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

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Reply to Comment on "Nonuniqueness of algebraic first-order density-matrix functionals"[Phys. Rev. A 92, 012520 (2015)]

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It is shown that symmetry considerations do not alter the conclusions of the original paper, that there exists an example of an electronic system for which at several geometries the one-matrix eigenvalues are identical, but the two-matrix spectrum is not. It is still therefore the case that JK and related functionals that depend on the one-matrix eigenvalues to model the two-matrix can not be made arbitrarily accurate.

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Using natural orbitals, the exact energy of an electronic system can be written as

$$E = Z + \sum_i h_{ii} n_i + \tfrac{1}{2} \sum_{ijkl} \Gamma_{ij,kl} \langle ij|kl\rangle \qquad (1)$$

where h_{ij} and $\langle ij|kl\rangle$ are the usual one- and two-electron integrals in the natural orbital basis, Z is the bare-nucleus Coulomb energy. In some realisations of reduced density matrix functional theory(RDMFT) [1–3] , one simply assumes that $\Gamma_{ij,kl}$ is a particular algebraic function of the occupation numbers $\{n_i\}$. In our previous paper[4], we considered two geometries for four hydrogen atoms: (a) the atoms at the corner of a square of side R_4; (b) an H_2 molecule with bond length R_2 plus two infinitely separated hydrogen atoms. For certain combinations of R_2 and R_4, they have the same one-matrix spectrum (i.e., identical $\{n_i\}$), but different two-matrix $\Gamma_{ij,kl}$. We concluded that a model functional based on $\Gamma_{ij,kl}(n)$ cannot be unique.

Gritsenko[5] argues that the conclusion presented in Ref. [4] does not hold, because the two cases have different point-group symmetry. For the square, the molecule has D_{4h} symmetry, and the ground-state wavefunction is $^1B_{1u}$; for dihydrogen, the molecular wavefunction is $^1\Sigma_g^+$ in $D_{\infty h}$, with the two ground-state hydrogen atoms singlet-spin-coupled. To avoid the nonuniqueness problem of $\Gamma_{ij,kl}(n)$, Gritsenko [5] pointed out that the density-matrix functional needs to be unique only within a given symmetry, and so that in the example system, one could in principle have different functionals for the two cases. It is not stated how one might construct such functionals.

However, it is straightforward to construct the counter-example so that the two cases have the same point-group symmetry, by defining the geometry such that the atoms are at the vertices of a rhombus whose diagonals are of length R_a, R_b. The square-planar configuration can be constructed via the $\delta = 0$ limit of $R_a = \sqrt{2}R_4 + \delta$, $R_b = \sqrt{2}R_4 - \delta$; dihydrogen with infinitely separated atoms is $R_a \to \infty$, $R_b = R_2$. The point group is D_{2h}. For reasonable values of R_2 and R_4, the ground term of the square-planar configuration is $^1B_{1g}$, whereas for the dihydrogen plus separated atoms it is ^1A_g. In both cases, the ground-state wavefunction has two natural-orbital occupation numbers that are exactly 1, even for finite δ, so the two cases still have the same one-matrix eigenvalues. However, the change of ground state on geometry change appears to support the conclusion of Ref. [5] that this example is invalid because it attempts to compare density-matrix functionals that could in principle be completely different because they represent ground states of different symmetries.

But one can easily reduce the symmetry further, by, for example, moving two of the hydrogen atoms by different infinitesimal amounts above the plane of the molecule. In the resulting C_1 point group, the ground state is of ^1A symmetry at both geometries, and they should be describable by the same universal density-matrix functional. One may then approach the D_{2h} configurations arbitrarily closely without changing this requirement.

The conclusion is that one can indeed argue that for certain high symmetries, our original argument is not strictly valid, but the practical consequences are somewhat insignificant. One would normally want to use a density-matrix functional that is continuous on passing from low to high symmetry, and at low symmetry the counter-example we presented previously is still valid.

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