Comment on “Density-matrix renormalization-group method for excited states”

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Abstract

In a recent paper (Phys. Rev. B 59, 9699 (1999)), Chandross and Hicks claim to present a new density matrix renormalisation group (DMRG) method for dealing with excited states of quantum lattice models. The proposed improvement to the DMRG—the inclusion of excited state wave functions in addition to the ground state in the density matrix when calculating excitations—is in fact standard practice, is clearly stated in White’s original papers, and has been used repeatedly by many groups to study excited states. The authors apply the method to the extended, dimerised Hubbard model for conjugated polymers. The criteria for determining whether states are bound or not are assessed. The authors claim that their results show that the optically important “1B_u” state is bound (excitonic), in contrast to a previous study. However, the discussion is qualitative, and the authors arrive at conclusions on the basis of results for one lattice size only. We show that when Chandross and Hicks’ criterion is developed into a quantitative definition of particle-hole separation, with the finite-size dependence analysed, the implication is that the 1B_u state is unbound, in keeping with the conclusions of a previous study.

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In a recent paper [1], Chandross and Hicks claim to present a new density matrix renormalisation group (DMRG) method [2,3] for dealing with excited states of quantum lattice models. They apply the method to the dimerised, extended Hubbard model for conjugated polymers. They claim that a previous study [5] of this model is flawed because it uses a “conventional” DMRG method which does not handle excitations correctly. The improvement that they suggest is to form a density matrix not only from the ground state, but from all the states being targeted in the calculation. This is in fact standard practice in DMRG calculations of excited states and the structure of the density matrix required to target excited states is given in White’s original papers on the method [3,4]. It has been used by many authors to target excitations in a variety of quantum lattice models (see, e.g., [6]) and was certainly used in [5] when various excitation energies and correlation functions were calculated for the extended Hubbard model. The comparisons presented in Fig. 1 and Fig. 2 of [1], between the “conventional” DMRG and Chandross and Hick’s “improvement” are therefore of limited value, as, to the best of our knowledge, all DMRG studies of excited states to date have incorporated the targeted excitations into the density matrix [7]. Unfortunately, a slightly different value for the Coulomb $V$ is used in [1] so a direct comparison with the results (e.g., for energies) tabulated in [5] is not possible. We have run a DMRG program which uses the algorithm used in [3] for targeting excited states with the parameters $U = 3t$, $V = t$, $\delta = 0.1$, used in [1], and found good agreement for the energies and correlation functions with the results plotted in Fig. 1(a) and Fig. 2(a) of [1]. For instance, we plot the $1B_u$ and $mA_g$ energies as functions of the lattice size $N$ in Fig. 1. The results compare very well with Fig. 1(a) of [1].
FIG. 1. The energies of the $1B_u$ (diamonds) and $mA_g$ (triangles) states of the dimerised, extended Hubbard model as a function of the lattice size $N$ for the parameter set used in [1]. The number of states retained per block [2,3] is $m = 270$.

In [1], Chandross and Hicks also examine criteria for deciding whether a particular excitation is bound (excitonic) or not. They claim that the average particle-hole separation, defined in [5] in terms of the density-density correlation function, is “too approximate” a quantity to determine whether a state is bound or not. They argue that by inspecting the centered correlation function as a function of distance (together with the profile of doubly occupied sites along the chain), for one particular lattice size ($N = 36$ sites), one can see that the $1B_u$ and $mA_g$ states are “different” in that the $1B_u$ ($mA_g$) has its strongest particle-hole correlations at short (long) distances. However, Chandross and Hicks do not present an alternative quantitative definition of the particle-hole separation, based on this observation. In [5], on the other hand, it is argued that a definition of particle-hole binding must take into account the way in which correlations scale with lattice size $N$. In [5] it is argued that this scaling is different for bound and unbound excitations, and that the scaling of the average
particle-hole separation with $N$ is but one manifestation of this.

Suppose we wish to take the average double occupancy of the $1B_u$ state (relative to the ground state) along the chain $\langle (n_i - 1)^2 \rangle_{1B_u} - \langle (n_i - 1)^2 \rangle_{1A_g}$ as an example (Fig. 2(a) in [1]). In Fig. 2 we plot this quantity for various lattice sizes $N$. We see that, although the concentration of doubly occupied sites is greatest in the middle of the chain, the distribution spreads out as $N$ is increased. The area under these curves rapidly converges to a non-zero value ($\approx 0.538$) as $N \to \infty$. This shows that the number of pairs of particles and holes in the $1B_u$, relative to the number in the ground state, approaches a constant. Our results could indicate that particle-hole pairs separate as $N$ is increased and are hence unbound, or they may simply indicate dispersion of a bound exciton in the $1B_u$. 

FIG. 2. The average number of doubly occupied sites of the $1B_u$ state relative to the ground state at distance $i$ from the center of the chain for various lattice sizes $N$. 

![Diagram showing the average number of doubly occupied sites for various lattice sizes](image-url)
FIG. 3. The averaged, centered, odd-site correlation function (relative to the ground state value, as defined in [5]) for the $1B_u$ state for $N = 42$ (diamonds), 62 (triangles), 82 (stars) and 102 (solid diamonds).

To address this, we again consider the averaged, centered, odd-site correlation function $C_{1B_u}^N(i)$, (again relative to the ground state value), defined in [5] and plotted for $N = 36$ in the inset to Fig. 2(a) in [1]. In Fig. 3 we plot this quantity for a number of values of $N$. We see that, although the correlations are generally strongest at short distances, they become increasingly spread out, and hence the particle-hole pair becomes increasingly separated, as $N$ is increased. Indeed, if one utilises $|C_{1B_u}^N(j)|$ to define a probability distribution for the particle-hole separation, as in [5], then one finds that the average particle-hole separation grows linearly with $N$, as shown in Fig. [4]. We note that any use of the density-density correlation function to describe particle-hole separation and the nature of exciton binding of excited states in the extended Hubbard model is merely plausible rather than rigorous [9], but Chandross and Hicks [1] do not offer an alternative quantitative definition of the particle-hole separation to the ones provided in [5].
FIG. 4. The (reduced) average particle-hole separation, as defined in [5] by using $|C_{1B_u}^N(i)|$ as a probability distribution, for the $1B_u$ state. Note the linear increase with $N$.

To summarise, Chandross and Hicks claim that, because the $1B_u$ and $mA_g$ have their greatest particle-hole correlations at short and long distances respectively (on the $N = 36$ lattice), the $1B_u$ is bound and the $mA_g$ is unbound. We would argue that it indicates that the particle-hole potential is more strongly attractive for the $1B_u$ state than for the $mA_g$. However, from the plausible, quantitative definition of the particle-hole separation given above, it would appear that the attraction between the particle and hole in the $1B_u$ state is not strong enough to bind them, and their separation increases throughout the range of lattice sizes studied.

Finally, we consider the structure of the density matrix when targeting excitations such as the $mA_g$ and $nB_u$. Chandross and Hicks argue that only four states—the $1A_g$ (ground state), the $1B_u$, the $mA_g$ and the $nB_u$—need be included in the density matrix. Our examinations of the dipole moments between the $A_g$ states and the $1B_u$ indicate that this approach is probably reasonable for the $mA_g$ which is well defined. That is, there is a reasonably abrupt jump in the magnitude of the dipole moment $\langle 1B_u|\hat{\mu}|jA_g \rangle$ at $j = m$. As shown in [5], this coincides with jump in the ionicity (the average number of doubly occupied sites) and in
the particle-hole separation. However, the \( nB_u \) state is less well defined in that there can be a number of \( B_u \) excitations that have a strong dipole moment with the \( mA_g \). This can be seen in Table I where we list the dipole moments \( \langle jB_u | \hat{\mu} | mA_g \rangle \) for \( N = 6, 10, 14 \) and 18, for the first five \( B_u \) states. Note that in no case is the \( nB_u \) state clearly defined, though there is a general trend whereby the \( 2B_u \) increases its relative dipole strength with the \( mA_g \) at the expense of the \( 4B_u \). Our contention here, as proposed in [5], is that, at least in terms of dipole moments or the density-density correlation function, the \( 1B_u \) state is the threshold of unbound states in the \( B_u \) sector and the “\( nB_u \)” is not well defined for this model.

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[4] Note also that the dipole operator method for calculating dipole-allowed singlet states within the DMRG proposed in [1], was actually first described in G. P. Zhang, T. F. George and L. N. Pandey, J. Chem. Phys. 109, 2562 (1998).

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[7] We note further that Chandross and Hicks [1] claim that including only the ground state in the density matrix leads to “grossly incorrect quantitative” results for excited states. Although it is illogical to include only the ground state in the density matrix when calculating excited states, for a given lattice size (e.g. \( N = 36 \)) it is in fact a mathematical certainty that the DMRG results for the excitations with a simple density matrix formed solely from the ground state projection operator will converge to the exact results as the number of states retained per block, \( m \), is increased. The phrase “less rapidly converging” is therefore more appropriate, as DMRG results should not be accepted if they have not converged with \( m \).

[8] The \( mA_g \) state is defined to be the excited state in the ground state symmetry sector that has the largest dipole moment with the \( 1B_u \) state, which is the lowest energy state in the dipole allowed symmetry sector.

[9] M. Yu. Lavrentiev and W. Barford, Phys. Rev. B 59, 15048 (1999). In this paper an alternative quantitative definition of the particle-hole separation is proposed using molecular
orbital operators. In terms of this definition there are indications that the $1B_u$ particle-hole separation grows less rapidly than linearly with $N$. 
TABLE I. Transition moments with the $m_A g$ states for the first five $B_u$ states (i.e. $\langle j_{B_u} | \hat{\mu} | m_A g \rangle$ for $j = 1, \ldots, 5$) for $N = 6, 10, 14$ and 18. Note that there is no clearly defined “$n B_u$” state.

| $N$ | $j = 1$ | $j = 2$ | $j = 3$ | $j = 4$ | $j = 5$ |
|-----|---------|---------|---------|---------|---------|
| 6   | 2.32    | 0.76    | 0.30    | 1.87    | 1.39    |
| 10  | 3.48    | 1.77    | 0.38    | 3.30    | 0.06    |
| 14  | 4.45    | 3.15    | 0.04    | 3.98    | 0.10    |
| 18  | 5.33    | 4.73    | 0.67    | 4.24    | 1.73    |