Symmetrized DMRG Method for Excited States of Hubbard Models

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Abstract

We extend the density matrix renormalization group method to exploit Parity, $C_2$ (rotation by $\pi$) and electron-hole symmetries of model Hamiltonians. We demonstrate the power of this method by obtaining the lowest energy states in all the eight symmetry subspaces of Hubbard chains with upto 50 sites. The ground-state energy, optical gap and spin gap of regular $U = 4t$ and $U = 6t$ Hubbard chains agree very well with exact results. This development extends the scope of the DMRG method and allows future applications to study of optical properties of low-dimensional conjugated polymeric systems.

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The Density Matrix Renormalization Group (DMRG) method \cite{1, 2} has proved to be an accurate technique for obtaining a few low-lying states of interacting model Hamiltonians with short-range interactions in low-dimensions\cite{3-5}. This technique would find wide applications in the electronic structure studies of conjugated polymers and donor-acceptor systems, if we can obtain excited eigenstates in different symmetry subspaces. However, the DMRG techniques reported in the literature for fermions can exploit only the conservation of the z-component of the total Spin ($S^z_{tot}$) and total number of particles ($N_{tot}$) in the system\cite{6-8}. Using these symmetries one can obtain a few (about ten) low-lying states in different $M_s$ and $N$ sectors\cite{2}. This is due to the limitation on the number of eigenstates that can be targeted effectively because of the large matrices that one encounters in the DMRG algorithm. Additionally, the Hamiltonians being spin conserving, the states with higher total spin repeat in many $M_s$ sectors. For example, triplet states will be present in the $M_s = 0$, $+1$ and $-1$ sectors. Therefore, obtaining the second singlet state usually requires targeting the third state in the $M_s = 0$ sector and eliminating the $M_s = 0$ intruder triplet state. Besides, with increasing system size, the number of intruders also increases. Thus the inclusion of just these symmetries is not sufficient to make detailed comparisons between theory and experiments that probe excited states.

In system with spatial symmetries, the states important from the point of view of optical (one-photon) spectroscopies always lie in a spatial symmetry subspace different from the subspace in which the ground state is found. For example, in Hubbard chains, the ground state is in the A subspace while the dipole allowed excited states are in the B subspace \cite{9}.

Hubbard chains at half-filling also possess electron-hole symmetry. This allows labelling of the states as either $'+$', corresponding to covalent subspace, or '$-$', corresponding to ionic subspace. The dipole allowed excited states are found in the $'-'$ subspace.
while the ground state is in the ′+′ subspace. The number of higher energy states in the ′+′ subspace intruding below the lowest ′−′ subspace state increases as the strength of electron correlation $U/t$ increases [10]. Hence, if this symmetry is not incorporated, many ′+′ space states intrude below the lowest ′−′ space state rendering the optically allowed excited state difficult to access computationally.

Obtaining the Hamiltonian in fully block-diagonal form, with respect to the above symmetries, is also necessary, if we wish to compute the dynamic nonlinear optic coefficients using correction vectors[11]. The correction vectors belong to symmetry determined subspaces and are obtained by solving a set of inhomogeneous linear algebraic equations which are defined by the Hamiltonian matrix. For example, the correction vector $\phi^{(1)}_i(\omega)$, required for computing first order nonlinearities, is defined by

$$(H - E_G + \omega)\phi^{(1)}_i(\omega) = \hat{\mu}_i|G\rangle$$

where $\hat{\mu}_i$ is the dipole displacement operator, $E_G$ and $|G\rangle$ are the ground state energy and eigenvector, and $\omega$ is the excitation frequency. The vector $\phi^{(1)}_i(\omega)$ lies in the $^{1}B^{+}$ space, if the Hamiltonian has $C_2$, electron-hole and spin symmetries. If the Hamiltonian matrix is not block diagonal then for small values of $\omega$ the system is near singular making it almost impossible to obtain the solution, $\phi^{(1)}_i(\omega)$.

In this communication, we briefly outline a new, symmetrized DMRG procedure which exploits fully the above symmetries in the context of DMRG. As an example of its utility, we present some excitation gaps for long Hubbard chains and compare them with the Bethe-ansatz solutions where possible.

In the implementation of the symmetrized DMRG scheme, we use the group theoretic projection operators for projecting the direct product functions onto different symmetry subspaces. The symmetries we have incorporated are the electron-hole symmetry, $\hat{J}$, end-
to-end interchange symmetry of chains,  $\hat{C}_2$ and parity, $\hat{P}$. The latter two symmetries have been employed within the DMRG scheme for spin chains. While the full spin symmetry classification can be incorporated into the scheme using Clebsch-Gordan coefficients, for the present we have only included parity which bifurcates the space of spin eigenvectors into even (e) and odd (o) spin spaces.

The electron-hole symmetry operator interchanges, with a phase, the creation and annihilation operators at a site,

$$a_i^\dagger = (-1)^i b_i$$  \hspace{1cm} (2)

Thus, the Fock space of a single site $i$, under electron-hole symmetry transforms as $\hat{J}_i|0> = |\uparrow\downarrow>$, $\hat{J}_i|\uparrow> = (-1)^i |\uparrow>$, $\hat{J}_i|\downarrow> = (-1)^i |\downarrow>$, $\hat{J}_i|\uparrow\downarrow> = (-1)|0>$. The full electron-hole symmetry operator, $\hat{J}$, is given by the direct product of the single site operators.

$$\hat{J} = \prod_i \hat{J}_i$$  \hspace{1cm} (3)

The parity operator, at a site $i$, $\hat{P}_i$, flips the electron spin at a site. Thus, $\hat{P}_i|0> = |0>$, $\hat{P}_i|\downarrow> = |\uparrow>$, $\hat{P}_i|\uparrow> = |\downarrow>$, $\hat{P}_i|\uparrow\downarrow> = (-1)|\uparrow\downarrow>$. The full parity operator for the system is also given by the direct product of the single site parity operators.

$$\hat{P} = \prod_i \hat{P}_i$$  \hspace{1cm} (4)

The $\hat{C}_2$ symmetry interchanges the states of the left and right halves of the system with a phase factor. Thus, $\hat{C}_2$ operating on the direct product state $|\mu, \sigma, \sigma', \mu'>>$ gives,

$$\hat{C}_2|\mu, \sigma, \sigma', \mu'> = (-1)^\gamma |\mu', \sigma', \sigma, \mu >; \ \gamma = (n_\mu + n_\sigma)(n_{\mu'} + n_{\sigma'})$$  \hspace{1cm} (5)

where, $\mu(\mu')$ refers to the $\mu^{th}(\mu'^{th})$ eigenvector of the left (right) density matrix while $\sigma(\sigma')$ refers to the Fock space state of the new left (right) site as in the standard DMRG procedure, and $n_\mu$, $n_{\mu'}$, $n_\sigma$ and $n_{\sigma'}$ are the occupancies in the states $|\mu>$, $|\mu'>$, $|\sigma>$ and $|\sigma'>$ respectively.
The operators $\hat{C}_2$, $\hat{J}$ and $\hat{P}$ commute amongst each other and the group formed by identity and these symmetries consists of eight elements with the remaining four elements, resulting from the closure condition. This group being abelian has eight irreducible representations which are labelled $eA^+$, $eA^-$, $oA^+$, $oA^-$, $eB^+$, $eB^-$, $oB^+$, $oB^-$.

The projection operator for a given irreducible representation, $\Gamma$, is given by

$$\hat{P}_\Gamma = \frac{1}{h} \sum_{\hat{R}} \chi_\Gamma(\hat{R}) \hat{R}$$

where $\hat{R}$'s are the symmetry operations, $\chi_\Gamma(\hat{R})$ is the character of $\hat{R}$ in $\Gamma$ and $h$ is the order of the group. The construction of the symmetry adapted direct product states consists in sequentially operating on each of the direct product states by the projection operator. The linear dependencies of the symmetry adapted combinations that result are eliminated by carrying out a Gram-Schmidt orthonormalization.

The computational procedure involves obtaining the matrix representation of the symmetry operators of the $(2n+2)$ site chain in the direct product basis. The matrix representation of both $\hat{J}$ and $\hat{P}$ for the new sites in the Fock space is known from their definitions. Similarly, the matrix representation of the operators $\hat{J}$ and $\hat{P}$ for the left (right) part of the system at the first iteration are also known in the basis of the corresponding Fock space states. These are then transformed to the density matrix eigenvectors basis. The matrix representation of the symmetry operators of the full system in the direct product space are obtained as the direct product of the corresponding matrices,

$$\langle \mu, \sigma, \sigma', \mu' | \hat{R}_{2n+2} | \nu, \tau, \tau', \nu' \rangle = <\mu | \hat{R}_n | \nu > <\sigma | \hat{R}_1 | \tau > <\sigma' | \hat{R}_1 | \tau' > <\mu' | \hat{R}_n | \nu '>$$

At the next iteration, we require the matrix representation of the symmetry operators in the basis of the eigenvectors of the new density matrix. This is achieved by obtaining the
matrix $\mathbf{R}$ as a direct product of $\mathbf{R}_n$ and $\mathbf{R}_1$ given by

$$< \mu, \sigma | \hat{R}_{n+1} | \nu, \tau > = < \mu | \hat{R}_n | \nu > < \sigma | \hat{R}_1 | \tau >$$

(6)

This matrix is renormalized by the transformation

$$\tilde{\mathbf{R}}_{n+1} = \mathbf{O}^\dagger \mathbf{R}_{n+1} \mathbf{O},$$

(7)

where $\mathbf{O}$ is the matrix whose columns are the chosen eigenvectors of the density matrix.

The matrix representation of $\hat{C}_2$ is quite straightforward in that each state $| \mu, \sigma, \sigma', \mu' >$ is mapped into a state $| \mu', \sigma', \sigma, \mu >$ with a phase factor. Thus, each row in the matrix of $\hat{C}_2$ contains only one element and the entire matrix can be represented by a correspondence vector. The matrices $\mathbf{J}$ and $\mathbf{P}$ are also rather sparse and can be stored in sparse form to avoid doing arithmetic with zeros. This aspect of the computation turns out to be crucial for the implementation of the scheme since the dimensionality of the direct product space is usually very large (about $10^5$).

The coefficients of the direct product functions in the symmetrized basis forms a matrix $\mathbf{S}$. The Hamiltonian matrix in the direct product basis can be transformed to the Hamiltonian in the symmetrized basis by the transformation

$$\tilde{\mathbf{H}}_{2n+2} = \mathbf{S}^\dagger \mathbf{H}_{2n+2} \mathbf{S}$$

(8)

The size of the symmetrized Hamiltonian matrix is of the order $\simeq 2000 \times 2000$ for a cut-off of $m = 100$. The low-lying eigenstates of this matrix can be obtained by Davidson’s algorithm.

The symmetry adaptation scheme described above has been implemented both within the infinite chain DMRG algorithm and within the finite system algorithm. In the latter,
we incorporate the $C_2$ symmetry only when the left and right parts of the system are identical, i.e. at the end of each finite system iteration. Without iterating over the density matrices of the fragments (i.e. within the infinite system algorithm), we find that the energy difference between a chain of length $N$ with $N+1$ and $N-1$ electrons is equal to the Hubbard parameter $U$ to an accuracy of $\approx 10^{-3}$. After three iterations of the finite system algorithm, the accuracy improves to $\approx 10^{-5}$, for a $U$ value of $4t$.

As an example of the use of the above technique, we present results of DMRG calculations for uniform Hubbard chains at half-filling, for $U/t$ of 4.0 and 6.0, with chain lengths of up to 50 sites. We have obtained the lowest energy states in all the eight subspaces (of $\hat{C}_2$, $\hat{J}$ and $\hat{P}$), keeping 70 to 150 eigenvectors of the density matrix. The extrapolated ground state energy per site of the infinite chain for both values of $U/t$ agrees with the exact values of $0.5737331t$ and $0.4200125t$ respectively to 5 decimal places.

The energy of the one-photon transition from the ground state (lying in the $^eA^+$ subspace) to the lowest energy state in the $^eB^-$ subspace defines the optical gap of the chain. In fig.1 we show a plot of optical gap vs. inverse chain length for $U/t = 4.0$ and 6.0 for different values of the cut-off $m$. The optical gaps for these values of $U/t$, from the Bethe ansatz solution for the infinite chain, are 1.2867$t$ and 2.8926$t$ respectively [12]. The corresponding extrapolated values from a polynomial fit in powers of $1/n$ from DMRG are 1.278$t$ and 2.895$t$, obtained with a cut-off of $m=150$ for $U/t = 4.0$ and $m=100$ for $U/t = 6.0$. We also find that the DMRG optical gap tends to saturate at shorter chain lengths as we decrease $m$. The fit of the optical gap to $1/n$ is a reasonably good straight line although the best fit is to a polynomial in this variable.

In fig.2 we plot the spin gap which we define as the energy gap between the lowest triplet state and the ground state singlet as a function of $1/n$. The Bethe ansatz solution
yields a vanishing spin gap in the thermodynamic limit of the uniform Hubbard chain. Polynomial fits to our DMRG data are consistent with this.

In fig. 3 we present the energy gaps, relative to the ground state, obtained by solving for the lowest energy state in each of the eight subspaces, for Hubbard chains with 40 to 50 sites, for the two values of $U/t$. The excitations clearly break up into two bands. The lower energy excitations correspond to states of different symmetry in the covalent subspace (i.e. predominantly spin excitations), while the higher energy excitations correspond to the ionic subspace (i.e. charge excitations). With increasing $U/t$ the states in the covalent subspace are less dispersed and so are the states in the ionic subspace. However, with increase in $U/t$ the gap between the two bands increases. This feature is in agreement with the basic physics of the Hubbard models.

To summarize, we have presented a symmetrized DMRG scheme for obtaining excitation gaps in different symmetry subspaces of a large model system. We have illustrated our scheme with applications to a uniform Hubbard model, wherein the known excitation gaps are very well reproduced. We expect that this scheme will prove invaluable in modelling the electronic state properties of polymers.

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References

1. S. R. White, Phys. Rev. Lett. 69, 2863 (1992); Phys. Rev. B 48, 10345 (1993).

2. R. M. Noack and S. R. White, Phys. Rev. B 47, 9243 (1993).

3. S. R. White and D. Huse, Phys. Rev B 48, 3844 (1993).

4. Erik S. Sorenson and Ian Affleck, Phys. Rev. B 49, 15771 (1994).

5. R. Chitra, Swapan K Pati, H. R. Krishnamurthy, Diptiman Sen and S. Ramasesha, Phys. Rev. B 52, 5681 (1995).

6. Hanbin Pang, Shoudan Liang and James F. Annett, Phys. Rev. Lett., 71, 4377 (1993).

7. Hanbin Pang and Shoudan Liang, Phys. Rev. B 51, 10287 (1995).

8. S. R. White, R. M. Noack and D. J. Scalapino, Phys. Rev. Lett., 73, 882 (1994).

9. Z. G. Soos and S. Ramasesha, Phys. Rev. B, 29, 5410 (1984).

10. Z. G. Soos, S. Ramasesha and D. S. Galvao, Phys. Rev. Lett., 71, 1609 (1993).

11. Z. G. Soos and S. Ramasesha, J. Chem. Phys., 90, 1067 (1989); S. Ramasesha and Z. G. Soos, Chem. Phys. Lett., 153, 171 (1988).

12. E. H. Lieb and F. Y. Wu, Phys. Rev. Lett., 20, 1445 (1968); A. A. Ovchinnikov, Sov. Phys - JETP, 30, 1160 (1970).
Figure Captions:

Fig.1:
Optical Gap as a function of inverse chain length for Hubbard chains with $U = 4.0t$ and $U = 6.0t$. $m$ corresponds to the number of density matrix eigenvectors retained in the DMRG procedure. Arrows indicate the model exact gaps for infinite chains.

Fig.2:
Spin Gap (defined in the text) as a function of $1/n$ for Hubbard chains with $U = 4.0t$ and $U = 6.0t$. $m$ corresponds to the DMRG cut-off. Model exact spin gaps vanish for infinite chains.

Fig.3:
Energy gaps (measured from the ground state) of the lowest state in each subspace for chain length varying from 40 to 50, for two different values of $U/t$. The level ordering is $E_{eA+} \downarrow E_{oA+} \downarrow E_{oB+} \downarrow E_{eB+} \downarrow E_{eA-} \downarrow E_{oB-} \downarrow E_{oA-}$. 

