MULTI-CONFIGURATIONAL SYMMETRIZED PROJECTOR QUANTUM MONTE CARLO METHOD FOR LOW-LYING EXCITED STATES OF THE HUBBARD MODEL

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ABSTRACT

We develop a novel multi-configurational Symmetrized Projector Quantum Monte Carlo (MSPQMC) method to calculate excited state properties of Hubbard models. We compare the MSPQMC results for finite Hubbard chains with exact results (where available) or with Density Matrix Renormalization Group (DMRG) results for longer chains. The energies and correlation functions of the excited states are in good agreement with those obtained from the alternate techniques.

1 Introduction

In recent years, numerical many-body techniques which have proved reliable for the study of the Hubbard model are the Projector Quantum Monte Carlo (PQMC) method[1, 2] and the Density Matrix Renormalization Group (DMRG)[3] method (for 1-D and quasi 1-D systems). These methods have been predominantly ground state techniques. The usual procedure for obtaining excited states of a many-body Hamiltonian in exact diagonalization schemes is to exploit the symmetries of the system and block-diagonalize the Hamiltonian[4]. The lowest few eigenvalues in each block can then be computed using standard numerical procedures. However, exact diagonalization schemes are limited to rather small system sizes, unlike either the DMRG scheme or the PQMC scheme. Implementation of symmetries in the latter schemes turns out to be nontrivial although desirable.

While the DMRG method could yield a few low-lying states, low-lying excited states of a chosen symmetry were inaccessible from this technique, until its recent extension to incorporate crucial symmetries of a system[5], which enables the method to target excited states as low-lying states in subspaces of a given irreducible representation of the symmetry group of the given system.

In contrast, the PQMC method has exclusively been a ground state technique for fermionic systems. Hitherto, it was not feasible to obtain even the ground state of the 2-D Hubbard model for arbitrary filling because of the open-shell structure of the non-interacting ground state[6]. Here, we present a novel multi-configurational symmetrized PQMC (MSPQMC) technique which makes it possible, for the first time, to obtain energies of excited states of the Hubbard Hamiltonian. The technique is also applicable to the ground state of open shell systems. We use the recently developed symmetrized PQMC method[7] to improve the Monte Carlo estimates of properties in the targeted state. In the next section, the formulation of the MSPQMC method will be presented. In section 3, we demonstrate the method by applying it to Hubbard chains. We also discuss numerical issues associated with the MSPQMC procedure.
2 The MSPQMC Method

The single band Hubbard Hamiltonian $\hat{H}$ for a system of $N$ sites, may be written as [8],

$$\hat{H} = \hat{H}_0 + \hat{H}_1 = -(\sum_{(ij),\sigma} t_{ij} \hat{a}_i^\dagger \hat{a}_j + h.c.) + U \sum_{i=1}^N \hat{n}_{i\uparrow} \hat{n}_{i\downarrow},$$  \hspace{1cm} (1)$$

where the symbols have their usual meanings.

Using the projection ansatz, the lowest eigenstate, $|\psi_0^\Gamma>\rangle$, in a given irreducible symmetry subspace $\Gamma$, of $\hat{H}$, can be projected from a trial wavefunction $|\phi^\Gamma>\rangle$ as

$$|\psi_0^\Gamma>\rangle = \lim_{\beta \to \infty} \frac{e^{-\beta \hat{H}}|\phi^\Gamma>\rangle}{\sqrt{<\phi^\Gamma|e^{-2\beta \hat{H}}|\phi^\Gamma>\rangle}},$$  \hspace{1cm} (2)$$

provided $|\phi^\Gamma>\rangle$ has a nonzero projection on to $|\psi_0^\Gamma>\rangle$. The trial wavefunction $|\phi^\Gamma>\rangle$ is usually formed from the molecular orbitals (MO) obtained as eigenfunctions of the non-interacting part, $\hat{H}_0$, of the full Hamiltonian. When the non-interacting ground state of a given system is a closed-shell state, the trial wavefunction $|\phi^\Gamma>\rangle$ for obtaining the interacting ground state can be chosen as a single nondegenerate electronic configuration in the MO basis. However, to obtain an excited state as the lowest eigenstate of the interacting model within a desired symmetry subspace $\Gamma$, of $\hat{H}$, can be chosen as a single nondegenerate electronic configuration as the trial wavefunction. Such a linear combination can be obtained by operating with the group theoretic projection operator [10] for the desired irreducible representation on a single excited MO-configuration. In order to fix the total spin of the target state, we use the Löwdin [9] projection operator to project out the desired spin state from the trial configuration transforming as $\Gamma$. The projection procedure in eqn. (2) conserves the symmetry of the initial state and hence projects out the lowest energy excited state of the interacting model with that symmetry from the trial state. The trial state $|\phi^\Gamma>\rangle$ in general takes the form,

$$|\phi^\Gamma>\rangle = \sum_{j=1}^p c_j^\Gamma |\phi_j^\Gamma>\rangle; \hspace{1cm} |\phi_j^\Gamma>\rangle = |\phi_{j,\sigma}^\Gamma>\rangle |\phi_{j,-\sigma}^\Gamma>\rangle,$$  \hspace{1cm} (3)$$

where $p$ is the number of degenerate MO-configurations in the symmetry adapted starting wavefunction. An MO-configuration with $M_\sigma$ fermions of spin $\sigma$ in second quantized form can be written as

$$|\phi_{j,\sigma}^\Gamma>\rangle = \prod_{m=1}^{M_\sigma} \left( \sum_{i=1}^N (\Phi^I_{\sigma})_{im} \hat{a}_i^\dagger \right) |0>,$$  \hspace{1cm} (4)$$
where \( \Phi_{j}^{\Gamma} \) is an \( N \times M_{\sigma} \) sub-matrix of the MO coefficients whose row index, \( i \), labels sites and the column index, \( m \), labels the MOs occupied by electrons of spin \( \sigma \), in the MO-configuration labelled by \( j \) and \( \Gamma \). The overlap of any two MO-configurations expressed in this form is given by

\[
\langle \phi_{j,\sigma}^{\Gamma} | \phi_{j',\sigma}^{\Gamma} \rangle = \det \left[ (\Phi_{j}^{\Gamma})^{T} (\Phi_{j'}^{\Gamma}) \right].
\]

In the PQMC method for the Hubbard model, the projection operator \( \exp(-\beta \hat{H}) \) is Trotter decomposed as \( (\exp(-\Delta \tau \hat{H}))^{L} \) with \( L \) imaginary time slices of width \( \Delta \tau \) \((\beta = L \times \Delta \tau)\). This is followed by a discrete Hubbard-Stratanovich (H-S) transformation\(^{11}\) of the on-site interaction Hamiltonian at each site \( i \) and each time-slice \( l \), in terms of Ising-like fields, \( s_{il} \), leading to the result

\[
e^{-\Delta \tau \hat{H}} = \sum_{\{s_{l}\}} \hat{X}_{\sigma}(l, s_{l}) \hat{X}_{-\sigma}(l, s_{l})
\]

where the summation is over all possible \( N \)-vectors \( s_{l} \) whose \( i^{th} \) components correspond to the H-S field, \( s_{it} \). \( \zeta_{\sigma} \) is \(+1\) \((-1\)) for electrons with \( \uparrow \) \((\downarrow)\) spin and the H-S parameter \( \lambda = 2 \text{arctanh} \sqrt{\tanh(\Delta \tau U / 4)} \). Thus,

\[
e^{-\beta \hat{H}} = \sum_{\{s\}} \hat{W}_{\sigma}(\{s\}) \hat{W}_{-\sigma}(\{s\}) = \sum_{\{s\}} \hat{W}(\{s\})
\]

The action of each of the terms in the summation in eqn. (6) on a trial state of the form in eqn. (4) can be obtained as the left multiplication of the \( N \times M_{\sigma} \) matrix \( \Phi_{j}^{\Gamma} \) by an \( N \times N \) matrix, \( B_{\sigma}(l, s_{l}) \), given by

\[
B_{\sigma}(l, s_{l}) = b_{0} b_{1\sigma}(l, s_{l}) b_{0}
\]

The matrix \( b_{0} \) is given by \( \exp[-\mathbf{K}] \), with \( K_{ij} = -\frac{\Delta \tau}{2} t_{ij} \). The matrix \( b_{1\sigma}(l, s_{l}) \) is diagonal with elements \( \delta_{ij} \frac{1}{2} \exp[\zeta_{\sigma} s_{il} - \frac{\Delta \tau}{2}] \).

To obtain the expectation value of an operator \( \hat{O} \) in the targetted state, when the trial state is a single MO-configuration, \( \langle \hat{O} \rangle = \langle \psi^{\Gamma} | \hat{O} | \psi^{\Gamma} \rangle / \langle \psi^{\Gamma} | \psi^{\Gamma} \rangle \) we define states \( |R(l, \{s_{R}\})\rangle \) and \( |L(l, \{s_{L}\})\rangle \). The former is obtained by projecting the trial wavefunction through the right Ising lattice \( \{s_{R}\} \) formed by time-slices 1 through \( l \), while
the latter is obtained by projecting its transpose through the left Ising lattice \( \{s_L\} \) time-slices \( L \) through \( L - l + 1 \),

\[
|\psi^F> \approx \sum_{\{s_R\}} |R^F(l, \{s_R\})> = \sum_{\{s_R\}} \hat{W}(\{s_R\})|\phi^F>
\]

(11)

\[
<\psi^F| \approx \sum_{\{s_L\}} <L^F(l, \{s_L\})| = \sum_{\{s_L\}} <\phi^F|\hat{W}(\{s_L\})
\]

(12)

This allows us to express \( <\hat{O}> \) as a weighted average, \( \sum_{\{s\}} \omega^F(\{s\})O^F(\{s\}) \), with weights given by,

\[
\omega^F(\{s\}) = \frac{<L^F(l, \{s_L\})|R^F(l, \{s_R\})>}{\sum_{\{s\}} <\phi^F|\hat{W}(\{s\})|\phi^F>}
\]

(13)

\[
O^F(\{s\}) = \frac{<L^F(l, \{s_L\})|\hat{O}|R^F(l, \{s_R\})>}{<L^F(l, \{s_L\})|R^F(l, \{s_R\})>}
\]

(14)

For example, if the operator \( \hat{O} \) is the single-particle operator \( \hat{a}^\dagger_{l\sigma} \hat{a}_{l\sigma} \), \( O^F(\{s\}) \) takes the form,

\[
O^F(\{s\}) = \left((R^F_\sigma(l, \{s\}))(L^F_\sigma(l, \{s\})R^F_\sigma(l, \{s\})^{-1}(L^F_\sigma(l, \{s\}))\right)_{kl}.
\]

(15)

which is the \( kl^{th} \) element of the single-particle Green function, \( G^F_\sigma(l, \{s\}) \). If we weight average the property over all the Ising-configurations, we would obtain the expectation value of that property in the targeted state, exact to within Trotter error. However, exhausting all Ising-configurations in an averaging procedure is impractical and the denominator in the eqn. (13) cannot be known explicitly. Therefore, we resort to an importance sampling Monte Carlo (MC) estimation in which a knowledge of the ratio of weights, \( r \), for any two configurations \( \{s'\} \) and \( \{s\} \), \( \omega^F(\{s'\})/\omega^F(\{s\}) \) is sufficient for obtaining property estimates. The ratio, \( r \) is given by the ratio of inner products of the right and left projected states (using eqn. (7)) for the two Ising-configurations,

\[
r = \prod_\sigma \frac{det\left(L^F_\sigma(l, \{s_L\})R^F_\sigma(l, \{s_R\})\right)}{det\left(L^F_\sigma(l, \{s_L\})R^F_\sigma(l, \{s_R\})\right)}
\]

(16)

Ising-configurations are generated by sequential single spin-flips through the lattice, examining each site at a given time slice, \( l \), before proceeding to the next. This allows efficient computation of the ratio, \( r \). Using the heat bath algorithm, the new configuration is accepted or rejected with a probability \( r/(1 + r) \).

The above procedure can be extended to a multi-configuration trial function \( (p > 1 \) in eqn.(3)) and the ratio of weights for Ising-configurations \( \{s'\} \) and \( \{s\} \) takes the form,

\[
\frac{\omega^F(\{s'\})}{\omega^F(\{s\})} = \frac{<L^F(l, \{s'\})|R^F(l, \{s'\})>}{<L^F(l, \{s\})|R^F(l, \{s\})>}
\]

(17)
where the projected states $|R^\Gamma(l, \{s_R\})>$ and $<L^\Gamma(l, \{s_L\})|$ are given by

$$
|R(l, \{s_R\})> = \sum_j c_j^\Gamma \prod_\sigma |R_{\sigma}^\Gamma(l, \{s_R\})>
$$

(18)

$$
<L(l, \{s_L\})| = \sum_j c_j^\Gamma \prod_\sigma <L_{\sigma}^\Gamma(l, \{s_L\})|
$$

(19)

with each state in the summations obtained in a manner analogous to the single-determinantal case. The ratio (eqn. (17)) is now given as the ratio of sums of determinants appearing in the numerator and denominator. Evaluating the ratio hence turns out to be more time consuming than in the single determinantal case.

Property estimates in the single-determinantal PQMC procedure, with a sequential, single spin-flip algorithm, are carried out by computing the Green function (eqn. (15)) at the time slice at which a spin-flip is attempted. This allows the use of an $O(N^2)$ updating algorithm for the Green function instead of the usual $O(N^3)$ direct algorithm. This is also applicable in the MSPQMC method, except when the states $<L_{\sigma}^\Gamma(l, \{s_L\})|$ and $|R_{\sigma}^\Gamma(l, \{s_R\})>$ are orthogonal. In this case we use the explicit method of calculating matrix elements of the single-particle Green function\cite{2}. The energies presented in this communication have been obtained from the Green function (eqn. (15)) estimated at the last time-slice, even when a spin flip is attempted at any intermediate time slice. Such an estimate of energy will be more accurate, although it precludes the use of an $O(N^2)$ updating algorithm. However, we still employ the single sequential spin-flip mechanism as it reduces the number of matrix multiplications involved in the computation of the Green function.

In the MSPQMC method for excited states, we encounter the negative sign problem even at half-filling although the number of occurrences of the negative signs even at large $U/t$ is insignificant (for $N = 20$, $U/t = 6$, the fraction of the sample for which negative signs are encountered is $\approx 10^{-4}$). The sign problem here arises because of the phases with which the configurations in the trial state are combined although products of individual determinants of up and down spin corresponding to $<L_{\sigma}^\Gamma(l, \{s_L\})|$ and $|R_{\sigma}^\Gamma(l, \{s_R\})>$ are positive. The MSPQMC method, besides being accurate for higher dimensional systems, also has the advantage in one-dimensional systems over the DMRG method in that the estimates of longer range correlations are as accurate as the nearest neighbour correlations.

One of the shortcomings of both single- and multi-configurational PQMC calculations carried out as described above is that the estimated properties do not reflect the symmetries of the system, as the sampled Ising-configurations do not have the full symmetry of the Hamiltonian. To obtain symmetrized property estimates, it is necessary to sample all symmetry related Ising-configurations of every Ising configuration that is sampled. We have achieved this by a symmetrized PQMC (SPQMC) procedure along the lines of the single-determinantal SPQMC method\cite{7}. Such a symmetrized sampling reduces errors in estimates as the sample size is increased by a factor which is of the order of the symmetry group, for a marginally small computational overhead.
3 Results and Discussion

The Hubbard chains and rings of $\leq 14$ sites can be solved exactly for energies of low-lying excitations in various symmetry subspaces. These results provide a strong check on the accuracy of the method. Besides, longer Hubbard chains can be solved to a high degree of accuracy by the DMRG method and we have compared our MSPQMC results against the DMRG results for longer chains ($N$ up to 20). We have computed the energies of the lowest excited singlet state connected to the ground state by a dipole transition as well the energies of the lowest triplet states for several values of the Hubbard parameter $U$ and chain length $N$. The projection parameter $\beta$ is set to 2.0 with a $\Delta \tau$ of 0.1, all in units of $t^{-1}$. All the estimates were carried out by averaging over 8000 spin flips per Ising spin after allowing 2000 spin flips per Ising spin for equilibration.

In table 1 we present the MSPQMC energies for three different values of $U/t$. We note that the MSPQMC energies are in very good agreement with exact results ($N \leq 12$) or high precision DMRG results for ($N > 12$). The agreement is better at lower correlation strengths. While the DMRG energies are better than the MSPQMC energies [5], for the chosen states, it is worth noting that the MSPQMC excitation gaps have a better accuracy than the absolute energies as the errors in the individual energies for the ground as well as the excited states are comparable and have the same sign.

In fig. (1), we have shown the dependence of the two excitation gaps (with respect to the ground state) as a function of $U/t$ for different chain lengths. The ’optical’ gap increases with $U/t$ while decreasing with $N$ for a fixed $U/t$. The ’spin’ gap decreases with $U/t$ with the dependence on $N$ being similar to the optical gap for a fixed $U/t$. This feature is in agreement with exact as well as DMRG calculations.

To conclude, we have shown that the PQMC method can be extended to excited states using the symmetries of the Hamiltonian via a multi-configurational formulation of the PQMC method. Property estimates can be improved by symmetrized sampling along the lines of a single-configuration SPQMC procedure. To characterize excited states, we have also calculated other quantities such as bond-orders, spin correlations and charge correlations. All these quantities are in good agreement with exact/DMRG results and will be presented in a longer paper.

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Figure Captions

Figure 1. "Optical" (filled symbols) and "Spin" (open symbols) gaps as a function of correlation strength \((U/t)\) for Hubbard chains of 16 (squares), 18 (circles) and 20 (triangles) sites, from the MSPQMC method.

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Table 1. MSPQMC energies (A) of lowest dipole allowed singlet and lowest triplet excitations (in units of $t$) for Hubbard chains of length 8 to 20 sites compared with exact/DMRG results (B). For chain lengths ($\geq$ 14 sites) comparison is with symmetrized DMRG results with a cut-off of 150. Data for $U/t$=6.0 is with $\Delta \tau = 0.05$.

| $U/t$ | $N$ | Singlet | | Triplet |
|-------|-----|---------|---|---------|
|       |     | A       | B | A       | B |
| 1.0   | 6   | -4.4766 | -4.4777 | -4.9331 | -4.9189 |
|       | 8   | -6.7881 | -6.7906 | -7.1378 | -7.1381 |
|       | 10  | -9.0185 | -9.0208 | -9.3066 | -9.3083 |
|       | 12  | -11.2030 | -11.2058 | -11.4470 | -11.4516 |
|       | 14  | -13.3581 | -13.3634 | -13.5767 | -13.5785 |
|       | 16  | -15.5007 | -15.5032 | -15.6858 | -15.6948 |
|       | 18  | -17.6262 | -17.6307 | -17.7970 | -17.8037 |
|       | 20  | -19.7429 | -19.7494 | -19.8998 | -19.9073 |
| 4.0   | 6   | -0.3987 | -0.4221 | -2.7088 | -2.6915 |
|       | 8   | -1.8982 | -1.9301 | -3.9462 | -3.9165 |
|       | 10  | -3.2633 | -3.3044 | -5.0796 | -5.1151 |
|       | 12  | -4.5378 | -4.6062 | -6.2310 | -6.2989 |
|       | 14  | -5.7782 | -5.8645 | -7.4085 | -7.4734 |
|       | 16  | -7.0329 | -7.0948 | -8.5557 | -8.6418 |
|       | 18  | -8.2260 | -8.3059 | -9.6945 | -9.8060 |
|       | 20  | -9.3868 | -9.5036 | -10.8457 | -10.9672 |
| 6.0   | 6   | 1.9294  | 1.9212 | -1.9793 | -1.9707 |
|       | 8   | 0.7405  | 0.6990 | -2.9178 | -2.8677 |
|       | 10  | -0.3477 | -0.3723 | -3.7362 | -3.7455 |
|       | 12  | -1.3415 | -1.3639 | -4.6146 | -4.6123 |
|       | 14  | -2.2349 | -2.3089 | -5.4068 | -5.4724 |
|       | 16  | -3.1609 | -3.2248 | -6.2614 | -6.3280 |
|       | 18  | -4.0374 | -4.1214 | -7.1203 | -7.1805 |
|       | 20  | -4.8692 | -5.0047 | -7.8726 | -8.0308 |
