

Up to now we considered
the use of small expansions,
'configuration interaction' to calculate
approximate

- ionization potentials
- electron affinities
- excitation energies

Using the difference of Variational
Result and Hartree-Fock
ground state energy

$E_{HF} = \langle HF | \hat{H} | HF \rangle$ is the
lowest possible energy for a
wave function that consists of a
single determinant: populate
an optimal set of molecular
orbitals.

This gives surprisingly good total
energies (at equilibrium geometries),
typically $> 99.9\%$ of the total
energy.

0.1% of ~ 100 Hartree ≈ 0.1 Hartree
 ≈ 65 kcal/mol ≈ 250 kJ/mol

On a chemical scale these
are huge errors.

We cannot use HF to calculate
reaction energies. They are quite
wrong. Geometries & frequencies

are typically more reasonable.

bottom line: we need to go beyond $|HF\rangle$, the simplest approach is to use the variational principle once again.

In what follows I will discuss briefly various approaches to the electronic structure problem. Let me give a brief outline first

(A): The basic approach: single reference Configuration Interaction; CISD, CISDT,

Problems with CI:

- not size-consistent: $E_{AB} \neq E_A + E_B$
for non-interacting systems A, B
- Does not describe bond breaking.

(B): Fixing the size-consistency problem: coupled cluster $\Psi = e^T |HF\rangle$

- CCSD(T) excellent for 'good' HF molecules
- fails for bond-breaking (multi-reference)
- Very poor convergence with size of one-particle basis set.

- ③ Solving the multi-reference problem (bond breaking)
- MR-CI
 - MR-CI + Q (\sim size-consistent)
 - MR-CC ??

- ④ Methods for excited states:
- Equation of Motion Coupled Cluster (also SAC-CI, CC-RT)
 - Similarity transformed EOM-CC

- ⑤ Wave function methods for large systems?
- local correlation
 - explicit r_{12} methods.
(solves the basis set convergence problem)

I anticipate that the remainder of the course will be discussing these items.

My own research is concerned with developing new methods in electronic structure theory, that can address various issues. I will give examples from this research environment.

(A) Configuration Interaction.

Conceptually the simplest approach would be to make the expansion

$$\begin{aligned} |\Psi\rangle &= c_0 |HF\rangle + \sum_{a} c_a^r \hat{r}_a^+ |HF\rangle \\ &+ \sum_{\substack{r,s \\ a,b}} c_{ab}^{rs} \hat{r}_a^+ \hat{s}_b^+ |HF\rangle + \dots \\ &= \sum_{\lambda} c_{\lambda} |\phi_{\lambda}\rangle \end{aligned}$$

in CISD we limit the expansion to go up to double substitution
CISDT -- go up to triple substitution
...

full CI : allow up to N-fold substitutions for N-electrons

Using the techniques we discussed, you could evaluate the matrix elements

	H	O	S	D	
H					
O					
S					
D					

elements → Singles → doubles
 formula

eg. $M_{SO} =$

$$\langle HF | \hat{b}^\dagger \hat{s} \hat{H} | HF \rangle$$

$$= \dots = h_{bs} + \sum_c \langle b c | s c \rangle$$

$$= f_{bs}$$

~~This~~ For Hartree-Fock Singles
this has a special meaning, as
HF orbitals can be shown to
satisfy $f_{bs} = 0 \quad \forall b, s$

This is called ~~Brillouin~~ the
Brillouin condition

It implies that the energy of
the Hartree Fock wave function
cannot be improved by mixing
in single excitations only.

H	HF	S
HF	E_{HF}	0
S	0	H_{SS}

This is equivalent to the fact
that the occupied orbitals
are optimal in HF.
(as an aside).

Other types of matrix-elements:

$$\begin{aligned} \langle HF | a^\dagger b^\dagger s r \quad H \quad \cancel{a}^\dagger | HF \rangle \\ = \langle ab || sr \rangle \Rightarrow H_{00} \end{aligned}$$

or H_{50}

$$\langle HF | (c^\dagger t) \quad H \quad (s^\dagger r^\dagger ab) | HF \rangle$$

All these ~~etc~~ matrix-elements can be evaluated using the 'line' algorithm we discussed. It does get tedious, but no new principles are involved.

If we have all matrix elements evaluated we can in principle diagonalise the resulting Hamiltonian.

This is not how it is done in practice. The Matrix is too large to store (even on disk).

Let us discuss what is done in practice (more or less).

i) Intermediate Normalization.

$$\text{We had } |\psi\rangle = C_0 |HF\rangle + \sum_{\lambda} C_{\lambda} |\phi_{\lambda}\rangle$$

$$H |\psi\rangle = E |\psi\rangle$$

(for finite set of configurations)

Hilbert

\hat{H} can always multiply $|\psi\rangle$ by a constant, and it is still an eigen vector.

$$\hat{H} |\psi\rangle \lambda = E |\psi\rangle \lambda$$

Let us choose this constant to be $\lambda = 1/c_0$, $c_\lambda \rightarrow c_\lambda / c_0$.

Then the wave function can be written

$$|\psi\rangle = |\phi_{HF}\rangle + \sum_\lambda c_\lambda |\psi_\lambda\rangle$$

normalization $\langle \phi_{HF} | \psi \rangle = 1$

This is called intermediate normalization.

$$|\psi\rangle \equiv (1 + \hat{C}) |\phi_{HF}\rangle$$

This also leads to a convenient formula for the energy

$$\langle \phi_{HF} | \hat{H} | \psi \rangle = \langle \phi_{HF} | E | \psi \rangle = E \langle \phi_{HF} | \psi \rangle = E$$

other equations:

$$\langle \phi_a^r | (\hat{H} - E) (1 + \hat{C}) | \phi_{HF} \rangle = 0$$

$$\langle \phi_{ab}^{rr} | (\hat{H} - E) (1 + \hat{C}) | \phi_{HF} \rangle = 0$$

In practice these equations are solved iteratively.

If I have a trial operator \tilde{C} , $\tilde{E} = \langle \phi_{HF} | H (1 + \tilde{C}) | \phi_{HF} \rangle$

$$\tilde{E}_1 = E_{HF} + \langle \phi_{HF} | H \tilde{C} | \phi_{HF} \rangle \\ = E_{HF} + \tilde{E}_c$$

$$E - E_{HF} = \langle \phi_{HF} | \hat{H} \hat{C} | \phi_{HF} \rangle = E_c$$

E_c is the so-called correlation energy, the piece extra

beyond Hartree Fock, due to the mixing in of additional determinants in the wave function.

Since the operator \tilde{C} is not (quite) correct, one can calculate the error

$$R_\lambda = \begin{cases} \langle \phi_a^r | (\hat{H} - \tilde{E}) (1 + \tilde{C}) | \phi_{HF} \rangle \\ \langle \phi_{ab}^{rc} | (\hat{H} - \tilde{E}) (1 + \tilde{C}) | \phi_{HF} \rangle \end{cases}$$

This essentially requires the calculation of $\hat{H} \hat{C}$, and this operation can be expressed using the 1- and 2-electron integrals and coefficients \tilde{C}_x .

The error of an efficient CI calculation is the calculation of the error vector.

From the error a correction vector

$$\Delta C_a^r = (\epsilon_a - \epsilon_r)^{-1} R_a^r$$

$$\Delta C_{ab}^{rs} = (\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s)^{-1} R_{ab}^{rs}$$

can be calculated, which brings the vector closer to convergence.

$$C^{(n+1)} = C^{(n)} + \Delta C^{(n)}$$

Various clever schemes exist to improve & accelerate convergence.

(acceleration)

All of this is cheap. The expensive part is the calculation of $\hat{H}\bar{C}$.

The most expensive contribution is

$$\sum_{ta} \langle rs || tu \rangle C_{ab}^{ta} \rightarrow R_{ab}^{rs}$$

which scales as $n_o^2 n_v^4$

where n_o : # of occupied orbitals
 n_v : # of virtual orbitals.

It is said that CI scales as n^6 . Doubling the size of the system increases the cost by a factor $2^6 = 64$.

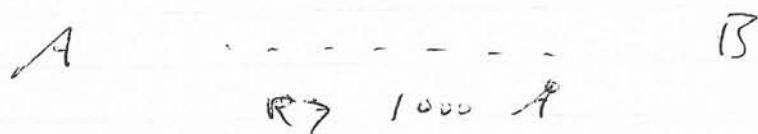
In contrast HF (or DFT) scales as n^3 . This is the reason (primarily) why DFT is so popular.

Size-consistency and CI.

CISD or higher order single-reference CI is hardly ever used in practice. It is conceptually straightforward, but it suffers from a major problem: lack of size-consistency.

Discussion:

Let us consider a system consisting of 2 non-interacting subsystems



orbitals are either localized on A, or on B. Integrals that contain orbitals on both sides (mixed) can be assumed 0.

$$\text{Then } \hat{H} = \hat{H}_A + \hat{H}_B$$

$$E = \hat{E}_A + \hat{E}_B$$

(assume proper antisymmetrization)

$$\psi = \psi_A \psi_B \equiv R(\psi_A \psi_B)$$

$$(\hat{H}_A + \hat{H}_B) \psi_A \psi_B = \hat{H}_A (\psi_A) \psi_B +$$

$$\psi_A (\hat{H}_B \psi_B) = (E_A + E_B) \psi_A \psi_B$$

(Some care is needed for antisymmetrization)

Hilroy

For the CI equations we would want a separate equation for \hat{C}_A and for \hat{C}_B

$$\langle \phi_x^A | (H_M^A - E_C^A) (1 + \hat{C}_A) | \phi_{HF} \rangle = 0$$

(note: $H_M = H - E_{HF}$)

$$\langle \phi_x^B | (H_M^B - E_C^B) (1 + \hat{C}_B) | \phi_{HF} \rangle = 0$$

This is more or less what the CI equations reduce to, except for one big difference:

instead of E_C^A , E_C^B the total correlation energy enters the equations. This breaks a very significant change, and introduces a large error.

The equations do not reduce to two decoupled equations for systems A and B.

An alternative one might think that a consistent wave function for the AB system should look like

$$\psi_{AB} \approx (1 + \hat{C}_A)(1 + \hat{C}_B) | \phi_{HF} \rangle$$

$$| \phi_{HF} \rangle = \underbrace{(a_1^+ \dots a_n^+)}_A \underbrace{(b_1^+ \dots b_m^+)}_B | vac \rangle$$

Separates properly.

$\hat{C}_A \hat{C}_B | \phi_{HF} \rangle \rightarrow$ quadruple excitations.

The size consistency problem ~~however~~ causes troubles in general.

Subsystem A and B could be the valence and deeper lying orbitals on a single atom, which are also weakly interacting. (think of Mg $(3s)$ _A $(2s 2p)$ _B)

In general, CI does not scale correctly with the size of the system. Correct scaling is called size-extensivity.

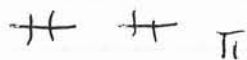
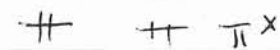
The scaling problem in CI can be solved using a different approach: Coupled Cluster.

Before we consider CC, I will address the other, independent problem in CI: The description of bond-breaking, e.g. in F_2

Around equilibrium the wave function is well described by the single determinant $|\text{HF}\rangle$, and $(1 + \hat{c}) |\text{HF}\rangle$ would give reasonable description (but for extensivity issues).

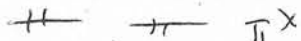
As the bond in F_2 breaks the qualitative wfn is given by

$$c_1 |-\sigma\bar{\sigma}| + c_2 |-\sigma^*\bar{\sigma}^*|$$

 $\frac{7}{4} \sigma$

at equilibrium.

11

 $\vdash \zeta$ 

in CISD we only include

 S_1 is excitations from the first

(17F) determinant

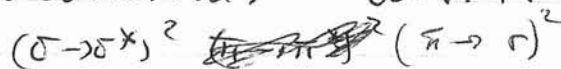
The second determinants and

Excitations out of it are

of equal importance.

These are often quadruplets

excitations w.r.t. M_F , eg



and these are not included

In a the wave function (CFSD)

Therefore the energy curves
are quite in error.

This problem occurs whenever
the wave function ~~is~~ needs
multiple determinants for its
qualitative description.

examples: $\left\{ \begin{array}{l} \text{bond-breaking} \\ \text{biradicals} \\ \text{transition metal systems} \\ \text{(low lying excited states)} \end{array} \right.$

Also for this problem, there is
a solution: multi-reference CI.
This approach still suffers (slightly)
from the size-consistency problem.

one additional note regarding
size-consistency:

If I do CI on n identical
non-interacting subsystems, e.g.
 n H_2 molecules, which ~~are~~ separated
then $E_C(n) \sim \sqrt{n} E_C(1)$
as $n \rightarrow \infty$ (see SRO: page 261)

The correct behaviour would of course
be $n E_C(1)$. This illustrates
again the poor behaviour of ~~any~~
truncated CI.

Coupled Cluster Theory (CC)

In CC theory, the same type of excitation operators are used as in CI

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots$$

$$\hat{T}_1 = \sum_{r,a} t_a^r \hat{r}^+ \hat{a} \quad \text{singles}$$

$$\hat{T}_2 = \frac{1}{4} \sum_{\substack{r,s \\ a,b}} t_{ab}^{rs} \hat{r}^+ \hat{a} \hat{s}^+ \hat{b} \quad \text{doubles}$$

$$\hat{T}_3 = \frac{1}{(3!)^2} \sum_{\substack{r,s,t \\ a,b,c}} t_{abc}^{rst} \hat{r}^+ \hat{a} \hat{s}^+ \hat{b} \hat{t}^+ \hat{c} \quad \text{(triples)}$$

In CCSD one includes \hat{T}_1, \hat{T}_2

In CC0 only \hat{T}_2

In CCSDT up to \hat{T}_3 , etc.

The difference with CI is the parametrization of the wave function (and the values of the coefficients)

The CC wavefunction:

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle$$

$|\Phi_0\rangle$: single determinant, typically (MF)

The simplest, physically meaningful case is $T = \hat{T}_2$ (CCD)

$$\begin{aligned}
 \text{Then } |\Psi\rangle &= e^{\hat{T}_2} |\phi_0\rangle \\
 &= \left(1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{3!} \hat{T}_2^3 + \dots \right) |\phi_0\rangle \\
 &= |\phi_0\rangle + \frac{1}{1} \sum_{\substack{r,s \\ a,b}} t_{ab}^{rs} \hat{r}^\dagger \hat{a} \hat{s}^\dagger \hat{b} |\phi_0\rangle \\
 &\quad + \frac{1}{2} \left(\frac{1}{1} \right)^2 \sum_{\substack{r,s \\ a,b}} \sum_{\substack{t,u \\ c,d}} t_{ab}^{rs} t_{cd}^{tu} \hat{r}^\dagger \hat{a} \hat{s}^\dagger \hat{b} \hat{t}^\dagger \hat{c} \hat{u}^\dagger \hat{d} |\phi_0\rangle \\
 &\quad + \frac{1}{3!} \left(\frac{1}{1} \right)^3 \sum_{\substack{r,s \\ a,b}} \sum_{\substack{t,u \\ c,d}} \sum_{\substack{v,w \\ e,f}} (\dots) |\phi_0\rangle
 \end{aligned}$$

Acting with the exponential includes higher excitations: doubles, quadruples, sextuples, octuples, ...

The coefficients of the higher excitations are determined by the elementary t_{ab}^{rs} coefficients.

It is fairly easy to verify that such an exponential Wfn is in principle exact, just as in FCI.

The identification of \hat{C} and \hat{T} is as follows

$$\hat{C}_1 = \hat{T}_1$$

$$\hat{T}_1 = \hat{C}_1$$

$$\hat{C}_2 = \hat{T}_2 + \frac{1}{2} \hat{T}_1^2$$

$$\hat{T}_2 = \hat{C}_2 - \frac{1}{2} \hat{T}_1^2$$

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \frac{1}{3!} \hat{T}_1^3$$

$$\hat{T}_3 = \hat{C}_3 - \hat{T}_1 \hat{T}_2 - \frac{1}{3!} \hat{T}_1^3$$

$$\hat{C}_4 = \hat{T}_4 + \hat{T}_1 \hat{T}_3 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{2} \hat{T}_2 \hat{T}_1^2 + \frac{1}{4!} \hat{T}_1^4$$

$$\hat{T}_4 = \hat{C}_4 - (-) \text{ disc.}$$

Hence if we would know the full CE coefficient we can easily extract the corresponding T -amplitudes.

This only establishes validity of the parameterization, why is it better as an approximation?

Let us consider the equations for truncated CE, and analyse from there:

$$\begin{aligned} \langle \phi_0 | e^{\hat{T}} | \phi_0 \rangle &= \langle \phi_0 | (1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \dots) | \phi_0 \rangle \\ &= \langle \phi_0 | \phi_0 \rangle = 1 \end{aligned}$$

$$\text{if exact: } \langle \phi_0 | H e^{\hat{T}} | \phi_0 \rangle = \langle \phi_0 | e^{\hat{T}} | \phi_0 \rangle E = E$$

→ intermediate normalization.

CC equations (derivation)

$$H e^{\hat{T}} |\phi_0\rangle = e^{\hat{T}} |\phi_0\rangle E$$

$$\Rightarrow \text{multiply by } e^{-\hat{T}} = (e^{\hat{T}})^{-1}$$

$$e^{-\hat{T}} H e^{\hat{T}} |\phi_0\rangle = e^{-\hat{T}} e^{\hat{T}} |\phi_0\rangle E$$

$$\text{or } e^{-\hat{T}} H e^{\hat{T}} |\phi_0\rangle = |\phi_0\rangle E$$

$$\bar{H} |\phi_0\rangle = |\phi_0\rangle E$$

$e^{\hat{T}}$ defines a transformation \hat{U}

as $\hat{U}^{-1} \hat{H} \hat{U}$ has same eigenvalues as \hat{H}

$$(\hat{U}^{-1} \hat{H} \hat{U}) \hat{U}^{-1} |\phi_\lambda\rangle = \hat{U}^{-1} H |\phi_\lambda\rangle = \hat{U}^{-1} |\phi_\lambda\rangle E_\lambda$$

$$\text{if } H |\phi_\lambda\rangle = E_\lambda |\phi_\lambda\rangle$$

$$\bar{H} = e^{-\hat{T}} H e^{\hat{T}} = \hat{U}^{-1} \hat{H} \hat{U}$$

The operator \hat{T} is to be defined / calculated such that $|\phi_0\rangle$, a single determinant, becomes eigenstate of \bar{H} !

Note: \bar{H} is non-hermitian as $e^{\hat{T}}$ is not unitary.

The equation $e^{-\hat{T}} H e^{\hat{T}} |\phi_0\rangle = E |\phi_0\rangle$
 can only be solved exactly
 if \hat{T} contains up to N -fold excitations

To obtain equations we project:

$$\begin{cases} \langle \phi_0 | e^{-\hat{T}} H e^{\hat{T}} | \phi_0 \rangle = \langle \phi_0 | \phi_0 \rangle E = E \\ \langle \phi_a^r | e^{-\hat{T}} H e^{\hat{T}} | \phi_0 \rangle = \langle \phi_a^r | \phi_0 \rangle E = 0 \\ \langle \phi_{ab}^{rs} | e^{-\hat{T}} H e^{\hat{T}} | \phi_0 \rangle = 0 \\ \vdots \end{cases}$$

project precisely as far as you
 have generator $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots$

An intriguing structure emerges

$$\langle \phi_x | e^{-\hat{T}} H e^{\hat{T}} | \phi_0 \rangle = 0 \quad \forall x$$

→ Solve for \hat{T} amplitudes from
 these equations: # eq's = # of unknowns

Once \hat{T} is known: ~~Solve~~ Calculate
 $E = \langle \phi_0 | e^{-\hat{T}} H e^{\hat{T}} | \phi_0 \rangle$

The equations that determine the
 amplitudes do not contain
 the energy E .
 This is the main reason CC
 is size-extensive.

Further analysis CC equations

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = \bar{H} =$$

$$H + [H, T] + \frac{1}{2} [[H, T], T] + \frac{1}{3!} [[[H, T], T], T] \\ + \frac{1}{4!} [[[[H, T], T], T], T]$$

"a nested commutator expansion"
This series terminates exactly
at order 4. This is it!

You can verify by expanding
 $e^{-T} H e^T =$

$$(1 - T + \frac{1}{2} T^2 - \frac{1}{3!} T^3 + \dots) H (1 + T + \frac{1}{2} T^2 + \frac{1}{3!} T^3 + \dots)$$

$$= H \\ + HT - TH \quad (= [H, T]) \\ + \frac{1}{2} T^2 H + \frac{1}{2} HT^2 - THT \quad = \frac{1}{2} [[H, T], T] \\ + \dots$$

$$\frac{1}{2} [(HT - TH)T - T(HT - TH)]$$

$$= \frac{1}{2} (HT^2 - THT - THT + T^2 H)$$

This nested commutator series
would go on forever. Why does
it terminate? ✓

Explanation:

$\frac{1}{T}$ contains operator $r^+ s^+, a, b$
that net excite out of $|\phi_0\rangle$
These operators commute.

Now consider $[H, T] = HT - TH$

Let us use the anti commutation
relations to bring the T operators
in HT to the left

$$\langle ij | H | kl \rangle \quad \langle ij | T | kl \rangle \quad T_{ab}^{rr} \quad r^+ s^+ b a$$

→ we would get 'contractions'
e.g. $\{r^+, r^+\} = r^+ r^+$
between components of H and T

$$HT = \overline{HT} + TH$$

at least an δ contraction, maybe
more

TH : Move all operators
without contraction. This yields
no net sign change (if flip
over 2/4 operators in H .)

$$\text{Hence } HT - TH = \overline{HT}$$

$$\text{Likewise: } \frac{1}{2} [\overline{HT}, T] = \frac{1}{2} [\overline{[H, T]}, T]$$

$$\overline{HTT} + T \overline{HT} - T \overline{HT} = \overline{HTT}$$

$$= \overline{H} T T$$

Only contributions survive in which each T is contracted at least once with an operator in H .

Operators in T $\hat{r}^+ \hat{s}^+$, \hat{r} , \hat{s}
all anti commute, since $r, s \rightarrow$ virtual,
 a, b occupied.

Since $\hat{H} = \hat{h} + \hat{V}$, and \hat{V}
contains at most 4 de-excitation
operators, i.e.: $(b a r s)$ $b^+ a^+ s r$



Each of these can be contracted
against one T -operator, but then
it stops

$e^{-T} H e^T$ contains at
most 4 de-excitation operators, from H .

→ The equations are finite and
truncate with 4 operators:

There is an other consequence:
every \hat{T} in $(e^{-T} H e^T) = \bar{H} = (H e^T)_c$
has at least one index in
common with \bar{H} .
this is indicated by $(H e^T)_c$ (connected)
(This nomenclature arises from
Hilbert)

a diagrammatic representation
of the contraction process.
So-called 'Feynman diagrams'
(more quantum field ingredients!)

Let us now return to the
extensivity question

two subsystems A, B , non-interacting
 $H = H_A + H_B$

\hat{H}_A : only integrals with all labels on A
 \hat{H}_B : all labels on B

all mixed integrals $\rightarrow 0$

Then the corresponding $T = T_A + T_B$
(no mixed T)

$$\begin{aligned} e^{-T} H e^T &= e^{-(T_A + T_B)} (H_A + H_B) e^{T_A + T_B} \\ &= e^{-T_B} (e^{-T_A} H_A e^{T_A}) e^{T_B} + e^{-T_A} (e^{-T_B} H_B e^{T_B}) e^{T_A} \\ &= \bar{H}_A + \bar{H}_B \end{aligned}$$

because $[\bar{H}_A, \hat{T}_B] = 0$

A and B have no common indices

also $e^{T_A + T_B} = e^{T_A} e^{T_B} = e^{T_B} e^{T_A}$

It is then easy to demonstrate
that $\hat{T} = \hat{T}_A + \hat{T}_B$ is the solution
to the combined set of equations

$$\langle \phi_{rs}^{ab} | \bar{H}_A + \bar{H}_B | \phi_0 \rangle = 0$$

\rightarrow if $(rs) \in A$: T_A solution

$(rs) \in B$: T_B solution

$(rs) \in AB$ (mixed) : equation

Vanished automatically: $\bar{H}_A + \bar{H}_B$ does
not contain mixed excitations.

\rightarrow In CC theory the combined AB
equation reduces to the isolated
subsystem equations. This is the
basis for locality in physics; this
is what we need to solve problems.

\Rightarrow Deep physical implication to this
exponential structure.

$$\text{Summary: } e^T |\phi_0\rangle = e^{T_A + T_B} |\phi_0\rangle$$

$$= e^{T_A} e^{T_B} |\phi_0\rangle \approx \psi_A \otimes \psi_B$$

The wavefunction takes the product form

$$E = \langle \phi_0 | \bar{H}_A + \bar{H}_B | \phi_0 \rangle = E_A + E_B$$

\Rightarrow Size-consistency is build into the theory.

How does CC theory work in practice?

- CCSD, $n_o^2 n_v^4$ scaling is fairly efficient, but is not quantitatively accurate.
- CCSDT $n_o^3 n_v^5$: prohibitively expensive only used for benchmarking (or very high accuracy calc)
- CCSD(T) $n_o^2 n_v^4$ iteratively (like CCSD)
 $n_o^3 n_v^4$ non-iterative

add a perturbative correction to CCSD. The (T) step is most expensive part typically, but still practical.

CCSD(T) in combination with large basis sets yields highly accurate results (for single reference situations)

- geometries
- vibrational frequencies
- thermochemistry
- reaction barriers (usually ok)

still, very expensive because of basis set requirements (→ CC-pvqz)

CCSD(T) is often referred to as gold standard in quantum chemistry.

However: This method cannot deal with general multireference situations:

- bond breaking
- biradicals (sometimes)
- transition metal systems.

CC methods for excited states

A straightforward extension allows the calculation of excited states using coupled cluster theory.

procedure: solve CCSD equations for the ground state

obtain transformed Hamiltonian

$$\bar{H} = e^{-T} H e^T$$

This \bar{H} is diagonalized over singles and double excited configurations.

\bar{H}	O	S	D	T
O	E_0	X	X	
S	O	X	X	
D	O	X	X	
T	X	\sim	X	

X: sizeable Matrix - elements
 O: rigorously 0
 \sim : small remainder

$$\begin{pmatrix} A & B \\ O & D \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} A \\ 0 \end{pmatrix} \quad \text{ground state.}$$

$$\begin{pmatrix} A & B \\ O & D \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} Ax + By \\ Dy \end{pmatrix} = E_\lambda \begin{pmatrix} x \\ y \end{pmatrix}$$

→ $Dy = E_\lambda y$: diagonalize S+D block. Don't couple to ground state.

This method is called
 Equation-of-Motion Coupled cluster
 or
 Coupled cluster linear response theory
 or
 (closely related) SAC-CI

SAC-CI was first. How in Gaussian.
 (1977)

Accuracy EOM-CCSD

~ 0.1 eV for Rydberg states
 ~ 0.3 eV for Valence states

only works for Singly excited states. Because "n" in \bar{H} matrix: small $S \rightarrow T$ block.

Calculation of IP's and EA's:
 ($E_H - E_{H-1}$ and $E_{H+1} - E_H$)

Essentially same procedure!
 Construct \bar{H} elements over ionized or electron-attached states

\bar{H}	1h	2h1p
1h	X	X
2h1p	X	X

IP-EOM-CCSD

$\sim 0.1 - 0.2$ eV accuracy for Koopmans' states

1h: $\hat{a} | HF \rangle$
 2h1p: $\hat{a}^\dagger \hat{r}^\dagger \hat{L} | HF \rangle$ } minimal set to get good accuracy.