ESTIMATION OF PROPERTIES OF LOW-LYING EXCITED STATES OF HUBBARD MODELS : A MULTI-CONFIGURATIONAL SYMMETRIZED PROJECTOR QUANTUM MONTE CARLO APPROACH [1]

Bhargavi Srinivasan[3], S. Ramasesha[3,5] and H. R. Krishnamurthy[4,5]   [2]

[3]*Solid State and Structural Chemistry Unit*
Indian Institute of Science, Bangalore 560 012, India

[4]*Department of Physics*
Indian Institute of Science, Bangalore 560 012, India

[5]*Jawaharlal Nehru Centre for Advanced Scientific Research*
Jakkur Campus, Bangalore 560 064, India

---

[2]e-mail: bhargavi@sscu.iisc.ernet.in, ramasesh@sscu.iisc.ernet.in,
hrkrish@physics.iisc.ernet.in

ABSTRACT

We present in detail the recently developed multiconfigurational symmetrized-projector quantum Monte Carlo (MSPQMC) method for excited states of the Hubbard model. We describe the implementation of the Monte Carlo method for a multiconfigurational trial wavefunction. We give a detailed discussion of issues related to the symmetry of the projection procedure which validates our Monte Carlo procedure for excited states. In this context we discuss various averaging procedures for the Green function and present an analysis of the errors incurred in these procedures. We study the ground state energy and correlation functions of the one-dimensional Hubbard model at half-filling to confirm these analyses. We then study the energies and correlation functions of excited states of Hubbard chains. Hubbard rings away from half-filling are also studied and the pair binding energies for holes of $4n$ and $4n + 2$ systems are compared with the Bethe ansatz results of Fye, Martins and Scalettar. Our study of the two-dimensional Hubbard model includes the 4×2 ladder and the 3×4 lattice with periodic boundary conditions. The 3×4 lattice is non-bipartite and amenable to exact diagonalization studies and is therefore a good candidate for checks on the method. We are able to reproduce accurately the energies of ground and excited states, both at and away from half-filling. We study the properties of the 4×2 Hubbard ladder with bond-alternation as the correlation strength and filling are varied. The method reproduces the correlation functions accurately. We also examine the severity of sign-problem for one- and two-dimensional systems.

1 Introduction

The study of the Hubbard model for understanding the basic physics underlying many electronic phenomena in the solid state continues to hold centerstage despite its apparent simplicity. While the model has exact solutions in very special limits [1, 2], more general and experimentally relevant regimes of the Hubbard model still defy exact solutions. This has led to the development of a variety of variational, perturbative and nonperturbative numerical many-body techniques. In recent years, efficient and reliable nonperturbative approaches have been developed to study the Hubbard model on finite lattices over a wide region of its parameter space. Amongst these, the projector quantum Monte Carlo (PQMC) method[3, 4] and the density matrix renormalization group (DMRG)[5] method (for 1-D and quasi 1-D systems) have allowed accurate studies of large Hubbard clusters. However, these methods have mainly been limited to obtaining ground state properties. Clearly, properties of the excited states and excitation gaps of the model are important for many purposes. Inspite of the importance of the excited states, there do not exist numerical many-body methods of sufficient generality to access these states of Hubbard-like models for large clusters.

The many-body excited states of small clusters can be obtained from exact diagonalization methods. The usual procedure for obtaining excited states in these methods is to exploit the symmetries of the system and block-diagonalize the Hamiltonian[6] in a convenient basis. The lowest few eigenvalues in each block can then be computed using numerical techniques such as the Davidson or modified Lanczos algorithms[7, 8].

The block-diagonalization of the Hamiltonian matrix in the DMRG scheme is non-trivial because of the choice of basis. 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 given system[9]. This has now made it possible to target excited states as low-lying states in a subspace of a chosen irreducible representation of the symmetry group of a given system.

The PQMC method has exclusively been a ground state technique for fermionic systems. Furthermore, even the ground state of the Hubbard model for arbitrary filling is inaccessible from the PQMC method when the non-interacting ground state has an open-shell structure. Employing a single configuration as a trial state for the ground state properties of the Hubbard model in such contexts results in inaccurate estimates of properties[10].

There have been a few attempts to obtain excited state properties via quantum Monte Carlo approaches. Ceperley and Bernu [11] introduced a scheme within a Green function Monte Carlo method for obtaining the rotational-vibrational spectra of polyatomic molecules for a given potential function. This approach is based on constructing a matrix representation of the Hamiltonian using approximate functions which under "time" evolution have progressively larger projections onto the space of low-lying eigenstates. However, this method has not been used in the context of the Hubbard model. Takahashi exploited the translational invariance of spin chains to obtain the des Cloizeaux-Pearson spectrum within a Green function Monte Carlo technique[12]. There has been no generalization of this technique to arbitrary symmetries and its use has been restricted to spin Hamiltonians.

In a recent paper we reported a novel multi-configurational symmetrized PQMC (MSPQMC) technique[13] which made it possible, for the first time, to obtain energies of *excited states* of the Hubbard Hamiltonian, within a Monte Carlo scheme. The method was illustrated for the excitation gaps of half-filled Hubbard chains. In this paper, we describe the MSPQMC method in detail including the symmetrized sampling procedure for accurate property estimates. We apply the technque to one- and two-dimensional Hubbard models to obtain properties of ground and excited states at various fillings and compare these with exact results for small systems. We also present a detailed discussion of the negative-sign problem encountered in the MSPQMC method. We summarize our results in the last section.

2 The MSPQMC Method

In this section we describe the multi-configurational symmetrized projector quantum Monte Carlo method for ground state properties of open shell systems and properties of excited states. In the first subsection, we give a brief description of the conventional PQMC algorithm to make this paper self-contained. The reader is referred to other papers[3, 4] for more details. We then describe the generalization of this method to multi-configurational trial states. However, in targetting an excited state, the validity of the approximations and transformations carried out in single configurational Monte Carlo procedure need to be re-examined. After describing the implementation of the MSPQMC method, this issue is dealt with in detail in subsection (2.2) and is shown to lead naturally to the idea of symmetrized sampling. Furthermore, the errors arising out of the averaging procedure are examined and the difference between the estimation of energy and other properties is highlighted. This section is concluded with a discussion of the negative-sign problem in the MSPQMC method.

2.1 Implementation of the MSPQMC method

The single band Hubbard Hamiltonian $\hat{H}$ for a system of N sites, may be written as[14],

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

where the symbols have their usual meanings.

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

$$|\psi_0^\Gamma\rangle = \lim_{\beta \to \infty} \frac{e^{-\beta \hat{H}} |\phi^\Gamma\rangle}{\sqrt{\langle \phi^\Gamma | e^{-2\beta \hat{H}} |\phi^\Gamma\rangle}}, \tag{2}$$

provided $|\phi^\Gamma\rangle$ has a nonzero projection on to $|\psi_0^\Gamma\rangle$. This principle was first used in diffusion Monte Carlo simulations of quantum systems wherein the trial state is evolved using a random walk algorithm to obtain a stationary solution corresponding to the ground state of the system[15]. In the context of the Hubbard model, however, this ansatz is implemented using the Trotter formula and the Hubbard-Stratanovich transformation to estimate expectation values of operators in the ground state of the Hamiltonian, without explicitly computing the ground state wavefunction.

In simulations of the Hubbard model, the trial wavefunction $|\phi^\Gamma\rangle$ is usually formed from the molecular orbitals (MOs) 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, $|\psi_0^\Gamma\rangle$, is usually chosen to be a single nondegenerate electronic configuration in the MO basis. Such a choice is adequate to ensure convergence to the ground state for reasonable values of the projection parameter, β and Monte Carlo parameters.

Within the framework of the projection ansatz, one can clearly target excited states as the lowest states in various symmetry subspaces, by choosing trial wavefunctions of the appropriate symmetry. However, for this purpose, a single MO-configuration is no longer an adequate trial wavefunction, since a symmetrized trial wavefunction, $|\phi^\Gamma\rangle$, is usually a symmetrized linear combination of *degenerate* excited MO-configurations. Such a linear combination corresponding to the desired irreducible representation, Γ, can be obtained, atleast formally, by operating with the group theoretic projection operator, $\hat{P}^\Gamma$[16]:

$$\hat{P}^\Gamma = \sum_{\hat{R}} \chi^\Gamma(\hat{R})\hat{R} \tag{3}$$

where $\chi^\Gamma(\hat{R})$ is the character of symmetry element $\hat{R}$ in the Γth irreducible representation, on a single excited MO-configuration. In particular, to fix the total spin, S of the target state, we use the Löwdin[17] projection operator, $\hat{P}_S$,

$$\hat{P}_S = \prod_{S'\neq S} [\hat{S}^2 - S'(S'+1)], \tag{4}$$

to project out the desired spin state from a trial configuration. The projection procedure in eqn. (2) conserves the symmetry of the initial state and hence projects out the lowest energy state of the interacting model of that symmetry subspace from the trial state. The trial state $|\phi^\Gamma\rangle$ in general takes the form,

$$|\phi^\Gamma\rangle = \sum_{j=1}^{p} c_j^\Gamma |\phi_j^\Gamma\rangle \;\; ; \;\; |\phi_j^\Gamma\rangle = |\phi_{j,\sigma}^\Gamma\rangle|\phi_{j,-\sigma}^\Gamma\rangle, \tag{5}$$

where p is the number of MO-configurations in the symmetry adapted starting wavefunction.

A single MO-configuration, $|\phi_{j,\sigma}^\Gamma\rangle$, with M_σ fermions of spin σ can be expressed in second quantized form as,

$$|\phi_{j,\sigma}^\Gamma\rangle = \prod_{m=1}^{M_\sigma} \Big(\sum_{i=1}^{N} (\mathbf{\Phi}_\sigma^{j\Gamma})_{im} \hat{a}_{i\sigma}^\dagger\Big)|0\rangle \tag{6}$$

where $\mathbf{\Phi}_\sigma^{j\Gamma}$ 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 σ, in the jth MO-configuration in the irreducible representation Γ. For example, a choice of multi-configurational trial wavefunction for the lowest singlet(S) and triplet(T) states in the

B^--space of the half-filled Hubbard chain of six sites with electron-hole and inversion symmetries can be written as

$$
\begin{aligned}
|\phi_S^{B^-}\rangle &= |\phi_1^{B^-}\rangle + |\phi_2^{B^-}\rangle \; ; \\
|\phi_T^{B^-}\rangle &= |\phi_1^{B^-}\rangle - |\phi_2^{B^-}\rangle \; ; \quad (7) \\
|\phi_1^{B^-}\rangle &= [b_{3\uparrow}^\dagger b_{2\uparrow}^\dagger b_{1\uparrow}^\dagger]|0\rangle [b_{4\downarrow}^\dagger b_{2\downarrow}^\dagger b_{1\downarrow}^\dagger]|0\rangle \quad (8) \\
|\phi_2^{B^-}\rangle &= [b_{4\uparrow}^\dagger b_{2\uparrow}^\dagger b_{1\uparrow}^\dagger]|0\rangle [b_{3\downarrow}^\dagger b_{2\downarrow}^\dagger b_{1\downarrow}^\dagger]|0\rangle, \quad (9)
\end{aligned}
$$

where $b^\dagger$'s are the creation operators for the MOs. The overlap of any two MO-configurations (eqn. (6)) is given by

$$
\langle \phi_{j,\sigma}^\Gamma | \phi_{j',\sigma}^\Gamma \rangle = det\Big[(\mathbf{\Phi}_\sigma^{j\Gamma})^T (\mathbf{\Phi}_\sigma^{j'\Gamma}) \Big]. \quad (10)
$$

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[18] of the on-site interaction Hamiltonian. The discrete H-S transformation applied to a single interaction term, $exp(\Delta\tau U \hat{n}_\uparrow \hat{n}_\downarrow)$, yields

$$
e^{\Delta\tau U \hat{n}_\uparrow \hat{n}_\downarrow} = \sum_{s=\pm 1} e^{\lambda s(\hat{n}_\uparrow - \hat{n}_\downarrow) - \frac{\Delta\tau U}{2}(\hat{n}_\uparrow + \hat{n}_\downarrow)} \quad (11)
$$

where s is a single H-S field and $\lambda = 2arctanh\sqrt{tanh(\Delta\tau U/4)}$ is the H-S parameter. Thus, at a given time-slice, l, the interaction term can be expressed as the exponential of a non-interacting Hamiltonian in terms of Ising-like fields, s_{il},

$$
e^{-\Delta\tau \hat{H}} = \sum_{\{\mathbf{s}_l\}} \hat{X}_\sigma(l, \mathbf{s}_l) \hat{X}_{-\sigma}(l, \mathbf{s}_l) \quad (12)
$$

$$
\hat{X}_\sigma(l, \mathbf{s}_l) = exp[\frac{-\Delta\tau}{2} \hat{H}_0] \left(\sum_{\{\mathbf{s}_l\}} exp[\zeta_\sigma \lambda \sum_i s_{il} \hat{n}_{i\sigma} - \frac{\Delta\tau U}{2}] \right) exp[\frac{-\Delta\tau}{2} \hat{H}_0] \quad (13)
$$

where the summation is over all possible N-vectors $\mathbf{s}_l$ whose i^{th} components correspond to the H-S field and s_{il}, ζ_σ is +1 (-1) for electrons with $\uparrow$ ($\downarrow$) spin. Thus,

$$
e^{-\beta \hat{H}} = \sum_{\{s\}} \hat{W}_\sigma(\{s\}) \hat{W}_{-\sigma}(\{s\}) = \sum_{\{s\}} \hat{W}(\{s\}) \quad (14)
$$

$$
\hat{W}_\sigma(\{s\}) = \hat{X}_\sigma(L, \mathbf{s}_L) \ldots \hat{X}_\sigma(1, \mathbf{s}_1) \quad (15)
$$

The action of each term in the summation in eqn. (12) on a single configuration j of the trial state of the form in eqn. (6) can be obtained as the left multiplication of the $N \times M_\sigma$ matrix $\mathbf{\Phi}_\sigma^{j\Gamma}$ by an $N \times N$ matrix, $\mathbf{B}_\sigma(l, \mathbf{s}_l)$, given by

$$
\mathbf{B}_\sigma(l, \mathbf{s}_l) = \mathbf{b}_0 \mathbf{b}_{1\sigma}(l, \mathbf{s}_l) \mathbf{b}_0 \quad (16)
$$

The matrix $\mathbf{b}_0$ is given by $exp[-\mathbf{K}]$, with $K_{ij} = -\frac{\Delta\tau}{2}t_{ij}$. The matrix $\mathbf{b}_{1\sigma}(l, \mathbf{s}_l)$ is diagonal with elements $\delta_{ij}\frac{1}{2}exp[\zeta_\sigma \lambda s_{il} - \frac{\Delta\tau U}{2}]$.

The expectation value of an operator $\hat{O}$ in the targetted state is given by

$$\langle \hat{O} \rangle = \frac{\langle \psi^\Gamma | \hat{O} | \psi^\Gamma \rangle}{\langle \psi^\Gamma | \psi^\Gamma \rangle}. \tag{17}$$

To compute such expectation values for a *single-configurational* trial wavefunction, we define right and left projected states $|R^\Gamma(l, \{s_R\})\rangle$ and $\langle L^\Gamma(l, \{s_L\})|$. 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 $\{s_L\}$ formed by time-slices L through $l+1$,

$$
\begin{aligned}
|R^\Gamma(l, \{s_R\})\rangle &= \hat{X}_\sigma(l, \mathbf{s}_l)\dots\hat{X}_\sigma(1, \mathbf{s}_1)|\phi^\Gamma\rangle \\
\langle L^\Gamma(l, \{s_L\})| &= \langle \phi^\Gamma | \hat{X}_\sigma(L, \mathbf{s}_L)\dots\hat{X}_\sigma(l+1, \mathbf{s}_l)
\end{aligned} \tag{18}
$$

The matrices $\mathbf{R}^\Gamma(l, \{s_R\})$ and $\mathbf{L}^\Gamma(l, \{s_L\})$ which generate the states $|R^\Gamma(l, \{s_R\})\rangle$ and $\langle L^\Gamma(l, \{s_L\})|$ in a manner analogous to eqn. (6) are given by

$$
\begin{aligned}
\mathbf{R}^\Gamma(l, \{s_R\}) &= \mathbf{B}_\sigma(l, \mathbf{s}_l)\dots\mathbf{B}_\sigma(1, \mathbf{s}_1)\mathbf{\Phi}_\sigma^{j\Gamma} \\
\mathbf{L}^\Gamma(l, \{s_L\}) &= \left(\mathbf{\Phi}_\sigma^{j\Gamma}\right)^T \mathbf{B}_\sigma(L, \mathbf{s}_L)\dots\mathbf{B}_\sigma(l+1, \mathbf{s}_{l+1})
\end{aligned} \tag{19}
$$

For $l \approx L/2$, the targetted state $|\psi^\Gamma\rangle$ can be approximated as

$$
\begin{aligned}
|\psi^\Gamma\rangle &\approx \sum_{\{s_R\}} |R^\Gamma(l, \{s_R\})\rangle \\
\langle \psi^\Gamma | &\approx \sum_{\{s_L\}} \langle L^\Gamma(l, \{s_L\})|
\end{aligned} \tag{20}
$$

This allows us to express $\langle \hat{O} \rangle$ as a weighted average over Ising configurations $\{s\}$,

$$\langle \hat{O}(l) \rangle = \sum_{\{s\}} \omega^\Gamma(\{s\})O^\Gamma(\{s\}) \tag{21}$$

where the weight $\omega^\Gamma(\{s\})$ is given by,

$$\omega^\Gamma(\{s\}) = \frac{\langle L^\Gamma(l, \{s_L\})|R^\Gamma(l, \{s_R\})\rangle}{\sum_{\{s\}} \langle \phi^\Gamma | \hat{W}(\{s\})|\phi^\Gamma\rangle} \tag{22}$$

$$\tag{23}$$

and $O^{\Gamma}(l, \{s\})$, the term in the expectation value corresponding to the Ising-configuration $\{s\}$ is given by,

$$O^{\Gamma}(l, \{s\}) = \frac{\langle L^{\Gamma}(l, \{s_L\})|\hat{O}|R^{\Gamma}(l, \{s_R\})\rangle}{\langle L^{\Gamma}(l, \{s_L\})|R^{\Gamma}(l, \{s_R\})\rangle}. \tag{24}$$

For example, we could estimate the equal time Green function, at the time-slice l, $\mathbf{G}_\sigma(l, \{s\})$, which we regard as a matrix in the Wannier basis, for spin σ, for an Ising-configuration $\{s\}$. The $(m, n)^{th}$ matrix element of $\mathbf{G}_\sigma(l, \{s\})$ is given by

$$(\mathbf{G}_\sigma(l, \{s\}))_{mn} = \frac{\langle L_\sigma(l, \{s\})|\hat{a}_{m\sigma}\hat{a}_{n\sigma}^\dagger|R_\sigma(l, \{s\})\rangle}{\langle L_\sigma(l, \{s\})|R_\sigma(l, \{s\})\rangle} \tag{25}$$

Thus, when the operator $\hat{O}$ is the single-particle operator, $\hat{a}_{m\sigma}\hat{a}_{n\sigma}^\dagger$ and the trial wavefunction is a single MO-configuration, $O^{\Gamma}(l, \{s\})$ can be shown to take the form[4],

$$O^{l,\Gamma}(l, \{s\}) = (\mathbf{G}_\sigma(l, \{s\}))_{mn} = \left(\mathbf{R}_\sigma^{\Gamma}(l, \{s\})(\mathbf{L}_\sigma^{\Gamma}(l, \{s\})\mathbf{R}_\sigma^{\Gamma}(l, \{s\})^{-1}\mathbf{L}_\sigma^{\Gamma}(l, \{s\})\right)_{mn}. \tag{26}$$

If we weight average the property over all the Ising-configurations, we would obtain the expectation value of that property in the targetted state, exact to within Trotter error. However, exhausting all Ising-configurations in an averaging procedure is impractical and the denominator in eqn. (23) 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 $\{s\}$, $\omega^{\Gamma}(\{s'\})/\omega^{\Gamma}(\{s\})$ is sufficient for obtaining property estimates. Using eqn. (10), this ratio can be written as

$$r = \prod_\sigma r_\sigma = \prod_\sigma \frac{det\left(\mathbf{L}_\sigma^{\Gamma}(l, \{s_L'\})\mathbf{R}_\sigma^{\Gamma}(l, \{s_R'\})\right)}{det\left(\mathbf{L}_\sigma^{\Gamma}(l, \{s_L\})\mathbf{R}_\sigma^{\Gamma}(l, \{s_R\})\right)} \tag{27}$$

Obtaining the ratio of determinants and the Green function, in practice, involves obtaining the inverse of a matrix which is an $O(N^3)$ operation for an $N \times N$ matrix. If a single spin flip mechanism is used, the ratio for flipping spin s_{il} in the configuration $\{s\}$ to s_{il}' obtain the configuration $\{s'\}$, r, can be expressed as

$$r = \prod_\sigma \frac{det(\mathbf{L}_\sigma^{\Gamma}(l, \{s_L'\})(1 + \mathbf{\Delta}_\sigma)R_\sigma^{\Gamma}(l, \{s_R'\}))}{det(\mathbf{L}_\sigma(l)\mathbf{R}_\sigma(l))} \tag{28}$$

where
$$\mathbf{\Delta}_{\sigma jj'} = \begin{cases} \delta_\sigma = exp(\lambda\zeta_\sigma(s_{il}' - s_{il})) - 1 & \text{for } j = j' = i \\ 0 & \text{otherwise} \end{cases} \tag{29}$$

The ratio of determinants r_σ can be written in terms of the Green function as,

$$r_\sigma = |1 + \delta_\sigma(\mathbf{G}_\sigma(l, \{s\}))_{ii}| \tag{30}$$

Once the new configuration $\{s'\}$ is accepted, its Green function $G'_\sigma(l)$ (dropping arguments for clarity) can be calculated from the Green function of the old configuration, $G_\sigma(l, \{s\})$ as

$$(\mathbf{G}'_\sigma(l))_{mn} = (\mathbf{\Delta}_\sigma \mathbf{b}_1)_{mm} (\mathbf{b}_1^{-1})_{mm} \left[(\mathbf{G}_\sigma(l))_{mn} - \frac{(\mathbf{G}_\sigma(l))_{mi} \delta_\sigma (\mathbf{G}_\sigma(l))_{in}}{1 + (\mathbf{G}_\sigma(l))_{ii} \delta_\sigma} \right] \tag{31}$$

In the ususal PQMC procedure, 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. The matrix elements of the Green function are computed at the time slice at which Ising spin flips are attempted. This allows the use of the $O(N^2)$ updating algorithm described above for the Green function instead of the $O(N^3)$ direct algorithm. Using the heat bath algorithm, the new configuration is accepted or rejected with a probability $r/(1+r)$. However, since the Green function is obtained through an updating procedure, it starts to degrade numerically as the number of spin flips increases. Therefore, at suitable intervals, we recompute the Green function, using eqn. (26). We use the modified Gram-Schmidt orthogonalization procedure of Imada and Hatsugai[4] to orthogonalize the columns (rows) of the right (left) projected trial wavefunction every few "time"-steps (usually 10). The use of an $O(N^2)$ updating algorithm forces estimation of the Green function at the time-slice at which a spin flip is attempted. Therefore, this algorithm yields properties as averages over all time- slices. However, the use of a direct $O(N^3)$ algorithm allows the possibility of estimating properties at any fixed time, independent of the time-slice at which the spin-flip is attempted. In such calculations, properties could be computed variously by choosing a particular time-slice l and obtaining all quantities at this time-slice, or by averaging over time-slices as in the procedure described above. We have implemented these methods and demonstrate in the next subsection that they have a direct bearing on the symmetry of the projection procedure and also discuss their relative merits.

We now discuss the extension of this method to a multiconfigurational trial wavefunction. In its implementation, the MSPQMC procedure is a generalization of the single configurational procedure and proceeds identically for ground states of open-shell systems and for excited states. However, at a formal level, issues related to conserving the symmetry of the trial state, essential for targetting excited states need to be clearly examined, in view of the randomness introduced by a Monte Carlo sampling procedure. These concerns will also be addressed in the next subsection.

Using the PQMC formalism, the Monte Carlo for open shells/ excited states proceeds as follows. The ratio of weights in the Monte Carlo procedure is no longer a simple ratio of determinants (eqn. (27)). The ratio of weights for Ising-configurations $\{s'\}$ and $\{s\}$ takes the form,

$$\frac{\omega^\Gamma(\{s'\})}{\omega^\Gamma(\{s\})} = \frac{\langle L^\Gamma(l, \{s'\}) | R^\Gamma(l, \{s'\}) \rangle}{\langle L^\Gamma(l, \{s\}) | R^\Gamma(l, \{s\}) \rangle} \tag{32}$$

where the projected states $|R^\Gamma(l, \{s_R\})\rangle$ and $\langle L^\Gamma(l, \{s_L\})|$ are also linear combinations of

states,

$$|R(l, \{s_R\})\rangle \ = \ \sum_j c_j^\Gamma \prod_\sigma |R_\sigma^{j\Gamma}(l, \{s_R\})\rangle \tag{33}$$

$$\langle L(l, \{s_L\})| \ = \ \sum_j c_j^\Gamma \prod_\sigma \langle L_\sigma^{j\Gamma}(l, \{s_L\})| \tag{34}$$

with each state in the summations obtained in a manner analogous to the single-determinantal case. The ratio (eqn. (32)) is now given as the ratio of sums of determinants appearing in the numerator and the denominator.

$$\frac{\omega^\Gamma(\{s'\})}{\omega^\Gamma(\{s\})} = \frac{\sum_{ij} \prod_\sigma c_i^\Gamma c_j^\Gamma det\left(\mathbf{L}_\sigma^{i\Gamma}(l, \{s'\})\mathbf{R}_\sigma^{j\Gamma}(l, \{s'\})\right)}{\sum_{ij} \prod_\sigma c_i^\Gamma c_j^\Gamma det\left(\mathbf{L}_\sigma^{i\Gamma}(l, \{s\})\mathbf{R}_\sigma^{j\Gamma}(l, \{s\})\right)} \tag{35}$$

Evaluating the ratio hence turns out to be more time consuming than in the single-determinantal case. The expectation value of a single-particle operator $\hat{O}_\sigma$ can be obtained from an importance sampling procedure, as in the single-configurational case, with

$$O_\sigma^\Gamma(\{s\}) = \frac{\sum_{i,j=1}^p c_i^\Gamma c_j^\Gamma \langle L_\sigma^{j\Gamma}(l, \{s\})|\hat{O}_\sigma|R_\sigma^{i\Gamma}(l, \{s\})\rangle\langle L_{-\sigma}^{j\Gamma}(l, \{s\})|R_{-\sigma}^{i\Gamma}(l, \{s\})\rangle}{\sum_{i,j=1}^p c_i^\Gamma c_j^\Gamma \langle L_\sigma^{j\Gamma}(l, \{s\})|R_\sigma^{i\Gamma}(l, \{s\})\rangle\langle L_{-\sigma}^{j\Gamma}(l, \{s\})|R_{-\sigma}^{i\Gamma}(l, \{s\})\rangle} \tag{36}$$

Estimates of two-particle properties can be obtained using Wick's theorem. The expectation value of a two-particle operator $\hat{Q} = \hat{O}_\sigma \hat{O}_{-\sigma}$ can be expressed as

$$Q^\Gamma(\{s\}) = \frac{\sum_{i,j=1}^p c_i^\Gamma c_j^\Gamma \langle L_\sigma^{j\Gamma}(l, \{s\})|\hat{O}_\sigma|R_\sigma^{i\Gamma}(l, \{s\})\rangle\langle L_{-\sigma}^{j\Gamma}(l, \{s\})|\hat{O}_{-\sigma}|R_{-\sigma}^{i\Gamma}(l, \{s\})\rangle}{\sum_{i,j=1}^p c_i^\Gamma c_j^\Gamma \langle L_\sigma^{j\Gamma}(l, \{s\})|R_\sigma^{i\Gamma}(l, \{s\})\rangle\langle L_{-\sigma}^{j\Gamma}(l, \{s\})|R_{-\sigma}^{i\Gamma}(l, \{s\})\rangle} \tag{37}$$

Property estimates in the MSPQMC procedure can be carried out as in the single configurational PQMC procedure. Estimates have been obtained at an extreme time-slice (usually chosen to be the last), at the middle-time slice and by averaging over all time-slices. We use the orthogonalization procedure on each of the left and right projected configurations in the multi-configurational trial wavefunction, every few time steps. Likewise, the Green function updating algorithm can be applied independently to each term in eqn. (36). We have carried out single- and multi-configurational PQMC simulations using the three averaging procedures for the Green function and other properties described above. An analysis of the errors involved in these procedures is presented in the next subsection.

2.2 Validity of the MSPQMC method and error analysis

While we have described a method for carrying out Monte Carlo simulations of excited states, the validity of such a procedure needs to be examined. In the MSPQMC method the trial wavefunction is a symmetrized linear combination of electron configurations. If the projection ansatz is employed without any further approximations, beyond employing a finite β, the projected state would continue to be in the initially chosen symmetry space. Employing a Trotter decomposition followed by a H-S transformation yields the approximation for the density operator $exp(-\beta\hat{H})$ given in eqns. (14,15). This procedure still retains the symmetry property of the density operator. However, in the Monte Carlo procedure, we only sample a fraction of all possible Ising- configurations. The operator $\hat{W}(\{s\})$ for an arbitrary Ising-configuration $\{s\}$ does not have the symmetry of the Hamiltonian.

Thus, it appears that the estimated properties would also have contributions from states belonging to symmetry subspaces other than the chosen space. In such a case, it is not enough to choose the symmetry of the trial wavefunction but is also necessary to prevent admixture with states of other symmetry in the MC procedure. While targetting the ground state, such an admixture would only slow down the convergence to the ground state since the admixture could involve intruder states of other symmetries lying between the ground state and the first excited state of the symmetry subspace of the ground state. On the other hand, while targetting excited states, the admixture could lead to intrusion of the ground state and projection would eventually lead to the ground state.

However, it is possible to retain the symmetry of the Hamiltonian, even when all the Ising-configurations are not sampled, using the following procedure. The set of Ising-configurations can be divided into disjoint invariant subsets. Any Ising- configuration in an invariant subset can be generated from any other configuration in the same subset by operating with an element $\hat{R}$ of the Schrödinger group. The operator $\hat{W}^{sym.}$, defined as

$$\hat{W}^{sym.}(\{s\}) = \sum_{\hat{R}} \hat{W}(\hat{R}\{s\}), \tag{38}$$

has the symmetry of the Hamiltonian. The estimates obtained from the projection procedure carried out using this symmetrized operator $\hat{W}^{sym.}$ exclude contributions from symmetries other than that of the initially chosen subspace. In the estimation of energy, the explicit use of the symmetrized operator, $\hat{W}^{sym.}$, is unnecessary for the following reason. The Hamiltonian of the system can be expressed as a linear combination of terms obtained by operating with the symmetry operators of the group on an irreducible operator, $\hat{H}^{irr.}$, which contains terms such as nearest-neighbour transfer operators and site-diagonal interactions to yield,

$$\hat{H} = \sum_{\hat{R}} \hat{R}\hat{H}^{irr.} \tag{39}$$

For example, for a Hubbard ring of N sites with periodic boundary conditions, $\hat{H}^{irr.}$ is given by

$$\hat{H}^{irr.} = (t_{i,i+1}\hat{a}_{i\sigma}^{\dagger}\hat{a}_{i+1\sigma} + h.c.) + U\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}, \tag{40}$$

where i is an arbitrary site. The Hamiltonian can be generated from $\hat{H}^{irr.}$ by adding up terms obtained by successive $\frac{2\pi}{N}$ rotations. For a system with a more complicated topology and non-equivalent nearest-neighbour bonds, such as C_{60} with bond-alternation, $\hat{H}^{irr.}$ is given by

$$\hat{H}^{irr.} = -\frac{1}{2}t_{hh}(\hat{a}_{i\sigma}^{\dagger}\hat{a}_{j\sigma} + h.c.) - t_{hp}(\hat{a}_{i\sigma}^{\dagger}\hat{a}_{k\sigma} + h.c.) + \frac{1}{2}U\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}. \tag{41}$$

where t_{hh} is the transfer integral for a hexagon-hexagon bond and t_{hp} is the transfer integral for a hexagon-pentagon bond. The label i corresponds to an arbitrary site on the truncated icosahedral lattice and j and k label nearest-neighbour sites corresponding to hexagon-hexagon and hexagon-pentagon bonds. The various terms in the Hamiltonian can be generated from $\hat{H}^{irr.}$ by operation with all the 120 elements of the icosahedral group. The estimate of the Hamiltonian for a single Ising-configuration in the MSPQMC procedure is given by

$$E^{\Gamma}(l, \{s\}) = \sum_{\hat{R}}\langle\phi^{\Gamma}|\hat{W}(\{s_L\})\hat{R}\hat{H}^{irr.}\hat{W}(\{s_R\})|\phi^{\Gamma}\rangle, \tag{42}$$

which can be rearranged to yield,

$$E^{\Gamma}(l, \{s\}) = \sum_{\hat{R}}\langle\phi^{\Gamma}|\hat{H}^{irr.}\sum_{\hat{R}}\hat{R}\hat{W}(\{s\})|\phi^{\Gamma}\rangle, \tag{43}$$

in doing which we have incurred a Trotter error. However, the operator acting on the ket conserves the symmetry of the initial state. The evaluation of energy on the last time slice is *a priori* symmetrized and does not involve the additional Trotter error.

For operators that do not have the symmetry of the Hamiltonian, we need to explicitly enforce the symmetrization of the estimates, even at the last time slice. By this, we would ensure that any property estimates would correspond to the excited state, targetted as the lowest state in a given symmetry subspace. This is done using the following procedure[19]. When a particular Ising-configuration is visited in the course of sampling, property estimates are obtained for all Ising-configurations related by symmetry. The symmetry of the Hamiltonian guarantees that the one–step transition probability between Ising-configurations $\{s\}$, $\{s'\}$ is the same as that between $\hat{R}\{s\}$ and $\hat{R}\{s'\}$,

$$p_{\{s\}\to\{s'\}} = p_{\hat{R}\{s\}\to\hat{R}\{s'\}} \tag{44}$$

Therefore, if an Ising configuration $\{s'\}$ is accepted (rejected) from an initial configuration $\{s\}$, the same result is expected from all symmetry related pairs of configurations $\hat{R}\{s'\}$ and $\hat{R}\{s\}$. This feature can be incorporated by constructing a symmetrized Green function as follows:

$$(\mathbf{G}_\sigma^{sym}(l, \{s\}))_{mn} = \frac{1}{h}\sum_{\hat{R}}(\mathbf{G}_\sigma(\hat{R}\{l, s\}))_{mn} \tag{45}$$

and $\hat{R}$ runs over all the h symmetry elements of the group.

It appears from the equation that we need to update the Green functions $\mathbf{G}_\sigma(\hat{R}\{s\})$ for every symmetry operation $\hat{R}$, which could be enormously computationally intensive. However, the Green functions $\mathbf{G}_\sigma(\hat{R}\{s\})$ and $\mathbf{G}_\sigma(\{s\})$ are related as

$$(\mathbf{G}_\sigma(l, \{s'\}))_{mn} = (\mathbf{G}_\sigma(l, \{s\}))_{m'n'} \tag{46}$$

$$\hat{R}: \{s\} \to \{s'\}; \tag{47}$$

$$\hat{R}^{-1}: i \to i' \;\; ; \;\; \hat{R}^{-1}: j \to j' \tag{48}$$

Thus, from the Green function of a single Ising configuration, we can generate the Green function of all Ising configurations related by the Schrödinger group of the system and thus ensure that property estimates are obtained in the irreducible representation Γ even for excited states.

The discussion so far seems to indicate that it is accurate to estimate the energy and other properties at an extreme time-slice since we do not incur the additional Trotter error. To analyze the errors arising from the updating and averaging procedures, we recognize that the ratio r (eqn. (27)) is independent of the time-slice l at which the lattice is notionally partitioned into left and right halves in both the single- and multi-configurational procedures. However, the matrix elements of the Green function depend on the time-slice at which they are computed. As seen from eqn. (20), *both* the right and left projected states are good approximations to the ground state only when they have both been sufficiently evolved, i.e. when $l \approx L/2$. Thus, we expect that the time-slice at which the averaging is carried out also determines the accuracy of the estimated properties. Because, if either the trial state or its transpose is insufficiently projected, contributions due to admixture with excited states of the same symmetry would lead to inaccurate estimates. For operators $\hat{O}$ that commute with the Hamiltonian, the ground-state expectation value can be obtained accurately *even* at the last time slice (for a non-degenerate ground-state) since,

$$\frac{\langle\phi|\hat{O}|\psi_0\rangle}{\langle\phi|\psi_0\rangle} = O_{00} \tag{49}$$

13

where

$$O_{ij} = \langle \psi_j | \hat{O} | \psi_i \rangle \tag{50}$$

$$|\phi\rangle = \sum_k a_k |\psi_k\rangle \tag{51}$$

and $|\psi_k\rangle$ are the eigenstates of the Hamiltonian. However, when $\hat{O}$ does not commute with the Hamiltonian, an estimate of its expectation value, carried out at the last time-slice would yield,

$$\frac{\langle \phi | \hat{O} | \psi_0 \rangle}{\langle \phi | \psi_0 \rangle} = O_{00} + \frac{1}{a_0} \sum_{k \neq 0} a_k O_{k0} \tag{52}$$

Thus the estimates of such properties are prone to be rather inaccurate towards either end of the Ising lattice. From this analysis we expect that the energy is most accurately estimated at an extreme time-slice, while other properties that do not have the symmetry of the Hamiltonian should be estimated at $l \approx L/2$. We have compared estimates obtained as time-slice averages and those obtained from measurements at a single time-slice with exact results, which we present in the next section.

In the MSPQMC method for excited states, we encounter the negative sign problem even at half-filling although the number of occurrences of negative signs even at large U/t is insignificant. In the usual quantum Monte Carlo methods, the sign problem arises only away from half-filling for bipartite lattices in any dimension. For, at half-filling in a bipartite lattice, the determinants for the up and down spins can be shown to have the same sign, if they occupy the same set of molecular orbitals. In the MSPQMC method, the sign problem could arise for two additional reasons. The individual up and down spin determinants could have different signs if the MOs occupied by the up and down spin electrons are not identical. Besides, the phases with which the configurations in the trial state are combined could also produce an overall negative sign even if the products of individual determinants of up and down spin corresponding to $\langle L_\sigma^{j\Gamma}(l, \{s_L\}) | R_\sigma^{j'\Gamma}(l, \{s_R\}) \rangle$ are positive. In what follows, we present data to show that the additional negative signs arising from the different up- and down-spin configurations as well as the phases are a negligible fraction. Besides, even the absolute numbers of negative signs appears to decrease with increasing system size for the excited states of half-filled systems.

3   Results and Discussion

In this section we first present our MSPQMC results on the ground and excited state properties of one-dimensional Hubbard systems at half-filling. We compare these with results from exact diagonalization studies, both for energies and correlation functions.

We also report results of studies carried out on the ground state of doped Hubbard systems and compare the binding energy obtained from these studies with Bethe ansatz results. We then report results on the excited states of the Hubbard chains. Results for the two-dimensional lattice include the 4×2 ladder and the 3×4 lattice. The 4×2 and 3×4 lattices are amenable to exact diagonalization studies and hence we have extensively studied various properties of these lattices for states of different symmetries at hole doping ranging from 2 to 4 holes.

In all these studies, we focus on two sources of error common to all PQMC procedures. The first one is that the projection as implemented via H-S fields does not retain the symmetry of the initial state for individual Ising configurations. However, it can be shown that the symmetry is retained if estimates are carried out at the last time slice. Except for the estimation of energy, estimates carried out in this manner contain contributions from excited states of the same symmetry. The error due to this could perhaps be reduced to some extent by the choice of trial wavefunction. As discussed before, there is an additional error of the order of Trotter error that is incurred by resorting to property estimates at intermediate time slices or by averaging over all time slices, as in the single configurational PQMC algorithms. In these procedures, however, the excited states are better filtered out due to projection being carried out on the trial state as well as its transpose. We have systematically studied the properties of the system obtained from (i) estimation at the last time slice (L) (ii) by averaging over estimates at all time slices (A) and (iii) estimation at the middle time slice (M). We have compared the results for energies and other correlation functions with exact results. We find that the energy estimates are most accurate on the last time slice while the estimates of correlation functions are accurate at the middle time slice. However, we find that the correlation functions at the last time slice for the chosen trial wavefunctions are reasonably accurate. More importantly, the accuracy of the estimates obtained at the middle time-slice and by averaging over all time slices can be improved by tuning the projection parameter which is consistent with the view that the errors in these two schemes are Trotter-like.

3.1   Ground state properties at half-filling for 1-D systems

We have computed the ground state properties of Hubbard rings at half-filling for various values of U/t, using different PQMC averaging procedures to find out the best suited algorithms for energies and other properties. The projection parameter β was set at 2.0 and $\Delta\tau$ was fixed at 0.05 for $U/t \geq 4.0$ and at 0.1 for smaller values of U/t.

In Table 1, we present the enrgies of rings of six and fourteen sites for various values of U/t. The agreement between exact and PQMC energies is very good for small and intermediate values of U/t from all the three averaging procedures. We note, howver, that for the larger ring averaging at the last time-slice gives best energy estimates. In Table 2, we compare, for the ring of six sites, spin correlations obtained from the three averag-

15

ing procedures in PQMC with those obtained from exact, variational Monte Carlo and symmetrized PQMC (with Green function updating) calculations. The PQMC estimates from middle-time slice as well as from averages over all time slice agree remarkably well with exact results. Green function updating, with judicious recomputation, yields results that are very similar to those obtained from the computationally more expensive explicit recomputation scheme followed in the all-time slice averaging procedure. In Table 3 we present the spin-spin and charge-charge correlation functions for weak, intermediate and strong electron-correlations. The charge and spin correlation even for strong electron correlations are well reproduced. Here again, we note that the average and middle time-slice estimates are better than the last time-slice estimates.

3.2 Excited state properties at half-filling for 1-D systems

In this subsection, we study the behaviour of the "optical" and "spin" gaps of Hubbard chains with increasing strength of electron correlations and compare these with exact results. The energies presented are obtained from the different averaging schemes. In an earlier paper, we reported some of the excitation gaps which were, however, obtained from energies calculated only at the last time-slice. The emphasis of this subsection is on comparing the various quantities computed using the different averaging schemes described earlier in this paper. Besides energies, these comparisons include various excited state correlation functions which have been studied for the first time using the MSPQMC procedure.

In Table (4), we present MSPQMC energies for the singlet excited states of Hubbard chains at weak and intermediate correlation strengths. We use a larger projection parameter in schemes (A) and (M). We observe that at small system sizes, the energies obtained from procedures (A) and (M) have slightly larger errors than those obtained from averaging at the last time-slice. Furthermore, the differences in estimates obtained from schemes (L), (A) and (M) decrease with increasing system size. We find that the estimates of the triplet excited state energy of the chain of 14 obtained from all the procedures ((L), (A) and (M)) are comparable. In Table (5) we present the diagonal and longer-range spin correlations in the singlet excited state of the chain of 6, for $U/t = 2.0$ and 6.0. Here, we find that the average time slice (A) and the middle time slice (M) values have smaller errors compared to the values calculated at the last time slice (L). This trend also holds for the charge correlations.

The above results show that it is indeed possible to obtain good estimates of *excited state* energies and other properties by averaging over all time-slices, if the Trotter error is controlled by sufficiently fine time-slicing. The wide applicability of the MSPQMC method would depend critically on the viability of this averaging method. For, it allows the use of the $O(N^2)$ Green function updating algorithm and thus makes larger system sizes computationally accessible.

3.3   Properties of doped 1-D systems

In this subsection we study Hubbard rings away from half-filling using the MSPQMC method. The quantity of interest in these systems is the pair binding energy of holes. The results presented here have been obtained using the Green function updating algorithm. Fye, Martins and Scalettar[20] obtained the pair binding energies for holes in doped Hubbard rings using the Sutherland-Shastry generalization of the Bethe ansatz equations for arbitrary boundary conditions. The binding energy for two holes in a system of N electrons is defined as $E(N)+E(N-2)-2E(N-1)$. They found that the binding-energies show non-monotonic behaviour with system size. The computation of these pair binding energies provides a very stringent test of any numerical scheme, as these quantities are small differences of relatively large numbers.

In Fig. (1) we plot the pair binding energies of periodic $4n$ and $4n + 2$ Hubbard rings against correlation strength. Our data compare well with the Bethe ansatz data, reproducing the important qualitative features. As observed earlier[20], $4n + 2$ systems doped with two holes do not show binding while $4n$ systems do exhibit negative binding energies over a certain parameter regime, in agreement with the Bethe ansatz results.

We now turn our attention to the negative sign problem for "open shell"/excited states of one-dimensional systems which arises due to the reasons discussed earlier. In the triplet state, the negative sign could arise either from non-identical occupancies of MOs for up and down spin electrons in the trial wavefunction or from the phase with which the terms in the trial wavefunction are combined. As seen in Table (6) the number of negative signs even for the excited triplet is not large. In fact, the number of occurances is a neglible fraction of the total number of configurations sampled and this decreases with increasing system size for the systems studied.

3.4   Properties of the two-dimensional Hubbard model

While it is possible to obtain properties of the Hubbard model on one-dimensional lattices from a variety of methods, both analytical and numerical, the two-dimensional Hubbard model has proved much harder to study. In this subsection, we illustrate the power of the MSPQMC method by studying in detail the 4×2 and the 3×4 clusters. These systems are easily amenable to exact diagonalization studies and provide the necessary checks. In Table (7) we present the energies of the 4×2 ladder with 6 electrons and the 3×4 system with 8 electrons. These fillings have open-shell non-interacting ground states. The 4×2 lattice has a triply degenerate HOMO while the 3×4 lattice has a doubly degenerate HOMO at the chosen fillings. The MSPQMC method accurately resolves the singlet and the triplet of the 4×2 and the 3×4 lattices with a trial wavefunction which is a symmetrized linear combination of properly chosen Slater determinants. We have also computed the ground state of the half-filled Hubbard Hamiltonian on the 4×4 lattice. In the non-interacting limit, this system has a six-fold degenerate MO at the Fermi level.

However, a muti-configurational trial wavefunction which is an appropriate symmetrized linear combination of just two MO-configurations yields a ground state energy which differs from the exact result by 1.4% for $U/t = 4.0$.

In Table (8), we study the effect of the three averaging schemes, (L), (A) and (M) described previously on the energy of the 3×4 lattice with 8 electrons at various values of the correlation strength. We used larger projection parameters for schemes A and M. As expected from our earlier analysis, we once again find that energies obtained at the last time slice are more accurate, but suitable tuning of the projection parameter allows us to reproduce energies from schemes A and M with comparable accuracy. This feature of the averaging schemes A and M is important, since we expect these two schemes to provide accurate correlation functions. In Fig. (2), we present the hole-binding energies for four holes on the 3×4 lattice. It is interesting to note that the 3×4 lattice does not show binding in the parameter regime studied. We also present the energy difference between the high and low spin states of 8 electrons on the 3×4 cluster and note that Hund's rule is obeyed over at weak and also in the intermediate correlation regime. Apart from the energy, other correlation functions like the spin-spin and charge-charge correlations charecterize the state of the system. We prefer to study these correlation functions for the 4×2 ladder, with bond-alternation, where the transfer integral of the rung, $t_{rung} = 0.9t$, where t is the transfer integral between two nearest-neighbours on each leg of the ladder. This choice of system and tranfer integrals has been made to ensure that the state studied is non-degenerate. In Table (9) we present the singlet spin correlations of the bond-alternated 4×2 ladder with 8 electrons obtained from the three averaging schemes, (L), (A) and (M). We observe that as expected from our analysis, correlation functions obtained from averaging at the middle time slice are significantly better than those obtained at the last time slice, both for weak and for intermediate correlation strengths. However, correlations obtained by averaging over all time slices, using the Green function updating algorithm are seen to be almost as accurate as those obtained from procedure (M). Thus, we expect that this method can be used to study much larger lattices. The charge correlations, also presented in Table (9) are seen to follow similar trends.

A major hindrance in the application of quantum Monte Carlo methods to the Hubbard model at large correlation strength and/or away from half-filling is the so-called 'negative-sign' problem. We have discussed the additional sign problem that arises even for one-dimensional systems when excited states are targetted. Bipartite lattices away from half-filling in 2-D suffer from the negative sign problem even when the ground state is the targetted state. Lattices which do not have charge-conjugation symmetry can have negative ratios of determinants even at half-filling. As discussed in the one-dimensional case, a multi-configurational trial wavefunction can lead to an additional sign problem when the configurations of electrons of up and down spin are not identical as well as through the phases with which terms in the wavefunction are combined. In Table (10), we present the actual numbers of negative signs we encountered in simulating the 4×2

and the 3×4 lattices with 6 and 8 electrons respectively. We observe that we are able to reduce the number of occurances of negative signs by a suitable choice of projection parameter and that a muti-configurational trial wavefunction does not appear to significantly worsen the sign problem in simulations of the two-dimensional Hubbard model, even of non-bipartite lattices.

4   Summary

We have described in detail the procedure for obtaining ground and excited states of open-shell systems, using a trial muti-configurational wavefunction within the projector quantum Monte Carlo method. A careful analysis of the method for excited states leads naturally to the idea of symmetrized sampling for correlation functions, developed earlier in the context of ground state simulations. It also leads to three possible averaging schemes, in which property estimates are carried out at the last time slice, over all time slices and at the middle time slice. We have analyzed the errors incurred in these various averaging procedures. From these analyses, we expect that the energy is best estimated at the last time slice. We also expect that the error incurred in the other procedures is Trotter like and can be reduced by increasing the projection parameter. Correlations that do not have the full symmetry of the Hamiltonian are better estimated at the middle time slice. We find that the energies and spin and charge correlations of one- and two-dimensional lattices, at and away from half-filling do exhibit this behaviour. We also find that upon increasing the projection parameter, properties obtained by averaging over all time slices and by averaging at the middle time slice have comparable accuracy. This observation allows the use of a Green function updating algorithm and makes larger system sizes accessible by the MSPQMC method. We have used this technique to study the hole-binding energies oftwo holes in $4n$ and $4n + 2$ systems, which compare well the Bethe ansatz data of Fye, Martins and Scalettar. We have also studied small clusters amenable to exact diagonalization studies in 2-D and have reproduced their energies and correlation functions by the MSPQMC method. We identify two ways in which a multiconfigurational trial wavefunction can lead to a negative sign problem. We observe that this effect is not severe in 1-D and tends to vanish with increasing system size. We also note that this does not enhance the severity of the sign problem in two dimensions. The MSPQMC method has been demonstrated to be capable of yielding reliable properties of ground and low-lying excited states of the Hubbard model.

References

[1] E. Lieb and F. Y. Wu, Phys. Rev. Lett., **20**, 1445 (1968).

[2] W. Metzner and D. Vollhardt, Phys. Rev. Lett., **62**, 324 (1989).

[3] S. Sorella, E. Tosatti, S. Baroni, R. Car and M. Parrinello, Int. J. Mod. Phys. B **1**, 993 (1988).

[4] M. Imada and Y. Hatsugai, J. Phys. Soc. Jpn. **58**, 3752 (1989).

[5] S. R. White, Phys. Rev. Lett. **69**, 2863 (1992); Phys. Rev. B **48**, 10345 (1993).

[6] Z. G. Soos and S. Ramasesha, ” Valence bond theory and Chemical structure”, ed. D. J. Klein and N. Trinajstic; Elsevier: Amsterdam (1990), p81.

[7] E. R. Davidson, J. Comput. Phys., **17**, 87 (1975).

[8] E. Dagotto and A. Moreo, Phys. Rev. D **31**, 865 (1985).

[9] S. Ramasesha, Swapan K. Pati, H. R. Krishnamurthy, Z. Shuai and J-L. Bredas (unpublished), preprint no. cond-mat/9603162.

[10] D. Bormann, T. Schneider and M. Frick, Z. Phys. B **87**, 1 (1992).

[11] D. M. Ceperley and B. Bernu, J. Chem. Phys., **89**, 6316 (1988); B. Bernu, D. M. Ceperley and W. A. Lester, Jr., *ibid.*, **93**, 552 (1990).

[12] M. Takahashi, Phys. Rev. Lett., **62**, 2313 (1989).

[13] Bhargavi Srinivasan, S.Ramasesha and H. R. Krishnamurthy, Phys. Rev. B**54** R2276 (1996).

[14] J. Hubbard, Proc. Roy. Soc. Lond. **238**, A276 (1964); *ibid.* **237**, A277 (1964); *ibid.*, **401**, A281 (1964).

[15] J. B. Anderson, J. Chem. Phys., **63**, 1499 (1975); *ibid.*, **65**, 4121 (1976).

[16] M. Tinkham, ”Group Theory and Quantum Mechanics”, McGraw-Hill Book Company (1964).

[17] P. O. Löwdin, Adv. Phys. **5**, 40 (1956).

[18] J. E. Hirsch, Phys. Rev. **B 28**, 4059 (1983).

[19] Bhargavi Srinivasan, S.Ramasesha and H. R. Krishnamurthy, Phys. Rev. B **54** , 1692 (1996).

[20] R. M. Fye, M. J. Martins and R. T. Scalettar, Phys. Rev. B **42**, 6809 (1990).

Table 1: MSPQMC energies of rings of 6 and 14 sites compared with exact calculations for averaging at last (lts), middle (mts) and all (ats) time slices for $U/t = 2.0, 4.0$ and 6.0. Data for $U/t = 4.0$ and 6.0 is with $\Delta\tau = 0.05$. Numbers in parantheses are the orders of magnitude of the statistical error. Data from procedures (A) and (M) have similar errors.

U/t	Energy-ring of 6				Energy-ring of 14			
	Exact	lts	ats	mts	$Exact$	lts	ats	mts
1.0	-6.601	-6.598	-6.605	-6.609	-14.715	$-14.710(10^{-4})$	-14.687	-14.718
4.0	-3.669	-3.657	-3.703	-3.685	-8.088	$-7.976(10^{-4})$	-8.247	-8.246
6.0	-2.649	-2.599	-2.704	-2.661	-5.916	$-5.875(10^{-3})$	-6.018	-5.983
10.0	-1.664	-1.525	-1.785	-1.768	-3.763	$-3.674(10^{-2})$	-4.004	-4.077

Table 2: Spin–Spin correlations ($4\langle s_i^z s_j^z \rangle$) of benzene for $U/t = 1.0$ and 4.0, from exact and MC calculations. The MC data is from variational MC (VMC), symmetrized PQMC (SPQMC) with green function updating and MSPQMC with explicit recalculation of the green function, followed by averaging at the last time slice (lts), over all time slices (ats) and at the middle time slice (mts). Data for $U/t = 4.0$ is with $\Delta\tau = 0.05$.

U/t	i,j	$4\langle s_i^z s_j^z \rangle$					
		Exact	VMC	SPQMC	lts	ats	mts
1.0	1,1	0.567	0.557	0.562	0.533	0.562	0.568
1.0	1,2	-0.267	-0.245	-0.264	-0.243	-0.262	-0.266
1.0	1,3	0.022	0.011	0.020	0.009	0.018	0.021
1.0	1,4	-0.077	-0.062	-0.074	-0.064	-0.073	-0.076
4.0	1,1	0.778	0.750	0.751	0.638	0.748	0.774
4.0	1,2	-0.435	-0.395	-0.412	-0.323	-0.412	-0.433
4.0	1,3	0.140	0.077	0.120	0.060	0.122	0.140
4.0	1,4	-0.188	-0.113	-0.167	-0.113	-0.169	-0.186

Table 3: Spin-Spin correlations ($4\langle s_i^z s_j^z \rangle$) and charge-charge correlations ($4\langle n_i^z n_j^z \rangle$) of the 6-site Hubbard ring exact and MC calculations. The MSPQMC values have been obtained by averaging at the last time slice (lts), over all time slices (ats) and at the middle time slice (mts). Data for $U/t = 4.0$ and 6.0 is with $\Delta\tau = 0.05$.

U/t	i,j	Spin				Charge			
		Exact	L	A	M	Exact	L	A	M
2.0	1,1	0.638	0.567	0.626	0.639	1.362	1.433	1.374	1.361
	1,2	-0.320	-0.267	-0.308	-0.317	0.849	0.814	0.844	0.850
	1,3	0.055	0.023	0.042	0.047	0.985	0.990	0.984	0.984
	1,4	-0.109	-0.079	-0.095	-0.100	0.972	0.960	0.967	0.970
6.0	1,1	0.873	0.700	0.844	0.873	1.127	1.300	1.159	1.127
	1,2	-0.516	-0.378	-0.496	-0.520	0.942	0.868	0.935	0.943
	1,3	0.202	0.103	0.186	0.202	0.996	0.991	0.996	0.995
	1,4	-0.244	-0.151	-0.224	-0.237	0.997	0.983	0.996	0.997

Table 4: MSPQMC energies of the excited singlet states of chains of 6 and 14 sites, compared with exact calculations for averaging at last (L), all (A) and middle (M) time slices for $U/t = 2.0$ and 6.0. Data for $U/t = 6.0$ is with $\Delta\tau = 0.05$.

N	$U/t = 2.0$				$U/t = 6.0$			
	Exact	L	A	M	Exact	L	A	M
6	3.0175	-3.0130	-3.0216	-3.0192	1.9212	1.9283	1.8874	1.9133
8	4.9958	-4.9893	-5.0010	-5.0044	0.6990	0.7405	0.6853	0.6259
10	-6.8718	-6.8615	-6.8645	-6.8502	-0.3723	-0.3477	-0.4378	-0.3794
12	8.6916	-8.6825	-8.6994	-8.7125	-1.3639	-1.3415	-1.4977	-1.4133
14	-10.4774	-10.4605	-10.4727	-10.4651	-2.3089	-2.2349	-2.4093	-2.4794

Table 5: MSPQMC spin and charge correlations of the excited singlet states of the chain of 6, compared with exact calculations for averaging at last (L), all (A) and middle (M) time slices for $U/t = 2.0$ and 6.0. Data for $U/t = 6.0$ is with $\Delta\tau = 0.05$.

U/t	i,j	spin				charge			
		Exact	L	A	M	Exact	L	A	M
2.0	1,1	0.498	0.431	0.477	0.490	1.502	1.569	1.535	1.510
	1,2	-0.248	-0.231	-0.251	-0.256	0.861	0.805	0.857	0.855
	1,3	-0.157	-0.124	-0.136	-0.152	1.017	1.052	1.048	1.021
	1,4	0.020	0.005	0.013	0.018	0.871	0.845	0.868	0.868
	1,5	-0.043	-0.034	-0.040	-0.043	0.939	0.978	0.957	0.947
	1,6	-0.071	-0.046	-0.056	-0.057	0.810	0.750	0.792	0.799
6.0	1,1	0.644	0.513	0.596	0.603	1.356	1.487	1.409	1.397
	1,2	-0.292	-0.266	-0.292	-0.295	0.952	0.878	0.943	0.943
	1,3	-0.242	-0.172	-0.214	-0.219	0.980	1.015	0.993	0.977
	1,4	0.056	0.027	0.026	0.025	0.899	0.862	0.885	0.883
	1,5	-0.038	-0.033	-0.024	-0.027	0.906	0.935	0.913	0.910
	1,6	-0.129	-0.070	-0.088	-0.087	0.907	0.823	0.884	0.890

Table 6: Number of occurances of negative signs for "open-shell"/ excited states in one-dimension. Sample size is $N \times 20 \times 5000$ for $U/t < 4.0$ and $N \times 40 \times 8000$ for $U/t \geq 4.0$.

U/t	$N = 6$		$N = 14$		$N = 18$		$N = 42$	
	singlet	triplet	singlet	triplet	singlet	triplet	singlet	triplet
1.0	14	0	0	0	0	0	0	0
2.0	532	14	1	0	0	0	0	0
3.0	1568	184	39	67	21	15	0	0
4.0	2414	693	224	371	71	192	0	0
5.0	3114	1131	901	1328	397	857	0	17
6.0	3638	1416	1325	1647	706	1085	0	127

Table 7: MSPQMC singlet and triplet energies of the 4×2 ladder, with 6 electrons, the 3×4 lattice with 8 electrons, compared with exact calculations.

U/t	system	N_e	Singlet		Triplet	
			Exact	MSPQMC	Exact	MSPQMC
2.0	4×2	6	-8.4059	-8.4261	-8.3270	-8.3725
2.0	3×4	8	-15.6745	-15.7533	-15.8619	-15.8533
4.0	4×2	6	-7.4171	-7.4318	-7.2358	-7.2837
4.0	3×4	8	-14.1782	-14.2698	-14.3631	-14.3768
6.0	4×2	6	-6.7880	-6.9182	-6.5556	-6.8617
6.0	3×4	8	-13.2061	-13.3083	-13.3422	-13.4012

Table 8: MSPQMC energies of the 3×4 lattice with 8 electrons, singlet compared with exact calculations for averaging at last (lts), middle (mts) and all (ats) time slices for $U/t = 1.0$ through 6.0. Data for $U/t = 6.0$ is with $\Delta\tau = 0.05$.

U/t	Singlet				Triplet			
	Exact	L	A	M	Exact	L	A	M
1.00	-16.7148	-16.7752	-16.7660	-16.7742	-16.8425	-16.8409	-16.8267	-16.8480
2.00	-15.6745	-15.7533	-15.7568	-15.7797	-15.8619	-15.8533	-15.8529	-15.8654
3.00	-14.8423	-14.9073	-14.9602	-14.9657	-15.0422	-15.0205	-15.0327	-15.0558
4.00	-14.1782	-14.2698	-14.3115	-14.3150	-14.3631	-14.3768	-14.4047	-14.4670
5.00	-13.6427	-13.7470	-13.7872	-13.8434	-13.8039	-13.8303	-13.8617	-13.8696
6.00	-13.2061	-13.3083	-13.3984	-13.4432	-13.3422	-13.4012	-13.4695	-13.4691

Table 9: MSPQMC spin and charge correlations of the excited singlet states of the 4×2 ladder with bond-alternation ($t_{rung} = 0.9t$, compared with exact calculations for averaging at last (L), all (A) and middle (M) time slices for $U/t = 2.0$ and 6.0. Data for $U/t = 6.0$ is with $\Delta\tau = 0.05$.

U/t	i,j	spin				charge			
		Exact	L	A	M	Exact	L	A	M
2.0	1,1	0.5940	0.551	0.592	0.595	0.9050	0.950	0.908	0.905
	1,2	-0.2369	-0.211	-0.224	-0.224	0.4681	0.452	0.469	0.468
	1,5	0.0204	0.008	0.020	0.012	0.5066	0.505	0.504	0.506
	1,6	-0.0787	-0.066	-0.070	-0.065	0.5504	0.555	0.549	0.549
	1,7	0.0088	0.006	0.012	0.013	0.5157	0.510	0.516	0.518
6.0	1,1	0.6873	0.618	0.682	0.689	0.8127	0.882	0.818	0.811
	1,2	-0.2775	-0.238	-0.198	-0.250	0.5056	0.476	0.495	0.502
	1,5	0.0549	0.003	0.002	0.011	0.5149	0.511	0.522	0.517
	1,6	-0.1002	-0.072	-0.029	-0.073	0.5406	0.548	0.545	0.546
	1,7	0.0136	0.022	0.010	0.021	0.5297	0.520	0.545	0.541

Table 10: Number of occurances of negative signs for "open-shell"/ excited states in two-dimensions. Sample size is $N \times 20 \times 5000$ for $U/t < 4.0$ and $N \times 40 \times 8000$ for $U/t \geq 4.0$.

U/t	4×2		3×4	
U/t	Singlet	Triplet	Singlet	Triplet
1.00	1	0	0	0
2.00	236	211	55	0
3.00	1162	1297	598	258
4.00	1980	2482	2444	1439
5.00	3321	3777	5676	4006
6.00	3894	4855	9818	7588

Figure Captions

Figure 1: Pair binding energies of two holes for $4n + 2$ and $4n$ Hubbard rings. Open symbols correspond to exact data and filled symbols to MSPQMC data (squares - ring of 6, triangles - ring of 14, circles - ring of 12 and diamonds - ring of 16).

Figure 2: Pair binding energy (triangles) of two holes in the 3×4 lattice with 10 electrons and difference between the high and low apin states (squares) of the 3×4 lattice with 8 electrons. Open symbols correspond to exact data and filled sysmbols to MSPQMC data.