Density Matrix Renormalization Group

using Matrix Product States

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Outline

Electron correlation

- Correlation energy:

$$E_{corr} = E_{exact} - E_{HF} \tag{1}$$

- Dynamic correlation: Absence of the "Coulomb hole"
- Static correlation: Nearly degenerate configurations, accounts for increased correlation energy at stretched geometries
- Use of single determinant wavefunction inadequate in strongly correlated systems

Possible remedies

- Configuration interaction:

$$|\Phi_0\rangle = c_0|\psi_0\rangle + \sum_{a,r} c_a^r|\Psi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \ldots \qquad (2)$$

- Total number of n-tuply excited determinants $= \binom{N}{n}\binom{2K-N}{n}$ ($2K$: no. of one electron spin orbitals, N: no. of electrons)
- FCI not feasible for large systems, truncations of FCI (viz. SDCI, QCI, etc.) fail to capture static correlation
- DMRG: Effectively targets a small part of the Hilbert space

Outline

Terminology

- The density operator of an ensemble of pure states is

$$\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i| \tag{3}$$

- Consider a bipartite system C made up of subsystems A and B. A pure state $|\psi\rangle$ of the system C is said to be separable if it can be written as

$$|\psi\rangle = |\psi_A\rangle \otimes |\psi_B\rangle \tag{4}$$

  A state entangled if and only if it is not separable.
- If ρ corresponds to the state $|\psi\rangle = \sum_{ij} \Psi_{ij} |i\rangle_A |j\rangle_B$, the reduced density matrices can be expressed as

$$\rho_A = \Psi\Psi^\dagger, \qquad \rho_b = \Psi^\dagger\Psi \tag{5}$$

Theorem (Singular value decomposition)

If $A \in M_{m,n}$, has rank r, then it may be written in the form

$$A = V\Sigma W^* \tag{6}$$

where $V \in M_m$ and $W \in M_n$ are unitary. The matrix $\Sigma = [\sigma_{ij}] \in M_{m,n}$ has $\sigma_{ij} = 0\ \forall i \neq j$ and $\sigma_{11} \geq \sigma_{22} \cdots \geq \sigma_{rr} > \sigma_{r+1,r+1} = \cdots = \sigma_{qq} = 0$ where $q = min\{m, n\}$ the numbers $\{\sigma_{ii} = \sigma_i\}$ are the nonnegative square roots of the eigenvalues of AA^*, and hence are uniquely determined. The columns of V are eigenvectors of AA^* and the columns of W are eigenvectors of A^*A.

Theorem (Schmidt decomposition)

Suppose $|\psi\rangle$ is a pure state of a composite system AB. Then there exist orthonormal states $|a\rangle_A$ for system A and orthonormal states $|a\rangle_B$ for system B such that

$$|\psi\rangle = \sum_a \lambda_a |a\rangle_A |a\rangle_B \tag{7}$$

- It follows that the reduced density matrices ρ_A and ρ_B have eigenvalues λ_a^2 with eigenvectors $|a\rangle_A$ and $|a\rangle_B$ respectively.
- The best rank k approximation of the state $|\psi\rangle$ is given by the state

$$|\tilde{\psi}\rangle = \sum_{a=1}^{k} \lambda_a |a\rangle_A |a\rangle_B \tag{8}$$

Outline

DMRG algorithm for spin lattice systems

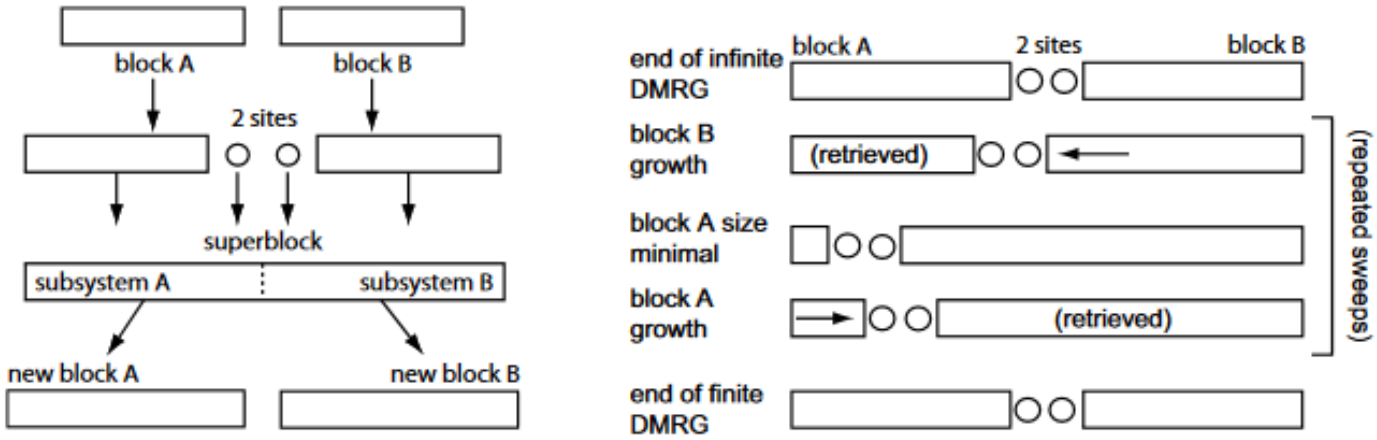

Figure: Pictorial representation of infinite (left) and finite (right) space DMRG

Source: Ulrich Schollwöck. "The density-matrix renormalization group in the age of matrix product states". In: *Annals of Physics* 326.1 (2011), pp. 96–192

- Consider a linear chain of L spins, with $s = 1/2$, interacting via the Heisenberg Hamiltonian

$$\hat{H} = \sum_{i=1}^{L-1} \frac{J}{2}(\hat{S}_i^+ \hat{S}_{i+1}^- + \hat{S}_i^- \hat{S}_{i+1}^+) + J^z \hat{S}_i^z \hat{S}_{i+1}^z \qquad (9)$$

Contd.

- Any state of the superblock can be written as

$$|\psi\rangle = \sum_{a_A \sigma_a a_B \sigma_b} \psi_{a_A \sigma_a a_B \sigma_b} |a\rangle_A |\sigma\rangle_A |\sigma\rangle_B |a\rangle_B = \sum_{i_A j_B} \psi_{i_A j_B} |i\rangle_A |j\rangle_B$$

  The Hamiltonian is now diagonalized in this space.

- Reduced density matrix of $A\bullet$ is given by

$$[\rho_{A\bullet}]_{ii'} = \sum_j \psi_{ij} \psi^*_{i'j} \tag{10}$$

  This reduced matrix is now diagonalized and the eigenvectors corresponding to largest D eigenvalues are retained and made into an orthonormal basis for $A\bullet$.

- Finite space DMRG: Very similar to the infinite system process
- Eigenvalue spectrum decays rapidly for one dimensional systems with gapped Hamiltonians

Outline

Matrix product states

- General state of a multi-electron system can be written in the occupation number representation as

$$|\psi\rangle = \sum_{n_{j\sigma}} C_{n_{1\uparrow} n_{1\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}} |n_{1\uparrow} n_{1\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}\rangle \tag{11}$$

- Product state (separable):

$$|\psi\rangle = \sum_{n_{j\sigma}} C[1]_{n_{1\uparrow} n_{1\downarrow}} \ldots C[L]_{n_{L\uparrow} n_{L\downarrow}} |n_{1\uparrow} n_{1\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}\rangle \tag{12}$$

  where $C^{[i]}_{n_{i\uparrow} n_{i\downarrow}}$ are scalars.

- Matrix product state (not separable):

$$|\psi\rangle = \sum_{n_{j\sigma}} A[1]_{n_{1\uparrow} n_{1\downarrow}} \ldots A[L]_{n_{L\uparrow} n_{L\downarrow}} |n_{1\uparrow} n_{1\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}\rangle \tag{13}$$

  where $A[i]_{n_{i\uparrow} n_{i\downarrow}}$ are matrices.

Matrix product states

- The expansion coefficients can be reshaped into a matrix Ψ of dimension $4 \times 4^{L-1}$as

$$\begin{aligned} C_{n_{1\uparrow} n_{1\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}} &= \Psi_{(n_{1\uparrow} n_{1\downarrow});(n_{2\uparrow} n_{2\downarrow} \ldots n_{L\uparrow} n_{L\downarrow})} \\ &= \sum_{\alpha_1}^{r_1} U[1]_{n_{1\uparrow} n_{1\downarrow};\alpha_1} s[1]_{\alpha 1} V[1]_{\alpha_1;n_{2\uparrow} n_{2\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}} \end{aligned}$$

Reshape $V[1]$ into a matrix Ψ of dimension $4r_1 \times 4^{L-2}$, to give

$$C_{n_{1\uparrow} n_{1\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}} = \sum_{\alpha_1}^{r_1} A[1]_{\alpha_1}^{n_{1\uparrow} n_{1\downarrow}} \Psi_{(\alpha_1 n_{2\uparrow} n_{2\downarrow});(n_{3\uparrow} n_{3\downarrow} \ldots n_{L\uparrow} n_{L\downarrow})} \quad (14)$$

- Continuing this procedure we eventually get the following contracted matrix product

$$C_{n_{1\uparrow} n_{1\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}} = \sum_{\alpha_1, \ldots, \alpha_{L-1}} A[1]_{\alpha_1}^{n_{1\uparrow} n_{1\downarrow}} A[2]_{\alpha_1;\alpha_2}^{n_{2\uparrow} n_{2\downarrow}} \ldots A[2]_{\alpha_{L-1}}^{n_{L\uparrow} n_{L\downarrow}} \quad (15)$$

- The matrices $A[i]$ obtained above are left-normalized

$$\sum_{n_{i\uparrow} n_{i\downarrow}} A[i]^{n_{i\uparrow} n_{i\downarrow}\dagger} A[i]^{n_{i\uparrow} n_{i\downarrow}} = I \tag{16}$$

- Mixed-canonical MPS used in DMRG

$$C_{n_{1\uparrow} n_{1\downarrow} \ldots n_{L\uparrow} n_{L\downarrow}} = A[1]^{n_{1\uparrow} n_{1\downarrow}} \ldots A[l]^{n_{l\uparrow} n_{l\downarrow}} SB[l{+}1]^{n_{l+1\uparrow} n_{l+1\downarrow}} \ldots B[L]^{n_{L\uparrow} n_{L\downarrow}} \tag{17}$$

  where $A[i]$ are left-normalized and $B[i]$ are right-normalized.

- A natural generalization of this representation can be made to operators (matrix product operators).

$$\hat{O} = \sum_{\mathbf{n},\mathbf{n'}} W^{n_1 n'_1} W^{n_2 n'_2} \ldots W^{n_L n'_L} |\mathbf{n}\rangle\langle\mathbf{n'}| \tag{18}$$

- When increasing the size from $l-1$ to l, the dimension of the new system is truncated to a constant D. If the new basis after truncation is $\{|a_l\rangle_A\}$, we have

$$|a_l\rangle_A = \sum_{a_{l-1}n_l} {}_A\langle a_{l-1}n_l|a_l\rangle_A|a_{l-1}\rangle_A|n_l\rangle \tag{19}$$

- Define

$$A^{n_l}_{a_{l-1}a_l} = {}_A\langle a_{l-1}n_l|a_l\rangle_A \tag{20}$$

  Recursing this procedure leads to

$$|a_l\rangle_A = \sum_{n_l\in A}(A^{n_1}A^{n_2}\dots A^{n_l})_{1,a_l}|n_1n_2\dots n_l\rangle \tag{21}$$

  DMRG actually finds the MPS that minimizes ground state energy.
- The maximum number of variables is LdD^2.

Outline

PPP model

- Pariser, Parr and Pople proposed a model Hamiltonian for π-conjugated systems in 1950's. The PPP Hamiltonian can be written as

$$H_{PPP} = \sum_{i,\sigma} \epsilon_i c^{\dagger}_{i\sigma} c_{i\sigma} + \sum_{<ij>,\sigma} t_{ij}(c^{\dagger}_{i\sigma} c_{j\sigma} + c^{\dagger}_{j\sigma} c_{i\sigma}) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \sum_{i<j} V_{ij}(n_i - 1)(n_j - 1)$$

- The molecular orbitals obtained by diagonalizing this Hamiltonian can be assumed to be placed on lattice sites. The DMRG procedure can then be applied to this system in an analogous way as with the spin lattice.

Two-site DMRG algorithm using MPS

- At each iteration two neighboring sites are simultaneously optimized.

$$\sum_{\alpha_i} A[i]^{n_i}_{\alpha_{i-1};\alpha_i} A[i+1]^{n_{i+1}}_{\alpha_i;\alpha_{i+1}} = C[i]^{n_i;n_{i+1}}_{\alpha_{i-1};\alpha_{i+1}} \tag{22}$$

- Minimizing

$$\mathcal{L} = \langle \Psi(C[i]) | \hat{H} | \Psi(C[i]) \rangle - \lambda \langle \Psi(C[i]) | \Psi(C[i]) \rangle \tag{23}$$

with respect to $C[i]$, we get

$$\mathbf{H}^{eff} C[i] = \lambda C[i] \tag{24}$$

- $C[i]$ is decomposed with SVD,

$$C[i]_{(\alpha_{i-1} n_i);(n_{i+1}\alpha_{i+1})} = \sum_{\beta} U[i]_{(\alpha_{i-1} n_i);\beta} s[i]_{\beta} V[i]_{\beta;(n_{i+1}\alpha_{i+1})}$$

β is truncated to D at each iteration.

- The system is sweeped from left to right. The direction is reversed when the process reaches the rightmost site.

Outline

t-PA results

- DMRG calculations of ground and low lying excited states of all-trans polyenes (also known as trans polyacetylene or t-PA) up to $C_{18}H_{20}$ (t-PA9)
- The PPP matrix elements were generated using a `FORTRAN 90` program written by Alok Shukla et.al. We used the free open source `C++` program `CheMPS2`, a spin adapted implementation of DMRG, developed by Sebastian Wouters et.al.[3]. The well known `MELD` package was used for CI calculations.
- Ths DMRG energies compare favorably with the CI energies (Full table of results in the report)

State	QCI	FCI	DMRG
$^1A_g1$	-16.8705045352	-16.872654897	-16.872654893347
$^1A_g2$	-13.0980180280	-13.1152751303	-13.115275153012
$^1A_g3$	-11.5287037281	-11.5418352844	-11.541835186370
$^1B_u1$	-12.3442194268	-12.3447199161	-12.344719931298
$^1B_u2$	-12.1580393892	-12.1656494667	-12.165649459403
$^1B_u3$	-10.2133324821	-10.2290160254	-10.229016052787
$^3B_u1$	-14.9617650290	-14.9632965985	-14.963296643552
$^3B_u2$	-13.0200987978	-13.0246444423	-13.024644378794
$^3B_u3$	-12.1165034330	-12.1233346617	-12.123334659033

Table: t-PA4 results

State	QCI	DMRG
$^1A_g1$	-34.50537	-34.53892
$^1A_g2$	-31.452610	-31.71369
$^1A_g3$	-30.477940	-30.68713
$^1B_u1$	-31.03991	-31.20570
$^1B_u2$	-30.83357	-30.87664
$^1B_u3$	-29.98617	-30.18422
$^3B_u1$	-32.93623	-33.01562
$^3B_u2$	-31.87445	-31.99596
$^3B_u3$	-30.94953	-31.10022

Table: t-PA8 results

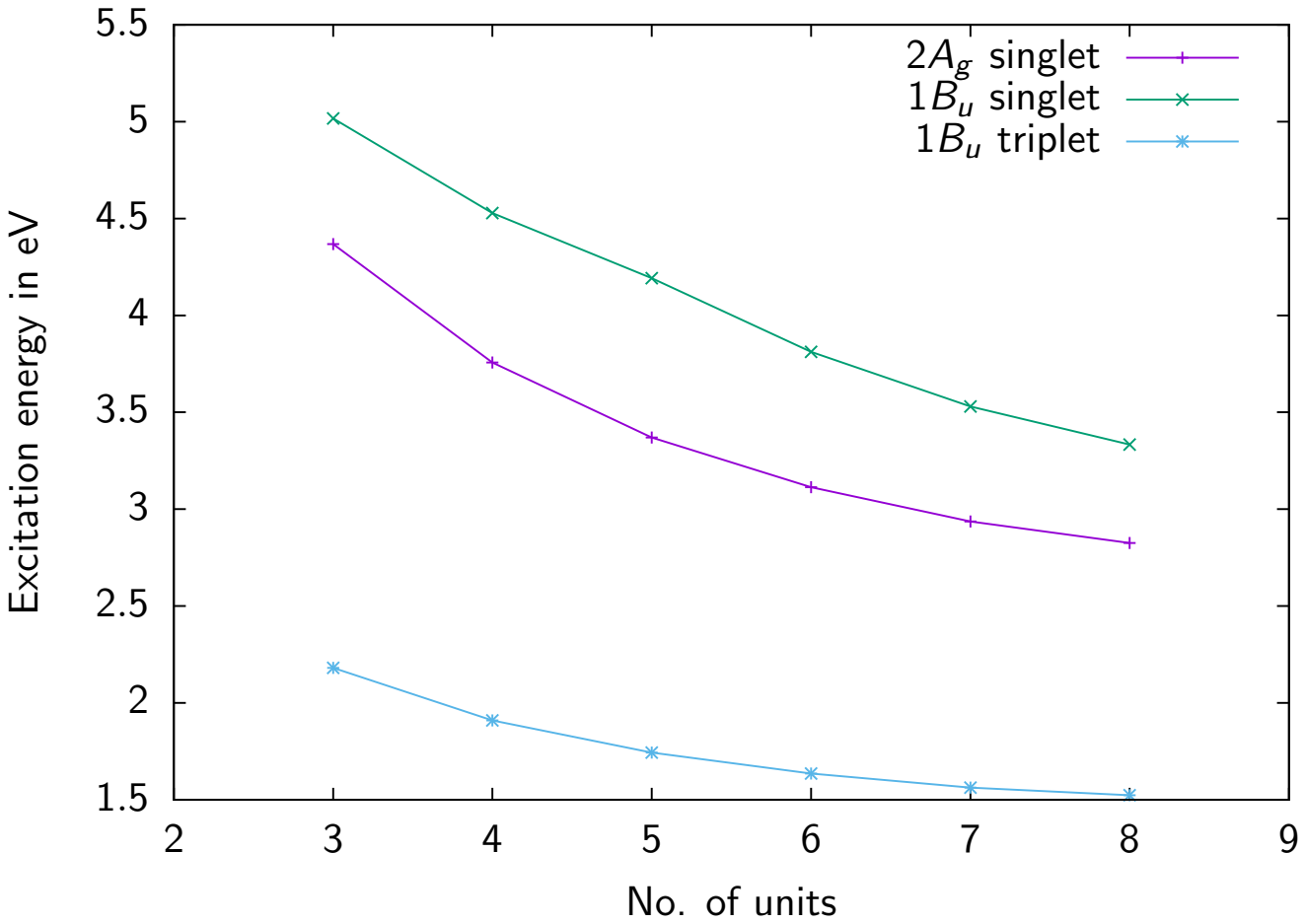

Figure: Excitation energies