

## Comment on “Nonuniqueness of algebraic first-order density-matrix functionals”

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Wang and Knowles (WK) [Phys. Rev. A **92**, 012520 (2015)] have given a counterexample to the conventional in reduced density-matrix functional theory representation of the second-order reduced density matrix (2RDM)  $\Gamma_{ij,kl}$  in the basis of the natural orbitals as a function  $\Gamma_{ij,kl}(n)$  of the orbital occupation numbers (ONs)  $n_i$ . The observed nonuniqueness of  $\Gamma_{ij,kl}$  for prototype systems of different symmetry has been interpreted as the inherent inability of ON functions to reproduce the 2RDM, due to the insufficient information contained in the 1RDM spectrum. In this Comment, it is argued that, rather than totally invalidating  $\Gamma_{ij,kl}(n)$ , the WK example exposes its symmetry dependence which, as well as the previously established analogous dependence in density functional theory, is demonstrated with a general formulation based on the Levy constrained search.

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In their recent work [1], Wang and Knowles (WK) have given a counterexample to a conventional representation of the electronic energy  $E$  in reduced density-matrix functional theory (RDMFT) [2–8]

$$E = \sum_i n_i h_{ii} + \frac{1}{2} \sum_{ijkl} \Gamma_{ij,kl}(n) \langle ij|kl \rangle. \quad (1)$$

Here,  $h_{ii}$  is the diagonal matrix element of the one-electron operator in the basis of the natural orbitals (NOs) and  $n_i$  is the occupation number (ON) of the NO  $\chi_i$ , with the former being the eigenvalue and the latter being the eigenfunction of the first-order reduced density matrix (1RDM)  $\gamma$ ,

$$\gamma(\mathbf{x}, \mathbf{x}') = \sum_i n_i \chi_i^*(\mathbf{x}) \chi_i(\mathbf{x}'). \quad (2)$$

Here,  $\mathbf{x}$  stands for both spatial  $\mathbf{r}$  and the spin  $s$  coordinates.  $\Gamma_{ij,kl}$  in (1) is the second-order RDM (2RDM) in the NO representation and for the present discussion it is essential, that  $\Gamma_{ij,kl}$  is conventionally expressed in RDMFT as a function  $\Gamma_{ij,kl}(n)$  of the ONs. To provide a counterexample to (1), WK have compared the ONs  $n_i$  and 2RDMs  $\Gamma_{ij,kl}$  obtained in the minimal basis set for the square-planar  $\text{H}_4$  (I) and the  $\text{H}_2 + 2\text{H}$  (II) systems from the corresponding ground-state wave functions. It has been shown that, for certain combinations of the length of the square side of I and the bond length of the  $\text{H}_2$  molecule in II, these systems possess the same ONs  $n_i$ , while their  $\Gamma_{ij,kl}$  are distinctly different.

In this Comment it is argued that, rather than invalidating the conventional RDMFT energy expression (1), the example given in [1] exposes the dependence of the function  $\Gamma_{ij,kl}(n)$  on the symmetry of the generic wave function. The symmetry dependence of functionals is a well-known feature of density functional theory (DFT) [9,10]. As was concluded in the celebrated Parr-Yang textbook [11], “...there is the unhappy fact that the Hohenberg-Kohn functional  $F[\rho]$  will in general differ from symmetry to symmetry” ( $\rho$  is the electron density and the definition of  $F[\rho]$  will be given below). Note that in DFT it was exclusively considered the dependence  $F^A[\rho]$  of

$F[\rho]$  on the irreducible representations (irreps)  $A$  of the generic ground- and lowest excited-state wave functions  $\Psi^A$  belonging to the same symmetry group  $S$  of a system.

This consideration can be extended to RDMFT and to different symmetry groups. To accomplish this for a system specified with the external potential  $v_{\text{ext}}(\mathbf{x})$ , one can apply the Levy constrained search [5] over all symmetry groups  $S$  and, within each group, over all its irreps  $A(S)$ . Within this search, the ground-state energy  $E_0$  is found as the double minimum

$$E_0 = \min_S \{ \min_{A(S)} \{ E^{A(S)} \} \} \quad (3)$$

over  $S$  and  $A(S)$  of the energies  $E^{A(S)}$ . Each  $E^{A(S)}$  is determined through the following minimization:

$$E^{A(S)} = \min_{\mu^{A(S)}} \left\{ F^{A(S)}[\mu^{A(S)}] + \int v_{\text{ext}}(\mathbf{x}) \rho^{A(S)}(\mathbf{x}) d\mathbf{x} \right\}, \quad (4)$$

which involves the above-mentioned Hohenberg-Kohn (HK) functional  $F^{A(S)}[\mu^{A(S)}]$

$$F^{A(S)}[\mu^{A(S)}] = \min_{\Psi^{A(S)} \rightarrow \mu^{A(S)}} \{ \langle \Psi^{A(S)} | \hat{T} + \hat{V}_{ee} | \Psi^{A(S)} \rangle \}. \quad (5)$$

In (4) and (5)  $\mu^{A(S)}$  is the electron density in the case of DFT,  $\mu^{A(S)} = \rho^{A(S)}$ , and it is the 1RDM in the case of RDMFT,  $\mu^{A(S)} = \gamma^{A(S)}$ . In the latter case  $\rho^{A(S)}$  in (4) is the diagonal part of  $\gamma^{A(S)}$ ,  $\rho^{A(S)}(\mathbf{x}) = \gamma^{A(S)}(\mathbf{x}, \mathbf{x})$ . The function  $\mu^{A(S)}$  is generated from the wave function  $\Psi^{A(S)}$  belonging to the irrep  $A$  of the symmetry group  $S$ .

Equations (3) and (4) show that the ground-state energy  $E_0$  is determined with the lowest  $E^{A(S)}$ , while other  $E^{A(S)}$  represent, in agreement with [9,10], the energies of the lowest excited states of the symmetries  $A(S)$ . The energies  $E^{A(S)}$  are obtained with the functionals  $F^{A(S)}$  of (5) which are, in general, different for the different combined symmetry indices  $A(S)$ . In the case of RDMFT the potential parts of the symmetry-specific functionals  $F^{A(S)}[\gamma^{A(S)}]$  determine the functions  $\Gamma_{ij,kl}^{A(S)}(n)$

$$\frac{1}{2} \sum_{ijkl} \Gamma_{ij,kl}^{A(S)}(n) \langle ij|kl \rangle^{A(S)} = \langle \Psi_m^{A(S)} | \hat{V}_{ee} | \Psi_m^{A(S)} \rangle, \quad (6)$$

which, in general, are also different for different  $A(S)$ . In (6)  $\Psi_m^{A(S)}$  minimizes (5), while  $n_i$  and  $\chi_i$  in the two-electron integrals are the eigenvalues and eigenfunctions of the corresponding  $\gamma^{A(S)}$ .

Based on (6), one can argue that, rather than totally invalidating (1), WK have exposed the dependence of  $\Gamma_{ij,kl}^{A(S)}(n)$  of  $\Gamma_{ij,kl}(n)$  on the symmetry  $A(S)$ . Let us assume, for a certainty, that four atoms H of II arrange a trapezoidal structure with the shorter of two parallel sides being the  $H_2$  bond, while the lengths of other sides of the trapezoid tend to infinity. The ground state of this system belongs to the symmetry  ${}^1A_1(C_{2v})$ , while the symmetry of the ground state of I is  ${}^1B_{1g}(D_{4h})$  [12]. Then, the fact that WK have obtained different 2RDMs for the same ONs of I and II can be interpreted as the explicit construction of the different functions  $\Gamma_{ij,kl}^{1B_{1g}(D_{4h})}(n)$  and  $\Gamma_{ij,kl}^{1A_1(C_{2v})}(n)$  for the different symmetries  ${}^1B_{1g}(D_{4h})$  and  ${}^1A_1(C_{2v})$ , respectively.

Note that the interpretation of the considered example in [1] appears to contradict the very idea of a reduced density-matrix functional. Indeed, according to WK, "... the information of the one-matrix spectrum is not enough to fix the wave function. Functional based on the one-matrix eigenvalues thus cannot generate a  $N$ -representable two-matrix for the square  $H_4$  system".

True, the one-electron 1RDM by itself and, especially, its spectrum contain much less information than the total  $N$ -electron wave function. But, from this does not automatically follow that a function of the ONs cannot represent 2RDM. To the contrary, the use of the reduced quantities with a limited information content as arguments of functions and functionals is a trademark of RDMFT. Then, the missing information is

supplied with the adequate functional dependence on these arguments. For instance, the present functions  $\Gamma_{ij,kl}^{A(S)}(n)$  can have a complicated, highly nonlinear form to adequately represent 2RDMs for different symmetries.

Unlike the original interpretation, the present interpretation of the results of [1] as a manifestation of the symmetry dependence  $\Gamma_{ij,kl}^{A(S)}(n)$  is based on the general formulation (3)–(6), which includes the previously established symmetry dependence of the DFT functional  $F[\rho]$  [9,10] as a special case. As the practice of RDMFT shows [8,13–17], when developing approximate two-index JK- or JKL-type functionals, one can, usually, neglect the symmetry dependence, applying symmetry-nonspecific approximations to systems of various symmetries. However, the present interpretation of WK results of [1] warns that for certain relatively high symmetries, such as  $D_{4h}$ , the development of the specialized symmetry-specific JK- or JKL-type RDMFT functionals might be necessary.

In particular, the system II can be considered as a combination of two two-electron systems, the  $H_2$  molecules, one of which is dissociated. In this case, to construct  $\Gamma_{ij,kl}(n)$  of a RDMFT functional for the  ${}^1A_1(C_{2v})$  symmetry, it is natural to use the square-root ON dependence  $\sqrt{n_p n_q}$  of the paradigmatic exact two-electron RDMFT functional of Löwdin and Shull [2]. In its turn, for the system I a proper approximate RDMFT functional for the  ${}^1B_{1g}(D_{4h})$  symmetry can use a more complicated  $\Gamma_{ij,kl}(n)$  dependence, such as that of the Padé approximant type employed in Ref. [15], in order to construct a JK-type functional. With such a dependence, a successful JK or JKL functional would not only approximate the corresponding elements of the generic 2RDM, but it would also effectively absorb the contributions from non-JK (or non-JKL) 2RDM elements.

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