Approximation Methods in Multi-Particle Quantum Dynamics

Othmar Koch

Vienna University of Technology

Time-Dependent Schrödinger Eqn. (TDSE)

$$\mathrm{i}\frac{\partial\psi}{\partial t}(x_1,\dots,x_f,t) = H(t)\psi(x_1,\dots,x_f,t).$$

- $f \gg 1$ electrons; $|\psi(x_1,\dots,x_f,t)|^2$ … probability density for electrons to be located at $x_1,\dots,x_f$ at time t.
- The fundamental equation of non-relativistic quantum mechanics. Its solution could answer many questions about the nature of matter.
- But: Exact solution impossible. Direct numerical integration computationally intractable in general for $f > 2 \Rightarrow$ need for model reduction.

MCTDHF

Multi-configuration time-dependent Hartree–Fock method: Approximate solution of TDSE by

$$\psi(x_1,\dots,x_f,t) \approx u := \sum_J a_J(t)\Phi_J(x,t)$$
$$= \sum_{j_1,\dots,j_f} a_{j_1,\dots,j_f}(t)\phi_{j_1}(x_1,t)\cdots\phi_{j_f}(x_f,t).$$

Dirac–Frenkel variational principle

$$\left\langle \delta u \left| \mathrm{i}\frac{\partial u}{\partial t} - Hu \right\rangle = 0 \quad \forall \text{ variations } \delta u.\right.$$

Additional constraints for uniqueness

$$\langle\phi_j|\phi_k\rangle = \delta_{j,k}, \quad \left\langle \phi_j \left| \frac{\partial\phi_k}{\partial t} \right\rangle = 0.\right.$$

This yields the equations of motion

$$\mathrm{i}\frac{da_J}{dt} = \sum_K \langle\Phi_J|H|\Phi_K\rangle a_K,$$
$$\mathrm{i}\frac{\partial\phi_j}{\partial t} = (I-P)\sum_k\sum_l \rho^{-1}_{j,l}\overline{H}_{l,k}\phi_k,$$

where

$$\psi_j := \langle\phi_j|u\rangle,$$
$$\rho_{j,l} := \langle\psi_j|\psi_l\rangle,$$
$$\overline{H}_{l,k} := \langle\psi_l|H|\psi_k\rangle,$$
$$P := \sum_j |\phi_j\rangle\langle\phi_j|.$$

ψ_j … single hole functions
ρ … "density matrix"
$\overline{H}$ … "meanfield operator matrix"

Numerical Solution

Test code for 1D problems — bounded potentials
Method of lines:

- Space discretization (for every t): Pseudospectral method: Collocation by plane waves on uniform grid; exponential convergence.
  Global basis functions unfavorable for parallelization, no grid adaptation!
- Time integration of large system of ODEs
  - Explicit Runge–Kutta methods. Unreliable for non-smooth problems, no geometric properties!
  - Variational splitting. Low order!

1D model

Electrons in strong, ultrafast laser field:

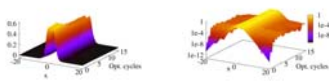
$$H(t) := \sum_{k=1}^{f}\left(\frac{1}{2}(-\mathrm{i}\nabla_k - A(t))^2 + U(x_k) + \sum_{l<k} V(x_k - x_l)\right),$$

$$A(t) := \mathrm{e}^{-t^2}\sin(\omega t),$$
$$U(x) := -\sum_{l=1}^{f} U_1\left(x - d\left(l - \frac{f+1}{2}\right)\right),$$
$$U_1(x) = \frac{1}{\sqrt{a^2+x^2}},$$
$$V(x-y) := \frac{1}{\sqrt{1+(x-y)^2}}.$$

Background: F. Kraus: Atto-second pulses Science (2002), Nature (2002); laser X-ray

Practical Simulation

- $f = 4$ electrons, 15 configurations
- Computations by Runge–Kutta, variable step-size, variable order method, pseudospectral space discretization at 1000 points, 15 optical cycles
- Electron density $\langle u|u\rangle_{f-1}$



Polarization, ionization and depletion
From: Koch, Kreuzer, Scrinzi (2005)

Project Aims

- Analytical properties of the solution: Extension of results for smooth potential to the singular (Coulomb) case. Domain of existence.
- Convergence of MCTDHF approximations as the number of configurations tends to infinity:
  Invertibility of density matrix ρ. Regularity bounds uniform in the number of configurations. Geometry of the approximation manifold.
- Code for 3D with cylindrical symmetry: Singular potentials.
- (Adaptive) finite elements for space discretization:
  Local basis functions favorable for parallelization.
- High order time integrator:
  Preserve "geometric" properties (e. g. orthonormality of orbitals ϕ_j). Splitting idea to treat separately fast and slow solution components.
- Speedup by "$\mathcal{H}$-matrices":
  Evaluation of meanfield terms includes inner products of the form

$$\langle\phi_i|V|\phi_j\rangle = \iint \overline{\phi_i(x)}V(x-y)\phi_j(y)\,dy\,dx.$$

"Correlation": The integrals have to be computed for many i, j! Discretization and low rank approximation may be boosted by use of "hierarchical matrices": Linear complexity for "asymptotically smooth" kernels (e. g. Coulomb interaction).

Collaborations

- Ch. Lubich, Univ. of Tübingen
  Numerical analysis, geometric (time) integration, convergence of the approximation, relationships with low rank approximation of time-dependent matrices.
- N. Mauser, Univ. of Vienna
  Analytical aspects of MCTDHF equations, convergence of the approximation.
- J. M. Melenk, D. Praetorius, Vienna Univ. of Technology
  Computational math., $\mathcal{H}$-matrices.
- A. Scrinzi, Vienna Univ. of Technology
  High performance computing, code development, applications.