Hartree-Fock and post-Hartree-Fock methods: Computational aspects

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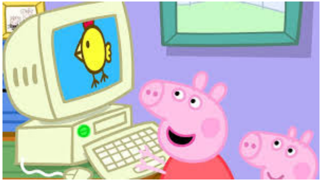


Today's program

- How to perform a Hartree-Fock (HF) calculation in practice?
  - Computation of integrals [Ahlrichs, PCCP 8 (2006) 3072]
  - Orthogonalization matrix [Szabo & Ostlund, Modern Quantum Chemistry]
  - Construction of the Coulomb matrix [White & Head-Gordon, JCP 104 (1996) 2620]
  - Resolution of the identity [Weigend et al. JCP 130 (2009) 164106]
  - DFT exchange via quadrature [Becke, JCP 88 (1988) 2547]

- Generalities on correlation methods
  - Configuration Interaction (CI) [Szabo & Ostlund, Modern Quantum Chemistry]
  - Perturbation theory [Szabo & Ostlund, Modern Quantum Chemistry]
  - Coupled-cluster (CC) theory [Jensen, Introduction to Computational Chemistry]

- Computing the 2nd-order Møller-Plesset (MP2) correlation energy
  - Atomic orbital (AO) to molecular orbital (MO) transformation [Frisch et al. CPL 166 (1990) 281]
  - Laplace transform [Almlöf, CPL 181 (1991) 319]

- Coupled cluster with doubles (CCD)
  - Introduction to CC methods [Shavitt & Bartlett, *"Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory"*]
  - Algorithm to compute the CCD energy [Pople et al. IJQC 14 (1978) 545]

How to perform a HF calculation in practice?

The SCF algorithm (p. 146)

① Specify molecule $\{\boldsymbol{r}_A\}$ and $\{Z_A\}$ and basis set $\{\phi_\mu\}$

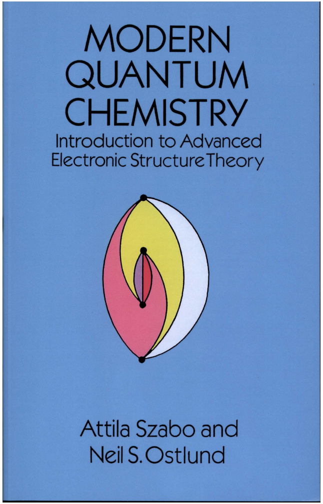
② Calculate integrals $S_{\mu\nu}$, $H_{\mu\nu}$ and $\langle\mu\nu|\lambda\sigma\rangle$

③ Diagonalize $\boldsymbol{S}$ and compute $\boldsymbol{X} = \boldsymbol{S}^{-1/2}$

④ Obtain guess density matrix for $\boldsymbol{P}$

1. Calculate $\boldsymbol{J}$ and $\boldsymbol{K}$, then $\boldsymbol{F} = \boldsymbol{H} + \boldsymbol{J} + \boldsymbol{K}$
2. Compute $\boldsymbol{F}' = \boldsymbol{X}^\dagger \cdot \boldsymbol{F} \cdot \boldsymbol{X}$
3. Diagonalize $\boldsymbol{F}'$ to obtain $\boldsymbol{C}'$ and $\boldsymbol{E}$
4. Calculate $\boldsymbol{C} = \boldsymbol{X} \cdot \boldsymbol{C}'$
5. Form a new density matrix $\boldsymbol{P} = \boldsymbol{C} \cdot \boldsymbol{C}^\dagger$
6. Am I converged? If not go back to 1.

⑤ Calculate stuff that you want, like E_{HF} for example


MODERN
QUANTUM
CHEMISTRY
Introduction to Advanced
Electronic Structure Theory

Attila Szabo and
Neil S. Ostlund

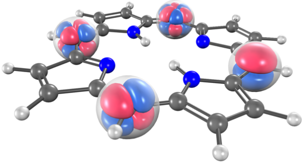
Let's talk about notations

- Number of occupied orbitals O
- Number of vacant orbitals V
- Total number of orbitals $N = O + V$

- i, j, k, l are occupied orbitals
- a, b, c, d are vacant orbitals
- p, q, r, s are arbitrary (occupied or vacant) orbitals
- $\mu, \nu, \lambda, \sigma$ are basis function indexes

One- and two-electron integrals

One-electron integrals: overlap & core Hamiltonian (Appendix A)



$$S_{\mu\nu} = \langle \mu | \nu \rangle = \int \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) d\mathbf{r} \tag{1}$$

$$H_{\mu\nu} = \langle \mu | \hat{H}^c | \nu \rangle = \int \phi_\mu(\mathbf{r}) \hat{H}^c(\mathbf{r}) \phi_\nu(\mathbf{r}) d\mathbf{r} \tag{2}$$

Chemist/Mulliken notation for two-electron integrals (p. 68)

$$(\mu\nu|\lambda\sigma) = \iint \phi_\mu(\mathbf{r}_1)\phi_\nu(\mathbf{r}_1) \frac{1}{r_{12}} \phi_\lambda(\mathbf{r}_2)\phi_\sigma(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \tag{3}$$

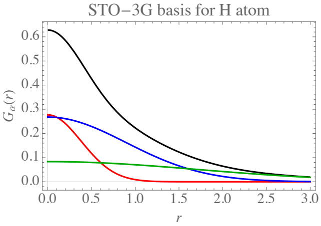
Physicist/Dirac notation for two-electron integrals (p. 68)

$$\langle \mu\nu|\lambda\sigma \rangle = \iint \phi_\mu(\mathbf{r}_1)\phi_\nu(\mathbf{r}_2) \frac{1}{r_{12}} \phi_\lambda(\mathbf{r}_1)\phi_\sigma(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \tag{4}$$

Computing the electron repulsion integrals (ERIs)

Four-center two-electron integrals

$$\begin{aligned}\langle \boldsymbol{a}_1\boldsymbol{a}_2|\boldsymbol{b}_1\boldsymbol{b}_2\rangle &\equiv \langle \boldsymbol{a}_1\boldsymbol{a}_2|r_{12}^{-1}|\boldsymbol{b}_1\boldsymbol{b}_2\rangle \\ &= \iint \phi_{\boldsymbol{a}_1}^{\boldsymbol{A}_1}(\boldsymbol{r}_1)\phi_{\boldsymbol{a}_2}^{\boldsymbol{A}_2}(\boldsymbol{r}_2)\,\frac{1}{r_{12}}\,\phi_{\boldsymbol{b}_1}^{\boldsymbol{B}_1}(\boldsymbol{r}_1)\phi_{\boldsymbol{b}_2}^{\boldsymbol{B}_2}(\boldsymbol{r}_2)\,d\boldsymbol{r}_1 d\boldsymbol{r}_2\end{aligned} \tag{5}$$



Formally, one has to compute $\mathcal{O}(N^4)$ ERIs!

Gaussian-type orbital (GTO)

$$\text{Contracted GTO} = |\boldsymbol{a}\rangle \equiv \phi_{\boldsymbol{a}}^{\boldsymbol{A}}(\boldsymbol{r}) = \sum_{k}^{K} D_k |\boldsymbol{a}]_k$$

$$\text{Primitive GTO} = |\boldsymbol{a}] = (x-A_x)^{a_x}(y-A_y)^{a_y}(z-A_z)^{a_z} e^{-\alpha|\boldsymbol{r}-\boldsymbol{A}|^2}$$

- **Exponent:** α
- **Center:** $\boldsymbol{A} = (A_x, A_y, A_z)$
- **Angular momentum:** $\boldsymbol{a} = (a_x, a_y, a_z)$ and total angular momentum $a = a_x + a_y + a_z$

The contraction problem

Primitive vs Contracted

- Same center $\boldsymbol{A}$
- Same angular momentum $\boldsymbol{a}$
- Different exponent α_k
- Contraction coefficient D_k and degree K

$$\underbrace{\langle \boldsymbol{a}_1\boldsymbol{a}_2|\boldsymbol{b}_1\boldsymbol{b}_2\rangle}_{\text{contracted ERI}} = \sum_{k_1}^{K_1}\sum_{k_2}^{K_2}\sum_{k_3}^{K_3}\sum_{k_4}^{K_4} D_{k_1}D_{k_2}D_{k_3}D_{k_4}\underbrace{[\boldsymbol{a}_{1,k_1}\boldsymbol{a}_{2,k_2}|\boldsymbol{b}_{1,k_3}\boldsymbol{b}_{2,k_4}]}_{\text{primitive ERI}} \tag{6}$$

One contracted ERI required $K_1 \times K_2 \times K_3 \times K_4$ primitive ERIs!

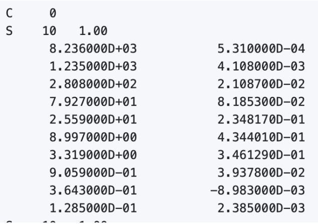
$$\boxed{|\boldsymbol{a}\rangle = \sum_{k}^{K} D_k |\boldsymbol{a}_k]} \tag{8}$$

https://www.basissetexchange.org

Dunning's cc-pVTZ basis for the carbon atom

$$\langle 1s1s|1s1s\rangle = \sum_{k_1}^{10}\sum_{k_2}^{10}\sum_{k_3}^{10}\sum_{k_4}^{10} D_{k_1}D_{k_2}D_{k_3}D_{k_4}[s_{k_1}^{\alpha_{k_1}} s_{k_2}^{\alpha_{k_2}}|s_{k_3}^{\alpha_{k_3}} s_{k_4}^{\alpha_{k_4}}] \tag{7}$$

The $\langle 1s1s|1s1s\rangle$ integral requires 10^4 s-type integrals!



```
C     0
S    10    1.00
      8.236000D+03               5.310000D-04
      1.235000D+03               4.108000D-03
      2.808000D+02               2.108700D-02
      7.927000D+01               8.185300D-02
      2.559000D+01               2.348170D-01
      8.997000D+00               4.344010D-01
      3.319000D+00               3.461290D-01
      9.059000D-01               3.937800D-02
      3.643000D-01              -8.983000D-03
      1.285000D-01               2.385000D-03
```

Gaussian product rule: *"The product of two gaussians is a gaussian"*

$$G_{\alpha,\boldsymbol{A}}(\boldsymbol{r}) = \exp\left(-\alpha|\boldsymbol{r}-\boldsymbol{A}|^2\right) \quad \text{and} \quad G_{\beta,\boldsymbol{B}}(\boldsymbol{r}) = \exp\left(-\beta|\boldsymbol{r}-\boldsymbol{B}|^2\right) \quad \text{then} \tag{9}$$

$$\boxed{G_{\alpha,\boldsymbol{A}}(\boldsymbol{r})G_{\beta,\boldsymbol{B}}(\boldsymbol{r}) = K\,G_{\zeta,\boldsymbol{P}}(\boldsymbol{r})} \quad \text{with} \quad \zeta = \alpha+\beta \quad \text{and} \quad \boldsymbol{P} = \frac{\alpha\boldsymbol{A}+\beta\boldsymbol{B}}{\alpha+\beta} \tag{10}$$

$$K = \exp\left(-\frac{\alpha\beta}{\alpha+\beta}|\boldsymbol{A}-\boldsymbol{B}|^2\right) \tag{11}$$

Gaussian product rule for ERIs

$$\begin{aligned}(\boldsymbol{ab}|\boldsymbol{cd}) &= \iint G_{\alpha,\boldsymbol{A}}(\boldsymbol{r}_1)G_{\beta,\boldsymbol{B}}(\boldsymbol{r}_1)\frac{1}{r_{12}}G_{\gamma,\boldsymbol{C}}(\boldsymbol{r}_2)G_{\delta,\boldsymbol{D}}(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\ &= K K \iint G_{\zeta,\boldsymbol{P}}(\boldsymbol{r}_1)\frac{1}{r_{12}}G_{\eta,\boldsymbol{Q}}(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2\end{aligned} \tag{12}$$

The number of "significant" ERIs in a large system is $\mathcal{O}(N^2)$!

Upper bounds for ERIs

A "good" upper bound must be

- tight (i.e., a good estimate)
- simple (i.e, cheap to compute)

$$\boxed{|(ab|cd)| \leq B} \tag{13}$$

Cauchy-Schwartz bound

$$|(ab|cd)| \leq \sqrt{(ab|ab)}\sqrt{(cd|cd)} \quad \text{or} \quad |(P|Q)| \leq \sqrt{(P|P)}\sqrt{(Q|Q)} \tag{14}$$

The family of generalized Hölder bounds

$$|(ab|cd)| \leq [(ab|ab)]^{1/m}[(cd|cd)]^{1/n} \quad \text{with} \quad \frac{1}{m} + \frac{1}{n} = 1 \quad \text{and} \quad m, n > 1 \tag{15}$$

Asymptotic scaling of two-electron integrals

Number of significant two-electron integrals

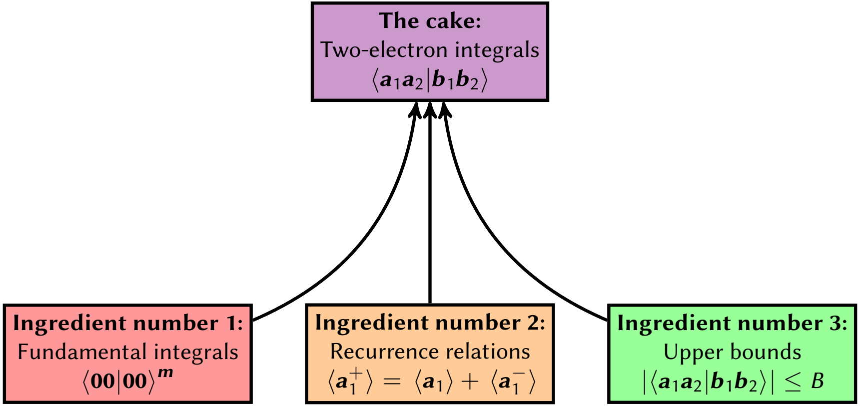
$$(\mathbf{ab}|\mathbf{cd}) \equiv (\mathbf{ab}|\mathcal{O}_2|\mathbf{cd}) \tag{16}$$

Long-range vs short-range operators

$$N_{\text{sig}} = c\, N^{\alpha} \tag{17}$$

Molecule	N	$\hat{\mathcal{O}} = r_{12}^{-1}$		$\hat{\mathcal{O}} = e^{-r_{12}^2}$	
		N_{sig}	α	N_{sig}	α
propene	12	1 625	—	1 650	—
butadiene	16	5 020	3.9	5 020	3.9
hexatriene	24	24 034	3.9	23 670	3.8
octatetraene	32	63 818	3.4	52 808	2.8
decapentaene	40	119 948	2.8	81 404	1.9
dodecaexaene	48	192 059	2.6	109 965	1.6

Recipe for computing two-electron integrals



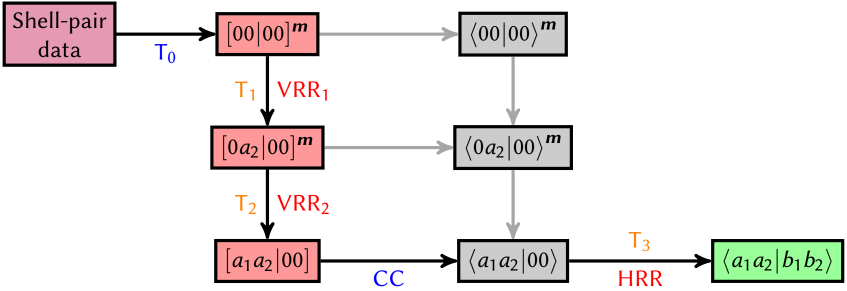
The cake:
Two-electron integrals
$\langle \boldsymbol{a}_1\boldsymbol{a}_2|\boldsymbol{b}_1\boldsymbol{b}_2\rangle$

Ingredient number 1:
Fundamental integrals
$\langle \mathbf{00}|\mathbf{00}\rangle^{\boldsymbol{m}}$

Ingredient number 2:
Recurrence relations
$\langle \boldsymbol{a}_1^+\rangle = \langle \boldsymbol{a}_1\rangle + \langle \boldsymbol{a}_1^-\rangle$

Ingredient number 3:
Upper bounds
$|\langle \boldsymbol{a}_1\boldsymbol{a}_2|\boldsymbol{b}_1\boldsymbol{b}_2\rangle| \leq B$

Late-contraction path algorithm (Head-Gordon-Pople & PRISM inspired)



- HRR = horizontal recurrence relation [Obara-Saika]
- VRR = vertical recurrence relation
- CC = bra contraction

Orthogonalization matrix

We are looking for a matrix in order to orthogonalize the AO basis, i.e. $\boldsymbol{X}^\dagger \cdot \boldsymbol{S} \cdot \boldsymbol{X} = \mathbf{1}$

Symmetric (or Löwdin) orthogonalization

$$\boldsymbol{X} = \boldsymbol{S}^{-1/2} = \boldsymbol{U} \cdot \boldsymbol{s}^{-1/2} \cdot \boldsymbol{U}^\dagger \text{ is one solution...} \tag{18}$$

Is it working?

$$\boldsymbol{X}^\dagger \cdot \boldsymbol{S} \cdot \boldsymbol{X} = \boldsymbol{S}^{-1/2} \cdot \boldsymbol{S} \cdot \boldsymbol{S}^{-1/2} = \boldsymbol{S}^{-1/2} \cdot \boldsymbol{S} \cdot \boldsymbol{S}^{-1/2} = \boldsymbol{I} \quad \checkmark \tag{19}$$

Canonical orthogonalization

$$\boldsymbol{X} = \boldsymbol{U} \cdot \boldsymbol{s}^{-1/2} \text{ is another solution (when you have linear dependencies)...} \tag{20}$$

Is it working?

$$\boldsymbol{X}^\dagger \cdot \boldsymbol{S} \cdot \boldsymbol{X} = \boldsymbol{s}^{-1/2} \cdot \underbrace{\boldsymbol{U}^\dagger \cdot \boldsymbol{S} \cdot \boldsymbol{U}}_{\boldsymbol{s}} \cdot \boldsymbol{s}^{-1/2} = \boldsymbol{I} \quad \checkmark \tag{21}$$

Computation of the Fock matrix and energy

Density matrix (closed-shell system)

$$P_{\mu\nu} = 2 \sum_{i}^{\text{occ}} C_{\mu i} C_{\nu i} \quad \text{or} \quad \boxed{\boldsymbol{P} = \boldsymbol{C} \cdot \boldsymbol{C}^{\dagger}} \tag{22}$$

Fock matrix in the AO basis (closed-shell system)

$$F_{\mu\nu} = H_{\mu\nu} + \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\nu|\lambda\sigma)}_{J_{\mu\nu} = \text{Coulomb}} \underbrace{- \frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\sigma|\lambda\nu)}_{K_{\mu\nu} = \text{exchange}} \tag{23}$$

HF energy in the AO basis (closed-shell system)

$$E_{\text{HF}} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\sigma|\lambda\nu) \right] P_{\lambda\sigma} \quad \text{or} \quad \boxed{E_{\text{HF}} = \frac{1}{2} \text{Tr}[\boldsymbol{P} \cdot (\boldsymbol{H} + \boldsymbol{F})]} \tag{24}$$

Computation of the Fock matrix and energy

```
procedure COMPUTING THE COULOMB MATRIX
    for $\mu = 1, N$ do
        for $\nu = 1, N$ do
            $J_{\mu\nu} = 0$                                        ▷ Initialization of the array
            for $\lambda = 1, N$ do
                for $\sigma = 1, N$ do
                    $J_{\mu\nu} = J_{\mu\nu} + P_{\lambda\sigma}(\mu\nu|\lambda\sigma)$     ▷ Accumulation step
                end for
            end for
        end for
    end for
end procedure                  ▷ This is a $\mathcal{O}(N^4)$ algorithm as it involves four loops
```

Resolution of the identity (RI)

$$\sum_{A=1}^{\infty} |A\rangle\langle A| = \hat{1} \quad \text{with} \quad \langle A|B\rangle = \delta_{AB} \quad \Leftrightarrow \quad \sum_{A=1}^{\infty} A(\boldsymbol{r}_1)A(\boldsymbol{r}_2) = \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) \tag{25}$$

Generalization to a two-body operator $\hat{\mathcal{O}}$

$$\sum_{\tilde{A}=1}^{\infty} |\tilde{A}\rangle\langle \tilde{A}| = \hat{\mathcal{O}} \quad \text{with} \quad \langle A|\hat{\mathcal{O}}|B\rangle = \delta_{AB} \quad \text{and} \quad \hat{\mathcal{O}}\,|A\rangle = |\tilde{A}\rangle \quad \Leftrightarrow \quad \sum_{\tilde{A}=1}^{\infty} \tilde{A}(\boldsymbol{r}_1)\tilde{A}(\boldsymbol{r}_2) = \hat{\mathcal{O}}(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{26}$$

RI in practice = RI approximation

$$\boxed{\sum_{A=1}^{\infty} |A\rangle\langle A| = \hat{1} \quad \text{and, in practice,} \quad \sum_{A=1}^{K} |A\rangle\langle A| \approx \hat{1}} \tag{27}$$

Computing the Coulomb matrix within the RI approximation

$$\begin{aligned} J_{\mu\nu} &= \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\nu|\lambda\sigma) \\ &\overset{\text{RI}}{=} \sum_{\lambda\sigma} P_{\lambda\sigma} \sum_{A} (\mu\nu|A)(A|\lambda\sigma) \\ &= \sum_{A} (\mu\nu|A) \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma} (A|\lambda\sigma)}_{\mathcal{O}(KN^2) \text{ and } K \text{ storage}} = \underbrace{\sum_{A} (\mu\nu|A) \rho_A}_{\mathcal{O}(KN^2)} \end{aligned} \tag{28}$$

Similar (more effective) approaches are named Cholesky decomposition, low-rank approximation, etc.

Computation of exact exchange

```
procedure COMPUTING THE EXCHANGE MATRIX
    for $\mu = 1, N$ do
        for $\nu = 1, N$ do
            $K_{\mu\nu} = 0$                                              ▷ Initialization of the array
            for $\lambda = 1, N$ do
                for $\sigma = 1, N$ do
                    $K_{\mu\nu} = K_{\mu\nu} + P_{\lambda\sigma}(\mu\sigma|\lambda\nu)$      ▷ Accumulation step
                end for
            end for
        end for
    end for
end procedure                ▷ This is a $\mathcal{O}(N^4)$ algorithm and it's hard to play games...
```

Computation of DFT exchange

LDA exchange (in theory) = cf ~~Julien’s~~ Manu’s lectures

$$K_{\mu\nu}^{\text{LDA}} = \int \phi_\mu(\boldsymbol{r}) v_{\text{x}}^{\text{LDA}}(\boldsymbol{r})\phi_\nu(\boldsymbol{r}) d\boldsymbol{r} = \frac{4}{3} C_{\text{x}} \overbrace{\int \phi_\mu(\boldsymbol{r})\rho^{1/3}(\boldsymbol{r})\phi_\nu(\boldsymbol{r})d\boldsymbol{r}}^{\text{no closed-form expression in general}} \tag{29}$$

$$\rho(\boldsymbol{r}) = \sum_{\mu\nu} \phi_\mu(\boldsymbol{r}) P_{\mu\nu} \phi_\nu(\boldsymbol{r}) \tag{30}$$

LDA exchange (in practice) = numerical integration via quadrature = $\int f(x)dx \approx \sum_k w_k f(x_k)$

$$\underbrace{K_{\mu\nu}^{\text{LDA}}}_{\mathcal{O}(N_{\text{grid}} N^2)} \approx \sum_{k=1}^{N_{\text{grid}}} \underbrace{w_k}_{\text{weights}} \phi_\mu(\boldsymbol{r}_k) v_{\text{x}}^{\text{LDA}}(\underbrace{\boldsymbol{r}_k}_{\text{roots}})\phi_\nu(\boldsymbol{r}_k) = \frac{4}{3} C_{\text{x}} \sum_{k=1}^{N_{\text{grid}}} w_k \phi_\mu(\boldsymbol{r}_k)\rho^{1/3}(\boldsymbol{r}_k)\phi_\nu(\boldsymbol{r}_k) \tag{31}$$

$$\underbrace{\rho(\boldsymbol{r}_k)}_{\mathcal{O}(N_{\text{grid}} N^2)} = \sum_{\mu\nu} \phi_\mu(\boldsymbol{r}_k) P_{\mu\nu} \phi_\nu(\boldsymbol{r}_k) \tag{32}$$

The correlation energy

- HF replaces the e-e interaction by an averaged interaction
- The error in the HF method is called the correlation energy

$$\boxed{E_c = E - E_{\text{HF}}}$$

- The correlation energy is small but cannot but neglected!
- HF energy roughly 99% of total but chemistry very sensitive to remaining 1%
- The correlation energy is always negative
- Computing E_c is one of the central problem of quantum chemistry
- In quantum chemistry, we usually “freeze” the core electrons for correlated calculations

Most common correlation methods in quantum chemistry

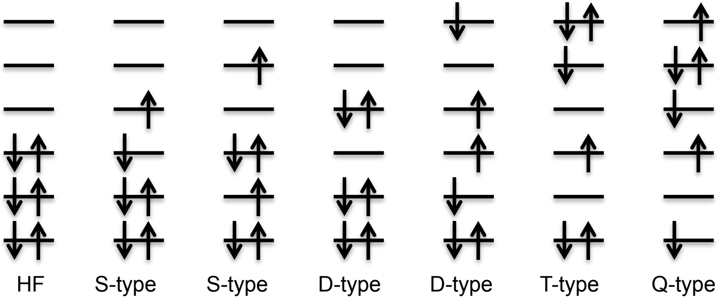
1. Configuration Interaction: CID, CIS, CISD, CISDTQ, etc.
2. Coupled Cluster: CCD, CCSD, CCSD(T), CCSDT, CCSDTQ, etc.
3. Møller-Plesset perturbation theory: MP2, MP3, MP4, MP5, etc.
4. Multireference methods: MCSCF, CASSCF, RASSCF, MRCI, MRCC, CASPT2, NEVPT2, etc. (C. Angeli & S. Knecht)
5. Density-functional theory: DFT, TDDFT, etc. (J. Toulouse/E. Fromager, F. Sottile)
6. Quantum Monte Carlo: VMC, DMC, FCIQMC, etc. (M. Caffarel)

Configuration Interaction (CI)

- This is the oldest and perhaps the easiest method to understand
- CI is based on the variational principle (like HF)
- The CI wave function is a linear combination of determinants
- CI methods use excited determinants to “improve” the reference (usually HF) wave function

$$|\Phi_0\rangle = \underbrace{c_0 |\Psi_0\rangle}_{\text{reference}} + \underbrace{\sum_{\substack{i\\a}} c_i^a |\Psi_i^a\rangle}_{\text{singles}} + \underbrace{\sum_{\substack{i<j\\a<b}} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle}_{\text{doubles}} + \underbrace{\sum_{\substack{i<j<k\\a<b<c}} c_{ijk}^{abc} |\Psi_{ijk}^{abc}\rangle}_{\text{triples}} + \underbrace{\sum_{\substack{i<j<k<l\\a<b<c<d}} c_{ijkl}^{abcd} |\Psi_{ijkl}^{abcd}\rangle}_{\text{quadruples}} + \ldots \quad (33)$$

Excited determinants



CI wave function

$$\boxed{|\Phi_0\rangle = c_0\,|0\rangle + c_S\,|S\rangle + c_D\,|D\rangle + c_T\,|T\rangle + c_Q\,|Q\rangle + \ldots} \tag{34}$$

Truncated CI

- When $|S\rangle$ (singles) are taken into account: **CIS**

$$|\Phi_{\text{CIS}}\rangle = c_0 |0\rangle + c_S |S\rangle \tag{35}$$

  NB: CIS is an excited state method

- When $|D\rangle$ (doubles) are taken into account: **CID**

$$|\Phi_{\text{CID}}\rangle = c_0 |0\rangle + c_D |D\rangle \tag{36}$$

  NB: CID is the cheapest CI method

- When $|S\rangle$ and $|D\rangle$ are taken into account: **CISD**

$$|\Phi_{\text{CISD}}\rangle = c_0 |0\rangle + c_S |S\rangle + c_D |D\rangle \tag{37}$$

  NB: CISD is the most commonly-used CI method

- When $|S\rangle$, $|D\rangle$ and $|T\rangle$ (triples) are taken into account: **CISDT**

$$|\Phi_{\text{CISDT}}\rangle = c_0 |0\rangle + c_S |S\rangle + c_D |D\rangle + c_T |T\rangle \tag{38}$$

- **CISDTQ**, etc.

- When all possible excitations are taken into account, this is called a Full CI calculation (**FCI**)

$$|\Phi_{\text{FCI}}\rangle = c_0 |0\rangle + c_{\text{S}} |\text{S}\rangle + c_{\text{D}} |\text{D}\rangle + c_{\text{T}} |\text{T}\rangle + c_{\text{Q}} |\text{Q}\rangle + \ldots \tag{39}$$

- FCI gives the exact solution of the Schrödinger equation within a given basis
- FCI is becoming more and more fashionable these days (e.g. FCIQMC and SCI methods)
- So, why do we care about other methods?
- Because FCI is super computationally expensive!

Size of CI Matrix

“Assume we have 10 electrons in 38 spin MOs: 10 are occupied and 28 are empty”

- There is C_{10}^{k} possible ways of selecting k electrons out of the 10 occupied orbitals

$$C_n^k = \frac{n!}{k!(n-k)!}$$

- There is C_{28}^{k} ways of distributing them out in the 28 virtual orbitals
- For a given excitation level k, there is $C_{10}^{k} C_{28}^{k}$ excited determinants
- The total number of possible excited determinant is

$$\sum_{k=0}^{10} C_{10}^{k} C_{28}^{k} = C_{38}^{10} = 472,733,756$$

- This is a lot...

For $n = 10$ and $N = 38$:

k	Num. of excitations
0	1
1	280
2	17,010
3	393,120
4	4,299,750
5	24,766,560
6	79,115,400
7	142,084,800
8	139,864,725
9	69,069,000
10	13,123,110
Tot.	472,733,756

The FCI matrix: before pruning

$$\boxed{|\Phi_0\rangle = c_0\,|\text{HF}\rangle + c_\text{S}\,|\text{S}\rangle + c_\text{D}\,|\text{D}\rangle + c_\text{T}\,|\text{T}\rangle + c_\text{Q}\,|\text{Q}\rangle + \ldots} \tag{40}$$

$$\boldsymbol{H} = \begin{array}{cccccccc}
 & |\text{HF}\rangle & |\text{S}\rangle & |\text{D}\rangle & |\text{T}\rangle & |\text{Q}\rangle & \cdots \\
\langle\text{HF}| & \langle\text{HF}|\hat{H}|\text{HF}\rangle & \langle\text{HF}|\hat{H}|\text{S}\rangle & \langle\text{HF}|\hat{H}|\text{D}\rangle & \langle\text{HF}|\hat{H}|\text{T}\rangle & \langle\text{HF}|\hat{H}|\text{Q}\rangle & \cdots \\
\langle\text{S}| & \langle\text{S}|\hat{H}|\text{HF}\rangle & \langle\text{S}|\hat{H}|\text{S}\rangle & \langle\text{S}|\hat{H}|\text{D}\rangle & \langle\text{S}|\hat{H}|\text{T}\rangle & \langle\text{S}|\hat{H}|\text{Q}\rangle & \cdots \\
\langle\text{D}| & \langle\text{D}|\hat{H}|\text{HF}\rangle & \langle\text{D}|\hat{H}|\text{S}\rangle & \langle\text{D}|\hat{H}|\text{D}\rangle & \langle\text{D}|\hat{H}|\text{T}\rangle & \langle\text{D}|\hat{H}|\text{Q}\rangle & \cdots \\
\langle\text{T}| & \langle\text{T}|\hat{H}|\text{HF}\rangle & \langle\text{T}|\hat{H}|\text{S}\rangle & \langle\text{T}|\hat{H}|\text{D}\rangle & \langle\text{T}|\hat{H}|\text{T}\rangle & \langle\text{T}|\hat{H}|\text{Q}\rangle & \cdots \\
\langle\text{Q}| & \langle\text{Q}|\hat{H}|\text{HF}\rangle & \langle\text{Q}|\hat{H}|\text{S}\rangle & \langle\text{Q}|\hat{H}|\text{D}\rangle & \langle\text{Q}|\hat{H}|\text{T}\rangle & \langle\text{Q}|\hat{H}|\text{Q}\rangle & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots
\end{array} \tag{41}$$

The FCI matrix: after pruning

$$\boxed{|\Phi_0\rangle = c_0\,|\mathrm{HF}\rangle + c_\mathrm{S}\,|\mathrm{S}\rangle + c_\mathrm{D}\,|\mathrm{D}\rangle + c_\mathrm{T}\,|\mathrm{T}\rangle + c_\mathrm{Q}\,|\mathrm{Q}\rangle + \ldots} \tag{42}$$

$$\boldsymbol{H} = \begin{array}{ccccccc}
 & |\mathrm{HF}\rangle & |\mathrm{S}\rangle & |\mathrm{D}\rangle & |\mathrm{T}\rangle & |\mathrm{Q}\rangle & \cdots \\
\langle\mathrm{HF}| & \langle\mathrm{HF}|\hat{H}|\mathrm{HF}\rangle & 0 & \langle\mathrm{HF}|\hat{H}|\mathrm{D}\rangle & 0 & 0 & \cdots \\
\langle\mathrm{S}| & 0 & \langle\mathrm{S}|\hat{H}|\mathrm{S}\rangle & \langle\mathrm{S}|\hat{H}|\mathrm{D}\rangle & \langle\mathrm{S}|\hat{H}|\mathrm{T}\rangle & 0 & \cdots \\
\langle\mathrm{D}| & \langle\mathrm{D}|\hat{H}|\mathrm{HF}\rangle & \langle\mathrm{D}|\hat{H}|\mathrm{S}\rangle & \langle\mathrm{D}|\hat{H}|\mathrm{D}\rangle & \langle\mathrm{D}|\hat{H}|\mathrm{T}\rangle & \langle\mathrm{D}|\hat{H}|\mathrm{Q}\rangle & \cdots \\
\langle\mathrm{T}| & 0 & \langle\mathrm{T}|\hat{H}|\mathrm{S}\rangle & \langle\mathrm{T}|\hat{H}|\mathrm{D}\rangle & \langle\mathrm{T}|\hat{H}|\mathrm{T}\rangle & \langle\mathrm{T}|\hat{H}|\mathrm{Q}\rangle & \cdots \\
\langle\mathrm{Q}| & 0 & 0 & \langle\mathrm{Q}|\hat{H}|\mathrm{D}\rangle & \langle\mathrm{Q}|\hat{H}|\mathrm{T}\rangle & \langle\mathrm{Q}|\hat{H}|\mathrm{Q}\rangle & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots
\end{array} \tag{43}$$

1. No coupling between HF ground state $|\mathrm{HF}\rangle$ and single excitations $|\mathrm{S}\rangle$
   $\Rightarrow$ Brillouin's theorem
$$\langle \mathrm{HF}|\hat{H}|\mathrm{S}\rangle = 0 \tag{44}$$
2. No coupling between $|\mathrm{HF}\rangle$ and triples $|\mathrm{T}\rangle$, quadruples $|\mathrm{Q}\rangle$, etc.
   $\Rightarrow$ Slater-Condon rules
$$\langle \mathrm{HF}|\hat{H}|\mathrm{T}\rangle = \langle \mathrm{HF}|\hat{H}|\mathrm{Q}\rangle = \ldots = 0 \tag{45}$$
$$\langle \mathrm{S}|\hat{H}|\mathrm{Q}\rangle = \ldots = 0 \tag{46}$$
3. $|\mathrm{S}\rangle$ have small effect but mix indirectly with $|\mathrm{D}\rangle$
   $\Rightarrow$ CID $\neq$ CISD
$$\langle \mathrm{HF}|\hat{H}|\mathrm{S}\rangle = 0 \quad \text{but} \quad \langle \mathrm{S}|\hat{H}|\mathrm{D}\rangle \neq 0 \tag{47}$$
4. $|\mathrm{D}\rangle$ have large effect and $|\mathrm{Q}\rangle$ more important than $|\mathrm{T}\rangle$
   $\Rightarrow$ CID gives most of the correlation energy
$$\langle \mathrm{HF}|\hat{H}|\mathrm{D}\rangle \gg \langle \mathrm{HF}|\hat{H}|\mathrm{Q}\rangle \gg \langle \mathrm{HF}|\hat{H}|\mathrm{T}\rangle \tag{48}$$
5. Of course, this matrix is never explicitly built in practice (Davidson algorithm)...

Example

Weights of excited configurations for Ne

Excit. level	Weight
0	9.6×10^{-1}
1	9.8×10^{-4}
2	3.4×10^{-2}
3	3.7×10^{-4}
4	4.5×10^{-4}
5	1.9×10^{-5}
6	1.7×10^{-6}
7	1.4×10^{-7}
8	1.1×10^{-9}

Correlation energy of Be and Method scaling

Method	ΔE_c	%	Scaling
HF	0	0	N^4
CIS	0	0	N^5
CISD	0.075277	96.05	N^6
CISDT	0.075465	96.29	N^8
CISDTQ	0.078372	100	N^{10}
FCI	0.078372	100	e^N

Size consistency and size extensivity

- Truncated CI methods are size inconsistent i.e.

$$2E_c(\mathrm{H}_2) \neq E_c(\mathrm{H}_2 \cdots \mathrm{H}_2)$$

- Size consistent defines for non-interacting fragment

- Size extensivity refers to the scaling of E_c with the number of electrons

- NB: FCI is size consistent and size extensive

Let's assume we want to find Ψ_0 and E_0, such as

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)})\Psi_0 = E_0 \Psi_0 \tag{49}$$

and that we know

$$\boxed{\hat{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}, \quad n = 0, 1, 2, \ldots, \infty} \tag{50}$$

Let's expand Ψ_0 and E_0 in term of λ:

$$E_0 = \lambda^0 E_0^{(0)} + \lambda^1 E_0^{(1)} + \lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \ldots \tag{51}$$

$$\Psi_0 = \lambda^0 \Psi_0^{(0)} + \lambda^1 \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \ldots \tag{52}$$

such as (intermediate normalization)

$$\left\langle \Psi_0^{(0)} \middle| \Psi_0^{(0)} \right\rangle = 1 \qquad \left\langle \Psi_0^{(0)} \middle| \Psi_0^{(k)} \right\rangle = 0, \quad k = 1, 2, \ldots, \infty \tag{53}$$

Gathering terms with respect to the power of λ:

$$\lambda^0 : \qquad \hat{H}^{(0)}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(0)} \tag{54}$$

$$\lambda^1 : \qquad \hat{H}^{(0)}\Psi_0^{(1)} + \hat{H}^{(1)}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(1)} + E_0^{(1)}\Psi_0^{(0)} \tag{55}$$

$$\lambda^2 : \qquad \hat{H}^{(0)}\Psi_0^{(2)} + \hat{H}^{(1)}\Psi_0^{(1)} = E_0^{(0)}\Psi_0^{(2)} + E_0^{(1)}\Psi_0^{(1)} + E_0^{(2)} \tag{56}$$

$$\lambda^3 : \qquad \hat{H}^{(0)}\Psi_0^{(3)} + \hat{H}^{(1)}\Psi_0^{(2)} = E_0^{(0)}\Psi_0^{(3)} + E_0^{(1)}\Psi_0^{(2)} + E_0^{(2)}\Psi_0^{(1)} + E_0^{(3)} \tag{57}$$

Using the intermediate normalization, we have

$$\lambda^0 : \qquad E_0^{(0)} = \left\langle \Psi_0^{(0)} \middle| \hat{H}^{(0)} \middle| \Psi_0^{(0)} \right\rangle \tag{58}$$

$$\lambda^1 : \qquad E_0^{(1)} = \left\langle \Psi_0^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_0^{(0)} \right\rangle \tag{59}$$

$$\lambda^2 : \qquad E_0^{(2)} = \left\langle \Psi_0^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_0^{(1)} \right\rangle \qquad \text{Wigner's (2n+1) rule!} \tag{60}$$

$$\lambda^3 : \qquad E_0^{(3)} = \left\langle \Psi_0^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_0^{(2)} \right\rangle = \left\langle \Psi_0^{(1)} \middle| \hat{H}^{(1)} - E_0^{(1)} \middle| \Psi_0^{(1)} \right\rangle \tag{61}$$

Rayleigh-Schrödinger perturbation theory (Part 2)

Expanding $\Psi_0^{(1)}$ in the basis $\Psi_n^{(0)}$ with $n = 0, 1, 2, \ldots, \infty$

$$\left|\Psi_0^{(1)}\right\rangle = \sum_n c_n^{(1)} \left|\Psi_n^{(0)}\right\rangle \quad \Rightarrow \quad c_n^{(1)} = \left\langle \Psi_n^{(0)} \middle| \Psi_0^{(1)} \right\rangle \tag{62}$$

Therefore,

$$\left|\Psi_0^{(1)}\right\rangle = \sum_{n\neq 0} \left|\Psi_n^{(0)}\right\rangle \left\langle \Psi_n^{(0)} \middle| \Psi_0^{(1)} \right\rangle \tag{63}$$

Using results from the previous slide, one can show that

$$\boxed{E_0^{(2)} = \sum_{n\neq 0} \frac{\left\langle \Psi_0^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_n^{(0)} \right\rangle^2}{E_0^{(0)} - E_n^{(0)}}} \tag{64}$$

$$\boxed{E_0^{(3)} = \sum_{n,m\neq 0} \frac{\left\langle \Psi_0^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_n^{(0)} \right\rangle \left\langle \Psi_n^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_m^{(0)} \right\rangle \left\langle \Psi_m^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_0^{(0)} \right\rangle}{\left(E_0^{(0)} - E_n^{(0)}\right)\left(E_0^{(0)} - E_m^{(0)}\right)} - E_0^{(1)} \sum_{n\neq 0} \frac{\left\langle \Psi_0^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_n^{(0)} \right\rangle^2}{\left(E_0^{(0)} - E_n^{(0)}\right)^2}} \tag{65}$$

Møller-Plesset (MP) perturbation theory

In Møller-Plesset perturbation theory, the partition is

$$\hat{H}^{(0)} = \sum_{i=1}^{N} f(i) = \sum_{i=1}^{N} [h(i) + v^{\mathrm{HF}}(i)], \qquad \hat{H}^{(1)} = \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i} v^{\mathrm{HF}}(i) \tag{66}$$

Therefore,

$$E_0^{(0)} = \sum_{i}^{\mathrm{occ}} \varepsilon_i, \qquad E_0^{(1)} = -\frac{1}{2} \sum_{ij}^{\mathrm{occ}} \langle ij||ij \rangle \quad \Rightarrow \quad \boxed{E_{\mathrm{HF}} = E_0^{(0)} + E_0^{(1)}} \tag{67}$$

The first information about the correlation energy is given by the second-order correction

$$\boxed{E_0^{(2)} = \sum_{i<j}^{\mathrm{occ}} \sum_{a<b}^{\mathrm{virt}} \frac{\langle ij||ab \rangle^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}} \quad \text{This is the MP2 correlation energy!!} \tag{68}$$

MP3 energy

The third-order correction is a bit ugly...

$$\boxed{\begin{aligned} E_0^{(3)} = & \frac{1}{8}\sum_{ijkl}\sum_{ab}\frac{\langle ij||ab\rangle\langle kl||ij\rangle\langle ab||kl\rangle}{(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_b)} \\ & + \frac{1}{8}\sum_{ij}\sum_{abcd}\frac{\langle ij||ab\rangle\langle ab||cd\rangle\langle cd||ij\rangle}{(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)(\varepsilon_i+\varepsilon_j-\varepsilon_c-\varepsilon_d)} \\ & + \sum_{ijk}\sum_{abc}\frac{\langle ij||ab\rangle\langle kb||cj\rangle\langle ac||ik\rangle}{(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)(\varepsilon_i+\varepsilon_k-\varepsilon_a-\varepsilon_c)} \end{aligned}}$$

- MP2 and MP3 only requires only doubly excited determinants
- MP4 does need singly, doubly, triply and quadruply excited determinants!

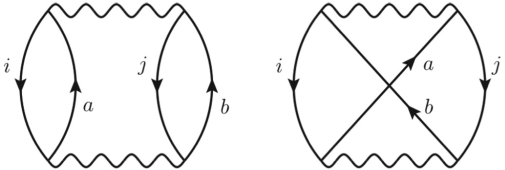
Correlation energy of Be in a 4s2p basis set

Scaling	Level	ΔE_c	%	Level	ΔE_c	%
N^5	MP2	0.053174	67.85			
N^6	MP3	0.067949	86.70	CISD	0.075277	96.05
N^7	MP4	0.074121	94.58			
N^8	MP5	0.076918	98.15	CISDT	0.075465	96.29
N^9	MP6	0.078090	99.64			
N^{10}	MP7	0.078493	100.15	CISDTQ	0.078372	100

- MPn is not a variational method, i.e. you can get an energy lower than the true ground state energy!
- MPn fails for systems with small HOMO-LUMO gap
- The MPn series can oscillate around the exact energy
- MPn is size-consistent!

MP2 is the simplest way of catching a good chunk of correlation:

$$\begin{aligned} E_c^{(2)} &= \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle \left(2\langle ij|ab\rangle - \langle ij|ba\rangle\right)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \\ &= \underbrace{2\sum_{ij}\sum_{ab} \frac{\langle ij|ab\rangle^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}_{\text{direct part}} - \underbrace{\sum_{ij}\sum_{ab} \frac{\langle ij|ab\rangle \langle ij|ba\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}_{\text{exchange part}} \end{aligned} \tag{69}$$



How much does it cost to compute the MP2 correlation energy?

```
procedure MP2 CORRELATION ENERGY
    $E_c^{(2)} = 0$
    for $i = 1, O$ do
        for $j = 1, O$ do
            for $a = 1, V$ do
                for $b = 1, V$ do
                    $\Delta = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$
                    $E_c^{(2)} = E_c^{(2)} + \left(2 \langle ij|ab\rangle^2 - \langle ij|ab\rangle \langle ij|ba\rangle\right) / \Delta$
                end for
            end for
        end for
    end for
end procedure                                   ▷ $\mathcal{O}(N^4)$ because there are four loops!
```

AO to MO transformation (Take 1)

The naive way...

$$\underbrace{(pq|rs)}_{\textbf{MO integrals}} = \sum_{\mu\nu\lambda\sigma} c_{\mu p} c_{\nu q} c_{\lambda r} c_{\sigma s} \underbrace{(\mu\nu|\lambda\sigma)}_{\textbf{AO integrals}} \quad (70)$$

```
procedure AO-to-MO Transformation
    for $p = 1, N$ do
        for $q = 1, N$ do
            for $r = 1, N$ do
                for $s = 1, N$ do
                    $(pq|rs) = 0$                                        ▷ Initialization of the array
                    for $\mu = 1, N$ do
                        for $\nu = 1, N$ do
                            for $\lambda = 1, N$ do
                                for $\sigma = 1, N$ do
                                    $(pq|rs) = (pq|rs) + c_{\mu p} c_{\nu q} c_{\lambda r} c_{\sigma s} (\mu\nu|\lambda\sigma)$   ▷ Accumulation step
                                end for
                            end for
                        end for
                    end for
                end for
            end for
        end for
    end for                                  ▷ This is a $\mathcal{O}(N^8)$ algorithm! You won't do much quantum chemistry with this...
end procedure
```

AO to MO transformation (Take 2)

Semi-direct algorithm...

$$(pq|rs) = \underbrace{\sum_{\mu p} c_{\mu p} \underbrace{\left\{ \sum_{\nu q} c_{\nu q} \underbrace{\left[\sum_{\lambda r} c_{\lambda r} \underbrace{\left(\sum_{\sigma s} c_{\sigma s} (\mu\nu|\lambda\sigma) \right)}_{\text{Step \#1}} \right]}_{\text{Step \#2}} \right\}}_{\text{Step \#3}}}_{\text{Step \#4}} \tag{71}$$

Semi-direct algorithm... Step #1

```
procedure SEMI-DIRECT ALGORITHM (STEP #1)
    Allocate temporary array $I$ of size $N^4$
    for $\mu = 1, N$ do
        for $\nu = 1, N$ do
            for $\lambda = 1, N$ do
                for $\sigma = 1, N$ do
                    for $s = 1, N$ do
                        $I_{\mu\nu\lambda s} = I_{\mu\nu\lambda s} + c_{\sigma s}(\mu\nu|\lambda\sigma)$
                    end for
                end for
            end for
        end for
    end for
end procedure
```

▷ Step #1 costs $\mathcal{O}\left(N^5\right)$ and $\mathcal{O}\left(N^4\right)$ storage

Semi-direct algorithm… Step #2

```
procedure SEMI-DIRECT ALGORITHM (STEP #2)
    Allocate temporary array $J$ of size $N^4$
    for $\mu = 1, N$ do
        for $\nu = 1, N$ do
            for $\lambda = 1, N$ do
                for $r = 1, N$ do
                    for $s = 1, N$ do
                        $J_{\mu\nu rs} = J_{\mu\nu rs} + c_{\lambda r} I_{\mu\nu\lambda s}$
                    end for
                end for
            end for
        end for
    end for
end procedure
```

▷ Step #2 costs $\mathcal{O}\left(N^5\right)$ and $\mathcal{O}\left(N^4\right)$ storage

Semi-direct algorithm... Step #3

```
procedure Semi-Direct Algorithm (Step #3)
    for $\mu = 1, N$ do
        for $\nu = 1, N$ do
            for $q = 1, N$ do
                for $r = 1, N$ do
                    for $s = 1, N$ do
                        $I_{\mu q r s} = I_{\mu q r s} + c_{\nu q} J_{\mu \nu r s}$
                    end for
                end for
            end for
        end for
    end for
end procedure
```

▷ Step #3 costs $\mathcal{O}\left(N^5\right)$ and no new storage

Semi-direct algorithm... Step #4

```
procedure Semi-Direct Algorithm (Step #4)
    for $\mu = 1, N$ do
        for $p = 1, N$ do
            for $q = 1, N$ do
                for $r = 1, N$ do
                    for $s = 1, N$ do
                        $(pq|rs) = (pq|rs) + c_{\mu p} I_{\mu qrs}$
                    end for
                end for
            end for
        end for
    end for
end procedure
```

▷ Step #4 costs $\mathcal{O}\left(N^5\right)$ and no new storage

Laplace transform

Almlöf’s trick

$$\boxed{\frac{1}{\Delta} = \int_0^\infty \exp(-\Delta t)\,dt} \tag{72}$$

$$\begin{aligned}
E_c^{(2)} &= \frac{1}{4}\sum_{ij}\sum_{ab}\frac{\langle ij||ab\rangle^2}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b} \\
&= \frac{1}{4}\int_0^\infty \sum_{ij}\sum_{ab}\langle ij||ab\rangle^2 \exp\left[-(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)t\right]dt \\
&= \frac{1}{4}\int_0^\infty \sum_{ij}\sum_{ab}\langle i(t)j(t)||a(t)b(t)\rangle^2 \overset{\text{quad.}}{\approx} \frac{1}{4}\sum_{k=1}^{N_{\text{grid}}} w_k \sum_{ij}\sum_{ab}\langle i(t_k)j(t_k)||a(t_k)b(t_k)\rangle^2
\end{aligned} \tag{73}$$

$$|p\rangle \equiv |\varphi_p(0)\rangle \quad \text{and} \quad |p(t)\rangle \equiv |\varphi_p(t)\rangle = |\varphi_p(0)e^{\pm\frac{1}{2}\epsilon_p t}\rangle \tag{74}$$

At this stage, one can play more games (e.g., localized orbitals, RI, stochastic sampling, quadrature, etc)

A few random thoughts about coupled cluster (CC)

- CC theory comes from nuclear physics
- The idea behind CC is to include all corrections of a given type to infinite order
- The CC wave function is an exponential *ansatz*
- The CC energy is size-extensive, but non-variational
- CC is considered as the gold standard for weakly correlated systems

Theory

- CC wave function

$$\Psi_{\mathrm{CC}} = e^{\hat{T}}\Psi_0 \quad \text{where } \Psi_0 \text{ is a reference wave function} \tag{75}$$

- Excitation operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_n \tag{76}$$

- Exponential *ansatz*

$$\begin{aligned} e^{\hat{T}} &= \hat{1} + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \ldots \\ &= \hat{1} + \hat{T}_1 + \left(\underbrace{\hat{T}_2}_{\text{connected}} + \frac{1}{2}\underbrace{\hat{T}_1^2}_{\text{disconnected}} \right) + \left(\hat{T}_3 + \hat{T}_2\hat{T}_1 + \frac{1}{6}\hat{T}_1^3 \right) \\ &+ \left(\underbrace{\hat{T}_4}_{\text{four electrons}} + \hat{T}_3\hat{T}_1 + \frac{1}{2}\underbrace{\hat{T}_2^2}_{\text{two pairs of electrons}} + \frac{1}{2}\hat{T}_2\hat{T}_1^2 + \frac{1}{24}\hat{T}_1^4 \right) + \ldots \end{aligned} \tag{77}$$

Excitation operators

- Singles

$$\hat{T}_1 = \sum_{ia} \underbrace{t_i^a}_{\text{amplitudes}} \hat{a}_a^\dagger \hat{a}_i \quad \Rightarrow \quad \hat{T}_1 \Psi_0 = \sum_{ia} t_i^a \Psi_i^a \tag{78}$$

- Doubles

$$\hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \quad \Rightarrow \quad \hat{T}_2 \Psi_0 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \underbrace{\Psi_{ij}^{ab}}_{\text{excited determinants}} \tag{79}$$

- FCI wave function

$$\Psi_{\mathrm{FCI}} = (\hat{1} + \hat{T}) \Psi_0 = (\hat{1} + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots) \Psi_0 \tag{80}$$

- Anticommutation relation of the annihilation and creation operators

$$\hat{a}_p^\dagger \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p^\dagger = 0 \qquad \hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = 0 \qquad \hat{a}_p^\dagger \hat{a}_q + \hat{a}_p \hat{a}_q^\dagger = \delta_{pq} \tag{81}$$

CC energies

- Schrödinger equation

$$\hat{H}\left|\Psi_{\mathrm{CC}}\right\rangle = E\left|\Psi_{\mathrm{CC}}\right\rangle \Rightarrow \hat{H}e^{\hat{T}}\left|\Psi_0\right\rangle = Ee^{\hat{T}}\left|\Psi_0\right\rangle \Rightarrow \underbrace{e^{-\hat{T}}\hat{H}e^{\hat{T}}}_{\bar{H} = \text{similarity transform}}\left|\Psi_0\right\rangle = E\left|\Psi_0\right\rangle \tag{82}$$

- Variational CC energy (factorial complexity)

$$E_{\mathrm{VCC}} = \frac{\langle\Psi_{\mathrm{CC}}|\hat{H}|\Psi_{\mathrm{CC}}\rangle}{\langle\Psi_{\mathrm{CC}}|\Psi_{\mathrm{CC}}\rangle} = \frac{\langle\Psi_0(e^{\hat{T}})^\dagger|\hat{H}|e^{\hat{T}}\Psi_0\rangle}{\langle\Psi_0(e^{\hat{T}})^\dagger|e^{\hat{T}}\Psi_0\rangle} \geq E_{\mathrm{exact}} \tag{83}$$

- (Traditional) projected CC energy (polynomial complexity)

$$E_{\mathrm{TCC}} = \frac{\langle\Psi_0|\bar{H}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} = \frac{\langle\Psi_0 e^{-\hat{T}}|\hat{H}|e^{\hat{T}}\Psi_0\rangle}{\langle\Psi_0 e^{-\hat{T}}|e^{\hat{T}}\Psi_0\rangle} \tag{84}$$

- Unitary CC energy (very expensive unless you have a quantum computer)

$$E_{\mathrm{UCC}} = \frac{\langle\Psi_0(e^{\hat{\tau}})^\dagger|\hat{H}|e^{\hat{\tau}}\Psi_0\rangle}{\langle\Psi_0(e^{\hat{\tau}})^\dagger|e^{\hat{\tau}}\Psi_0\rangle} = \frac{\langle\Psi_0 e^{-\hat{\tau}}|\hat{H}|e^{\hat{\tau}}\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} \quad \text{where } \hat{\tau} = \hat{T} - \hat{T}^\dagger \text{ is anti-Hermitian} \tag{85}$$

Similarity-transformed Hamiltonians

- The similarity-transformed Hamiltonian $\bar{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$ is **not** Hermitian:

$$(e^{-\hat{T}}\hat{H}e^{\hat{T}})^\dagger = (e^{\hat{T}})^\dagger \hat{H}^\dagger (e^{-\hat{T}})^\dagger = e^{\hat{T}^\dagger}\hat{H}e^{-\hat{T}^\dagger} \neq e^{-\hat{T}}\hat{H}e^{\hat{T}} \tag{86}$$

- The similarity-transformed Hamiltonian $e^{-\hat{\tau}}\hat{H}e^{\hat{\tau}}$ is Hermitian:

$$(e^{-\hat{\tau}}\hat{H}e^{\hat{\tau}})^\dagger = (e^{\hat{\tau}})^\dagger \hat{H}^\dagger (e^{-\hat{\tau}})^\dagger = e^{\hat{\tau}^\dagger}\hat{H}e^{-\hat{\tau}^\dagger} = e^{-\hat{\tau}}\hat{H}e^{\hat{\tau}} \quad \text{because} \quad \hat{\tau}^\dagger = -\hat{\tau} \tag{87}$$

The two most important equations in CC theory

- The energy equation

$$\boxed{\langle\Psi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle = E} \tag{88}$$

- The amplitude equation

$$\boxed{\langle\Psi_{ij\ldots}^{ab\ldots}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle = 0 \quad \Rightarrow \quad t_{ij\ldots}^{ab\ldots}} \tag{89}$$

Let's build the CISD and CCSD Hamiltonian matrix in the basis of $|0\rangle$, $|\mathrm{S}\rangle$, and $|\mathrm{D}\rangle$:

CISD Hamiltonian

$$\hat{H}_{\text{CISD}} = \begin{pmatrix} E_{\text{HF}} & 0 & H_{0\text{D}} \\ 0 & H_{\text{SS}} & H_{\text{SD}} \\ H_{\text{D}0} & H_{\text{DS}} & H_{\text{DD}} \end{pmatrix} \tag{90}$$

CCSD Hamiltonian

$$\bar{H}_{\text{CCSD}} = \begin{pmatrix} E_{\text{CC}} & \bar{H}_{0\text{S}} & \bar{H}_{0\text{D}} \\ 0 & \bar{H}_{\text{SS}} & \bar{H}_{\text{SD}} \\ 0 & \bar{H}_{\text{DS}} & \bar{H}_{\text{DD}} \end{pmatrix} \tag{91}$$

NB: This is the equation-of-motion (EOM) CCSD Hamiltonian!

The Hausdorff expansion

Campbell-Baker-Hausdorff formula

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \dots \tag{92}$$

$$\hat{H} = \sum_{pq} h_{pq}\hat{a}_p^\dagger \hat{a}_q + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle\, \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \tag{93}$$

$$\left[\hat{a}_p^\dagger \hat{a}_q, \hat{a}_a^\dagger \hat{a}_i\right] = \hat{a}_p^\dagger \underbrace{\hat{a}_q \hat{a}_a^\dagger}_{\delta_{qa} - \hat{a}_a^\dagger \hat{a}_q} \hat{a}_i - \hat{a}_a^\dagger \underbrace{\hat{a}_i \hat{a}_p^\dagger}_{\delta_{ip} - \hat{a}_p^\dagger \hat{a}_i} \hat{a}_q = \hat{a}_p^\dagger \delta_{qa} \hat{a}_i - \hat{a}_a^\dagger \delta_{ip} \hat{a}_q \tag{94}$$

- At the TCC level, the BCH expansion truncates naturally after the first five terms
- At the VCC level, the BCH expansion does not truncate but terminates
- At the UCC level, the BCH expansion does not terminate

For more details about normal-ordered operators, Wick's theorem, and diagrammatic techniques, see Crawford & Schaefer, Reviews in Computational Chemistry, Vol. 14, Chap. 2, 2000.

Projected CC energy

Assuming that $\langle \Psi_0 | \Psi_0 \rangle = 1$, we have

$$
\begin{aligned}
E_{\mathrm{CC}} &= \langle \Psi_0 | \hat{H} e^{\hat{T}} | \Psi_0 \rangle \\
&= \langle \Psi_0 | \hat{H} (\hat{1} + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2) | \Psi_0 \rangle \\
&= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | \hat{H} \hat{T}_1 | \Psi_0 \rangle + \langle \Psi_0 | \hat{H} \hat{T}_2 | \Psi_0 \rangle + \frac{1}{2} \langle \Psi_0 | \hat{H} \hat{T}_1^2 | \Psi_0 \rangle \\
&= E_0 + \sum_i \sum_a t_i^a \langle \Psi_0 | \hat{H} | \Psi_i^a \rangle + \frac{1}{4} \sum_{ij} \sum_{ab} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle \Psi_0 | \hat{H} | \Psi_{ij}^{ab} \rangle
\end{aligned}
\tag{95}
$$

HF reference wave function

- $E_0 = E_{\mathrm{HF}}$
- $\langle \Psi_0 | \hat{H} | \Psi_i^a \rangle = \langle i | f | a \rangle = 0$ ⇔ Brillouin's theorem
- $\langle \Psi_0 | \hat{H} | \Psi_{ij}^{ab} \rangle = \langle ij || ab \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle$ ⇔ Two-electron integrals

$$\boxed{E_{\mathrm{CC}} = E_{\mathrm{HF}} + \frac{1}{4} \sum_{ij} \sum_{ab} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle ij || ab \rangle} \tag{96}$$

CC with doubles (CCD)

- Only doubles, doubles of doubles, etc $\Rightarrow \hat{T} = \hat{T}_2$
- Still an infinite series

$$e^{\hat{T}_2} = \hat{1} + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{6}\hat{T}_2^3 + \frac{1}{24}\hat{T}_2^4 + \dots \tag{97}$$

- CCD energy

$$E_{\text{CCD}} = E_{\text{HF}} + \frac{1}{4}\sum_{ij}\sum_{ab} t_{ij}^{ab} \langle ij||ab\rangle \tag{98}$$

CCD equations

- Projection of similarity-transformed Hamiltonian onto doubles

$$\langle \Psi_{ij}^{ab} | \bar{H} | \Psi_0 \rangle = E_{\text{CC}} \langle \Psi_{ij}^{ab} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad \langle \Psi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle = 0 \tag{99}$$

- Residual equation

$$\boxed{r_{ij}^{ab} = \langle ij || ab \rangle + \Delta_{ij}^{ab} t_{ij}^{ab} + u_{ij}^{ab} + v_{ij}^{ab} = 0} \quad \Rightarrow \quad \boxed{t_{ij}^{ab} = - \frac{\langle ij || ab \rangle + u_{ij}^{ab} + v_{ij}^{ab}}{\Delta_{ij}^{ab}}} \tag{100}$$

- Energy differences

$$\Delta_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j \tag{101}$$

- Linear array

$$u_{ij}^{ab} = f(t_{ij}^{ab}) = \mathcal{O}(N^6) \tag{102}$$

- Quadratic array

$$v_{ij}^{ab} = f(t_{ij}^{ab}) = \underbrace{\mathcal{O}(N^6)}_{\text{smart}} \text{ or } \underbrace{\mathcal{O}(N^8)}_{\text{dumb}} \tag{103}$$

Linear array

Each term of the linear term can be computed in $\mathcal{O}(N^6)$:

$$\begin{aligned} u_{ij}^{ab} = {} & \frac{1}{2}\sum_{cd} \underbrace{\langle ab||cd\rangle}_{VVVV} t_{ij}^{cd} + \frac{1}{2}\sum_{kl} \underbrace{\langle kl||ij\rangle}_{OOOO} t_{kl}^{ab} \\ & + \sum_{kc}\left[- \underbrace{\langle kb||jc\rangle}_{OVOV} t_{ik}^{ac} + \langle ka||jc\rangle t_{ik}^{bc} - \langle ka||ic\rangle t_{jk}^{bc} + \langle kb||ic\rangle t_{jk}^{ac} \right] \end{aligned} \tag{104}$$

NB: CCD($v_{ij}^{ab} = 0$) = linear CCD (LCCD)

Quadratic array: the dumb way

The quadratic term is the computational bottleneck of CCD:

$$v_{ij}^{ab} = \frac{1}{4} \sum_{klcd} \underbrace{\langle kl||cd\rangle}_{OOVV} \Big[t_{ij}^{cd} t_{kl}^{ab} - 2(t_{ij}^{ac} t_{kl}^{bd} + t_{ij}^{bd} t_{kl}^{ac}) - 2(t_{ik}^{ab} t_{jl}^{cd} + t_{ik}^{cd} t_{jl}^{ab}) + 4(t_{ik}^{ac} t_{jl}^{bd} + t_{ik}^{bd} t_{jl}^{ac}) \Big] \tag{105}$$

The “formal” scaling of the quadratic term is $\mathcal{O}(N^8)$

Quadratic array: the smart way

One can “sacrifice” storage to gain in scaling:

$$\underbrace{\langle kl|X_1|ij\rangle}_{\mathcal{O}(N^6)} = \sum_{cd} \langle kl||cd\rangle\, t_{ij}^{cd} \qquad \underbrace{\langle b|X_2|c\rangle}_{\mathcal{O}(N^5)} = \sum_{kld} \langle kl||cd\rangle\, t_{kl}^{bd} \tag{106}$$

$$\underbrace{\langle k|X_3|j\rangle}_{\mathcal{O}(N^5)} = \sum_{lcd} \langle kl||cd\rangle\, t_{jl}^{cd} \qquad \underbrace{\langle il|X_4|ad\rangle}_{\mathcal{O}(N^6)} = \sum_{kc} \langle kl||cd\rangle\, t_{ik}^{ac} \tag{107}$$

Now, the quadratic term can be computed in $\mathcal{O}(N^6)$

$$\begin{aligned} v_{ij}^{ab} &= \frac{1}{4}\sum_{kl} \langle kl|X_1|cd\rangle\, t_{kl}^{ab} - \frac{1}{2}\sum_{c}\left[\langle b|X_2|c\rangle t_{ij}^{ac} + \langle a|X_2|c\rangle t_{ij}^{cb}\right] \\ &- \frac{1}{2}\sum_{k}\left[\langle k|X_3|j\rangle t_{ik}^{ab} + \langle k|X_3|i\rangle t_{kj}^{ab}\right] + \sum_{kc}\left[\langle ik|X_4|ac\rangle t_{jk}^{bc} + \langle ik|X_4|bc\rangle t_{kj}^{ac}\right] \end{aligned} \tag{108}$$

CCD algorithm

CCD subroutine

```
procedure ITERATIVE CCD ALGORITHM
    Perform HF calculation to get $\epsilon_p$ and $\langle pq||rs\rangle$
    Set $u_{ij}^{ab} = 0$, and $v_{ij}^{ab} = 0$
    Compute amplitudes $t_{ij}^{ab} = -\langle ij||ab\rangle / \Delta_{ij}^{ab}$ (MP2 guess)
    while $\max |r_{ij}^{ab}| > \tau$ do
        Form linear array $u_{ij}^{ab}$
        Compute intermediate arrays $\langle kl|X_1|ij\rangle$, $\langle b|X_2|c\rangle$, $\langle k|X_3|j\rangle$, and $\langle il|X_4|ad\rangle$.
        Form quadratic array $v_{ij}^{ab}$
        Compute residues: $r_{ij}^{ab} = \langle ij||ab\rangle + \Delta_{ij}^{ab} t_{ij}^{ab} + u_{ij}^{ab} + v_{ij}^{ab}$
        Update amplitudes: $t_{ij}^{ab} \leftarrow t_{ij}^{ab} - r_{ij}^{ab} / \Delta_{ij}^{ab}$
    end while
    Compute CCD energy: $E_{CCD} = E_{HF} + \frac{1}{4}\sum_{ij}\sum_{ab} t_{ij}^{ab}\langle ij||ab\rangle$
end procedure
```

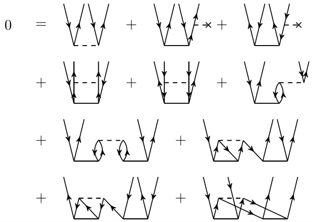


Illustration for the Be atom

Correlation energy of Be in a 4s2p basis set

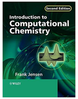
Scaling	Level	ΔE_c	%	Level	ΔE_c	%	Level	ΔE_c	%
N^5	MP2	0.053174	67.85						
N^6	MP3	0.067949	86.70	CISD	0.075277	96.05	CCSD	0.078176	99.75
N^7	MP4	0.074121	94.58				CCSD(T)	0.078361	99.99
N^8	MP5	0.076918	98.15	CISDT	0.075465	96.29	CCSDT	0.078364	99.99
N^9	MP6	0.078090	99.64						
N^{10}	MP7	0.078493	100.15	CISDTQ	0.078372	100	CCSDTQ	0.078372	100

As a rule of thumb:

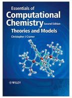
$\text{HF} \ll \text{MP2} < \text{CISD} < \text{MP4(SDQ)} \sim \text{CCSD} < \text{MP4} < \text{CCSD(T)}$

Good books

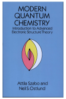
- Introduction to Computational Chemistry (Jensen)



- Essentials of Computational Chemistry (Cramer)



- Modern Quantum Chemistry (Szabo & Ostlund)



- Molecular Electronic Structure Theory (Helgaker, Jorgensen & Olsen)