TCCM lectures – Advanced Computational Techniques

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Overview of computational methods

- Hartree-Fock to start with ... or Hückel?
- Multiconfigurational SCF
- Perturbation theory for electron correlation
- CISD and derivates (CEPA, ACPF)
- Coupled-Cluster Theory
- Full CI
- Density-Functional methods
- Atoms-In-Molecules, Non-Covalent-Interactions etc
- Quantum Monte-Carlo methods
- Quantum chemistry for periodic systems
- Molecular dynamics, potential surfaces, finite-temperature methods ...

What are the bottle-necks? What are sources of errors?

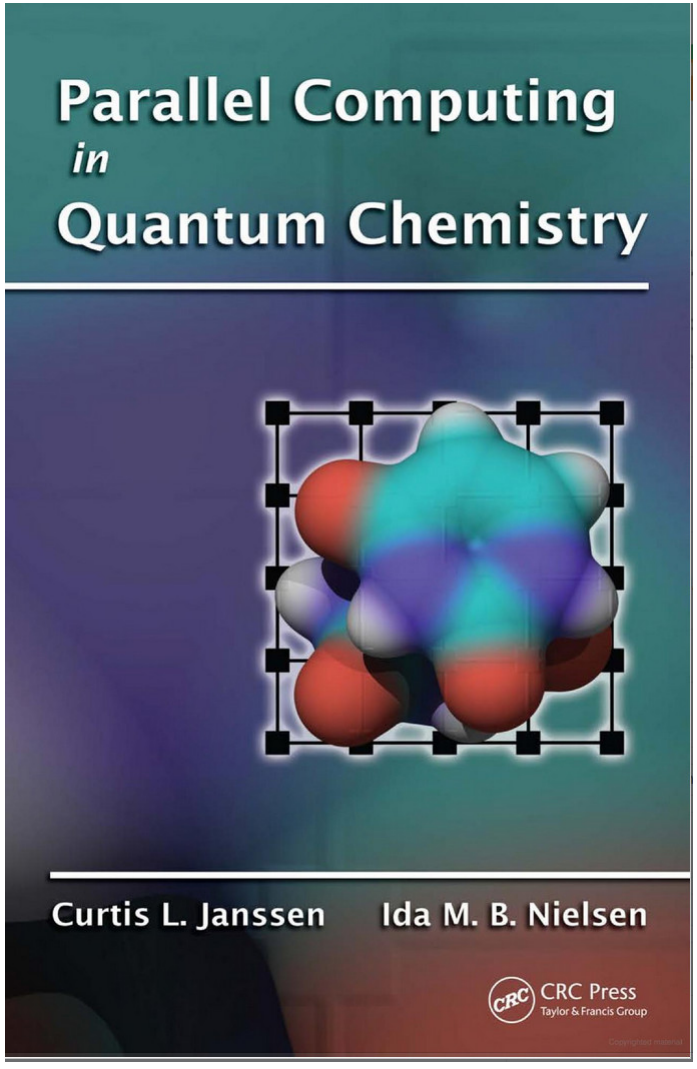
Overview of computational methods

Ingredients

- Atom-centered basis sets
- Precalculated integrals for one- and two-electron operators
- Storage and diagonalization of operator matrices
- Storage and matrix elements between excited determinants
- Matrix and vector operations in high dimensions
- Four-index integral transformation $(\alpha\beta|\gamma\delta) \rightarrow (ij|kl)$
- Scaling well beyond N or $N \log N$
- Random numbers
- Algebra in the complex plane (periodic systems)
- Numerical integration on grids
- Numerical interpolation in multidimensional spaces

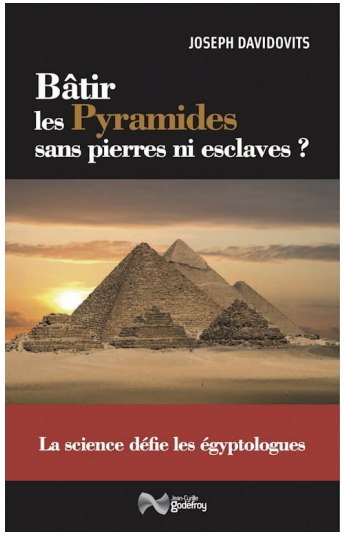
Overview of computational methods

What can be parallelized on 100 processors, on 10 000 processors?



Overview of computational methods

- Calculation of integrals? $N^4 \longrightarrow$ 100 procs
- Fock matrix elements? N^2, 10 procs
- Double excitations? $n_o^2 N_v^2$
- Matrix elements between double excitations? N^6, 100 procs, but ...
- Matrix elements between triple excitations? N^8
- Strange situation .... known already in ancient Egypt, 4500 years ago



Way out: Localized orbitals or Density-Functional Theory !

Overview of computational methods

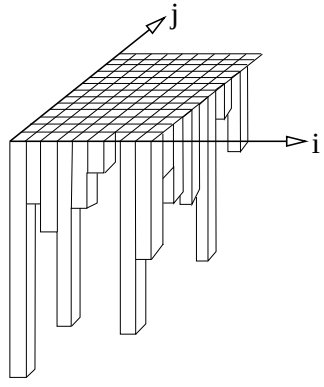
Integral-driven or Configuration-driven ?

$$\langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ij}^{cd} \rangle = (ac|bd) - (ad|bc)$$

Loop over configurations Φ_{ij}^{ab} or over integrals $(ab|cd)$.

- In which category are less elements?
- CISD: many orbitals, but only 2 electrons $\rightarrow$ integral-driven
- CAS-CI: a few orbitals, but many configurations $\rightarrow$ configuration-driven

One may rearrange configurations with common indexes:



The matrix elements within each 1D “rod” need evaluation.

Hash tables and bisection

- Bi-electronic integrals $(ij|kl)$, many are small or even zero, no need to store them.
- Canonical ordering: $i \leq j, k \leq l, i \leq k$, if $i = k$ then $j \leq l$ to avoid double storage
- Schwartz inequality: $(ij|kl) \leq \sqrt{(ij|ij)(kl|kl)}$
- Calculate first the N^2 integrals $(ij|ij)$
- Maximum number of different integrals:

$$\frac{1}{8}N(N+1)(N(N+1)+2) = \frac{1}{8}N\left(N^3+2N^2+3N+2\right)$$

- Exact address in memory is a complicated polynomial of 4th order in the first index
- Integrals may be cast into index classes, occ–virt, all different or not
- All integrals have to fit into memory.
- Storage with indexes or in an order?
- How to find a needed integral $(ij|kl)$ rapidly?

Hash tables and bisection

Hash tables

- Integrals are stored with their indexes in a list
- Allocate a hash table (N, depth)
- For each integral create a number from the 4 indexes as a key
- Store the index of the integral at this place
- If a second index combination generates the same number, it is stored with a second index
- Rapid access $\longleftrightarrow$ memory needs for the hash table
- No need for integral ordering, or definition of classes
- How to generate the key?
  - $\lambda(ijkl) = l + \alpha(k + \alpha(j + \alpha\, i))$ with a given α
  - position = $\mathrm{mod}(\lambda, N) + 1$
  - store in the last non-occupied depth
- 3rd-order polynomial = 3 multiplications + 3 additions

Hash tables and bisection

Typical situation

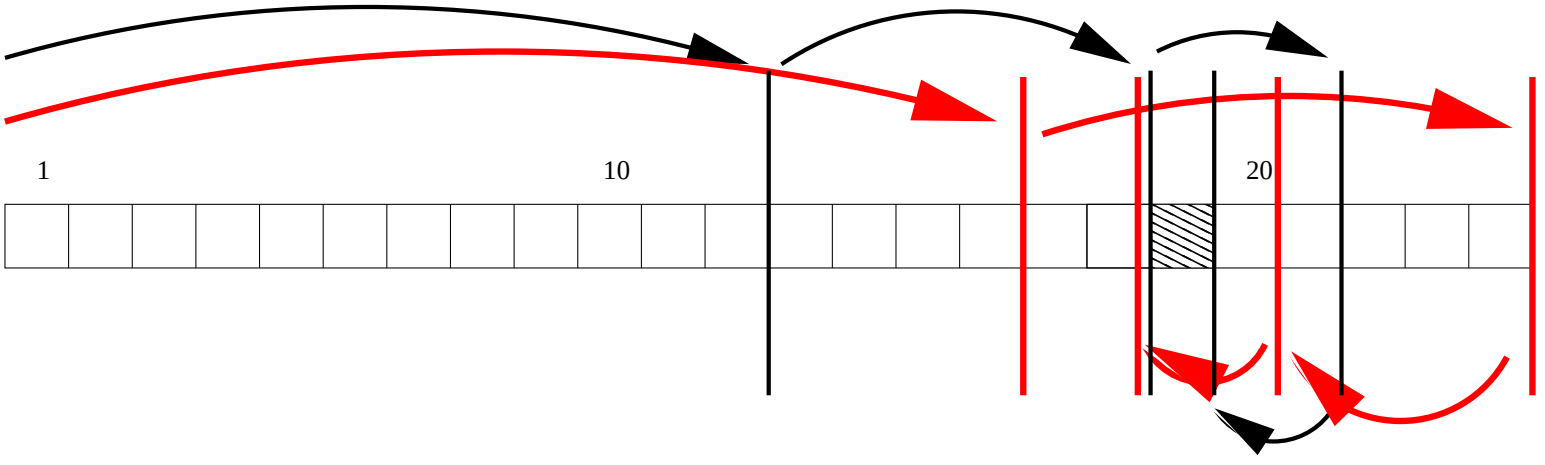
```
 NBAS =           46  NOCC =            4  NVIRT =           42

 updating the hash table
   deepest hashing =            4


  statistics of the hash table

          0      626804
          1       73162
          2        2360
          3          52
          4           1
          5           0
          6           0
          7           0
          8           0
          9           0



 read in total        78042  integrals in core

NUMBER OF INTEGRALS IN THE DIFFERENT CLASSES:
 TYPE         N1          N2
             (AABC)      (ABCD)
------------------------------
  OOOO          22           0
  OOOV         415          84
  OVOV        1322        2713
  OOVV        1373        1337
  OVVV        5157       37506
  VVVV       28113           0
 ------------------------------
```

For $N = 46$ we would need 4 477 456 instead of the minimal 584 821 places. And we have "only" 78 042 relevant integrals to store (13 %).

Hash tables and bisection

Bisection

- Order data lexically
- Use for instance `heapsort`, no additional memory needed
- No need for additional tables neither
- Regroup integrals for reducing the search amplitudes, e.g. wrt to 1st index
- Start at $N/2$, look where your data should be, divide interval by 2 etc.
- For 2^n data an item is found in n steps.
- Need for n steps as well to find that an integral is not present



Full CI – why not?

- We have a set of molecular orbitals $\{\phi_i(\vec{r})\}$ and determinants $\{\Phi_I\}$
- Full CI means that we run over all orbitals and all determinants
- Look for the lowest eigenvalue of the matrix $H_{IJ} = \langle\Phi_I|\hat{H}|\Phi_J\rangle$
- What is the action of $\hat{H}$ on a given wavefunction $\Psi = \sum_J c_J \Phi_J$?
- We write $\hat{H}|\Psi\rangle = \sum_I c'_I |\Phi_I\rangle = \sum_J c_J \hat{H}|\Phi_J\rangle$ or

$$c'_I = \sum_J c_J \langle\Phi_I|\hat{H}|\Phi_J\rangle$$

- The matrix elements of $\hat{H}$ may be written as

$$c'_I = \sum_{tu} \tilde{h}_{tu} \sum_J c_J A^{IJ}_{tu} + \frac{1}{2} \sum_{tuvx} (tu|vx) \left[\sum_J c_J \left(\sum_K A^{IK}_{tu} A^{KJ}_{vx} \right) - \delta_{uv} A^{IJ}_{tx} \right]$$

- Generator matrix elements $A^{IJ}_{tu} = \langle\Phi_I|\hat{E}_{tu}|\Phi_J\rangle$ (destroy an electron in orbital ϕ_u and create one in ϕ_t, very sparse matrix!)

Full CI – why not?

- Auxiliary matrices

$$
\begin{aligned}
D^K_{tu} &= \sum_J c_J A^{KJ}_{tu} \\
E^K_{tu} &= \sum_{vx} (tu|vx) D^K_{vx}
\end{aligned}
$$

- Final expression

$$
c'_I = \sum_{tu} \left\{ \left(\tilde{h}_{tu} - \frac{1}{2} \sum_r (tr|ru) \right) D^I_{tu} + \frac{1}{2} \sum_K A^{IK}_{tu} E^K_{tu} \right\}
$$

- Matrices D and E with 3 indices, matrix A very sparse and precalculated
- Ready for iterative solution

$$
|\Psi\rangle \to \hat{H}|\Psi\rangle \to |Q\rangle = (\hat{H} - \langle\Psi|\hat{H}|\Psi\rangle)|\Psi\rangle \to \ldots
$$

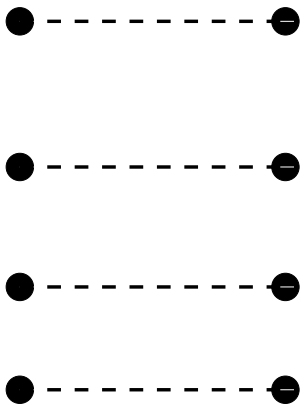
Perturbation theory

$$
\begin{aligned}
E_0^{(1)} &= \langle\, \Phi_0 \,|\, V \,|\, \Phi_0 \,\rangle = \langle 0|\hat{V}|0\rangle = \langle 0|\hat{H} - \hat{H}_0|0\rangle \\
E_0^{(2)} &= \langle\, \Phi_0 \,|\, V \,|\, \Psi^{(1)} \,\rangle = \sum_{k\neq 0} \langle 0|\hat{V} \frac{|k\rangle\langle k|}{E_0^{(0)} - E_k^{(0)}} \hat{V}|0\rangle \\
E_0^{(3)} &= \langle\, \Phi_0 \,|\, V \,|\, \Psi^{(2)} \,\rangle \\
&= \sum_{k,l\neq 0} \langle 0|\hat{V} \frac{|k\rangle\langle k|}{E_0^{(0)} - E_k^{(0)}} \hat{V} \frac{|l\rangle\langle l|}{E_0^{(0)} - E_l^{(0)}} \hat{V}|0\rangle \\
&\quad - E_0^{(1)} \sum_{k\neq 0} \left(\frac{\langle\, 0 \,|\, V \,|\, k \,\rangle}{E_0^{(0)} - E_k^{(0)}} \right)^2
\end{aligned}
$$

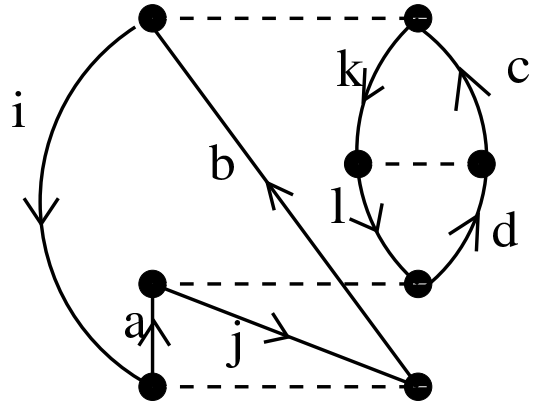
There is a systematic structure in the equations ...

Perturbation theory

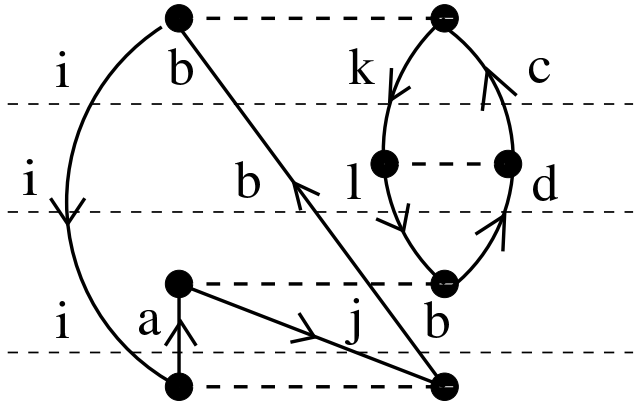
Graphical approach: a 4-th order diagram as example



(1)



(2)

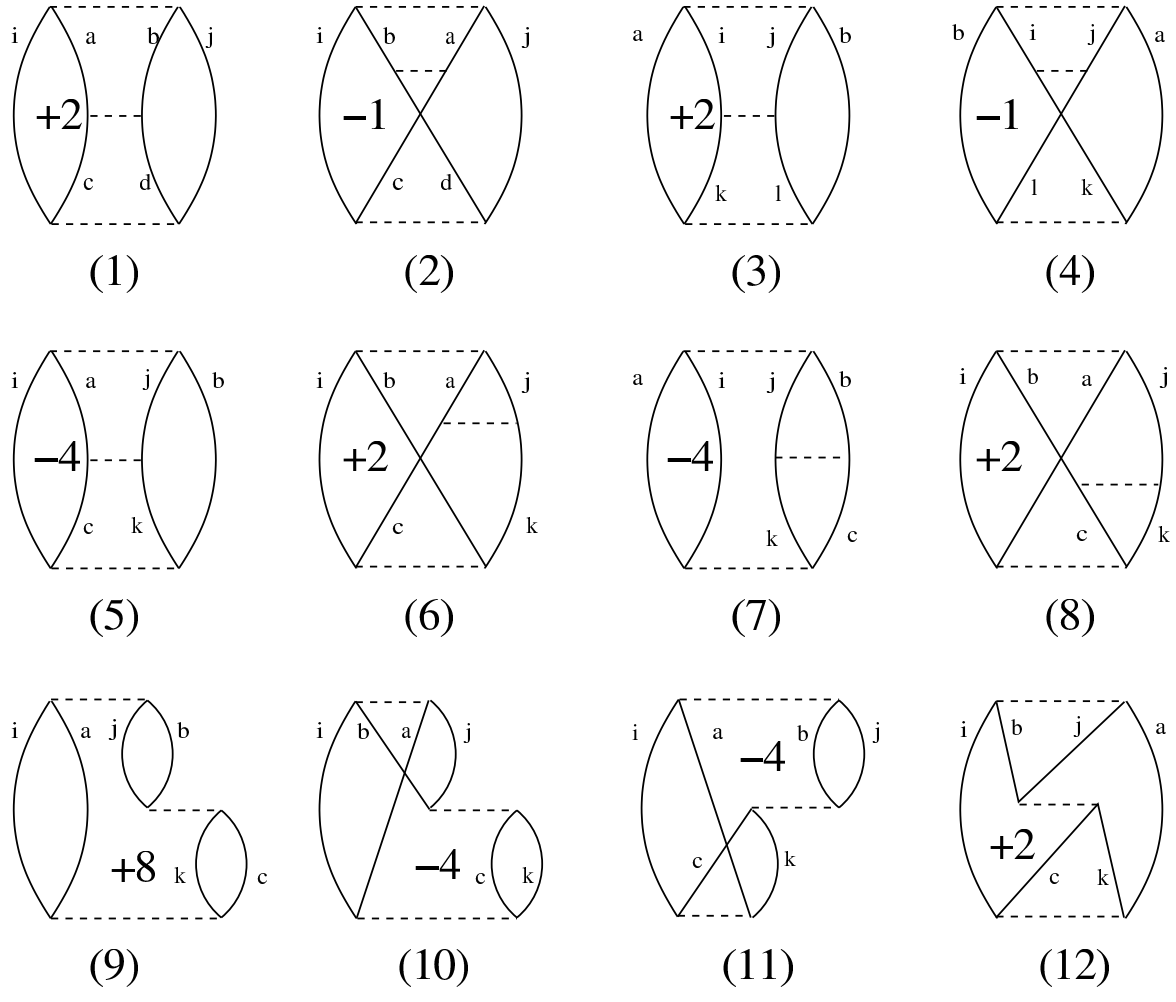


(3)

$$\sum_{ijkl}\sum_{abcd}(-1)^{2+4}\,2^2\,\frac{(ib|kc)(kl|cd)(ja|ld)(ia|jb)}{(\epsilon_i+\epsilon_k-\epsilon_b-\epsilon_c)(\epsilon_i+\epsilon_l-\epsilon_b-\epsilon_d)(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)}$$

Perturbation theory

All third-order diagrams



Density Functional Theory

Integration grids needed for numerical integration of the functionals

- Spherical around atoms
- Logarithmic radial grids
- Space-filling between atoms

Chemical Physics Letters
Volume 209, Issues 5–6, 16 July 1993, Pages 506-512

A standard grid for density functional calculations

Peter M.W Gill [1] ✉, Benny G Johnson, John A Pople

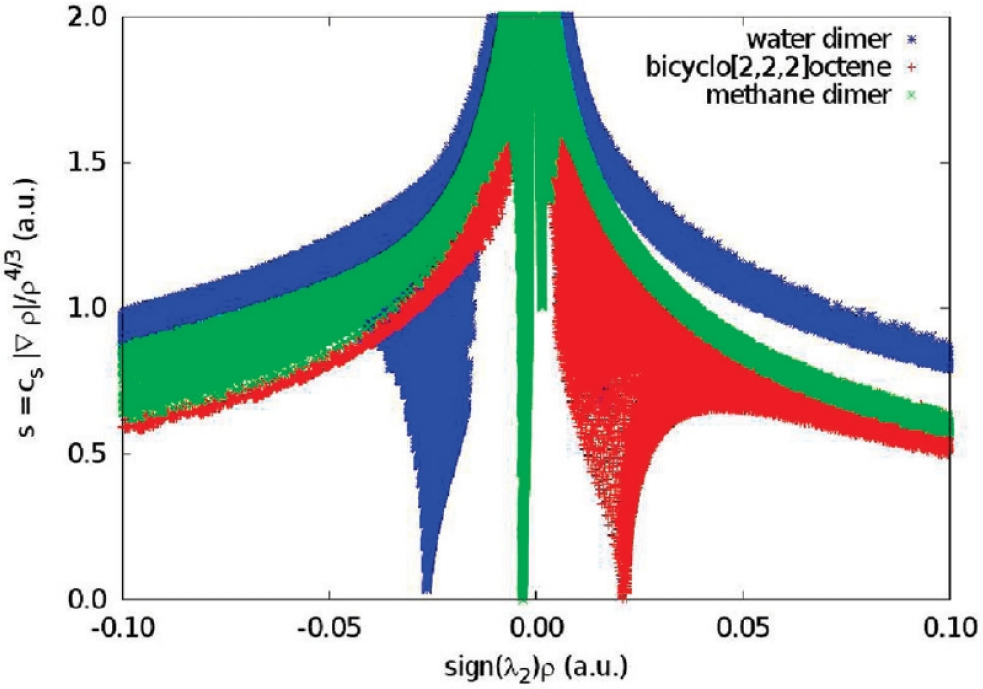
Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA

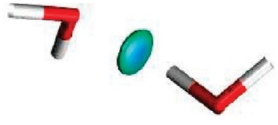
AIM, ELF, NCI etc

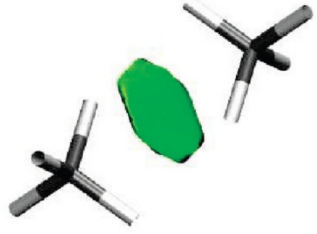
Evaluation of orbitals, densities etc on grids

- Domain boundaries difficult to localize in space
- Description of hypersurfaces, e.g. $\Delta\rho = 0$
- Huge data volumes, however good compressibility
- Data should be plotted in 3D: `.cube` format

AIM, ELF, NCI etc







Repulsive H bond Dispersion

Integrals and Determinants

MP2 and the 4-index transformation

- Sparse matrices
- Canonical orbitals and localized orbitals
- Orbital-invariant MP2
- The 4-index transformation
- Laplace-transformed MP2

Sparse matrices

- Storage of an $n \times n$ matrix (CRS = compressed row storage): three 1D arrays, one holding the number of non-zero elements in a row, one with the column indexes, and one with the matrix elements.
- Matrix-matrix operations, matrix-vector operations:

```
do i = 1, n
  y(i) = 0
  do j = row_ptr(i), row_ptr(i+1) - 1
    y(i) = y(i) + val(j) * x(col_ind(j))
  end do
end do
```

- Atomic orbitals are local, molecular orbitals are not
- The Hamilton matrix in the base of determinants is not really sparse neither
- Spin-free generator matrices $\langle \Phi_I | \hat{E}_{ij} | \Phi_J \rangle$ are VERY sparse, and matrix elements are 2, 1, 0, or -1.

$$\hat{E}_{ij} = \hat{a}^\dagger_{i,\alpha} \hat{a}_{j,\alpha} + \hat{a}^\dagger_{i,\beta} \hat{a}_{j,\beta}$$

- See for instance the package `librsb-dev` on Ubuntu

Sparse matrices

Example

$$A = \begin{pmatrix} 1 & 0 & 0 & 0 & 3 \\ 0 & 1 & 2 & 0 & 0 \\ 1 & 0 & 2 & 0 & 7 \\ 0 & 0 & 0 & 4 & 0 \\ 1 & 2 & 3 & 0 & 3 \end{pmatrix}$$

The three 1D arrays:

$$\begin{aligned} R &= (1, 3, 5, 8, 9, 12) \\ C &= (1, 5, 2, 3, 1, 3, 5, 4, 1, 2, 3, 5) \\ V &= (1, 3, 1, 2, 1, 2, 7, 4, 1, 2, 3, 3) \end{aligned}$$

for example $R(2) = 3$, i.e. the 2nd row starts with the 3rd element of C (=2nd column with value 1)

Sparse matrices

The generator matrices

$$\langle \Phi_I | \hat{E}_{pq} | \Phi_J \rangle = \langle \Phi_I | \hat{a}^\dagger_{p,\alpha} \hat{a}_{q,\alpha} + \hat{a}^\dagger_{p,\beta} \hat{a}_{q,\beta} | \Phi_J \rangle$$

- Orbital q (and/or $\bar{q}$) must be occupied in $|\Phi_I\rangle$, and orbital p (and/or $\bar{p}$) empty
- From $|\Phi_I\rangle$ the generator may produce either one or two determinants $|\Phi_J\rangle$, multiplied with ± 1 or ± 2
- Store in one array `A(I,p,q)` if there is a result
- Store in a second array `S(I,p,q)` whether there is a second possible result
- Store the results J in an array `R(2,I,p,q)` and the multiplicators `M(2,I,p,q)`

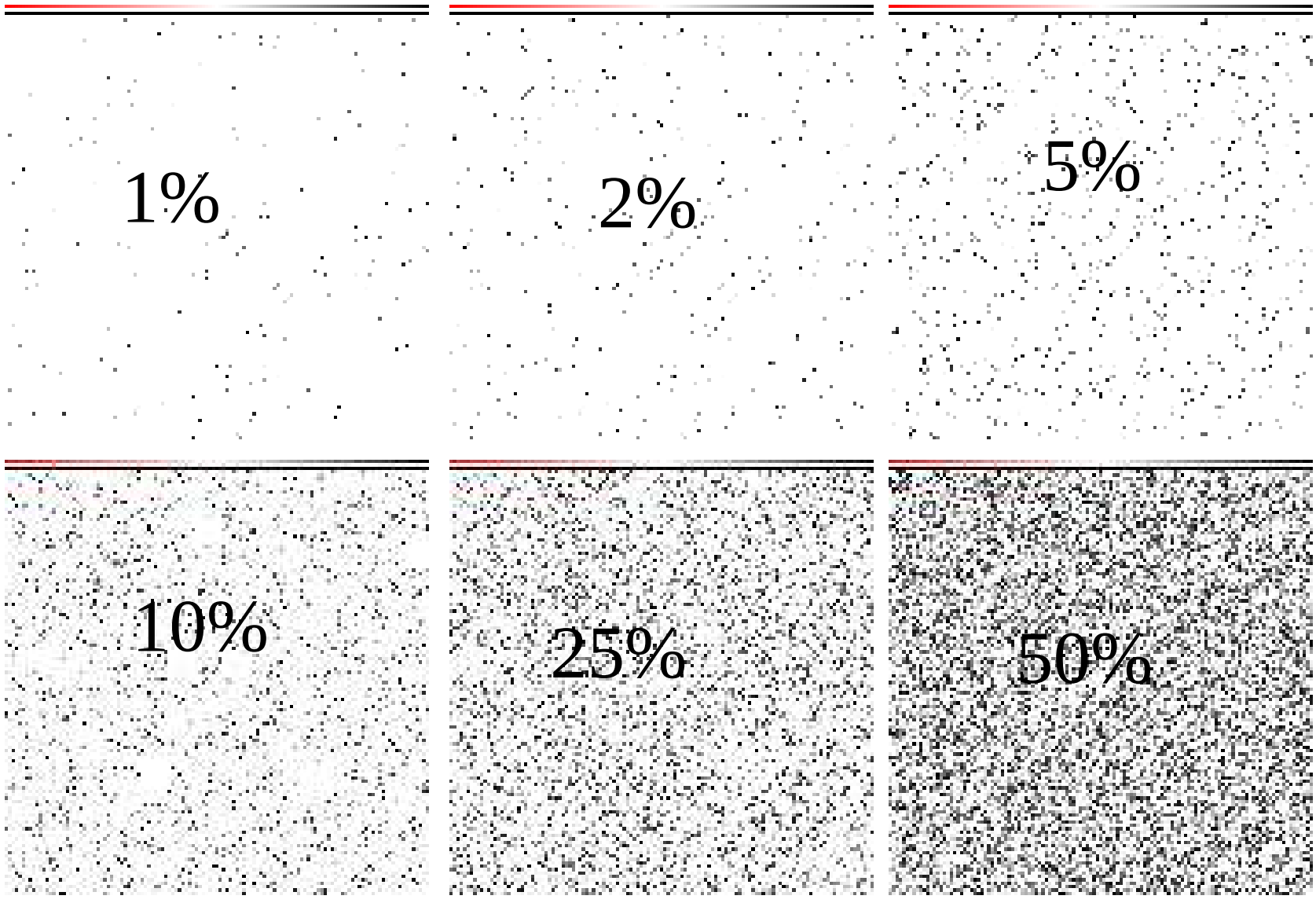
How to calculate now $c_I = \sum_J c_J \langle \Phi_I | \hat{h} | \Phi_J \rangle$?

Sparse matrices

$$c_I = \sum_J c_J \sum_{pq} h_{pq} \langle \Phi_I | \hat{E}_{pq} | \Phi_J \rangle = \sum_{pq} h_{pq} \sum_J c_J \langle \Phi_I | \hat{E}_{pq} | \Phi_J \rangle$$

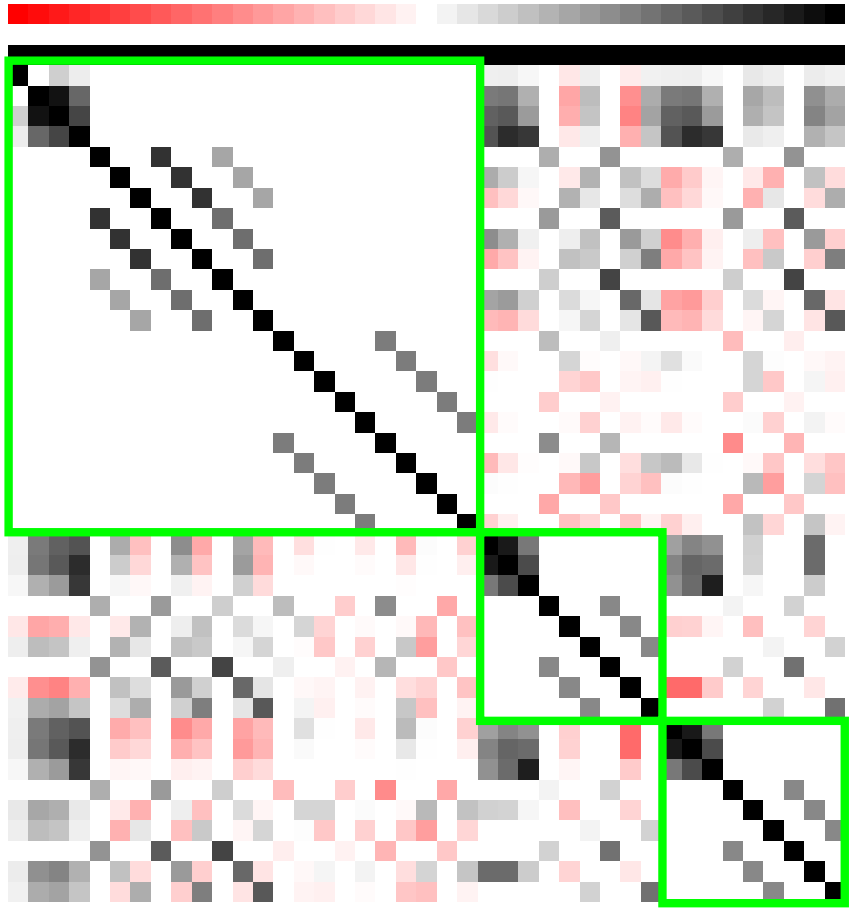
```
do p,q = 1,nbas
 calculate h_pq
 do I=1,Ndets
  if (A(I,p,q) then
   find first J
   get the multiplicator
   add c_J * h_pq * m to c_I
   if (S(I,p,q) then
    find possible second J
    get the multiplicator
    add c_J * h_pq * m to c_I
close the if's and the do's
```

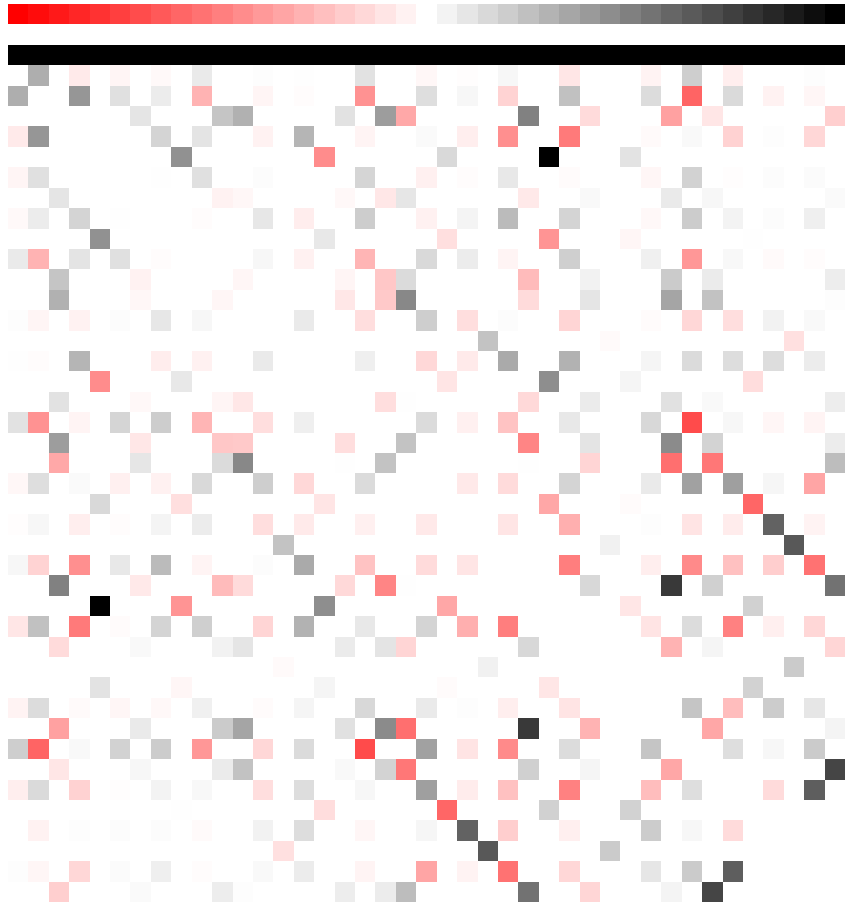
Sparse matrices



Sparse matrices

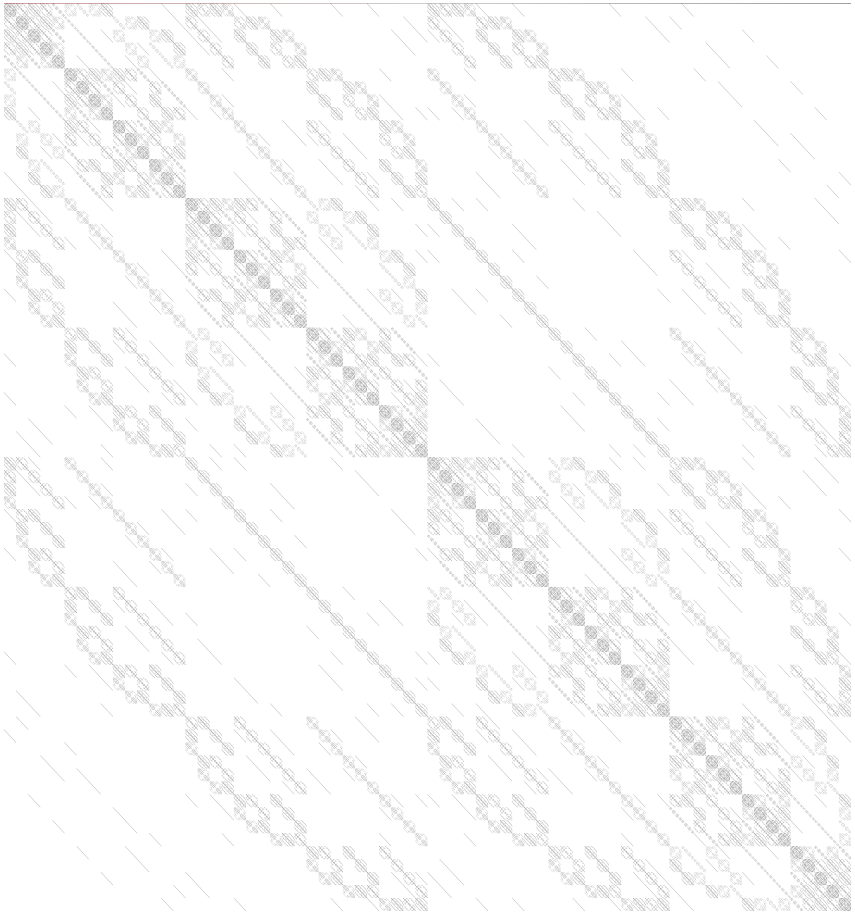
Water molecule: overlap (AOs), Fock matrix (MOs), DZP





Sparse matrices

Water molecule: Hamilton Matrix FCI (8 electrons / 8 orbitals, ≈ 5000 dets.)



Canonical orbitals versus localized orbitals

- Diagonalization of F = delocalization of orbitals
- N^2 integrals $(ii|jj)$ scale as $1/N \longrightarrow E \sim N$
- Localized orbitals: N integrals $(ii|ii)$ remain constant
- However: Fock matrix is not any more diagonal
- Need for orbital-invariant methods (CISD, CEPA–0, ACPF, Coupled-Cluster, Full CI)

Perturbation theory: define $\hat{H}_0$ and $\hat{V}$

$$\hat{H} = \sum_i F_{ii} \hat{a}_i^\dagger \hat{a}_i + \sum_i \sum_{j \neq i} F_{ij} \hat{a}_i^\dagger \hat{a}_j \; + \; \text{bielectronic operator}$$

- Sum additional series to infinity or approximate
- Include $\sum_i \sum_{j \neq i} F_{ij} \hat{a}_i^\dagger \hat{a}_j$ in $\hat{H}_0$: system of linear equations to be solved

Canonical orbitals versus localized orbitals

Orbital invariant MP2:

- Schrödinger equation $(\hat{H}_0 + \lambda\hat{V}) \sum_i \lambda^i \Psi^{(i)} = \sum_j \lambda^j E^{(j)} \sum_k \lambda^k \Psi^{(k)}$
- First order wavefunction $\Psi^{(1)} = \sum_I c_I^{(1)} \Phi_I$, projection on Φ_K

$$\sum_I c_I^{(1)} \langle \Phi_K | \hat{H}_0 - E_0^{(0)} | \Phi_I \rangle + \langle \Phi_K | \hat{V} | \Phi_0 \rangle = 0$$

Observation of Hylleraas 1930:

- Define a functional

$$h = 2\langle \Psi^{(1)} | \hat{V} | \Psi^{(0)} \rangle + \langle \Psi^{(1)} | \hat{H}_0 - E_0^{(0)} | \Psi^{(1)} \rangle$$

- Put derivatives to zero (minimize h)

$$\frac{\partial h}{\partial c_K} = 2 \langle \Phi_K | \hat{V} | \Phi_0 \rangle + \sum_I 2\, c_I \langle \Phi_K | \hat{H}_0 - E_0^{(0)} | \Phi_I \rangle = 0$$

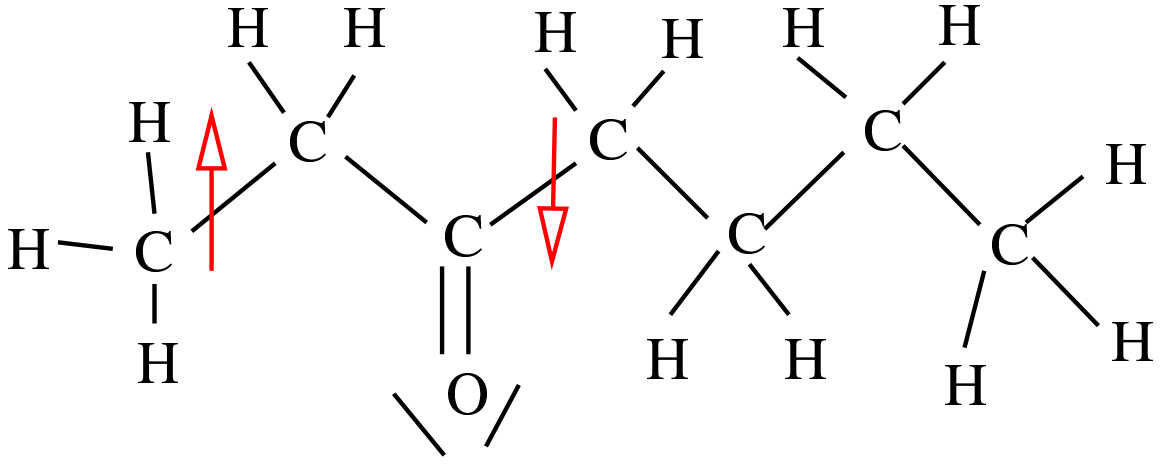
- Insert into functional: $h = \langle \Psi^{(1)} | \hat{V} | \Psi^{(0)} \rangle = E_0^{(2)}$

Canonical orbitals versus localized orbitals

- System of linear equations

$$\langle \Phi_K | \hat{H} | \Phi_0 \rangle + \sum_{c \in virt} \left(c_{ij}^{cb} F_{ac} + c_{ij}^{ac} F_{bc} \right) - \sum_{k \in occ} \left(c_{kj}^{ab} F_{ik} + c_{ik}^{ab} F_{jk} \right) = 0$$

- Evaluate integrals and Fock matrix in any set of Hartree-Fock orbitals
- Energy will be always the same as the coefficients minimize a functional.
- Formulas more complicated than standard MP2, but hope for linear scaling



Matrix-dressing techniques

Start with CI of Singles and Doubles

$$(\mathbf{H} - \mathbf{E_0}).\Psi = E_{\mathrm{corr}}..\Psi$$

- 1st row/column: $\langle \Phi_0 | \hat{H} | \Phi_I \rangle$, $\Phi_0 = \Phi_{\mathrm{HF}}$, Φ_I= di-excited determinant
- Add effects of higher excitations to the diagonal: $H_{ii} \rightarrow H_{ii} + \Delta_i$
- $\Delta_i = E_{\mathrm{corr}}$: CEPA–0 (Coupled electron pair approximation)
- $\Delta_i = E_{\mathrm{corr}}\,(1 - 2/n)$: ACPF (Averaged Coupled Pair Functional, n = number of correlated electrons)
- $\Delta_i = E_{\mathrm{corr}} - \sum_{J \in \mathrm{EPV}} \langle \Phi_I | \hat{H} | \Phi_{I+J} \rangle$: CEPA–2, CEPA–3, Full CEPA=(SC)^{2}CI
- As $\langle \Phi_I | \hat{H} | \Phi_{I+J} \rangle = \langle \Phi_0 | \hat{H} | \Phi_I \rangle$, no additional cost
- Restores size-consistence of the CISD equations

Matrix-dressing techniques

Coupled-Cluster equations

$$\langle \Phi_I \,|\, \hat{H} \left(1 + \hat{T}_2 + \frac{1}{2}\,\hat{T}_2^2 \right) \,|\, \Phi_0 \,\rangle = (E_{\rm HF} + E_{\rm corr})\, c_I$$

with $\hat{T}_2\hat{T}_2|\Phi_0\rangle = 2\sum_{klcd}(c_{ij}^{ab} * c_{kl}^{cd})\,|\Phi_{ijkl}^{abcd}\rangle$ and

$$\begin{aligned} c_{ij}^{ab} * c_{kl}^{cd} &= c_{ij}^{ab}\, c_{kl}^{cd} - \langle c_{ij}^{ab} * c_{kl}^{cd} \rangle \\ &= c_{ij}^{ab}\, c_{kl}^{cd} - c_{ik}^{ab}\, c_{jl}^{cd} + c_{il}^{ab}\, c_{jk}^{cd} - c_{ij}^{ac}\, c_{kl}^{bd} + c_{ik}^{ac}\, c_{jl}^{bd} - c_{il}^{ac}\, c_{jk}^{bd} \\ &\quad + c_{ij}^{ad}\, c_{kl}^{bc} - c_{ik}^{ad}\, c_{jl}^{bc} + c_{il}^{ad}\, c_{jk}^{bc} + c_{ij}^{cd}\, c_{kl}^{ab} - c_{ik}^{cd}\, c_{jl}^{ab} + c_{il}^{cd}\, c_{jk}^{ab} \\ &\quad - c_{ij}^{bd}\, c_{kl}^{ac} + c_{ik}^{bd}\, c_{jl}^{ac} - c_{il}^{bd}\, c_{jk}^{ac} + c_{ij}^{bc}\, c_{kl}^{ad} - c_{ik}^{bc}\, c_{jl}^{ad} + c_{il}^{bc}\, c_{jk}^{ad} \end{aligned}$$

- Rearrange as

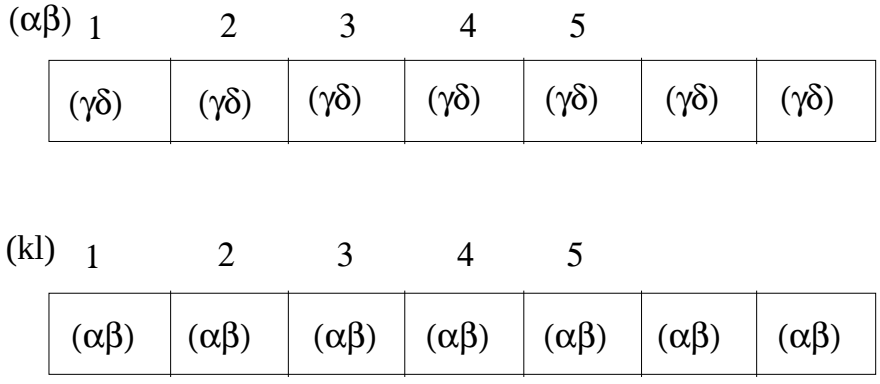
$$(H_{0I} - \sum_J H_{0J}\,\langle c_I * c_J \rangle) + \langle \Phi_I | \hat{H} - E_{HF} | \Phi_I \rangle\, c_I + \sum_{J \neq I} H_{IJ}\, c_J = 0$$

- Dressing of the first column, scales as N^8 $(ijkl\,abcd)$

Four-index transformation

$$(ij|kl) = \sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta} c_{\alpha i} c_{\beta j} c_{\gamma k} c_{\delta l} (\alpha\beta|\gamma\delta)$$

- Scales in this form as N^8
- Transform index after index, store intermediates, reduce scaling to N^5
- Sort integrals, one index couple $\alpha\beta$ on one file/processor
- Distribute — transform — assemble — distribute — transform — assemble



- Only non-zero integrals are stored
- In localized orbitals at the limit linear scaling.

Four-index transformation

$$(ij|kl) = \sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta} c_{\alpha i} c_{\beta j} c_{\gamma k} c_{\delta l} (\alpha\beta|\gamma\delta)$$

Alternative: Laplace transformation for perturbation theory (*M. Häser*, Theor.Chim.Acta, **87** (1993) 1147)

$$E^{(2)} = -\frac{1}{4}\sum_{ijab}\frac{\langle ab\,\|ij\rangle^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \qquad (1a)$$

$$= -\frac{1}{4}\int_0^\infty dt \sum_{ijab} \langle ab\,\|ij\rangle^2 e^{-(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t} \qquad (1b)$$

$$= \int_0^\infty e^{(2)}(t)\,dt, \qquad (1c)$$

May be used with atomic orbitals!

Exercise

Verify that the index function

$$
\begin{aligned}
p(i,j,k,l;n) \quad = \quad & (k-1)(n-1) - \frac{(k-1)(k-2)}{2} + l \\
& + \frac{n(n+1)}{2}(j-1) - \frac{j(j-1)}{2} \\
& + (i-1)\left(n\left(\frac{n(n-1)}{2}+1\right) - j(n-1) - 1\right) \\
& + \frac{(i-1)(i-2)}{2}\left(j - \frac{n(3n-7)}{2} - 4\right) \\
& + \frac{(i-1)(i-2)(i-3)}{2}(n-2) - \frac{(i-1)(i-2)(i-3)(i-4)}{8}
\end{aligned}
$$

produces indeed the position of a given integral $(ij|kl)$ in a complete list of bielectronic integrals in canonical ordering, i.e.

- $0 < i, j, k, l \leq n$
- $i \leq j$, $k \leq l$, $i \leq k$
- if $i = k$ then $j \leq l$

Exercise

Alternative formulation

$$
\begin{aligned}
p(i,j,k,l;n) \quad = \quad & \frac{1}{8}\left[-i^4 + i^3(4n+2) + i^2(4j - 2n(3n+5) - 3) + \right. \\
& +2i(2n+1)(-2j + n(n+3) + 1) \\
& -4\left(j^2 - j(n(n+3)+1) + n(n(n+3) - 2k) + \right. \\
& \left.\left.(k-1)k - 2l + 4n\right)\right]
\end{aligned}
$$

You may consider the expression as a polynomial in i, to be evaluated as

$$P_4(i) = a_0 + i(a_1 + i(a_2 + i(a_3 + i\,a_4)))$$