

Introduction to Electron Correlation

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Molecular Orbitals Aren't Real...

Molecular orbitals are the eigenvectors of the Fock matrix in Hartree-Fock theory. Hartree-Fock is just an approximation, *even if a complete orbital basis is used*. Why? Two reasons, equivalent to each other:

- It *assumes* the wavefunction can be written as *one* Slater determinant. This is wrong!
- It *assumes* that each electron interacts with an average charge distribution due to the other electrons. This is wrong!

Electron Correlation

- Electrons repel each other according to Coulomb's law, with the repulsion energy r_{ij}^{-1} .
- Hartree-Fock *replaces* this instantaneous electron-electron repulsion with the repulsion of each electron with an *average* electron charge cloud.
- This introduces an *error* in the wavefunction and the energy. The energy error is called the *total correlation energy*. The error in the total energy is about 1 eV per electron pair in a bond or lone pair.
- Dispersion forces are due to electron correlation; expect Hartree-Fock to fail badly for van der Waals complexes.

Correlation Energy

- The *correlation energy* is defined as the difference between the true energy and the Hartree-Fock energy in a complete basis (“Hartree-Fock limit”)

$$E_{corr} = \mathcal{E}_{exact} - E_{HF}^{\infty}$$

- Usually we don’t know the exact energy \mathcal{E}_{exact} , but sometimes we can compute the exact energy *for a given one-electron basis set*. This lets us compute the *basis set correlation energy* (or just “correlation energy” for short...)

$$E_{corr}^{basis} = E_{exact}^{basis} - E_{HF}^{basis}$$

Why it's called Electron Correlation

The Hartree Product

$$\Psi^{HP}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \cdots \chi_k(\mathbf{x}_N)$$

is *completely uncorrelated*, in the sense that the probability of simultaneously finding electron 1 at \mathbf{x}_1 , electron 2 at \mathbf{x}_2 , etc., is given by $|\Psi^{HP}(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 \cdots d\mathbf{x}_N$ and is just

$$|\chi_i(\mathbf{x}_1)|^2 d\mathbf{x}_1 |\chi_j(\mathbf{x}_2)|^2 d\mathbf{x}_2 \cdots |\chi_k(\mathbf{x}_N)|^2 d\mathbf{x}_N,$$

which is the probability of finding electron 1 at \mathbf{x}_1 *times* the probability of finding electron 2 at \mathbf{x}_2 , etc....the product of the probabilities. This makes the Hartree Product an *independent particle model*. Electrons move independently; their motion is uncorrelated.

Correlation in Hartree-Fock

- *Hartree-Fock is usually defined as “uncorrelated.” However, the electron motions are no longer completely independent.*
- For two electrons with the same spin
- For two electrons with different spins, $|\Psi_1(\mathbf{r}_1)\alpha(\omega_1)\Psi_2(\mathbf{r}_2)\beta(\omega_2)\rangle$, the probability of finding electron 1 at \mathbf{r}_1 and electron 2 at \mathbf{r}_2 is

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 &= d\mathbf{r}_1 d\mathbf{r}_2 \int d\omega_1 d\omega_2 |\Psi|^2 \\ &= \frac{1}{2} \left[|\Psi_1(\mathbf{r}_1)|^2 |\Psi_2(\mathbf{r}_2)|^2 + |\Psi_1(\mathbf{r}_2)|^2 |\Psi_2(\mathbf{r}_1)|^2 \right] d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned}$$

The electrons are uncorrelated.

- For two electrons with the same spin, $|\Psi_1(\mathbf{r}_1)\alpha(\omega_1)\Psi_2(\mathbf{r}_2)\alpha(\omega_2)\rangle$, the probability of finding electron 1 at \mathbf{r}_1 and electron 2 at \mathbf{r}_2 is

$$\begin{aligned}
 P(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 &= \frac{1}{2} \left(|\Psi_1(\mathbf{r}_1)|^2 |\Psi_2(\mathbf{r}_2)|^2 + |\Psi_1(\mathbf{r}_2)|^2 |\Psi_2(\mathbf{r}_1)|^2 \right. \\
 &\quad - [\Psi_1^*(\mathbf{r}_1)\Psi_2(\mathbf{r}_1)\Psi_2^*(\mathbf{r}_2)\Psi_1(\mathbf{r}_2) \\
 &\quad \left. + \Psi_1(\mathbf{r}_1)\Psi_2^*(\mathbf{r}_1)\Psi_2(\mathbf{r}_2)\Psi_1^*(\mathbf{r}_2)] \right) d\mathbf{r}_1 d\mathbf{r}_2
 \end{aligned}$$

Now $P(\mathbf{r}_1, \mathbf{r}_1) = 0$. No 2 electrons with same spins can be at the same place. “Fermi hole.” *Same-spin electrons are correlated in Hartree-Fock, different-spin electrons are not.*

The N -electron Basis

- A collection of atom-centered Gaussian functions can be used as a basis set for expanding one-electron functions (molecular orbitals).
- We need to solve the electronic Schrödinger equation to get $\Psi_e(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$, a function of N electrons. What can we use as a basis for expanding Ψ_e ?
- *Slater determinants* are proper N -electron basis functions: they are functions which can be used to expand any (antisymmetric) N -electron function.
- In the limit of an infinite number of Slater determinants, *any* N -electron function can be expanded exactly.

What Other Determinants?

If it takes an infinite number of determinants to exactly represent the wavefunction, taking *only one*, as in Hartree-Fock theory, is not necessarily a decent approximation!

For a given set of MO's, other determinants can be formed by *putting electrons in different orbitals*. These other determinants will generally belong to *different electron configurations*.

Example: Minimal Basis H₂

There are four possible determinants, one for each spin-orbital configuration:

$$(\sigma_g)^2 \quad (\sigma_g\alpha)(\sigma_u^*\beta) \quad (\sigma_g\beta)(\sigma_u^*\alpha) \quad (\sigma_u^*)^2$$

Note that the middle two correspond to the same *spatial orbital configuration* but are different *spin orbital configurations* or Slater determinants.

Note also that the middle two determinants *can be discarded* in any expansion of the $^1\Sigma_g^+$ state of H₂. Why??

Using Symmetry

We only need determinants with the right symmetries. This includes: *spatial symmetry*, \hat{S}_z symmetry, and \hat{S}^2 symmetry. Determinants with values different than the desired state *cannot contribute* to the total wavefunction.

Of the four given determinants for H_2 ,

$$(\sigma_g)^2 \quad (\sigma_g\alpha)(\sigma_u^*\beta) \quad (\sigma_g\beta)(\sigma_u^*\alpha) \quad (\sigma_u^*)^2,$$

all have $M_s = 0$. The first and last are also eigenfunctions of \hat{S}^2 , but the middle two are not – we would need to take +/- combinations of them. *Configuration State Functions* (CSF's) are combinations of one or more Slater determinants with the proper values of spatial symmetry, M_s , and S .

Configuration Interaction (CI)

Configuration Interaction: Express the wavefunction as a linear combination of Slater determinants. Usually obtain expansion coefficients variationally. $|\Phi\rangle = \sum_I c_I |\Phi_I\rangle$.

Complete CI: Arrange all electrons in all possible ways (consistent with symmetry requirements) in a complete (i.e., infinite) orbital basis set. Unattainable.

Full CI: Arrange all electrons in all possible ways (w/ symmetry) for a finite orbital basis set. **Very costly!**

How Many Determinants Could There Be?

Ignoring \hat{S}^2 and spatial symmetry, but keeping \hat{S}_z symmetry, how many determinants can be formed? If there are N_α (N_β) electrons with α (β) spin, in n orbitals, one can keep M_s fixed by moving the α and β electrons separately.

There are very many ways to do this!

$$N_{det} = \binom{n}{N_\alpha} \binom{n}{N_\beta}.$$

Number of $M_s = 0$ Determinants (CSF's in parentheses)

Orbitals	Number of electrons			
	6	8	10	12
10	14.4×10^3 (4.95×10^3)	44.1×10^3 (13.9×10^3)	63.5×10^3 (19.4×10^3)	44.1×10^3 (13.9×10^3)
20	1.30×10^6 (379×10^3)	23.5×10^6 (5.80×10^6)	240×10^6 (52.6×10^6)	1.50×10^9 (300×10^6)
30	16.5×10^6 (4.56×10^6)	751×10^6 (172×10^6)	20.3×10^9 (4.04×10^9)	353×10^9 (62.5×10^9)

Full CI is Impractical

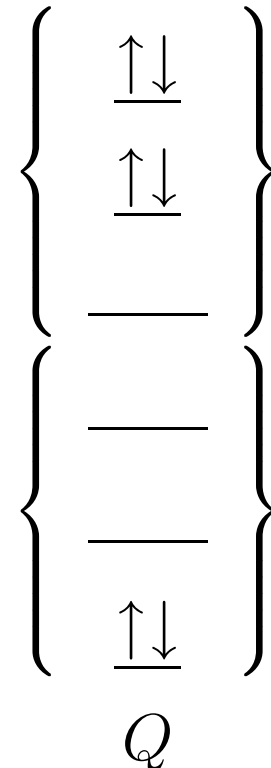
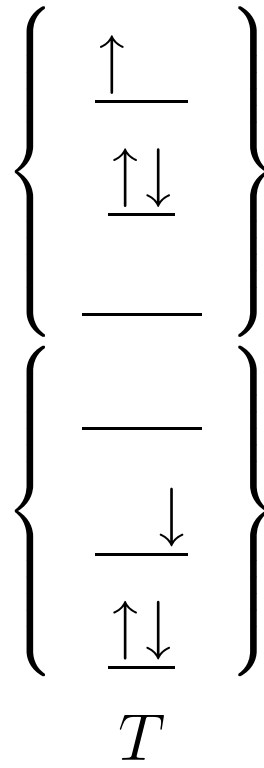
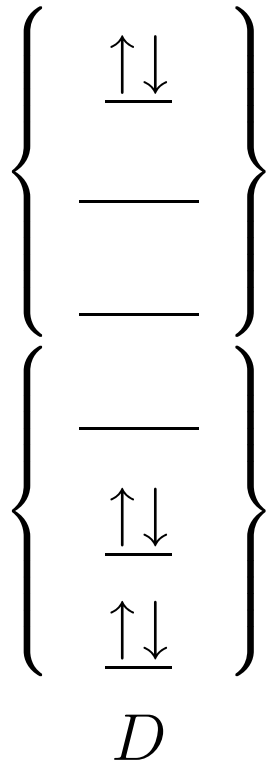
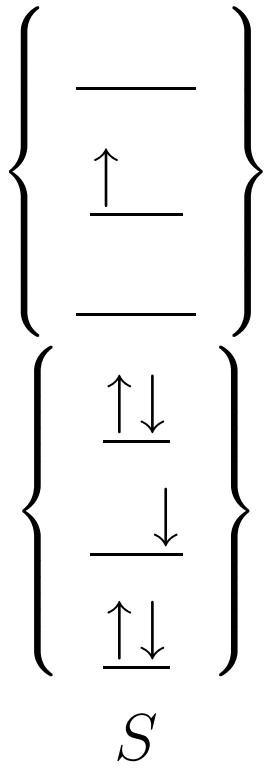
- About 1 billion determinants is the limit of what can be reached today for Full CI computations. This requires highly optimized computer code!
- For a determinant basis, this means about 12 electrons in 20 orbitals, or 10 electrons in 30 orbitals. *Mostly diatomics.*
- Need to separate the “more important” determinants from the “less important.” A common way: truncate CI expansion according to excitation level.

Classification by Substitution (“Excitation”) Classes

The Hartree-Fock “reference” determinant $|\Phi_0\rangle$ should be the leading term. Expect the importance of other configurations to drop off rapidly as they substitute more orbitals. Let $|\Phi_{ij\dots k}^{ab\dots c}\rangle$ denote a determinant which differs from $|\Phi_0\rangle$ by replacing orbitals $ij\dots k$ with $ab\dots c$.

$$\begin{array}{ccccccccccc} |\Psi\rangle & = & c_0|\Phi_0\rangle & + & \sum c_i^a|\Phi_i^a\rangle & + & \sum c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle & + & \sum c_{ijk}^{abc}|\Phi_{ijk}^{abc}\rangle & \dots \\ & & \text{Reference} & & \text{Singles} & & \text{Doubles} & & \text{Triples} & \dots \end{array}$$

Examples of Excitation Levels



How to obtain Coefficients?

- *Variationally*: This is the *configuration interaction* method. Find the coefficients which minimize the total energy. Equivalent to diagonalizing \hat{H} is the basis of determinants.
- *(Many-Body) Perturbation Theory*: Treat the Hartree-Fock determinant $|\Psi_0\rangle$ as the zeroth-order solution, $E^{(0)} = \sum \epsilon_i$, $E^{(1)} = E_{HF}$, doubles (and singles for open-shell) contribute to $|\Psi^{(1)}\rangle$ and $E^{(2)}$, etc.

Need to truncate expansion of determinants to make it practical.

Configuration Interaction

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum c_i^a|\Phi_i^a\rangle + \sum c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \sum c_{ijk}^{abc}|\Phi_{ijk}^{abc}\rangle \dots$$

Reference Singles Doubles Triples ...

Usually truncate expansion at a given excitation level.

CISD: CI with singles and doubles. Scales as $\mathcal{O}(N^6)$.

CISDT: CI with singles, doubles, triples. Scales as $\mathcal{O}(N^8)$.

Can keep going until Full CI limit; *more accurate as more terms are added*, but also more costly! (Why no CIS?)

Configuration Interaction Matrices

It's easy to prove that the coefficients c_I which minimize the total energy E_{CI} are the *same* as the eigenvectors of the electronic Hamiltonian in the same basis of determinants.

Simple strategy for CI: form the Hamiltonian matrix \mathbf{H} and diagonalize it. In actuality, we do this cleverly to avoid extra work.

Evaluate the matrix elements $H_{IJ} = \langle \Phi_I | \hat{H} | \Phi_J \rangle$ using *Slater's Rules*. Determinants differing by more than two spin orbitals are 0.

$$\mathbf{H} = \begin{bmatrix}
\langle \Phi_0 | \hat{H} | \Phi_0 \rangle & 0 & \langle \Phi_0 | \hat{H} | D \rangle & 0 & 0 & \dots \\
0 & \langle S | \hat{H} | S \rangle & \langle S | \hat{H} | D \rangle & \langle S | \hat{H} | T \rangle & 0 & \dots \\
\langle D | \hat{H} | \Phi_0 \rangle & \langle D | \hat{H} | S \rangle & \langle D | \hat{H} | D \rangle & \langle D | \hat{H} | T \rangle & \langle D | \hat{H} | Q \rangle & \dots \\
0 & \langle T | \hat{H} | S \rangle & \langle T | \hat{H} | D \rangle & \langle T | \hat{H} | T \rangle & \langle T | \hat{H} | Q \rangle & \dots \\
0 & 0 & \langle Q | \hat{H} | D \rangle & \langle Q | \hat{H} | T \rangle & \langle Q | \hat{H} | Q \rangle & \dots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots
\end{bmatrix}$$

Slater's Rules for Matrix Elements

Identical Determinants: If the determinants are identical, then

$$\langle \Phi_1 | \hat{H} | \Phi_1 \rangle = \sum_m^N \langle m | \hat{h} | m \rangle + \sum_{m>n}^N \langle mn || mn \rangle$$

Determinants that Differ by One Spin Orbital:

$$|\Phi_1\rangle = |\cdots mn \cdots\rangle$$

$$|\Phi_2\rangle = |\cdots pn \cdots\rangle$$

$$\langle \Phi_1 | \hat{H} | \Phi_2 \rangle = \langle m | \hat{h} | p \rangle + \sum_n^N \langle mn || pn \rangle$$

Determinants that Differ by Two Spin Orbitals:

$$|\Phi_1\rangle = |\cdots mn \cdots\rangle$$

$$|\Phi_2\rangle = |\cdots pq \cdots\rangle$$

$$\langle \Phi_1 | \hat{H} | \Phi_2 \rangle = \langle mn || pq \rangle$$

Determinants that differ by More than Two Spin Orbitals:

$$|\Phi_1\rangle = |\cdots mno \cdots\rangle$$

$$|\Phi_2\rangle = |\cdots pqr \cdots\rangle$$

$$\langle \Phi_1 | \hat{H} | \Phi_2 \rangle = 0$$

Molecule	Percent Corr. Energy ^a		
	CISD	CISDT	CISDTQ
BH	94.91	n/a	99.97
H ₂ O(R _e)	94.70	95.47	99.82
H ₂ O(1.5 R _e)	89.39	91.15	99.48
H ₂ O(2.0 R _e)	80.51	83.96	98.60
NH ₃	94.44	95.43	99.84
HF	95.41	96.49	99.86
H ₇ ⁺	96.36	96.87	99.96

^aData from Harrison *et al.*, 1983, except H₇⁺ data from Fermann *et al.*, 1994.

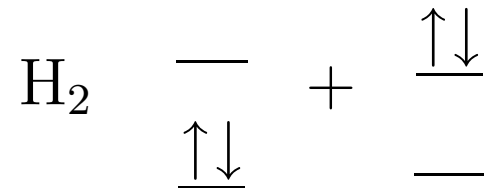
Size of CI space vs Excitation Level

Molecule	CSF's required ^a			
	CISD	CISDT	CISDTQ	FCI
BH	568	n/a	28 698	132 686
H ₂ O	361	3 203	17 678	256 473
NH ₃	461	4 029	19 925	137 321
HF	552	6 712	48 963	944 348
H ₇ ⁺	1 271	24 468	248 149	2 923 933

^aData from Harrison *et al.*, 1983, except for H₇⁺ data from Fermann *et al.*, 1994.

Configuration Interaction Is Not Size Extensive

CISD is exact for a two-electron system like H_2



...But not exact for two noninteracting H_2 's.



Would need Quadruple excitations! Should be able to express quadruple as product of doubles, but not in CISD.

Many-Body (or Møller-Plesset) Perturbation Theory

A size-extensive approach. As always in perturbation theory, we split the problem into a part we can solve easily and a perturbation, i.e.,

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}'$$

The solution is expressed as a Taylor series in λ , the perturbation strength, as

$$\mathcal{E}_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots$$

$$|\Psi_i\rangle = |\Psi_i^{(0)}\rangle + \lambda|\Psi_i^{(1)}\rangle + \lambda^2|\Psi_i^{(2)}\rangle + \dots$$

The Fock operator is zeroth-order Hamiltonian; difference between the real r_{ij}^{-1} repulsion and the Fock operator becomes the perturbation (“fluctuation potential”) \hat{H}' .

$$\begin{aligned}\hat{H}_0 &= \sum f(i) \\ &= \sum [h(i) + v^{HF}(i)]\end{aligned}$$

$$\begin{aligned}\hat{H}' &= \sum_{i<j} r_{ij}^{-1} - \mathcal{V}_{HF} \\ &= \sum_{i<j} r_{ij}^{-1} - \sum v^{HF}(i)\end{aligned}$$

$$v^{HF}(1)\chi_p(\mathbf{x}_1) = \sum_i \langle i|r_{12}^{-1}|i\rangle \chi_p(\mathbf{x}_1) - \sum_i \langle i|r_{12}^{-1}|p\rangle \chi_i(\mathbf{x}_1)$$

$$\langle p|v^{HF}|q\rangle = v_{pq}^{HF} = \sum_i \langle pi||qi\rangle$$

Hartree-Fock energy is Sum of Zero and First Order Energies

$$\begin{aligned}\hat{H}_0|\Psi_0\rangle &= E_0^{(0)}|\Psi_0\rangle \\ E_0^{(0)} &= \sum_i \epsilon_i \\ E_0^{(1)} &= \langle\Psi_0|\mathcal{H}'|\Psi_0\rangle \\ &= \langle\Psi_0|\sum_{i<j} r_{ij}^{-1}|\Psi_0\rangle - \langle\Psi_0|\sum_i v^{HF}(i)|\Psi_0\rangle \\ &= \frac{1}{2}\sum_{ij}\langle ij||ij\rangle - \sum_i \langle i|v^{HF}|i\rangle \\ &= -\frac{1}{2}\sum_{ij}\langle ij||ij\rangle \\ E_0^{HF} &= E_0^{(0)} + E_0^{(1)}\end{aligned}$$

Second-Order Energy Expression

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

The numerator is zero for all other determinants except double excitations.

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

Second-order energy correction is negative; electron correlation stabilizes the energy. Usually perturbation theory is taken through second order, MBPT(2) (or simply MP2), which scales as $\mathcal{O}(N^5)$.

Coupled-Cluster Theory

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

CCSD: $\hat{T} = \hat{T}_1 + \hat{T}_2$. Cost $\mathcal{O}(N^6)$.

CCSD(T): Adds perturbative correction for \hat{T}_3 at cost $\mathcal{O}(N^7)$.

- Improves over CISD, etc., by using products of excitations
- Size extensive version of CI: CCSD exact for N noninteracting H_2 's
- Contains higher-order “disconnected” substitutions



If $\hat{H} = \hat{H}^A + \hat{H}^B$, should have $E = E^A + E^B$ and $|\Psi\rangle = |\Psi^A\rangle|\Psi^B\rangle$. Unfortunately,

$$\begin{aligned}
 |\Psi_{CID}\rangle &\neq |\Psi_{CID}^A\rangle|\Psi_{CID}^B\rangle \\
 (1 + \hat{T}_2^A + \hat{T}_2^B)|\Phi_0^A\rangle|\Phi_0^B\rangle &\neq \left\{ (1 + \hat{T}_2^A)|\Phi_0^A\rangle \right\} \left\{ (1 + \hat{T}_2^B)|\Phi_0^B\rangle \right\}
 \end{aligned}$$

However,

$$\begin{aligned}
 e^{\hat{T}_2^A + \hat{T}_2^B} |\Phi_0^A\rangle|\Phi_0^B\rangle &= \left\{ e^{\hat{T}_2^A} |\Phi_0^A\rangle \right\} \left\{ e^{\hat{T}_2^B} |\Phi_0^B\rangle \right\} \\
 |\Psi_{CCD}\rangle &= |\Psi_{CCD}^A\rangle|\Psi_{CCD}^B\rangle
 \end{aligned}$$

Excitation Operators

Coupled-cluster theory makes use of excitation operators that act on a reference determinant to generate excited determinants times coefficients

$$\hat{T}_1 = \sum_{ia} t_i^a |\Phi_i^a\rangle$$

$$\hat{T}_2 = \sum_{ijab} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle$$

With this notation, CISD is just

$$|\Psi_{CISD}\rangle = (1 + \hat{T}_1 + \hat{T}_2)|\Phi_0\rangle$$

This makes the CCSD wavefunction

$$\begin{aligned}
 |\Psi_{CCSD}\rangle &= e^{\hat{T}_1 + \hat{T}_2} |\Phi_0\rangle \\
 &= (1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \dots) |\Phi_0\rangle \\
 &= |\Phi_0\rangle + \sum_{ia} t_i^a |\Phi_i^a\rangle + \sum_{ij}^{ab} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \\
 &+ \frac{1}{2} \sum_i^a t_i^a \sum_j^b t_j^b |\Phi_{ij}^{ab}\rangle + \sum_i^a t_i^a \sum_{jk}^{bc} t_{jk}^{bc} |\Phi_{ijk}^{abc}\rangle \\
 &+ \frac{1}{2} \sum_{ij}^{ab} t_{ij}^{ab} \sum_{kl}^{cd} t_{kl}^{cd} |\Phi_{ijkl}^{abcd}\rangle + \dots
 \end{aligned}$$

Coupled-Cluster Theory: An *Ab Initio* Success Story

Expected Errors for Large-Basis CCSD(T)

Bond lengths	$\pm 0.004 \text{ \AA}$
Bond angles	$\pm 0.3^\circ$
Harmonic frequencies	+2%
Dipole moments	$\pm 0.05 \text{ D}$
IR intensities	$\pm 20\%$
Excitation energies	$\pm 0.2 \text{ eV}$

Convergent *ab initio* Methods

- *Ab initio* methods such as CI and MBPT can be improved, in principle, by including more and more terms (and simultaneously increasing one-electron basis set size).
- CI and CC become more accurate as higher substitution levels are included (although cost grows dramatically).
- MBPT does not always improve at higher orders; the series is not guaranteed to converge. Current conventional wisdom is to stop at second order.
- Density functional theory methods are *nonconvergent* methods in that no one knows how to improve them systematically to get more and more accurate results.

Convergence and Pauling Points

Method	Basis Set					
	STO-3G	6-31G*	cc-pVTZ	cc-pVQZ	...	∞
SCF		x				
MP2		x	x			
CISD		x	x			
CCSD		x	x			
CCSD(T)			x	x		
CCSDT			x	x		
...						
Full CI						Truth