

# Tensor product methods and entanglement opt for ab initio quantum chemistry

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## 1 introduction

Trade off between accuracy and computational complexity. No method of choice solution for finding a sufficiently accurate data sparse rep of the exact many body wavefunction if electrons are strongly correlated. open shell transition metal complexes for example.

Due to many electron interactions strongly correlated problems cannot be described by small perturbations of a single Slater determinant. Treatment of other many particle systems have been proposed resulting in matrix product states MPS. These rep wavefunctions of a system of  $d$  components by forming products of  $d$  matrices, each one component. complexity dictated by size of the matrices related to eigenvalue spectrum of the corresponding subsystem density matrix characterizing a formal way the so called entanglement among the different components.

MPS has linear arrangement of components. More recently approach called Tensor Network States more flexible connection of components

Identical approaches devised in numerical mathematics under name tensor product approx, where low rank factorization of matrices is generalized to higher-order tensors.

Using data sparse representation an accurate rep of electronic structure will be possible in polynomial if the exact wfn can be approx to be a sufficient extent by moderately entangled TNS representations. The underlying MO basis can be optimized by well known techs of multiconfigurational methods which constitutes a tensor approximation method as well as the level of first quantization.

Entanglement based methods have been developed in quantum chemistry. A promising direction is to develop and implement efficient quantum chemistry algorithm based on tree tensor network states. Enabling the treatments in quantum chem that are intractable by standard DFT or CC particularly interesting. Paper gives pedagogical intro into field and provides underlying benefits through numerical application.

## 2 Tensor product methods in quantum chemistry

Multiparticle Schrödinger type equations suffer curse of dimensionality. Circumventing the problem challenge of modern numerical analysis covering Schrödinger equation Fokker-Planck equation and chemical master equation.

In 1992 S. R. White introduced DMRG allows chemists to determine the physical properties of low-dimensional correlated systems such as quantum spin chains or chains of interacting itinerant electrons. DMRG has gone through major algorithmic developments in the past decade. One direction is the post DMRG treatment of dynamic correlation. DMRG can be considered as a CAS-CI technique can recover static correlation and dynamic correlation depending on the size of the active space.

DMRG can be used to calculate ground and excited states. DMRG is flexible and can be used in situations when the wfn character changes dynamically. Ansatz is size consistent by construction and symmetries as particle number, spin projection spin reflection abelian point group and non abelian symmetries can be factored out explicitly.

Recently MPS and further tensor product approximations have been applied to post-HF methods to decompose the 2 electron integrals, the AO-MO transformation and MP2 energy expression

MPS methods scale by matrices size used to approximate wfn. controlled based on truncation. Systems with identical sites feature is directly connected to scaling of entanglement when subsystems include larger and larger portion of the system, called area law.

More complicated in Quantum chem since rank depends on the ordering of the matrices. different orderings lead to better or worse results if ranks are kept fixed. Basis optimization and initialization also affect the results.

HOSVD have made MPS the basis of variational frameworks and revealed a profound connection to quantum information theory.

MPS corresponds to systems arranged in linear topology, quantum states more complex topologies so use of TNS. Applications in small systems called complete graph tensor network state approach and tree tensor network states. QC-TTNS combine features general concept of data-sparsity allow for efficient rep of bigger class of wfns. Ansatz can span full CI space.

## 2.1 entanglement

Entanglement is synonymous to correlation. QC-DMRG and QC-TTNS algorithms approx composite systems with strong interactions btwn pairs of orbitals, Quantum information theory can be used to understand their convergence criteria.

total correlation can be char by single-orbital entropy sum of all soe gives total correlation. orbital entropy provides chemical information about system especially bond formation and nature of static / dynamic correlation.

Two orbital information can yeild a weighted graph of the overall 2-orbital correlation.

## 2.2 Tensor Decomp in math

Recent analysis shows that beyond matrix almost all tensor problems, even that of finding the best rank-1 approximation, are in general NP hard. Though this means tensor product approx difficult a variety of complex concepts for the approximation of solutions of certain problem have been proposed.

Tucker format attains sparsity via a subspace approximation. Multiconfig methods are tucker approximations in framework of antisymmetry. Unfav scaling worked around using Hierarchical subspace approximation framework corresponding to TTNS. Tensor trains developed independ formal version of MPS with open boundary conditions. TNS and MPS have desirable properties from matrix factorization. In general the robustness and quasi-best approximation of the HOSVD and the one site DMRG as simple and efficient numerical methods are now well-understood.

## 3 Quantum Chemistry

Quantum system of N nonrel electrons described by a state-function  $\Psi$  depending on 3 spatial variables together with N discrete spin variables. The wavefunction belongs to the hilbert space  $L_2((\mathbb{R}^3 \times \{+ - 1/2\})^N)$  has an inner product as I know with the norm as the sqrt of the inner product. The Pauli antisymmetric principle states that the wfn of fermions in perticular electrons must be antisymmetric wrt permutation of variables.

These wave-functions are elements of the antisymmetric tensor subspace in the paper. The pauli exclusion principle immediatly follows  $\Psi$  must vansih for the points in the hilbert space which have the corrdinates  $r_a=r_b$  and  $s_a=s_b$  for some  $a \neq b$  fermions.

In quantum mechanics interested in wfn definite energies, stationary schrodinger equation  $H\Psi = E\Psi$  wfn an eigenfunction of a differential operation, Hamiltonian, the eigenvalue  $E \in \mathbb{R}$  is energy of state of the wavefunction. Most important is lowest ground state energy.

Born-Oppenheimer approximation considers a nonrelativistic quantum mechanical system of N electrons in an exterior field generated by K nuclei. In this case H is defined as

$$H = K + V, \text{ where } V = V_{ext} + V_{int}$$

$$K = \sum_{a=1}^N -1/2 \Delta_a, V_{ext} = \sum_{a=1}^N \sum_{c=1}^K \frac{Z_c}{|R_c - r_a|}, V_{in} = 1/2 \sum_{a,b=1}^N \sum_{a \neq b} \frac{1}{r_b - r_a}$$

H is second order linear diff op, analysis for electronic schrodinger eqn already established to a certain extent.

Some basic results from the literature:

Sobolev spaces are defined as the spaces of functions for which all derivatives up to order  $m$  are in  $H^0$  defined as the original hilbert space. Therefore  $H$  maps the sobolev space  $H^1$  continuously into a dual space  $H^{-1}$  boundedly.

The potential operator maps the Sobolev space  $H^1$  continuously into  $H^0$  boundedly. The electronic schrodinger operator admits a complicated spectrum. Interested mainly in the ground state energy. For neutral systems  $E_0$  is an eigenvalue of finite multiplicity of the kinetic energy operator.

Assume  $E_0$  a simple eigenvalue of multiplicity 1. This case is stationary electronic schro eqn in nonrelativistic and born-opp setting, can assume wfn is real valued. According to mini-max principle ground state energy and corresponding wfn satisfy the Rayleigh-Ritz variational principle, ie lowest eigenvalue is the min of the Rayleigh quotient  $\frac{\langle \Psi, H \Psi \rangle}{\langle \Psi, \Psi \rangle}$

### 3.1 Full CI and Ritz-Galerkin approximation

A convenient way to approximate the wavefunction is to use an antisymmetric tensor product of basis function depending on a single particle variables realized by determinants. Consider a finite subset of an orthonormal set of basis function. These functions called spin orbitals because they depend on the spin variable and spatial variable.

Build slater determinants of an  $N$ -electron system by selecting  $N$  different indices out of a larger set of orbitals. By this we have chosen  $N$  orthonormal spin orbitals to define the slater determinant.

Full CI space for an  $N$  electron system is as the finite dimensional  $V_N$  spanned by the slatter determinants  $\dim V_N$  about  $O(d^N)$

To obtain an approximate solution one may apply Ritz-Galerkin method using the finite dimensional subspace. that is considered a finite dimensional eigenvalue problem projected by an  $L^2$  orthogonal projection. The Ritz-Galerkin method provides an upper bound for the exact energy value. The eigenvalue converges quadratically compared to the convergence of the eigenfunction. Since the dimension of full CI is  $i = O(2^N)$  full CI scales exponentially wrt  $N$ . Therefore the molecules this approach can practically compute is very small.

### 3.2 Fock spaces

Embedding the full CI space of  $N$ -electrons into a larger space  $F_d$  called discrete fock space where we do not care about the number of electrons. its dimension is  $2^d$ . The fock space is a hilbertspace with same inner product.

The full fock space is when infinite dimensions. The Hamiltonian now acts on different number of electrons and the whole fock space. It is convenient to define the creator operator which given on slater determinants. This connects the subspaces with different number of particles in the fock space. Also an annihilation operator. Fermionic anticommutation relations:

$$\{a_i^\dagger, a_j^\dagger\} = 0, \{a_i, a_j\} = 0, \{a_i, a_j^\dagger\} = \delta_{ij}$$

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