


Self-consistent-field method for correlation calculation within density-matrix-functional theory

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The self-consistent-field method proposed recently [Wang *et al.*, *Phys. Rev. Lett.* **128**, 013001 (2022)] is discussed in more detail. The method leads to self-consistent eigenvalue equations for the natural spin orbitals and Fermi-Dirac distribution for the orbital occupation numbers. The entropic functional contains two parameters (κ and b), which can be fitted to various experimental or theoretical data such as the dissociation energy, entropy, and total energy at a given geometry, etc. Calculations are demonstrated on the square H₄ and hydrogen chains of H₅₀, which are representative cases of degenerate or nondynamically correlated systems.

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I. INTRODUCTION

In the configuration interaction (CI) method, the wave function is expressed as a linear combination of Slater determinants Φ_i

$$\Psi(12 \cdots N) = \sum_i c_i \Phi_i(12 \cdots N). \quad (1)$$

The coefficients c_i satisfy an eigenvalue problem

$$\sum_j \langle \Phi_i | H | \Phi_j \rangle c_j = E c_i. \quad (2)$$

For an N -electron system spanned by $2M$ spin orbitals, the total number of possible Slater determinants is on the order of $\binom{M}{N/2}^2$ for a spin-unpolarized system. For example, for a system with $N = 50$ electrons, using minimum basis set such as STO-3G, there will be $M = 100$ spin orbitals, the number of possible determinants will be on the order of 10^{46} . Symmetry restrictions may reduce this number, but the resulting size of matrix $\langle \Phi_i | H | \Phi_j \rangle$ or the number of expansion coefficients c_i will still be too large for today's computer technology.

Many determinants (or configurations) have almost zero coefficients c_i , but usually it is difficult to find them and get rid of them from the beginning. Alavi *et al.* [1] once designed a Monte Carlo algorithm, i.e., a game of life, death, and annihilation, to eliminate such determinants.

The contribution of each determinant to the energy state is roughly weighted by $|c_k|^2$, so each orbital in the k th determinant can be assigned the weight $|c_k|^2$. A quantity that measures the total contribution of an orbital to the energy state is

$$\langle \Psi | a_i^\dagger a_i | \Psi \rangle = \sum_k |c_k|^2, \quad \text{with orbital, } i \in \Phi_k, \quad (3)$$

where a_i^\dagger and a_j are the creation and annihilation operators for the one-particle basis $\{\varphi_i\}$ that generates the CI wave function.

The above quantity includes contribution from all the related determinants, even those with nearly zero c_i which account for the weak dynamic correlation. If one takes $\langle \Psi | a_i^\dagger a_i | \Psi \rangle$ as variables, one need not worry about how to select the effective configurations (or active space), to get rid of the vast number of configurations with nearly zero coefficient c_i .

A more elegant quantity is the one-particle reduced density matrix (1RDM) [2,3],

$$\gamma(1, 1') = \sum_{ij} \langle \Psi | a_i^\dagger a_j | \Psi \rangle \varphi_i^*(1) \varphi_j(1'). \quad (4)$$

The matrix elements $\langle \Psi | a_i^\dagger a_j | \Psi \rangle$ are Hermitian and depend on the CI expansion coefficients c_i . Diagonalization of the matrix $\gamma(1, 1')$ leads to an eigenvalue expansion

$$\gamma(1, 1') = \sum_i n_i \chi_i^*(1) \chi_i(1') \quad (5)$$

with the eigenfunctions, $\chi_i(1)$, named as the natural (spin) orbitals and the eigenvalues, n_i , their occupation numbers, which has the property $\sum n_i = N$, and $1 \geq n_i \geq 0$. The natural orbitals and their occupation numbers have the nice feature that they are nearly invariant under a variety of choices of basis set, i.e., the wave function expressed in the natural orbitals is almost invariant to the choice of the basis set [4,5].

The natural orbital expansion allows one to express the electronic energy of atoms and molecules in a concise form

$$E = \sum_i n_i h_{ii} + \int \frac{\Gamma(1, 2)}{r_{12}} d1 d2, \quad (6)$$

where $h_{ii} = \langle \chi_i | \hat{h} | \chi_i \rangle$ is the one-electron energy with the operator

$$\hat{h} = -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \quad (7)$$

in atomic units. Note that only the diagonal terms h_{ii} survive.

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The pair density $\Gamma(1, 2)$ can be expressed as

$$\begin{aligned}\Gamma(1, 2) &= \frac{1}{2} \sum_{ijkl} \langle \Psi | a_i^\dagger a_j^\dagger a_l a_k | \Psi \rangle \chi_i^*(1) \chi_j^*(2) \chi_k(1) \chi_l(2) \\ &= \sum_{ijkl} \Gamma_{ij,kl} \chi_i^*(1) \chi_j^*(2) \chi_k(1) \chi_l(2),\end{aligned}\quad (8)$$

where $\Gamma_{ij,kl}$ are quadratic functions of the CI expansion coefficient c_i . Some properties of the coefficients $\Gamma_{ij,kl}$ are obvious from its definition. Since it is the expectation value of the operator $a_i^\dagger a_j^\dagger a_l a_k$, it is both Hermitian and antisymmetric, $\Gamma_{ij,kl} = -\Gamma_{ji,kl}$.

In the density-matrix functional theory (DMFT) [6], the natural orbitals and their occupation numbers are taken as the variables. Both the kinetic energy and the nucleus-electron Coulomb energy are expressed exactly with 1RDM, only the two-electron repulsion energy need be modeled as a functional of 1RDM.

In his original paper of DMFT, Gilbert [6] tried to derive the eigenvalue equation for the orbitals as the Kohn-Sham equation in the density-functional theory (DFT) [7]. To his surprise, he found that the orbital energies for orbitals with fractional occupancy are all degenerate. In his own words, it is “unexpected and paradoxical.” The degeneracy problem was later further investigated by Pernal [8], and a level-shift method was proposed to accelerate the solution of the pseudoeigenvalue problem. Piris and Ugalde [9] proposed an alternative method for the pseudoeigenvalue problem. Without proper eigenvalue for the orbital energy, it is sometimes awkward to interpret energy levels in molecules or band structure in solids [10,11].

A genuine eigenvalue equation for the spin orbitals in DMFT was recently obtained with the observation that the correlation energy in DMFT is proportional to the information entropy for 1RDM [12],

$$S = - \sum_i [n_i \ln n_i + (1 - n_i) \ln (1 - n_i)]. \quad (9)$$

For $1 > n_i > 0$, the logarithmic function is negative, then $S > 0$. For $n_i = 0$ or 1 , $S = 0$. The method is thus named as *i*-DMFT for its connection to information entropy [13].

Besides the eigenvalue equation for the spin orbitals, it also leads to efficient calculation for the occupation numbers as a Fermi-Dirac distribution. Previously, the Fermi-Dirac distribution is invoked as *ad hoc* convenience to accelerate convergence [14,15] or to introduce fractional virtual orbitals heuristically in DFT exchange-correlation functional [16,17]. In Ref. [12], the Fermi-Dirac distribution becomes a rigorous solution derived from the variational Lagrangian function.

The purpose of this paper is to present more detail of the *i*-DMFT method and its application to prototypical non-dynamically correlated systems, i.e., the square H_4 and the linear chains of 50 hydrogen atoms. The square H_4 system is interesting because both Hartree-Fock and DFT fail due to the frustration in assigning electron occupation to the degenerate orbitals, while the linear chains of 50 hydrogen atoms have too many determinants for the full CI method.

II. CUMULANT ENTROPIC FUNCTIONAL

The *i*-DMFT method is based on the cumulant decomposition of the pair density [18–20].

$$\Gamma(1, 2) = \frac{1}{2} [\gamma(1, 1)\gamma(2, 2) - \gamma(1, 2)\gamma(2, 1)] + \lambda(1, 2). \quad (10)$$

The two-electron energy is then written as

$$\int \frac{\Gamma(1, 2)}{r_{12}} d1d2 = Y + E_{\text{cum}}, \quad (11)$$

where Y contains the direct and exchange parts of the two-electron energy, both are functional of 1RDM,

$$\begin{aligned}Y &= \frac{1}{2} \iint \frac{\gamma(1, 1)\gamma(2, 2) - \gamma(1, 2)\gamma(2, 1)}{r_{12}} d1d2 \\ &= \frac{1}{2} \sum_{ij} n_i n_j [\langle ij|ij \rangle - \langle ij|ji \rangle].\end{aligned}\quad (12)$$

The cumulant energy is then defined by

$$E_{\text{cum}} = \int \frac{\lambda(1, 2)}{r_{12}} d1d2, \quad (13)$$

which has been identified as the correlation energy in DMFT [21]. The exact form of E_{cum} is unknown, however, it has a rigorous bound

$$E_{\text{cum}} \leq 0 \quad (14)$$

as a consequence of Lieb’s theorem [22]. The nonpositive property of E_{cum} relieves one from the phase dilemma in functional reconstruction of $\Gamma_{ij,kl}$ in DMFT [23,24].

The conventional strategy of functional modeling in DMFT is to reconstruct the matrix elements of pair density or its cumulant term by term with functionals of 1DM. Based on the paradigm of two-electron theory [25], the square-root functional $\sqrt{n_i}$ is popular among various functional models [26–39]. A close functional form is the power function n_i^α with optimized $\alpha \approx 0.656$ [40–42]. According to Eq. (8), there are four indexes $\{ij, kl\}$ in $\Gamma_{ij,kl}$, the number of different elements is in the order of M^4 , where M is the number of orbitals, symmetry consideration may reduce distinct elements of $\Gamma_{ij,kl}$, but still there are too many elements to be modeled. So in real practice, only a limited number of elements are modeled, typically the *JK* elements [43], while other elements are neglected.

After the careful comparison of DMFT functional models with the pair density from the wave function [44,45], we found some general shortcomings in conventional DMFT models, regarding nonuniqueness, symmetry dependence, and universality. To overcome those shortcomings, and at the same time, to go beyond *JK*-only functional type and avoid the phase dilemma problem, we try to model the integral of Eq. (13) as a whole, instead of modeling elements of $\lambda(1, 2)$ term by term.

Collins [46] once conjectured the correlation energy was proportional to the information entropy. In his conjecture, the correlation energy is defined as $E_{\text{cor}} = E_{\text{exact}} - E_{\text{HF}}$ as in traditional quantum chemistry [47]. The information entropy used was based on Shannon’s definition for probabilities [48],

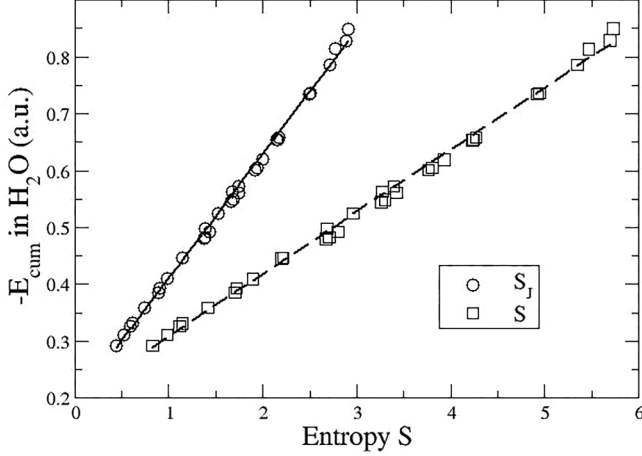


FIG. 1. The cumulant energy with respect to the entropies, S_J and S , from wave function analysis with the basis set cc-pVDZ. S_J is from Table II of Ref. [12].

or more exactly Jaynes' definition for the density matrix [49],

$$S_J = - \sum_i n_i \ln n_i, \quad (15)$$

which is also in the spirit of von Neumann entropy [50].

However, Collins's conjecture has not been substantiated, with, for instance, large deviations for the simple H_2 molecule along the internuclear coordinate [51,52]. After making a careful analysis on each part of the total energy, including the kinetic energy, two-electron energy, and cumulant energy [12,53], we found that the cumulant energy has the expected linear relationship with the information entropy S_J .

However, the entropy form of S_J leads to Boltzmann distribution for the occupation numbers [54],

$$n_i = \exp\left[\frac{\mu - \epsilon_i}{\kappa} - 1\right] = n_0 \exp\left[-\frac{\epsilon_i}{\kappa}\right]. \quad (16)$$

In this form, it is possible that some n_i becomes greater than 1, which violates the Pauli principle. Because electrons are identical and indistinguishable particles, which follows the Fermi-Dirac statistics, the desirable entropy is Eq. (9) [55]. The additional term from $1-n_i$ increases the entropy S over S_J . Does the entropy S also hold a linear relation with the cumulant energy? In Table I, we employ the same data set as used for H_2O in Ref. [12], recalculate the entropy using Eq. (9). The cumulant energies with respect to both entropies, S_J and S , are compared in Fig. 1. To a good approximation, a linear relation still holds, only the slope has changed,

$$E_{\text{cum}} = -\kappa S - b, \quad (17)$$

where κ and b are constant depending on the system.

The above relation is physically appealing because electron correlation reduces the energy, the negative minimum correlation energy can be sought through the positive maximum entropy. The cumulant is extensive, the cumulant energy is also an extensive quantity [20]. The information entropy is also additive for independent events or groups [48,56]. In this respect, the equation is consistent.

TABLE I. Entropy and the correlation energy E_{cum} (in a.u.) of H_2O in different geometries, calculated with the basis set cc-pVDZ. R_1 and R_2 are the two H-O bond lengths in bohr. θ is the angle between R_1 and R_2 in degree. In the column $\kappa S + b$, $\kappa = 0.10928$ and $b = 0.19872$. The error is $\Delta = -E_{\text{cum}} - (\kappa S + b)$.

R_1	R_2	θ	S	$-E_{\text{cum}}$	$\kappa S + b$	error Δ
1.5	1.5	104	0.827369	0.292481	0.289132	0.003349
1.8	1.8	104	0.980903	0.310823	0.305910	0.004913
2.0	2.0	104	1.117670	0.326621	0.320856	0.005765
2.0	2.0	90	1.143829	0.331368	0.323715	0.007653
2.0	2.5	104	1.414363	0.359273	0.353279	0.005994
1.5	3.0	104	1.703884	0.385724	0.384919	0.000805
2.5	2.5	104	1.720543	0.393399	0.386739	0.006660
2.0	3.0	104	1.892864	0.409800	0.405571	0.004229
2.5	3.0	90	2.201364	0.445860	0.439284	0.006576
2.5	3.0	104	2.213900	0.446331	0.440654	0.005677
3.0	3.0	90	2.674029	0.480264	0.490938	-0.010674
3.0	3.0	80	2.683345	0.498437	0.491956	0.006481
3.0	3.0	104	2.705745	0.482863	0.494404	-0.011541
3.0	3.0	120	2.801007	0.492003	0.504814	-0.012811
2.0	4.0	104	2.959595	0.524455	0.522145	0.002310
3.0	3.5	90	3.259834	0.544781	0.554956	-0.010175
3.0	3.5	80	3.273371	0.562797	0.556435	0.006362
3.0	3.5	104	3.303197	0.548979	0.559694	-0.010715
2.0	5.0	104	3.396455	0.572692	0.569886	0.002806
3.0	3.5	120	3.420204	0.561060	0.572481	-0.011421
3.0	4.0	90	3.762673	0.601068	0.609907	-0.008839
3.0	4.0	104	3.800557	0.604960	0.614047	-0.009087
3.5	3.5	104	3.929460	0.619154	0.628133	-0.008979
3.0	5.0	80	4.229828	0.653541	0.660958	-0.007417
3.0	5.0	104	4.243364	0.654838	0.662437	-0.007599
3.0	5.0	120	4.269684	0.657830	0.665314	-0.007484
4.0	4.0	80	4.923086	0.734728	0.736719	-0.001991
4.0	4.0	104	4.945478	0.736814	0.739166	-0.002352
4.0	5.0	90	5.350569	0.785682	0.783435	0.002247
4.0	4.5	104	5.472077	0.813650	0.796713	0.016937
5.0	5.0	104	5.695376	0.828640	0.821116	0.007524

If we compare it to the free energy $F = E - TS$ [57,58], κ can be considered as playing the role of the effective temperature T . A system with a large value of κ is effectively in a state of high temperature or strong correlation. While we focus on the cumulant energy in i -DMFT, a noninteracting kinetic free energy at the fictitious temperature is introduced along with the entropy in the thermally assisted occupation DFT (TAO-DFT) method [17]. Obviously, the entropy there is used to add more flexibility in the modeling of noninteracting kinetic energy.

Recently, Mazziotti *et al.* [59,60] introduced a functional of $\sum_i n_i - n_i^2 = N - \sum_i n_i^2$ to correct the noninteracting kinetic energy in DFT. For Hartree-Fock approximation, $n_i = 1$ or 0, then $n_i = n_i^2$, which is idempotent [2]. When $1 > n_i > 0$, then $n_i > n_i^2$. Thus nonidempotency has been proposed as a measure of correlation [51,61]. Interestingly, they showed that the nonidempotency can be derived from Eq. (9) using the Taylor expansion of the logarithmic function,

$$S \approx \frac{5}{2} \sum_i n_i - n_i^2. \quad (18)$$

TABLE II. The parameters κ and b for atoms in the basis set cc-pVDZ. κ is determined by the entropy of the occupation numbers from CI wave function, b is calibrated to the total energy. All quantities are in atomic unit.

Atom	Entropy	Energy	κ	b
He	0.188572	-2.887594	0.23812	0.024864
Li	0.003391	-7.432637	0.01192	0.000201
Be	1.455016	-14.617409	0.05938	0.024798
B	1.247217	-24.590629	0.06582	0.042337
C	3.793661	-37.707295	0.09138	0.030535
N	3.333223	-54.380166	0.14643	-0.076230
O	3.594539	-74.833036	0.13776	0.037254
F	0.716118	-99.529518	0.124295	0.134215
Ne	0.698732	-128.680881	0.27169	0.158932

This suggests another reason why the entropy functional is also relevant to the correlation energy. However, one should be aware that this function does not lead to the Fermi-Dirac distribution during Lagrange variation with respect to n_i .

Since the parameters κ and b are introduced in i -DMFT based on empirical observation between E_{cum} and S , there is no first-principles derivation yet. In practice, there are several ways to choose the parameters. In general, one may choose two or several points on the potential energy curve (or surface), then optimize the parameters via the cost function

$$\Delta E = \sum_i |E_i^{\text{CI}} - E_i^{\text{iDMFT}}(\kappa, b)|, \quad (19)$$

where E_i^{CI} is the total energy from CI calculations.

Since parameter b is a constant shift in the total energy, it does not affect the difference of two energies, such as dissociation energy (D_e), which is the difference between two energies, one at equilibrium and another at the dissociation limit. Experimental D_e is available for many small molecules [62]. One can set $b = 0$ at the beginning. From the energy difference of two geometries, the optimal parameter κ can be adjusted by simple trial and error. Once κ is obtained, b can be calibrated by the total energy at any geometry.

The parameter b also does not enter the eigenvalue equations for the orbitals, so it does not affect the orbital energies, and so the entropy. In principle, the occupation numbers from i -DMFT should reproduce those of 1RDM from the wave function. So κ can also be fitted to the entropy of 1RDM from wave function calculation. In the TAO-DFT method [17], the fractional occupation numbers are defined with the Kohn-Sham orbital energies through the Fermi-Dirac distribution, they are not connected with the eigenvalues of 1RDM, so the parameter of fictitious temperature can not be determined from the knowledge of 1RDM.

At the dissociation limit, the total energy and entropy can be readily obtained by adding the individual values of the atoms. Table II lists the relevant data for atoms from the MOLPRO code [63] with the basis set cc-pVDZ. The parameter κ is chosen to reproduce the entropy of 1RDM, and b is then calibrated to the total energy. The data can be of help in search of κ for molecules. The rule of thumb for the parameters κ from one molecular system to another is still to be studied. It

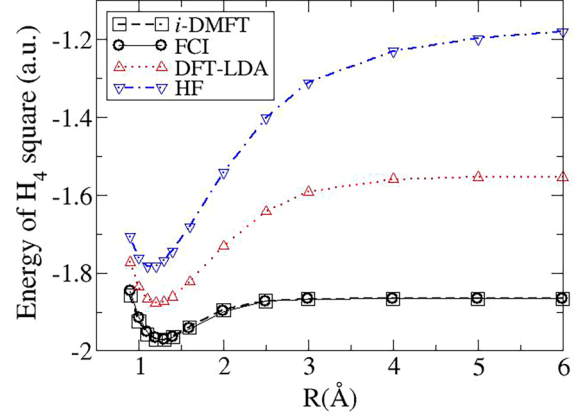


FIG. 2. The total energy curves of different methods for the ground state of H_4 square with the basis set STO-3G. The parameters in i -DMFT are $\kappa = 0.149623$ and $b = -0.0550800366$ (a.u.).

is possible in the future to search the parameter κ by machine learning from a large data set [64].

III. UNIFORM STRETCHING OF SQUARE H_4

The H_4 model has been a classic model system to test various computational methods [65–67]. Study on linear H_4 has been reported with the i -DMFT method [60]. Here we concentrate on the square H_4 model under uniform stretching with a minimum basis set (STO-3G). There are four symmetry-adapted orbitals a_{1g} , e_{ux} , e_{uy} , and b_{2g} . Because e_{ux} and e_{uy} are degenerate, the assignment of four electrons in the orbitals is frustrated in the closed-shell single-determinant description of the Hartree-Fock or the Kohn-Sham DFT method. As Fig. 2 shows, both the Hartree-Fock and the DFT local density approximation (LDA) lead to too high energies from equilibrium distance all the way to the dissociation limit.

There are a total of $\binom{M}{N/2}^2 = 36$ determinants in the full CI wave function. For the ${}^1B_{1g}$ ground state with the D_{4h} symmetry, the wave function is reduced to the following Slater determinants built from the orbitals [44],

$$\Psi_4 = c_1 (|a_{1g}^2 e_{ux}^2| - |a_{1g}^2 e_{uy}^2|) + c_2 (|b_{2g}^2 e_{ux}^2| - |b_{2g}^2 e_{uy}^2|) + c_3 \left| a_{1g} e_{ux} e_{uy} b_{2g} \frac{1}{2\sqrt{3}} [\alpha\alpha\beta\beta + \beta\beta\alpha\alpha + \alpha\beta\alpha\beta + \beta\alpha\beta\alpha - 2(\alpha\beta\beta\alpha + \beta\alpha\alpha\beta)] \right|, \quad (20)$$

with $c_3 = \sqrt{1 - 2c_1^2 - 2c_2^2}$. The eigenvalues of the 1RDM are then, for $\sigma = \alpha$ or β ,

$$n_{a_{1g}}^\sigma = \frac{1}{2} + c_1^2 - c_2^2, \quad (21)$$

$$n_{b_{2g}}^\sigma = 1 - n_{a_{1g}}^\sigma, \quad (22)$$

$$n_{e_{ux}}^\sigma = n_{e_{uy}}^\sigma = \frac{1}{2}. \quad (23)$$

Thus the spin-summed occupation number for the orbital of either e_{ux} or e_{uy} is exactly 1.

TABLE III. The HF, DFT-LDA, FCI, and *i*-DMFT total energies (in a.u.) for the ground state of H₄ on a square with the internuclear distance *R*, calculated with the basis set STO-3G. The *i*-DMFT data are calculated with $\kappa = 0.149623$ and $b = -0.0550800366$ (a.u.).

<i>R</i> (Å)	HF	DFT-LDA	FCI	<i>i</i> -DMFT
0.9	-1.706763	-1.772384	-1.846741	-1.856366
1	-1.761075	-1.835708	-1.915107	-1.922480
1.1	-1.782551	-1.866981	-1.951594	-1.956456
1.2	-1.782361	-1.877366	-1.967550	-1.969922
1.3	-1.767816	-1.874061	-1.970377	-1.970376
1.4	-1.743877	-1.861757	-1.965081	-1.963195
1.6	-1.680637	-1.822578	-1.942939	-1.938919
2	-1.541255	-1.730882	-1.897849	-1.894355
2.5	-1.400853	-1.642249	-1.873174	-1.872071
3	-1.311334	-1.592107	-1.867495	-1.867296
4	-1.229731	-1.559107	-1.866348	-1.866345
5	-1.198050	-1.554575	-1.866328	-1.866328
6	-1.179943	-1.554165	-1.866327	-1.866327

In the *i*-DMFT method, there are two parameters: κ and b . Since b is only a shift in the total energy, it does not affect the difference of two energies, such as the dissociation energy D_e . Here we approximate the dissociation limit with $R = 6$ Å. One can use experimental or theoretical D_e to determine κ . For the square H₄, the full CI calculation gives $D_e = |-1.970377$ (at $R = 1.3$ Å) $-(-1.866327$ (at $R = 6$ Å)) = 0.104050 (a.u.). After a few trial-and-error calculations (starting from, say $\kappa = 0.1$), we find $\kappa = 0.149623$ will give $D_e = 0.104049$ (a.u.). Since *i*-DMFT calculation is fast, it does not take much time to find κ . Once κ is settled, one can use the CI total energy at $R = 6$ Å to calibrate b , which is just a shift to match to the corresponding CI energy. Table III lists all the total energy values with different methods, which are displayed in Fig. 2.

TABLE IV. The occupation numbers of the a_{1g} , b_{2g} , e_{ux} , and e_{uy} orbitals (spin summed) in H₄ calculated with the *i*-DMFT and full CI methods using the basis set STO-3G. The parameters in *i*-DMFT are $\kappa = 0.149623$ and $b = -0.0550800366$ (a.u.).

<i>R</i> (Å)	<i>i</i> -DMFT			full CI		
	a_{1g}	b_{2g}	e_{ux}, e_{uy}	a_{1g}	b_{2g}	e_{ux}, e_{uy}
0.9	1.98993	0.00327	1.00346	1.96026	0.03974	1
1	1.98215	0.00818	1.00483	1.94773	0.05227	1
1.1	1.97000	0.01784	1.00608	1.93220	0.06780	1
1.2	1.95350	0.03366	1.00642	1.91292	0.08708	1
1.3	1.93150	0.05747	1.00551	1.88908	0.11092	1
1.4	1.90305	0.08904	1.00328	1.85988	0.14012	1
1.6	1.82367	0.18387	0.99624	1.78269	0.21731	1
2	1.58045	0.44425	0.98764	1.55801	0.44199	1
2.5	1.27460	0.73859	0.99340	1.27480	0.72520	1
3	1.10755	0.89620	0.99812	1.11176	0.88824	1
4	1.01234	0.98777	0.99994	1.01340	0.98660	1
5	1.00099	0.99900	0.99999	1.00111	0.99889	1
6	1.00092	0.99907	1.00000	1.00006	0.99994	1

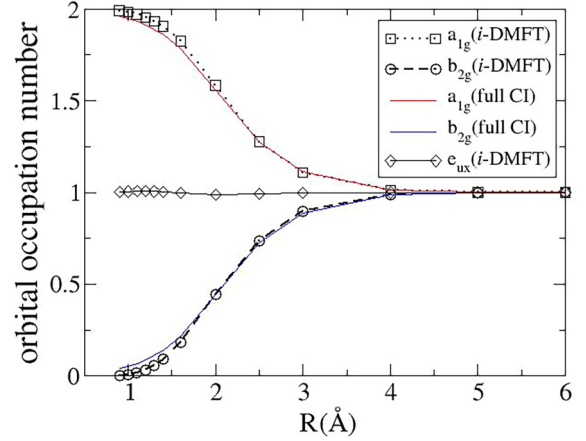


FIG. 3. The occupation numbers of the a_{1g} , b_{2g} , and e_{ux} orbitals of H₄ square as a functional of nuclear separation. The occupation number of the e_{uy} orbital (not shown in the figure) equals that of e_{ux} . For the CI case, the occupation number of the e_{ux} orbital is exactly 1. The data are calculated with the basis set STO-3G. The parameters in *i*-DMFT are $\kappa = 0.149623$ and $b = -0.0550800366$ (a.u.).

Table IV compares the spin-summed occupation numbers from both the *i*-DMFT method and the full CI method, which are displayed in Fig. 3. The overall agreement with the full CI results is quite good. Even though $n_{e_{ux}}$ and $n_{e_{uy}}$ in *i*-DMFT do not give exactly the number 1 from the Fermi-Dirac distribution, they are very close to the wave function result. The system thus provides a simple yet interesting model to compare with Hartree-Fock and DFT calculations, and benchmark the *i*-DMFT method.

IV. LINEAR CHAIN OF 50 HYDROGEN ATOMS

The linear chain of hydrogen atoms is a prototype example of strong electronic correlation [68–71]. It is known that one needs fractional occupation number to describe the static or nondynamic correlation even in H₂ [16,72]. The density matrix renormalization group (DMRG) method is particularly

TABLE V. Total energies for symmetric dissociation of H₅₀ with the basis set STO-6G. The RHF and DMRG energies are from Ref. [68]. *i*-DMFT energies are calculated with $\kappa = 0.14251$ and $b = 0.219552$ (a.u.). Δ is the difference of DMRG and *i*-DMFT energies. All energies are in a.u..

<i>R</i> (bohr)	RHF	DMRG	<i>i</i> -DMFT	Δ
1.0	-16.864876	-17.284066	-16.964971	-0.319095
1.2	-22.461267	-22.947647	-22.703113	-0.244534
1.4	-25.029763	-25.593783	-25.430992	-0.162791
1.6	-26.062253	-26.719443	-26.640413	0.079030
1.8	-26.265983	-27.038653	-27.038653	0.000000
2.0	-26.008202	-26.926092	-26.994034	0.067942
2.4	-24.835761	-26.160571	-26.313916	0.153345
2.8	-23.360813	-25.274803	-25.439828	0.165025
3.2	-21.896331	-24.568281	-24.691067	0.122786
3.6	-20.574288	-24.102768	-24.165967	0.063199
4.2	-18.955948	-23.749708	-23.749940	0.000232

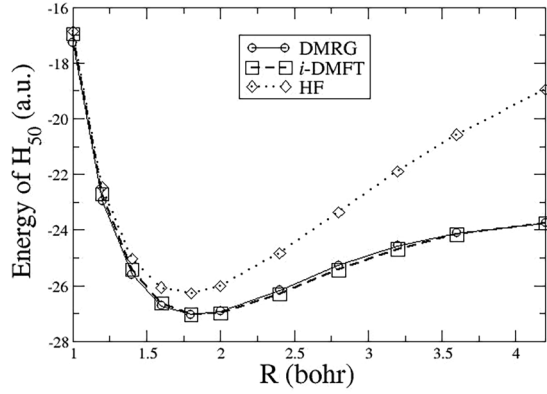


FIG. 4. The potential energy curves for symmetric dissociation of H_{50} with the basis set STO-6G. In the i -DMFT calculation, $\kappa = 0.14251$ and $b = 0.219552$ (a.u.).

adapted to one-dimensional problems, previously the linear hydrogen chain of H_{50} has been studied by Chan *et al.* using the DMRG method [68].

Following Chan *et al.*, we consider two cases, one is symmetric dissociation with all 49 bonds of 50 equidistant H atoms symmetrically and simultaneously stretching, and another is asymmetric dissociation with alternating bonds of R_{inter} and R_{intra} , with R_{intra} kept fixed at 1.4 bohr. Thus the structure models 25 equidistant H_2 molecules distributed on a line. The calculations are carried out in the basis set of STO-6G.

Table V and Fig. 4 show the results of symmetric bond stretching. The i -DMFT result is obtained with $\kappa = 0.14251$ and $b = 0.219552$ (a.u.). The parameters are chosen by fitting to two DMRG energies, one at $R = 1.8$ bohr and another at $R = 4.2$ bohr. First, the parameter κ is chosen to reproduce the energy difference of the two energies, then b is used to shift the energy at $R = 1.8$ bohr to the corresponding DMRG value. In Table VI and Fig. 5, the results of asymmetric dissociation are displayed. The i -DMFT result is obtained with $\kappa = 0.06$ and $b = 0.50916936$ (a.u.). The parameters are chosen by fitting to the DMRG energies at $R = 1.4$ bohr and $R = 1.6$ bohr. One may choose two different energy points on the curve

TABLE VI. Total energies for asymmetric dissociation of H_{50} with the basis set STO-6G. The RHF and DMRG energies are from Ref. [68]. i -DMFT energies are calculated with $\kappa = 0.06$ and $b = 0.50916936$ (a.u.). Δ is the difference of DMRG and i -DMFT energies. All energies are in a.u..

R (bohr)	RHF	DMRG	i -DMFT	Δ
1.4	-25.029763	-25.593783	-25.593783	0.000000
1.6	-25.963707	-26.487377	-26.487990	0.000613
1.8	-26.617685	-27.127165	-27.133553	0.006388
2.0	-27.071820	-27.577320	-27.584640	0.007320
2.4	-27.609241	-28.117611	-28.119937	0.002326
2.8	-27.873616	-28.387066	-28.383616	-0.003450
3.2	-28.004679	-28.521239	-28.514377	-0.006862
3.6	-28.069652	-28.587362	-28.579196	-0.008166
4.2	-28.111003	-28.628583	-28.620434	-0.008149

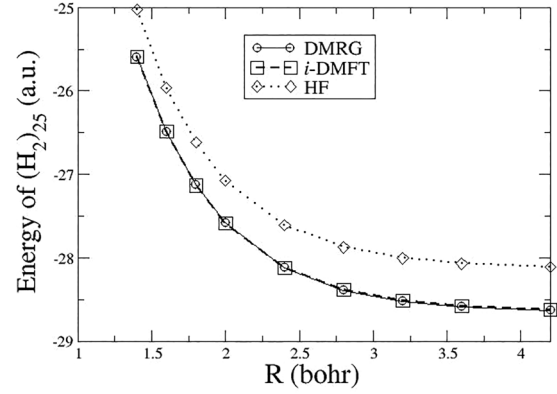


FIG. 5. The potential energy curves for asymmetric dissociation of H_{50} with the basis set STO-6G. In the i -DMFT calculation, $\kappa = 0.06$ and $b = 0.50916936$ (a.u.).

to determine the parameter set, it is possible to find slightly different values for the parameters, but the result is almost the same quality.

In the i -DMFT method, all electrons are correlated in the full orbital space in the functional manner. Because the DMRG method also introduces approximation in setting the size of the renormalized density matrix, some difference in the total energy between DMRG and i -DMFT methods is expected. However, the overall agreement with the DMRG results is still impressive.

V. DISCUSSION AND CONCLUSION

Electron correlation has been the focus of many theoretical and computational efforts over the past decades [73–87]. One of the challenging problems is the N -representability problem of the density matrix [88,89]. The N -representability problem of 1RDM has been almost solved thanks to Klyachko [90,91]. It is now clear that there are additional constraints on the natural orbital occupation numbers, besides $1 \geq n_i \geq 0$ to comply with the Pauli principle. The 1RDM in DMFT is only constrained by $1 \geq n_i \geq 0$ at the moment, so some discrepancy with the wave function result of occupation number is expected [92].

In the i -DMFT method [13], the eigenvalue equation for the natural spin orbital is

$$\left[\hat{h} + \sum_j n_j (\hat{J}_j - \hat{K}_j) \right] \chi_i(1) = \epsilon_i \chi_i(1), \quad (24)$$

where \hat{J}_j and \hat{K}_j are the Coulomb and exchange operators as in the Hartree-Fock method [93]. When the occupation numbers n_j are either 1 or 0, it becomes the Hartree-Fock equation. So the equation looks like just a natural extension of the Hartree-Fock equation to the general case when n_i become fractional. One can implement i -DMFT calculation with minimal modification of the existing Hartree-Fock code. The method can be readily extended to open-shell systems [94], just as the unrestricted Hartree-Fock method [95] extends the restricted Hartree-Fock method [96].

As the Hartree-Fock equation, the above equation is a mean-field approximation. The exact equation satisfied by the natural spin orbital is much more complicated [2]. There is certainly room to improve the *i*-DMFT method, such as a first-principles estimation of the parameter set κ and b , and invoking orbital dependence in the cumulant energy. The advantage of the current form is its cost efficiency. As a correlation method, it is much cheaper than the full CI or other correlated wave function method.

The DFT method has been widely used for electronic structure calculations, especially near equilibrium geometry. Its shortcoming is in the description of static electron correlation, which may be improved by combining with the DMFT

method [97,98]. The calculations with the square H_4 and hydrogen chain of H_{50} demonstrate that the *i*-DMFT method is able to achieve reasonable results across weak (or dynamic) and strong (or static) correlation regions.

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