Reply to "Comment on 'Generalization of the Kohn-Sham system that can represent arbitrary one-electron density matrices’’

Hubertus J. J. van Dam
Brookhaven National Laboratory, Upton, NY 11973-5000
(Dated: August 20, 2017)

Our paper [Phys. Rev. A 93, 052512 (2016)], proposing a novel form of single determinant wave function that admits non-idempotent 1-electron density matrices, has recently received a Comment [Phys. Rev. A ??, 0????? (2017)] suggesting a number of flaws:

1. The form of the 1-electron density matrix that we proposed is deemed invalid;
2. None of the currently known functionals are given in terms of the 1-electron density matrix but known only in the basis where the density matrix is diagonal;
3. In NOFT the energy is not invariant with respect to unitary transformations of the orbitals;
4. The Müller functional we used suffers from serious shortcomings;
5. In NOFT the detachment energies should be obtained from the extended Koopmans theorem.

Below we will address these criticisms in sequence.
I. INTRODUCTION

In our paper [1] we proposed a single determinant wave function and an associated electron probability density so as to enable formulating an effective 1-electron model that can generate the exact 1-electron density matrix (1RDM). In addition this wave function requires only $O(N^2)$ coefficients, where $N$ is the dimension of the basis, so that the memory requirements are of the same order as those of the 1RDM. Such a wave function is desirable for a number of reasons:

- Single determinant wave functions do not incorporate correlation effects and therefore correlation can be accounted for by introducing a suitable functional, without risking double counting problems;
- Single determinant wave functions have easily identified 1-electron states facilitating the application of excitation operators;
- The cost of storing such a wave functions is twice that of storing the Hartree-Fock or Kohn-Sham wave function which is a manageable overhead;
- The requirement that the wave function can generate the exact electron density, as required by the Hohenberg-Kohn theorems, can be fulfilled whereas with the conventional Kohn-Sham wave function this is not strictly possible.

In order to demonstrate the capabilities of this wave function an energy expression that generates fractionally occupied natural orbitals was needed. Rohr [2] has stated that density functionals usually fail to describe this kind of correlations well. Instead the Müller functional has been previously demonstrated to favor such outcomes. Piris and Pernal, in their comment, explain that there are qualitatively better functionals that could have been used. We accept that such functionals exist and should be considered for real applications. Nevertheless, for the purpose of demonstrating the capabilities of the wave function we proposed, the Müller functional is sufficient and its simplicity is beneficial so as not to distract from the main topic of our publication.

II. POINT 1

Piris and Pernal [Phys. Rev. A ??, 0???? (2017)] claim that my Eq.(16) is a mistake and invalid, instead they suggest that their Eq.(5) should be used. In addition it has been commented that "the 1RDM of a single Slater determinant has rather specific properties: the orbitals that appear in the Slater determinant are natural orbitals with occupation one, and the remaining space is described by empty orbitals." Admittedly, this comment states how we have conventionally used Slater determinants, in that the orbitals used are eigenfunctions of the 1RDM and the associated probability density for finding an electron at position $r$ is given by

$$p(r) = \sum_{a,b=1}^{n_b} \sum_{i=1}^{n_e} \chi_a(r)N_{ai} N_{bi}^* \chi_b^*(r)$$

(1)

where $n_b$ is the number of basis functions and $n_e$ is the number of electrons (considering without loss of generality only spin-up electrons as the properties for the spin-down electrons can be evaluated in the same way). However, when Slater introduced the wavefunctions we have come to know as Slater determinants he proposed determinants of spin-orbitals as a convenient way to formulate wave functions with the proper anti-symmetric behavior under electron permutations. The key here is that the orbitals are (normalizable) functions of a single electron (see pages 1294, 1299-1300). As orbitals he considered 1-electron eigen functions of a Hamiltonian with spherical symmetry and hence it was appropriate to characterize the orbitals by the corresponding quantum numbers $n$, $l$, $m_l$ and $m_s$. However, as these quantum numbers are specifically suited to the study of single atom wavefunctions we may assume that using such orbitals is not a general requirement.

If our understanding is that a Slater determinant is a wave function represented as a determinant of 1-electron (spin) wave functions then in principle we have considerable freedom in the kind of 1-electron wave functions we may choose. The most important constraint is that the 1-electron wave functions be normalizable. In addition if the 1-electron wave functions form an orthonormal set we also have that the determinantal wave function is normalized as long as every orbital appears only once.

With these considerations in mind we proposed the generalized 1-electron wave function of our Eq.(8). In addition we deliberately chose our Eq.(16) to express the density matrix for a single electron. This 1-electron wave function was shown to be normalizable (our Eqs.(11) to (14)). Hence we maintain that we have satisfied all requirements for valid 1-electron wave functions.
A determinantal wave function constructed from this (our Eq.(17)) contains only the occupied generalized orbitals, all other generalized orbitals remain unoccupied. While the generalized orbitals are either occupied or unoccupied the correlation functions we introduced distribute a single electron over multiple natural orbitals. By these means we are able to formulate a single determinantal wave function that generates a density matrix with fractional occupation numbers. Admittedly these choices are rather unconventional but we maintain that unless they lead to inconsistencies or results that conflict with observations they are permissible.

To provide some background to this choice consider that in order to change the occupation numbers of a 1RDM (but without changing the natural orbitals) some additional degrees of freedom are required. The correlation functions were introduced to provide this additional freedom. Updating these functions using regular unitary transformations it is ensured that the orthonormality of the correlation functions is maintained. Now if a Fock matrix of the form of our Eq.(9) were used then Eq.(5) of Piris and Pernal would result. In that case, however, the rotation of correlation functions would just be an additional rotation to the ones on the natural orbitals. In fact, this would eliminate every possible benefit of the correlation functions and there would be no reason to introduce them in the first place, which is main objection of Piris and Pernal.

If instead the Fock matrix is cast form of our Eq.(44) then the corresponding density matrix assumes the form of our Eq.(16). Essentially this form entails a projection that eliminates off-diagonal terms that would reduce transformations of the correlation function to simple rotations. Instead the combination of rotation and projection creates a new kind of transformation. The projection chosen does preserve critically important properties such as the lower and upper limits on the occupation numbers as well as the trace of the density matrix. With this choice in place conventional unitary transformations ensure that orthonormality of the 1-electron wave functions is preserved, the trace and eigenvalue limits of the density matrix are preserved, yet non-trivial transformations that are cannot be formulated in an N-dimensional space can now be expressed straightforwardly on the 1RDM. A worked example of this approach is discussed in the supplementary material, Section I, where it is shown how this technique can used to transform a 1RDM of a single electron from

\[
D = \begin{pmatrix}
1 & 0 \\
0 & 0
\end{pmatrix}
\]

(2)

to

\[
D' = \begin{pmatrix}
1/2 & 0 \\
0 & 1/2
\end{pmatrix}
\]

(3)

It is also shown that such a transformation cannot be represented in a 2-dimensional space.

Piris and Pernal have also raised the issue of the N-representability of NOFT and pointed to the fact that attempts to express the 2RDM by means of a reconstruction functional have failed (we will come back to that in Section III). The reason being that the ensemble N-representability conditions of the 1RDM are easily implemented but that they are not sufficient to guarantee that the reconstructed 2RDM is N-representable. As we believe that we can maintain an approach until properly falsified and as a wave function should by construction generate N-representable density matrices let us consider the same spin part of the 2RDM as a test for our proposed approach (the opposite spin part is essentially trivial as the exchange terms vanish). To summarize a single determinant wave function is defined of the form (Eq.(17) of [1]):

\[
\Psi(r_1, \ldots, r_n_e) = |G_1(r_1)G_2(r_2) \ldots G_n_e(r_n_e)|
\]

(4)

where \(G(r)\) are the generalized orbitals we proposed given by (Eq.(8) of [1]):

\[
|G_s(r)\rangle = \sum_{a,i=1}^{n_b} N_{ai}C_{is}|\chi_a(r)\rangle
\]

(5)

The 1-electron density matrix of Eq.(16) of [1] is adopted as given by

\[
\sum_{a,b=1}^{n_b} |\chi_a(r'_1)\rangle D_{ab} |\chi_b(r''_1)\rangle = \left( \begin{array}{c} n_c \\ 1 \end{array} \right) \int \cdots \int \Psi(r'_1, r_2, \ldots, r_n_e)\Psi^*(r''_1, r_2, \ldots, r_n_e) dr_2 \ldots dr_n_e
\]

(6)

\[
D_{ab} = \sum_{i=1}^{n_b} \sum_{s=1}^{n_s} N_{ai}C_{is}C^*_{is}N^*_s
\]

(7)

furthermore the 2RDM is defined by

\[
\sum_{a,b,c,d=1}^{n_b} |\chi_a(r'_1)\chi_b(r'_2)\rangle \Gamma_{abcd} |\chi_c(r''_1)\chi_d(r''_2)\rangle = \left( \begin{array}{c} n_c \\ 2 \end{array} \right) \int \cdots \int \Psi(r'_1, r'_2, \ldots, r_n_e)\Psi^*(r''_1, r''_2, \ldots, r_n_e) dr_3 \ldots dr_n_e
\]

(8)
Obviously, Eq.\((7)\) cannot be used directly in evaluating \(\Gamma_{abcd}\) as for the 2RDM we have to consider cross terms between orbitals. To accommodate these cross terms Eq.\((7)\) is trivially generalized as
\[
D_{ab}^{st} = \sum_{i=1}^{n_e} N_{ai} C_{i\alpha} C_{i\alpha}^* N_{bi}^*
\]  
(9)

Note that because of the orthonormality of the correlation functions the trace of Eq.\((9)\) is
\[
\text{tr} \left( D_{ab}^{st} \right) = \delta_{st}
\]  
(10)

which will play an important role in considering the exchange terms. In addition as the generalized orbitals are defined as in Eq.\((5)\) anti-symmetric permutations among generalized orbitals have to be defined as
\[
P(1, 2)G_1(r_1)G_2(r_2) = P(1, 2) \sum_{a,b=1}^{n_b} \sum_{i,j=1}^{n_b} N_{ai} C_{i\alpha}(r_1) N_{bj} C_{j\beta}(r_2)
\]  
(11)
\[
= - \sum_{a,b=1}^{n_b} \sum_{i,j=1}^{n_b} N_{ai} C_{i\alpha}(r_2) N_{bj} C_{j\beta}(r_1)
\]  
(12)

in other words the permutation operator implies exchanging units of \(\sum_i N_{ai} C_{i\alpha}\) in its entirety. Alternatives such as exchanging only the correlation functions are not valid as they do not treat the entire generalized orbital as an integral unit. Based on Eq.\((8)\), Eq.\((9)\) and Eq.\((12)\) the 2RDM can be written as
\[
\Gamma_{abcd} = \frac{1}{4} \left\{ \sum_{s,t=1}^{n_e} \left( \sum_{i=1}^{n_b} N_{ai} C_{i\alpha} C_{i\alpha}^* N_{bi}^* \right) \left( \sum_{j=1}^{n_b} N_{bj} C_{j\beta} C_{j\beta}^* N_{dj}^* \right) 
- \sum_{s,t=1}^{n_e} \left( \sum_{i=1}^{n_b} N_{ai} C_{i\alpha} C_{i\alpha}^* N_{bi}^* \right) \left( \sum_{j=1}^{n_b} N_{bj} C_{j\beta} C_{j\beta}^* N_{dj}^* \right) 
- \sum_{s,t=1}^{n_e} \left( \sum_{i=1}^{n_b} N_{bi} C_{i\alpha} C_{i\alpha}^* N_{bi}^* \right) \left( \sum_{j=1}^{n_b} N_{aj} C_{j\beta} C_{j\beta}^* N_{dj}^* \right) 
+ \sum_{s,t=1}^{n_e} \left( \sum_{i=1}^{n_b} N_{bi} C_{i\alpha} C_{i\alpha}^* N_{bi}^* \right) \left( \sum_{j=1}^{n_b} N_{aj} C_{j\beta} C_{j\beta}^* N_{dj}^* \right) \right\}
\]  
(14)

Given the expressions above the N-representability conditions may be addressed. They are:

1. The trace of the 2RDM must be equal to the number of electron pairs \(n_e(n_e-1)/2\);

2. The matrix must non-negative, i.e. all eigenvalues must be equal to or larger than 0, or equivalently all electron pair probability functions must be non-negative;

3. Integrating the coordinates of 1 electron out, must produce the 1RDM according to \(D_1(r_1; r_1') = \frac{2}{N_e} \int D_2(r_1, r_2; r_1', r_2) dr_2\)

4. The 2RDM must be anti-symmetric, i.e. \(D_2(r_1, r_2; r_1', r_2') = -D_2(r_1, r_2; r_2', r_1') = -D_2(r_2, r_1; r_1', r_2') = D_2(r_2, r_1; r_2', r_1)\)

Below this points are tackled in turn.

**A. The trace of the 2RDM**

The trace of the 2RDM given by Eq.\((14)\) can be evaluated by considering and adding the traces of the various terms because \(\text{tr}(A + B) = \text{tr}(A) + \text{tr}(B)\) based simply on the fact that the trace of a matrix is the sum of its diagonal
elements. For the first and the fourth term of Eq. (14) the traces are given by

\[ \text{tr}(\text{term}_1) = \sum_{s,t=1}^{n_e} \sum_{i,j=1}^{n_b} C_{is}^* C_{jt}^* C_{ij} \]  
\[ = \sum_{s,t=1}^{n_e} \delta_{ss} \delta_{tt} \]  
\[ = n_e^2 \]  
\[ \text{tr}(\text{term}_4) = \sum_{s,t=1}^{n_e} \sum_{i,j=1}^{n_b} C_{it}^* C_{js}^* C_{ij} \]  
\[ = n_e^2 \]  

For the second and third terms of Eq. (14) the traces \( \text{tr}(\text{term}_2) = -\sum_{s,t=1}^{n_e} \sum_{i,j=1}^{n_b} C_{is}^* C_{it}^* C_{js} \) and \( \text{tr}(\text{term}_3) = -\sum_{s,t=1}^{n_e} \sum_{i,j=1}^{n_b} C_{it}^* C_{js}^* C_{ij} \) are obtained. Combining the results of Eqs. (17, 19, 22, 24) with the prefactor of Eq. (14) the result

\[ \text{tr} (\Gamma_{abcd}) = \frac{1}{4} \left( n_e^2 - n_e - n_e + n_e^2 \right) \]  
\[ = n_e(n_e - 1) \]  

is obtained which proves that the first N-presentability condition is met.

### B. The non-negativity of the 2RDM

To prove that the 2RDM of Eq. (13) is non-negative it has to be shown that the Coulomb terms (terms 1 and 4) are larger than the exchange terms (terms 2 and 3). The key is to show that the diagonal elements are non-negative. Once that is established one can always show that the pair probability density is non-negative as well, which implies that the density matrix must be non-negative. The proof is based on the Gauchy-Schwarz inequality which is given by

\[ \left( \sum_{i=1}^{n} x_i y_i^* \right)^2 \leq \left( \sum_{j=1}^{n} x_j^2 \right) \left( \sum_{k=1}^{n} y_k^2 \right) \]  

The diagonal elements of Eq. (14) are given by

\[ d_{ij} = \frac{1}{4} \sum_{s,t=1}^{n_e} \left( C_{is} C_{jt}^* C_{ij} - C_{is} C_{it} C_{js}^* - C_{it} C_{is} C_{js}^* + C_{it} C_{jt} C_{js}^* \right) \]  

Obviously terms 1 and 4 and terms 2 and 3 are essentially the same and therefore the expression can be reduced to two terms as

\[ d_{ij} = \frac{1}{2} \sum_{s,t=1}^{n_e} \left( C_{is} C_{jt}^* C_{ij} - C_{is} C_{it} C_{js} \right) \]
At which point Eq. (33) can be used to demonstrate all electron pair probability functions are non-negative term-by-term as well. Note that here only the evaluation of the term coming from the block. Calculating the $\alpha\alpha$ part of the 2RDM is considered. This differs by a constant from the calculation of the $\alpha\beta$ part of the 2RDM. In the latter case there is a term coming from the $\alpha\alpha$ block as well as from the $\alpha\beta$ block. Calculating the $\alpha\beta$ part of the 2RDM is considered.

From the Gauchy-Schwarz inequality one immediately obtains that

$$d_{ij} \geq 0$$

(33)

Obviously the argument given leaves the factors stemming from the natural orbitals out and as they are different in different terms this makes the outcome less clear. To resolve this matter the pair probability density is considered

$$p(r_1, r_2) = \frac{1}{2} \sum_{s,t=1}^{n_e} \left[ \left( \sum_{a,c=1}^{n_a} \sum_{i=1}^{n_b} \chi_a(r_1) N_{ai} C_{is} C_{it}^* N_{cj}^* \chi_c(r_1) \right) \left( \sum_{b,d=1}^{n_b} \sum_{j=1}^{n_b} \chi_b(r_2) N_{bj} C_{jt}^* N_{dj}^* \chi_d(r_2) \right) \right]$$

(34)

Relabeling the basis function indeces in the exchange terms gives

$$p(r_1, r_2) = \frac{1}{2} \sum_{s,t=1}^{n_e} \left[ \left( \sum_{a,c=1}^{n_a} \sum_{i=1}^{n_b} \chi_a(r_1) N_{ai} C_{is} C_{it}^* N_{cj}^* \chi_c(r_1) \right) \left( \sum_{b,d=1}^{n_b} \sum_{j=1}^{n_b} \chi_b(r_2) N_{bj} C_{jt}^* N_{dj}^* \chi_d(r_2) \right) \right]$$

(35)

At which point Eq. (33) can be used to demonstrate that

$$p(r_1, r_2) \geq 0$$

(36)

For the Gauchy-Schwarz inequality to hold there is no need to integrate over all electrons. The inequality also holds for every term separately, i.e. $n = 1$ in Eq. (28). Hence we also have

$$p^{st}(r_1, r_2) = \frac{1}{2} \left[ \left( \sum_{a,c=1}^{n_a} \sum_{i=1}^{n_b} \chi_a(r_1) N_{ai} C_{is} C_{it}^* N_{cj}^* \chi_c(r_1) \right) \left( \sum_{b,d=1}^{n_b} \sum_{j=1}^{n_b} \chi_b(r_2) N_{bj} C_{jt}^* N_{dj}^* \chi_d(r_2) \right) \right]$$

(37)

At which point Eq. (33) can be used to demonstrate all electron pair probability functions are non-negative

$$p^{st}(r_1, r_2) \geq 0, \ \forall s, t \leq n_e$$

(38)

The result of Eq. (38) proves that the second N-representability condition is met.

C. Obtaining the 1RDM by integration of the 2RDM

The integration of the one set of coordinates from the 2RDM of Eq. (14) to calculate the 1RDM can be tackled term-by-term as well. Note that here only the evaluation of the $\alpha\alpha$-electron 1RDM from the $\alpha\alpha$-part of the 2RDM is considered. This differs by a constant from the calculation of the $\alpha\beta$-1RDM from the whole 2RDM. In the latter case there is a term coming from the $\alpha\alpha$ block as well as from the $\alpha\beta$ block. Calculating the $\alpha\beta$-1RDM from the $\alpha\beta$ block
is trivial hence the more involved calculation from the $\alpha \alpha$ block is considered here. Use is made of the fact that the natural orbitals are normalized such that

$$
\delta_{ij} = \sum_{a,b=1}^{n_b} N_{ai} \langle \chi_a(r_1) | \chi_b(r_1) \rangle N_{bj}
$$

Integrating out electron 2 for the first and fourth term gives

$$
T_1 = \left( \sum_{i=1}^{n_b} \sum_{s=1}^{n_e} N_{ai} C_{is} C_{is}^* N_{ci} \right) \left( \sum_{j=1}^{n_b} \sum_{t=1}^{n_e} N_{bj} C_{jt} C_{jt}^* N_{dj} \right) \langle \chi_b(r_2) | \chi_d(r_2) \rangle
$$

$$
= \left( \sum_{i=1}^{n_b} \sum_{s=1}^{n_e} N_{ai} C_{is} C_{is}^* N_{ci} \right) \left( \sum_{j=1}^{n_b} \sum_{t=1}^{n_e} C_{jt} C_{jt}^* \right) n_e
$$

$$
= D_{\alpha \epsilon} n_e
$$

$$
T_4 = \left( \sum_{i=1}^{n_b} \sum_{t=1}^{n_e} N_{bi} C_{it} C_{it}^* N_{di} \right) \left( \sum_{j=1}^{n_b} \sum_{s=1}^{n_e} N_{aj} C_{js} C_{js}^* N_{cj} \right) \langle \chi_a(r_2) | \chi_c(r_2) \rangle
$$

$$
= \left( \sum_{i=1}^{n_b} \sum_{t=1}^{n_e} N_{bi} C_{it} C_{it}^* N_{di} \right) \left( \sum_{j=1}^{n_b} \sum_{s=1}^{n_e} C_{js} C_{js}^* \right) n_e
$$

$$
= \left( \sum_{i=1}^{n_b} \sum_{t=1}^{n_e} N_{bi} C_{it} C_{it}^* N_{di} \right) n_e
$$

$$
= D_{\alpha \delta} n_e
$$

Integrating out electron 2 for the second and third term gives

$$
T_2 = - \sum_{s,t=1}^{n_e} \left( \sum_{i=1}^{n_b} N_{ai} C_{is} C_{is}^* N_{di} \right) \left( \sum_{j=1}^{n_b} \sum_{c=1}^{n_e} N_{bj} C_{jt} C_{jt}^* N_{cj} \right) \langle \chi_b(r_2) | \chi_c(r_2) \rangle
$$

$$
= - \sum_{s,t=1}^{n_e} \left( \sum_{i=1}^{n_b} N_{ai} C_{is} C_{is}^* N_{di} \right) \left( \sum_{j=1}^{n_b} C_{jt} C_{jt}^* \right) \delta_{ts}
$$

$$
= - D_{\alpha \delta}
$$

$$
T_3 = - \sum_{s,t=1}^{n_e} \left( \sum_{i=1}^{n_b} N_{bi} C_{it} C_{it}^* N_{di} \right) \left( \sum_{j=1}^{n_b} \sum_{d=1}^{n_e} N_{aj} C_{jd} C_{jd}^* N_{dj} \right) \langle \chi_a(r_2) | \chi_d(r_2) \rangle
$$

$$
= - \sum_{s,t=1}^{n_e} \left( \sum_{i=1}^{n_b} N_{bi} C_{it} C_{it}^* N_{di} \right) \left( \sum_{j=1}^{n_b} C_{jd} C_{jd}^* \right) \delta_{st}
$$

$$
= - D_{\alpha \epsilon}
$$
Combining the results of Eqs. [13] [17] [51] [55] with the prefactor gives

\[
\begin{align*}
D &= \frac{1}{4} \frac{2}{n_e - 1} (n_e D - D - D + n_e D) \\
&= \frac{1}{4} \frac{2}{n_e - 1} 2D(n_e - 1) \\
&= D
\end{align*}
\]

This result proves that the third N-representability condition is met.

**D. The anti-symmetry of the 2RDM**

In order to demonstrate the anti-symmetry of the 2RDM the condition given in Eq. [12] for the permutation symmetry is enforced. This means that exchanging two labels requires exchanging the whole orbital expression. Note that this is the same condition we enforced in the 2RDM construction. With that

\[
\Gamma_{abcd} = \frac{1}{4} \left\{ \sum_{s,t=1}^{n_e} \left( \sum_{i=1}^{n_b} N_{ai} C_{is} C_{is}^{*} N_{di}^{*} \right) \left( \sum_{j=1}^{n_b} N_{bj} C_{jt} C_{jt}^{*} N_{cj}^{*} \right) \right. \\
- \sum_{s,t=1}^{n_e} \sum_{i=1}^{n_b} N_{ai} C_{is} C_{is}^{*} N_{ci}^{*} \left( \sum_{j=1}^{n_b} N_{bj} C_{jt} C_{jt}^{*} N_{dj}^{*} \right) \\
- \sum_{s,t=1}^{n_e} \sum_{i=1}^{n_b} N_{bd} C_{it} C_{it}^{*} N_{di}^{*} \left( \sum_{j=1}^{n_b} N_{aj} C_{js} C_{js}^{*} N_{cj}^{*} \right) \\
+ \sum_{s,t=1}^{n_e} \sum_{i=1}^{n_b} N_{bi} C_{it} C_{it}^{*} N_{ci}^{*} \left( \sum_{j=1}^{n_b} N_{aj} C_{js} C_{js}^{*} N_{dj}^{*} \right) \left\} \\
&= -\Gamma_{abcd}
\]

With Eq. [61] it is demonstrated that the fourth N-representability condition is met.

**E. Summary of 2RDM results**

Based on the arguments above it would seem that the approach proposed in [1] provides both N-representable 1RDM and 2RDM without generating logical inconsistencies. Therefore even applying our approach to the 2RDM does not lead to a breakdown that invalidates the wave function we proposed. In addition to ref. [1] the exact 1RDM of a system of interacting electrons can be represented. Of course the exact 2RDM of a system of interacting electrons cannot be obtained as such an RDM would have to account for electron correlation (the approach suggested here is merely a Hartree-Fock theory with funky orbitals, i.e. one that admits fractional occupations of the natural orbitals). As the wave function used here is just a single determinant wave function it cannot capture electron correlation at all. This is also clear from the fact that the 2RDM presented here has anti-symmetrized products of natural orbitals.
as eigenfunctions rather than proper geminals. In addition the pair occupation numbers are limited to the range \([0, 1]\) whereas in the exact 2RDM they may exceed 1.\(^\text{[4]}\)

In fact if the wave function we proposed in \(^\text{[1]}\) is simply inserted into the Schrödinger equation and the energy minimized a wave function that is equivalent to the conventional Hartree-Fock wave function will be obtained. To account for electron correlation special terms that model electron correlation as a function of the natural orbital occupation numbers would have to be introduced. In NOFT and \(^\text{[1]}\) the 2-electron interaction is effectively replaced with a functional of the natural orbitals and occupation numbers.

### III. POINT 2

To address the criticism that none of the currently known functionals are given in terms of the 1RDM but known only in the basis where the density matrix is diagonal two things need to be considered:

- The equivalence between functions expressed on eigenvalues and matrix functions
- Show that multiple 1RDM functionals have been proposed that can be recast in such a way as to rely on matrix functions

The first point is a well known result from the mathematics of matrix functions. If \(M\) is a Hermitian matrix and \(\{v_1, \ldots, v_i, \ldots, v_n\}\) are its eigenvectors with eigenvalues \(\{d_1, \ldots, d_i, \ldots, d_n\}\) then a function \(f\) applied to the matrix can be obtained as

\[
 f(M) = \sum_{i=1}^{n} v_i f(d_i) v_i^T
\]

This is a well known property of matrix functions. From this we have that even if a 1-electron density matrix functional is given in terms of functions applied to occupation numbers then, as long as the same function is applied to all occupation numbers, this function can be rewritten as a function on the 1RDM. In the latter form no explicit mention of the occupation numbers is even needed.

For the second point we need show that there are multiple 1RDM functionals that are expressed either directly in terms of the 1RDM or (equivalently) that are expressed in terms of functions on the occupation numbers where the same function is applied to all occupation numbers. Some examples of such functionals are:

- First of all Piris and Pernal have admitted that the Hartree-Fock energy expression is an explicit density matrix functional, albeit a rather trivial one and one that does not account for electron correlation at all.
- The Müller functional\(^\text{[6]}\) and variants thereof\(^\text{[7]}\).
- The functional of Csányi and Arias\(^\text{[8]}\) where the authors explicitly state on page 7350 in the first paragraph of the subsection “Representation of the functionals” that “The corresponding energy functionals may be represented either directly in terms of the one-body density matrix for use with direct density-matrix methods, or in terms of the spectral (natural orbital representation of the density matrix.”
- Herbert and Harriman\(^\text{[9]}\) consider a range of different functionals including direct and implicit density matrix functionals (including the ones by Müller and Csányi and generalizations thereof). They refer to these functionals as \(CH(\zeta)\), \(CHF(\zeta)\), and \(MCHF(\zeta)\).

Admittedly this list is not a very extensive one but at least there are a few. Hence the claim that no such functionals exist seems exaggerated.

### IV. POINT 3

The criticism that the energy in NOFT is not invariant to orbital transformations seems to need some additional information. The authors Piris and Pernal make distinctions between implicit and explicit 1-electron density functionals. Based on what we have seen regarding this issue we conclude that Piris and Pernal refer to explicit 1-electron density matrix functionals when a functional can be represented in a form that involves functions of the 1RDM as in the left-hand-side of Eq.(62). In functionals where different functions may be applied to different occupation numbers, i.e. where the functional cannot be expressed using matrix functions, they refer to those expressions as implicit 1RMD functionals or Natural Orbital Functionals (NOF).
We have no experience or expertise related to implicit 1RDM functionals and therefore we will not comment on those functionals and any specific requirements related to their energy optimization. On the topic of explicit 1RDM functionals Piris and Pernal agree that the optimization method we used is valid. As for the Löwdin paper [10] this problem applies to the Langrangian associated with the natural orbitals but not to the Lagrangian of the correlation functions. The correlation functions are either occupied or unoccupied. The 1RDM is invariant under rotations amongst the occupied correlation functions, and invariant under rotations amongst the unoccupied correlation functions. This leaves ample freedom to diagonalize the matrix of Lagrangian multipliers for the correlation functions. In addition the correlation function energies (or equivalently the generalized orbital energies) are the proper one-electron energies. Hence the duality issue that Piris and Pernal face in their natural orbital driven formulation does not arise here.

V. POINT 4

As stated in Section I we accept that the Müller functional has short comings. It was only chosen for its simplicity to demonstrate the ability to generate fractional occupation numbers with the approach proposed in our paper [1]. For real applications other functionals should be chosen. We do not claim any expertise on the question which functional is most appropriate in reduced density matrix methods.

VI. POINT 5

The issue with the detachment energies is that the orbital energies of a correlated electron system are the same for all correlated electrons. In a way this suggests a collective behavior of the correlated electrons and therefore the associated energy is not a good measure for a single electron response. Hence we proposed to calculate these single electron energies from an effective 1-electron (i.e. uncorrelated) energy expression instead. This choice does not preclude that there other and possibly better ways to do this.

ACKNOWLEDGMENTS

This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy.

[1] Hubertus J. J. van Dam. Generalization of the kohn-sham system that can represent arbitrary one-electron density matrices. Phys. Rev. A, 93:052512, May 2016.
[2] Daniel R. Rohr, Julien Toulouse, and Katarzyna Pernal. Combining density-functional theory and density-matrix-functional theory. Phys. Rev. A, 82:052502, Nov 2010.
[3] J. C. Slater. The theory of complex spectra. Phys. Rev., 34:1293–1322, Nov 1929.
[4] Fukashi Sasaki. Eigenvalues of fermion density matrices. Phys. Rev., 138:B1338–B1342, Jun 1965.
[5] Nicholas J. Higham. Functions of Matrices: Theory and Computation. Society for Industrial and Applied Mathematics, Philadelphia, PA, USA, 2008.
[6] A.M.K. Müller. Explicit approximate relation between reduced two- and one-particle density matrices. Physics Letters A, 105(9):446, Nov 1984.
[7] N. N. Lathiotakis, S. Sharma, J. K. Dewhurst, F. G. Eich, M. A. L. Marques, and E. K. U. Gross. Density-matrix-power functional: Performance for finite systems and the homogeneous electron gas. Physical Review A, 79(4):040501(R), Apr 2009.
[8] Gábor Csányi and T. A. Arias. Tensor product expansions for correlation in quantum many-body systems. Phys. Rev. B, 61:7348–7352, Mar 2000.
[9] John M Herbert and John E Harriman. Self-interaction in natural orbital functional theory. Chemical Physics Letters, 382(12):142 – 149, 2003.
[10] Per-Olov Löwdin. Quantum theory of many-particle systems, i. physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction. Phys. Rev., 97:1474–1489, Mar 1955.