Insights into the structure of many-electron wave functions of Mott-insulating antiferromagnets: The three-band Hubbard model in full configuration interaction quantum Monte Carlo

Lauretta R. Schwarz,[1] George H. Booth,[1,2] and Ali Alavi[1,3]

[1]*University of Cambridge, Chemistry Department, Lensfield Road, Cambridge CB2 1EW, United Kingdom*
[2]*King's College London, Theory and Simulation of Condensed Matter, The Strand, London WC2R 2LS, United Kingdom*
[3]*Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany*

We investigate the ground-state wave function of a prototypical strongly correlated system, a three-band (*p-d*) Hubbard model of cuprates, using full configuration interaction quantum Monte Carlo. We show that the configuration interaction description of the exact ground state wave function is profoundly affected by the choice of single-particle representation, in a counterintuitive manner. Thus a broken-symmetry unrestricted Hartree-Fock basis, which at a single configuration level produces a qualitatively correct description of the antiferromagnet, results in a highly entangled exact solution consisting of high particle-hole excitations of the reference. This wave function is found to be very difficult to approximate using subspace diagonalizations. Conversely, a restricted Hartree-Fock basis, which yields at a single configuration level a qualitatively incorrect paramagnetic metal, results in a relatively rapidly converging configuration interaction expansion. Convergence can be further accelerated by adopting a natural orbital representation. Our results suggest that with the correct single-particle basis, such strongly correlated systems may be described by relatively compact wave functions.

Introduction. Mott-insulating antiferromagnets are ubiquitously found in the parent compounds of many strongly correlated materials, including cuprates and 3*d* transition metal mono-oxides. It is well known that their electronic properties arise in large part from electron correlation: spin-restricted band theory such as the local density approximation (LDA) of density functional theory wrongly predicts such compounds to be paramagnetic metals [1]. By allowing spin symmetry to break at a mean-field level [2], it is possible to recover antiferromagnetic behavior, but only at the cost of unphysical spin contamination, and such band theory does not provide a viable route to study the metal-insulator transition. Mott-insulating behavior can be obtained within the framework of dynamical mean field theory (DMFT) [3], through a mapping of the interacting system onto a cluster of sites embedded in a dynamical bath, but the lack of fine resolution in momentum space of the correlation effects [4,5] is a serious drawback. There is therefore growing interest in using wave function methods, including density matrix renormalization group [6] and configuration-interaction (CI) methods [7], such as full configuration interaction quantum Monte Carlo, (*i*)-FCIQMC [8,9], applied to periodic clusters to describe such systems [10–12].

While wave functions of strongly correlated molecular systems primarily build on restricted one-particle bases, the general approach in condensed matter physics communities is to start from a qualitatively correct broken-symmetry solution. In this study, we therefore ask how the structure of the many-electron wave function of a typical Mott insulator depends on the representation of the single-particle basis used to describe the configuration space of the system. On the face it, such a question appears to be more of a mathematical rather than a physical one: a unitary transformation of a basis cannot change the physical content of the wave function, any more than a rotation of a Cartesian system of coordinates changes the physical content of a tensorial quantity. However, we will show that the choice of basis impacts the convergence of the

exact full configuration interaction (FCI) [13] expansion of the many-electron wave function in a dramatic and counterintuitive manner. Thus a broken-symmetry mean-field basis (UHF), which produces a qualitatively correct description of the antiferromagnet, is shown to provide an extremely poor basis to construct the exact FCI wave function: the CI coefficients decay very slowly with increasing particle-hole excitation of the reference, resulting in a highly complex wave function which is very difficult to approximate. In contrast, we find that the qualitatively incorrect band structure of spin-restricted mean-field theory (RHF) provides a rapidly convergent CI expansion, which is much more amenable to approximation. Natural orbitals, which diagonalize the exact one-particle density matrix, provide yet more rapidly converging, compact wave functions. Our results suggest that with the correct single-particle basis, such strongly correlated systems may be amenable to powerful single-reference wave function methods, opening a new direction of theoretical research for these systems [14,15].

Model. The physics of copper oxide planes can be described by a three-band (*p-d*) Hubbard Hamiltonian [16–18]. This model describes the dynamics of holes in a CuO_2 plane which is represented by a $3d_{x^2-y^2}$ orbital centered on the copper site and two O $2p_\sigma$ orbitals, a $2p_x$ on an oxygen atom displaced in the *x* direction from the copper site, and a $2p_y$ on the O site displaced along the *y* direction. The Hamiltonian comprises kinetic energy and hole interaction terms,

$$\hat{H} = \sum_{i,j,\sigma} t_{ij} a^\dagger_{i,\sigma} a_{j,\sigma} + \sum_{i,j,\sigma\sigma'} U_{ij} a^\dagger_{i,\sigma} a_{i,\sigma} a^\dagger_{j,\sigma'} a_{j,\sigma'}, \quad (1)$$

where $a^\dagger_{i,\sigma}$ creates a hole with spin σ in the Cu 3*d* or O $2p_v$ orbital at site *i* and $a_{i,\sigma}$ annihilates such a hole. The site-diagonal terms t_{ii} represent the energy levels of the Cu, $\epsilon_d = 0.00$, and O, $\epsilon_p = 3.60$, orbitals, while $t_{pd} = 1.30$ and $t_{pp} = 0.65$ describe nearest-neighbor hopping processes between Cu 3*d* and O $2p_{x/y}$ orbitals with the phase convention

of Ref. [19]. Local on-site repulsions are taken into account by the site-diagonal U_{ii}, $U_d = 10.50$ and $U_p = 4.00$, whereas nearest-neighbor repulsions are represented by $U_{dp} = 1.20$ and $U_{pp} = 0.00$. We present results for a tilted lattice with $10 \, CuO_2$ unit cells, populated by $N = 10$ holes, which corresponds to an undoped system at half filling. The full Hilbert space encompasses 20.3×10^9 determinants. The chosen parameters (all in eV) were obtained with a constrained first-principles calculation for La_2CuO_4 by Hybertsen *et al.* [20].

Method. In FCIQMC [8] the wave function $|\Psi\rangle$ is sampled by an ensemble of N_w signed walkers which stochastically evolve in a combinatorially large Hilbert space of N-particle Slater determinants constructed from an orthonormal one-particle basis set of size M. Application of the imaginary-time evolution propagator to an initial state, $|\Psi\rangle = \lim_{\tau \to \infty} e^{-\tau(\hat{H} - E_0)}|\Phi\rangle$, projects out the exact ground state wave function which is written as an FCI expansion in the orthogonal basis of Slater determinants $|D_\mathbf{i}\rangle$,

$$|\Psi\rangle = \sum_\mathbf{i} C_\mathbf{i}|D_\mathbf{i}\rangle. \tag{2}$$

Stochastic sampling of $|\Psi\rangle$ by discrete walkers exploits the sparsity of this FCI representation, thereby avoiding storage of the large number of $C_\mathbf{i}$ coefficients which scales combinatorially in both N and M [13]. The imaginary-time evolution of walkers is given by

$$C_{\mathbf{i}, \tau + \delta\tau} = [1 - \delta\tau\,(H_{\mathbf{ii}} - E_0)]\,C_{\mathbf{i}, \tau} - \delta\tau \sum_{\mathbf{j} \neq \mathbf{i}} H_{\mathbf{ij}} C_{\mathbf{j}, \tau}, \tag{3}$$

where the first term increases or decreases the walker population on determinant $|D_\mathbf{i}\rangle$ and the second causes transitions of walkers from determinant $|D_\mathbf{j}\rangle$ to $|D_\mathbf{i}\rangle$ ($H_{\mathbf{ij}} = \langle D_\mathbf{i}|\hat{H}|D_\mathbf{j}\rangle$). Since contributions to each determinant can be of either sign, a fermion sign problem results in the form of an exponential increase in noise [21]. The discrete basis allows for effective cancellation algorithms [22], such that for sufficiently large walker populations N_w, the fermion sign problem can be controlled. A substantial reduction in the computational costs of FCIQMC [8] has been achieved by the initiator adaptation, i-FCIQMC [9], which maintains a high cancellation rate and controls the propagation of noise at the cost of a systematically improvable initiator error. However, as N_w increases, i-FCIQMC converges to the FCI limit within stochastic errors, with a reduced scaling compared to traditional FCI (exact diagonalization) [10–12,23–25].

The invariance of the FCI energy to unitary transformations of the one-particle basis set enables a choice between a variety of the latter. The purpose of this study is to investigate the impact of this choice on the resulting $C_\mathbf{i}$ coefficients, which may lead to a compact and sparse FCI representation of $|\Psi\rangle$ that is more amenable to treatment with configuration-based methods. A natural measure for the sparsity of a wave function is the L_1 norm, $L_1 = \sum_\mathbf{i} |C_\mathbf{i}|$, which within (i)-FCIQMC is quantified, up to a normalization constant, by the total walker number, $L_1 \propto N_w$. We therefore seek a representation of $|\Psi\rangle$ in which the L_1 norm and level of complexity are small, once the energy has converged to within small error bars. For this purpose, we investigate two widely available sources of single-
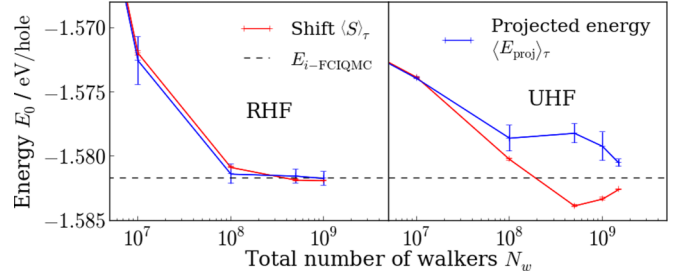

FIG. 1. (Color online) The convergence of ground-state energy E_0 (eV/hole) for RHF and UHF basis sets as measured by the shift $\langle S \rangle_\tau$ and projected energy $\langle E_{\text{proj}} \rangle_\tau$ [8].

particle orbitals, restricted and unrestricted Hartree-Fock spin orbitals (RHF, UHF), which we also compare with restricted and unrestricted natural orbitals (RNO, UNO), which have been shown to give rapidly converging FCI expansions [26–30].

In the independent-particle HF approximation, $|\Psi_{\text{HF}}\rangle$ is written as a single Slater determinant whose energy is variationally minimized with respect to unitary transformations of the one-particle states. Solving a set of effective one-particle Schrödinger equations, the Roothan-Hall equations [31] and Pople-Nesbet [32] equations, leads to the RHF and UHF spin orbitals, respectively. The eigenvectors which diagonalize the exact one-particle density matrix, $\gamma = \mathbf{U}\omega\mathbf{U}^\dagger$ (whose elements $\gamma_q^p = \langle\Psi|a_p^\dagger a_q|\Psi\rangle$ are evaluated from the i-FCIQMC wave function [33]), are referred to as natural orbitals (NO) and their eigenvalues, ω_p, as NO occupation numbers. Whereas restricted HF and NO orbitals, $\phi_{i,\text{R}}$, restrict the spatial distributions $\psi_i(\mathbf{r})$ to be equal for α and β channels,

$$\phi_{i,\text{R}} = \begin{cases} \psi_i(\mathbf{r})\,\alpha(\sigma), \\ \psi_i(\mathbf{r})\,\beta(\sigma), \end{cases} \quad \phi_{i,\text{U}} = \begin{cases} \psi_i^\alpha(\mathbf{r})\,\alpha(\sigma), \\ \psi_i^\beta(\mathbf{r})\,\beta(\sigma), \end{cases} \tag{4}$$

unrestricted spin orbitals, $\phi_{i,\text{U}}$, are characterized by relaxation of this constraint, $\psi_i^\alpha(\mathbf{r}) \neq \psi_i^\beta(\mathbf{r})$ [34].

Since the exact Hamiltonian commutes with the total (S^2) and projected (S_z) spin operators, the FCI wave function is a simultaneous eigenfunction of both. However, approximate wave functions, such as UHF, may not necessarily display the full symmetry. Imposing symmetry constraints to fulfill this criterion may raise the energy, a situation referred to as the symmetry dilemma [34,35]. By contrast, the RHF wave function $|\Psi_{\text{RHF}}\rangle$ is an eigenfunction of S^2 with $S = 0$ by virtue of being a closed-shell determinant.

Results and discussion. To begin with, we establish convergence to the FCI limit with walker number N_w (Fig. 1). Working with RHF orbitals leads to a $|\Psi\rangle$ with a smaller L_1 norm ($L_1 = 723.6$) given that for a tenfold growth in walker number to $N_w = 1.0 \times 10^9$ the energy changes by < 0.4 meV which is on the order of statistical errors. In contrast, for UHF spin orbitals the energy still changes significantly at $N_w = 1.5 \times 10^9$ and a larger L_1 norm ($L_1 = 1059.5$) results for $|\Psi\rangle$.

Ground states. In order to shed light on the reasons behind this, we examine the i-FCIQMC, RHF, and UHF ground states (Table I). Whereas the UHF approximation is able to

TABLE I. Ground-state energies E_0 (eV/hole), energy of the lowest-energy determinant E_D (eV/hole), percentage of correlation energy $p_{corr} = \frac{E_0 - E_D}{E_{exact} - E_D}$ (%) captured by $|\Psi_{CAS}\rangle$, average hole densities per atom $\langle n_{at} \rangle$ (holes/atom), staggered magnetization $\langle M^2 \rangle$, square magnitude of spin $\langle S^2 \rangle$. Errors in the previous digit are presented in parentheses [36]. Local spin-spin correlation function $\langle \Psi_{FCI} | \mathbf{S}_i \cdot \mathbf{S}_j | \Psi_{FCI} \rangle$ ($i = 1$) (right) of the correlated i-FCIQMC wave function $|\Psi_{FCI}\rangle$ in the metallic RHF one-particle basis.

Wave function	$|\Psi_{FCI}\rangle$	$|\Psi_{RHF}\rangle$	$|\Psi_{UHF}\rangle$	$|\Psi_{CAS}\rangle$				
One-particle basis	RHF/UHF	RHF	UHF	RHF	UHF	RNO	UNO	$\langle \Psi_{FCI} | \mathbf{S}_i \cdot \mathbf{S}_j | \Psi_{FCI} \rangle$
E_0	−1.5817 (5)	−0.9521	−1.5291	−1.3399	−1.5341	−1.5586	−1.5587	
E_D				−0.9521	−1.5291	−0.7636	−0.8350	
p_{corr}				61.6	9.5	97.2	97.0	
$\langle n_{Cu} \rangle$	0.70	0.49	0.73	0.53	0.73	0.71	0.73	
$\langle n_O \rangle$	0.15	0.25	0.14	0.24	0.14	0.15	0.14	
$\langle M^2 \rangle$	0.118	0.000	0.113	0.056		0.130		
$\langle S^2 \rangle$	0.00	0.00	4.37	0.00		0.00		

capture ∼97% of the true i-FCIQMC ground-state energy, the RHF approximation only accounts for ∼60%. Similarly, the UHF wave function only slightly overestimates the degree of ionicity in the system while the RHF wave function largely overestimates the degree of covalency.

Like previous studies [37–42], we find that the exact i-FCIQMC ground state establishes an antiferromagnetic long-range order across the copper sites, illustrated by the staggered magnetization, $\langle M^2 \rangle = \frac{1}{N} \sum_{ij} (-1)^{(x_i + y_i) + (x_j + y_j)} \langle \Psi_{FCI} | \mathbf{S}_i \cdot \mathbf{S}_j | \Psi_{FCI} \rangle$ (Table I). Again, UHF theory reproduces this closely by separating α and β orbitals on two sublattices while yielding identical band structures for both channels. Since RHF cannot describe an antiferromagnetic order by construction, it yields a metallic paramagnetic phase (Fig. 2) where most orbitals are delocalized over all lattice sites. Yet, the UHF wave function contains a significant amount of spin contamination and $|\Psi_{RHF}\rangle$ and $|\Psi_{UHF}\rangle$ constitute a clear example of the symmetry dilemma. While the UHF basis provides a physically closer single-determinant description of the antiferromagnetic ground state, it breaks spin symmetry leading to an inherent spin contamination. In contrast, the spin-symmetry-conserving RHF basis yields a qualitatively incorrect metallic ground state, but is still found to be a much more effective basis for correlated calculations within i-FCIQMC.

Orbital occupation numbers and correlation entropy. A clue with the difficulty introduced by the UHF basis can be obtained by considering the orbital occupation numbers γ_p^p in the four basis sets (RHF, UHF, RNO, and UNO) (Fig. 3). While for the RHF, RNO, and UNO bases the

occupation numbers decay roughly monotonically with mean-field orbital energy ϵ_p (Fig. 3), a sharp increase in γ_p^p is observed for the N highest UHF virtuals, which are also far higher in energy than those of any other basis. These highest energy virtuals correspond to spin-flipped counterparts of the occupied UHF orbitals. This is achieved by changing sublattices for the orbital coefficients on copper atoms, resulting in orbitals with antibonding character which split the Hubbard bands far apart (Fig. 2). It has been observed that for obtaining rapidly converging CI expansions it is beneficial for orbitals which ought to correlate with each other to possess spatial distributions $\psi_i^\sigma (\mathbf{r})$ which have their greatest amplitudes concentrated in similar regions of space while simultaneously providing suitable nodal surfaces [7]. By breaking spin symmetry, UHF theory leads to a set of single-particle states characterized by localized $\psi_i^\sigma (\mathbf{r})$ which strongly differ in their spatial extent. While this enables $|\Psi_{UHF}\rangle$ to provide a qualitatively correct single-determinant description, introducing correlation into $|\Psi_{UHF}\rangle$ requires very high energy orbitals. In contrast, the metallic RHF orbitals are very delocalized and hence exhibit similar spatial distributions $\psi_i (\mathbf{r})$. This facilitates correlation of the single-particle states, thereby favoring a more rapidly converging CI expansion in comparison to UHF orbitals. Additionally, the RHF orbital energies cover a smaller energy range than their UHF counterparts which leads to a smaller energy range covered by determinants with significant amplitudes in $|\Psi\rangle$ (Fig. 3). This seems to be an advantageous characteristic given that it is also shared by both NO bases which are known to yield less entangled representations of $|\Psi\rangle$ [26,30]. A quantitative measure of the configurational mixing present in the wave function representations is provided by the correlation entropy per hole [44], $S_{CE} = -\frac{1}{N} \sum_p \gamma_p^p \ln \gamma_p^p$. With $S_{CE} = 0.6421$ for RNOs and $S_{CE} = 0.6115$ for UNOs, the entanglement in $|\Psi\rangle$ is smallest in NO bases. Whereas the UHF basis produces the wave function with the largest configurational mixing ($S_{CE} = 0.8846$), the metallic spin-symmetry-conserving RHF basis leads to a significantly less entangled $|\Psi\rangle$ with a smaller S_{CE} ($S_{CE} = 0.7635$), even when describing a strikingly physically different antiferromagnet to which the spin-symmetry-broken UHF ground state is a far better approximation.

Subspace diagonalizations. Examination of FCIQMC descriptions of $|\Psi\rangle$ (Fig. 3) shows that all are highly
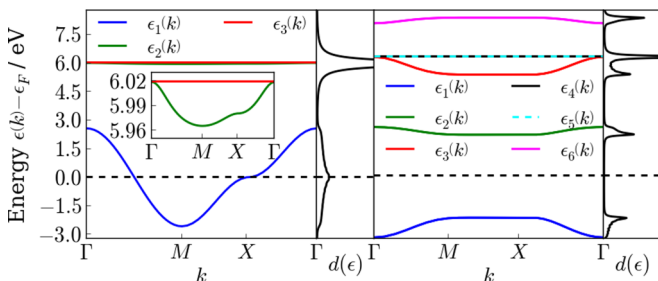

FIG. 2. (Color online) Metallic RHF (left) and insulating UHF (right) band structure $\epsilon(k) - \epsilon_F$ (eV) and density of states $d(\epsilon)$ (a.u.).
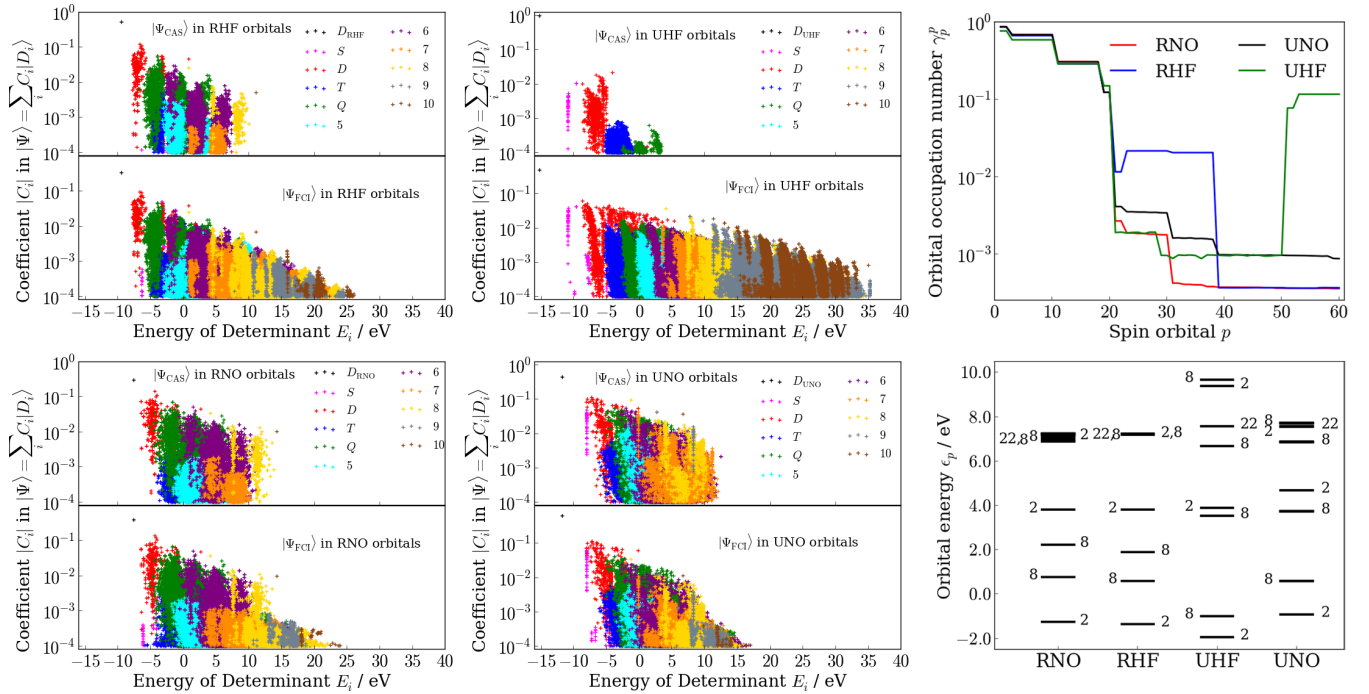
FIG. 3. (Color online) The magnitude of coefficients $|C_i| \geqslant 0.0001$ in the FCI expansion $|\Psi\rangle = \sum_i C_i |D_i\rangle$ shown against the respective determinant energy E_i for RHF (upper left), RNO (lower left), UHF (upper middle), and UNO (lower middle) basis sets. The amplitudes of determinants within the full space $|\Psi\rangle$ are depicted in the lower panels while those of determinants within the (10,10)-CAS space $|\Psi_{CAS}\rangle$ are shown in the top panels. The colors distinguish the x-fold excitations ($x \in \{1, 2, \ldots, N\}$) of the reference. The orbital occupation numbers γ_p^p (upper right) and mean-field orbital energies ϵ_i (diagonal elements of mean-field generalized Fock matrix) (lower right) [34,43]. The numbers indicate degeneracies which are exact for HF and approximate for NO spin orbitals.

multiconfigurational with a large number of single- to N-fold particle-hole excitations of the reference with $|C_i|$ decaying approximately exponentially with determinant energy. Yet, comparing RHF and UHF bases shows that the $|\Psi\rangle$ expansion is both sparser within the RHF space and more strongly weighted towards lower particle-hole excitations of the reference. Thus in the UHF expansion a plethora of 10-fold excitations contribute to $|\Psi\rangle$, the amplitudes of which are extremely difficult to sample. By contrast, the RHF, and more so RNO and UNO bases, are strongly weighted towards the low particle-hole excitations which are easy to sample. The latter are more amenable to accurate treatment of correlations via a compact set of explicit configurations.

Remarkably, $|\Psi_{FCI}\rangle$ in the RHF basis can be well approximated by simple subspace diagonalizations in a (10,10)-CAS space (complete active space); i.e., 10 holes are distributed in 10 orbitals about the Fermi level [45], resulting in a Hilbert space of 63 504 determinants. This is also the case for RNO and UNO spaces where $|\Psi_{CAS}\rangle$ captures a majority of the respective correlation energy (Table I) and basic structure of $|\Psi\rangle$. However, in the UHF space barely any correlation energy at all is captured by this subspace. This is a consequence of the fact that determinant weight is entirely absent from high particle-hole excitation when compared to $|\Psi\rangle$ despite the fact that many of the significant high-excitation determinants are in fact included in the CAS space. This suggests that orbitals outside the CAS space, especially the N highest-energy virtuals, are

essential for establishing the basic structure of $|\Psi\rangle$ in the UHF basis.

Conclusions. We have analyzed the FCI wave function representation in different single-particle basis sets and their amenability to accurate correlation treatments using i-FCIQMC and the strongly correlated three-band Hubbard model as an example. It has been shown that, counterintuitively, the effectiveness of single-particle basis sets for rapidly converging CI expansions is not necessarily paralleled by their ability to reproduce the physics of the system within a single-determinant description. While the UHF determinant represents qualitatively the correct insulating antiferromagnet, imposing spin symmetry in the RHF basis gives an RHF determinant describing a qualitatively incorrect metal. Yet, in this basis the FCI representation of $|\Psi\rangle$ is sparser, and converges rapidly with particle-hole excitations of the reference. Our results therefore suggest that with an appropriate single-particle description, it may be possible to describe the many-electron wave function of strongly correlated materials based on single-reference quantum chemical methodologies [34], which opens up a vast array of powerful many-body techniques for the study of such systems.

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