Ding, Liebert and Schilling (DLS) submitted a critical comment [1] on our recent publication [2] which describes a procedure called i-DMFT.

DLS state that we make three claims regarding our method: (i) that it is a method within DMFT (ii) that it is capable of describing accurately molecules at various geometries, in particular the dissociation limit; (iii) that it is based on a distinctive information-theoretic approximation of the 2RDM cumulant. They then argue that these claims are unjustified. We address their points in order.

(i) As for the first claim, from the further elaboration it is clear that the authors mean that we claim to offer a method that tries to reproduce the exact one-particle reduced density matrix (1RDM) using a universal functional of the natural orbitals (NOs) and occupation numbers (ONs). But we do not claim to approximate the exact 1RDM and we clearly do not offer a universal functional and do not claim to do so.

Our method is clearly an orbital method, or self-consistent field method, as the Hartree-Fock and Kohn-Sham methods are. The crucial point, however, is that we employ fractional occupation numbers (a density matrix) in order to invoke the electron-electron interaction energy giving for the electron-electron interaction energy

\[ E_{ee} = Y - \kappa S |\psi]\]

with \( Y \) the direct and exchange parts of the energy

\[ Y = \frac{1}{2} \int \int \gamma(1,2)\gamma(2,1) r^{-1}_1 r^{-1}_2 d1d2. \]  

The fractional occupation numbers help us to solve the notorious molecular dissociation problem. DFT has the problem that the electron density is rather insensitive to electron correlation. At near dissociation the local density on a weakly bonded fragment in practice is not revealing its entanglement with the rest of the system. Involvement of virtual orbitals solves this entanglement problem, which is also a motivation for the application of density-matrix functional theory (DMFT) in general. We have referred to related attempts in DFT [6–10] to invoke virtual orbitals by fractional occupation schemes.

DLS question our results for the dissociation of molecules using the example of the two-electron molecules \( \text{H}_2 \) and \( \text{HeH}^+ \). For \( \text{H}_2 \) and \( \text{HeH}^+ \), we do find, using exact NOs and
ONs, the remarkable linear relationship [16, 17] of $E_{\text{cum}}$ vs. $S(n)$ which was the inspiration for our approach. However, they stress that the 1DM we obtain for H$_2$ differs from the exact/FCI 1RDM, judging from the deviation of the Frobenius norm $\sqrt{\text{Tr}(\gamma - \gamma')^2}$ from zero, where $\gamma'$ is from $i$-DMFT and $\gamma$ form CI calculations. This is especially true at the dissociation limit.

As discussed in (i), a difference of the 1DM of the $i$-DMFT calculation from the 1RDM of the exact wave function is in general to be expected. This is certainly the case for H$_2$, as already detailed in the supplementary information (SI) of [2]. It is useful to expand on this point, also in connection with the complaint of DLS about the nonuniversality of our [2]. It is well-known that the fundamental problem of the HF model is the presence of ionic terms in the wavefunction, which lead to too much on-site electron-electron repulsion in general and particularly at the dissociation limit. When substituting the HF 1RDM

$$\gamma_{\text{HF}}^{(1, 1')} = \sum_{\sigma = a, b} 1.0 \sigma_g(r_1) \sigma^*(r_1') \sigma(s_1) \sigma^*(s_1')$$

(3)

into the HF expression for the electron-electron energy, $Y$, the ionic terms show up when expanding the $\sigma_g$ orbital in the atomic orbitals (AOs), $\sigma_g = (1/\sqrt{2})(1s_L + 1s_g)$. DLS make the point that when the exact 1RDM is used,

$$\gamma_{\text{DMFT}}^{(1, 1')} = \sum_{\sigma = a, b} 0.5 \sigma_g(r_1) \sigma^*(r_1') \sigma(s_1) \sigma^*(s_1')$$

+ $\sum_{\sigma = a, b} 0.5 \sigma_u(r_1) \sigma^*(r_1') \sigma(s_1) \sigma^*(s_1')$

(4)

$$= \sum_{\sigma = a, b} 0.5 [1s_L(r_1)1s_L(r_1') + 1s_g(r_1)1s_g(r_1')] \sigma(s_1) \sigma^*(s_1')$$

the $Y$ of Eq. (2) with $\gamma_{\text{DMFT}}$ would again yield wrong on-site electron repulsion terms. They ascribe this to the electron-electron energy $E_{ee}$ of Eq. (1) referring only to the regime of weak correlations. But Eq. (1) is remarkably successful for strong correlation. It is just the purpose of the entropic term in Eq. (1) to correct for the correlation error also and in particular for strong (nondynamical) correlation. The excellent total energies that are obtained with $i$-DMFT, along the complete dissociation coordinate, prove that the entropic term does have this effect. Actually, the deviation of the Frobenius norm from zero has a different origin. As has been discussed at some length in our paper [2] and the SI, there is an error in the orbitals and the electron density for H$_2$, notably at the dissociation limit. It is worthwhile to highlight this point here. We have stressed that our SCF equation, being very similar to the HF one, leads to the too diffuse orbitals and density that are characteristic of the HF model due to the too high on-site electron-electron repulsion (making the electronic potential part of the Fockoperator too repulsive) [18, 19]. That manifests itself in the too high orbital energy (not negative enough), see Table V and Fig. 1 of SI. Such an orbital energy implies a too slow asymptotic decay. The diffuse nature of the HF $\sigma_g$ orbital, and the $i$-DMFT $\sigma_g$ (and $\sigma_u$) orbitals compared to the $\sigma_g$ (and $\sigma_u$) NOs is evident from Fig. 1 of this work. The orbital energy at the dissociation limit should be $-0.5$ a.u. in order to have the correct shape and decay like the density of a H atom.

The too diffuse orbitals and density show up in the Frobenius norm

$$\text{Tr}(\gamma - \gamma') = \sum_{\mu} \langle \chi_{\mu} | (\gamma - \gamma')^2 | \chi_{\mu} \rangle$$

(5)

where $\{\chi_{\mu}\}$ is some complete basis. The terms $(\gamma')^2$ and $\gamma^2$ can be reduced to the sums over the squares of the occupation numbers by choosing the basis either the NOs (for $\gamma^2$)
TABLE I. The entropy, cumulant energy, HF, CI energies in HeH+ from the wave functions calculated with the basis set cc-pVDZ. The $i$-DMFT energies are obtained with $\kappa=0.015$ and $b=0.03244$ (in a.u.).

| $R$  | $S$        | $E_{cum}$ | HF        | CI        | $i$-DMFT   |
|------|------------|-----------|-----------|-----------|------------|
| 0.40 | -0.066769  | -2.613107 | -2.643258 | -2.645547 |
| 0.50 | -0.073258  | -2.809079 | -2.841901 | -2.841519 |
| 0.60 | -0.078466  | -2.889631 | -2.924526 | -2.922072 |
| 0.70 | -0.082393  | -2.918503 | -2.954909 | -2.950943 |
| 0.80 | -0.084944  | -2.923532 | -2.960888 | -2.955972 |
| 0.90 | -0.086032  | -2.918065 | -2.955797 | -2.950506 |
| 1.00 | -0.077492  | -2.869870 | -2.904148 | -2.902311 |
| 1.25 | -0.074961  | -2.862084 | -2.895344 | -2.894524 |
| 1.50 | -0.073826  | -2.858529 | -2.891332 | -2.890969 |
| 2.00 | -0.073105  | -2.856088 | -2.888605 | -2.888528 |
| 2.50 | -0.072941  | -2.855461 | -2.887913 | -2.887896 |
| 3.00 | -0.072894  | -2.855214 | -2.887648 | -2.887648 |

or the eigenfunctions of $\gamma'$ (for $(\gamma')^2$). As shown in, for example, Fig. 2 of our paper [2] those two sets of occupation numbers are very close, so these terms are not the source of the Frobenius norm discrepancy. However, the cross terms $\gamma\gamma'$ and $\gamma\gamma$ depend on the orbitals from two different calculations. Choosing the set $\{\chi_{\mu}\}$ to be the NOs of the wave function, $\gamma\chi_{\mu} = n_{\mu}\chi_{\mu}$, and inserting the identity as a sum over eigenfunctions of $\gamma'$,

$$\sum_{\mu, k} \langle \chi_{\mu} | \gamma | \psi_k \rangle \langle \psi_k | \gamma | \chi_{\mu} \rangle = \sum_{\mu, k} n_{\mu} S_{\mu k} n_{\mu} S_{k \mu}$$  \quad (6)

we see that the trace depends on the overlaps $S_{\mu k}$ of the two orbital sets from different calculations. Due to the different shapes of the $i$-DMFT orbitals and the exact NOs, the overlaps are not delta functions and the Frobenius norm will differ from zero.

To remedy this particular HF error in the orbitals (for which dissociated H$_2$ is the worst case), an expedient modification of our functional is possible. Also the nonuniversality of our functional is an issue: the system dependence of the $\kappa$ parameter should eventually be replaced by functionals of the orbitals and occupation numbers (density matrix) in order to arrive at a universal functional. As an example of how to address these points we introduce orbital dependence into the entropic term through the exchange energy as a factor,

$$E_{cum} = AE_x S - b$$  \quad (7)

where $E_x = -\frac{1}{2} \sum_{i,j} n_i n_j \langle ji | ji \rangle$. This leads to a new eigenvalue problem for the orbitals,

$$\hat{F} \chi_i(1) = \epsilon_i \chi_i(1)$$  \quad (8)

where the operator $\hat{F}$ is,

$$\hat{F} = \hat{h} + \sum_j n_j [\hat{J}_j - (1 + A S) \hat{K}_j].$$  \quad (9)

The occupation numbers are approximated with a Fermi-Dirac type of dependence on the orbital energies.

As shown in Fig. 2 the orbital energies of the $\sigma_g$ and $\sigma_u$ orbitals now approach correctly the value of $-0.5$. This is because the electronic potential in the new Fock operator no longer includes the erroneous on-site repulsion of HF (when the reference electron is at site A, there is still 1/2 of the other electron at that site in the HF model). It has electron correlation built in in the sense that when the reference electron is at site A, the other electron is fully at site B. This new Fock operator incorporates the potential of the full
exchange-correlation hole, not just the exchange. It shares this property with the exact Kohn-Sham potential. The reference electron for which the orbital is determined by Eq. (8), then sees when at site A the nucleus A unscreened and the electron density acquires the correct shape of the H atom density at site A (and similarly at site B). This remedies the main source of the discrepancy signaled by the Frobenius norm differing from zero at long internuclear distance. This development also points the way to reducing the nonuniversality of the i-DMFT functional. Of course the functional of Eq. (7), with a system dependent constant $A$, has deficiencies and is certainly not yet universal. It is just a first example of the further refinement of the i-DMFT functional with density and orbital dependent terms. Ultimately one would strive for any remaining constants to be system independent, or, as is common practice in present day density functional development, to be determined by minimum deviations over appropriate benchmark sets of molecules.

DLS also signal a special problem for the HeH$^+$ molecule: they state that for HeH$^+$ there is not a single-valued dependence of $E_{\text{cum}}$ on $S$ and “thus i-DMFT would fail to describe its chemical behavior”. In reality there is no problem with HeH$^+$. The upper and middle panels of Fig. 3 clearly show an impressive scaling behaviour between $E_{\text{cum}}$ and the entropy, $E_{\text{cum}} \propto -\kappa S$. In Fig. 4 we show the linear regression for $E_{\text{cum}}$ vs $S$ with the data points obtained from a CI calculation (see data in Table I), as in the middle panel of Fig. 1 of DLS. Note that the points below the straight line belong to the long distance regime (beyond 1 Å), and the points above the straight line belong to the short distance regime (below 1 Å). In both regimes, there is a close linear relation, with a similar slope, between $E_{\text{cum}}$ and $S$ calculated from the CI wavefunction. This is the interpretation of the middle panel of DLS’ Fig. 1.

It is to be noted that the chemical behavior of HeH$^+$ is different from the dissociations of covalent bonds in H$_2$, He$_2^+$, and He$_2^2+$. At long internuclear distance this molecule dissociates to a proton (H$^+$) and a He atom (slightly polarized by the proton). Then we do not have large nondynamical correlation, like in the covalently bound molecules at long distance, but only the dynamical correlation of the He atom. When the H$^+$ approaches the He atom, some charge delocalization towards H$^+$ takes place and there is at shorter distance than ca. 1 Å a covalent component (or rather donor-acceptor component) to the bonding. In contrast to dissociating covalent bonds, like H$_2$ and He$_2^+$, HeH$^+$ is pretty well described by the HF model along the entire dissociation coordinate. So both $E_{\text{cum}}$ and $S$ are relatively small. This explains why the axis scale for HeH$^+$ in the middle panel of Fig. 1 of DLS (both for $S$ and for $E_{\text{cum}}$) is almost an order of magnitude smaller than that in the left panel for the covalently bonded H$_2$ and He$_2^+$. The differences in slope of the $E_{\text{cum}}$ vs $S$ lines in the two different distance and bonding regimes shown in Fig. 4 are not large and a good dissociation curve is obtained with just one choice for $\kappa$ in Fig. 3, bottom panel. Rather than failing for such a special system, with different bonding behavior in different distance regimes, the i-DMFT method can evidently cope with this situation.

(iii) DLS state that in the dissociation limit of H$_2$ other theoretical forms would serve better than our entropic $S(n)$, with the weak condition that they be Schur-convex. There is no objection to other forms, of course, but the challenge is to prove that such a form works well over the entire range of the dissociation coordinate where the requirement is not just simple “maximal mixedness” of a limited set of orbitals. We reiterate that, since our orbitals are not NOs, the small occupation numbers are not expected to be equal to NO occupations, and a scaling condition like $\partial \mathcal{F} / \partial n_i \sim -1/\sqrt{n_i}$ does not apply.

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