TCCM lectures – Advanced Computational Techniques

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Thursday morning — II

- Common quantum chemistry problems

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?

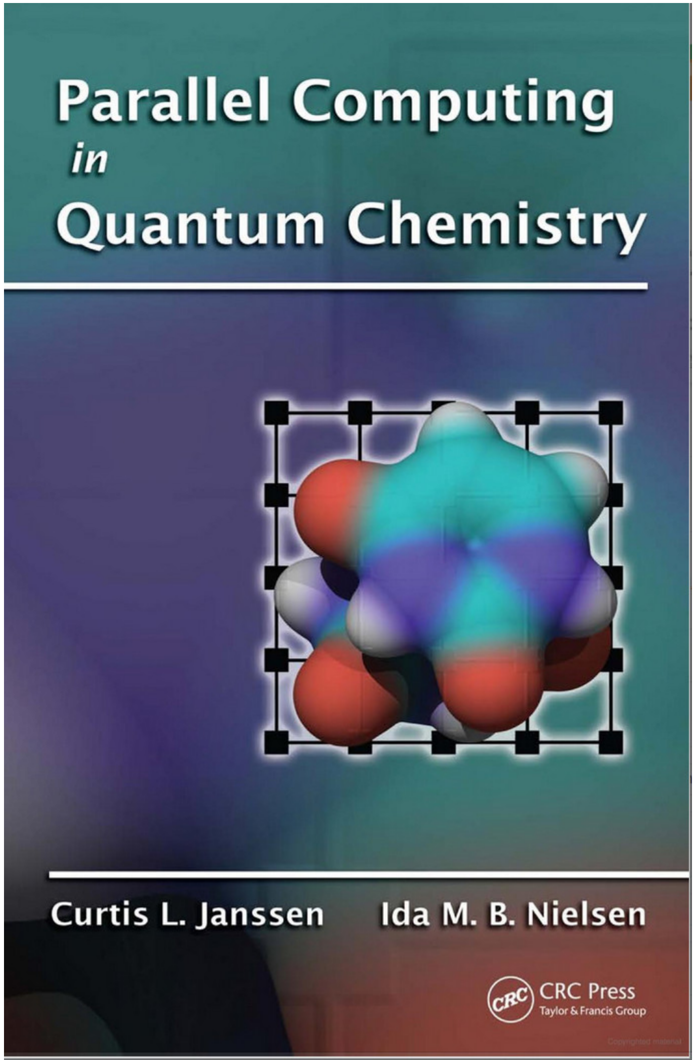
Overview of computational methods

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

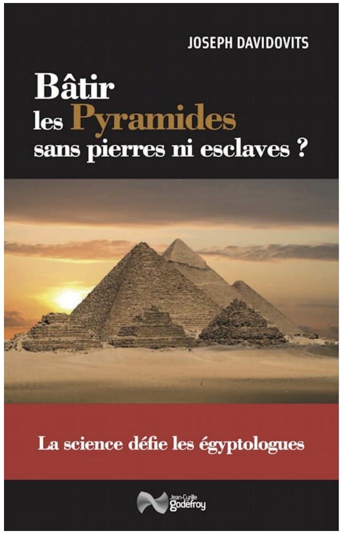
Overview of computational methods

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

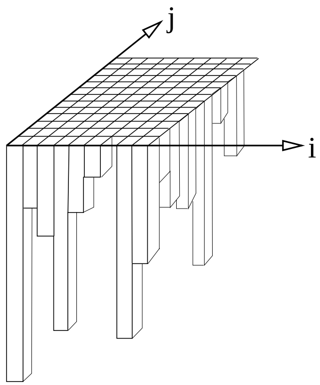
Integral-driven or Configuration-driven ?

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

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

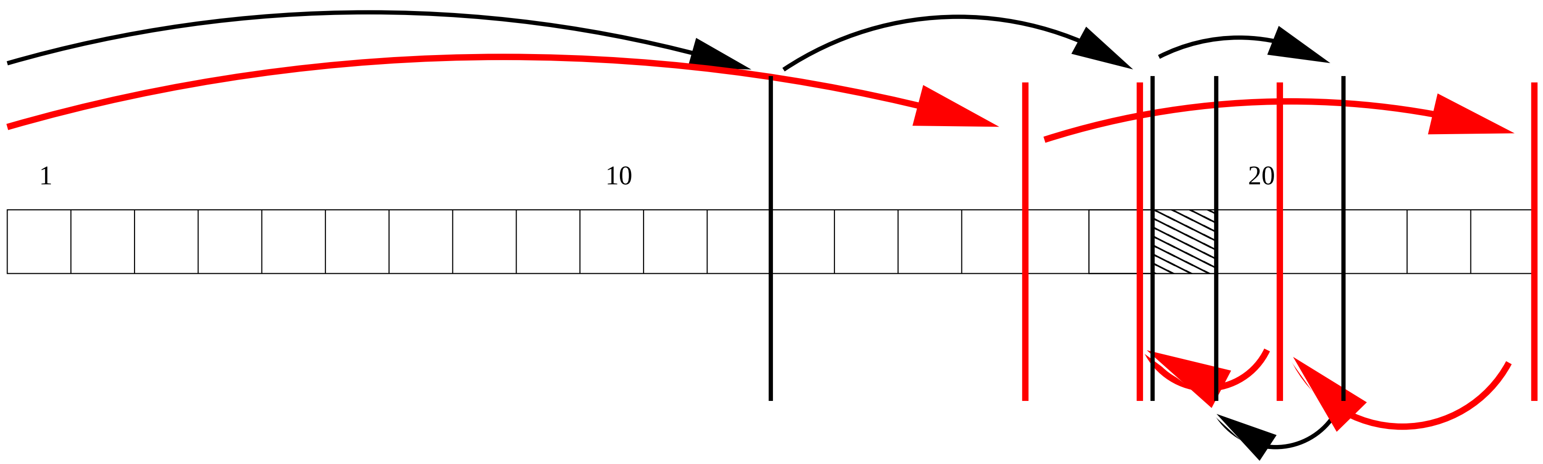
```
NBAS =           46  NOCC =            4  NVIRT =           42

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

$$D_{tu}^{K} = \sum_{J} c_J A_{tu}^{KJ}$$

$$E_{tu}^{K} = \sum_{vx} (tu|vx) D_{vx}^{K}$$

- Final expression

$$c'_I = \sum_{tu} \left\{ \left(\tilde{h}_{tu} - \frac{1}{2} \sum_{r} (tr|ru) \right) D_{tu}^{I} + \frac{1}{2} \sum_{K} A_{tu}^{IK} E_{tu}^{K} \right\}$$

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

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

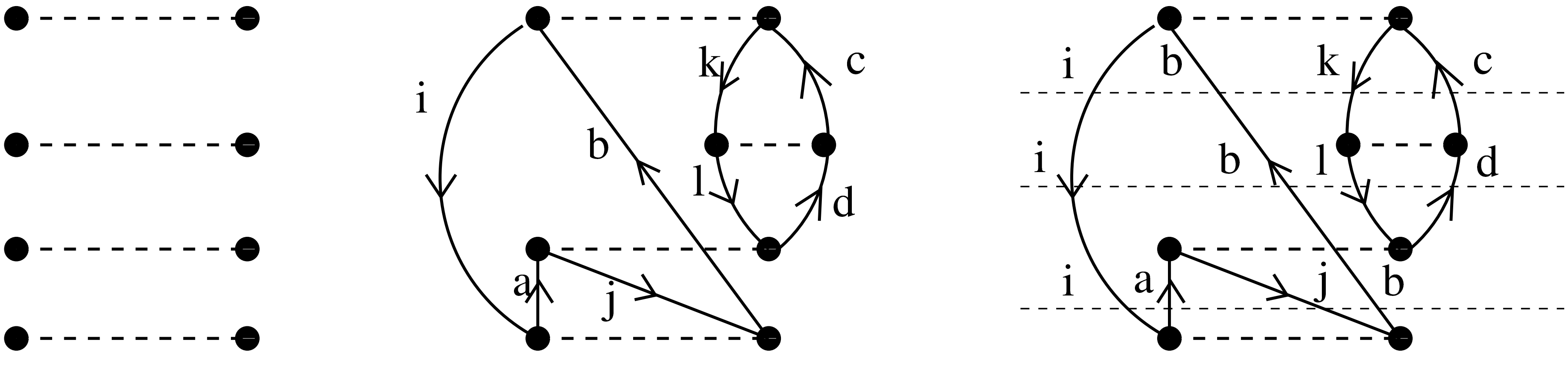
Perturbation theory

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

There is a systematic structure in the equations ...

Perturbation theory

Graphical approach: a 4-th order diagram as example

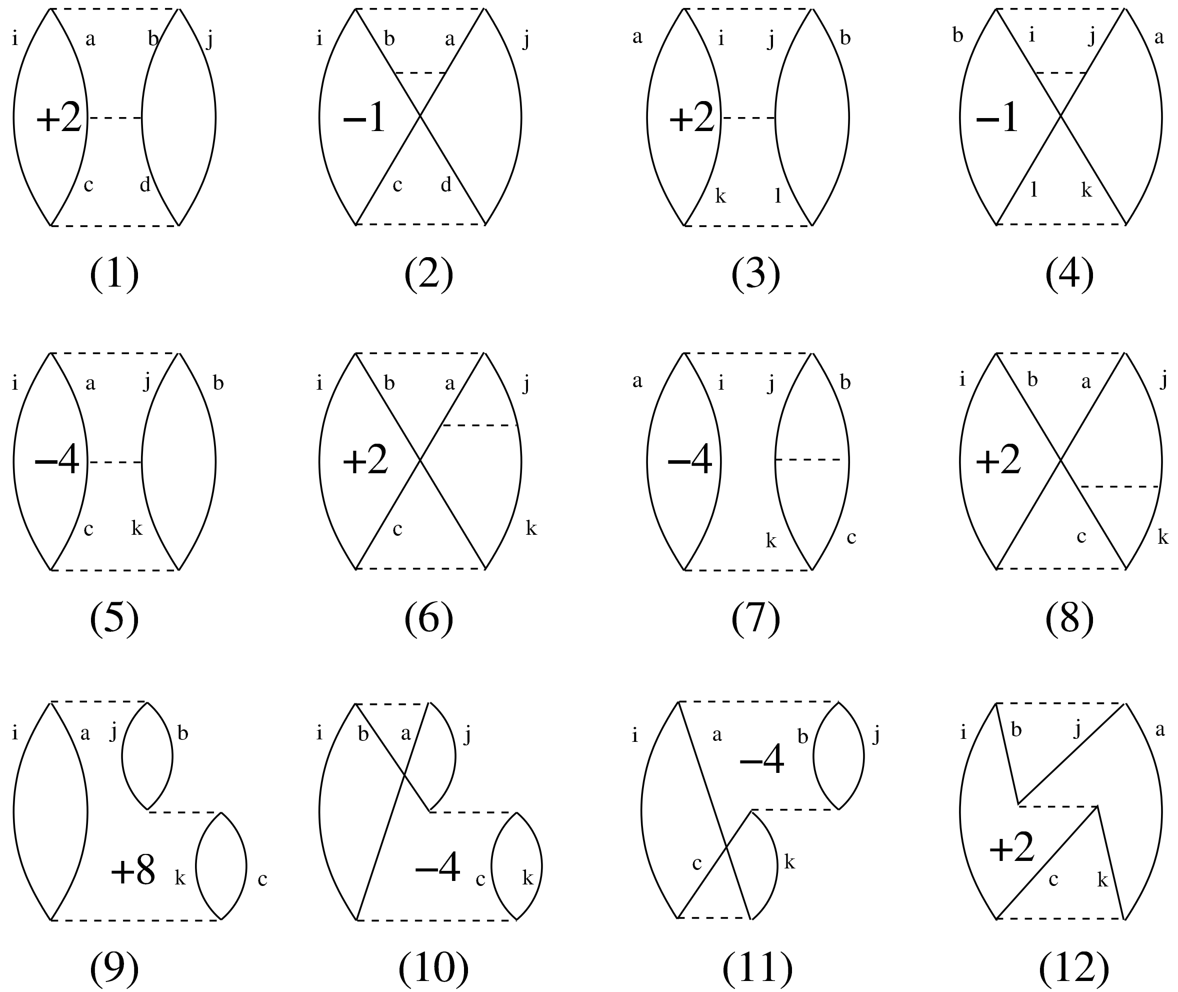


(1) (2) (3)

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

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

ELSEVIER

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

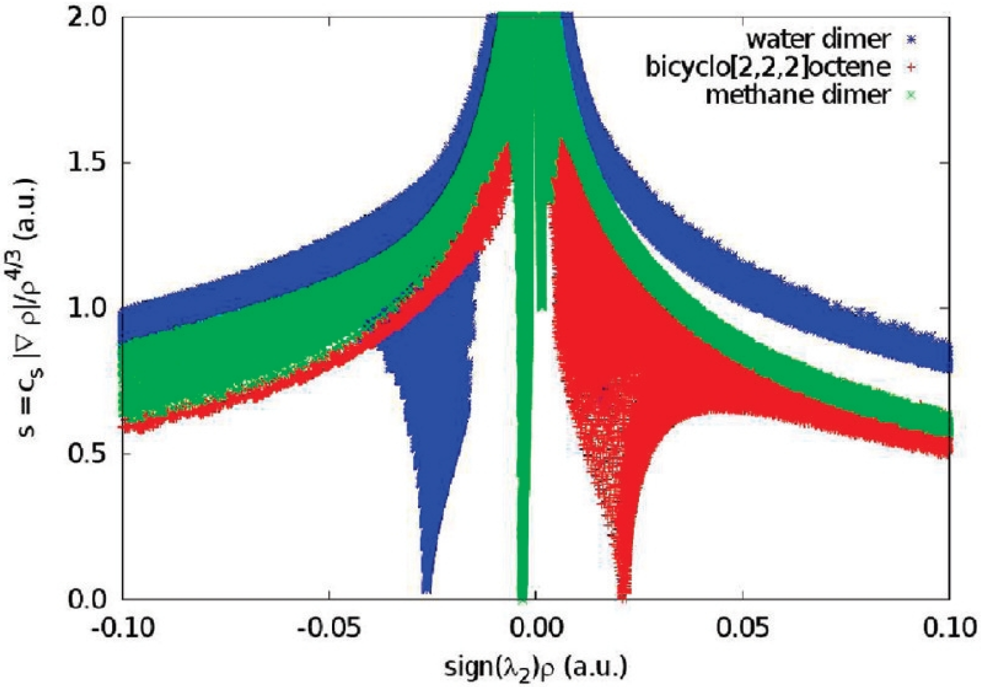
Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA

AIM, ELF, NCI etc

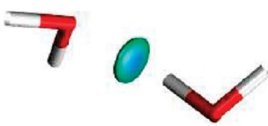
Evaluation of orbitals, densities etc on grids

- 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

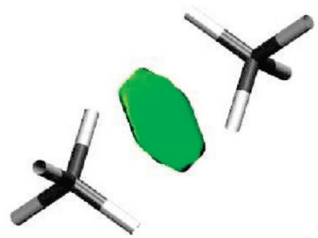
AIM, ELF, NCI etc



Repulsive



H bond



Dispersion

Quantum Monte-Carlo methods

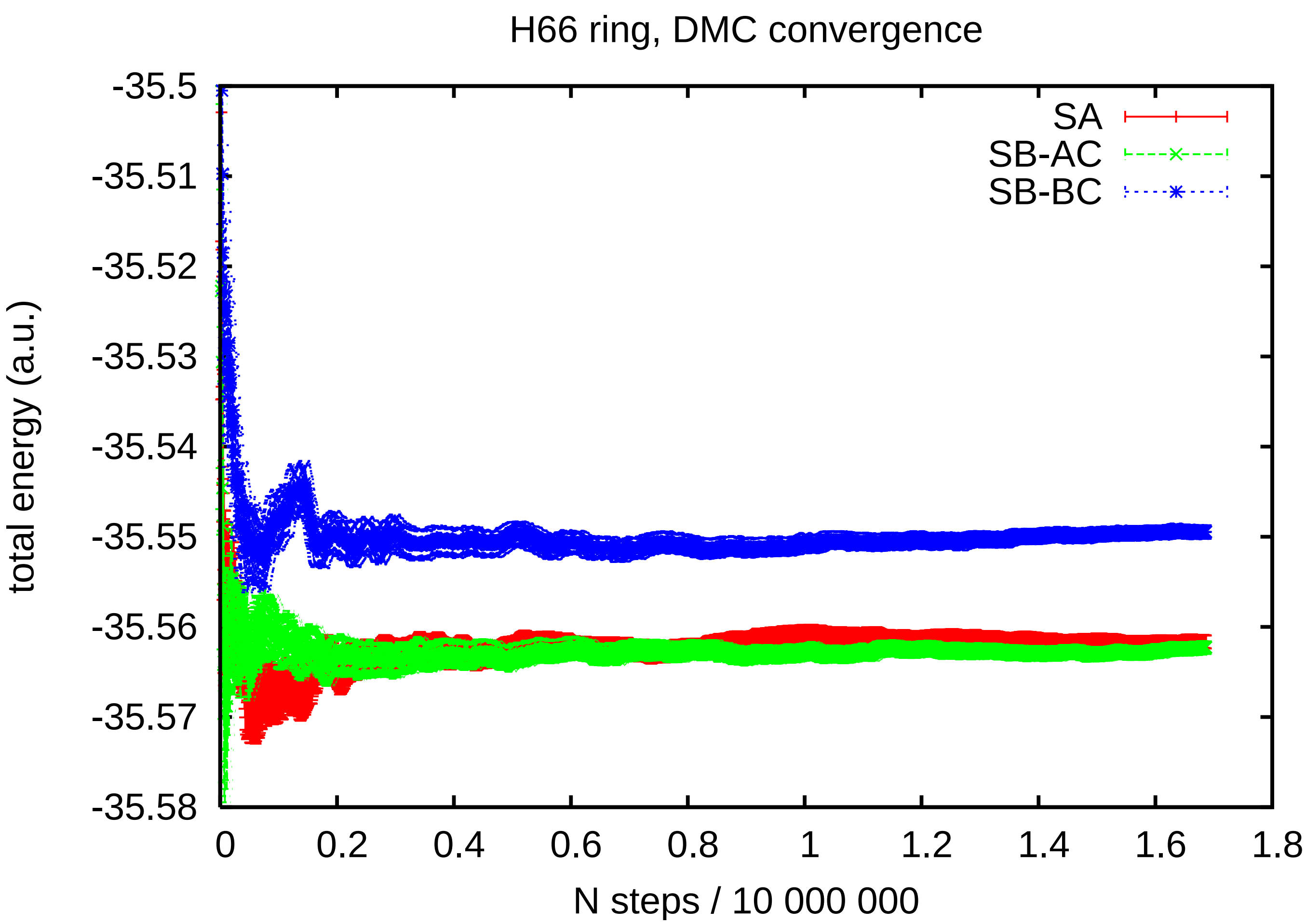
Evaluation of $(\hat{H}\Psi)/\Psi$ for calculating

$$E = \langle\Psi|\hat{H}|\Psi\rangle = \int |\Psi|^2 \left(\frac{\hat{H}\Psi}{\Psi}\right) dx^{3N} = \sum_i w_i \, E_{\mathrm{local}}(\{\vec{r}_j\}_i)$$

- $|\Psi|^2$ is a probability distribution
- $(\hat{H}\Psi)/\Psi$ is a $3N$-dimensional function; we need the Laplacian of the wavefunction with respect to every electron, and the potential energy
- Create a number of initial electron distributions
- calculate the total energy
- displace electrons, recalculate the energy E_{local}
- accept the suggested displacement with a probability $P(E_{\mathrm{local}})$
- sum over all generated configurations $\{\vec{r}_j\}_i$
- trivially parallelizable

Quantum Monte-Carlo methods

Statistical error bar well-known, but not the expectation value $E = \langle \Psi | \hat{H} | \Psi \rangle$



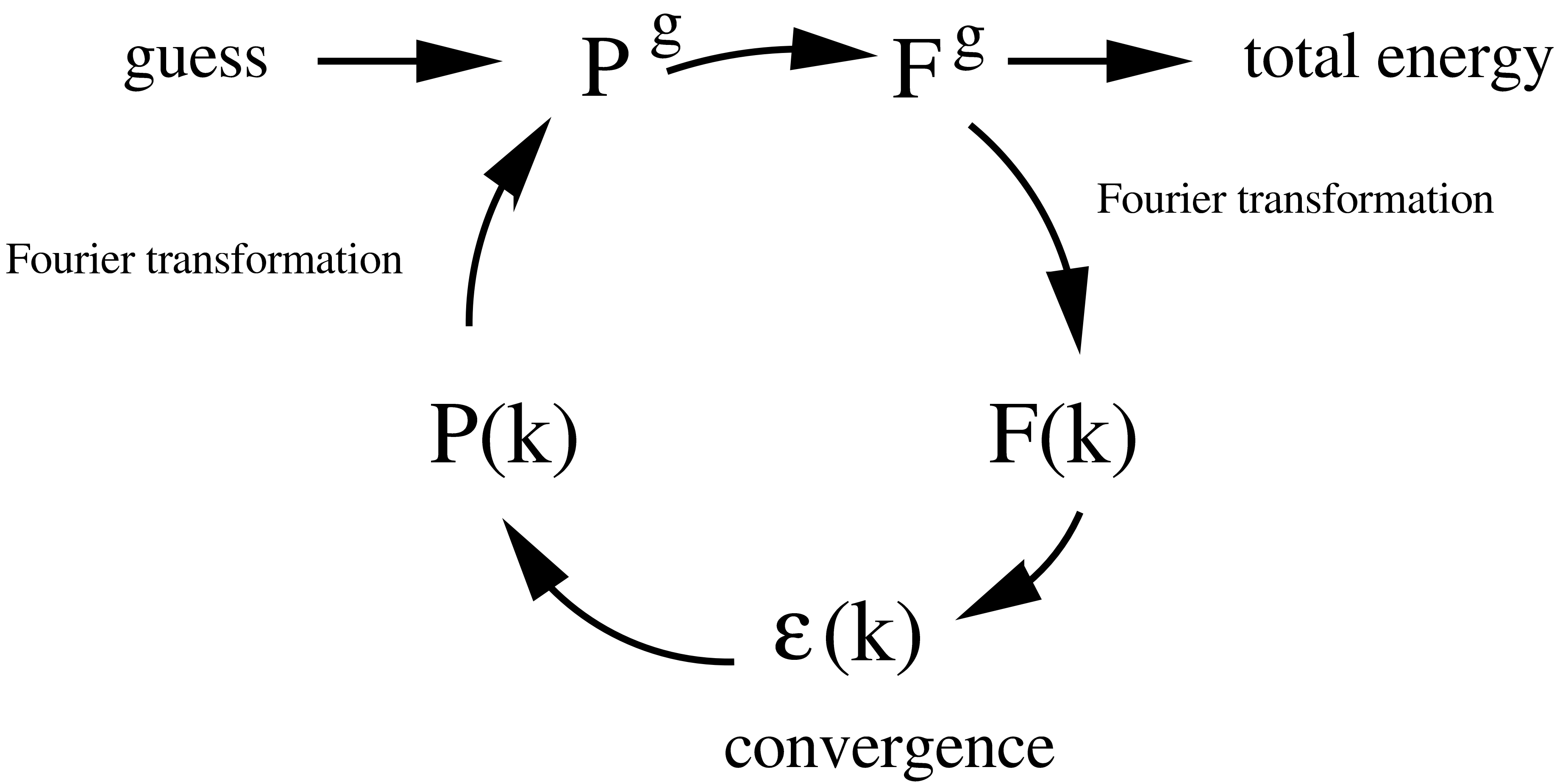
Quantum Chemistry for periodic systems

Infinite summations over unit cells

- Electrostatic interactions
  - nuclear-nuclear: repulsive
  - nuclear-electron: attractive
  - electron-electron: repulsive

  has to sum to a finite value per unit cell
- Exchange interactions have to converge on their own
- additional index for quantities needed: cell vector
- Fourier transform for k-space: complex numbers via $e^{ik\cdot g}$
- construct Fock matrix in real space, transform to k-space, diagonalize, transform density matrix back to real space
- parallel computation by symmetry of crystals and k points

Quantum Chemistry for periodic systems



SCF-scheme for a Hartree-Fock program for periodic systems (Pisani/Del Re 1967)

Molecular dynamics

Classical dynamics with an ab-initio potential surface

- Initial geometry of N atoms in space, inital positions and momenta given
- Potential surface in $3N - 6$ dimensions given
- Calculate forces on atoms as $\vec{F}_i = -\vec{\nabla}_i V(\vec{r}_1, \ldots, \vec{r}_N)$
- Calculate new positions and momenta after an acceleration period of Δt
- Recalculate forces, recalculate displacements etc

Sources of "errors"

- Approximate potential surfaces
- Neglect of intrinsic quantum effects
- Discrete time steps
- Integration algorithms (Euler, Runge-Kutta, Cash-Karp, Verlet, etc)
- Limited number of trajectories of limited length in time for statistical treatment

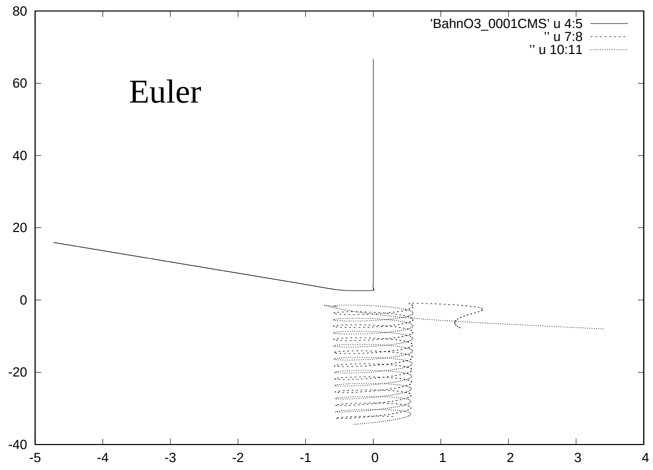
Molecular dynamics

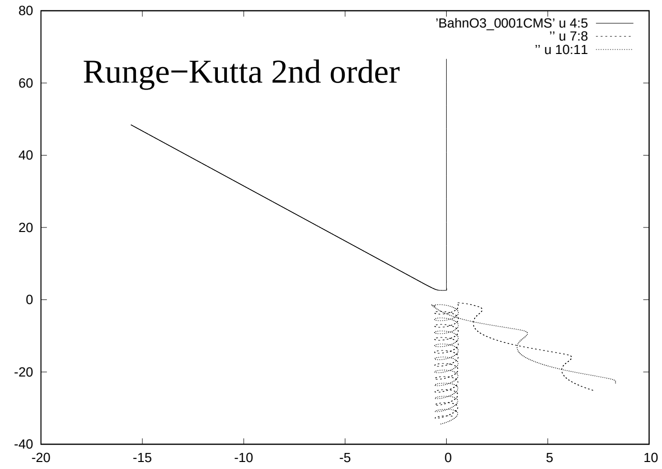
Control mechanisms

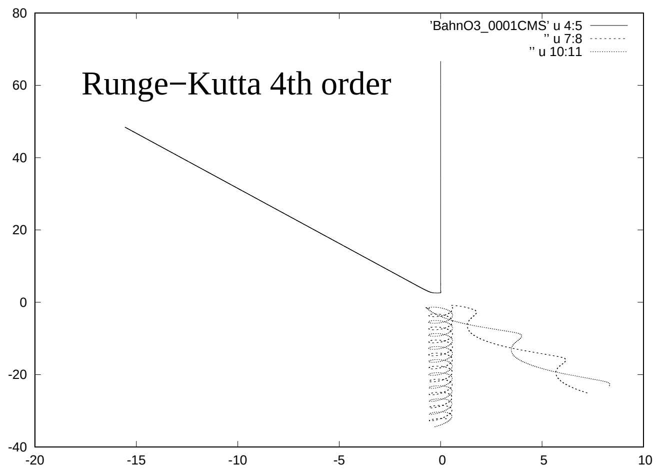
- Correct total energy after each time step via kinetic energy
- Watch total angular momentum as conserved quantity of movement
- Try different time steps

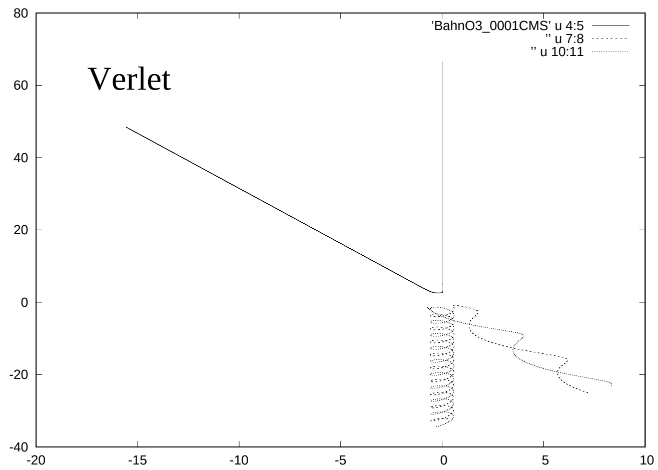
Molecular dynamics

O + O2 scattering − Schinke surface









Molecular dynamics

O + O2 scattering − Tyutereev surface