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Implementation of single-reference correlation methods

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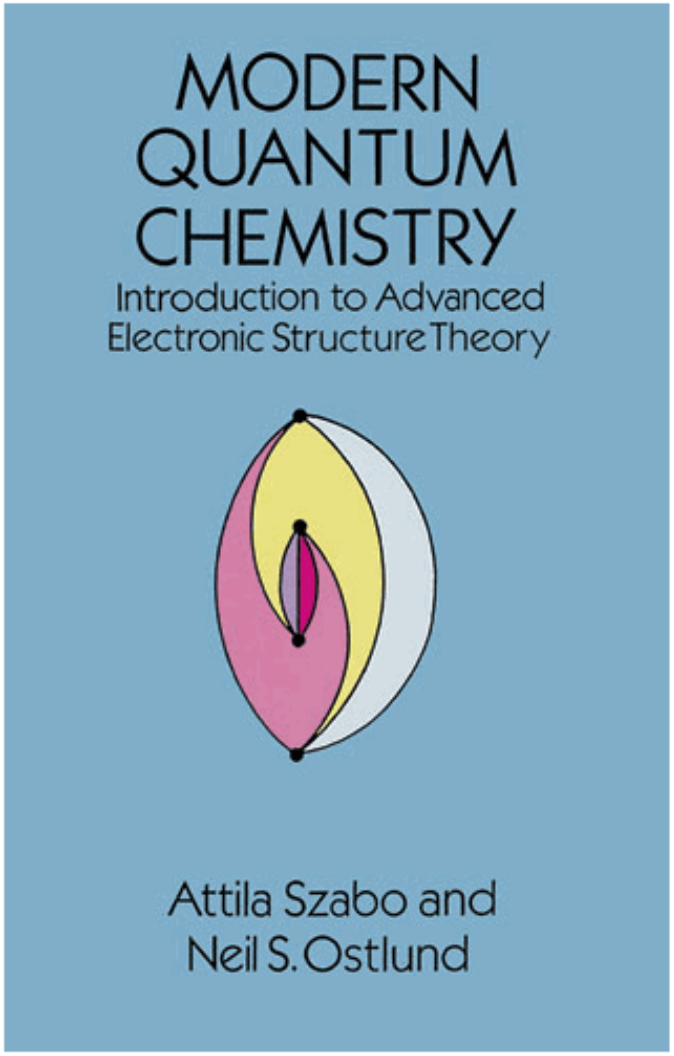
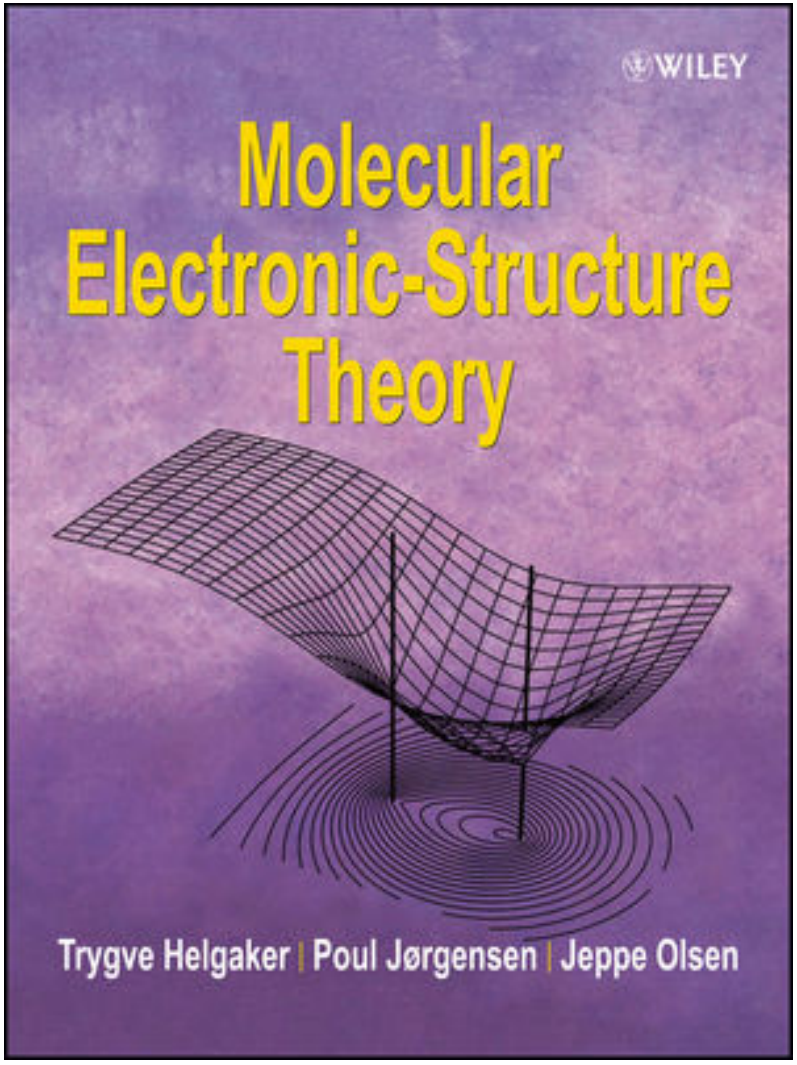
Catalog

- **Introduction**
  - **Second quantization**
- **Single reference methods**
  - **CID**
  - **CCD/MP2**
  - **Spin-adaptation**
- **Low scaling correlation methods**

Wave function, Matrix element, Programming

Reference


MODERN
QUANTUM
CHEMISTRY
Introduction to Advanced
Electronic Structure Theory
Attila Szabo and
Neil S. Ostlund


WILEY
Molecular
Electronic-Structure
Theory
Trygve Helgaker | Poul Jørgensen | Jeppe Olsen

Resources

- Various BBS, mailing list: CCL (jobs), Orca forum….

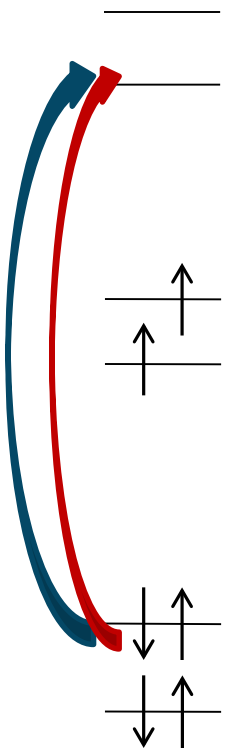
- Sherrill's notes

  http://vergil.chemistry.gatech.edu/notes/
- C++ Programming Tutorial in Chemistry

  https://github.com/CrawfordGroup/ProgrammingProjects
- Computer Physics Communications

  https://data.mendeley.com/journal/00104655?CPC
- GitHub:
  - https://github.com/guoyang0123/QCQC-python
  - PYSCF, Libint, MolSSI, Libxc

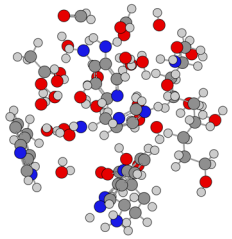
Symbols

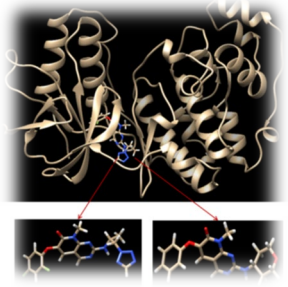


- a, b, c, d Virtual MOs
- t, u, v, w Active MOs
- i, j, k, l Doubly occupied MOs
- p, q, r, s arbitrary MOs

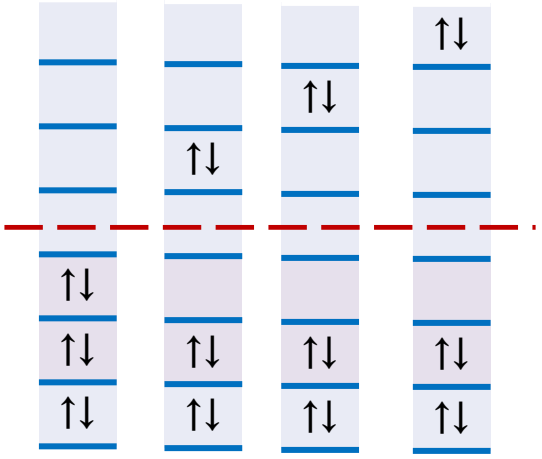
Wave function methods

Single reference





HF/DFT, MP2, CCSD(T),…



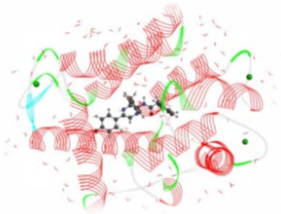
$|\Psi\rangle = c_0\,|\Psi_0\rangle + c_2\,|\Psi_2\rangle$

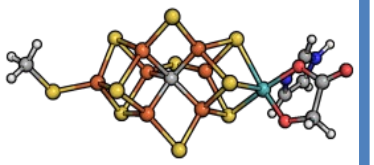
Multi reference

Bond breaking

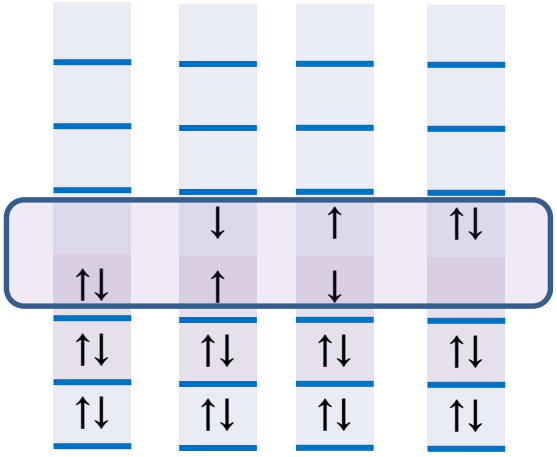
Excited state

Metal complex





CASSCF,MR-DFT, MRPT2, MRCI…



Active space

$|\Psi\rangle = c_0|\Psi_0\rangle + c_1|\Psi_1\rangle + \cdots + c_n|\Psi_n\rangle$

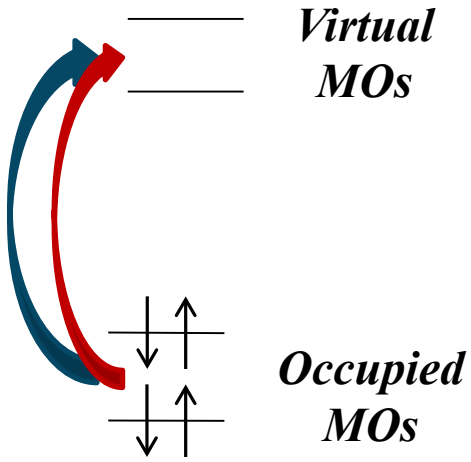
Single-reference methods

Correlation energy (dynamic correlation):

$$\left|\Psi_{ij}^{ab}\right\rangle = a_a^+ a_b^+ a_j \; a_i \; \left|\Psi_{HF}\right\rangle$$

$$E_{cor} = E_{FCI} - E_{HF} = \langle\Psi_{FCI}|H|\Psi_{FCI}\rangle - \langle\Psi_{HF}|H|\Psi_{HF}\rangle$$

$$\left|\Psi_{FCI}\right\rangle = C_{HF}\left|\Psi_{HF}\right\rangle + C_i^a\left|\Psi_i^a\right\rangle + C_{ij}^{ab}\left|\Psi_{ij}^{ab}\right\rangle \cdots\cdots$$



Truncated wave function:

$$\left|\Psi_{MP2/CCD}\right\rangle = \left|\Psi_{HF}\right\rangle + C_{ij}^{ab}\left|\Psi_{ij}^{ab}\right\rangle$$

	Examples	Variational	Unitary invariant	Size consistent
Perturbation theory	MP2/MP4	No	Yes	Yes
Configuration interaction	CID/CISD	Yes	Yes	No
Coupled cluster	CCD/CCSD	No	Yes	Yes

Per-Olov Löwdin, ***Phys. Rev.*** **97**, 1509 (1955)

Determinant

- Let $\{\phi_P(x)\}$ be a basis of M orthonormal spin orbitals. A Slater determinant is a normalized, anti-symmetrized product of spin orbitals

$$|\Psi| = \frac{1}{\sqrt{N!}} \begin{bmatrix} \chi_1(\overrightarrow{r_1}) & \cdots & \chi_N(\overrightarrow{r_1}) \\ \vdots & \ddots & \vdots \\ \chi_1(\overrightarrow{r_N}) & \cdots & \chi_N(\overrightarrow{r_N}) \end{bmatrix}$$

- In Fock space, a determinant is represented by an occupation-number vector

$$|\Psi\rangle = |k_1 k_2 \cdots k_N\rangle \qquad k_i = \begin{matrix} 1 & \chi_i \; is \quad occupied \\ 0 & \chi_i \; is \; unoccupied \end{matrix}$$

Second quantization

- Creation & Annihilation operator

Vacuum state	$\|0\rangle$	$\langle 0\|0\rangle = 1$
Creation	$a_p^\dagger\|0\rangle = \|\chi_p\rangle$	$\langle 0\|a_p = \langle\chi_p\|$
Annihilation	$a_p\|0\rangle = 0$	$\langle 0\|a_p^\dagger = 0$

- Determinant

$$|\Phi_0\rangle = |HF\rangle = a_p^\dagger a_q^\dagger a_r^\dagger \ldots |\,\rangle = |\chi_p\chi_q\chi_r \ldots\rangle$$

$$a_p^\dagger|\chi_1\chi_2\chi_3 \ldots \chi_p \ldots \chi_N\rangle = 0 \quad a_p^\dagger|\chi_1\chi_2\chi_3 \ldots 0_p \ldots \chi_N\rangle = (-1)^X|\chi_1\chi_2\chi_3 \ldots \chi_p \ldots \chi_N\rangle$$

$$a_p\,|\chi_1\chi_2\chi_3 \ldots 0_p \ldots \chi_N\rangle = 0 \quad a_p\,|\chi_1\chi_2\chi_3 \ldots \chi_p \ldots \chi_N\rangle = (-1)^X|\chi_1\chi_2\chi_3 \ldots 0_p \ldots \chi_N\rangle$$

- Anti-commutator

$$\{a_p\,, a_q^\dagger\} = a_p\,a_q^\dagger + a_q^\dagger a_p \;= \delta_{pq} \qquad \{a_p\,, a_q\,\} = a_p\,a_q \;+ a_q\,a_p \;= 0$$

$$\{a_p^\dagger, a_q\,\} = a_p^\dagger a_q \;+ a_q\,a_p^\dagger \;= \delta_{pq} \qquad \{a_p^\dagger, a_q^\dagger\} = a_p^\dagger a_q^\dagger + a_q^\dagger a_p^\dagger \;= 0$$

Operators

- One-body operator

$$\hat{F} = h_{pq} a_p^\dagger a_q \qquad h_{pq} = \int \chi_p^* f(x) \chi_q dx$$

- Two-body operator

$$\hat{G} = \frac{1}{2} \langle pr|qs\rangle a_p^\dagger a_r^\dagger a_s \; a_q \qquad \langle pr|qs\rangle = \iint \chi_p^* \chi_r^* g(x_1, x_2) \chi_q \chi_s dx_1 dx_2$$

- Electronic Hamiltonian

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q \; + \frac{1}{2} \sum_{pqrs} \langle pr|qs\rangle a_p^\dagger a_r^\dagger a_s \; a_q$$

Normal ordering

- Normal ordered

  Annihilation operators standing to the right of all creation operators

$$\langle 0|a_p^\dagger = 0 \qquad\qquad a_p\,|0\rangle = 0$$

- Example (two electron system)

$$|K\rangle = |\chi_p\chi_q\rangle = a_p^\dagger a_q^\dagger|0\rangle \qquad \langle K| = \langle 0|a_q\ a_p$$
$$|L\rangle = |\chi_r\chi_s\rangle = a_r^\dagger a_s^\dagger|0\rangle$$

$$\langle K|L\rangle = \langle 0|a_q\ a_p\ a_r^\dagger a_s^\dagger|0\rangle = \langle 0|a_q\ (\delta_{pr} - a_r^\dagger a_p\ )a_s^\dagger|0\rangle$$
$$= \delta_{pr}\langle 0|a_q\ a_s^\dagger|0\rangle - \langle 0|a_q\ a_r^\dagger a_p\ a_s^\dagger|0\rangle$$
$$= \delta_{pr}\langle 0|(\delta_{qs} - a_s^\dagger a_q\ )|0\rangle - \langle 0|a_q\ a_r^\dagger(\delta_{ps} - a_s^\dagger a_p\ )|0\rangle$$
$$= \delta_{pr}\delta_{qs}\ - \langle 0|a_s^\dagger a_q\ |0\rangle - \delta_{ps}\langle 0|a_q\ a_r^\dagger|0\rangle$$
$$= \delta_{pr}\delta_{qs}\ - \delta_{ps}\langle 0|(\delta_{qr} - a_r^\dagger a_q\ )|0\rangle$$
$$= \delta_{pr}\delta_{qs}\ - \delta_{ps}\delta_{qr}$$

Normal ordered Hamiltonian

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} \langle pr|qs\rangle a_p^\dagger a_r^\dagger a_s \, a_q$$

$$\sum_{pqrs} \langle pr|qs\rangle a_p^\dagger a_r^\dagger a_s \, a_q = \sum_{pqrs} \langle pr|sq\rangle a_p^\dagger a_r^\dagger a_s \, a_q$$

$$= -\sum_{pqrs} \langle pr|sq\rangle a_p^\dagger a_r^\dagger a_q \, a_s$$

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \{\langle pr|qs\rangle - \langle pr|sq\rangle\} a_p^\dagger a_r^\dagger a_s \, a_q$$

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pr||qs\rangle a_p^\dagger a_r^\dagger a_s \, a_q$$

$$\langle pr||qs\rangle = \langle pr|qs\rangle - \langle pr|sq\rangle$$

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} (pq|rs) a_p^\dagger a_r^\dagger a_s \, a_q$$

$$\langle pr|qs\rangle = (pq|rs)$$

Fermi vacuum

- Creation & Annihilation operator

$$|\Phi_0\rangle = |HF\rangle = a_i^\dagger\, a_j^\dagger\, a_k^\dagger \ldots |\,\rangle = |\chi_i\chi_j\chi_k \ldots\rangle$$

Creation $\quad a_a^\dagger\,|HF\rangle = |\chi_a\chi_i\chi_j\chi_k \ldots\rangle \qquad a_i\;|HF\rangle = |\chi_j\chi_k \ldots\rangle$

Annihilation $\quad a_a\,|HF\rangle = 0 \qquad a_i^\dagger|HF\rangle = a_i^\dagger|\chi_i\chi_j\chi_k \ldots\rangle = 0$

- Anti-commutator

$$\{a_a\,, a_b^\dagger\} = a_a\, a_b^\dagger + a_b^\dagger a_a\; = \delta_{ab} \qquad \{a_i\;, a_j^\dagger\} = a_i\; a_j^\dagger + a_j^\dagger a_i\; = \delta_{ij}$$

$$\{a_a^\dagger, a_b\;\} = a_a^\dagger a_b\; + a_b\, a_a^\dagger = \delta_{ab} \qquad \{a_i^\dagger, a_j\;\} = a_i^\dagger a_j\; + a_j\; a_i^\dagger = \delta_{ij}$$

$$\{a_a^\dagger, a_b^\dagger\} = a_a^\dagger a_b^\dagger + a_b^\dagger a_a^\dagger = 0 \qquad \{a_i^\dagger, a_j^\dagger\} = a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$$

$$\{a_a\,, a_b\;\} = a_a\, a_b\; + a_b\, a_a\; = 0 \qquad \{a_i\;, a_j\;\} = a_i\; a_j\; + a_j\; a_i\; = 0$$

$$\{a_a^\dagger, a_i^\dagger\} = \{a_i^\dagger, a_a^\dagger\} = 0 \qquad \{a_a\,, a_i^\dagger\} = \{a_i^\dagger, a_a\;\} = 0$$

$$\{a_a\,, a_i\;\} = \{a_i\;, a_a\;\} = 0 \qquad \{a_i\;, a_a^\dagger\} = \{a_a^\dagger, a_i\;\} = 0$$

Normal ordering

- Normal ordered

  Annihilation operators standing to the right of all creation operators

  Move $a_a^\dagger$ and a_i to left, $a_i^\dagger$ and a_a to right

- Example

  Single excitation: $|K\rangle = a_a^\dagger a_i \ |HF\rangle$ and $|L\rangle = a_b^\dagger a_j \ |HF\rangle$

$$\langle K|L\rangle = \langle HF|a_i^+ a_a \ a_b^\dagger a_j \ |HF\rangle = \langle HF|a_a \ a_b^+ a_i^+ a_j \ |HF\rangle$$

$$= \delta_{ab}\langle HF|a_i^+ a_j \ |HF\rangle - \langle HF|a_a \ a_b^\dagger a_i^+ a_j \ |HF\rangle$$

$$= \delta_{ij}\delta_{ab} - \langle HF|a_j \ a_i^+|HF\rangle - \delta_{ij}\langle HF|a_a \ a_b^\dagger|HF\rangle + \langle HF|a_a \ a_b^\dagger a_j \ a_i^+|HF\rangle$$

$$= \delta_{ij}\delta_{ab} - 0 - 0 - \langle HF|a_a \ a_j \ a_b^\dagger a_i^+|HF\rangle$$

$$= \delta_{ij}\delta_{ab}$$

CI doubles (CID)

- Wave function

$$\left|\Psi_{CID}\right\rangle = C_{HF}\left|\Psi_{HF}\right\rangle + \left(\frac{1}{2!}\right)^2 \sum_{ijab} C_{ij}^{ab} a_a^+ a_b^+ a_j \; a_i \; \left|\Psi_{HF}\right\rangle$$

$$= C_{HF}\left|\Psi_{HF}\right\rangle + \sum_{i>j,a>b} C_{ij}^{ab} \Psi_{ij}^{ab}$$

- Energy expression

$$E_{CID} = \frac{\left\langle \Psi_{CID}\middle|H\middle|\Psi_{CID}\right\rangle}{\left\langle \Psi_{CID}\middle|\Psi_{CID}\right\rangle} \qquad H(kC) = E(kC)$$

- Intermediate normalization

$$\left|\Psi_{CID}\right\rangle = \left|\Psi_{HF}\right\rangle + \sum_{i>j,a>b} C_{ij}^{ab} a_a^+ a_b^+ a_j \; a_i \; \left|\Psi_{HF}\right\rangle$$

CID

- Working equation

$$H\left\{\left|\Psi_{HF}\right\rangle+\sum_{i>j,a>b}C_{ij}^{ab}\left|\Psi_{ij}^{ab}\right\rangle\right\}=E\left\{\left|\Psi_{HF}\right\rangle+\sum_{i>j,a>b}C_{ij}^{ab}\left|\Psi_{ij}^{ab}\right\rangle\right\}\qquad(HC=EC)$$

Project $\langle\Psi_{HF}|$ on left

$$\langle\Psi_{HF}|H|\Psi_{HF}\rangle+\sum_{i>j,a>b}C_{ij}^{ab}\langle\Psi_{HF}|H|\Psi_{ij}^{ab}\rangle=E\langle\Psi_{HF}|\Psi_{HF}\rangle$$

$$\sum_{i>j,a>b}C_{ij}^{ab}\langle\Psi_{HF}|H|\Psi_{ij}^{ab}\rangle=E_{cor}\quad(E=E_{cor}+E_{HF})$$

Project $\left\langle\Psi_{i'j'}^{a'b'}\right|$ on left

$$\left\langle\Psi_{i'j'}^{a'b'}\middle|H\middle|\Psi_{HF}\right\rangle+\sum_{i>j,a>b}C_{ij}^{ab}\left\langle\Psi_{i'j'}^{a'b'}\middle|H\middle|\Psi_{ij}^{ab}\right\rangle=E\sum_{i>j,a>b}C_{ij}^{ab}\left\langle\Psi_{i'j'}^{a'b'}\middle|\Psi_{ij}^{ab}\right\rangle$$

Storage of C_{ij}^{ab}: $4o^2v^2$, integral: (vv|vv), bottleneck: o^2v^4

o and v are no. of spatial occ. and vir. MOs

$$C_{ij}^{cd}(ac|bd)\rightarrow R_{ij}^{ab}$$

Coupled cluster doubles (CCD)

- Wave function

$$\left|\Psi_{CCD}\right\rangle = e^{T_2}\left|\Psi_{HF}\right\rangle$$

$$T_2 = \sum_{i>j,a>b} C_{ij}^{ab} a_a^+ a_b^+ a_j \; a_i \qquad e^{T_2} = 1 + T_2 + \frac{1}{2}T_2^2 + \ldots$$

- Working equation

$$He^{T_2}\left|\Psi_{HF}\right\rangle = Ee^{T_2}\left|\Psi_{HF}\right\rangle$$

Project $\langle\Psi_{HF}|$ on left

$$\left\langle\Psi_{HF}\middle|He^{T_2}\middle|\Psi_{HF}\right\rangle = E\left\langle\Psi_{HF}\middle|e^{T_2}\Psi_{HF}\right\rangle \quad \left\langle\Psi_{HF}\middle|H(1+T_2)\middle|\Psi_{HF}\right\rangle = E\left\langle\Psi_{HF}\middle|e^{T_2}\Psi_{HF}\right\rangle$$

$$\left\langle\Psi_{HF}\middle|HT_2\middle|\Psi_{HF}\right\rangle = E_{cor} \quad (E = E_{cor} + E_{HF})$$

Project $\left\langle\Psi_{i'j'}^{a'b'}\right|$ on left

$$\left\langle\Psi_{i'j'}^{a'b'}\middle|H(1+T_2+\frac{1}{2}T_2^2)\middle|\Psi_{HF}\right\rangle = E\left\langle\Psi_{i'j'}^{a'b'}\middle|e^{T_2}\Psi_{HF}\right\rangle$$

Too many disconnected terms!

Storage of C_{ij}^{ab}: $4o^2v^2$, integral: (vv|vv), bottleneck: o^2v^4

o and v are no. of spatial occ. and vir. MOs

BCH expansion

- Baker–Campbell–Hausdorff expansion

$$H^{eff} = e^{-T} H e^{T} = H + [H,T] + \frac{1}{2}[[H,T],T] \ldots + \frac{1}{N!}[..[H,T],..T]$$

$$H e^{T_2} \left|\Psi_{HF}\right\rangle = E e^{T_2} \left|\Psi_{HF}\right\rangle$$

Project $\langle \Psi_{HF} | e^{-T_2}$ on left

$$\langle \Psi_{HF} | H \left|\Psi_{HF}\right\rangle + \left\langle \Psi_{HF}\right| [H,T_2] \left|\Psi_{HF}\right\rangle = E$$

$$\left\langle \Psi_{HF}\right| [H,T_2] \left|\Psi_{HF}\right\rangle = E_{cor} \quad (E = E_{cor} + E_{HF})$$

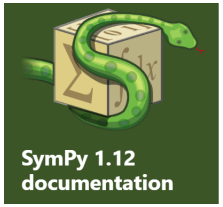
Project $\left\langle \Psi_{i'j'}^{a'b'} \right| e^{-T_2}$ on left

$$\left\langle \Psi_{i'j'}^{a'b'} \right| H + [H,T_2] + \frac{1}{2}[[H,T_2],T_2] \left|\Psi_{HF}\right\rangle = 0$$

No disconnected terms!

Matrix element evaluation

- Sympy



Welcome to SymPy's documentation!

A PDF version of these docs is also available.

SymPy is a Python library for symbolic mathematics. If you are new to SymPy, start with the introductory tutorial.

```
1   #!/usr/bin/env python
2
3   """
4   Calculates the Coupled-Cluster energy- and amplitude equations
5   See 'An Introduction to Coupled Cluster Theory' by
6   T. Daniel Crawford and Henry F. Schaefer III.
7
8   Other Resource : http://vergil.chemistry.gatech.edu/notes/sahan-cc-2010.pdf
9   """
10
11  from sympy.physics.secondquant import (AntiSymmetricTensor, wicks,
12          F, Fd, NO, evaluate_deltas, substitute_dummies, Commutator,
13          simplify_index_permutations, PermutationOperator)
14  from sympy import (
15      symbols, Rational, latex, Dummy
16  )
17
18  > pretty_dummies_dict = {
22      }...
23
```

https://github.com/sympy/sympy/blob/master/examples/intermediate/coupled_cluster.py

Matrix elements evaluation

```
24
25  def get_CC_operators():
26      """
27      Returns a tuple (T1,T2) of unique operators.
28      """
29      i = symbols('i', below_fermi=True, cls=Dummy)
30      a = symbols('a', above_fermi=True, cls=Dummy)
31      t_ai = AntiSymmetricTensor('t', (a,), (i,))
32      ai = NO(Fd(a)*F(i))
33      i, j = symbols('i,j', below_fermi=True, cls=Dummy)
34      a, b = symbols('a,b', above_fermi=True, cls=Dummy)
35      t_abij = AntiSymmetricTensor('t', (a, b), (i, j))
36      abji = NO(Fd(a)*Fd(b)*F(j)*F(i))
37
38      T1 = t_ai*ai
39      T2 = Rational(1, 4)*t_abij*abji
40      return (T1, T2)
41
42
43  def main():
44      print()
45      print("Calculates the Coupled-Cluster energy- and amplitude equations")
```

https://github.com/sympy/sympy-notebooks/blob/1878319fce86df62bb8944492b8a211e259c8078/intermediate/coupled_cluster.py

So far so good?
How about closed-shell systems?

Spin-adaption

- Single excitation of RHF $\left| i_\alpha i_\beta \right\rangle$

  Spin-flip excitation: $\left| i_\alpha \quad a_\alpha \right\rangle, \left| i_\beta \quad a_\beta \right\rangle, {}^{1}/_{\sqrt{2}} \left(\left| i_\alpha \quad a_\beta \right\rangle + \left| i_\beta \quad a_\alpha \right\rangle \right)$

  Spin-free excitation: ${}^{1}/_{\sqrt{2}} \left(\left| i_\alpha \quad a_\beta \right\rangle - \left| i_\beta \quad a_\alpha \right\rangle \right)$

- Spin-free excitation operator

$$\hat{E}_{pq} = a^\dagger_{p_\alpha} a_{q_\alpha} + a^\dagger_{p_\beta} a_{q_\beta}$$

$$\hat{E}_{ai} \left| i_\alpha i_\beta \right\rangle = \left| a_\alpha \quad i_\beta \right\rangle - \left| a_\beta \quad i_\alpha \right\rangle = \left| i_\alpha \quad a_\beta \right\rangle - \left| i_\beta \quad a_\alpha \right\rangle$$

- Singles and Doubles

$$T_i^a = \sum_{ia} C_{ia} \hat{E}_{ai}$$

$$T_{ij}^{ab} = \frac{1}{2} \sum_{ijab} C_{ij}^{ab} \hat{E}_{bj} \hat{E}_{ai}$$

Spin-free operator

- Hamiltonian (Spin-orbital)

$$\hat{H} = \sum_{pq}^{2N} h_{pq} a_p^\dagger a_q \; + \frac{1}{2} \sum_{pqrs}^{2N} (pq|rs) a_p^\dagger a_r^\dagger a_s \; a_q$$

- Hamiltonian (Spatial-orbital)

$$\hat{E}_{pq} = a_{p_\alpha}^\dagger a_{q_\alpha} + a_{p_\beta}^\dagger a_{q_\beta}$$

$$\hat{H} = \sum_{pq}^{N} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs}^{N} (pq|rs) \left(\hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} \right)$$

N : number of spatial MOs

Normal ordering

- Normal ordered

"Shift to left" $\hat{E}_{pi}|HF\rangle = 2\delta_{ip}|HF\rangle \qquad \langle HF|\hat{E}_{ap} = 0$

"Shift to right" $\langle HF|\hat{E}_{ip} = \langle HF|2\delta_{ip} \qquad \hat{E}_{pa}|HF\rangle = 0$

- Commutator (Boson)

$$\left[\hat{E}_{pq}, \hat{E}_{rs}\right] = \hat{E}_{pq}\hat{E}_{rs} - \hat{E}_{rs}\hat{E}_{pq} = \delta_{rq}\hat{E}_{ps} - \delta_{ps}\hat{E}_{rq}$$

- Normal ordering

$$\hat{E}_{jb}\hat{E}_{ai} = \hat{E}_{ai}\hat{E}_{jb} + \delta_{ab}\hat{E}_{ij} - \delta_{ij}\hat{E}_{ab}$$

$$\left\langle HF\middle|\hat{E}_{jb}\hat{E}_{ai}\middle|HF\right\rangle = 2\delta_{ab}\delta_{ij}$$

Two electron excitation operator

$$\hat{e}_{pq,rs} = \hat{e}_{rs,pq} = \sum_{\sigma\tau} a^{\dagger}_{p_\sigma} a^{\dagger}_{r_\tau} a_{s_\sigma} a_{q_\sigma} = \hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}$$

$$\left[\hat{E}_{pq}, \hat{e}_{rs,xy}\right] = \delta_{rq}\hat{e}_{ps,xy} + \delta_{qx}\hat{e}_{rs,py} - \delta_{ps}\hat{e}_{rq,xy} - \delta_{py}\hat{e}_{rs,xq}$$

$$\left[a_{q_\sigma}, \hat{E}_{rs}\right] = \delta_{rq} a_{s_\sigma}$$

$$\left[a_{q_\sigma}, \hat{e}_{rs,xy}\right] = \delta_{rq}\hat{E}_{xy} a_{s_\sigma} + \delta_{qx}\hat{E}_{rs} a_{y_\sigma}$$

$$\left[a^{\dagger}_{p_\sigma}, \hat{E}_{rs}\right] = -\delta_{ps} a^{\dagger}_{r_\sigma}$$

$$\left[a^{\dagger}_{p_\sigma}, \hat{e}_{rs,xy}\right] = -\delta_{ps} a^{\dagger}_{r_\sigma}\hat{E}_{xy} - \delta_{py} a^{\dagger}_{x_\sigma}\hat{E}_{rs}$$

Y. Guo, N. Zhang, W. Liu, ***J. Chem. Theory Comput.*** 19, 6668 (2023)

Example

- MP2 wave function

$$\left|\Psi_{MP2}\right\rangle = \left|\Psi_{HF}\right\rangle + \left|\Psi_1\right\rangle = \left|\Psi_{HF}\right\rangle + \frac{1}{2}\sum_{ijab} C_{ij}^{ab}\hat{E}_{bj}\hat{E}_{ai}\left|\Psi_{HF}\right\rangle$$

- Working equations

$$\frac{1}{2}\sum_{ijab} C_{ij}^{ab}\left\langle\Psi_{HF}\middle|H\hat{E}_{bj}\hat{E}_{ai}\middle|\Psi_{HF}\right\rangle = E_{cor}$$

$$\left\langle\Psi_{HF}\middle|\hat{E}_{i'a'}\hat{E}_{j'b'}H\middle|\Psi_{HF}\right\rangle + \frac{1}{2}\sum_{ijab} C_{ij}^{ab}\left\langle\Psi_{HF}\middle|\hat{E}_{i'a'}\hat{E}_{j'b'}(H_0 - E_{HF})\hat{E}_{bj}\hat{E}_{ai}\middle|\Psi_{HF}\right\rangle = 0$$

$$H_0 = \sum_{ij} f_{ij}\hat{E}_{ij} + \sum_{ab} f_{ab}\hat{E}_{ab} + E_{HF} - 2\sum_{ii} f_{ii}$$

Contravariant configuration

- Doubles

$$\Psi_{ij}^{ab} = \hat{E}_{bj}\hat{E}_{ai}\left|\Psi_{HF}\right\rangle$$

$$\left\langle \Psi_{i'j'}^{a'b'} \middle| \Psi_{ij}^{ab} \right\rangle = \delta_{aa'}\delta_{bb'}\left(4\delta_{ii'}\delta_{jj'} - 2\delta_{ji'}\delta_{ij'}\right) + \delta_{ab'}\delta_{ba'}\left(4\delta_{ij'}\delta_{ji'} - 2\delta_{ii'}\delta_{jj'}\right)$$

- Contravariant doubles

$$\tilde{\Psi}_{ij}^{ab} = \frac{1}{6}(2\Psi_{ij}^{ab} + \Psi_{ji}^{ab})$$

$$\left\langle \tilde{\Psi}_{i'j'}^{a'b'} \middle| \Psi_{ij}^{ab} \right\rangle = \delta_{aa'}\delta_{bb'}\delta_{ii'}\delta_{jj'} + \delta_{ab'}\delta_{ba'}\delta_{ij'}\delta_{ji'}$$

- Singles

$$\Psi_{i}^{a} = \hat{E}_{ai}\left|\Psi_{HF}\right\rangle \qquad \tilde{\Psi}_{i}^{a} = \frac{1}{2}\Psi_{i}^{a} \qquad \left\langle \tilde{\Psi}_{i'}^{a'} \middle| \Psi_{i}^{a} \right\rangle = \delta_{aa'}\delta_{ii'}$$

MP2

- Project $\langle \tilde{\Psi}_{ij}^{ab} |$ on left

$$\langle \tilde{\Psi}_{ij}^{ab} | H | \Psi_{HF} \rangle + \langle \tilde{\Psi}_{ij}^{ab} | (H_0 - E_{HF}) | \Psi_1 \rangle = 0$$

Easy to validate: $\langle \tilde{\Psi}_{ij}^{ab} | H | \Psi_{HF} \rangle = (ia|jb)$ $\quad$ $\langle \tilde{\Psi}_{ij}^{ab} | \Psi_1 \rangle = C_{ij}^{ab}$

$$(ia|jb) + \sum_c (f_{ac} C_{ij}^{cb} + f_{cb} C_{ij}^{ac}) - \sum_k (f_{ik} C_{kj}^{ab} + f_{kj} C_{ik}^{ab}) = 0$$

$$|\Psi_1\rangle = \frac{1}{2} \sum_{ijab} C_{ij}^{ab} \hat{E}_{bj} \hat{E}_{ai} |\Psi_{HF}\rangle = \frac{1}{2} \sum_{ijab} \tilde{C}_{ij}^{ab} \left| \tilde{\Psi}_{ij}^{ab} \right\rangle$$

$$\tilde{C}_{ij}^{ab} = 2C_{ij}^{ab} - C_{ij}^{ba}$$

$$E_{cor} = \langle \Psi_{HF} | H | \Psi_1 \rangle = \frac{1}{2} \sum_{ijab} \tilde{C}_{ij}^{ab} \langle \Psi_{HF} | H | \tilde{\Psi}_{ij}^{ab} \rangle = \frac{1}{2} \sum_{ijab} \tilde{C}_{ij}^{ab} (ia|jb)$$

Storage of C_{ij}^{ab} : no , integral: (ov|ov), bottleneck: $(o+v)^4 o$

o and v are no. of spatial occ. and vir. MOs

Programming MP2

- Two-electron integral

$$(pq|rs) = \sum_{\mu}\sum_{\nu}\sum_{\lambda}\sum_{\sigma} C_{\mu}^{p} C_{\nu}^{q} (\mu\nu|\lambda\sigma) C_{\lambda}^{r} C_{\sigma}^{s} \qquad (N^8)$$

  - Intermediates

$$(pq|rs) = \sum_{\mu} C_{\mu}^{p} \left[\sum_{\nu} C_{\nu}^{q} \left[\sum_{\lambda} C_{\lambda}^{r} \left[\sum_{\sigma} C_{\sigma}^{s} (\mu\nu|\lambda\sigma) \right] \right] \right] \qquad (4N^5)$$

- Energy

$$E_{\mathrm{MP2}} = \sum_{ij}\sum_{ab} \frac{(ia|jb)\left[2(ia|jb) - (ib|ja)\right]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \qquad (N^4)$$

https://github.com/CrawfordGroup/ProgrammingProjects/tree/master/Project%2304#project-4-the-second-order-moller-plesset-perturbation-mp2-energy

Programming CCSD

- CCD code

$$\left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| \tilde{\hat{H}} + [\tilde{\hat{H}}, \hat{T}_2] + \frac{1}{2}[[\tilde{\hat{H}}, \hat{T}_2], \hat{T}_2] \middle| \mathrm{HF} \right\rangle$$

$$\left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| \tilde{\hat{H}} \middle| \mathrm{HF} \right\rangle = \tilde{g}_{aibj}$$

$$\frac{1}{2}\left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| [[\tilde{\hat{H}}, \hat{T}_2], \hat{T}_2] \middle| \mathrm{HF} \right\rangle = R_1 + R_2 + R_3$$

$$\left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| [\tilde{\hat{H}}, \hat{T}_2] \middle| \mathrm{HF} \right\rangle = Q_1 + Q_2$$

$$Q_1 = \sum_{cdkl} t_{kl}^{cd} \left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| E_{ck}[\tilde{\hat{H}}, E_{dl}] \middle| \mathrm{HF} \right\rangle$$

$$Q_2 = \frac{1}{2}\sum_{cdkl} t_{kl}^{cd} \left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| [[\tilde{\hat{H}}, E_{ck}], E_{dl}] \middle| \mathrm{HF} \right\rangle$$

$$R_1 = \frac{1}{2}\sum_{\substack{cdef \\ klmn}} t_{kl}^{cd} t_{mn}^{ef} \left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| E_{ck}E_{em}[[\tilde{\hat{H}}, E_{dl}], E_{fn}] \middle| \mathrm{HF} \right\rangle$$

$$R_2 = \frac{1}{2}\sum_{\substack{cdef \\ klmn}} t_{kl}^{cd} t_{mn}^{ef} \left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| E_{ck}[[[\tilde{\hat{H}}, E_{dl}], E_{em}], E_{fn}] \middle| \mathrm{HF} \right\rangle$$

$$R_3 = \frac{1}{8}\sum_{\substack{cdef \\ klmn}} t_{kl}^{cd} t_{mn}^{ef} \left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| [[[[\tilde{\hat{H}}, E_{ck}], E_{dl}], E_{em}], E_{fn}] \middle| \mathrm{HF} \right\rangle$$

$$Q_1 = P_{ij}^{ab}\left(\sum_c t_{ij}^{ac}\,{}^1\tilde{F}_{bc} - \sum_k t_{ik}^{ab}\,{}^1\tilde{F}_{kj} + \sum_{ck} t_{ik}^{ac}\tilde{L}_{bjkc}\right)$$

$$R_1 = P_{ij}^{ab}\sum_{cdkl} t_{ik}^{ac} t_{jl}^{bd}\tilde{L}_{kcld}$$

$$Q_2 = -P_{ij}^{ab}\sum_{ck}(t_{kj}^{ac}\tilde{g}_{bcki} + t_{ki}^{ac}\tilde{g}_{bjkc}) + \sum_{cd} t_{ij}^{cd}\tilde{g}_{acbd} + \sum_{kl} t_{kl}^{ab}\tilde{g}_{kilj}$$

$$R_2 = -P_{ij}^{ab}\sum_{cdkl}(t_{ik}^{ab} t_{lj}^{cd}\tilde{L}_{lckd} + t_{ik}^{ac} t_{lj}^{bd}\tilde{L}_{kcld} + t_{ij}^{ac} t_{kl}^{bd}\tilde{L}_{kcld})$$

$$R_3 = \tfrac{1}{2}P_{ij}^{ab}\sum_{cdkl}(t_{kl}^{ab} t_{ij}^{cd} + t_{ki}^{ac} t_{lj}^{bd} + t_{kj}^{ad} t_{li}^{bc})\tilde{g}_{kcld}$$

- Include singles by “dressing” Hamiltonian

<Molecular electronic-structure theory>

Useful reference

- Manuscript

RESEARCH ARTICLE | JANUARY 17 2013

An efficient and near linear scaling pair natural orbital based local coupled cluster method

Special Collection: JCP 90 for 90 Anniversary Collection

Christoph Riplinger; Frank Neese

Check for updates

+ Author & Article Information

J. Chem. Phys. 138, 034106 (2013)

Journal of Chemical Theory and Computation > Vol 3/Issue 4 > Article

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ARTICLE | June 6, 2007

Parallel Calculation of Coupled Cluster Singles and Doubles Wave Functions Using Array Files

Tomasz Janowski, Alan R. Ford, and Peter Pulay

Journal of Chemical Theory and Computation

Cite this: *J. Chem. Theory Comput.* 2007, 3, 4, 1368−1377

https://doi.org/10.1021/ct700048u

Published June 6, 2007

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ARTICLE | November 27, 2019

Integral-Direct and Parallel Implementation of the CCSD(T) Method: Algorithmic Developments and Large-Scale Applications

László Gyevi-Nagy*, Mihály Kállay, and Péter R. Nagy*

Journal of Chemical Theory and Computation

Cite this: *J. Chem. Theory Comput.* 2020, 16, 1, 366−384

https://doi.org/10.1021/acs.jctc.9b00957

Published November 27, 2019

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- Code
  - https://github.com/piecuch-group/ccpy (by Piotr)
  - https://github.com/devinamatthews/aquarius/tree/stable/src/cc (by Matthews)

Local property based methods

- Local density based methods
  - Divide and Conquer (D&C)
  - Fragment molecular orbital (FMO)
  - Primitive fragment LMOs (pFLMOs)
- Local fragment energy based methods
  - Systematic Molecular Fragmentation (SMF)
  - Generalized Energy Based Fragment (GEBF)
  - Many body expansion

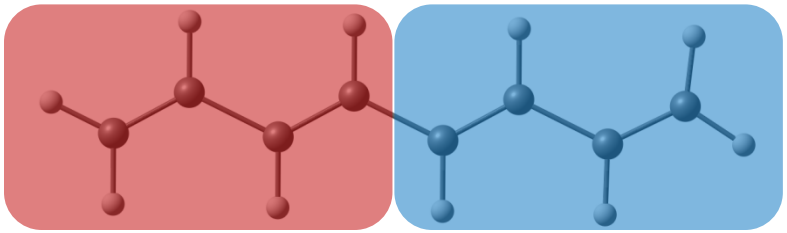
Not based on the Hartree-Fock wave functions of whole systems!

M. A. Collins, and R. P. A. Bettens, *Chem. Rev.* 115 (2015).

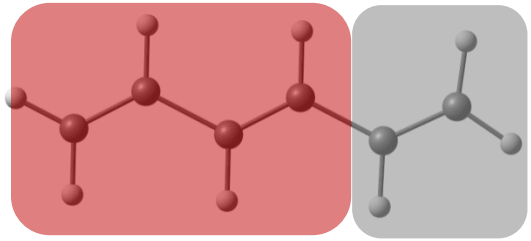
Principle of Fragment based methods

Subsys A **Subsys B**

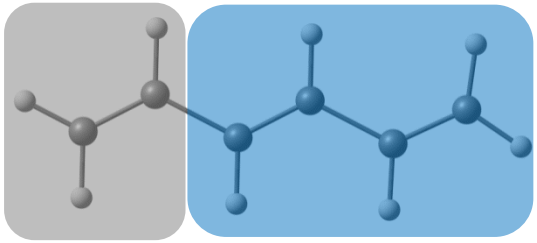
Target molecule



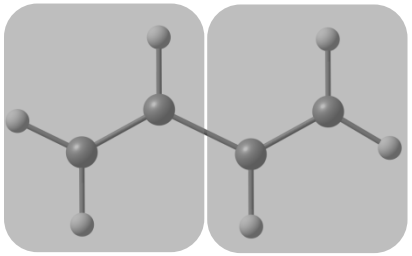
E_A=Subsys A+ Env A



E_B=Subsys B+ Env B



E_C=Env A+ Env B



$$E_{Total} \approx E_A + E_B - E_C$$

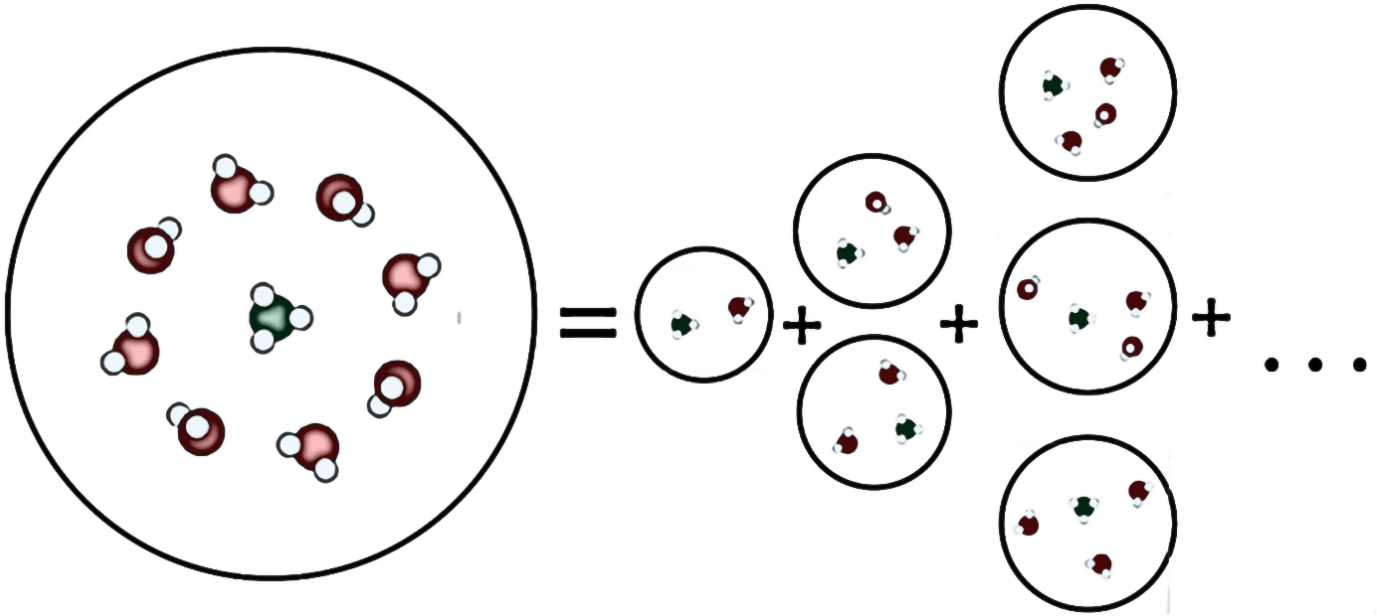
No calculation involving the whole system
High parallel efficiency

Many-body expansion

$$E = \sum_{I}^{N} E_I + \sum_{I<J}^{N} \Delta E_{IJ} + \sum_{I<J<K}^{N} \Delta E_{IJK} + \cdots .$$

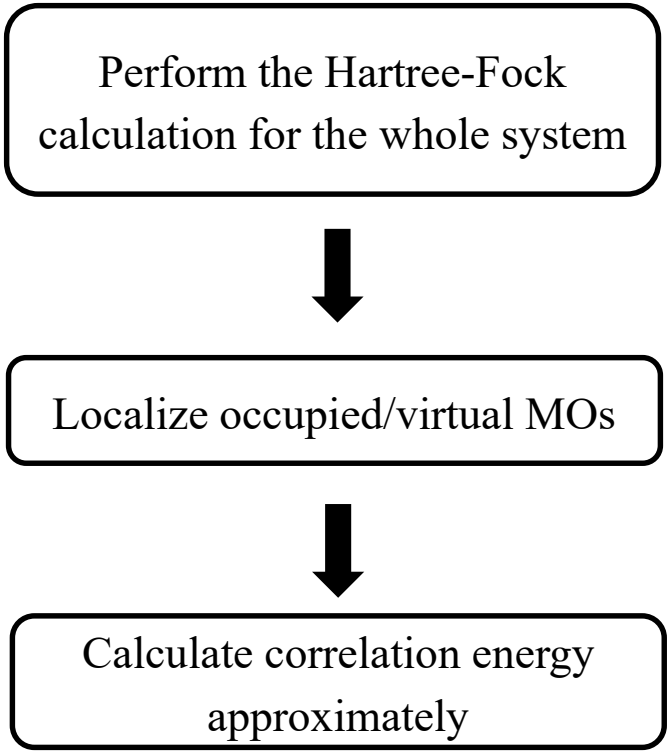
$$\Delta E_{IJ} = E_{IJ} - E_I - E_J,$$

$$\Delta E_{IJK} = E_{IJK} - \Delta E_{IJ} - \Delta E_{IK} - \Delta E_{JK} - E_I - E_J - E_K,$$



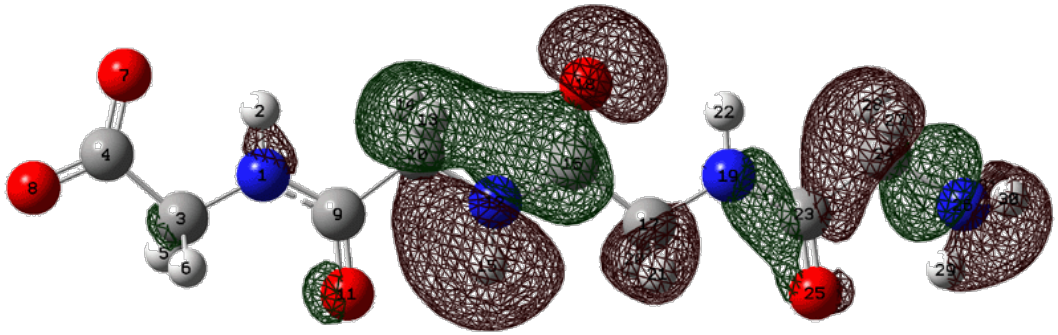
Local correlation methods

- Direct local correlation methods
  - Pulay's and Werner's local correlation methods (LMO+PAO)
  - Domain-based Local Pair Natural Orbital (DLPNO) method by Neese
- "Fragment" based local correlation methods
  - Cluster-in-molecule (CIM) by Li
  - Local natural orbital (LNO) by Kallay
  - Divide-expend-consolidate (DEC) by Jørgensen
  - Incremental

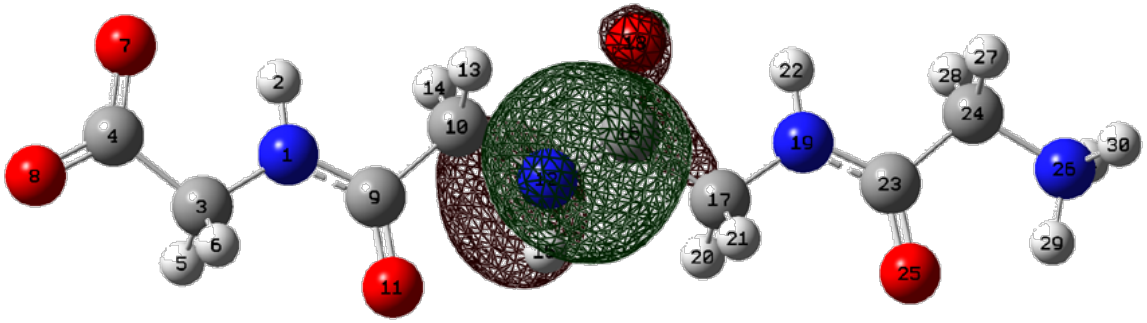


A schematic picture of a LMO

A canonical MO (CMO)



A LMO



A LMO is distributed over a few atoms !

Correlation energies of LMO pairs

$$E^{cor} = \sum_{ijab} [2(ia|jb) - (ib|ja)] C_{ij}^{ab} = \sum_{ij} E_{ij}^{cor}$$

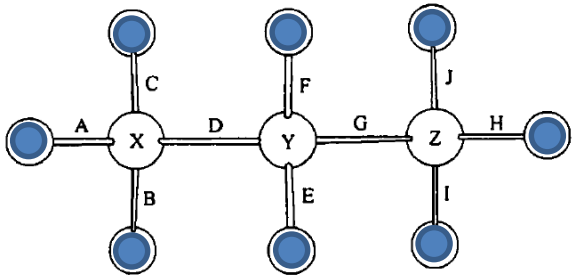


Table 1 Negative of pair correlation energies (in milliHatree) for the ground state of propane at the CCD(full)/6-31G* // HF/6-31G* level

	X	Y	Z	A	B	C	D	E	F	G	H	I	J
X	2.48												
Y	0.00	2.55											
Z	0.00	0.00	2.48										
A	0.54	0.01	0.00	22.84									
B	0.53	0.01	0.00	11.14	22.81								
C	0.53	0.01	0.00	11.14	11.13	22.81							
D	0.53	0.54	0.01	10.55	10.58	10.58	22.88						
E	0.01	0.55	0.01	0.73	0.73	0.83	10.58	22.99					
F	0.01	0.55	0.01	0.73	0.83	0.73	10.58	11.19	22.99				
G	0.01	0.54	0.53	0.79	0.68	0.68	9.93	10.58	10.58	22.88			
H	0.00	0.01	0.54	0.22	0.17	0.17	0.79	0.73	0.73	10.55	22.84		
I	0.00	0.01	0.53	0.17	0.26	0.15	0.68	0.73	0.83	10.58	11.14	22.81	
J	0.00	0.01	0.53	0.17	0.15	0.26	0.68	0.83	0.73	10.58	11.14	11.13	22.81

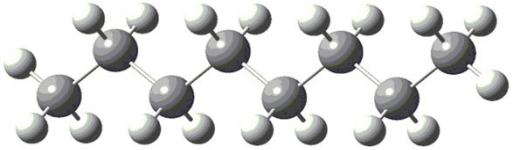
$$\varepsilon_{ij} \sim e^{-K|\bar{r}_i - \bar{r}_j|}$$

S. Li, W. Li, J. Ma, ***Chin. J. Chem.*** 21, 1422 (2003)

Direct local method

$$E^{cor} = \sum_{ijab} [2(ia|jb) - (ib|ja)] C_{ij}^{ab} = \sum_{ij} E_{ij}^{cor}$$

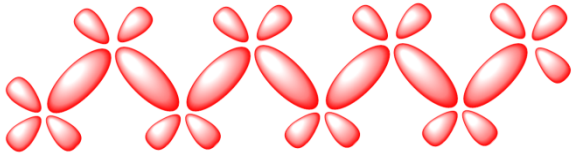
Molecule C_8H_{18}

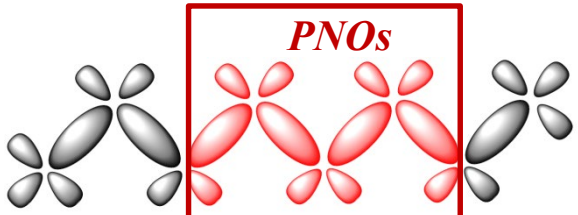


Truncation of occupied pairs (Pre-screen)

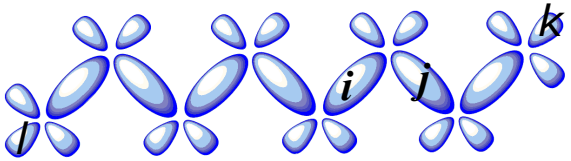
Truncation of virtual space (PNO) For each pair

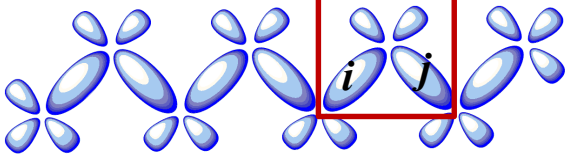
Virtual MOs





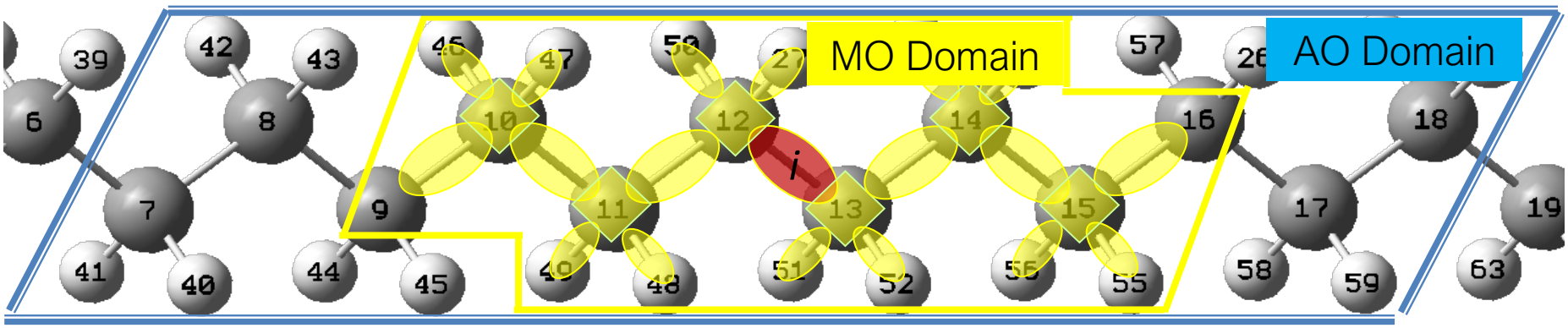
Occupied LMOs





Fragment local method

$$E^{cor} = \sum_{ijab} [2(ia|jb) - (ib|ja)] C_{ij}^{ab} = \sum_{ij} E_{ij}^{cor} = \sum_{i} E_{i}^{cor}$$



Y. Guo, W. Li, and S. Li, *J. Phys. Chem. A* **118**, 8996 (2014).

Thank you for your attention!