Pair-state analysis of the eigenstates of an N-electron system

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(Dated: May 6, 2002)

The foundation of the electronic structure of atoms, molecules, and solids is conceptionally and computationally based on single-electron basis representations. It is also known that the energies of these systems can be exactly represented as a sum of pair-state energies (eigenvalues of the two-particle reduced Hamiltonian) weighted by two-particle density matrix elements, implying that these two-electron basis functions should provide a natural alternative basis for analyzing and evaluating electronic structure. This paper demonstates the notion of a "pair-state" decomposition for a simple system as a function of its electron-electron interaction strength.

INTRODUCTION

Consider a system of N electrons consisting of one-electron ($h(i)$) and two-electron ($g(i,j)$) contributions to the total Hamiltonian:

$$\mathcal{H}(1,2,\ldots,N) = \sum_{i=1}^{N} h(i) + \sum_{i=1}^{N}\sum_{j<i} g(i,j). \qquad (1)$$

It can be shown that an eigenvalue E^α of this Hamiltonian can be evaluated in the form:

$$E^\alpha = \frac{N(N-1)}{2}\sum_a E^P_a \Gamma^{2\alpha}_{aa} \quad \text{where} \quad \sum_a \Gamma^{2\alpha}_{aa} = 1. \quad (2)$$

In this expression E^P_a denotes the a^{th} eigenvalue of the two-particle "reduced" Hamiltonian:

$$H^P(i,j) \equiv \frac{1}{N-1}\Big(h(i)+h(j)\Big) + g(i,j), \qquad (3)$$

with the eigenvalue equation

$$H^P(i,j)\ \phi_a(i,j) = E^P_a\ \phi_a(i,j) \qquad (4)$$

defining the pair states $\phi_a(i,j)$ and their corresponding energies E^P_a. The pair weight factor $\Gamma^{2\alpha}_{aa}$ in Eq. 2 is defined as the diagonal matrix element of the two particle density matrix evaluated in the pair-state basis:

$$\Gamma^{2\alpha}_{aa} \equiv \int d1d2d1'd2' \phi^*_a(1,2)\Gamma^{2\alpha}(1,2;1',2')\phi_a(1',2'). \qquad (5)$$

Here, the two-particle density matrix for the N-particle system can be defined in terms of the many-electron eigenstate $\Psi^\alpha(1,2,3,\ldots,N)$:

$$\Gamma^{2\alpha}(1,2;1',2') \equiv \int d3\ldots dN \Psi^{\alpha\,*}(1,2,3,\ldots,N)\Psi^\alpha(1',2',3,\ldots,N). \qquad (6)$$

The form of the pair-state expansion (2) implies that the eigenvalue spectrum $\{E^P_a\}$ of the pair Hamiltonian, weighted by the corresponding diagonal two-particle density matrix elements $\Gamma^{2\alpha}_{aa}$, can represent any eigenstate of the N-electron system. In this way, the eigenvalues and eigenvectors of the pair Hamiltonian (3) provides a natural and, in some sense, universal basis for representing a many-electron system.

These observations have been known for more than 40 years.[1–4] Bopp[1] evaluated the pair-state expansion (2) with a simple approximation for $\Gamma^{2\alpha}_{aa}$. However it was later realized[2, 3, 5] that the two-particle density matrix has a non-trivial "representability" problem[4]. Valdemoro used quantum chemistry techniques to analyze an expression similar to (2) for the ground states of Li and Be atoms and their isoelectronic ions[6, 7]. Coleman studied the mathematical properties of these functions, using the terms "pairon" and "eigengeminal" to describe the pair eigenstates $\phi_a(i,j)$. This work and related work on properties of the two-particle density matrix are summarized in the proceedings of a symposium held in his honor[4].

Despite the compelling simplicity of Eq. (2) and the long history of its study, pair-state analysis has not been readily incorporated into the repertory of popular numerical techniques for analyzing and solving many-body systems. One reason for this neglect is the difficulty of evaluating the two-particle density matrix. Some recent advances in density matrix theory[8, 9] may make it more practical to evaluate Eq. (6). In fact, the many-electron eigenvalue can be evaluated in terms of the trace expression $E^\alpha = \mathrm{Tr}(H^P\Gamma^{2\alpha})$ in any convenient representation.[2, 3] However, the pair-state representation of $\Gamma^{2\alpha}$ has have some analytical as well as numerical advantages. Another reason that pair-state analysis has not yet been adopted is the difficulty of solving the pair-state eigenvalue problem (4). Advances in computer hardware and software may make it possible to solve a two-body differential equation reasonably efficiently. The analogous one-body approaches to electronic structure calculations, such as density functional or Hartree-Fock theory, need less computational work. However, more advanced theories which include correlation and/or excitation effects[10–12] require additional computationally intensive steps. It may be the case that as the need for more accurate treatments of correlation effects grows, pair-state analysis may become computationally as well as analytically attractive.

Before investing a substantial effort in developing pair-state analysis methods, it is prudent to first address the question of how quickly the pair-state expansion (2) might converge. If it is necessary to include the entire pair-state spectrum in the representation of the ground state of the many-electron system, then the pair-state analysis will not be very convenient. On the other hand, the pair-state expansion promises to be a very attractive analysis and computational tool if a relatively small number of pair-states can be used to represent the ground and first few excited states of the many-electron system. The answer to this question will undoubtedly depend upon the system to be studied. In the present work, the pair-state decomposition is applied to a very simple system which has well-defined correlation effects but which can be evaluated exactly – the one-dimensional Hubbard model[13] for a finite number of sites. This system has been well studied[14, 15] and is known to demonstrate non-trivial correlation effects.

HUBBARD MODEL EXAMPLE

The Hubbard model is formulated in terms a Wannier basis. In second-quantized form with n denoting the site index and $\sigma(\uparrow,\downarrow)$ representing spin, the Hubbard Hamiltonian can be written

$$\mathcal{H}(t,U) = -t\sum_{n\sigma}\sum_{(n')} C^\dagger_{n\sigma}C_{n'\sigma} + U\sum_n C^\dagger_{n\uparrow}C_{n\uparrow}C^\dagger_{n\downarrow}C_{n\downarrow}, \tag{7}$$

where the parameters t and U represent the electron hopping and Coulomb repulsion matrix elements, respectively. The operators $C^\dagger_{n\sigma}$ and $C_{n\sigma}$ represent creation and annihilation operators respectively. The sum over n is taken over the N_a sites of the lattice (3 or 4 in this case). The sum over n' is restricted to nearest neighbors of n. If the pair eigenstates $\phi_a(i,j)$ are represented as linear combinations of two-electron states of the form $C^\dagger_{n_1}C^\dagger_{n_2}|0\rangle$, where $|0\rangle$ denotes the "vacuum" state, then the pair-state Hamiltonian appropriate for the Hubbard model for N electrons can be written in the form:

$$H^P(t,U) = \mathcal{H}\Big(\frac{t}{N-1},U\Big) = \frac{t}{N-1}\mathcal{H}\Big(1,\frac{(N-1)U}{t}\Big). \tag{8}$$

For the simplest non-trivial case, $N_a = N = 3$. There are a total of $\frac{6!}{3!3!} = 20$ three-electron states for this system. These states can be further characterized as 1 four-fold degenerate state with total spin $S^\alpha = 3/2$ and energy $E^\alpha = 0$ and 8 two-fold degenerate states with total spin $S^\alpha = 1/2$. The full spectrum of this system is shown in Fig. 1. For all values of the coupling strength U/t, the lowest energy state has spin $S^\alpha = 1/2$ and $E^\alpha < 0$. The pair-state spectrum for this system consists of $\frac{6!}{4!2!} = 15$ states including 6 singlet states and 3 triplet states. As

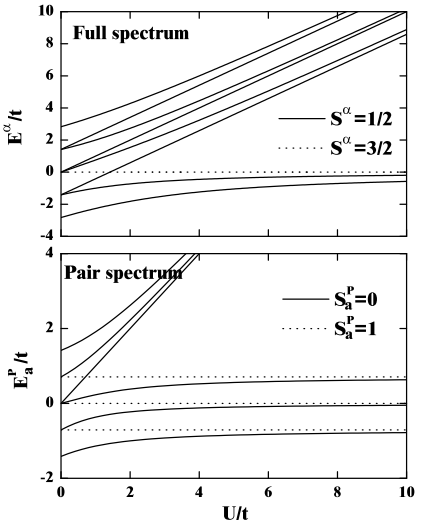

FIG. 1: Plot of the eigenvalues E^α (upper panel) and the corresponding pair eigenvalues E^P_a (lower panel) for the 3-site and 3-particle Hubbard model plotted as a function of the scaled Coulomb repulsion U/t.

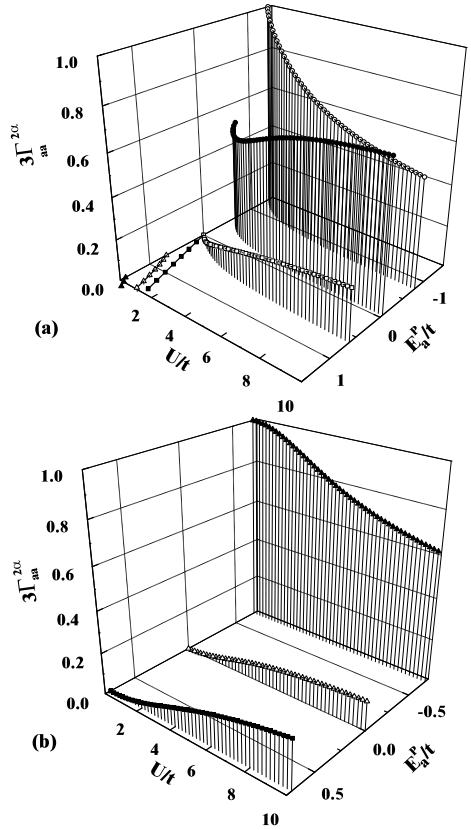

FIG. 2: Three dimensional plot of the pair weight functions $\Gamma^{2\alpha}_{aa}$ (scaled by $N(N-1)/2 = 3$) for the lowest eigenstate ($S^\alpha = 1/2, M^\alpha = 1/2$) of the $N_a = N = 3$ Hubbard model, as a function of the Coulomb repulsion U/t and of the pair energy E^P_a/t. Panel (a) represents the $S^P_a = 0$ and panel (b) represents the $S^P_a = 1, M^P_a = 1$ pair decompositions.

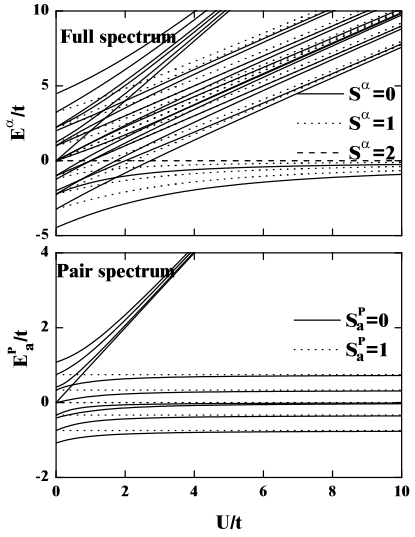

FIG. 3: Plot of the eigenvalues E^α (upper panel) and the corresponding pair eigenvalues E_a^P (lower panel) for the 4-site and 4-particle Hubbard model plotted as a function of the scaled Coulomb repulsion U/t.

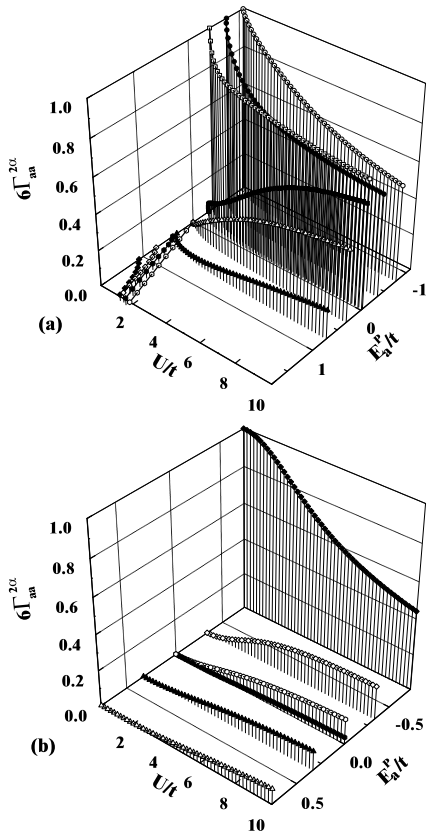

FIG. 4: Three dimensional plot of the pair weight functions $6\Gamma_{aa}^{2\alpha}$ for the lowest eigenstate ($S^\alpha = 0$) of the $N_a = N = 4$ Hubbard model, as a function of the Coulomb repulsion U/t and of the pair energy E_a^P/t. Panel (a) represents the $S_a^P = 0$ and panel (b) represents the $S_a^P = 1, M_a^P = 1$ pair decompositions.

the coupling parameter U/t increases, three of the singlet pair energies E_a^P converge to corresponding constant triplet energies, while the remaining 3 singlet pair states increase rapidly, as shown in the lower panel of Fig. 1.

The pair-state analysis was applied to the lowest energy eigenstate ($S^\alpha = 1/2, M^\alpha = 1/2$). The pair weight coefficients $\Gamma_{aa}^{2\alpha}$ are shown in Fig. 2a, for the the singlet contributions and in 2b for the $S_a^P = 1, M_a^P = 1$ triplet contributions. Additional triplet contributions from the $S_a^P = 1, M_a^P = 0$ pair states are exactly 1/2 the values of those shown in Fig. 2b. These results show that the pair weights are strong functions of the coupling parameter U/t. For $U = 0$ there are only 4 pair states with non-trivial weights (including the $S_a^P = 1, M_a^P = 0$ contributions which are not shown). As U/t increases, 5 additional pair states increase their contributions. The remaining 3 singlet pair states contribute only a small amount throughout the range of U/t, with a peak total weight of less that 2% at $U/t \approx 3$. In summary, 9 out of the total of 15 pair states contribute to the ground state energy of the 3-site 3-electron Hubbard model for most of the range of U/t. Three of the triplet states ($S_a^P = 1, M_a^P = -1$) are 0 because of symmetry and 3 of the singlet states contribute only a small amount.

For the second example, $N_a = N = 4$. There are a total of $\frac{8!}{4!4!} = 70$ four-electron states for this system. These states can be further characterized as 1 five-fold degenerate state with total spin quantum number $S^\alpha = 2$ and energy $E^\alpha = 0$, 15 three-fold degenerate states with total spin $S^\alpha = 1$, and 20 $S^\alpha = 0$ states. The full spectrum of this system is shown in Fig. (3). The lowest 2 energy eigenstates have $S^\alpha = 0$ and $S^\alpha = 1$, respectively. The pair-state spectrum for this system consists of $\frac{8!}{6!2!} = 28$ states with 10 singlet states and 6 triplet states. As the coupling parameter U/t increases, 6 of the singlet pair-state energies converge to the corresponding triplet energies[16] which are constant, and 4 singlet pair-state energies increase rapidly, as shown in the lower panel of Fig. 3.

The pair-state analysis was applied to the lowest singlet energy $S^\alpha = 0$ eigenstate. The pair weights are shown in Fig. 4a for the singlet contributions and in 4b for the $S_a^P = 1, M_a^P = 1$ triplet contributions. Additional non-trivial triplet contributions from the $S_a^P = 1, M_a^P = 0$ states are not shown. The results are qualitatively similar to the 3-site case. The 6 lowest energy singlet pair weights $\Gamma_{aa}^{2\alpha}$ have significant contributions throughout the range of U/t, while the 4 highest energy singlet pair states have very small values, peaking at less than 3% at $U/t \approx 2$. The 6 triplet pair states for $S_a^P = 1, M_a^P = 1$ shown in Fig. (4) as well as the 6 triplet pair states for $S_a^P = 1, M_a^P = 0$ (not shown) all contribute to the ground state eigenstate energy throughout

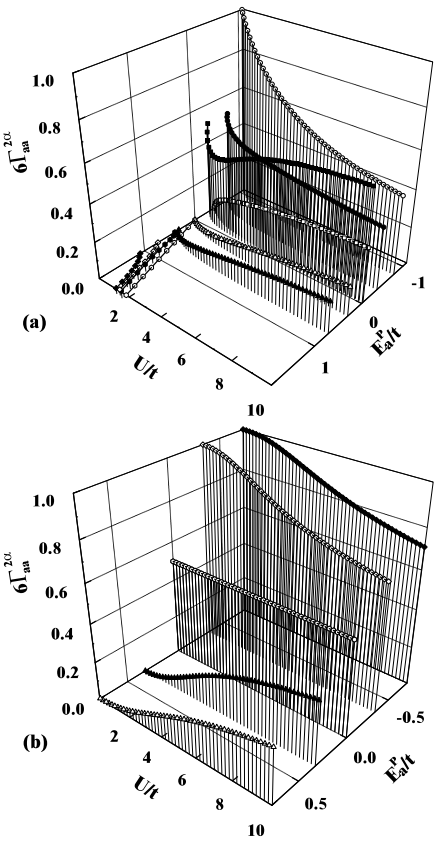

FIG. 5: Three dimensional plot of the pair weight functions $6\Gamma_{aa}^{2\alpha}$ for the next to lowest eigenstate ($S^\alpha = 1, M^\alpha = 1$) of the $N_a = N = 4$ Hubbard model, as a function of the Coulomb repulsion U/t and of the pair energy E_a^P/t. Panel (a) represents the $S_a^P = 0$ and panel (b) represents the $S_a^P = 1, M_a^P = 1$ pair decompositions.

the range of U/t. In Fig. (5) the pair state decomposition is shown for the lowest energy triplet state of this system. While the general pattern of the results are very similar to that of the singlet case, the greater contribution from the triplet pair weights is evident. In summary, 18 of the total of the 28 pair states contribute to the lowest two energy states of the 4-site 4-electron Hubbard model for most of the range of U/t. Six of the triplet states states ($S_a^P = 1, M_a^P = -1$) have zero contributions because of spin symmetry and 4 of the singlet states contribute only a small amount. As in the 3-site case, the "excluded" pair states are those which contain appreciable amplitudes of doubly occupied Wannier states of the form $C_{n\uparrow}^\dagger C_{n\downarrow}^\dagger|0\rangle$ at strong correlation (large U/t).

OUTLOOK

The results of this study give valuable insight into the convergence of a pair-state decomposition. Specifically, while more than the minimum number of pair-states are needed to represent the low energy states of a highly correlated system (as represented in this model by large values of U/t), a significant number of pair states are reasonably well excluded.

The Hubbard model represents only a small part of the numerical challenges of the "typical" many-electron problem. In order to further study the pair-state formalism, numerical methods for solving the pair-state eigenvalue equation (4) must be developed for atoms, molecules, and solids. The fact that the equation depends only on the fundamental interactions ($h(i)$ and $g(i,j)$) of the system, and has convenient scaling properties[3] should provide numerical advantages. It will also be necessary to develop algorithms for evaluating the two-particle density matrix elements in the pair basis. As pointed out by Coleman[2, 4], the pair weight factors $\Gamma_{aa}^{2\alpha}$ are considerably more complicated than occupation numbers that appear in Hartree-Fock or density functional theory. On the other hand, because of the form of the pair-state decomposition equation (2), all of the electronic configuration information for the N-electron state is contained within the pair weight $\Gamma_{aa}^{2\alpha}$ coefficients.

This work was supported by NSF grant No. DMR-9706575 and a SUR grant from IBM. W. C. Kerr and E. Carlson contributed helpful comments.

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