Coupled-Cluster Theory

Lecture Series in Electronic Structure Theory, Summer 2010

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References

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Introduction

The purpose of all many-body methods is to describe *electron correlation*.

- Löwdin definition of correlation energy

$$\Delta E = E_{exact} - E_{HF}. \quad (1)$$

Since the variationally optimized Hartree-Fock energy is an upper bound to the exact energy, the correlation energy must be a negative value.

- There are three main methods for calculating electron correlation:
  - Configuration Interaction (CI)
  - Many-Body Perturbation Theory (MBPT) or (MPPT)
  - Coupled-Cluster Theory (CC)

HF theory recovers 99% of overall energy.

But,

lots of important chemistry happen in the remaining 1%.

Conventions and Notation

Level	Symbol	Name	Alternative
1	S	singles	mono-substitutions
2	D	doubles	di–substitutions
3	T	triples	tri–substitutions
4	Q	quadraples	tetra–substitutions
5	P/5	pentuples	penta–substitutions
6	H/6	hextupels	hexa–substitutions

$i, j, k, \ldots$ occupied orbitals or holes.

$a, b, c, \ldots$ virtual, unoccupied orbitals or particles.

$p, q, r, \ldots$ generic orbitals

$\hat{i}, \hat{a}, \hat{F}, \hat{H}, \ldots$ or $\mathscr{H}, \mathscr{F}, \mathscr{V}, \mathscr{W}, \ldots$ or $\Lambda, \Omega, \ldots$

ϕ or φ

Φ_0 or Ψ_0 or $|0\rangle$

Extensivity and Consistencivity

- Size-extensive
  - The energy of a non-interacting system computed with this model scales correctly with the size of the system, which satisfy

$$E(N\text{He}) = NE(\text{He})$$

.

- Size-consistency
  - The energies of two systems A and B and of the combined system AB with A and B very far apart, computed in equivalent ways, satisfy

$$E(\text{AB}) = E(\text{A}) + E(\text{B})$$

.

The Exponential Ansatz

The essential idea in CC theory is the ground state wave function $|\Psi_0\rangle$ can be given by the exponential ansatz

$$
\begin{aligned}
|\Psi_{CC}\rangle &= e^{\hat{T}}|\Phi_0\rangle, && (2)\\
&= \left(1+\hat{T}+\frac{\hat{T}^2}{2!}+\frac{\hat{T}^3}{3!}+\dots\right)|\Phi_0\rangle. && (3)
\end{aligned}
$$

$$
\begin{aligned}
\hat{T} &= \hat{T}_1+\hat{T}_2+\hat{T}_3+\dots, && (4)\\
\hat{T}_1|\Phi_0\rangle &= \sum_{i,a} t_i^a \Phi_i^a, && (5)\\
\hat{T}_2|\Phi_0\rangle &= \sum_{\substack{i>j\\a>b}} t_{ij}^{ab}\Phi_{ij}^{ab}, && (6)\\
\hat{T}_2^2|\Phi_0\rangle &= \sum_{\substack{i>j\\a>b}}\sum_{\substack{k>l\\c>d}} t_{ij}^{ab}t_{kl}^{cd}\Phi_{ijkl}^{abcd} && (7)
\end{aligned}
$$

Basic Considerations in CC Theory

The non-relativistic time-independent Schrödinger equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle, \tag{8}$$

and can be written as

$$\begin{aligned} \hat{H}e^{\hat{T}}|\Phi_0\rangle &= Ee^{\hat{T}}|\Phi_0\rangle, \\ e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle &= Ee^{-\hat{T}}e^{\hat{T}}|\Phi_0\rangle \\ e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle &= E|\Phi_0\rangle. \end{aligned} \tag{9}$$

The energy and amplitude expressions can be obtained from Eq. 9 left-multiplying by the reference and an excited state determinant, respectively, and integrating over all space

$$\langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E, \tag{10}$$

$$\langle\Phi_{ij\ldots}^{ab\ldots}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0. \tag{11}$$

CCD Equations

If we consider,

$$\Psi_{\text{CCD}} = e^{\hat{T}_2}|\Phi_0\rangle \tag{12}$$

and substitute to $\hat{H}\Psi = E\Psi$, we can get

$$\hat{H}e^{\hat{T}_2}|\Phi_0\rangle = E_{\text{CCD}}e^{\hat{T}_2}|\Phi_0\rangle \tag{13}$$

$$\langle\Phi_0|\hat{H} - E_{\text{CCD}}|e^{\hat{T}_2}\Phi_0\rangle = 0 \tag{14}$$

$$\langle\Phi_0|\hat{H} - E_{\text{CCD}}|\left(1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2{}^2 + \frac{1}{3!}\hat{T}_2{}^3 + \ldots.\right)\Phi_0\rangle = 0 \tag{15}$$

$$\begin{aligned} E_{\text{CCD}} &= \langle\Phi_0|\hat{H}|\Phi_0\rangle + \langle\Phi_0|\hat{H}\hat{T}_2|\Phi_0\rangle, & (16)\\ &= E_{\text{HF}} + \sum_{\substack{i>j\\a>b}} \langle\Phi_0|\hat{H}|\Phi_{ij}^{ab}\rangle t_{ij}^{ab}, & (17)\\ &= E_{\text{HF}} + \sum_{\substack{i>j\\a>b}} \langle ij||ab\rangle t_{ij}^{ab}. & (18) \end{aligned}$$

CCD Equations

$$\langle\Phi_{ij}^{ab}|\hat{H}-E_{\text{CCD}}|e^{\hat{T}_2}\Phi_0\rangle = 0 \tag{19}$$

$$\langle\Phi_{ij}^{ab}|\hat{H}|\Phi_0\rangle + \langle\Phi_{ij}^{ab}|\hat{H}-E_{\text{CCD}}\hat{T}_2|\Phi_0\rangle + \langle\Phi_{ij}^{ab}|\hat{H}-E_{\text{CCD}}\frac{1}{2}\hat{T}_2^2|\Phi_0\rangle = 0 \tag{20}$$

$$\langle\Phi_{ij}^{ab}|\hat{H}|\Phi_0\rangle + \langle\Phi_{ij}^{ab}|\hat{H}-E_{\text{CCD}}|\Phi_{kl}^{cd}\rangle t_{kl}^{cd} + \frac{1}{2}\sum_{\substack{k>l>m>n\\c>d>e>f}}\langle\Phi_{ij}^{ab}|\hat{H}-E_{\text{CCD}}|\Phi_{klmn}^{cdef}\rangle t_{kl}^{cd}t_{mn}^{ef} = 0 \tag{21}$$

$\hat{T} = \hat{T}_2 \longrightarrow$ CCD

$\hat{T} = \hat{T}_1 + \hat{T}_2 \longrightarrow$ CCSD

$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \longrightarrow$ CCSDT

Full CI *vs.* Full CC

$$\Psi_{\mathrm{CI}} = \left(1 + \hat{C}\right)|\Phi_0\rangle \qquad \Psi_{\mathrm{CC}} = e^{\hat{T}}|\Phi_0\rangle$$

$$\hat{C} = \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \hat{C}_4 + \cdots \qquad \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots$$

$$\begin{aligned} e^{\hat{T}} &= 1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2{}^2 + \frac{1}{3!}\hat{T}_2{}^3 + \cdots \\ &= 1 + \left(\hat{T}_1 + \hat{T}_2 + \cdots\right) + \frac{1}{2}\left(\hat{T}_1 + \hat{T}_2 + \cdots\right)^2 + \cdots \\ &= 1 + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right) + \left(\hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3\right) + \qquad (22) \\ &\quad \left(\hat{T}_4 + \hat{T}_1\hat{T}_3 + \frac{1}{2!}\hat{T}_2^2 + \frac{1}{2!}\hat{T}_1^2\hat{T}_2 + \frac{1}{4!}\hat{T}_1^4\right) + \cdots \qquad (23) \end{aligned}$$

$$|\Psi\rangle = |\Psi_0\rangle + \sum_S c_{\mathrm{S}}|S\rangle + \sum_D c_{\mathrm{D}}|D\rangle + \sum_T c_{\mathrm{T}}|T\rangle + \sum_Q c_{\mathrm{Q}}|Q\rangle + \cdots$$

Second Quantization

Second-quantization techniques evolved primarily for problems in which the number of particles is not fixed or known and in the context of independent-particle models.

We assumes the existence of an unspecified number of functions in a given fixed ***one-particle basis***, say

$$\{\phi_i\} = \{\phi_1, \phi_2, \phi_3, \ldots\}\,, \tag{24}$$

In general, the functions ψ_i are ***spinorbitals***, and we assume that the basis is orthonormal

$$\langle\phi_i|\phi_j\rangle = \delta_{ij} \tag{25}$$

The given one-particle basis generates ***Hilbert spaces*** for $N = 1, 2, ...$ particles, for which the basis functions are products of N one-particle basis functions. However, since we are dealing with fermions, we will restrict the many-particle functions to be antisymmetric and thus assume a many-particle basis constructed of Slater determinants made up of the one-particle basis functions.

Creation and Annihilation Operators

The representation of a normalized Slater determinant

$$\Phi = \Phi_{ijk\ldots} \equiv \mathcal{A}(\varphi_i \varphi_j \varphi_k \cdots) \equiv |\varphi_i \varphi_j \varphi_k \cdots\rangle \equiv |ijk \cdots\rangle \tag{26}$$

where $\mathcal{A}$ is the antisymmetrizer and each φ is a spinorbital in our one-particle basis.

The Slater determinant (SD) Φ is represented in ***second-quantized*** form by specifying the ***occupancies*** (or ***occupation numbers***) $n1, n2, \ldots$ of the basis spinorbitals $\varphi_1, \varphi_2, \ldots$ in the determinant.

$$n_i\,(\Phi) = \begin{cases} 0 & \text{if } \phi_i \text{ is empty} \\ 1 & \text{if } \phi_j \text{ is occupied} \end{cases}, (i = i, 2, \ldots) \tag{27}$$

The determinant itself (and various operators on it) are represented in terms of a set of *creation and annihilation operators*.

- Creation operator for φ_i, $\hat{X}_i^\dagger$, $\hat{c}_i^\dagger$, $\hat{i}_i^\dagger$ or $\hat{a}_i^\dagger$
- Annihilation operator for φ_i, $\hat{X}_i$, $\hat{c}$, $\hat{i}_i$ or $\hat{a}_i$

Here we shall use $\hat{a}_i^\dagger$ and $\hat{a}_i$.

Creation and Annihilation Operators

- An annihilation operator which is the adjoin of the creation operator

$$\left(\hat{a}_i^\dagger\right)^\dagger = \hat{a}_i \tag{28}$$

- Creation and annihilation operators defined in terms of their action on SD

$$\hat{a}_i^\dagger|jk\cdots\rangle = |ijk\cdots\rangle \tag{29}$$

$$\hat{a}_i|ijk\cdots\rangle = |jk\cdots\rangle \tag{30}$$

- A given SD may be written as a chain of creation operators acting on the true vacuum

$$\hat{a}_p^\dagger\hat{a}_q^\dagger\cdots\hat{a}_s^\dagger|\ \rangle = |\phi_p\phi_q\cdots\phi_s\rangle. \tag{31}$$

- An annihilation operator acting on the vacuum state gives a zero result,

$$\hat{a}_p|\ \rangle = 0. \tag{32}$$

$$\hat{a}_i^\dagger|\Phi\rangle = 0 \qquad \text{if } n_i(\Phi) = 1, \tag{33}$$

$$\hat{a}_i|\Phi\rangle = 0 \qquad \text{if } n_i(\Phi) = 0, \tag{34}$$

Permutation Operator and Anticommutation Relations

- It is convenient to arrange the spinorbitals in an SD in lexical order as $|ijk\cdots\rangle$, where $i > j > k > \cdots$ and therefore it is necessary define ***permutation operator***

$$\hat{P}|ijk\cdots\rangle = (-1)^{\sigma(\hat{P})}|ijk\cdots\rangle, \tag{35}$$

- Pairwise permutations of the operators introduce changes in the sign of the resulting determinant,

$$\hat{a}_q^\dagger \hat{a}_p^\dagger|\ \rangle = |\phi_q\phi_p\rangle = -|\phi_p\phi_q\rangle = -\hat{a}_p^\dagger \hat{a}_q^\dagger|\ \rangle. \tag{36}$$

- The ***anticommutation relation*** for a pair of creation operators is simply

$$\left[\hat{a}_p^\dagger, \hat{a}_q^\dagger\right]_+ = \hat{a}_p^\dagger \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p^\dagger = \hat{0}. \tag{37}$$

- The analogous relation for a pair of annihilation operators is

$$\left[\hat{a}_p, \hat{a}_q\right]_+ = \hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = \hat{0}. \tag{38}$$

- The anticommutation relation for the “mixed” product is

$$\left[\hat{a}_p^\dagger, \hat{a}_q\right]_+ = \left[\hat{a}_p, \hat{a}_q^\dagger\right]_+ = \hat{a}_p^\dagger \hat{a}_q + \hat{a}_q \hat{a}_p^\dagger = \hat{\delta}_{pq}, \tag{39}$$

Normal Order for Second Quantized Operators

- "all annihilation operators ($\hat{a}_i^\dagger$ and $\hat{a}_a$) standing to the right of all creation operators ($\hat{a}_i$ and $\hat{a}_a^\dagger$) ."

$$\begin{aligned}\hat{A} &= \hat{a}_p\hat{a}_q^\dagger\hat{a}_r\hat{a}_s^\dagger \\ &= \delta_{pq}\hat{a}_r\hat{a}_s^\dagger - \hat{a}_q^\dagger\hat{a}_p\hat{a}_r\hat{a}_s^\dagger \\ &= \delta_{pq}\delta_{rs} - \delta_{pq}\hat{a}_s^\dagger\hat{a}_r - \delta_{rs}\hat{a}_q^\dagger\hat{a}_p + \hat{a}_q^\dagger\hat{a}_p\hat{a}_s^\dagger\hat{a}_r \\ &= \delta_{pq}\delta_{rs} - \delta_{pq}\hat{a}_s^\dagger\hat{a}_r - \delta_{rs}\hat{a}_q^\dagger\hat{a}_p + \delta_{ps}\hat{a}_q^\dagger\hat{a}_r - \hat{a}_q^\dagger\hat{a}_s^\dagger\hat{a}_p\hat{a}_r . \qquad (40)\end{aligned}$$

The quantum mechanical expectation value of this operator in the true vacuum state, $|\,\rangle$,

$$\begin{aligned}\langle\,|\hat{A}|\,\rangle &= \langle\,|\delta_{pq}\delta_{rs}|\,\rangle - \langle\,|\delta_{pq}\hat{a}_s^\dagger\hat{a}_r|\,\rangle - \langle\,|\delta_{rs}\hat{a}_q^\dagger\hat{a}_p|\,\rangle + \langle\,|\delta_{ps}\hat{a}_q^\dagger\hat{a}_r|\,\rangle - \langle\,|\hat{a}_q^\dagger\hat{a}_s^\dagger\hat{a}_p\hat{a}_r|\,\rangle \\ &= \delta_{pq}\delta_{rs}, \qquad (41)\end{aligned}$$

The matrix element of $\hat{A}$ between the single-particle states, $\langle\phi_t|$ and $|\phi_u\rangle$, $\langle\phi_t|\hat{A}|\phi_u\rangle = \langle\,|\hat{a}_t\hat{A}\hat{a}_u^\dagger|\,\rangle$ and a new operator, $\hat{B} \equiv \hat{a}_t\hat{A}\hat{a}_u^\dagger$, we can express

$$\langle\phi_t|\hat{A}|\phi_u\rangle = \langle\,|\hat{B}|\,\rangle = \delta_{tu}\delta_{pq}\delta_{rs} + \delta_{tq}\delta_{ps}\delta_{ru} - \delta_{tq}\delta_{pu}\delta_{rs} - \delta_{ts}\delta_{pq}\delta_{ru}. \qquad (42)$$

Contraction

A contraction between two arbitrary annihilation/creation operators, A and B, is defined as

$$\overbrace{AB} \equiv AB - \{AB\} \tag{43}$$

where the notation $\{AB\}$ indicates the normal-ordered form of the pair.

- Case I

$$\overbrace{\hat{a}_p \hat{a}_q} = \hat{a}_p \hat{a}_q - \{\hat{a}_p \hat{a}_q\} = \hat{a}_p \hat{a}_q - \hat{a}_p \hat{a}_q = 0\ . \tag{44}$$

- Case II

$$\overbrace{\hat{a}_p^\dagger \hat{a}_q^\dagger} = \hat{a}_p^\dagger \hat{a}_q^\dagger - \{\hat{a}_p^\dagger \hat{a}_q^\dagger\} = \hat{a}_p^\dagger \hat{a}_q^\dagger - \hat{a}_p^\dagger \hat{a}_q^\dagger = 0\ . \tag{45}$$

- Case III

$$\overbrace{\hat{a}_p^\dagger \hat{a}_q} = \hat{a}_p^\dagger \hat{a}_q - \{\hat{a}_p^\dagger \hat{a}_q\} = \hat{a}_p^\dagger \hat{a}_q - \hat{a}_p^\dagger \hat{a}_q = 0\ . \tag{46}$$

- Case IV

$$\overbrace{\hat{a}_p \hat{a}_q^\dagger} = \hat{a}_p \hat{a}_q^\dagger - \{\hat{a}_p \hat{a}_q^\dagger\} = \hat{a}_p \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p = \delta_{pq}\ . \tag{47}$$

Wick's theorem

An arbitrary string of annihilation and creation operators, $ABCDE\cdots$, may be written as a linear combination of normal-ordered strings

$$\begin{aligned} ABCDE\cdots = & \{ABCDE\cdots\} + \sum_{singles} \{ABCDE\cdots\}\{ABCDE\cdots\} + \\ & \sum_{doubles} \{ABCDE\cdots\}\{ABCDE\cdots\} + \\ & \sum_{triples} \{ABCDEF\cdots\}\{ABCDEF\cdots\} + \cdots + \sum_{\substack{fully\\contracted\\terms}} \{\cdots\} \end{aligned} \tag{48}$$

$$\langle \Phi_0 | \{ABCD\cdots\} | \Phi_0 \rangle = 0 \tag{49}$$

$$\langle \Phi_0 | \{ABCD\cdots\} | \Phi_0 \rangle = \sum_{\substack{fully\\contracted\\terms}} \{ABC\ldots\} \tag{50}$$

Wick's theorem - Example

$$
\begin{aligned}
\langle\Phi_0|\{ABCD\}|\Phi_0\rangle = & \cancel{\langle\Phi_0|\{ABCD\}|\Phi_0\rangle} + \cancel{\langle\Phi_0|\{\wick{\c1 A \c1 B C D}\}|\Phi_0\rangle} + \\
& \cancel{\langle\Phi_0|\{\wick{A \c1 B \c1 C D}\}|\Phi_0\rangle} + \cancel{\langle\Phi_0|\{\wick{A B \c1 C \c1 D}\}|\Phi_0\rangle} + \\
& \cancel{\langle\Phi_0|\{\wick{\c1 A B \c1 C D}\}|\Phi_0\rangle} + \cancel{\langle\Phi_0|\{\wick{A \c1 B C \c1 D}\}|\Phi_0\rangle} + \\
& \cancel{\langle\Phi_0|\{\wick{\c1 A B C \c1 D}\}|\Phi_0\rangle} + \langle\Phi_0|\{\wick{\c1 A \c1 B \c2 C \c2 D}\}|\Phi_0\rangle + \\
& \langle\Phi_0|\{\wick{\c1 A \c2 B \c2 C \c1 D}\}|\Phi_0\rangle + \langle\Phi_0|\{\wick{\c1 A \c2 B \c1 C \c2 D}\}|\Phi_0\rangle
\end{aligned} \tag{51}
$$

The Fermi Vacuum and the Particle-Hole Formalism

A complete set of operators required to generate $|\Phi_0\rangle$ from the true vacuum

$$|\Phi_0\rangle = \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k^\dagger \ldots |\,\rangle \tag{52}$$

- ***Quasiparticle*** (*q-particle*) operators.
  - $\hat{a}_i^\dagger$ and $\hat{a}_a$ annihilate holes and particles.
  - $\hat{a}_i$ and $\hat{a}_a^\dagger$ create holes and particles

$$\overbracket{\hat{a}_i^\dagger \hat{a}_j} = \hat{a}_i^\dagger \hat{a}_j - \{\hat{a}_i^\dagger \hat{a}_j\} = \hat{a}_i^\dagger \hat{a}_j + \hat{a}_j \hat{a}_i^\dagger = \delta_{ij} \tag{53}$$

and

$$\overbracket{\hat{a}_a \hat{a}_b^\dagger} = \hat{a}_a \hat{a}_b^\dagger - \{\hat{a}_a \hat{a}_b^\dagger\} = \hat{a}_a \hat{a}_b^\dagger + \hat{a}_b^\dagger \hat{a}_a = \delta_{ab} \; . \tag{54}$$

$$\overbracket{\hat{a}_a^\dagger \hat{a}_b} = \overbracket{\hat{a}_i \hat{a}_j^\dagger} = 0. \tag{55}$$

$$\overbracket{\hat{a}_a^\dagger \hat{a}_i} = \overbracket{\hat{a}_i \hat{a}_a^\dagger} = \overbracket{\hat{a}_a \hat{a}_i^\dagger} = \overbracket{\hat{a}_i^\dagger \hat{a}_a} = \overbracket{\hat{a}_a^\dagger \hat{a}_i^\dagger} = \overbracket{\hat{a}_i^\dagger \hat{a}_a^\dagger} = \overbracket{\hat{a}_a \hat{a}_i} = \overbracket{\hat{a}_i \hat{a}_a} = 0 \; . \tag{56}$$

The Normal-Ordered Electronic Hamiltonian

One-electron operator

Using Wick's theorem, $\hat{a}_p^\dagger \hat{a}_q = \{\hat{a}_p^\dagger \hat{a}_q\} + \overline{\hat{a}_p^\dagger \hat{a}_q}$, we can write one-electron operator $\hat{F}$ as

$$\begin{aligned}
\hat{F} &= \sum_{pq} \langle p|\hat{f}|q\rangle \hat{a}_p^\dagger \hat{a}_q \\
&= \sum_{pq} \langle p|\hat{f}|q\rangle \{\hat{a}_p^\dagger \hat{a}_q\} + \sum_{pq} \langle p|\hat{f}|q\rangle \delta_{pq} \\
&= \sum_{pq} \langle p|\hat{f}|q\rangle \{\hat{a}_p^\dagger \hat{a}_q\} + \sum_{i} \langle i|\hat{f}|i\rangle \\
&= \hat{\mathscr{F}}_N + \sum_{i} \langle i|\hat{f}|i\rangle
\end{aligned} \tag{57}$$

where $\mathscr{F}_{\mathcal{N}}$ is the normal-product form of the operator.

$$\hat{\mathscr{F}}_N = \sum_{pq} \langle p|\hat{f}|q\rangle \{\hat{a}_p^\dagger \hat{a}_q\} \tag{58}$$

The Normal-Ordered Electronic Hamiltonian

$$\hat{\mathscr{F}}_N = \sum_{pq} \langle p|\hat{f}|q\rangle \{\hat{a}_p^\dagger \hat{a}_q\}, \tag{59}$$

Since $\langle 0|\hat{\mathscr{F}}_N|0\rangle = 0$, we have

$$\langle 0|\hat{\mathscr{F}}_N|0\rangle = \sum_i \langle i|\hat{f}|i\rangle, \qquad \hat{F} = \hat{\mathscr{F}}_N + \langle 0|\hat{F}|0\rangle, \tag{60}$$

and $\hat{\mathscr{F}}_N$ represents the difference between F and its Fermi-vacuum expectation value

$$\hat{\mathscr{F}}_N = \hat{F} - \langle 0|\hat{F}|0\rangle. \tag{61}$$

$\hat{\mathscr{F}}_N$ contains hole-hole, particle-particle and hole-particle terms,

$$\begin{aligned} \hat{\mathscr{F}}_N &= \sum_{ij} \hat{f}_{ij}\{\hat{a}_i^\dagger \hat{a}_j\} + \sum_{ab} \hat{f}_{ab}\{\hat{a}_a^\dagger \hat{a}_b\} + \sum_{ia} \hat{f}_{ia}\{\hat{a}_i^\dagger \hat{a}_a\} + \sum_{ia} \hat{f}_{ai}\{\hat{a}_a^\dagger \hat{a}_i\} \\ &= -\sum_{ij} \hat{f}_{ij}\hat{a}_j \hat{a}_i^\dagger + \sum_{ab} \hat{f}_{ab}\hat{a}_a^\dagger \hat{a}_b + \sum_{ia} \hat{f}_{ia}\hat{a}_i^\dagger \hat{a}_a + \sum_{ia} \hat{f}_{ai}\hat{a}_a^\dagger \hat{a}_i \end{aligned} \tag{62}$$

$\hat{\mathscr{F}}_N$ can be separated into diagonal and off-diagonal parts,

$$\begin{aligned} \hat{\mathscr{F}}_N &= \hat{\mathscr{F}}_N^d + \hat{\mathscr{F}}_N^o, \\ \hat{\mathscr{F}}_N^d &= \sum_p \hat{f}_{pp}\hat{a}_p^\dagger \hat{a}_p = \hat{\mathscr{F}}^d - \langle 0|\hat{F}^d|0\rangle, \\ \hat{\mathscr{F}}_N^o &= \sum_{pq} \hat{f}_{pq}\hat{a}_p^\dagger \hat{a}_q = \hat{\mathscr{F}}^o - \langle 0|\hat{F}^o|0\rangle = \hat{\mathscr{F}}^o. \end{aligned} \tag{63}$$

The Normal-Ordered Electronic Hamiltonian

Two-electron operator

$$\hat{\mathscr{W}}_N = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle \hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r \tag{64}$$

$$\overbrace{\hat a_p^\dagger \hat a_q^\dagger} = \overbrace{\hat a_p \hat a_q} = 0, \qquad \overbrace{\hat a_i^\dagger \hat a_j} = \delta ij, \qquad \overbrace{\hat a_a^\dagger \hat a_b} = 0 \tag{65}$$

We obtain,

$$\begin{aligned}\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r =& \{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\} + \cancel{\{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\}_{(p^\dagger q^\dagger)}} + \{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\}_{(q^\dagger s)} + \cancel{\{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\}_{(s r)}} + \{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\}_{(p^\dagger s)} + \\ & \{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\}_{(q^\dagger r)} + \{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\}_{(p^\dagger r)} + \cancel{\{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\}_{(p^\dagger q^\dagger)(s r)}} + \{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\}_{(p^\dagger s)(q^\dagger r)} + \{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\}_{(p^\dagger r)(q^\dagger s)} \\ =& \{\hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r\} + \delta_{qs}\{\hat a_p^\dagger \hat a_r\} - \delta_{ps}\{\hat a_q^\dagger \hat a_r\} + \\ & - \delta_{qr}\{\hat a_p^\dagger \hat a_s\} + \delta_{pr}\{\hat a_q^\dagger \hat a_s\} + -\delta_{ps}\delta_{qr} + \delta_{pr}\delta_{qs}\end{aligned} \tag{66}$$

$$\begin{aligned}\hat{\mathscr{W}} =& \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle \hat a_p^\dagger \hat a_q^\dagger \hat a_s \hat a_r + \frac{1}{4}\sum_{pqi}\langle pi||ri\rangle \hat a_p^\dagger \hat a_r - \frac{1}{4}\sum_{qri}\langle iq||ri\rangle \hat a_q^\dagger \hat a_r \\ & - \frac{1}{4}\sum_{psi}\langle pi||is\rangle \hat a_p^\dagger \hat a_s + \frac{1}{4}\sum_{qsi}\langle iq||is\rangle \hat a_q^\dagger \hat a_s - \frac{1}{4}\sum_{ij}\langle ij||ji\rangle + \frac{1}{4}\sum_{ij}\langle ij||ij\rangle\end{aligned} \tag{67}$$

The Normal-Ordered Electronic Hamiltonian

Using antisymmetrized two-electron integrals in Dirac's notation, $\langle pq||rs\rangle = -\langle pq||sr\rangle = -\langle qp||rs\rangle = \langle qp||sr\rangle$, we re-index sums and combine terms where appropriate to obtain

$$\hat{\mathscr{W}} = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\} + \sum_{pri}\langle pi||ri\rangle\{\hat{a}_p^\dagger\hat{a}_r\} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle. \tag{68}$$

The complete Hamiltonian is therefore

$$\begin{aligned}\hat{H} \quad = \quad & \sum_{pq}\langle p|h|q\rangle\{\hat{a}_p^\dagger\hat{a}_q\} + \sum_{pri}\langle pi||ri\rangle\{\hat{a}_p^\dagger\hat{a}_r\} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\} \\ & + \sum_i\langle i|h|i\rangle + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle.\end{aligned} \tag{69}$$

$$\hat{H} = \sum_{pq} f_{pq}\{\hat{a}_p^\dagger\hat{a}_q\} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\} + \langle\Phi_0|\hat{H}|\Phi_0\rangle \tag{70}$$

or

$$\hat{H} = \hat{\mathscr{F}}_N + \hat{\mathscr{V}}_N + \langle\Phi_0|\hat{H}|\Phi_0\rangle, \tag{71}$$

The Normal-Ordered Electronic Hamiltonian

The normal-ordered Hamiltonian (canonical HF) is

$$\hat{\mathscr{H}}_N = \hat{H} - \langle \Phi_0 | \hat{H} | \Phi_0 \rangle. \qquad (72)$$

where, $\hat{\mathscr{H}}_N = \hat{\mathscr{F}}_N + \hat{\mathscr{V}}_N$
But, more generally,

$$\hat{\mathscr{V}}_N = \hat{\mathscr{F}}_N^o + \hat{\mathscr{W}}_N \qquad (73)$$

The total normal-product Hamiltonian

$$\hat{\mathscr{H}}_N = \hat{\mathscr{F}}_N + \hat{\mathscr{W}}_N = \hat{\mathscr{F}}_N^d + \hat{\mathscr{F}}_N^o + \hat{\mathscr{W}}_N = \hat{\mathscr{F}}_N^d + \hat{\mathscr{V}}_N \qquad (74)$$

Simplification of the Coupled Cluster Hamiltonian

$$
\begin{aligned}
|\Psi_{CC}\rangle &= e^{\hat{T}}|\Phi_0\rangle, && (75)\\
&= \left(1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \ldots\right)|\Phi_0\rangle. && (76)
\end{aligned}
$$

$$
\begin{aligned}
\hat{H}e^{\hat{T}}|\Phi_0\rangle &= Ee^{\hat{T}}|\Phi_0\rangle,\\
\left(\hat{H} - \langle\Phi_0|\hat{H}|\Phi_0\rangle\right)e^{\hat{T}}|\Phi_0\rangle &= \left(E - \langle\Phi_0|\hat{H}|\Phi_0\rangle\right)e^{\hat{T}}|\Phi_0\rangle,\\
\hat{\mathscr{H}}_N e^{\hat{T}}|\Phi_0\rangle &= \Delta E e^{\hat{T}}|\Phi_0\rangle,\\
e^{-\hat{T}}\hat{\mathscr{H}}_N e^{\hat{T}}|\Phi_0\rangle &= \Delta E e^{-\hat{T}}e^{\hat{T}}|\Phi_0\rangle\\
e^{-\hat{T}}\hat{\mathscr{H}}_N e^{\hat{T}}|\Phi_0\rangle &= \Delta E|\Phi_0\rangle. && (77)
\end{aligned}
$$

$$
\begin{aligned}
\langle\Phi_0|e^{-\hat{T}}\hat{\mathscr{H}}_N e^{\hat{T}}|\Phi_0\rangle &= \Delta E, && (78)\\
\langle\Phi_{ij\ldots}^{ab\ldots}|e^{-\hat{T}}\hat{\mathscr{H}}_N e^{\hat{T}}|\Phi_0\rangle &= 0. && (79)
\end{aligned}
$$

Simplification of the Coupled Cluster Hamiltonian

$$\hat{T}_1 \equiv \sum_i \hat{t}_i = \sum_{ia} t_i^a \hat{a}_a^\dagger \hat{a}_i, \tag{80}$$

and

$$\hat{T}_2 \equiv \frac{1}{2} \sum_{ij} \hat{t}_{ij} = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i, \tag{81}$$

More generally, an n-orbital cluster operator may be defined as

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{ij\ldots ab\ldots}^{n} t_{ij\ldots}^{ab\ldots} \hat{a}_a^\dagger \hat{a}_b^\dagger \ldots \hat{a}_j \hat{a}_i. \tag{82}$$

Similarity-Transformed Normal-Ordered Hamiltonian

$$\hat{H}\Psi_k = E\Psi_k \tag{83}$$

$$\hat{H}\Omega\Omega^{-1}\Psi_k = E\Psi_k \tag{84}$$

$$\Omega^{-1}\hat{H}\Omega \;\; \Omega^{-1}\Psi_k = E\Omega^{-1}\Psi_k \tag{85}$$

$$\bar{H}\bar{\Psi_k} = E\bar{\Psi_k} \tag{86}$$

This change eigenvectors but not the eigenvalues of the operator.
The similarity-transformed normal-ordered Hamiltonian, $\bar{H} \equiv e^{-\hat{T}}\hat{H}_N e^{\hat{T}}$, we obtain

$$\begin{aligned}\bar{H} \quad = \quad & \hat{H} + \left[\hat{H},\hat{T}\right] + \frac{1}{2!}\left[\left[\hat{H},\hat{T}\right],\hat{T}\right] + \frac{1}{3!}\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right] + \\ & \frac{1}{4!}\left[\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right],\hat{T}\right] + \cdots .\end{aligned} \tag{87}$$

Campbell-Baker-Hausdorff Relationship

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \left(\hat{H}_N e^{\hat{T}}\right)_C \tag{88}$$

$$\langle\Phi_0| \left(\hat{H}_N e^{\hat{T}}\right)_C |\Phi_0\rangle = \Delta E, \tag{89}$$

$$\langle\Phi_{ij\ldots}^{ab\ldots}| \left(\hat{H}_N e^{\hat{T}}\right)_C |\Phi_0\rangle = 0. \tag{90}$$

The energy and T amplitudes can be obtained by solving equations 89 and 90, respectively.

In order to satisfy the generalized Hellmann–Feynman theorem and to calculate molecular properties, CC equations can be reformulated while introducing an antisymmetrized, perturbation-independent, deexcitation operator Λ

$$\Lambda = \Lambda_1 + \Lambda_2 + \ldots + \Lambda_n, \tag{91}$$

$$\Lambda_n = \left(\frac{1}{n!}\right)^2 \sum_{ij\ldots ab\ldots}^{n} \lambda_{ab\ldots}^{ij\ldots} \left\{i^\dagger j^\dagger \ldots ba\right\}. \tag{92}$$

$$\langle 0| \left(1+\Lambda\right) \left(\hat{H}_N e^{\hat{T}}\right)_C |0\rangle = \Delta E, \tag{93}$$

$$\langle 0| \left(1+\Lambda\right) \left(\hat{H}_N e^{\hat{T}}\right)_C - \Delta E|\Phi_{ij\ldots}^{ab\ldots}\rangle = 0. \tag{94}$$

The CCSD Energy Equation

$$\langle\Phi_0|\left(\hat{H}_N e^{(\hat{T}_1+\hat{T}_2)}\right)_C|\Phi_0\rangle = \Delta E, \tag{95}$$

$$\begin{aligned}\bar{H} = \hat{H}_N \Big(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \\ \frac{1}{2}\hat{T}_1\hat{T}_2^2 + \frac{1}{6}\hat{T}_2^3 + \frac{1}{24}\hat{T}_1^4 + \frac{1}{6}\hat{T}_1^3\hat{T}_2 + \frac{1}{4}\hat{T}_1^2\hat{T}_2^2 + \frac{1}{6}\hat{T}_1\hat{T}_2^3 + \frac{1}{24}\hat{T}_2^4\Big)_c\end{aligned} \tag{96}$$

but only survives,

$$\hat{H}_N\left(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right)_C \tag{97}$$

$$(\hat{F}_N + \hat{V}_N)\left(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right)_C \tag{98}$$

$$\left(\hat{F}_N + \hat{V}_N + \hat{F}_N\hat{T}_1 + \hat{F}_N\hat{T}_2 + \frac{1}{2}\hat{F}_N\hat{T}_1^2 + \hat{V}_N\hat{T}_1 + \hat{V}_N\hat{T}_2 + \frac{1}{2}\hat{V}_N\hat{T}_1^2\right)_C \tag{99}$$

The CCSD Energy Equation

We have,

$$\hat{F}_N = \sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} \quad (100)$$

$$\hat{V}_N = \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle\{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} \quad (101)$$

$$\hat{T}_1 = \frac{1}{2}\sum_{ai} t_i^a\{\hat{a}_a^\dagger \hat{a}_i\} \quad (102)$$

$$\hat{T}_2 = \frac{1}{4}\sum_{abij} t_{ij}^{ab}\{\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i\} \quad (103)$$

$$\hat{T}_1^2 = \frac{1}{4}\sum_{aibj} t_i^a t_j^b\{\hat{a}_a^\dagger \hat{a}_i\}\{\hat{a}_b^\dagger \hat{a}_j\} \quad (104)$$

The CCSD Energy Equation

$$\left(\hat{F}_N + \hat{V}_N + \hat{F}_N\hat{T}_1 + \hat{F}_N\hat{T}_2 + \frac{1}{2}\hat{F}_N\hat{T}_1^2 + \hat{V}_N\hat{T}_1 + \hat{V}_N\hat{T}_2 + \frac{1}{2}\hat{V}_N\hat{T}_1^2\right)_C \tag{105}$$

$$\hat{F}_N\hat{T}_1 = \frac{1}{2}\sum_{pq}\sum_{ai} f_{pq} t_i^a \{\hat{a}_p^\dagger \hat{a}_q\}\{\hat{a}_a^\dagger \hat{a}_i\} \tag{106}$$

$$\begin{aligned}
\{\hat{a}_a^\dagger \hat{a}_i\}\{\hat{a}_p^\dagger \hat{a}_q\} &= \{\hat{a}_a^\dagger \hat{a}_i \hat{a}_p^\dagger \hat{a}_q\} \\
&= \{\hat{a}_p^\dagger \hat{a}_q \hat{a}_a^\dagger \hat{a}_i\} + \{\overline{\hat{a}_p^\dagger \hat{a}_q \hat{a}_a^\dagger \hat{a}_i}\} + \{\hat{a}_p^\dagger \overline{\hat{a}_q \hat{a}_a^\dagger} \hat{a}_i\} + \{\overline{\hat{a}_p^\dagger \overline{\hat{a}_q \hat{a}_a^\dagger} \hat{a}_i}\} \\
&= \{\hat{a}_p^\dagger \hat{a}_q \hat{a}_a^\dagger \hat{a}_i\} + \delta_{pi}\{\hat{a}_q \hat{a}_a^\dagger\} + \delta_{qa}\{\hat{a}_p^\dagger \hat{a}_i\} + \delta_{pi}\delta_{qa}.
\end{aligned} \tag{107}$$

$$\hat{F}_N\hat{T}_1 = \sum_{ai} f_{ia} t_i^a, \tag{108}$$

The CCSD Energy Equation

$$
\begin{aligned}
\left(\hat{F}_N \hat{T}_2\right)_c &= \frac{1}{4}\sum_{pq}\sum_{aibj} f_{pq} t_{ij}^{ab} \{a_p^\dagger a_q\}\{a_a^\dagger a_b^\dagger a_j a_i\} \\
&= \frac{1}{4}\sum_{pq}\sum_{aibj} f_{pq} t_{ij}^{ab} \Big(\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \\
&\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \\
&\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} \Big).
\end{aligned}
$$

$$
\begin{aligned}
\left(\hat{V}_N \hat{T}_1\right)_c &= \frac{1}{4}\sum_{pqrs}\sum_{ia} \langle pq||rs\rangle t_i^a \{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_i\} \\
&= \frac{1}{4}\sum_{pqrs}\sum_{ia} \langle pq||rs\rangle t_i^a \Big(\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i\} + \\
&\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i\} + \\
&\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i\} \Big).
\end{aligned}
$$

The CCSD Energy Equation

$$\langle\Phi_0|\left(\hat{V}_N\hat{T}_2\right)_c|\Phi_0\rangle = \frac{1}{16}\sum_{pqrs}\sum_{aibj}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_b^\dagger a_j a_i\}|\Phi_0\rangle$$

$$= \frac{1}{16}\sum_{pqrs}\sum_{aibj}\langle pq||rs\rangle t_{ij}^{ab}\Big(\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\} +$$

$$\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\}\Big)$$

$$= \frac{1}{16}\sum_{pqrs}\sum_{aibj}\langle pq||rs\rangle t_{ij}^{ab}\left(\delta_{pi}\delta_{qj}\delta_{ra}\delta_{sb} + \delta_{pj}\delta_{qi}\delta_{rb}\delta_{sa} - \delta_{pj}\delta_{qi}\delta_{ra}\delta_{sb} - \delta_{pi}\delta_{qj}\delta_{rb}\delta_{sa}\right)$$

$$= \frac{1}{4}\sum_{aibj}\langle ij||ab\rangle t_{ij}^{ab}.$$

The CCSD Energy Equation

$$\frac{1}{2}\langle\Phi_0|\left(\hat{V}_N\hat{T}_1^2\right)_c|\Phi_0\rangle = \frac{1}{8}\sum_{pqrs}\sum_{ai}\sum_{bj}\langle pq||rs\rangle t_i^a t_j^b \langle\Phi_0|\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_i\}\{a_b^\dagger a_j\}|\Phi_0\rangle$$

$$= \frac{1}{8}\sum_{pqrs}\sum_{aibj}\langle pq||rs\rangle t_i^a t_j^b \Big(\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\} +$$

$$\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\}\Big)$$

$$= \frac{1}{8}\sum_{pqrs}\sum_{aibj}\langle pq||rs\rangle t_i^a t_j^b \left(-\delta_{pj}\delta_{qi}\delta_{ra}\delta_{sb} + \delta_{pj}\delta_{qi}\delta_{rb}\delta_{sa} + \delta_{pi}\delta_{qj}\delta_{ra}\delta_{sb} - \delta_{pi}\delta_{qj}\delta_{rb}\delta_{sa}\right)$$

$$= \frac{1}{2}\sum_{aibj}\langle ij||ab\rangle t_i^a t_j^b. \qquad [133$$

The CCSD Energy Equation

$$\left(\hat{F}_N + \hat{V}_N + \hat{F}_N\hat{T}_1 + \hat{F}_N\hat{T}_2 + \frac{1}{2}\hat{F}_N\hat{T}_1^2 + \hat{V}_N\hat{T}_1 + \hat{V}_N\hat{T}_2 + \frac{1}{2}\hat{V}_N\hat{T}_1^2\right)_C \tag{109}$$

$$\hat{F}_N = \sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} = 0 \tag{110}$$

$$\hat{V}_N = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\} = 0 \tag{111}$$

$$\hat{F}_N\hat{T}_1 = \frac{1}{2}\sum_{pq}\sum_{ai} f_{pq}t_i^a\{\hat{a}_p^\dagger\hat{a}_q\}\{\hat{a}_a^\dagger\hat{a}_i\} = \sum_{ai} f_{ia}t_i^a, \tag{112}$$

$$\hat{F}_N\hat{T}_2 = \frac{1}{4}\sum_{pq}\sum_{abij} f_{pq}t_{ij}^{ab}\{\hat{a}_p^\dagger\hat{a}_q\}\{\hat{a}_a^\dagger\hat{a}_b^\dagger\hat{a}_j\hat{a}_i\} = 0, \tag{113}$$

$$\frac{1}{2}\hat{F}_N\hat{T}_1^2 = \frac{1}{4}\sum_{pq}\sum_{aibj} f_{pq}t_i^a t_j^b\{\hat{a}_p^\dagger\hat{a}_q\}\{\hat{a}_a^\dagger\hat{a}_i\}\{\hat{a}_b^\dagger\hat{a}_j\} = 0, \tag{114}$$

$$\hat{V}_N\hat{T}_1 = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\}\frac{1}{2}\sum_{ai} t_i^a\{\hat{a}_a^\dagger\hat{a}_i\} = 0, \tag{115}$$

$$E_{\text{CCSD}} - E_0 = \sum_{ia} f_{ia}t_i^a + \frac{1}{4}\sum_{aibj}\langle ij||ab\rangle t_{ij}^{ab} + \frac{1}{2}\sum_{aibj}\langle ij||ab\rangle t_i^a t_j^b. \tag{116}$$

The CCSD Amplitude Equations

$$\langle\Phi_i^a|\left(\hat{H}_N e^{(\hat{T}_1+\hat{T}_2)}\right)_C|\Phi_0\rangle = 0 \tag{117}$$

$$\langle\Phi_{ij}^{ab}|\left(\hat{H}_N e^{(\hat{T}_1+\hat{T}_2)}\right)_C|\Phi_0\rangle = 0 \tag{118}$$

$$\langle\Phi_i^a|\left(\hat{F}_N+\hat{V}_N\right)|\Phi_0\rangle = \tag{119}$$

$$\sum_{pq} f_{pq}\langle\Phi_0|\{\hat{a}_i^\dagger\hat{a}_a\}\{\hat{a}_p^\dagger\hat{a}_q\}|\Phi_0\rangle + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_0|\{\hat{a}_i^\dagger\hat{a}_a\}\{\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\}|\Phi_0\rangle.$$

$$\begin{aligned}\langle\Phi_i^a|\hat{F}_N|\Phi_0\rangle &= \sum_{pq} f_{pq}\langle\Phi_0|\{\hat{a}_i^\dagger\hat{a}_a\}\{\hat{a}_p^\dagger\hat{a}_q\}|\Phi_0\rangle \\ &= \sum_{pq} f_{pq}\{\hat{a}_i^\dagger\hat{a}_a\hat{a}_p^\dagger\hat{a}_q\} \\ &= \sum_{pq} f_{pq}\delta_{iq}\delta_{ap} \\ &= f_{ai}.\end{aligned} \tag{120}$$

The CCSD Amplitude Equations

$$\langle\Phi_{ij}^{ab}|\left(\hat{F}_N+\hat{V}_N\right)|\Phi_0\rangle = \tag{121}$$

$$\sum_{pq} f_{pq}\langle\Phi_0|\{\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_b\hat{a}_a\}\{\hat{a}_p^\dagger\hat{a}_q\}|\Phi_0\rangle+\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_0|\{\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_b\hat{a}_a\}\{\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\}|\Phi_0\rangle.$$

$$\begin{aligned}
\langle\Phi_{ij}^{ab}|\hat{V}_N|\Phi_0\rangle &= \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_0|\{a_i^\dagger a_j^\dagger a_b a_a\}\{a_p^\dagger a_q^\dagger a_s a_r\}|\Phi_0\rangle \\
&= \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\Big(\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\}+ \\
&\qquad \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\}\Big) \\
&= \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left(\delta_{pa}\delta_{qb}\delta_{ri}\delta_{sj}-\delta_{pb}\delta_{qa}\delta_{ri}\delta_{sj}-\delta_{pa}\delta_{qb}\delta_{rj}\delta_{si}+\delta_{pb}\delta_{qa}\delta_{rj}\delta_{si}\right) \\
&= \langle ab||ij\rangle.
\end{aligned}$$

The CCSD Amplitude Equations

$$\langle\Phi_i^a|\left(\left[\hat{F}_N+\hat{V}_N\right]\hat{T}_1\right)_c|\Phi_0\rangle = \sum_{pq}\sum_{jb} f_{pq}t_j^b\langle\Phi_0|\{\hat{a}_i^\dagger\hat{a}_a\}\left(\{\hat{a}_p^\dagger\hat{a}_q\}\{\hat{a}_b^\dagger\hat{a}_j\}\right)_c|\Phi_0\rangle + \frac{1}{4}\sum_{pqrs}\sum_{jb}\langle pq||rs\rangle t_j^b\langle\Phi_0|\{\hat{a}_i^\dagger\hat{a}_a\}\left(\{\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\}\{\hat{a}_b^\dagger\hat{a}_j\}\right)_c|\Phi_0\rangle,$$

$$\begin{aligned}\langle\Phi_i^a|\left(\hat{V}_N\hat{T}_1\right)_c|\Phi_0\rangle &= \frac{1}{4}\sum_{pqrs}\sum_{jb}\langle pq||rs\rangle t_j^b\langle\Phi_0|\{a_i^\dagger a_a\}\left(\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_b^\dagger a_j\}\right)_c|\Phi_0\rangle \\ &= \frac{1}{4}\sum_{pqrs}\sum_{jb}\langle pq||rs\rangle t_j^b\Big(\{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j\} + \\ &\qquad \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j\}\Big) \\ &= \frac{1}{4}\sum_{pqrs}\sum_{jb}\langle pq||rs\rangle t_j^b\left(-\delta_{pa}\delta_{qj}\delta_{rb}\delta_{si}+\delta_{pj}\delta_{qa}\delta_{rb}\delta_{si}+\delta_{pa}\delta_{qj}\delta_{ri}\delta_{sb}-\delta_{pj}\delta_{qa}\delta_{ri}\delta_{sb}\right) \\ &= \sum_{jb}\langle ja||bi\rangle t_j^b.\end{aligned}$$

The CCSD Amplitude Equations

$$\langle \Phi_{ij}^{ab} | \left(\hat{V}_N \hat{T}_1 \right)_c | \Phi_0 \rangle = \frac{1}{4} \sum_{pqrs} \sum_{kc} \langle pq||rs \rangle t_k^c \langle \Phi_0 | \{ a_i^\dagger a_j^\dagger a_b a_a \} \left(\{ a_p^\dagger a_q^\dagger a_s a_r \} \{ a_c^\dagger a_k \} \right)_c | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{pqrs} \sum_{kc} \langle pq||rs \rangle t_k^c \Big(\{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} +$$

$$\{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} + \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} + \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} +$$

$$\{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} + \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} + \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} +$$

$$\{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} + \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} + \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} +$$

$$\{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} + \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} + \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} +$$

$$\{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} + \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} + \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k \} \Big)$$

$$= \sum_c \left(\langle ab||cj \rangle t_i^c - \langle ab||ci \rangle t_j^c \right) + \sum_k \left(\langle ij||bk \rangle t_k^a - \langle ij||ak \rangle t_k^b \right)$$

The CCSD Amplitude Equations

$\hat{T}_1$ Contribution,

$$
\begin{aligned}
0 = \; & f_{ai} + \sum_{c} f_{ac} t_i^c - \sum_{k} f_{ki} t_k^a + \sum_{kc} \langle ka||ci\rangle t_k^c + \sum_{kc} f_{kc} t_{ik}^{ac} + \frac{1}{2}\sum_{kcd} \langle ka||cd\rangle t_{ki}^{cd} - \\
& \frac{1}{2}\sum_{klc} \langle kl||ci\rangle t_{kl}^{ca} - \sum_{kc} f_{kc} t_i^c t_k^a - \sum_{klc} \langle kl||ci\rangle t_k^c t_l^a + \sum_{kcd} \langle ka||cd\rangle t_k^c t_i^d - \qquad (122) \\
& \sum_{klcd} \langle kl||cd\rangle t_k^c t_i^d t_l^a + \sum_{klcd} \langle kl||cd\rangle t_k^c t_{li}^{da} - \frac{1}{2}\sum_{klcd} \langle kl||cd\rangle t_{ki}^{cd} t_l^a - \frac{1}{2}\sum_{klcd} \langle kl||cd\rangle t_{kl}^{ca} t_i^d,
\end{aligned}
$$

The CCSD Amplitude Equations

$$
\begin{aligned}
0 \quad = \quad & \langle ab||ij\rangle + \sum_c \left(f_{bc}t_{ij}^{ac} - f_{ac}t_{ij}^{bc}\right) - \sum_k \left(f_{kj}t_{ik}^{ab} - f_{ki}t_{jk}^{ab}\right) + \frac{1}{2}\sum_{kl}\langle kl||ij\rangle t_{kl}^{ab} \\
& + \frac{1}{2}\sum_{cd}\langle ab||cd\rangle t_{ij}^{cd} + P(ij)P(ab)\sum_{kc}\langle kb||cj\rangle t_{ik}^{ac} + P(ij)\sum_c\langle ab||cj\rangle t_i^c - P(ab)\sum_k\langle kb||ij\rangle t_k^a \\
& + \frac{1}{2}P(ij)P(ab)\sum_{klcd}\langle kl||cd\rangle t_{ik}^{ac}t_{lj}^{db} + \frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_{ij}^{cd}t_{kl}^{ab} - P(ab)\frac{1}{2}\sum_{klcd}\langle kl||cd\rangle t_{ij}^{ac}t_{kl}^{bd} \\
& - P(ij)\frac{1}{2}\sum_{klcd}\langle kl||cd\rangle t_{ik}^{ab}t_{jl}^{cd} + P(ab)\frac{1}{2}\sum_{kl}\langle kl||ij\rangle t_k^a t_l^b + P(ij)\frac{1}{2}\sum_{cd}\langle ab||cd\rangle t_i^c t_j^d \\
& P(ab)\sum_{kc} f_{kc}t_k^a t_{ij}^{bc} + P(ij)\sum_{kc} f_{kc}t_i^c t_{jk}^{ab} P(ij)\sum_{klc}\langle kl||ci\rangle t_k^c t_{lj}^{ab} + P(ab)\sum_{kcd}\langle ka||cd\rangle t_k^c t_{ij}^{db} + \\
& P(ij)P(ab)\sum_{kcd}\langle ak||dc\rangle t_i^d t_{jk}^{bc} + P(ij)P(ab)\sum_{klc}\langle kl||ic\rangle t_l^a t_{jk}^{bc} - P(ij)P(ab)\sum_{kc}\langle kb||ic\rangle t_k^a t_j^c + \\
& P(ij)\frac{1}{2}\sum_{klc}\langle kl||cj\rangle t_i^c t_{kl}^{ab} - P(ab)\frac{1}{2}\sum_{kcd}\langle kb||cd\rangle t_k^a t_{ij}^{cd} - \\
& P(ij)P(ab)\frac{1}{2}\sum_{kcd}\langle kb||cd\rangle t_i^c t_k^a t_j^d + P(ij)P(ab)\frac{1}{2}\sum_{klc}\langle kl||cj\rangle t_i^c t_k^a t_l^b - \\
& P(ij)\sum_{klcd}\langle kl||cd\rangle t_k^c t_i^d t_{lj}^{ab} - P(ab)\sum_{klcd}\langle kl||cd\rangle t_k^c t_l^a t_{ij}^{db} + \\
& P(ij)\frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_i^c t_j^d t_{kl}^{ab} + P(ab)\frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_k^a t_l^b t_{ij}^{cd} + \\
& P(ij)P(ab)\sum_{klcd}\langle kl||cd\rangle t_i^c t_l^b t_{kj}^{ad} + P(ij)P(ab)\frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_i^c t_k^a t_j^d t_l^b .
\end{aligned}
\tag{123}
$$