

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

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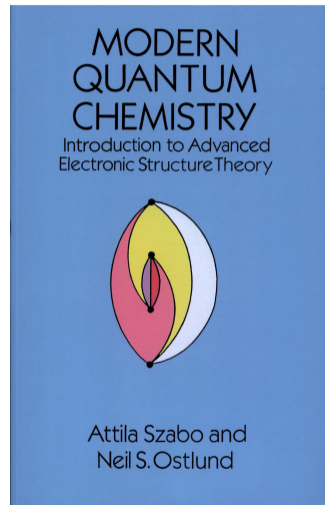
- How to perform a Hartree-Fock (HF) calculation in practice?
 - Computation of integrals [Ahlrichs, PCCP 8 (2006) 3072]
 - Orthogonalization matrix [Szabo & Ostlund, Modern Quantum Chemistry]
 - Construction of the Coulomb matrix [White & Head-Gordon, JCP 104 (1996) 2620]
 - Resolution of the identity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

- Computing the 2th-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]

The SCF algorithm (p. 146)

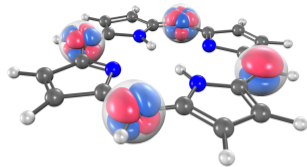
- 1 Specify molecule $\{\mathbf{r}_A\}$ and $\{Z_A\}$ and basis set $\{\phi_\mu\}$
- 2 Calculate integrals $S_{\mu\nu}$, $H_{\mu\nu}$ and $\langle\mu\nu|\lambda\sigma\rangle$
- 3 Diagonalize \mathbf{S} and compute $\mathbf{X} = \mathbf{S}^{-1/2}$
- 4 Obtain guess density matrix for \mathbf{P}
 1. Calculate \mathbf{J} and \mathbf{K} , then $\mathbf{F} = \mathbf{H} + \mathbf{J} + \mathbf{K}$
 2. Compute $\mathbf{F}' = \mathbf{X}^\dagger \cdot \mathbf{F} \cdot \mathbf{X}$
 3. Diagonalize \mathbf{F}' to obtain \mathbf{C}' and \mathbf{E}
 4. Calculate $\mathbf{C} = \mathbf{X} \cdot \mathbf{C}'$
 5. Form a new density matrix $\mathbf{P} = \mathbf{C} \cdot \mathbf{C}^\dagger$
 6. Am I converged? If not go back to 1.
- 5 Calculate stuff that you want, like E_{HF} for example



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

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

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



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

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

$$(\mu\nu||\lambda\sigma) = (\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu) \quad (4)$$

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

$$\langle \mu\nu | \lambda\sigma \rangle = \iint \phi_{\mu}(\mathbf{r}_1) \phi_{\nu}(\mathbf{r}_2) \frac{1}{r_{12}} \phi_{\lambda}(\mathbf{r}_1) \phi_{\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (5)$$

$$\langle \mu\nu || \lambda\sigma \rangle = \langle \mu\nu | \lambda\sigma \rangle - \langle \mu\nu | \sigma\lambda \rangle \quad (6)$$

Four-center two-electron integrals

$$\begin{aligned} \langle \mathbf{a}_1 \mathbf{a}_2 | \mathbf{b}_1 \mathbf{b}_2 \rangle &\equiv \langle \mathbf{a}_1 \mathbf{a}_2 | r_{12}^{-1} | \mathbf{b}_1 \mathbf{b}_2 \rangle \\ &= \iint \phi_{\mathbf{a}_1}^{\mathbf{A}_1}(\mathbf{r}_1) \phi_{\mathbf{a}_2}^{\mathbf{A}_2}(\mathbf{r}_2) \frac{1}{r_{12}} \phi_{\mathbf{b}_1}^{\mathbf{B}_1}(\mathbf{r}_1) \phi_{\mathbf{b}_2}^{\mathbf{B}_2}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (7)$$

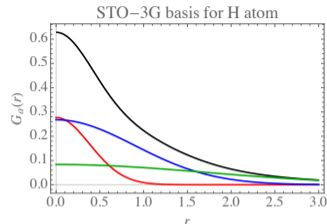
Formally, one has to compute $\mathcal{O}(N^4)$ ERIs!

Gaussian-type orbital (GTO)

$$\text{Contracted GTO} = |\mathbf{a}\rangle \equiv \phi_{\mathbf{a}}^{\mathbf{A}}(\mathbf{r}) = \sum_k^K D_k |\mathbf{a}\rangle_k$$

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

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



Primitive vs Contracted

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

$$\underbrace{\langle \mathbf{a}_1 \mathbf{a}_2 | \mathbf{b}_1 \mathbf{b}_2 \rangle}_{\text{contracted ERI}} = \sum_{k_1}^{K_1} \sum_{k_2}^{K_2} \sum_{k_3}^{K_3} \sum_{k_4}^{K_4} D_{k_1} D_{k_2} D_{k_3} D_{k_4} \underbrace{[\mathbf{a}_{1,k_1} \mathbf{a}_{2,k_2} | \mathbf{b}_{1,k_3} \mathbf{b}_{2,k_4}]}_{\text{primitive ERI}} \quad (8)$$

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

Dunning's cc-pVTZ basis for the carbon atom

$$\langle 1s1s | 1s1s \rangle = \sum_{k_1}^{10} \sum_{k_2}^{10} \sum_{k_3}^{10} \sum_{k_4}^{10} D_{k_1} D_{k_2} D_{k_3} D_{k_4} [s_{k_1}^{\alpha_{k_1}} s_{k_2}^{\alpha_{k_2}} | s_{k_3}^{\alpha_{k_3}} s_{k_4}^{\alpha_{k_4}}] \quad (9)$$

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

$$|\mathbf{a}\rangle = \sum_k^K D_k |\mathbf{a}_k\rangle \quad (10)$$

<https://www.basissetexchange.org>

```

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”

$$G_{\alpha, \mathbf{A}}(\mathbf{r}) = \exp(-\alpha |\mathbf{r} - \mathbf{A}|^2) \quad \text{and} \quad G_{\beta, \mathbf{B}}(\mathbf{r}) = \exp(-\beta |\mathbf{r} - \mathbf{B}|^2) \quad \text{then} \quad (11)$$

$$\boxed{G_{\alpha, \mathbf{A}}(\mathbf{r}) G_{\beta, \mathbf{B}}(\mathbf{r}) = K G_{\zeta, \mathbf{P}}(\mathbf{r})} \quad \text{with} \quad \zeta = \alpha + \beta \quad \text{and} \quad \mathbf{P} = \frac{\alpha \mathbf{A} + \beta \mathbf{B}}{\alpha + \beta} \quad (12)$$

$$K = \exp\left(-\frac{\alpha\beta}{\alpha + \beta} |\mathbf{A} - \mathbf{B}|^2\right) \quad (13)$$

Gaussian product rule for ERIs

$$\begin{aligned} (\mathbf{ab} | \mathbf{cd}) &= \iint G_{\alpha, \mathbf{A}}(\mathbf{r}_1) G_{\beta, \mathbf{B}}(\mathbf{r}_1) \frac{1}{r_{12}} G_{\gamma, \mathbf{C}}(\mathbf{r}_2) G_{\delta, \mathbf{D}}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= K K \iint G_{\zeta, \mathbf{P}}(\mathbf{r}_1) \frac{1}{r_{12}} G_{\eta, \mathbf{Q}}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (14)$$

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

A “good” upper bound must be

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

$$|(\mathbf{ab}|\mathbf{cd})| \leq B \quad (15)$$

Cauchy-Schwartz bound

$$|(\mathbf{ab}|\mathbf{cd})| \leq \sqrt{(\mathbf{ab}|\mathbf{ab})} \sqrt{(\mathbf{cd}|\mathbf{cd})} \quad \text{or} \quad |(P|Q)| \leq \sqrt{(P|P)} \sqrt{(Q|Q)} \quad (16)$$

The family of generalized Hölder bounds

$$|(\mathbf{ab}|\mathbf{cd})| \leq [(\mathbf{ab}|\mathbf{ab})]^{1/m} [(\mathbf{cd}|\mathbf{cd})]^{1/n} \quad \text{with} \quad \frac{1}{m} + \frac{1}{n} = 1 \quad \text{and} \quad m, n > 1 \quad (17)$$

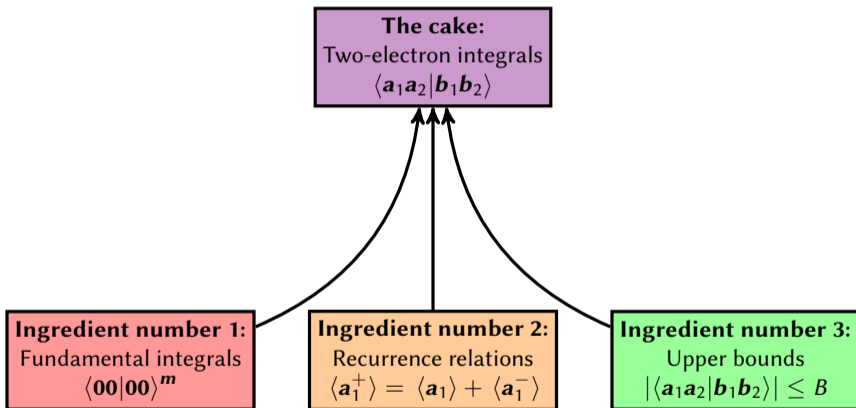
Number of significant two-electron integrals

$$(\mathbf{ab}|\mathbf{cd}) \equiv (\mathbf{ab}|\mathcal{O}_2|\mathbf{cd}) \quad (18)$$

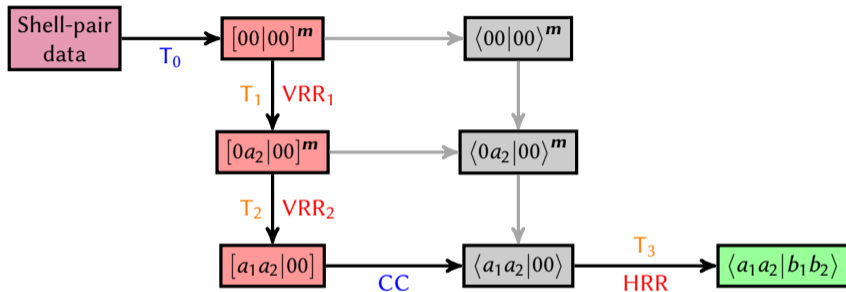
Long-range vs short-range operators

$$N_{\text{sig}} = c N^\alpha \quad (19)$$

Molecule	N	$\mathcal{O}_2 = r_{12}^{-1}$		$\mathcal{O}_2 = e^{-\lambda r_{12}^2} (\lambda = 1)$	
		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



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



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

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

Symmetric (or Löwdin) orthogonalization

$$\mathbf{X} = \mathbf{S}^{-1/2} = \mathbf{U} \cdot \mathbf{s}^{-1/2} \cdot \mathbf{U}^\dagger \text{ is one solution...} \quad (20)$$

Is it working?

$$\mathbf{X}^\dagger \cdot \mathbf{S} \cdot \mathbf{X} = \mathbf{S}^{-1/2} \cdot \mathbf{S} \cdot \mathbf{S}^{-1/2} = \mathbf{S}^{-1/2} \cdot \mathbf{S} \cdot \mathbf{S}^{-1/2} = \mathbf{I} \quad \checkmark \quad (21)$$

Canonical orthogonalization

$$\mathbf{X} = \mathbf{U} \cdot \mathbf{s}^{-1/2} \text{ is another solution (when you have linear dependencies)...} \quad (22)$$

Is it working?

$$\mathbf{X}^\dagger \cdot \mathbf{S} \cdot \mathbf{X} = \mathbf{s}^{-1/2} \cdot \underbrace{\mathbf{U}^\dagger \cdot \mathbf{S} \cdot \mathbf{U}}_{\mathbf{s}} \cdot \mathbf{s}^{-1/2} = \mathbf{I} \quad \checkmark \quad (23)$$

Density matrix (closed-shell system)

$$P_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{\mu i} C_{\nu i} \quad \text{or} \quad \boxed{\mathbf{P} = \mathbf{C} \cdot \mathbf{C}^\dagger} \quad (24)$$

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

$$F_{\mu\nu} = H_{\mu\nu} + \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\nu|\lambda\sigma)}_{J_{\mu\nu} = \text{Coulomb}} - \frac{1}{2} \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\sigma|\lambda\nu)}_{K_{\mu\nu} = \text{exchange}} \quad (25)$$

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

$$E_{\text{HF}} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\sigma|\lambda\nu) \right] P_{\lambda\sigma} \quad \text{or} \quad \boxed{E_{\text{HF}} = \frac{1}{2} \text{Tr}[\mathbf{P} \cdot (\mathbf{H} + \mathbf{F})]} \quad (26)$$

```

procedure COMPUTING THE COULOMB MATRIX
  for  $\mu = 1, N$  do
    for  $v = 1, N$  do
       $J_{\mu v} = 0$ 
      for  $\lambda = 1, N$  do
        for  $\sigma = 1, N$  do
           $J_{\mu v} = J_{\mu v} + P_{\lambda\sigma}(\mu v | \lambda\sigma)$ 
        end for
      end for
    end for
  end for
end procedure

```

▷ Initialization of the array

▷ Accumulation step

▷ **This is a $\mathcal{O}(N^4)$ algorithm as it involves four loops**

Resolution of the identity (RI) = a fancy way of writing 1

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

Computing the Coulomb matrix with the RI

$$\begin{aligned} J_{\mu\nu} &= \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\nu|\lambda\sigma) \\ &\stackrel{\text{RI}}{=} \sum_{\lambda\sigma} P_{\lambda\sigma} \sum_A (\mu\nu|A)\langle A|\lambda\sigma\rangle \\ &= \sum_A (\mu\nu|A) \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma} \langle A|\lambda\sigma\rangle}_{\mathcal{O}(KN^2) \text{ and } K \text{ storage}} = \sum_A (\mu\nu|A) \underbrace{I_A}_{\mathcal{O}(KN^2)} \end{aligned} \quad (28)$$

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

```

procedure COMPUTING THE EXCHANGE MATRIX
  for  $\mu = 1, N$  do
    for  $v = 1, N$  do
       $K_{\mu v} = 0$ 
      for  $\lambda = 1, N$  do
        for  $\sigma = 1, N$  do
           $K_{\mu v} = K_{\mu v} + P_{\lambda\sigma}(\mu\sigma|\lambda v)$ 
        end for
      end for
    end for
  end for
end procedure

```

▷ Initialization of the array

▷ Accumulation step

▷ **This is a $\mathcal{O}(N^4)$ algorithm and it's hard to play games...**

LDA exchange (in theory) = cf Julien's lectures

$$K_{\mu\nu}^{\text{LDA}} = \int \phi_{\mu}(\mathbf{r}) v_x^{\text{LDA}}(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r} = \frac{4}{3} C_x \overbrace{\int \phi_{\mu}(\mathbf{r}) \rho^{1/3}(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r}}^{\text{no closed-form expression in general}} \quad (29)$$

$$\rho(\mathbf{r}) = \sum_{\mu\nu} \phi_{\mu}(\mathbf{r}) P_{\mu\nu} \phi_{\nu}(\mathbf{r}) \quad (30)$$

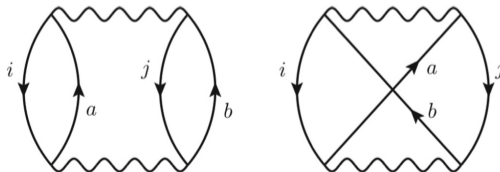
LDA exchange (in practice) = numerical integration via quadrature = $\int f(x) dx \approx \sum_k w_k f(x_k)$

$$\underbrace{K_{\mu\nu}^{\text{LDA}}}_{\mathcal{O}(N_{\text{grid}} N^2)} \approx \sum_{k=1}^{N_{\text{grid}}} \underbrace{w_k}_{\text{weights}} \phi_{\mu}(\mathbf{r}_k) v_x^{\text{LDA}}(\mathbf{r}_k) \phi_{\nu}(\mathbf{r}_k) = \frac{4}{3} C_x \sum_{k=1}^{N_{\text{grid}}} w_k \phi_{\mu}(\mathbf{r}_k) \rho^{1/3}(\mathbf{r}_k) \phi_{\nu}(\mathbf{r}_k) \quad (31)$$

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

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

$$\begin{aligned}
 E_c^{(2)} &= \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab \rangle (2\langle ij|ab \rangle - \langle ij|ba \rangle)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \\
 &= \underbrace{2 \sum_{ij} \sum_{ab} \frac{\langle ij|ab \rangle^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}_{\text{direct part}} - \underbrace{\sum_{ij} \sum_{ab} \frac{\langle ij|ab \rangle \langle ij|ba \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}_{\text{exchange part}}
 \end{aligned} \tag{33}$$



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**

$$\Delta = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$$

$$E_c^{(2)} = E_c^{(2)} + (2 \langle ij|ab \rangle^2 - \langle ij|ab \rangle \langle ij|ba \rangle) / \Delta$$

end for

end for

end for

end for

end procedure

▷ $\mathcal{O}(N^4)$ because there are four loops!

The naive way...

$$\underbrace{(pq|rs)}_{\text{MO integrals}} = \sum_{\mu\nu\lambda\sigma} c_{\mu p} c_{\nu q} c_{\lambda r} c_{\sigma s} \underbrace{(\mu\nu|\lambda\sigma)}_{\text{AO integrals}} \quad (34)$$

```
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
          for μ = 1, N do
            for ν = 1, N do
              for λ = 1, N do
                for σ = 1, N do
                  (pq|rs) = (pq|rs) + cμpcνqcλrcσs(μν|λσ)
                end for
              end for
            end for
          end for
        end for
      end for
    end for
  end for
end procedure
```

▷ Initialization of the array

▷ Accumulation step

▷ This is a $\mathcal{O}(N^8)$ algorithm! You won't do much quantum chemistry with this...

Semi-direct algorithm...

$$(pq|rs) = \sum_{\mu p} c_{\mu p} \left\{ \sum_{\nu q} c_{\nu q} \left[\sum_{\lambda r} c_{\lambda r} \left(\underbrace{\sum_{\sigma s} c_{\sigma s} (\mu\nu|\lambda\sigma)}_{\text{Step \#1}} \right) \right] \right\} \quad (35)$$

Step #2
Step #3
Step #4

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 $\mathcal{O}(N^5)$ and $\mathcal{O}(N^4)$ 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
             $J_{\mu\nu r s} = J_{\mu\nu r s} + c_{\lambda r} I_{\mu\nu\lambda s}$ 
          end for
        end for
      end for
    end for
  end for
end procedure

```

▷ Step #2 costs $\mathcal{O}(N^5)$ and $\mathcal{O}(N^4)$ 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
             $l_{\mu q r s} = l_{\mu q r s} + c_{\nu q} j_{\mu \nu r s}$ 
          end for
        end for
      end for
    end for
  end for
end procedure

```

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

Almlöf's trick

$$\frac{1}{\Delta} = \int_0^{\infty} \exp(-\Delta t) dt \quad (36)$$

$$\begin{aligned} E_c^{(2)} &= \frac{1}{4} \sum_{ij} \sum_{ab} \frac{\langle ij || ab \rangle^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \\ &= \frac{1}{4} \int_0^{\infty} \sum_{ij} \sum_{ab} \langle ij || ab \rangle^2 \exp[-(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)t] dt \end{aligned} \quad (37)$$

$$\begin{aligned} &= \frac{1}{4} \int_0^{\infty} \sum_{ij} \sum_{ab} \langle i(t)j(t) || a(t)b(t) \rangle^2 \stackrel{\text{quad.}}{\approx} \frac{1}{4} \sum_{k=1}^{N_{\text{grid}}} w_k \sum_{ij} \sum_{ab} \langle i(t_k)j(t_k) || a(t_k)b(t_k) \rangle^2 \\ &\quad |p\rangle \equiv |\varphi_p(0)\rangle \quad \text{and} \quad |p(t)\rangle \equiv |\varphi_p(t)\rangle = |\varphi_p(0)\rangle e^{\pm \frac{1}{2} \epsilon_p t} \end{aligned} \quad (38)$$

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** (Thank you 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

- CC wave function

$$\Psi_{\text{CC}} = e^{\hat{T}} \Psi_0 \quad (39)$$

- Excitation operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n \quad (40)$$

- Exponential *ansatz*

$$\begin{aligned} e^{\hat{T}} &= \hat{1} + \hat{T} + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \dots \\ &= \hat{1} + \hat{T}_1 + \left(\underbrace{\hat{T}_2}_{\text{connected}} + \frac{1}{2} \underbrace{\hat{T}_1^2}_{\text{disconnected}} \right) + \left(\hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{1}{6} \hat{T}_1^3 \right) \\ &\quad + \left(\hat{T}_4 + \hat{T}_3 \hat{T}_1 + \frac{1}{2} \underbrace{\hat{T}_2^2}_{\text{two pairs of electrons}} + \frac{1}{2} \hat{T}_2 \hat{T}_1^2 + \frac{1}{24} \underbrace{\hat{T}_1^4}_{\text{four electrons}} \right) + \dots \end{aligned} \quad (41)$$

- Singles

$$\hat{T}_1 \Psi_0 = \sum_i \sum_a \underbrace{t_i^a}_{\text{amplitudes}} \Psi_i^a \quad (42)$$

- Doubles

$$\hat{T}_2 \Psi_0 = \sum_{i < j} \sum_{a < b} t_{ij}^{ab} \underbrace{\Psi_{ij}^{ab}}_{\text{excited determinants}} \quad (43)$$

- FCI wave function

$$\Psi_{\text{FCI}} = (\hat{1} + \hat{T}) \Psi_0 = (\hat{1} + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots) \Psi_0 \quad (44)$$

- Schrödinger equation

$$\hat{H}|\Psi_{CC}\rangle = E|\Psi_{CC}\rangle \Rightarrow \hat{H}e^{\hat{T}}|\Psi_0\rangle = Ee^{\hat{T}}|\Psi_0\rangle \Rightarrow \underbrace{e^{-\hat{T}}\hat{H}e^{\hat{T}}}_{\bar{H}}|\Psi_0\rangle = E|\Psi_0\rangle \quad (45)$$

\bar{H} = similarity transform

- Variational CC energy (**factorial complexity**)

$$E_{VCC} = \frac{\langle\Psi_{CC}|\hat{H}|\Psi_{CC}\rangle}{\langle\Psi_{CC}|\Psi_{CC}\rangle} = \frac{\langle e^{\hat{T}}\Psi_0|\hat{H}|e^{\hat{T}}\Psi_0\rangle}{\langle e^{\hat{T}}\Psi_0|e^{\hat{T}}\Psi_0\rangle} \quad (46)$$

- Projected CC energy

$$\langle\Psi_0|\hat{H}|\Psi_{CC}\rangle = E_{CC}\langle\Psi_0|\Psi_{CC}\rangle \Rightarrow \boxed{E_{CC} = \frac{\langle\Psi_0|\hat{H}e^{\hat{T}}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}} \quad (47)$$

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

$$\begin{aligned}
 E_{CC} &= \langle \Psi_0 | \hat{H} e^{\hat{T}} | \Psi_0 \rangle \\
 &= \langle \Psi_0 | \hat{H} (\hat{1} + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2) | \Psi_0 \rangle \\
 &= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | \hat{H} \hat{T}_1 | \Psi_0 \rangle + \langle \Psi_0 | \hat{H} \hat{T}_2 | \Psi_0 \rangle + \frac{1}{2} \langle \Psi_0 | \hat{H} \hat{T}_1^2 | \Psi_0 \rangle \\
 &= E_0 + \sum_i \sum_a t_i^a \langle \Psi_0 | \hat{H} | \Psi_i^a \rangle + \frac{1}{4} \sum_{ij} \sum_{ab} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle \Psi_0 | \hat{H} | \Psi_{ij}^{ab} \rangle
 \end{aligned} \tag{48}$$

HF reference wave function

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

$$E_{\text{CC}} = E_{\text{HF}} + \frac{1}{4} \sum_{ij} \sum_{ab} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle ij || ab \rangle \quad (49)$$

CC with doubles (CCD)

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

$$e^{\hat{T}_2} = \hat{1} + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{6}\hat{T}_2^3 + \frac{1}{24}\hat{T}_2^4 + \dots \quad (50)$$

- CCD energy

$$E_{\text{CCD}} = E_{\text{HF}} + \frac{1}{4} \sum_{ij} \sum_{ab} t_{ij}^{ab} \langle ij || ab \rangle \quad (51)$$

- Projection of similarity-transformed Hamiltonian onto doubles

$$\langle \Psi_{ij}^{ab} | \bar{H} | \Psi_0 \rangle = E_{\text{CC}} \langle \Psi_{ij}^{ab} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad \langle \Psi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle = 0 \quad (52)$$

- Residual equation

$$\boxed{r_{ij}^{ab} = \langle ij || ab \rangle + \Delta_{ij}^{ab} t_{ij}^{ab} + u_{ij}^{ab} + v_{ij}^{ab} = 0} \quad \Rightarrow \quad \boxed{t_{ij}^{ab} = -\frac{\langle ij || ab \rangle + u_{ij}^{ab} + v_{ij}^{ab}}{\Delta_{ij}^{ab}}} \quad (53)$$

- Energy differences

$$\Delta_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j \quad (54)$$

- Linear array

$$u_{ij}^{ab} = f(t_{ij}^{ab}) = \mathcal{O}(N^6) \quad (55)$$

- Quadratic array

$$v_{ij}^{ab} = f(t_{ij}^{ab}) = \underbrace{\mathcal{O}(N^6)}_{\text{smart}} \text{ or } \underbrace{\mathcal{O}(N^8)}_{\text{dumb}} \quad (56)$$

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

$$\begin{aligned}
 u_{ij}^{ab} = & \frac{1}{2} \sum_{cd} \underbrace{\langle ab||cd \rangle}_{VVVV} t_{ij}^{cd} + \frac{1}{2} \sum_{kl} \underbrace{\langle kl||ij \rangle}_{OOOO} t_{kl}^{ab} \\
 & + \sum_{kc} \left[- \underbrace{\langle kb||jc \rangle}_{OVOV} t_{ik}^{ac} + \langle ka||jc \rangle t_{ik}^{bc} - \langle ka||ic \rangle t_{jk}^{bc} + \langle kb||ic \rangle t_{jk}^{ac} \right]
 \end{aligned} \tag{57}$$

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

The quadratic term is the computational bottleneck of CCD:

$$v_{ij}^{ab} = \frac{1}{4} \sum_{klcd} \underbrace{\langle kl || cd \rangle}_{OOVV} \left[t_{ij}^{cd} t_{kl}^{ab} - 2(t_{ij}^{ac} t_{kl}^{bd} + t_{ij}^{bd} t_{kl}^{ac}) \right. \\ \left. - 2(t_{ik}^{ab} t_{jl}^{cd} + t_{ik}^{cd} t_{jl}^{ab}) + 4(t_{ik}^{ac} t_{jl}^{bd} + t_{ik}^{bd} t_{jl}^{ac}) \right] \quad (58)$$

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

One can “sacrifice” storage to gain in scaling:

$$\underbrace{\langle kl|X_1|ij \rangle}_{\mathcal{O}(N^6)} = \sum_{cd} \langle kl||cd \rangle t_{ij}^{cd} \qquad \underbrace{\langle b|X_2|c \rangle}_{\mathcal{O}(N^5)} = \sum_{kld} \langle kl||cd \rangle t_{kl}^{bd} \quad (59)$$

$$\underbrace{\langle k|X_3|j \rangle}_{\mathcal{O}(N^5)} = \sum_{lcd} \langle kl||cd \rangle t_{jl}^{cd} \qquad \underbrace{\langle il|X_4|ad \rangle}_{\mathcal{O}(N^6)} = \sum_{kc} \langle kl||cd \rangle t_{ik}^{ac} \quad (60)$$

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

$$\begin{aligned} v_{ij}^{ab} = & \frac{1}{4} \sum_{kl} \langle kl|X_1|cd \rangle t_{kl}^{ab} - \frac{1}{2} \sum_c \left[\langle b|X_2|c \rangle t_{ij}^{ac} + \langle a|X_2|c \rangle t_{ij}^{cb} \right] \\ & - \frac{1}{2} \sum_k \left[\langle k|X_3|j \rangle t_{ik}^{ab} + \langle k|X_3|i \rangle t_{kj}^{ab} \right] + \sum_{kc} \left[\langle ik|X_4|ac \rangle t_{jk}^{bc} + \langle ik|X_4|bc \rangle t_{kj}^{ac} \right] \end{aligned} \quad (61)$$

CCD subroutine

procedure ITERATIVE CCD ALGORITHM

 Perform HF calculation to get ϵ_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**

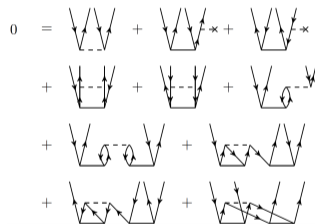
 Form linear array u_{ij}^{ab}

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


- Introduction to Computational Chemistry (Jensen)
- Essentials of Computational Chemistry (Cramer)
- Modern Quantum Chemistry (Szabo & Ostlund)
- Molecular Electronic Structure Theory (Helgaker, Jorgensen & Olsen)

