Efficient and accurate treatment of electron correlations from first-principles

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We present an efficient ab initio method for calculating the electronic structure and total energy of strongly correlated electron systems. The method extends the traditional Gutzwiller approximation for one-particle operators to the evaluation of the expectation values of two particle operators in a full many-electron Hamiltonian. The method is free of adjustable Coulomb parameters, and has no double counting issues in the calculation of total energy, and has the correct atomic limit. We demonstrate that the method describes well the bonding and dissociation behaviors of the hydrogen and nitrogen clusters. We also show that the method can satisfactorily tackle great challenging problems faced by the density functional theory recently discussed in the literature. The computational workload of our method is similar to the Hartree-Fock approach while the results are comparable to high-level quantum chemistry calculations.

It is one of the outstanding challenges in physics, chemistry, and materials science to develop robust and efficient theoretical and computational methods to accurately calculate the electronic structure and total energy of materials containing strongly correlated electrons [1]. While accurate methods are available from quantum chemistry approaches (e.g., configuration interaction (CI)), these methods are too expensive for condensed matter systems. On the other hand, density functional theory (DFT) and related computational codes based on the Kohn-Sham approach [2, 3] have been well developed, and are highly effective and successful for predicting the structures and properties of many materials, but they fail for systems with strongly correlated electrons. In the last three decades, there have been intensive efforts in developing new approaches to solve the outstanding problems in correlated electron systems [4–20]. Among these new developments, local-density approximation plus on-site Coulomb interaction parameter U (LDA+U) [4, 5], LDA+dynamical mean field theory [6–8], and LDA+Gutzwiller [12, 13, 15–20] have emerged as the most popular methods for treating strongly-correlated electron systems. The method extends the traditional Gutzwiller approximation form

\[ H = \sum_i E_i \Gamma_i \langle \Gamma_i \rangle + \sum_{i \sigma \beta \gamma} t_{i \sigma j \beta} c_{i \alpha \sigma}^{\dagger} c_{j \beta \gamma} + \frac{1}{2} \sum_{i \sigma j \beta \gamma l \delta \sigma'} U_{i \sigma j \beta \gamma l \delta} c_{i \alpha \sigma}^{\dagger} c_{j \beta \gamma}^{\dagger} c_{k \gamma \sigma'} c_{l \delta \sigma} \]

(1)

Here \( i, j, k, l \) are the atomic site indices. \( \alpha, \beta, \gamma, \delta \) are orbital indices and \( \sigma \) is the spin index. \( \{ \Gamma_i \} \) are eigenstates of the local many-body Hamiltonian. The first term is the local on-site part which has been singled out for exact treatment, \( E_i \) is the energy of the local many-electron configuration \( \{ \Gamma_i \} \). The second and third terms describe the non-local one-body and two-body contributions. All interactions are included in this Hamiltonian without any adjustable parameters. When evaluating this Hamilto-

In this letter, we present an ab initio method for the electronic structure and total energy calculations of strongly correlated electron systems without adjustable Coulomb parameters. In our approach, the commonly-adopted Gutzwiller approximation (GA) for evaluating the one particle density matrix \( \langle \Gamma_i \rangle \) is extended to treat the evaluation of the two-particle correlation matrix of the system. This approximation, which we call the correlation matrix renormalization (CMR) approximation [26], allows the expectation value of a many-electron Hamiltonian with respect to Gutzwiller variational wave function (GWF) to be evaluated with reduced computational complexity. We show that the method describes well the bonding and dissociation behaviors of hydrogen and nitrogen clusters in comparison with the accurate and expensive quantum chemistry calculations. Furthermore, some of the most challenging problems faced by Kohn-Sham DFT-based calculations recently discussed in the literature [27, 28] can also be readily solved by our method. The method has no double counting issues in the calculation of total energy, and produces the correct atomic limit. The computational workload scales as \( N^4 \) or better for systems of size \( N \), similar to the HF calculations [26].

We start with the full ab initio Hamiltonian for an interacting many-electron system in the second quantization form

\[ \mathcal{H} = \sum_i E_i \Gamma_i \langle \Gamma_i \rangle + \sum_{i \sigma \beta \gamma} t_{i \sigma j \beta} c_{i \alpha \sigma}^{\dagger} c_{j \beta \gamma} + \frac{1}{2} \sum_{i \sigma j \beta \gamma l \delta \sigma'} U_{i \sigma j \beta \gamma l \delta} c_{i \alpha \sigma}^{\dagger} c_{j \beta \gamma}^{\dagger} c_{k \gamma \sigma'} c_{l \delta \sigma} \]

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nian with the full CI wave function, one obtains an exact expression of the total energy which consists of non-local one-particle and two-particle density matrices in addition to the local on-site contributions. In our CMR approach, we evaluate the Hamiltonian in Eq. 1 with the GWF of the form

$$\Psi_{GWF} = \prod_i \left( \sum_{\Gamma} g_{\Gamma} | \Gamma_i \rangle \langle \Gamma_i | \right) | \Psi_0 \rangle$$  \hspace{1cm} (2)

Where $| \Psi_0 \rangle$ is a non-interacting electron wavefunction, which has been assumed.

$$E = \sum_{i\Gamma} E_{i\Gamma} P_{i\Gamma} + \sum_{i\alpha j\beta} t_{i\alpha j\beta} z_{i\alpha\sigma}^{j\beta} \left< c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} \right>_0$$

$$+ \frac{1}{2} \sum_{i\alpha j\beta k\gamma l\delta} U_{i\alpha j\beta}^{k\gamma l\delta} \left< c_{i\alpha\sigma}^\dagger c_{i\alpha\sigma}^\dagger c_{k\gamma\sigma} c_{l\delta\sigma} \right>_0 z_{j\beta\sigma}^{k\gamma} \left< c_{j\beta\sigma}^\dagger c_{k\gamma\sigma} \right>_0 z_{i\alpha\sigma}^{l\delta} \left< c_{j\beta\sigma}^\dagger c_{l\delta\sigma} \right>_0$$

$$+ E_c$$  \hspace{1cm} (3)

where $P_{i\Gamma}$ is the occupation weight of the configuration $| \Gamma_i \rangle$. $z_{i\alpha\sigma}^{j\beta}$ can be evaluated following the standard GA rule for one-particle hopping operators, i.e., $z_{i\alpha\sigma}^{j\beta} = z_{i\alpha\sigma} z_{j\beta\sigma}$ if $(i\alpha) \neq (j\beta)$ and 1 otherwise. To reach the expression Eq. 3, the validity of Wick’s theorem has been assumed. $E_c$ is the residual correlation energy due to the approximation involved in the CMR approach. In general, $E_c$ can be determined by comparing the total energies from the CMR with that from accurate CI or quantum Monte Carlo calculations for some exactly solvable structures. Since the dominant local onsite electron correlation effect has been taken into account by the GWF, the residual correlation energy due to the CMR approximation is expected to be small. In the test cases to be shown in this letter, we find that one way to include the effects of $E_c$ is to modify the renormalization $z$-factor obtained from the GA.

We first demonstrate the CMR method by studying the dissociation behavior of the hydrogen molecules. The dissociation behavior of these hydrogen molecules has been the testing ground of methods for correlated electron calculations, because the electron correlation changes from the weak to strong regime as the hydrogen bond length increases. For these systems, the residual correlation energy is included by replacing the renormalization $z$-factor obtained using the density-density type GA [24] by the functional of $z$, i.e., $f(z)$. The $f(z)$ is determined by requiring that the total energy (without explicit $E_c$ term) and the probability of the local double occupancy for a H$_2$ dimer obtained from the CMR calculation to be the same as our CI results. We first performed the test using the minimal basis set (one $s$ orbital for each H atom). In this case, the total energy and double occupancy probability from the CI calculation can be solved analytically and the $f(z)$ has an analytical form in term of $z$. Using the $f(z)$ analytically determined from the reference system H$_2$, CMR calculations are performed for H$_{10}$-ring, H$_8$-ring, H$_{10}$-ring and H$_8$-cube structures. The results from our CMR calculations are presented in Fig. 4 in comparison with the full CI or the highly accurate multi-configurational self-consistent field (MCSCF) results. We found the bonding and dissociation behavior of the hydrogen clusters calculated from the CMR method agrees very well with the result from the high level quantum chemistry calculations. In contrast, the HF results show large systematic errors, especially at large separations where the electron correlation effect becomes prominent, as evidenced by the strong suppression of the energetically unfavorable local electron double occupancy weight.

We further tested the CMR method for the dissociation behavior of hydrogen clusters using a large basis set of 6-311G**, which contains 3 s-orbitals plus 3 p-orbitals. In this case, the $f(z)$ needs to be determined numerically by fitting the CMR energies and the local configuration occupation probabilities of the H$_2$ dimer to the exact CI results. Using such a numerically constructed functional $f(z)$, we have performed the CMR calculations for H$_{10}$-ring, H$_8$-ring, and H$_8$-cube with the same large basis set. In Fig. 2 we show that the CMR method yields again very good bonding and dissociation curves in close agreement with the MCSCF calculations. The inset of Fig. 2 shows the behavior of $f(z)$, which scales like $\sqrt{z}$ at small
FIG. 1: (Color online) The total energy (upper panel) and double occupancy weight (lower panel) of H$_n$ clusters as a function of bond length calculated from the CMR method, which agree very well with the results from the exact CI calculations. The CMR results are also much better than the HF results. The calculations are done using a minimal basis set.

$z$ and approaches $z$ as $z$ goes to 1.

Very recently, Cohen, et al used some prototype systems to show the dramatic errors in the DFT-based calculations. These errors stem from the fact that the current approximations used in DFT calculations miss the energy derivative discontinuity with respect to the total electron number [27–29]. The prototype systems to reveal the failure of DFT are the stretched few-electron systems, e.g., one-electron systems like HZ$^{1e}$ and HZH$^{1e}$ and two-electron systems like HZ$^{2e}$ with $Z$ being the proton with nucleus charge $Z$ varying between 0 and 2. While the electron density from the exact calculations shows dramatic discontinuous changes in real space with a slight variation of $Z$ near some critical points at large separations, all the DFT calculations predict an artificial continuous variation of the electron density [27]. Remarkably, our CMR method gives exact solutions for any single-electron systems, as it can be easily proved that the orbital renormalization factors are constantly one and the method reproduces the HF results, which are exact in the special class of one-electron systems. It is also remarkable that our CMR method yields the exact bonding and dissociation behaviors for both HZ$^+$ and H$_2$ (see Fig. 2), while all the available DFT calculations can hardly describe both cases equally well [28]. One can further show that because the CMR method reaches the correct atomic solutions at the large separation limit, the exact discontinuous electron transfer observed in the HZ$^{2e}$ system at large separations can be well reproduced. In Fig. 3 we compare the electron occupation and double occupancy weight of Z atom from the CMR, HF, DFT with the generalized gradient approximation (GGA) and CI. Although all the methods predict similar results near equilibrium bond length ($\sim$0.75Å), the CMR method shows significant improvements over the mean field HF and GGA and follows closely the exact CI results with increasing separations, even at the chemically crucial bond breaking region ($\sim$2Å) and beyond. The underlying physics for the large errors of the simple mean field approaches like the HF and GGA can be understood by noting that the mean field double occupancy weight evaluated using the CI orbital occupation, shown as the dotted line in the lower panel of Fig. 3 can severely deviate from the exact CI double occupancy weight—
manifesting the multi-configuration nature of the exact solution which is beyond the simple Slater determinant description.

Another challenging prototype system is the H₈ cluster with varying electron filling [28]. The exact solution predicts a relatively big energy gap for the system at large separations and half-filling \( N_e = 8 \); while all the DFT calculations fail to reproduce this result because of the incapability to treat the strong electron correlation effects. In Fig. 4 we show the total energy of the H₈ cube from the CMR, HF, GGA and MCSCF calculations as a function of even number of electron filling, which keeps the system to have the closed shell ground state solution [28]. While all the four theories give similar total energies at the small bond length, the discrepancy between them becomes increasingly large with expanding the H₈ cluster. Remarkably, the CMR energies agree with the highly accurate MCSCF results very well for all the bond separations and electron fillings, which proves that the key many-body correlation physics in this system has been perfectly captured by the CMR method. A better comparison between the four levels of theories is presented by the energy gap, defined as the second order finite difference \( \Delta_2 E = E(N_e + 2) + E(N_e - 2) - 2E(N_e) \), as shown in the insets of Fig. 4. Clearly, as the bond length increases, or the electron correlation effects become stronger, the simple mean field HF and GGA energy gap shows larger deviations from the exact gap, especially the gap at half filling. In contrast, the CMR calculations yield energy gaps in excellent agreement with the MCSCF results in all the cases.

The CMR method is also successfully applied to systems with atoms containing multiple correlated orbitals, e.g., nitrogen clusters. For computational convenience, we describe the nitrogen atom with the minimum basis set and choose the 2s and 2p as the correlated orbitals. The same idea can be equally well carried over to the large basis calculations as shown previously for the hydrogen clusters. Two functionals, \( f_s(z_s) \) and \( f_p(z_p) \), are introduced to modify the renormalization coefficients of 2s and 2p orbitals. The specific functional forms, following the procedure in the calculations of hydrogen clusters, are determined by matching the CMR total energy, \( E \), and local correlated Fock state occupation probabilities, \( p_r \), with the exact CI results of the N₂ dimer. We apply the method to calculate binding energy curves of three nitrogen clusters of different geometries, i.e., the square, diamond and tetragonal shapes. In Fig. 5 we show the total energy as a function of bond length from the CMR, HF and MCSCF calculations. The good agreement between the CMR and MCSCF energies for all the structures demonstrates the good transferability of our method.

In summary, we have developed an efficient method for calculating the electronic structure and total energy of the systems with strong electron correlations. The method is based on the Gutzwiller type variational wavefunction and adopts a correlation matrix renormalization approximation in which both one-particle density and two-particle correlation matrices at mean field level are renormalized according to the local electron correlation effects. While the computation workload of this new approach is similar to that in HF calculations, the calcu-
lution results are much more accurate. The benchmark results for the bonding and dissociation behaviors of the hydrogen and nitrogen clusters show that our method well reproduces the results from the accurate and yet expensive quantum chemistry CI and MCSCF calculations. The CMR method is also demonstrated to be accurate for treating the electron correlation effects in some prototype systems where the current DFT and HF calculations fail. The extension of the method to crystalline solids is straightforward and promising. The work along this direction is underway.

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