Reply to "Comment on 'Family of modified contracted Schrödinger equations' "

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The preceding Comment by Yasuda [Phys. Rev. A **79**, 016101 (2009)] on our earlier paper [Phys. Rev. A **64**, 062105 (2001)] raises several objections about the modified contracted Schrödinger equations (MCSEs) to which we reply here. In his comment, Yasuda also questions the possibility of obtaining the exact solution of the fourth-order MCSE due to its indeterminacy. We maintain the opposite, at least from a theoretical point of view.

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Here we respond to the preceding Comment [1] by Yasuda, where he raises several objections to our paper [2] about the modified contracted Schrödinger equations (MCSEs).

Our apparent neglect of the N-representability conditions. Let us start by emphasizing that the problem of the *N*-representability conditions [3] is common to all the reduced density matrix (RDM) based methods and, of course, to the self-consistent iterative solution of the MCSEs [2,4,5].

In our paper [2] we did not neglect the need for handling *N*-representable matrices. This problem was referred to as follows.

After Eq. (21) [2] we ask, "how to impose the constraints on the correlation matrices implied by them?"

At the end of Sec. V C [2] we say, "Although these relations are exact it should be noted that they do not have the RDM's antisymmetry built in. This point will be discussed in some detail in the last section."

In Sec. VI D [2] we make clear that all matrices must be *N*-representable and that *N*-representability constraints must be imposed. Let us stress this point by also calling attention to the paper [4], where several theorems, concerning the MCSEs, underline the need for the matrices involved to be *N*-representable. Let us moreover add that the need to purify the fourth-order correlation matrix (4-CM), and hence the 4-RDM is not a simple matter, as will be discussed in more detail below, and in practice, it has hampered our work on this subject.

Indeterminacy of the second-order contracted Schrödinger equation. Let us recall the second-order contracted Schrödinger equation (2-CSE) structure. This equation can be written as [6,7]:

$$
\begin{aligned}
2!E^2D_{rs;pq} = {} & 2!2\sum_{i,j} {}^2D_{rs;ij}\,{}^0H_{ij;pq} \\
& + 3!2\sum_{i,j,k} ({}^3D_{rsk;ijq}\,{}^0H_{ij;pk} + {}^3D_{rsk;ijp}\,{}^0H_{ij;kq}) \\
& + 4!\sum_{i,j,k,l} {}^4D_{klrs;ijpq}\,{}^0H_{ij;kl} \equiv {}^2\mathcal{M}_{rs;pq}, \qquad (1)
\end{aligned}
$$

where

$$
{}^0H_{ij;kl} = \frac{1}{2}\left(\frac{\delta_{i,k}\epsilon_{j;l} + \delta_{j,l}\epsilon_{i;k}}{N-1} + \langle ij|kl\rangle\right). \qquad (2)
$$

The symbol ϵ represents the one-electron integral matrix while the $\langle ij|kl\rangle$ is the two-electron repulsion integral in the Condon and Shortley notation. The 2-RDM, 3-RDM, and 4-RDM which appear in Eq. (1) must, of course, be *N*-representable, otherwise they would not be RDMs. That is, the *N*-representability of these matrices may be assumed when considering the 2-CSE [similarly as when one speaks about the Schrödinger equation (SE) it is assumed that the wave-function is an element of the Hilbert space, single-valued, etc.]. The reminder of this condition in Nakatsuji's statement of his 1976 theorem [8], whose second quantization equivalent was given by Mazziotti [9], can be considered to be just an extra clarification addressed to the potential method to be applied to solve the equation.

As Nakatsuji pointed out [10], the 2-CSE is not indeterminate. This is so because it has the same solutions as the SE and only these. This implies that the 2-RDM, 3-RDM, and 4-RDM that solve the 2-CSE for a given Hamiltonian eigenstate are unique. Therefore, the type of the 2-CSE indeterminacy is not an essential but an operational one. This 2-CSE operational indeterminacy is due to the *apparent* dependence of the 2-CSE on more variables than the number of available equations. That is, this operational indeterminacy derives from our ignorance of the exact constructing algorithms which express the 3-RDM and 4-RDM in terms of the 2-RDM.

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Existence of the high-order RDMs constructing functionals. We wish to recall that the existence of functionals for constructing third and fourth order N-representable matrices in terms of the 2-RDM has not, to our knowledge, been questioned. When replacing these functionals into the 2-CSE, the new equation would just depend on second-, first-, and zeroth-order matrices and would be nonlinear. The fact that the constructing algorithm—when applied outside from the equation framework—could generate in the excited states case more than one 3-RDM or 4-RDM would not, in our opinion, matter because the equation which only depends now on an unknown second-order N-representable matrix, the 2-RDM, would yield the correct answer.

Unfortunately, we ignore the exact algorithms leading from a 2-RDM to a 3-RDM and to a 4-RDM. This is the problem which is avoided when iteratively solving the fourth-order MCSE.

Modified contracted Schrödinger equation. As we explain in Ref. [2], the MCSEs are not new equations but linear combinations of several lower-order CSEs, as Yasuda points out, but also of terms depending on correlation matrices which Yasuda's development does not show explicitly. Moreover, the 4-MCSE is analytically equal to the 4-CSE and hence *different* from the 2-CSE. Thus,

$$E4!^4D = \langle \hat{H}^4\hat{\Gamma}\rangle \equiv {}^4\mathcal{M}, \tag{3}$$

where ${}^4\hat{\Gamma}$ stands for a fourth-order density operator and ${}^4\mathcal{M}$ is a functional of the 4-RDM, 5-RDM, and 6-RDM. As shown in our paper, this equation can be expressed in terms of the 2-CSE as

$$\begin{aligned} E4!^4D_{ijkl;pqrs} &= {}^2\mathcal{M}_{ij;pq}2!^2D_{kl;rs} + (\delta_{l,q}\delta_{k,p} - \delta_{k,q}\delta_{l,p})^2\mathcal{M}_{ij;rs} + (\delta_{k,q}\delta_{l,r} - \delta_{l,q}\delta_{k,r})^2\mathcal{M}_{ij;ps} + (\delta_{l,p}\delta_{k,r} - \delta_{k,p}\delta_{l,r})^2\mathcal{M}_{ij;qs} \\ &+ (\delta_{l,q}{}^1D_{s;k} - \delta_{k,q}{}^1D_{s;l})^2\mathcal{M}_{ij;pr} + (\delta_{k,p}{}^1D_{l;s} - \delta_{l,p}{}^1D_{k;s})^2\mathcal{M}_{ij;qr} + \delta_{l,q}(E^{(3;2,1)}\mathcal{C}_{ijk;prs} + {}^{(5;2,2,1)}0_{ijk;prs}) \\ &+ \delta_{k,p}(E^{(3;2,1)}\mathcal{C}_{ijl;qrs} + {}^{(5;2,2,1)}0_{ijl;qrs}) - \delta_{k,q}(E^{(3;2,1)}\mathcal{C}_{ijl;prs} + {}^{(5;2,2,1)}0_{ijl;prs}) - \delta_{l,p}(E^{(3;2,1)}\mathcal{C}_{ijk;qrs} + {}^{(5;2,2,1)}0_{ijk;qrs}) \\ &+ E^{(4;2,2)}\mathcal{C}_{ijkl;pqrs} + {}^{(6;2,2,2)}0_{ijkl;pqrs} = {}^4\mathcal{M}_{ijkl;pqrs}, \end{aligned} \tag{4}$$

where ${}^{(p;2,x,y,\ldots)}\mathcal{C}$ stands for a p-order correlation matrix (p-CM) [2] and

$$\begin{aligned} &{}^{(p;2,x,y,\ldots)}0_{v_1,\ldots,v_xt_1,\ldots,t_y,\ldots;w_1,\ldots,w_xz_1,\ldots,z_y,\ldots} \\ &\equiv \sum_{i,j,k,l} {}^0H_{ij;kl}{}^{(p;2,x,y,\ldots)}\mathcal{C}_{ijv_1,\ldots,v_xt_1,\ldots,t_y,\ldots;klw_1,\ldots,w_xz_1,\ldots,z_y,\ldots}, \end{aligned} \tag{5}$$

with $p=2+x+y+\cdots$. Now, because of Alcoba's theorem [4], when the 4-RDM corresponds to a Hamiltonian eigenstate not only the ${}^{(4;2,2)}0$ matrix vanishes but also the ${}^{(5;2,2,1)}0$ and ${}^{(6;2,2,2)}0$ ones.

The resulting equation is exact and both the energy and the RDMs correspond to the eigenstates which are solutions of the SE and the 2-CSE. This is so because of both Nakatsuji's and Alcoba's theorems. By solving iteratively this equation one avoids the operational indeterminacy arising from our ignorance of the exact constructing algorithms, and at convergence, the solution corresponds to that of the SE. We wish to stress that the 4-MCSE is self-contained not because it is not a hierarchy equation, but because the higher-order terms can be neglected since at convergence they vanish and none of the other matrices involved has a higher order than 4.

The price to be paid for bypassing the need for the constructing algorithms is that the N-representability purification procedure that has to be applied to the fourth-order matrix obtained at each iteration is rather complex. Let us, for instance, focus in just one of the many questions that a RDM purification procedure must accomplish and analyze the degree of relative complexity in the 2-RDM and in the 4-RDM cases. When purifying a trial 2-RDM [11–14] one has to guarantee that three different but inter-related matrices be positive semidefinite—the D, Q, and G conditions (in this latter case the positive or negative character of the G-spin components has also been included in our purification procedure [12–14])—while in the 4-RDM case one has to guarantee that at least eight inter-related matrices be positive semidefinite [15]. This high complexity of the purification procedure is what renders the 4-MCSE approach, in spite of its higher accuracy, non competitive with other RDM-based methods.

Possibility to distinguish whether a solution is spurious. We agree that within Yasuda's approach it is rather complex to judge which are the genuine solutions, but this is not the case in our 4-MCSE method. Thus, when convergence of 4-MCSE is achieved, one carries out the following operations.

(1) The fourth-order matrix obtained, which should be the 4-RDM, is contracted to the two-electron space to obtain the corresponding approximated 2-RDM. This new 2-RDM candidate is tested for all the N-representability conditions which are known at present [12–14,16].

(2) The 4-CM which is derived from the 4-RDM is then contracted to the two-electron space in order to obtain the 2-CM. This latter matrix should coincide with that derived from the 2-RDM yielded by the previous test.

(3) The ${}^{(4;2,2)}0$ is constructed from the 4-CM. This matrix should be equal to zero.

If these essential tests have a positive answer, there are

still other important properties which the 4-RDM obtained should fulfill and which can be added to this verification. Clearly, an spurious solution can be easily spotted.

The SE and N-MCSE are the same equation. Let us suppose that the studied system has only four electrons. In this case the 4-MCSE will be exact since the $^{(5;2,2,1)}0$ and the $^{(6;2,2,2)}0$ vanishing terms are null by hypothesis. Hence, in this case, the 4-MCSE is certainly equivalent to the SE and its solution coincides with the full-configuration-interaction (FCI) one, for a finite space of representation. Moreover, this latter case is not an exception. Thus, for any number of electrons N, according to Alcoba's theorem, the N-MCSE, which only depends on the 2-CSE and the N- and lower-order CMs, is equivalent to the SE and its solution coincides with the FCI one. Even more, as is pointed out in the paragraph (2) in Sec. VI C of our article, the FCI result is a stationary point in the iterative process of the 4-MCSE because no additional N-representability conditions are required. This is not so in the 2-CSE case because, although the FCI 2-RDM, 3-RDM, and 4-RDMs satisfy the equation, the iterative process requires a reconstruction of higher order RDMs and, hence, the next set of matrices deviate from exact fulfilment of the 2-CSE due to the approximations implicit in their reconstruction. That is, the FCI results satisfy the 2-CSE but they are not stationary points in the iterative process.

It can be concluded that 2-CSE and 4-MCSE, although having the same set of solutions, are not operatively equivalent. The 2-CSE requires the 2-RDM N-representability conditions *and* the constructing algorithms which are not N-representability conditions and which at present can only be considered good approximations. On the other hand, no construction algorithms are needed for solving the 4-MCSE since the $^{(5;2,2,1)}0$ and the $^{(6;2,2,2)}0$ terms vanish when the exact solution is attained. Therefore, the 4-RDM N-representability conditions are the only constraints (as we refer to in our paper) that need to be imposed at each iteration upon the 4-MCSE. Note that in Yasuda's approach all the variables are assumed to be independent, which is not the case.

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