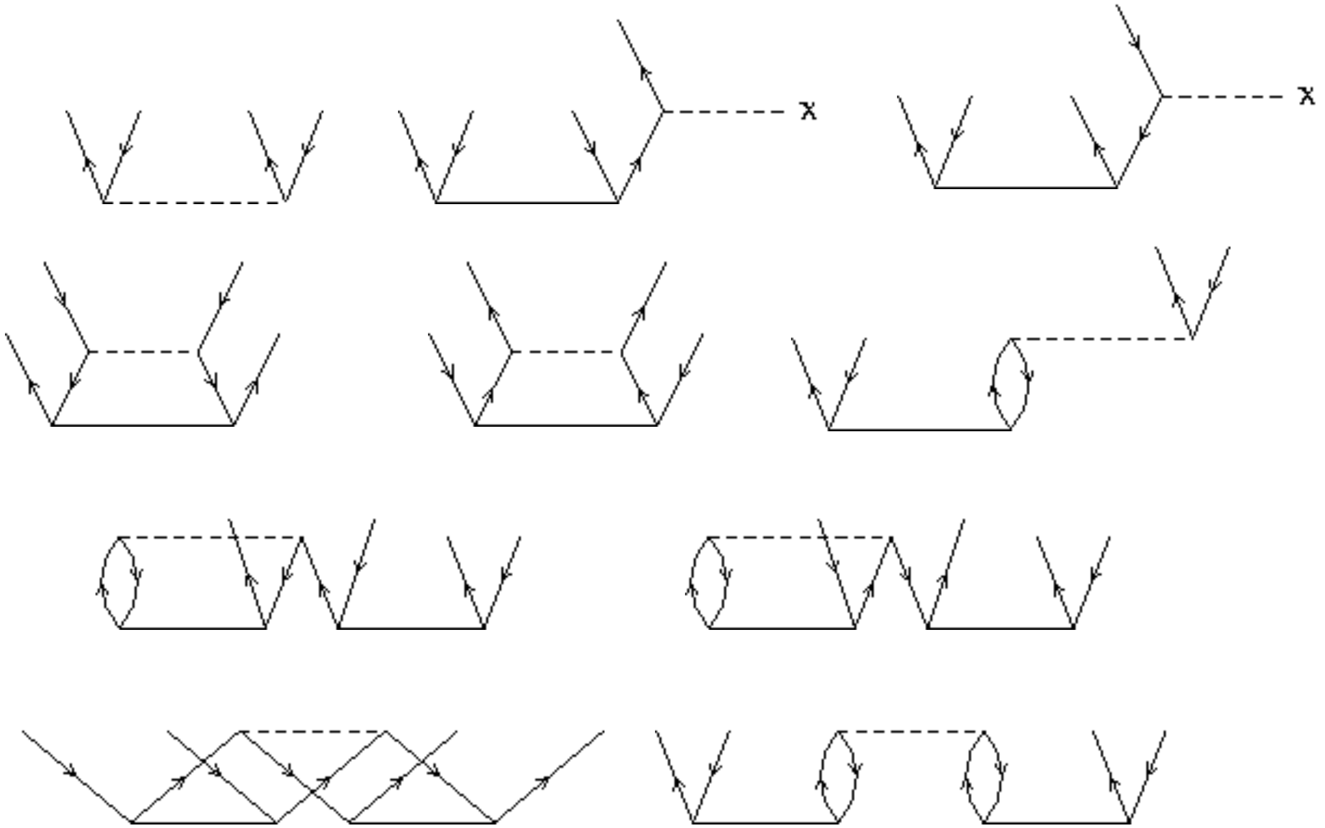
$$P_-(ab)\ Z(a,b)\ \ =\ \ Z(a,b)\ -\ Z(b,a)$$

Diagrammatic Representation of the CCD Model

CC energy:



CC equations:



CCD: Algebraic Expressions

CC energy:

$$\Delta E = \frac{1}{4}\sum_{ij}\sum_{ab} \langle ij||ab\rangle \, t_{ij}^{ab}$$

CC equations:

$$\begin{aligned}
0 = {} & \langle ab||ij\rangle + P_-(ab)\sum_{e} f_{ae}\, t_{ij}^{eb} - P_-(ij)\sum_{m} f_{mi}\, t_{mj}^{ab} \\
& + \frac{1}{2}\sum_{mn} \langle mn||ij\rangle\, t_{mn}^{ab} + \frac{1}{2}\sum_{ef} \langle ab||ef\rangle\, t_{ij}^{ef} \\
& + P_-(ij)P_-(ab)\sum_{m}\sum_{e} \langle mb||ej\rangle\, t_{im}^{ae} \\
& - \frac{1}{2}P_-(ab)\sum_{mn}\sum_{ef} \langle mn||ef\rangle\, t_{mn}^{af}\, t_{ij}^{eb} - \frac{1}{2}P_-(ij)\sum_{mn}\sum_{ef} \langle mn||ef\rangle\, t_{in}^{ef}\, t_{mj}^{ab} \\
& + \frac{1}{4}\sum_{mn}\sum_{ef} \langle mn||ef\rangle\, t_{mn}^{ab}\, t_{ij}^{ef} + \frac{1}{2}P_-(ij)P_-(ab)\sum_{mn}\sum_{ef} \langle mn||ef\rangle\, t_{im}^{ae}\, t_{jn}^{bf}
\end{aligned}$$

X.

Computational Realization of CC Approaches

Solution of CC Equations

- no direct solution of (non-linear) CC equations possible

=> **iterative schemes**

- rewrite CC equations

CCD: $$0 = (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)t_{ij}^{ab} + Z_{ij}^{ab}(t_{ij}^{ab})$$

zeroth-order term **higher-order terms**

- iterative sequence

$$t_{ij}^{ab(n+1)} = \frac{Z_{ij}^{ab}(t_{ij}^{ab(n)})}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

new amplitudes

computed with old amplitudes

initial guess via MP2, convergence acceleration using DIIS

CC equations:

zeroth-order term

$$
\begin{aligned}
0 \;=\; & \langle ab||ij\rangle + P_{-}(ab)\sum_{e} f_{ae}\, t_{ij}^{eb} - P_{-}(ij)\sum_{m} f_{mi}\, t_{mj}^{ab} \\
& + \frac{1}{2}\sum_{mn} \langle mn||ij\rangle\, t_{mn}^{ab} + \frac{1}{2}\sum_{ef} \langle ab||ef\rangle\, t_{ij}^{ef} \\
& + P_{-}(ij)P_{-}(ab)\sum_{m}\sum_{e} \langle mb||ej\rangle\, t_{im}^{ae} \\
& - \frac{1}{2}P_{-}(ab)\sum_{mn}\sum_{ef} \langle mn||ef\rangle\, t_{mn}^{af}\, t_{ij}^{eb} - \frac{1}{2}P_{-}(ij)\sum_{mn}\sum_{ef} \langle mn||ef\rangle\, t_{in}^{ef}\, t_{mj}^{ab} \\
& + \frac{1}{4}\sum_{mn}\sum_{ef} \langle mn||ef\rangle\, t_{mn}^{ab}\, t_{ij}^{ef} + \frac{1}{2}P_{-}(ij)P_{-}(ab)\sum_{mn}\sum_{ef} \langle mn||ef\rangle\, t_{im}^{ae}\, t_{jn}^{bf}
\end{aligned}
$$

higher-order terms

Computational Cost

$$\sum_{m<n} \langle mn||ij\rangle \; t_{mn}^{ab} \Longrightarrow Z_{ij}^{ab}$$

target indices i,j,a,b

do it for all i<j and a<b

→ $\frac{1}{2}\, n_{occ}^{2} * \frac{1}{2}\, N_{virt}^{2}$

summation over m < n → $\frac{1}{2}\, n_{occ}^{2}$

=> total cost is $1/8\; n_{occ}^{4} * N_{virt}^{2}$

CCD

linear terms: $1/8\; n_{occ}^{4} * N_{virt}^{2} + 1/8\; n_{occ}^{2} * N_{virt}^{4} + n_{occ}^{3} * N_{virt}^{3}$

=> N^6 computational cost

non-linear terms: $\sum_{m<n} \sum_{e<f} \langle mn||ef\rangle \; t_{mn}^{ab} \; t_{ij}^{ef} \Longrightarrow Z_{ij}^{ab}$ N^8 cost???

CCD equations:

linear terms

$$\begin{aligned} 0 \;=\;& \langle ab||ij\rangle + P_{-}(ab)\sum_{e} f_{ae}\, t_{ij}^{eb} - P_{-}(ij)\sum_{m} f_{mi}\, t_{mj}^{ab} \\ &+ \frac{1}{2}\sum_{mn}\langle mn||ij\rangle\, t_{mn}^{ab} + \frac{1}{2}\sum_{ef}\langle ab||ef\rangle\, t_{ij}^{ef} \\ &+ P_{-}(ij)P_{-}(ab)\sum_{m}\sum_{e}\langle mb||ej\rangle\, t_{im}^{ae} \\ &- \frac{1}{2}P_{-}(ab)\sum_{mn}\sum_{ef}\langle mn||ef\rangle\, t_{mn}^{af}\, t_{ij}^{eb} - \frac{1}{2}P_{-}(ij)\sum_{mn}\sum_{ef}\langle mn||ef\rangle\, t_{in}^{ef}\, t_{mj}^{ab} \\ &+ \frac{1}{4}\sum_{mn}\sum_{ef}\langle mn||ef\rangle\, t_{mn}^{ab}\, t_{ij}^{ef} + \frac{1}{2}P_{-}(ij)P_{-}(ab)\sum_{mn}\sum_{ef}\langle mn||ef\rangle\, t_{im}^{ae}\, t_{jn}^{bf} \end{aligned}$$

CCD equations:

$$
\begin{aligned}
0 \; = \; & \langle ab||ij\rangle + P_-(ab)\sum_{e} f_{ae}\, t_{ij}^{eb} - P_-(ij)\sum_{m} f_{mi}\, t_{mj}^{ab} \\
& + \frac{1}{2}\sum_{mn}\langle mn||ij\rangle\, t_{mn}^{ab} + \frac{1}{2}\sum_{ef}\langle ab||ef\rangle\, t_{ij}^{ef} \\
& + P_-(ij)P_-(ab)\sum_{m}\sum_{e}\langle mb||ej\rangle\, t_{im}^{ae} \\
& - \frac{1}{2}P_-(ab)\sum_{mn}\sum_{ef}\langle mn||ef\rangle\, t_{mn}^{af}\, t_{ij}^{eb} - \frac{1}{2}P_-(ij)\sum_{mn}\sum_{ef}\langle mn||ef\rangle\, t_{in}^{ef}\, t_{mj}^{ab} \\
& + \frac{1}{4}\sum_{mn}\sum_{ef}\langle mn||ef\rangle\, t_{mn}^{ab}\, t_{ij}^{ef} + \frac{1}{2}P_-(ij)P_-(ab)\sum_{mn}\sum_{ef}\langle mn||ef\rangle\, t_{im}^{ae}\, t_{jn}^{bf}
\end{aligned}
$$

non-linear terms

Factorization of Terms

$$\sum_{m<n} \sum_{e<f} \langle mn||ef\rangle \; t_{mn}^{ab} \; t_{ij}^{ef} \quad \Longrightarrow \quad Z_{ij}^{ab}$$

one-step evaluation => N^8 computational cost

a) $$\sum_{e<f} \langle mn||ef\rangle \; t_{ij}^{ef} \quad \Longrightarrow \quad Y_{ij}^{mn}$$

factorization

b) $$\sum_{m<n} Y_{ij}^{mn} \; t_{mn}^{ab} \quad \Longrightarrow \quad Z_{ij}^{ab}$$

two-step evaluation => 2 N^6 computational cost

Definition of Intermediates

- **straightforward implementation (term by term)**

$$\left.\begin{array}{ccc} \displaystyle\sum_{m<n} \langle mn||ij\rangle \; t^{ab}_{mn} & + & \displaystyle\sum_{m<n}\sum_{e<f} \langle mn||ef\rangle \; t^{ef}_{ij} \; t^{ab}_{mn} \\ \textbf{N}^6\textbf{ cost} & & \textbf{2 N}^6\textbf{ cost} \end{array}\right\} \textbf{3 N}^6\textbf{ cost}$$

- **via intermediates**

$$\left.\begin{array}{lll} \textbf{intermediate} & \widetilde{\mathcal{W}}_{mnij} = \langle mn||ij\rangle + \displaystyle\sum_{e<f} \langle mn||ef\rangle t^{ef}_{ij} & \\ & \qquad\qquad\qquad\qquad \textbf{N}^6\textbf{ cost} & \\ \textbf{contraction} & \displaystyle\sum_{m<n} \widetilde{\mathcal{W}}_{mnij} \; t^{ab}_{mn} & \textbf{N}^6\textbf{ cost} \end{array}\right\} \textbf{2 N}^6\textbf{ cost}$$

CCD Formulated via Intermediates

CC energy:

$$\Delta E = \frac{1}{4}\sum_{i,j}\sum_{a,b}\langle ij||ab\rangle\, t_{ij}^{ab}$$

CC equations:

$$\begin{aligned} 0 = \langle ab||ij\rangle &+ P_-(ab)\sum_e \widetilde{\mathcal{F}}_{ae}\, t_{ij}^{eb} - P_-(ij)\sum_m \widetilde{\mathcal{F}}_{mi}\, t_{mj}^{ab} \\ &+ \frac{1}{2}\sum_{m,n}\mathcal{W}_{mnij}\, t_{mn}^{ab} + \frac{1}{2}\sum_{e,f}\langle ab||ef\rangle\, t_{ij}^{ef} \\ &+ P_-(ij)P_-(ab)\sum_m\sum_e \widetilde{\mathcal{W}}_{mbej}\, t_{im}^{ae} \end{aligned}$$

intermediates:

$$\widetilde{\mathcal{F}}_{mi} = f_{mi} + \frac{1}{2}\sum_n\sum_{e,f}\langle mn||ef\rangle\, t_{in}^{ef} \qquad \mathcal{W}_{mnij} = \langle mn||ij\rangle + \frac{1}{2}\sum_{e,f}\langle mn||ef\rangle\, t_{ij}^{ef}$$

$$\widetilde{\mathcal{F}}_{ae} = f_{ae} - \frac{1}{2}\sum_{m,n}\sum_f\langle mn||ef\rangle\, t_{mn}^{af} \qquad \widetilde{\mathcal{W}}_{mbej} = \langle mb||ej\rangle + \frac{1}{2}\sum_n\sum_f\langle mn||ef\rangle\, t_{jn}^{bf}$$

Computational Cost

leading terms of CCD + CCSD

linear terms: $1/8\ n_{occ}^{4} * N_{virt}^{2} + 1/8\ n_{occ}^{2} * N_{virt}^{4} + n_{occ}^{3} * N_{virt}^{3}$

non-linear terms: $1/8\ n_{occ}^{4} * N_{virt}^{2} + n_{occ}^{3} * N_{virt}^{3}$

---

total: $1/4\ n_{occ}^{4} * N_{virt}^{2} + 1/8\ n_{occ}^{2} * N_{virt}^{4} + 2\ n_{occ}^{3} * N_{virt}^{3}$

=> N^{6} computational cost

less than 2 times as expensive as CID and CISD (linear terms only!)

Standard CC Approaches

truncation of the cluster operator T:

cluster operator	approximation	cost
$T=T_1+T_2$	CCSD	N^6
$T=T_1+T_2+T_3$	CCSDT	N^8
$T=T_1+T_2+T_3+T_4$	CCSDTQ	N^{10}
$T=T_1+T_2+T_3+T_4+T_5$	CCSDTQP	N^{12}
…	…	…
$T=T_1+T_2+\ldots+T_N$	FCI	

Accuracy of CC Methods

deviation from FCI (in mH) for CO

	CI	CC
SD	30.804	12.120
SDT	21.718	1.009
SDTQ	1.775	0.061
SDTQP	0.559	0.008
SDTQPH	0.035	0.002

calculations with cc-pVDZ basis, frozen core

E(FCI) = -113.055853 H

Historical Remarks

CC theory	Čížek, 1966
first CC computations (semiempirical, min. basis)	Čížek, 1966 Čížek, Paldus, Shavitt, 1972
CCD implementation	Pople and co-workers, 1978 Bartlett, Purvis, 1978
CCSD implementation	Purvis, Bartlett, 1982
efficient closed-shell CCSD	Schaefer and co-workers, 1987
CCSDT implementation	Noga, Bartlett, 1987 Scuseria and Schaefer, 1988
CCSDTQ implementation	Oliphant, Adamowicz, 1991 Kucharski, Bartlett, 1991
general CC models	Olsen, 2000, Kállay, Surján, 2001, Hirata, 2003

XI.

Approximate Treatment of Higher Excitations

Need for Higher Excitations

High-Accuracy Calculations:

1 kJ/mol or better in thermochemical applications

0.1 pm accuracy in computed bond distances

...

require considerations of excitations beyond singles and doubles

=> triples, quadruples, ...

CCSDT Equations

$$H \;=\; E_{HF} \;+\; f_N \;+\; W_N \qquad\qquad T \;=\; T_1 \;+ T_2 \;+\; T_3$$

$$E \;=\; E_{HF} \;+\; \langle 0|(f_N T_1)_c \;+\; (W_N T_2)_c \;+\; \frac{1}{2!}((W_N T_1)_c)T_1)_c \;|0\rangle$$

projection on singly excited determinants

additional term due to T_3

$$\begin{aligned} 0 \;=& \langle \Phi_S|\; f_N \\ &+(f_N T_1)_c + (W_N T_1)_c \\ &+(f_N T_2)_c + (W_N T_2)_c + \frac{1}{2}((f_N T_1)_c T_1)_c + \frac{1}{2}((W_N T_1)_c T_1)_c \\ &+((W_N T_2)_c T_1)_c + \frac{1}{3!}(((W_N T_1)_c T_1)_c)T_1)_c + (W_N T_3)_c|0\rangle \end{aligned}$$

CCSDT Equations

$$H = E_{HF} + f_N + W_N \qquad T = T_1 + T_2 + T_3$$

projection on doubly excited determinants

$$\begin{aligned}
0 = \langle \Phi_D | \; W_N \\
&+(W_N T_1)_c \\
&+(f_N T_2)_c + (W_N T_2)_c + \frac{1}{2}((W_N T_1)_c T_1)_c \\
&+((f_N T_2)_c T_1)_c + ((W_N T_2)_c T_1)_c + \frac{1}{3!}(((W_N T_1)_c T_1)_c T_1)_c \\
&\qquad +(f_N T_3)_c + (W_N T_3)_c \\
&+\frac{1}{2}((W_N T_2)_c T_2)_c + \frac{1}{2}(((W_N T_2)_c T_1)_c T_1)_c + \frac{1}{4!}((((W_N T_1)_c T_1)_c T_1)_c T_1)_c \\
&\qquad +((W_N T_3)_c T_1)_c |0\rangle
\end{aligned}$$

additional terms due to T_3

CCSDT Equations

$$H \;=\; E_{HF} \;+\; f_N \;+\; W_N \qquad\qquad T \;=\; T_1 \;+\; T_2 \;+\; T_3$$

projection on triply excited determinants

$$\begin{aligned}0 \;=\; \langle\Phi_T|&(W_NT_2)_c+(f_NT_3)_c+(W_NT_3)_c+((W_NT_2)_cT_1)_c\\&+((f_NT_3)_cT_1)_c+\frac{1}{2}((f_NT_2)_cT_2)_c+\frac{1}{2}((W_NT_2)_cT_2)_c+((W_NT_3)_cT_1)_c\\&+\frac{1}{2}(((W_NT_2)_cT_1)_cT_1)_c+((W_NT_3)_cT_2)_c+\frac{1}{2}(((W_NT_2)_cT_1)_cT_1)_c\\&+\frac{1}{2}((W_NT_3)_cT_1)_cT_1)_c+\frac{1}{3!}((((W_N)T_2)_cT_1)_cT_1)_cT_1)_c|0\rangle\end{aligned}$$

shorthand notation

$$((W_NT_2)_cT_1)_c \;\equiv\; (W_NT_2T_1)_c$$

in the sense that all Ts are connected to f_N or W_N

CCSDT Equations

projection on triply excited determinants

$$\begin{aligned} 0 \;=\; \langle \Phi_T | \; & (W_N T_2)_c \;+\; (f_N T_3)_c \;+\; (W_N T_3)_c \\ & + (W_N T_2 T_1)_c \;+\; (f_N T_3 T_1)_c + \frac{1}{2}(f_N T_2^2)_c \\ & + \frac{1}{2}(W_N T_2^2)_c \;+\; (W_N T_3 T_1)_c + \frac{1}{2}(W_N T_2 T_1^2)_c \\ & + (W_N T_3 T_2)_c \;+\; \frac{1}{2}(W_N T_2^2 T_1)_c + \frac{1}{2}(W_N T_3 T_1^2)_c \\ & + \frac{1}{3!}(W_N T_2 T_1^3)_c \; |0\rangle \end{aligned}$$

„problems“ with CCSDT

- computational cost : N^8
- storage of triples amplitudes: N^6

CCSD for comparison

- computational cost : N^6
- storage of doubles amplitudes: N^4

two orders of magnitudes more expensive

Iterative Approximations to CCSDT

additional approximations in the amplitude equations

- **no storage** of amplitudes for highest excitation
- **reduced scaling** in computational cost

=> CCSDT-n (n=1-3)

Bartlett and co-workers
(1984, 1987)

=> CC3 (within CCn hierarchy)

Jørgensen and co-workers
(1997)

Iterative Approximations to CCSDT

triples equations

$$
\begin{aligned}
0 \;=\; \langle\Phi_T|\, (W_N T_2)_c \;+\; (f_N T_3)_c \;+\; \underline{(W_N T_3)}_c \\
+\, (W_N T_2 T_1)_c \;+\; \underline{(f_N T_3 T_1)}_c + \frac{1}{2}(f_N T_2^2)_c \\
+\, \frac{1}{2}(W_N T_2^2)_c \;+\; \underline{(W_N T_3 T_1)}_c + \frac{1}{2}(W_N T_2 T_1^2)_c \\
+\, \underline{(W_N T_3 T_2)}_c \;+\; \frac{1}{2}(W_N T_2^2 T_1)_c + \frac{1}{2}\underline{(W_N T_3 T_1^2)}_c \\
+\, \frac{1}{3!}(W_N T_2 T_1^3)_c \;|0\rangle
\end{aligned}
$$

N⁸ terms: ▬ **to be skipped in all cases**

Iterative Approximations to CCSDT

reduced scaling

all N^8 terms involve contractions with T_3 in the triples equations

only remaining term with T_3

$(f_N T_3)_c$ → T_3 equation; $(\varepsilon_a + \varepsilon_b + \varepsilon_c - \varepsilon_i + \varepsilon_j + \varepsilon_k)\ t_{ijk}^{abc}$

scaling of remaining terms

terms in the T3 equations: **N^7** **(dominates cost)**

$((W_N + W_N T_1) T_3)_c$ → T_2 equation: **N^7** **(dominates cost)**

$(W_N\, T_3)_c$ → T_1 equation: **N^6**

overall cost : $O(N^7)$ per iteration

Iterative Approximations to CCSDT

storage of *T_3* amplitudes

$$t_{ijk}^{abc\,(n+1)} = \frac{Z_{ijk}^{abc}(t_i^{a\,(n)}, t_{ij}^{ab\,(n)})}{(\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c)}$$

compute the triples „on the fly“

independent of *T_3*

followed by immediate calculation of *T_3* contribution to singles and doubles

(without storage)

Iterative Approximations to CCSDT

triples equations

$$
\begin{aligned}
0 \;=\; \langle\Phi_T|\; & \underline{(W_N T_2)_c} \;+\; \underline{(f_N T_3)_c} \;+\; (W_N T_3)_c \\
& + \underline{\underline{(W_N T_2 T_1)_c}} \;+\; (f_N T_3 T_1)_c + \frac{1}{2}\underline{\underline{(f_N T_2^2)_c}} \\
& + \frac{1}{2}\underline{(W_N T_2^2)_c} \;+\; (W_N T_3 T_1)_c + \frac{1}{2}\underline{\underline{(W_N T_2 T_1^2)_c}} \\
& + (W_N T_3 T_2)_c \;+\; \frac{1}{2}\underline{(W_N T_2^2 T_1)_c} + \frac{1}{2}(W_N T_3 T_1^2)_c \\
& + \frac{1}{3!}\underline{\underline{(W_N T_2 T_1^3)_c}}\; |0\rangle
\end{aligned}
$$

CCSDT-1: 🟦

CCSDT-2: 🟦 + 🟩

CCSDT-3: 🟦 + 🟩 + ⬛

CC3: 🟦 + ⬜

Accuracy of Approximate Treatments of Triples

deviation from FCI and CCSDT (in mH) for CO

	Δ(FCI)	Δ(CCSDT)
CCSD	12.12	11.11
CCSDT-1	0.13	-0.88
CCSDT-2	1.52	0.51
CCSDT-3	1.47	0.46
CC3	0.12	-0.89

calculations with cc-pVDZ basis, frozen core

Non-Iterative Approximations to CCSDT

two-step procedure:

- perform CCSD calculation

$$T = T_1 + T_2$$

- add perturbative corrections due to T_3

$$E = E(CCSD) + \Delta E(T)$$

use of converged T_1 and T_2 amplitudes

→ CCSD+T(CCSD), CCSD(T), ...

Coupled-Cluster and Perturbation Theory

perturbative expansion of CC energy and equations

$$\begin{aligned} H_0 &= E_{HF} + f_N & \qquad E &= E^{(0)} + E^{(1)} + E^{(2)} + \dots \\ H^{(1)} &= W_N & T &= T^{(1)} + T^{(2)} + T^{(3)} + \dots \end{aligned}$$

- recovers Møller-Plesset (MP) perturbation theory
- CCSD contains all second- and third-order terms, lacks some higher-order terms
- CC sums certain terms (via iterative solution) to infinite order
- correct CC energy for missing terms using perturbation theory

Coupled-Cluster and Perturbation Theory

perturbative triples correction to energy

$$\Delta E_T \quad = \quad \langle 0 |\; T_3^{\dagger\,(2)} \;\; f_N \; T_3^{(2)} \;\; | 0 \rangle$$

second-order T_3, from MP4

compute T_3 with converged CCSD amplitudes

$$\Delta E_T \quad = \quad \langle 0 |\; T_3^{\dagger} \; f_N \; T_3 \; | 0 \rangle$$

defines CCSD+T(CCSD)

Urban, Noga, Cole, Bartlett, 1985

Coupled-Cluster and Perturbation Theory

additional consideration of a singles contribution

$$\Delta E \quad = \quad \langle 0|\; {T_1^\dagger}^{(2)} \; W_N \; T_3^{(2)} \; |0\rangle$$

fifth-order term!

triples correction to energy (converged amplitudes)

$$\Delta E_T \quad = \quad \langle 0|\; (T_3^\dagger \; f_N \; + \; T_1^\dagger \; W_N) \; T_3 \; |0\rangle$$

defines CCSD(T)

Raghavachari, Trucks, Pople, Head-Gordon, 1989

CCSD(T)

perturbative corrections on top of CCSD

- **fourth-order contribution**

$$\Delta E_T(4) = \frac{1}{36} \sum_{i,j,k} \sum_{a,b,c} \frac{|w_{ijk}^{abc}|^2}{(\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c)}$$

$$w_{ijk}^{abc} = P(ij/k)P(ab/c) \left\{ \sum_e \langle bc||ek\rangle \; t_{ij}^{ae} - \sum_m \langle mc||jk\rangle \; t_{im}^{ab} \right\}$$

computed with CCSD amplitudes

- **fifth-order contribution**

$$\Delta E_T(5) = \frac{1}{36} \sum_{i,j,k} \sum_{a,b,c} \frac{w_{ijk}^{abc} \widetilde{w}_{ijk}^{abc}}{(\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c)}$$

$$\widetilde{w}_{ijk}^{abc} = P(ij/k)P(ab/c) \; \langle bc||jk\rangle \; t_i^a$$

permutation operator: $P(pq/r) \; Z(pqr) = Z(pqr) + Z(qrp) + Z(rpq)$

CCSD(T)

computational cost

$$w_{ijk}^{abc} \quad = \quad P(ij/k)P(ab/c)\left\{\sum_{e} \langle bc||ek\rangle \; t_{ij}^{ae} - \sum_{m} \langle mc||jk\rangle \; t_{im}^{ab}\right\}$$

one summaton index (e or m)

six target index (i,j,k,a,b,c)

=>

cost scale with $n_{occ}^{3}N_{virt}^{4}$

CCSD(T): cost N^6 per iteration, N^7 for non-iterative step

no need to store T_3 amplitudes

„gold standard“ of quantum chemistry

Accuracy of Approximate Treatments of Triples

deviation from FCI and CCSDT (in mH) for CO

	Δ(FCI)	Δ(CCSDT)
CCSD	12.12	11.11
CCSDT-1	0.13	-0.88
CCSDT-2	1.52	0.51
CCSDT-3	1.47	0.46
CC3	0.12	-0.89
CCSD(T)	1.47	0.46
CCSD+T	-0.05	-1.06

calculations with cc-pVDZ basis, frozen core

Further Developments

perturbative triples

- **Λ-CCSD(T)** Crawford, Stanton, 1999

  replaces $T_3^\dagger$ by Λ_3 Kucharski, Bartlett, 1999

  slightly more stable

- **CCSD(T-n), n=2,3,4,...** Eriksen et al., 2014

  most rigorous treatment

  n=4 required to match CCSD(T)

perturbative quadruples

- **CCSDT(Q)** Bomble et al., 2005

  non-iterative N^9 analogue to CCSD(T)

- **CCSDT(Q-n), n=2,3,4,...** Eriksen et al., 2015

  most rigorous treatment

XII.

Computational Thermochemistry: A Perfect Playground for CC Theory

Computational Thermochemistry

quantum-chemical calculation of thermochemical energies via energy differences

most often computed:

atomization energies **heats of formation**

calculation involves:

electronic part **non-electronic part**

e.g. vibrational corrections

Chemical Accuracy

accuracy required for realistic chemical predictions

1 kcal/mol $\widehat{=}$ **4.184 kJ/mol**

$4.33 \cdot 10^{-2}$ eV

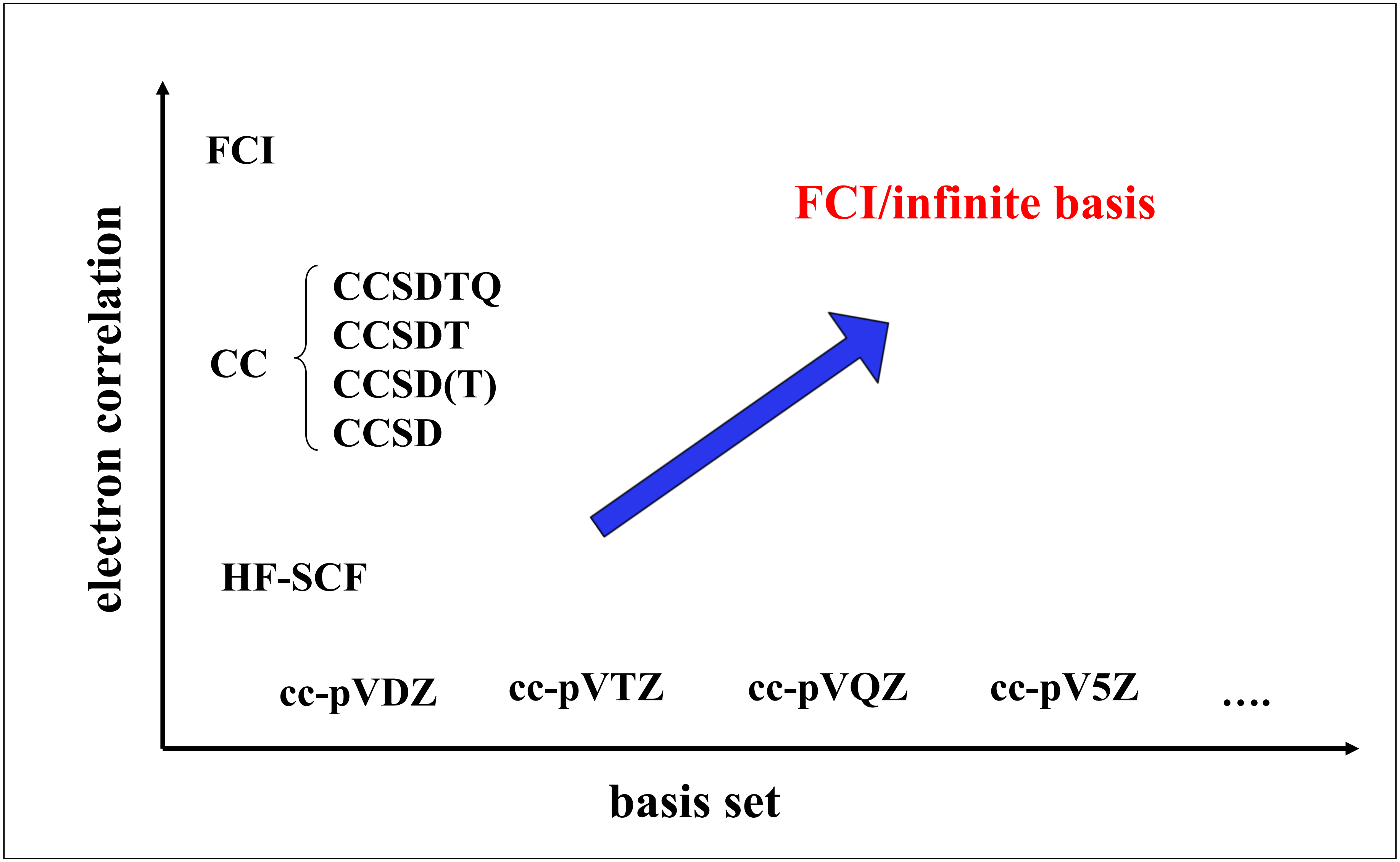
350 cm^{-1}

1.59 mHartree

sub-chemical accuracy: **1 kJ/mol and better**

density-functional theory not accurate enough

Approximate Quantum Chemistry



electron correlation

FCI

FCI/infinite basis

CC

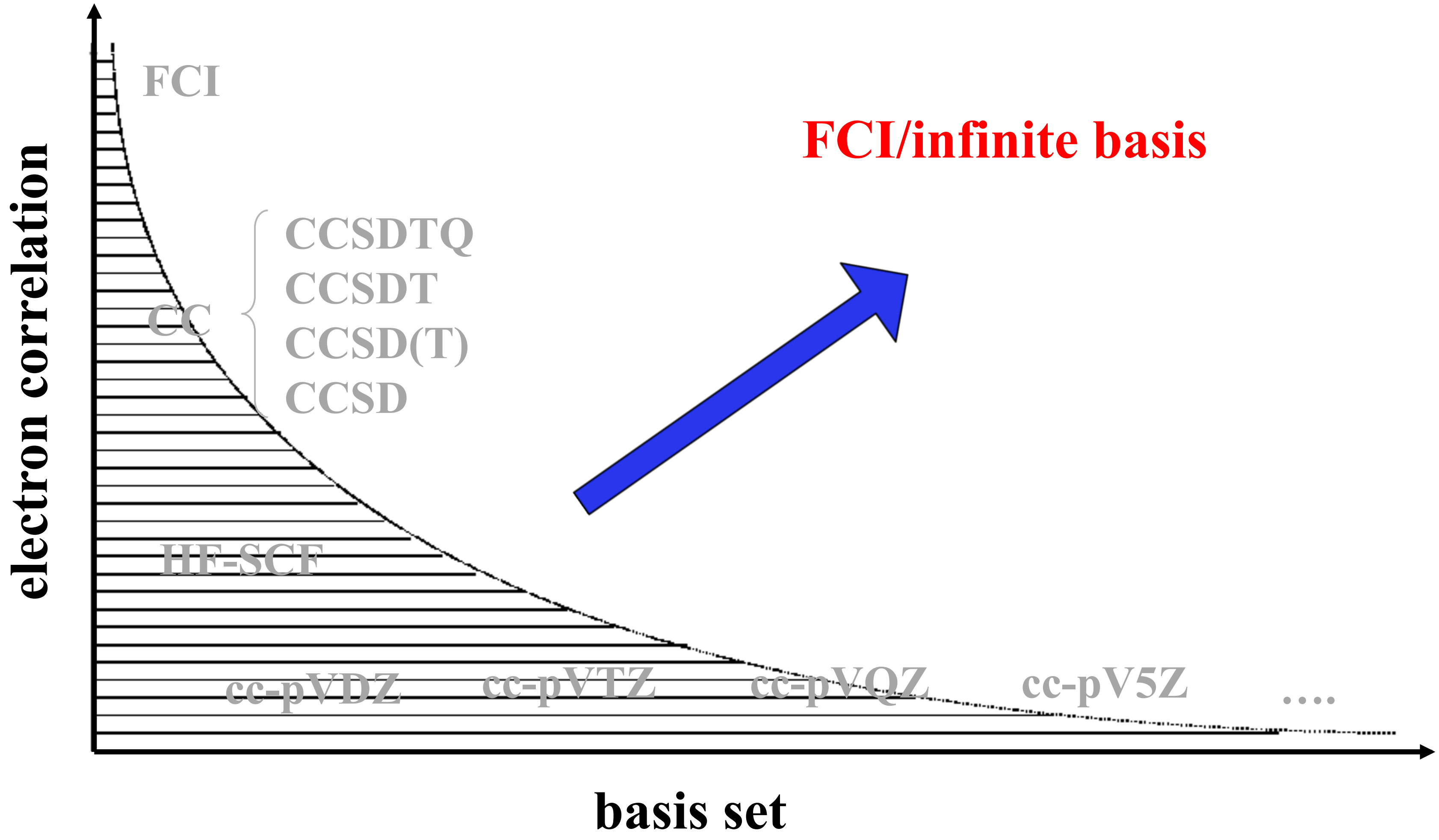
- CCSDTQ
- CCSDT
- CCSD(T)
- CCSD

HF-SCF

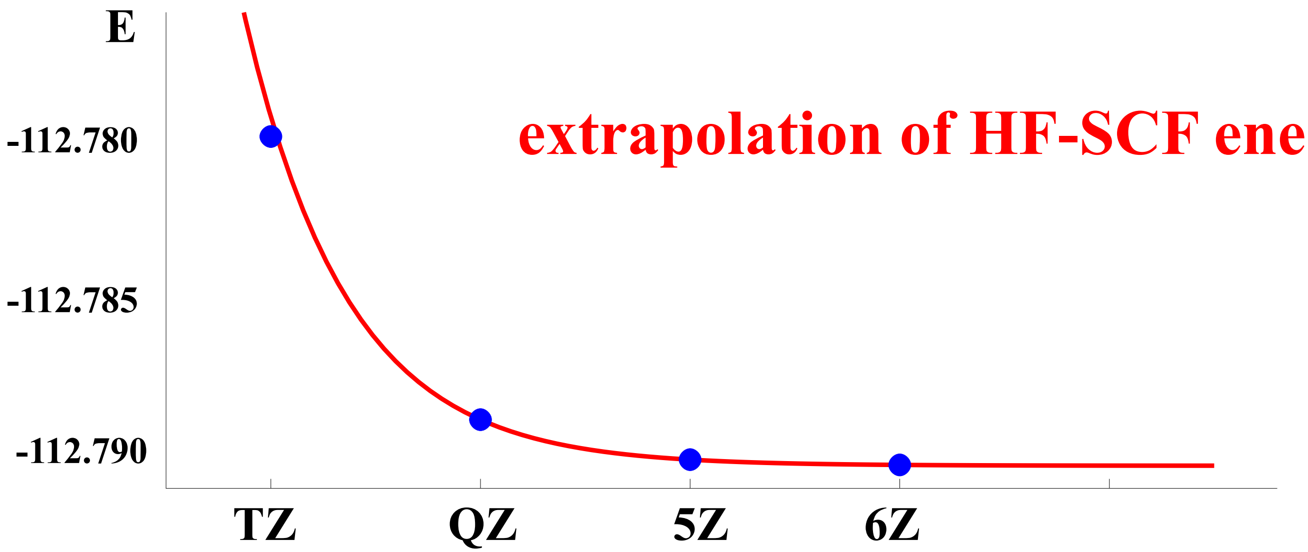
cc-pVDZ cc-pVTZ cc-pVQZ cc-pV5Z ….

basis set

Approximate Quantum Chemistry



Basis-Set Extrapolation: HF Energy



extrapolation of HF-SCF energy

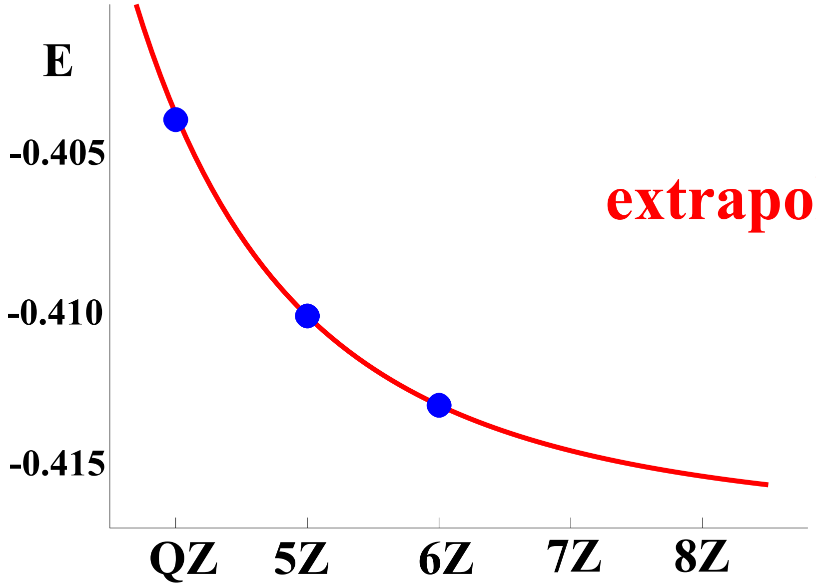
$$E(\text{HF-SCF/aug-cc-pVXZ}) = E^{\infty}(\text{HF-SCF}) + a \exp(-bX)$$

extrapolated value

***a*, *b*, and *E*∞(HF-SCF) from 3 HF-SCF energies**

D. Feller, *J. Chem. Phys.* **98**, 7059 (1993)

Basis-Set Extrapolation: Correlation Energy



extrapolation of CC energy

$$\Delta E^{\infty}(\mathrm{CC}) = \Delta E(\mathrm{CC/aug\text{-}cc\text{-}pVXZ}) - \frac{c}{X^3}$$

extrapolated value

c and $\Delta E\infty(\mathrm{CC})$ from 2 CC energies

Helgaker et al., *J. Chem. Phys.* **106**, 9639 (1997)

High-accuracy Extrapolated Ab-initio Thermochemistry

HF-SCF	extrapolated (Q56)
+ ΔCCSD(T)	extrapolated (ae, 56)
+ ΔCCSDT	extrapolated (fc, TQ)
+ ΔCCSDTQ	fc, cc-pVDZ
+ ΔCCSDTQP	fc, cc-pVDZ
+ scalar relativistic	CCSD(T)/aug-cc-pCVTZ
+ SO splittings	MRCISD/cc-pVDZ+PP
+ ZPE (anharm.)	CCSD(T)/cc-pVQZ
+ DBOC	CCSD/aug-cc-pCVQZ

Tajti et al., *J. Chem. Phys*. **121**, 11599 (2004)

Bomble et al., *J. Chem. Phys*. **125**, 064108 (2006) Harding et al., *J. Chem. Phys*. **128**, 114111 (2008)

HEAT: Atomization Energy of CO

HF-SCF	730.13	extrapolated (Q56)
ΔCCSD(T)	356.53	extrapolated (ae, 56)
ΔCCSDT	-2.37	extrapolated (fc, TQ)
ΔCCSDTQ	2.22	fc, cc-pVDZ
ΔCCSDTQP	0.13	fc, cc-pVDZ
scalar relativistic	-0.65	**CCSD(T)/aug-cc-pCVTZ**
SO splittings	-1.20	**MRCISD/cc-pVDZ+PP**
ZPE (anharm.)	-12.99	**CCSD(T)/cc-pVQZ**
DBOC	0.02	**CCSD/aug-cc-pCVQZ**
Sum (Theory)	1071.83	
Experiment	1072.13±0.09	

all energies in kJ/mol

Harding et al., *J. Chem. Phys*. **128**, 114111 (2008)

Statistical Evaluation

High-accuracy **E**xtrapolated **A**b-initio **T**hermochemistry

atomization energies of

N_2, H_2, F_2, CO, O_2, C_2H_2, CCH, CH_2, CH, CH_3,
CO_2, H_2O_2, H_2O, HCO, HF, HO_2, NO, OH

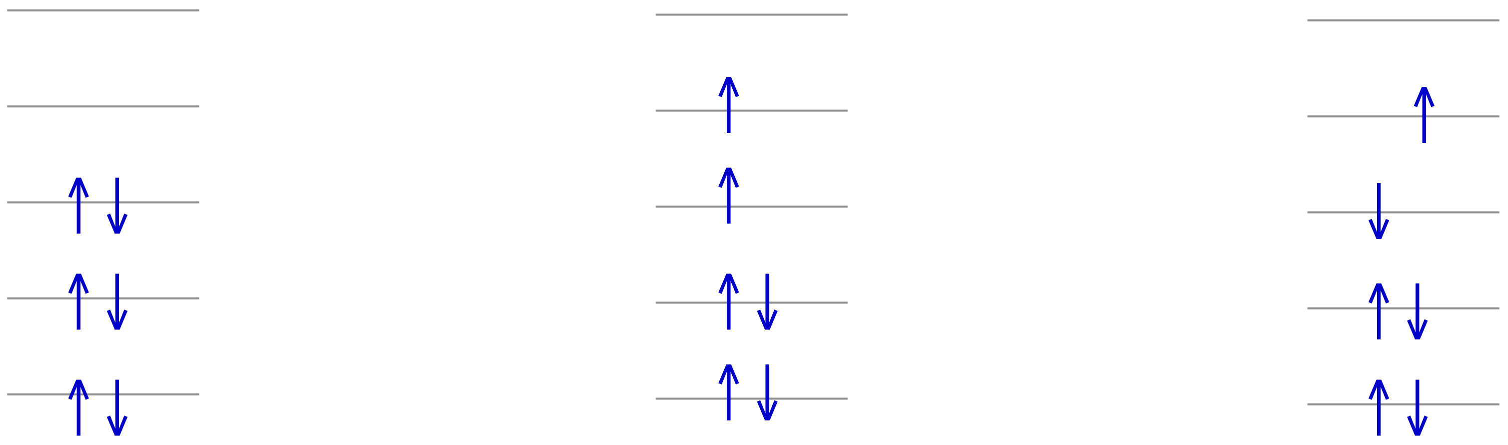
mean error	max. error	RMS error
-0.24	0.87	0.42

Harding et al., *J. Chem. Phys*. **128**, 114111 (2008)

XIII.

Closed- and Open-Shell CC Methods

Closed- and Open-Shell Systems



closed shell

⇒ RHF reference

spin-adapted
CC formalism

high-spin
open-shell

⇒ UHF, ROHF reference

spin-orbital
CC formalism

low-spin
open-shell

⇒ multi-
determinantal
description

no routine
CC treatment

Closed-Shell CC Approaches

restricted HF reference

$$|0\rangle \;\hat{=}\; \frac{1}{\sqrt{N!}}\,|\phi_1\bar{\phi}_1 \;\ldots\; \phi_{N/2}\bar{\phi}_{N/2}|$$

doubly occupied spatial orbitals

α spin orbital

β spin orbital

=> relationships among two-electron integrals

$$\langle pq|rs\rangle = \langle\bar{p}\bar{q}|\bar{r}\bar{s}\rangle = \langle p\bar{q}|r\bar{s}\rangle = \ldots$$

$$\langle pq||rs\rangle = \langle p\bar{q}|r\bar{s}\rangle - \langle p\bar{q}|s\bar{r}\rangle$$

Closed-Shell CC Approaches

non-vanishing spin cases for amplitudes

$$t_i^a = t_{\bar i}^{\bar a} \qquad t_{ij}^{ab} = t_{\bar i\bar j}^{\bar a\bar b} \qquad t_{i\bar j}^{a\bar b} = t_{\bar j i}^{\bar b a} = -t_{i\bar j}^{\bar b a} = -t_{\bar j i}^{a\bar b}$$

αα ββ αααα ββββ αβαβ βαβα αββα βααβ

in addition

$$t_{ij}^{ab} = t_{i\bar j}^{a\bar b} - t_{i\bar j}^{b\bar a} \qquad t_{i\bar j}^{a\bar b} = t_{j\bar i}^{b\bar a}$$

only αα (singles) and αβαβ (doubles) required

Closed-Shell CC: Spin Integration

closed-shell CCD

- **consider only αβαβ amplitude equations**

$$0 \quad = \quad \langle \Phi_{i\bar{j}}^{a\bar{b}} | \;\exp(-T_2)\; H \;\exp(T_2)\; |0\rangle$$

- **consider only non-zero contributions based on spin cases**

$$\cdots + \sum_{e} \widetilde{\mathcal{F}}_{ae}\, t_{i\bar{j}}^{e\bar{b}} \; + \xcancel{\sum_{e} \widetilde{\mathcal{F}}_{a\bar{e}}\, t_{i\bar{j}}^{\bar{e}\bar{b}}} + \;\ldots$$

- **rewrite all terms using αα and αβαβ quantities**

$$\widetilde{\mathcal{W}}_{m\bar{b}e\bar{j}}\, t_{im}^{ae} \;+\; \widetilde{\mathcal{W}}_{\bar{m}\bar{b}\bar{e}\bar{j}}\, t_{i\bar{m}}^{a\bar{e}}$$

$$= \quad \frac{1}{2}(2\,\widetilde{\mathcal{W}}_{m\bar{b}e\bar{j}} \;+\; \widetilde{\mathcal{W}}_{m\bar{b}\bar{e}j})\;(2\, t_{i\bar{m}}^{a\bar{e}} \;-\; t_{i\bar{m}}^{e\bar{a}}) \;+\; \frac{1}{2}\,\widetilde{\mathcal{W}}_{m\bar{b}\bar{e}j}\, t_{i\bar{m}}^{e\bar{a}}$$

=> **CCD equations in terms of $\mathbf{f_{pq}}, \langle \mathbf{p\bar{q}} | \mathbf{r\bar{s}} \rangle$, and $\mathbf{t_{ij}^{ab}}$**

Closed-Shell CCD

- **amplitude equations**

$$\begin{aligned} 0 \;=\; & \langle a\bar{b}|i\bar{j}\rangle \;+\; P_-(ab)\sum_e \widetilde{\mathcal{F}}_{ae} t^{e\bar{b}}_{i\bar{j}} \;-\; P_-(ij)\sum_m \widetilde{\mathcal{F}}_{mi}\, t^{a\bar{b}}_{m\bar{j}} \\ & + \sum_{m,n} \mathcal{W}_{m\bar{n}i\bar{j}}\, t^{a\bar{b}}_{m\bar{n}} \;+\; \sum_{e,f} \langle a\bar{b}|e\bar{f}\rangle\, t^{e\bar{f}}_{i\bar{j}} \\ & + \frac{1}{2} P_+(ia,jb) \sum_m \sum_e \Big[(2\,\widetilde{\mathcal{W}}_{m\bar{b}e\bar{j}} \;+\; \widetilde{\mathcal{W}}_{m\bar{b}\bar{e}j})\,(2\,t^{a\bar{e}}_{i\bar{m}} \;-\; t^{a\bar{e}}_{m\bar{i}}) \\ & \qquad\qquad + \frac{1}{2}\,\widetilde{\mathcal{W}}_{m\bar{b}\bar{e}j}\, t^{a\bar{e}}_{m\bar{i}} - \widetilde{\mathcal{W}}_{m\bar{b}\bar{e}i}\, t^{a\bar{e}}_{m\bar{j}} \Big] \end{aligned}$$

- **actual (optimal) computational cost**

$$\frac{\mathbf{1}}{\mathbf{2}}\; \mathbf{n}^{\mathbf{4}}_{\mathbf{occ}} \mathbf{N}^{\mathbf{2}}_{\mathbf{virt}} \;+\; \mathbf{4}\; \mathbf{n}^{\mathbf{3}}_{\mathbf{occ}} \mathbf{N}^{\mathbf{3}}_{\mathbf{virt}} \;+\; \frac{\mathbf{1}}{\mathbf{4}}\; \mathbf{n}^{\mathbf{2}}_{\mathbf{occ}} \mathbf{N}^{\mathbf{4}}_{\mathbf{virt}}$$

- **automatically spin adapted**

Open-Shell CC Approaches: UHF-CC

unrestricted HF reference

$$|0\rangle \;\hat{=}\; \frac{1}{\sqrt{(N_\alpha + N_\beta)!}}\,|\phi_1^\alpha \;\ldots\; \phi_{N_\alpha}^\alpha \bar{\phi}_1^\beta \;\ldots\; \bar{\phi}_{N_\beta}^\beta|$$

different spatial parts for α and β spin orbitals

non-vanishing spin cases for amplitudes

t_i^a	$t_{\bar{i}}^{\bar{a}}$	t_{ij}^{ab}	$t_{\bar{i}\bar{j}}^{\bar{a}\bar{b}}$	$t_{i\bar{j}}^{a\bar{b}} =$	$t_{\bar{j}i}^{\bar{b}a} =$	$-t_{i\bar{j}}^{\bar{b}a} =$	$-t_{\bar{j}i}^{a\bar{b}}$
αα	ββ	αααα	ββββ	αβαβ	βαβα	αββα	βααβ

αα and ββ (singles) and αααα, ββββ, and αβαβ (doubles) required

Open-Shell CC Approaches: UHF-CC

spin-integrated UHF-CCD equations

αααα /ββββ spin cases

$$
\begin{aligned}
0 \quad = \quad & \langle ab|ij\rangle \; + \; P_-(ab)\sum_e \widetilde{\mathcal{F}}_{ae} t_{ij}^{eb} \; - \; P_-(ij)\sum_m \widetilde{\mathcal{F}}_{mi}\, t_{mj}^{ab} \\
& + \sum_{m<n} \mathcal{W}_{mnij}\, t_{mn}^{ab} \; + \sum_{e<f} \langle ab|ef\rangle\, t_{ij}^{ef} \\
& + P_-(ij)P_-(ab)\left(\sum_m\sum_e \widetilde{\mathcal{W}}_{mbej} t_{im}^{ae} + \sum_{\bar{m}}\sum_{\bar{e}} \widetilde{\mathcal{W}}_{\bar{m}b\bar{e}j} t_{i\bar{m}}^{a\bar{e}}\right)
\end{aligned}
$$

equations are not spin adapted!

Open-Shell CC Approaches: UHF-CC

αβαβ spin case

$$
\begin{aligned}
0 \; = \; & \langle a\bar{b}|i\bar{j}\rangle + \sum_{e} \widetilde{\mathcal{F}}_{ae} t_{i\bar{j}}^{e\bar{b}} + \sum_{\bar{e}} \widetilde{\mathcal{F}}_{\bar{b}\bar{e}} t_{i\bar{j}}^{a\bar{e}} - \sum_{m} \widetilde{\mathcal{F}}_{mi}\, t_{m\bar{j}}^{a\bar{b}} - \sum_{\bar{m}} \widetilde{\mathcal{F}}_{\bar{m}\bar{j}}\, t_{i\bar{m}}^{a\bar{b}} \\
& + \sum_{m,n} \mathcal{W}_{m\bar{n}i\bar{j}}\, t_{m\bar{n}}^{a\bar{b}} + \sum_{e,f} \langle a\bar{b}|e\bar{f}\rangle\, t_{i\bar{j}}^{e\bar{f}} \\
& + \sum_{m}\sum_{e} \widetilde{\mathcal{W}}_{m\bar{b}e\bar{j}} t_{im}^{ae} + \sum_{\bar{m}}\sum_{\bar{e}} \widetilde{\mathcal{W}}_{\bar{m}\bar{b}\bar{e}\bar{j}} t_{i\bar{m}}^{a\bar{e}} + \sum_{m}\sum_{e} \widetilde{\mathcal{W}}_{maei} t_{m\bar{j}}^{e\bar{b}} \\
& + \sum_{\bar{m}}\sum_{\bar{e}} \widetilde{\mathcal{W}}_{\bar{m}a\bar{e}i} t_{\bar{m}\bar{j}}^{\bar{e}\bar{b}} + \sum_{\bar{m}}\sum_{e} \widetilde{\mathcal{W}}_{\bar{m}ae\bar{j}} t_{i\bar{m}}^{e\bar{b}} + \sum_{m}\sum_{\bar{e}} \widetilde{\mathcal{W}}_{m\bar{b}\bar{e}i} t_{m\bar{j}}^{a\bar{e}}
\end{aligned}
$$

actual (optimal) computational cost

$$\frac{5}{2}\ \mathrm{n}_{\mathrm{occ}}^{4}\mathrm{N}_{\mathrm{virt}}^{2} + 20\ \mathrm{n}_{\mathrm{occ}}^{3}\mathrm{N}_{\mathrm{virt}}^{3} + \frac{3}{2}\ \mathrm{n}_{\mathrm{occ}}^{2}\mathrm{N}_{\mathrm{virt}}^{4}$$

4-5 times more expensive than RHF-CCD/CCSD

Open-Shell CC Approaches: ROHF-CC

restricted open-shell HF (ROHF) reference

$$|0\rangle \;\hat{=}\; \frac{1}{\sqrt{(N_\alpha + N_\beta)!}} \, |\phi_1 \; \ldots \; \phi_{N_\alpha} \bar{\phi}_1 \; \ldots \; \bar{\phi}_{N_\beta}|$$

same spatial parts for α and β spin orbitals

αα and ββ (singles) and αααα, ββββ, and αβαβ (doubles) required

actual (optimal) computational cost

$$2.5\, n_{occ}^{4} N_{virt}^{2} + 20\, n_{occ}^{3} N_{virt}^{3} + 1.5\, n_{occ}^{2} N_{virt}^{4}$$

essentially the same cost as UHF-CC

Spin-Orbital Based CC Methods

- T contains spin-orbital excitations
- no spin properties enforced
- since $[S^2, T] \neq 0$ in case of open-shell systems

$\Rightarrow$ **truncated CC wavefunctions no spin eigenfunctions**

- **UHF-CC**

$$\langle S^2 \rangle_{UHF} \neq s(s+1) \quad \text{and} \quad \langle S^2 \rangle_{CC} \neq s(s+1)$$

- **ROHF-CC**

$$\langle S^2 \rangle_{ROHF} = s(s+1) \quad \text{but} \quad \langle S^2 \rangle_{CC} \neq s(s+1)$$

Spin-Adaption in CC Theory

- generators of the unitary group

$$[S^2, E_i^a] = 0 \quad \textbf{with} \quad E_i^a = \sum_{\sigma=\alpha,\beta} a^\dagger_{a\sigma}\, a_{i\sigma}$$

summation
over spins

- closed-shell CC
  - T can be rewritten in terms of $\mathrm{E_i^a}$
  - spin adaptation trival
- open-shell CC
  - usage of $\mathrm{E_i^a}$ leads to non-commuting excitation operators

$$T_1 = \sum_i \sum_a t_i^a\, E_i^a, \quad \dots \quad => \quad [E_i^a, E_j^b] = \delta_{ib} E_j^a - \delta_{aj} E_i^b$$

singly occupied orbital appears as occupied and virtual

Current Status of Open-Shell CC Theory

- spin-orbital approaches (UHF, ROHF reference)
  - standard choice
- unitary-group based approaches
  - rigorously spin adapted
  - complicated, automatized implementations

Janssen, Schaefer, 1991

Li, Paldus, 1994

- partially spin-adapted approaches
  - open-shell orbital(s) not spin adapted
  - much simpler

Janssen, Schaefer, 1991

Knowles, Hampel, Werner, 1993

Neogrády, Urban, Hubač, 1994

- spin-restricted approaches
  - exact CC spin-expectation value

Szalay, Gauss, 1997

- spin-free combinatoric approaches
  - unitary group based, spin adapted
  - modified exponential ansatz

Datta, Mukherjee, 2008

XIII.

Analytic Energy Derivatives in CC Theory

CC Lagrangian

- **CC theory is nonvariational**
  - **direct differentiation of CC energy involves derivatives of amplitudes**

    => computationally inefficient!!
  - **efficient formulation of CC gradients via so-called CC Lagrangian**

- **CC Lagrangian**

Lagrange multipliers

$$L_{CC} = \langle 0|\exp(-T)H\exp(T)|0\rangle + \sum_I \lambda_I \langle \Phi_I|\exp(-T)H\exp(T)|0\rangle$$

energy

CC equations as constraints

Lambda Operator

$$L_{CC} = \langle 0|\exp(-T)H\exp(T)|0\rangle + \sum_I \lambda_I \, \langle \Phi_I|\exp(-T)H\exp(T)|0\rangle$$

compact notation

$$L_{CC} = \langle 0| \; (1+\Lambda) \; \exp(-T) \; H \; \exp(T) \; |0\rangle$$

Λ deexcitation operator

$$\Lambda = \Lambda_1 + \Lambda_2 + \ldots$$

$$\Lambda_1 = \sum_i \sum_a \lambda_a^i \; a_i^\dagger a_a \qquad \Lambda_2 = \frac{1}{4} \sum_{i,j} \sum_{a,b} \lambda_{ab}^{ij} \; a_i^\dagger a_a a_j^\dagger a_b$$

diagrammatic representation

Stationarity Conditions

wrt λ-amplitudes

$$\frac{\partial L_{CC}}{\partial \lambda_I} = 0 \qquad \Rightarrow \qquad 0 \;=\; \langle \Phi_I |\, \exp(-T) H \exp(T) | 0 \rangle$$

CC equations

wrt t-amplitudes

$$\frac{\partial L_{CC}}{\partial t_I} = 0 \qquad \Rightarrow \qquad 0 \;=\; \langle 0 | (1 \;+\; \Lambda) \; (\exp(-T) H \exp(T) \;-\; E) | \Phi_I \rangle$$

Λ equations

stationarity => (2n+1) rule for t-amplitudes and (2n+2) for λ-ampliutudes

CC Gradients

- **differentiate CC Lagrangian wrt perturbation *x***

$$L_{CC} = \langle 0|\ (1+\Lambda)\ \exp(-T)\ H\ \exp(T)\ |0\rangle$$

- **exploit (2n+1) and (2n+2) rule**

$$\frac{\partial E}{\partial x} = \langle 0|\ (1\ +\ \Lambda)\ \exp(-T)\ \frac{\partial H}{\partial x}\ \exp(T)\ |0\rangle$$

no perturbed t- and λ-amplitudes required!

CCD Gradients

- **cluster operator** $T = T_2$
- **Lambda operator** $\Lambda = \Lambda_2$
- **CCD Lagrangian**

$$L_{CCD} = \langle 0 | \ (1 + \Lambda_2) \ \exp(-T_2) \ H \ \exp(T_2) \ | 0 \rangle$$

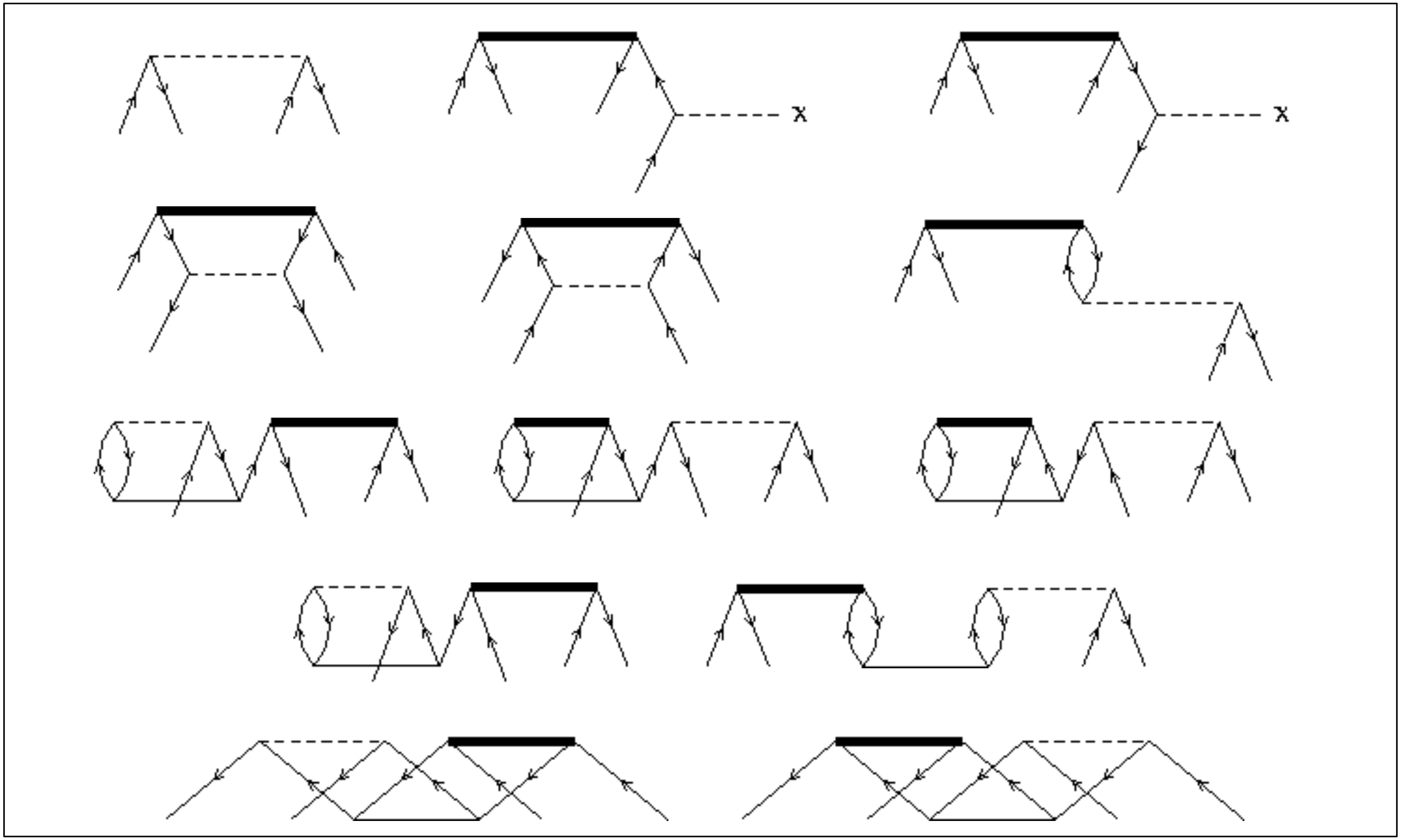
- **CCD amplitude equations**

$$0 = \langle \Phi_D | \ \exp(-T_2) \ H \ \exp(T_2) \ | 0 \rangle$$

- **CCD lambda equations**

$$0 = \langle 0 | \ (1 + \Lambda_2) \ (\exp(-T_2) \ H \ \exp(T_2) \ - \ E_{CCD}) \ | \Phi_D \rangle$$

Λ Equations for CCD: Diagrams



Λ Equations for CCD: Algebraic Form

$$\begin{aligned}
0 \;=\; & \langle ij||ab\rangle \;+\; P_{-}(ab)\sum_{e}\;\lambda^{ij}_{eb}\,\Big\{f_{ea} \;-\; \frac{1}{2}\sum_{m,n}\sum_{f}\,\langle mn||af\rangle\; t^{ef}_{mn}\Big\} \\
& -\; P_{-}(ij)\sum_{m}\;\lambda^{mj}_{ab}\,\Big\{f_{im} \;+\; \frac{1}{2}\sum_{n}\sum_{e,f}\; t^{ef}_{mn}\,\langle in||ef\rangle\Big\} \\
& +\; \frac{1}{2}\sum_{mn}\;\lambda^{mn}_{ab}\,\Big\{\langle ij||mn\rangle \;+\; \frac{1}{2}\sum_{ef}\,\langle ij||ef\rangle\; t^{ef}_{mn}\Big\} \\
& +\; \frac{1}{2}\sum_{ef}\;\lambda^{ij}_{ef}\,\Big\{\langle ef||ab\rangle \;+\; \frac{1}{2}\sum_{mn}\,\langle mn||ab\rangle\; t^{ef}_{mn}\Big\} \\
& +\; P_{-}(ij)P_{-}(ab)\sum_{m}\sum_{e}\;\lambda^{im}_{ae}\,\Big\{\langle ej||mb\rangle \;+\; \sum_{n}\sum_{f}\,\langle nj||fb\rangle\; t^{ef}_{mn}\Big\} \\
& -\; \frac{1}{2}P_{-}(ab)\sum_{mn}\sum_{ef}\,\langle ij||eb\rangle\; t^{ef}_{mn}\;\lambda^{mn}_{af} \;-\; \frac{1}{2}P_{-}(ij)\sum_{mn}\sum_{ef}\,\langle mj||ab\rangle\; t^{ef}_{mn}\;\lambda^{in}_{ef}
\end{aligned}$$

(perturbation independent) linear equations for λ amplitudes

Density Matrices in CC Gradient Theory

introduction of density matrices

$$\frac{\partial E}{\partial x} = \langle 0|\ (1 + \Lambda)\ \exp(-T)\ \frac{\partial H}{\partial x}\ \exp(T)\ |0\rangle$$

$$= \sum_{p,q} D_{pq} \frac{\partial f_{pq}}{\partial x} + \frac{1}{4} \sum_{p,q,r,s} \Gamma_{pqrs} \frac{\partial \langle pq||rs\rangle}{\partial x}$$

reduced one-particle density matrix

$$\langle 0|(1+\Lambda)\exp(-T)\{a_p^\dagger a_q\}\exp(T)|0\rangle$$

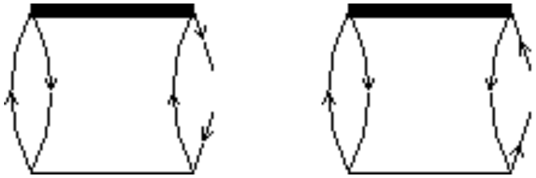
reduced two-particle density matrix

$$\langle 0|(1+\Lambda)\exp(-T)\{a_p^\dagger a_q^\dagger a_s a_r\}\exp(T)|0\rangle$$

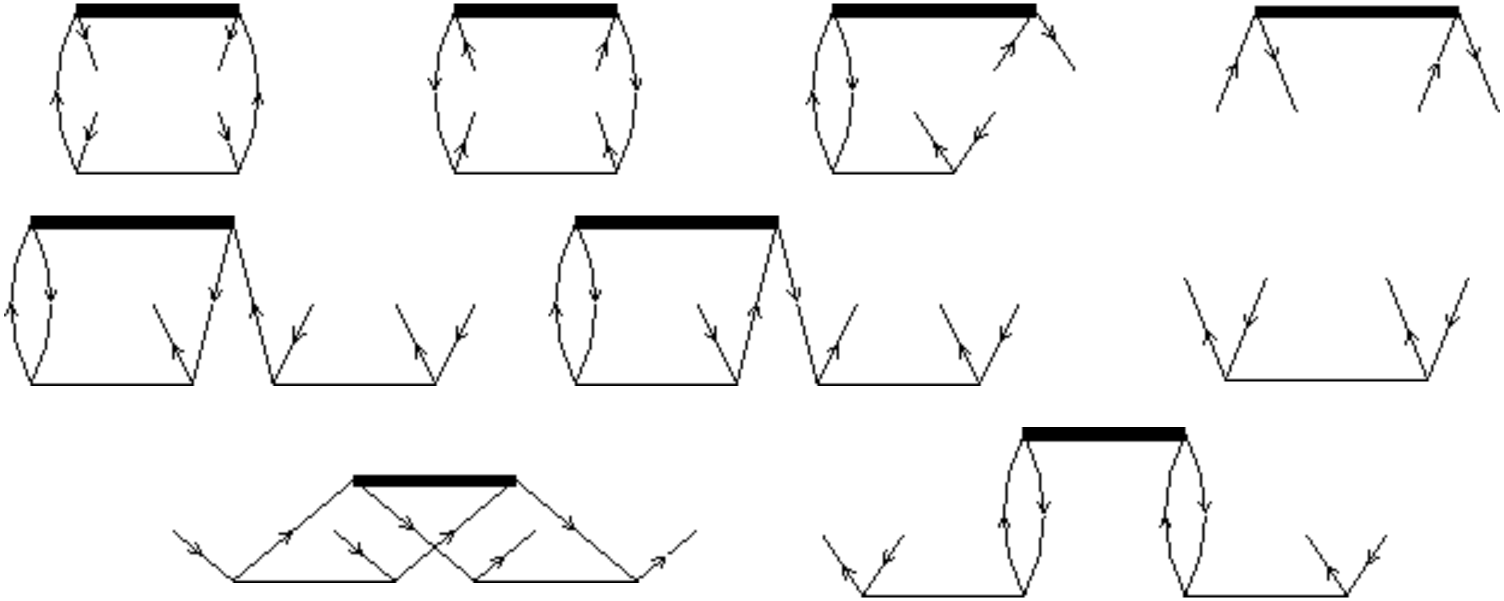
gradients in terms of integral derivatives and density matrices

Diagrams for CCD Density Matrices

- **one-particle density matrix**



- **two-particle density matrix**



Algebraic Expressions for CCD Density Matrices

- **one-particle density matrix**

$$D_{ij} = -\frac{1}{2}\sum_{m}\sum_{e,f} \lambda^{jm}_{ef}\, t^{ef}_{im} \qquad D_{ab} = \frac{1}{2}\sum_{m,n}\sum_{e} \lambda^{mn}_{ae}\, t^{be}_{mn}$$

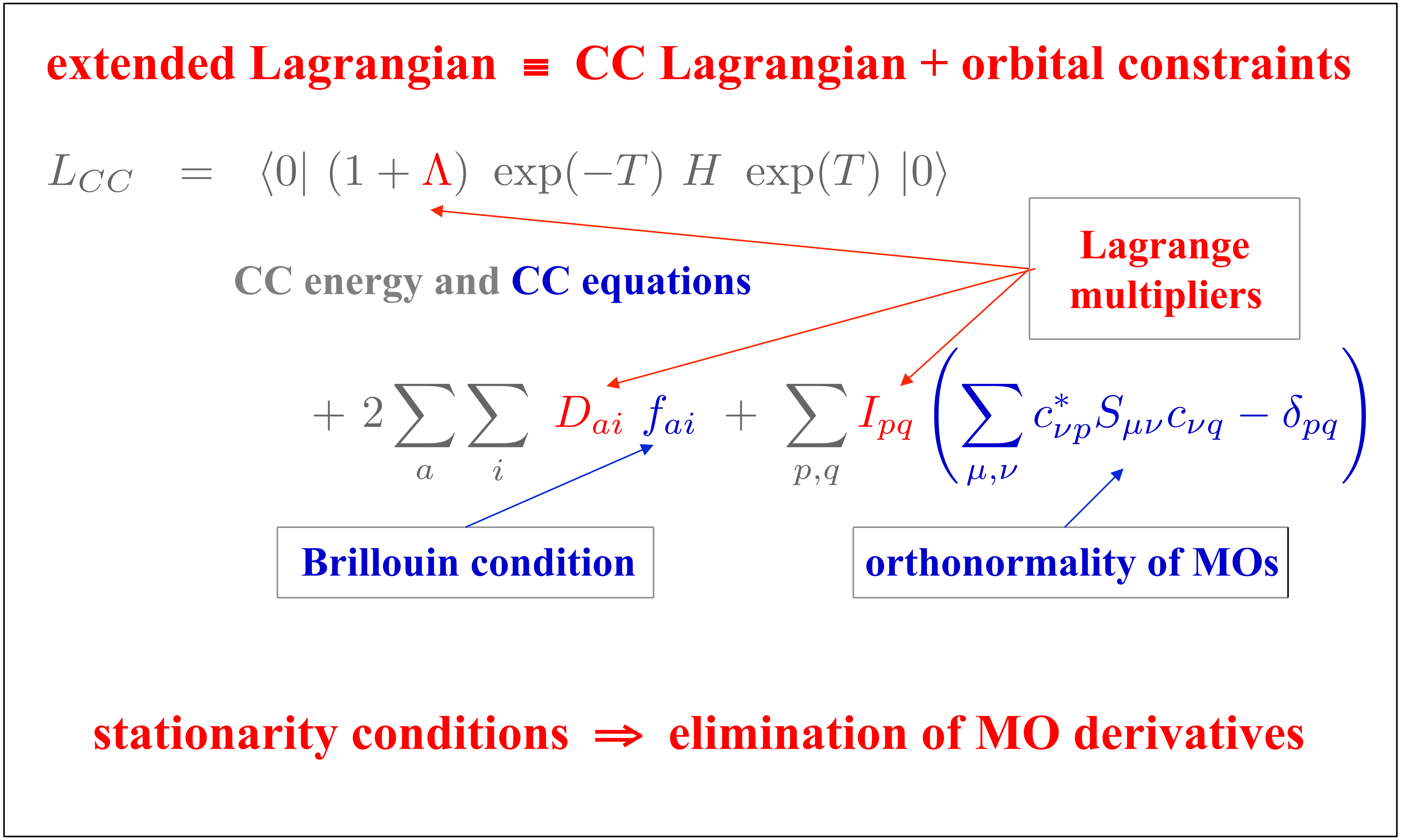
- **two-particle density matrix**

$$\Gamma_{ijkl} = \frac{1}{2}\sum_{e,f} \lambda^{kl}_{ef}\, t^{ef}_{ij} \qquad \Gamma_{abcd} = \frac{1}{2}\sum_{m,n} \lambda^{mn}_{ab}\, t^{cd}_{mn}$$

$$\Gamma_{ajib} = \sum_{m}\sum_{e} \lambda^{im}_{ae}\, t^{be}_{jm} \qquad \Gamma_{abij} = \lambda^{ij}_{ab}$$

$$\begin{aligned}\Gamma_{ijab} = {} & t^{ab}_{ij} + \frac{1}{4}\sum_{m,n}\sum_{e,f} \lambda^{mn}_{ef}\, t^{ef}_{ij}\, t^{ab}_{mn} + \frac{1}{2}P_{-}(ij)P_{-}(ab)\sum_{m,n}\sum_{e,f} \lambda^{mn}_{ef}\, t^{ae}_{im}\, t^{bf}_{jm} \\ & - \frac{1}{2}P_{-}(ab)\sum_{m,n}\sum_{e,f} \lambda^{mn}_{ef}\, t^{eb}_{mn}\, t^{af}_{ij} - \frac{1}{2}P_{-}(ij)\sum_{m,n}\sum_{e,f} \lambda^{mn}_{ef}\, t^{ef}_{mj}\, t^{ab}_{in}\end{aligned}$$

CC Gradients with Orbital Relaxation



extended Lagrangian ≡ CC Lagrangian + orbital constraints

$$L_{CC} = \langle 0| \; (1+\Lambda) \; \exp(-T) \; H \; \exp(T) \; |0\rangle$$

CC energy and CC equations

Lagrange multipliers

$$+ \, 2 \sum_{a} \sum_{i} D_{ai} \; f_{ai} \; + \sum_{p,q} I_{pq} \left(\sum_{\mu,\nu} c^{*}_{\nu p} S_{\mu\nu} c_{\nu q} - \delta_{pq} \right)$$

Brillouin condition

orthonormality of MOs

stationarity conditions ⇒ elimination of MO derivatives

CC Gradients with Orbital Relaxation

parameterization of orbital changes

$$c'_{\mu p} = \sum_q c_{\mu q} \, T_{qp}$$

matrix *T*

$$\left(\begin{array}{c|c} \text{occ-occ} & \text{occ-vrt} \\ \hline \text{vrt-occ} & \text{vrt-vrt} \end{array}\right)$$

general (non-unitary) transformation

stationarity requirements

(1) $$\frac{\partial L_{CC}}{\partial T_{ab}} = 0 \implies \underline{I_{ab}}$$

(2) $$\frac{\partial L_{CC}}{\partial T_{ia}} = 0 \implies \underline{I_{ai} + I_{ia}}$$

(3) $$\frac{\partial L_{CC}}{\partial T_{ai}} = 0 \implies$$ **Z-vector equations for D$_{ai}$**

(4) $$\frac{\partial L_{CC}}{\partial T_{ij}} = 0 \implies \underline{I_{ij}}$$

Z-Vector Equations for CC Gradients

Z-vector equations

$$\sum_m \sum_e D_{em}[\langle ae||im\rangle \ + \ \langle am||ie\rangle \ + \ \delta_{ae}\,\delta_{im}\,(\varepsilon_a \ - \varepsilon_i)] \ = \ -X_{ai}$$

with

$$\begin{aligned} X_{ai} \ &= \ \frac{1}{4}\sum_{p,q,r}(\Gamma_{ipqr}\ \langle ap||qr\rangle \ + \ \Gamma_{qrip}\ \langle qr||ap\rangle) \\ &- \ \frac{1}{4}\sum_{p,q,r}(\Gamma_{apqr}\ \langle ip||qr\rangle \ + \ \Gamma_{qrap}\ \langle qr||ip\rangle) \\ &+ \ \frac{1}{2}\sum_{p,q} D_{pq}\ (\langle pa||qi\rangle \ + \ \langle pi||qa\rangle) \end{aligned}$$

linear equations for orbital relaxation contribution to D_{ai}

CC Gradients with Orbital Relaxation

differentiation of „extended“ CC Lagrangian

Hamiltonian with AO derivative integrals

$$\begin{aligned}\frac{\partial L_{CC}}{\partial x} &= \langle 0|\,(1 + \Lambda)\,\exp(-T)\,H^{x}\,\exp(T)\,|0\rangle \\ &+ 2\sum_{i}\sum_{a} D_{ai}\sum_{\mu,\nu} c_{\mu a}\left\{\frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma,\rho} D^{SCF}_{\sigma\rho}\,\frac{\partial\langle\mu\sigma||\nu\rho\rangle}{\partial x}\right\} c_{\nu i} \\ &+ \sum_{p,q} I_{pq}\sum_{\mu,\nu} c^{*}_{\mu p}\,\frac{\partial S_{\mu\nu}}{\partial x}\,c_{\nu q}\end{aligned}$$

AO derivative integrals

contains no derivative of wavefunction parameters

AO Formulation of CC Gradients

differentiation of „extended“ energy functional

$$\frac{\partial E}{\partial x} = \sum_{p,q} D_{pq}\, f_{pq}^{(x)} + \frac{1}{4}\sum_{p,q,r,s} \Gamma_{pqrs}\, \langle pq||rs\rangle^{x} + \sum_{p,q} I_{pq}\, S_{pq}^{x}$$

integral derivatives contain no MO derivative contributions

reformulation in AO representation

$$\frac{\partial E}{\partial x} = \sum_{\mu\nu} D_{\mu\nu}\left(\frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma,\rho} D_{\sigma\rho}^{SCF}\frac{\partial\langle\mu\sigma||\nu\rho\rangle}{\partial x}\right) + \frac{1}{4}\sum_{\mu,\nu,\sigma,\rho}\Gamma_{\mu\nu\sigma\rho}\frac{\partial\langle\mu\sigma||\nu\rho\rangle}{\partial x} + \sum_{\mu,\nu} I_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial x}$$

density matrices and intermediates back transformed to AO basis

Implementation of CC Gradients

required steps for gradients

CC and Λ equations ($\sim N^6, N^8, \ldots$)

CC density matrices ($\sim N^6, N^8, \ldots$)

MO → AO transformation of density matrices ($\sim N^5$)

contraction with integral derivatives (**no storage**, $\sim N^4$)

computational cost do not scale with N_{pert}

Historical Remarks

– **CC Lambda operator**	Arponen, 1983 Adamowicz, Bartlett, 1984
– **Z-vector method**	Handy, Schaefer, 1984
– **Lagrangian technique**	Jørgensen, Helgaker, 1988
– **CCSD gradients**	Schaefer and co-workers, 1987
– **open-shell CCSD gradients**	Gauss, Stanton, Bartlett 1991
– **CCSD(T) gradients**	Scuseria, 1991, Lee, Rendell 1991 Watts, Gauss, Bartlett, 1992
– **CCSDT gradients**	Gauss, Stanton 2001
– **general CC gradients**	Kállay, Szalay, Gauss, 2003

Accuracy of CC Geometrical Parameters

calculated r(OH) for H_2O (in Å)

	CI	CC
SD	0.96131	0.96435
SD(T)		0.96575
SDT	0.96251	0.96583
SDTQ	0.96593	0.96614
SDTQP	0.96606	0.96616
SDTQPH	0.96616	0.96616
FCI	0.96616	

calculations with cc-pVDZ basis

XIV.

Availability and Applicability

Standard CC Approaches

CCSD	N^6	many programs such as
CCSD(T)	N^7	ACES2, ACES3, CFOUR, DALTON, GAUSSIAN, GAMESS, MOLCAS, MOLPRO, NWCHEM, ORCA, PSI, PySCF, Q-CHEM, TURBOMOLE, …
CCSDT	N^8	ACES2, CFOUR, NWCHEM
CCSDT(Q)	N^9	CFOUR, MRCC
CCSDTQ	N^{10}	
…		

XV.

What is Still Missing?

Further Topics (not covered)

large molecules (linear scaling)

e.g., local CC methods (→ F. Neese)

explicitly-correlated CC methods

R12-CC and F12-CC

higher excitations in CC theory

general CC
automatized implementation
string-based methods

relativistic effects

4- and 2-component CC (→ L. Visscher)

multi-reference treatments

e.g., Mk-MRCC, ic-MRCC (not routine!)

properties via CC methods

analytic CC derivatives
response theory
(→ T. Helgaker, J. Olsen)

excited states via CC methods

equation-of-motion (EOM) CC
CC response theory (→ Friday)

other open-shell CC methods

EOM-IP-CC
Fock-space CC