Tensor product approximation and the numerical solution of the Electronic Schrödinger equation

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Introduction

Electronic Schrödinger Equation
Quantum mechanics

**Goal:** Calculation of physical and chemical properties on a microscopic (atomic) length scale.

- E.g. atoms, molecules, clusters, solids
- E.g. chemical behaviour, bonding energies, ionization energies, conduction properties, essential material properties
Electronic structure calculation
Reduction of the problem to the computation of an electronic wave function $\Psi$ for given fixed nuclei.

The electronic Schrödinger equation, describes the stationary nonrelativistic behaviour of system of $N$ electrons in an electrical field

$$\hat{H}\Psi = E\Psi.$$ 

Electronic structure determines e.g.

- bonding energies,
- reactivity,
- ionization energies,
- conductivity,
- in a wider sense molecular geometry, dynamics,...

of atoms, molecules, solids etc.
**Electronic Schrödinger equation**

\[
N \text{ nonrelativistic electrons} + \text{Born Oppenheimer approximation}
\]

\[
H\psi = E\psi
\]

The Hamilton operator in atomic units

\[
H = -\frac{1}{2} \sum_i \Delta_i - \sum_i \sum_{\nu=1}^{K} \frac{Z_\nu}{|x_i - a_\nu|} + \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|x_i - x_j|}
\]

acts on *anti-symmetric* wave functions (Pauli principle)

\[
\psi(x_1, s_1, \ldots, x_N, s_N) \in \mathbb{R}, \quad x_i = (x_i, s_i) \in \mathbb{R}^3 \times \{\pm \frac{1}{2}\},
\]

\[
\psi(\ldots; x_i, s_i; \ldots; x_j, s_j; \ldots) = -\psi(\ldots; x_j, s_j; \ldots; x_i, s_i; \ldots)
\]
Variational formulation

**Input:** position $a_{\nu}$ of the $\nu$'s atom, nuclear charge $Z_{\nu}$, number of electrons $N$.

**Output:** We are mainly interested in the ground-state energy, i.e. the lowest eigenvalue in the configuration space

$$\psi \in \mathcal{V} = H^1(\mathbb{R}^3 \times \{\pm \frac{1}{2}\})^N \cap \bigwedge_{i=1}^N L^2(\mathbb{R}^3 \times \{\pm \frac{1}{2}\})^N.$$ 

$$E_0 = \min_{\langle \psi, \psi \rangle = 1} \langle H\psi, \psi \rangle, \quad \psi = \arg\min_{\langle \psi, \psi \rangle = 1} \langle H\psi, \psi \rangle$$

- Energy surfaces $E = E(a_1, \ldots a_k)$. (Add nuclear repulsion potential $\sum_{\nu \neq \mu} \frac{Z_{\nu} Z_{\mu}}{2|a_\nu - a_\mu|}!$)

- Atomic forces $\frac{\partial E}{\partial a_\nu} \Rightarrow$ molecular geometry

- Bonding and ionization energies etc.

- These quantities are (small) differences $E_{0,a} - E_{0,b}$

- Accuracy is limited due to neglecting relativistic and non-Born-Openheimer effects

.. is beyond the present presentation
Example in quantum chemistry

$O_2$ binding to hemoglobin modeled by a Fe-prophyrin complex (heme) $1E_h \approx 27,2114\text{eV}$ Hartree

![Image](Kopie.jpg)
Facts to know

The ES has been well studied in Analysis or Mathematical Physics

- Kato, ... (.. 60..), The energy space is: \( V : H^1((\mathbb{R}^3 \times \{\pm \frac{1}{2}\})^{N'}) \)
i.e. the Hamilton operator maps \( H : V \rightarrow V' \) boundedly.
- HVZ-Theorem ( ..60..), \( E_0 \) is an eigenvalue of finite multiplicity: \( -\infty < E_0 < \inf \sigma_{\text{ess}}(H) \) if \( N' \leq Z := \sum_{\nu=1}^{K} Z_{\nu} \)
- Agmon ( .. 70 .. ), exponential decay at infinity:
  \( \psi(x) = O(e^{-a|x|}) \) if \( |x| \rightarrow \infty \).
- Kato, T.- von Ostenhoff & T. Soerensen ... (98),
cusp-singularities:
e.g. electron-nucleon (e-N) cusp \( O(|x_i - a_\nu|) \)
and electron-electron (e-e) cusp \( O(|x_i - x_j|) \)
- Yserentant (03) mixed regularity \( \psi \in H^{1,s}, s \leq \frac{1}{2} \), resp. 1
Basic Problem - Curse of dimensions

- linear eigenvalue problem, but extremely high-dimensional
- + anti-symmetry constraints + lack of regularity.
- traditional approximation methods (FEM, Fourier series, polynomials, MRA etc.):
  approximation error in $\mathbb{R}^1$: $\lesssim n^{-s}$, s- regularity $\sim$, $\mathbb{R}^{3N'}$: $\lesssim n^{-s}3N'$, ($s < \frac{5}{2}$) with $n$ DOFs
- Curse of dimensionality
- in principle, deterministic approximation methods are scaling exponentially with $N$.
- Nondeterministic methods: Quantum Monte Carlo methods have problems with fermions

For large systems $N' >> 1$ ($N' > 1$) the electronic Schrödinger equation seems to be intractable! But 70 years of impressive progress has been awarded by the Nobel price 1998 in Chemistry: Kohn, Pople.

For extended systems, the method of choice is Density Functional Theory (DFT). However this will be deferred to my colloquium lecture.

In the sequel, we will consider only discretized equations and high dimensional functions.
For sake of simplicity, we keep all vector spaces finite dimensional.
Further motivations: PDE’s in higher dimensions

Equations describing complex systems with multi-variate solution spaces, e.g.

- stationary/instationary Schrödinger type equations

\[ i\hbar \frac{\partial}{\partial t} \psi(t, x) = \left( -\frac{1}{2} \Delta + V \right) \psi(t, x), \quad H \psi(x) = E \psi(x) \]

-describing quantum-mechanical many particle systems

- stochastic DEs (SDEs) and the Fokker-Planck equation, 

\[ \frac{\partial p(t, x)}{\partial t} = \sum_{i=1}^{d} \frac{\partial}{\partial x_i} (f_i(t, x)p(t, x)) + \frac{1}{2} \sum_{i,j=1}^{d} \frac{\partial^2}{\partial x_i \partial x_j} (B_{i,j}(t, x)p(t, x)) \]

-describing mechanical systems in stochastic environment,

- chemical master equations, parametric PDEs, machine learning, …

Solutions depend on \( x = (x_1, \ldots, x_d) \), where usually, \( d \gg 3 \)!
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describing mechanical systems in stochastic environment,

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Solutions depend on \( x = (x_1, \ldots, x_d) \), where usually, \( d \gg 3! \)
Setting - Tensors of order $d$

**Goal:** Generic perspective on methods for high-dimensional problems, i.e. problems posed on tensor spaces,

$$\mathcal{V} := \bigotimes_{i=1}^{d} V_i, \quad \text{today: } \mathcal{V} = \bigotimes_{i=1}^{d} \mathbb{R}^n = \mathbb{R}^{(n^d)}$$

**Notation:** $(x_1, \ldots, x_d) \mapsto U = U(x_1, \ldots, x_d) \in \mathcal{V}$

**Main problem:**

$$\dim \mathcal{V} = \mathcal{O}(n^d) \quad \leftarrow \quad \text{Curse of dimensionality!}$$

* e.g. $n = 100, d = 10 \leadsto 100^{10}$ basis functions,  
  $\leadsto$ coefficient vectors of $800 \times 10^{18}$ Bytes $= 800$ Exabytes

**Approach:** Some higher order tensors can be constructed (data-) sparsely from lower order quantities.

**As for matrices, incomplete SVD:**

$$A(x_1, x_2) \approx \sum_{k=1}^{r} \sigma_k(u_k(x_1) \otimes v_k(x_2))$$
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**Approach:** Some higher order tensors can be constructed (data-) sparsely from lower order quantities.

$$\leadsto \textbf{Canonical decomposition for order-}d\text{-tensors:}$$

$$U(x_1, \ldots, x_d) \approx \sum_{k=1}^r \sigma_k \left( \bigotimes_{i=1}^d u_{i,k}(x_i) \right).$$
Further application of TP approximation

- approximation of multi-parametric functions
- e.g. machine learning
- signal processing
- parametric PDE’s, (boundary value problems with uncertain coefficients)
- high dimensional integration
- computational finance
- quantum information theory
- algebraic geometry (see book Landsberg)
- vector tensorization
- ...

Although these issues could not be discussed here in detail.

Major challenge: How to avoid the curse of dimensionality?
- Tensor product approximation seems to be promising?
- Question: what is an appropriate generalization of SVD to higher order tensors?
Content and time line

Part I - Tensor Approximation
1. Classical and novel tensor formats
2. Tensor networks, TT and HT tensors - - Recovery, approximation and optimization
3. ALS and MALS for TT and related formats – Matrix product states and DMRG algorithm
4. Geometry of the hierarchical Tucker format (including TT and Tucker)
5. Dynamical low rank approximation
6. vector tensorization and QTT tensors

Part 2 - Numerical solution of the electronic Schrödinger equation
1. Slater determinants, Full CI and discrete Fock spaces,
2. Hartree Fock approximations and multi-configurational SCF
3. Matrix product states (TT tensors) and DMRG
4. Coupled Cluster method I
5. Coupled Cluster method II and simplifications: MP2, RPA and CEPA
6. Reduced density matrices and Greens functions
Thank you
for your attention.

References:


T. G. Kolda, B. W. Bader, *Tensor decompositions and applications*, SIAM Review Vol. 51, 3, 455-500,