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Self-Consistent-Field Method for Correlated Many-Electron Systems with an Entropic Cumulant Energy

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A self-consistent field method is presented within density matrix functional theory. The computational cost for a correlated many-electron calculation is reduced to that of the self-consistent-field Hartree-Fock method, while the accuracy still reaches that of sophisticated configuration interaction based methods. In this method, the two-electron cumulant energy is measured with an information entropy associated with the Fermi-Dirac distribution of the occupation numbers. An eigenvalue equation for the orbitals is obtained, with the eigenvalues (orbital energies) connected to the occupation numbers through the Fermi-Dirac distribution. The occupation numbers for the strongly occupied orbitals are very close to the natural orbital occupation numbers from wave function methods. It covers in a single scheme the nondynamical correlation in weak or breaking bonds as well as the dynamical correlation at all distances. The method is well suited to large-scale potential energy surface calculation and molecular dynamics simulation.

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Arguably the most important problem in electronic structure theory is the accurate yet efficient rendering of the electron correlation energy. Specializing to atoms and molecules, a range of methods and implementations has been explored. *Ab initio* methods, i.e., Hartree-Fock (HF) plus some form of configuration interaction (CI), have been developed over a long time and can now be pushed to high accuracy, although at the expense of large amounts of computer time. They do not scale well for large systems. Density functional theory (DFT) [1,2] has enjoyed great popularity because of a good compromise between accuracy and efficiency [3]. It can be applied, in its Kohn-Sham (KS) form, to large systems, but the accuracy is still insufficient for many purposes. In particular for geometries that deviate from the equilibrium geometry (bond dissociation, transition states, general potential energy surfaces) it often falls short of the required accuracy. It is known that the exact exchange-correlation functional is nonlocal, and this nonlocality is particularly important when the (partial) spreading of exchange and correlation holes over the atoms of the dissociating bond plays a role. It is difficult to incorporate the nonlocality correctly in actual functionals. It appears that one has to invoke the virtual KS orbitals in order to achieve this [4–7]. Density matrix functional theory (DMFT) [8] has been investigated in the last decades for its potential to describe potential energy surfaces much better, also those of excited states. The primary reason is the natural incorporation of nonlocality effects by the involvement of “virtual” natural orbitals (NOs) through the NO occupation numbers (ONs) [9]. In spite of some successes for small systems [10,11], DMFT has not become a main

stream methodology due to theoretical and computational obstacles (see below).

We present in this Letter a new method for correlated calculations. It is a variant of DMFT in that it involves the “virtual orbitals” in a natural manner by their ONs (which are similar to the NO ONs). But it solves the practical computational problems of DMFT in that it requires just a self-consistent field procedure to obtain the orbitals, and therefore is as cost-effective as HF or KS calculations. It still delivers correlated energies by a new Ansatz for the electron cumulant energy (the correlation energy in the DMFT context) which is cast in the form of a function of the ONs which is inspired by information theoretic (Shannon entropy) concepts [12,13]. It will be shown to offer accurate correlated energies at essentially HF (or KS) computational expense.

In DMFT the variable is the one-particle reduced density matrix (1RDM) $\gamma(1, 1')$ which has the spectral expansion

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

The eigenvectors $\{\chi_i\}$ are called the natural orbitals, and the eigenvalues $\{n_i\}$ are their occupation numbers (ONs), which sum to the number of electrons $\sum n_i = N$. For a single-determinant wave function (HF or KS), n_i are either 0 or 1. For a correlated system with the wave function expanded as a linear combination of Slater determinants, the occupation numbers are fractional numbers, $0 < n_i < 1$. The diagonal element of the 1RDM, i.e., $\gamma(1, 1)$, is the electron density. The kinetic energy and electron-nucleus Coulomb energy can be expressed exactly with the

exact 1RDM. While progress has been made over the last two decades with optimization schemes for the NOs and ONs, and with the development of suitable 1RDM functionals [14–19], there are still theoretical and computational obstacles to overcome for DMFT to become a successful computational method.

In his seminal paper on DMFT, Gilbert constructed an eigenvalue problem for the natural spin orbitals

$$h^G \chi_i = \epsilon_i \chi_i. \quad (2)$$

The one-electron Gilbert Hamiltonian h^G is related to the functional $E(\gamma)$ as $h^G = \delta E(\gamma) / \delta \gamma(1, 1')$. To his surprise, Gilbert [8] noted “an unexpected and paradoxical result for the one-particle reduced ensemble density kernel,” “that all partially occupied natural spin orbitals must belong to the same degenerate eigenvalue ($\epsilon_i = \mu$).” Gilbert concluded: “If the operator h^G can be constructed, it must be quite different from the one-electron orbital operators that occur in self-consistent-field theories” (original quotation). This degeneracy problem is not prohibitive but still inconvenient. In the case that (an approximation to) the electron-electron energy is given in terms of the natural orbitals and occupation numbers, Pernal [20] has applied the chain rule to show that an effective one-electron operator h^G can be explicitly derived. The degeneracy of the orbital energies in DMFT remains, for which a level-shift method was proposed, but successful implementation is still somewhat empirical. Conceptually the lack of meaningful orbital energies (cf. for estimates of excitation energies or band structures) is inconvenient. Computational inconveniences in current DMFT implementations compared with DFT are the occurrence of expensive four-index transformations to evaluate the exchange-correlation functional expressed in the NOs and ONs, and the required separate optimization of the ONs.

Here we take a different route, which is based on a correlation energy functional associated with the two-electron cumulant. The two-electron cumulant follows from the well-known decomposition of the two-particle reduced density matrix (here its diagonal element, the pair density) in terms of 1RDM contributions, plus a remainder,

$$\Gamma(1, 2) = \frac{1}{2} [\gamma(1, 1)\gamma(2, 2) - \gamma(1, 2)\gamma(2, 1)] + \lambda(1, 2). \quad (3)$$

The first term is the independent-particle contribution to the pair density, and the second term accounts for the exchange effect. The $\lambda(1, 2)$ term is called the two-electron cumulant [21,22]. The Hartree-Fock (HF) approximation is characterized by $\lambda(1, 2) = 0$. It has been proven that if $\lambda(1, 2)$ is neglected and the total energy is optimized with only direct and exchange terms, an idempotent 1RDM will result [23]. We will call the energy associated with the two-electron cumulant

$$E_{\text{cum}} = \int \frac{\lambda(1, 2)}{r_{12}} d1d2 \quad (4)$$

the cumulant correlation energy. It is to be distinguished from the traditional quantum chemical definition of correlation energy as the difference between the exact total energy and the HF energy, $E_{\text{cor}} = E_{\text{exact}} - E_{\text{HF}}$.

Entropy is a key concept of statistical mechanics. In quantum statistical mechanics, von Neumann [24] formulated the entropy using the density matrix (ρ) as $S = -\text{Tr} \rho \ln \rho$. This leads for states Ψ_j occurring with probabilities p_j in an ensemble to the expression $S = -\sum_j p_j \ln p_j$. In his information theory, Shannon [25] arrived at a similar expression for the uncertainty connected with a probability distribution $\{p_i\}$ for events. It is therefore also denoted as Shannon entropy or information entropy. Jaynes [26] has investigated the basic assumptions of statistical mechanics (entropy maximization) from the viewpoint of information entropy being the more fundamental concept.

Collins [27] once conjectured that an “entropy” evaluated with the 1RDM eigenvalues $S = -\sum_i n_i \ln n_i$ would be proportional to the traditional correlation energy E_{cor} . However, this has not been substantiated, with for instance, large deviations for the simple H_2 molecule along the internuclear coordinate [28–30]. However, in our recent work [12] we have established that this is different for the cumulant energy as a measure of correlation energy: when varying the geometry of a molecule the cumulant energy proves to have an almost perfect linear relationship with the entropy $S = -\sum_i n_i \ln n_i$:

$$E_{\text{cum}} = -\kappa S - b \quad (5)$$

where κ and b are constants depending on the system. Note that the correlation energy E_{cum} is a negative quantity [31].

In statistical physics, the entropy for fermions has been derived as [32,33] (apart from the k_B factor)

$$S = -\sum_i [n_i \ln n_i + (1 - n_i) \ln (1 - n_i)] \quad (6)$$

where the n_i are the (average) occupations of the one-electron states. This form of the entropy has been discussed for the uniform electron gas [34]. It has recently been established that the linear relationship with the cumulant energy mentioned above also exists with the entropy of Eq. (6) (to distinguish it from the entropy $S = -\sum_i n_i \ln n_i$) [13]. In the Hartree-Fock approximation, n_i are either 0 or 1, so the entropy is zero. For a correlated system, $0 < n_i < 1$, the entropy is positive.

These investigations suggest a DMFT functional for the total energy using Eq. (5) and Eq. (6),

$$E[\{n_i\}, \{\chi_i\}] = \sum_i n_i h_{ii} + Y - \kappa S - b \quad (7)$$

where Y is

$$\begin{aligned} Y &= \frac{1}{2} \iint \frac{\gamma(1,1)\gamma(2,2) - \gamma(1,2)\gamma(2,1)}{r_{12}} d1d2 \\ &= \frac{1}{2} \sum_{ij} n_i n_j [\langle ij|ij \rangle - \langle ij|ji \rangle] = \frac{1}{2} \sum_{ij} n_i n_j \langle ij||ij \rangle. \end{aligned} \quad (8)$$

The problem of optimizing the energy $E[\{n_i\}, \{\chi_i\}]$ under the constraint $\sum n_i = N$ and with orthonormality conditions for the spin orbitals leads to the Lagrangian

$$\begin{aligned} \Omega(\{n_i\}, \{\chi_i\}) &= E[\{n_i\}, \{\chi_i\}] - \mu \left(\sum_i n_i - N \right) \\ &\quad - \sum_{ij} \lambda_{ij} (\langle \chi_i | \chi_j \rangle - \delta_{ij}) \end{aligned} \quad (9)$$

where μ and λ_{ij} are Lagrange multipliers. The Euler-Lagrange equations $\delta\Omega/\delta\chi_i^*(1) = 0$ for the orbitals yield

$$n_i \left[\hat{h} + \sum_j n_j (\hat{J}_j - \hat{K}_j) \right] \chi_i(1) = \sum_k \lambda_{ik} \chi_k(1) \quad (10)$$

and the corresponding complex conjugated set of equations. Here \hat{h} is the one-electron operator (in atomic units)

$$\hat{h} = -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \quad (11)$$

and \hat{J}_j and \hat{K}_j are the Coulomb and exchange operators as in the Hartree-Fock method [35].

The conditions $\partial\Omega/\partial n_i = 0$ for the occupation numbers yield [using Eq. (6) for the entropy]

$$h_{ii} + \sum_j n_j \langle ij||ij \rangle + \kappa [\ln n_i - \ln(1 - n_i)] = \mu \quad (12)$$

The Hermitian property of Lagrange multipliers λ_{ki} requires $\lambda_{ik} = \lambda_{ki}^*$, i.e., $(n_i - n_k) \langle k|\hat{f}|i \rangle = 0$, which implies an eigenvalue problem for the orbitals

$$\hat{f} \chi_i(1) = \epsilon_i \chi_i(1) \quad (13)$$

where the operator \hat{f} is

$$\hat{f} = \hat{h} + \sum_j n_j [\hat{J}_j - \hat{K}_j]. \quad (14)$$

Except for the additional factor n_j , this is exactly the Fock operator in the Hartree-Fock method. When the occupation numbers are close to 1 and 0 (dynamical correlation only)

the eigenvalues ϵ_i (the orbital energies) are expected to be close to the HF orbital energies.

Once the eigenvalue problem is solved, we insert the eigenvalues ϵ_i into Eq. (12) to obtain

$$\epsilon_i + \kappa [\ln n_i - \ln(1 - n_i)] = \mu. \quad (15)$$

Note that Gilbert's "paradox" of all ϵ_i being equal, $\epsilon_i = \mu$, does not recur here; instead, the above equation leads to

$$n_i = \frac{1}{1 + \exp[(\epsilon_i - \mu)/\kappa]} \quad (16)$$

which is just the Fermi-Dirac distribution. The Lagrange multiplier μ is fixed by the sum rule $\sum n_i = N$. The distribution n_i can be updated from the eigenvalues ϵ_i immediately after the solution of the eigenvalue equations for the orbitals; no extra optimization procedure for n_i is required. This makes the computation effort of this method nearly the same as the Hartree-Fock method. Since this variant of the density matrix functional method is based on entropy, with statistical mechanical and information theoretic connotations [25,26], we denote it here as *i*-DMFT.

Investigations like the one by Levy [31] of scaling relations and constraints for $E_{\text{cum}}[\gamma]$ may offer a route to first-principles determination of κ . Here we take a pragmatic approach. Since κ controls the distribution $\{n_i\}$ via Eq. (16) and so the entropy of Eq. (6) as well, one can simply determine κ by fitting to the entropy of Eq. (6) from a wave function calculation at a single (e.g., equilibrium) geometry.

In case the eigenvalue analysis of the 1RDM is not available from the wave function, there is another way to obtain κ . Since the entropy at dissociation is larger than that at equilibrium geometry [30], doing *i*-DMFT calculations while varying κ , one will get different estimates of $E_{\text{cum}}^{\text{eq}} - E_{\text{cum}}^{\infty}$, and so different values of the total energy difference $E^{\text{eq}} - E^{\infty} = -D_e$. By comparing to the CI or experimental value of D_e , one can find the optimal value of κ . Tables I and II of the Supplemental Material [36] lists such optimal values of κ for H_2 under different basis sets. As expected, there is some variation due to the different quality and dimension of the basis sets.

The constant b is immaterial for orbital energies and energy differences such as D_e . One can start the *i*-DMFT calculation with any value of b . In case the absolute value of the energy is required, b can be simply obtained by calibrating to the CI or experimental value at some geometry.

Figure 1 shows the E vs R curves of H_2 from restricted HF, full CI (FCI), and the *i*-DMFT method. It is clear that the method reproduces the FCI curve very well and in particular avoids the notorious restricted HF problem of much too high energy in the dissociation limit. This problem is alleviated in (spin- and symmetry-restricted)

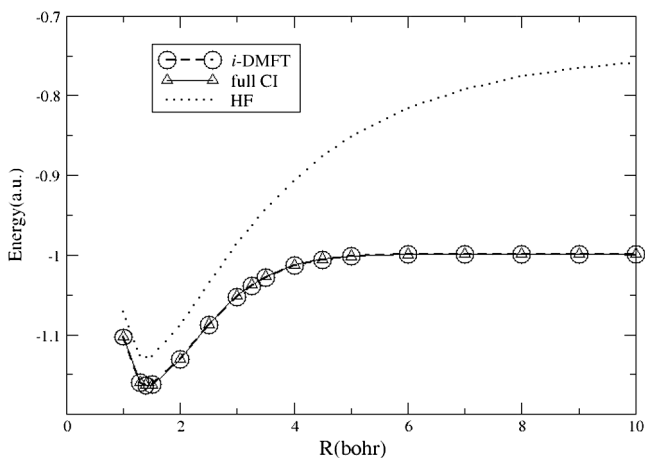


FIG. 1. Total energy curves for HF, full CI, and i -DMFT calculations along the dissociation coordinate of H_2 . Basis set cc-pVDZ, $\kappa = 0.094681$, and $b = 0.0286186$.

local density approximation (LDA) and generalized gradient approximation (GGA) calculations, but is still serious with these density functional approximations [5]. The numerical data for H_2 are collected in Table IV of the Supplemental Material [36]. It is to be noted that the errors around $R_e = 1.4$ bohr are exceedingly small, indicating that R_e and ω_e are reproduced very accurately.

In Fig. 2 (and Table III of the Supplemental Material [36]) the occupation numbers of the $1\sigma_g$ and $1\sigma_u$ orbitals are displayed for both the i -DMFT method and the FCI methods. They are obviously very close. Apparently, the Fermi-Dirac distribution recovers these occupation numbers for the strong nondynamical correlation case almost perfectly. Figure 1 and Table V in the Supplemental Material [36] show the behavior of the orbital energies of both the HF and the i -DMFT methods as a function of R . These energies are close but not identical. The i -DMFT $1\sigma_g$ and $1\sigma_u$ orbital energies converge to the same value at a shorter distance (9–10 bohr) than the HF orbital energies do. The latter differ by a $1/R$ term which only slowly decays. This difference is important for the correct behavior of the occupation numbers in Fig. 2 which also become equal at 9–10 bohr. However, at long distance the orbitals do not have shapes close to the NOs. They are HF-like, and it is known the HF orbitals and density are too diffuse [37]. Further elucidation is given in the Supplemental Material [36].

Figure 3 shows the energy along the dissociation coordinate for the multiply bonded N_2 molecule. The parameters κ and b are fitted to reproduce the total energies at $R_e = 2.21$ bohr and $R = 10$ bohr of the CI calculations. Again the i -DMFT curve closely follows the CI one. The corresponding numerical data are in Table VI of the Supplemental Material [36]. Since a FCI calculation and analysis is expensive, we approximate it with the MCSCF method using the Molpro package [38], in which eight

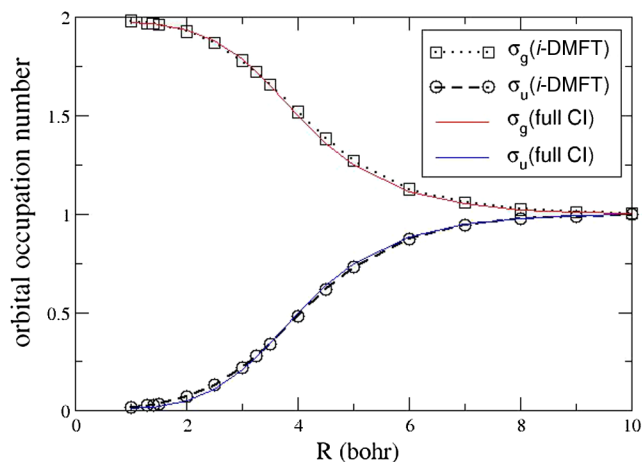


FIG. 2. Occupation numbers of the σ_g and σ_u orbitals in H_2 as a function of the nuclear separation R . The data are calculated with the basis set cc-pVDZ, $\kappa = 0.094681$, and $b = 0.0286186$.

electrons are fixed in four closed-shell orbitals, while six electrons are correlated in 24 active orbitals. In our i -DMFT calculations, all 14 electrons are taken into consideration for correlation in all 30 orbitals available for the cc-pVDZ basis set. Table VII of the Supplemental Material [36] shows the occupation numbers at 10 bohr. Both i -DMFT and MCSCF methods demonstrate that each of the three broken bonds leads to two orbitals with $n_i \sim 1.0$ for the + and - combinations of the corresponding atomic orbitals.

The water molecule has three internal coordinates: two O–H bond lengths (R_1 and R_2) and a bond angle (θ). To see the performance of our method in water under various geometries, we compare the total energies of a few representative geometries with the MCSCF calculations in Table I. The equilibrium structure is around $R_1 = R_2 = 1.82$ bohr, while $\theta = 104^\circ$. The parameters $\kappa = 0.1109136$ and $b = 0.18121047$ are fitted to the total energy

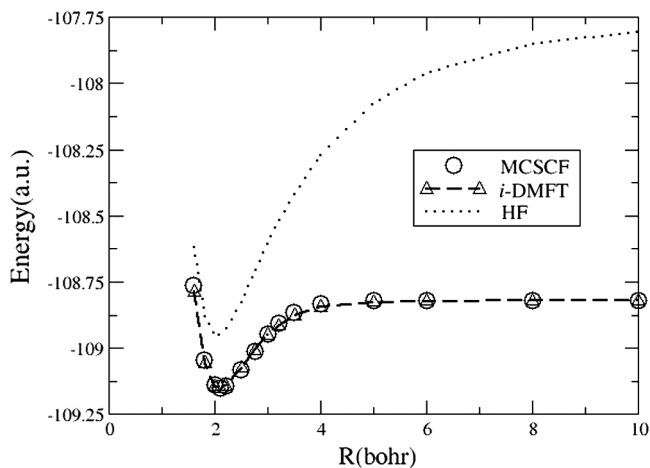


FIG. 3. Total energy curves of N_2 for HF, MCSCF and i -DMFT methods as a function of the nuclear separation R . Basis set cc-pVDZ, $\kappa = 0.122499$, and $b = 0.143913$.

TABLE I. Total energies at selected geometries in H₂O, 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. $\kappa = 0.1109136$ and $b = 0.18121047$ are used in the i -DMFT calculations. The difference between the i -DMFT and MCSCF data is also listed.

R_1	R_2	θ	MCSCF	i -DMFT	Difference
1.82	1.82	60	-76.183023	-76.177566	-0.005457
1.82	1.82	90	-76.237984	-76.235450	-0.002534
1.82	1.82	104	-76.241954	-76.241954	0
1.82	1.82	120	-76.234485	-76.237427	0.002942
1.82	1.82	180	-76.181646	-76.194224	0.012578
1.82	3	104	-76.131279	-76.134458	0.003179
1.82	3	60	-76.115868	-76.113687	-0.002181
3	3	104	-76.032078	-76.029051	-0.003027
1.82	6	104	-76.059787	-76.072413	0.012625
6	6	104	-75.909726	-75.920715	0.010989

(-76.241954) and the entropy (1.326550) at this geometry. The MCSCF values were done with eight electrons correlated in 23 active orbitals in the cc-pVDZ basis set. The i -DMFT calculations are done with all ten electrons correlated in all available orbitals.

It is not immediately apparent that the present simple entropic Ansatz for the cumulant energy would also apply to the dispersion energy. This is a rather different type of correlation than the (nondynamical) mostly left-right correlation in a molecular bond, and the (dynamic) angular and in-out correlations in an atom. However, tests on the Van der Waals interaction energy curves for He₂ and Ne₂ led to potential energy minima (with almost correct well depths D_e and bond distance R_e) even with a moderate basis set cc-pVTZ and choosing the parameter κ around 0.11. Details will be reported elsewhere.

We conclude that the i -DMFT method provides accurate potential energy surfaces. It achieves the incorporation of electron configuration effects along the complete dissociation coordinate at no more computational expense than an independent particle method like Hartree-Fock or Kohn-Sham. In wave function methods electron correlation is brought in by adding more configurations. In view of the rapidly increasing number of possible configurations with system size (and primitive basis) many choices have to be made in order to keep the problem tractable. This concerns the level of the CI, as exemplified by strategies such as CCSD(T), or MR-CI, CASSCF, CASPT2, as well as the choice of active orbital space etc. The size of the problem increases rapidly anyhow. Here we do not need to make any distinction between active and inactive orbital space, or dynamical and nondynamical correlation. The involvement of the “virtual” orbitals, which is a definite requirement to transcend the independent particle level, is governed by the occupation numbers [nonidempotency of $\gamma(1, 1')$]. These occupation numbers follow a Fermi-Dirac distribution

which is obtained directly from the variational problem for the orbitals and occupation numbers of the energy expression [Eq. (7)]. Here the correlation energy, which in DMFT is the two-electron cumulant energy [Eq. (4)], is brought in by the entropic Ansatz [Eq. (6)]. The power of this entropic correlation energy is that it leads to a simple SCF problem. The method is therefore efficient, and we have demonstrated it to be accurate as well.

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