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COMMENT

Reply to the 'Comment on "Multiconfigurational perturbation theory can predict a false ground state"' by J. Soto, F. Avila, J. C. Otero and J. F. Arenas, *Phys. Chem. Chem. Phys.*, 2011, DOI: 10.1039/C0CP01917H

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The conclusions of our recent communication [*Phys. Chem. Chem. Phys.* 2010, **12**, 5058] are reaffirmed in the present response to a comment. Popular variants of multireference perturbation theory used in conjunction with the intruder-state removing techniques (aka shift techniques) are capable of predicting a false ground state for seemingly simple chemical systems.

In our recent communication[1] we have demonstrated that popular variants of multireference perturbation theory (CASPT2[2,3] and MRMP[4,5]) can predict a false ground state for a remarkably simple chemical system: the scandium dimer. The MRMP and CASPT2 calculations on Sc_2 using a reduced valence (12o, 6e) active space were found to suffer severely from intruder states (*i.e.*, the quasi-degeneracies in the spectrum of the zeroth-order Hamiltonian[6]); employing intruder state removal techniques[7–9] helped us to obtain smooth and continuous potential energy curves. Unfortunately, the shape of the curves and their energy order depended strongly on the magnitude of the shift parameter σ; for small values of σ, MRMP and CASPT2 predicted that the ground state of Sc_2 is $^3\Sigma_u^-$, while for large values of σ, they predicted $^5\Sigma_u^-$. Thus, we concluded our research by stating that CASPT2 and MRMP used in conjunction with the intruder-state removal techniques *are capable* of predicting a false ground state for the scandium dimer. Analogous calculations performed with NEVPT2—a recent variant[10] of multireference perturbation theory (MRPT) free from the intruder state problem owing to a partially bielectronic definition of the zeroth-order Hamiltonian—showed clearly that the ground state is $^5\Sigma_u^-$.

The comment by Soto *et al.*[11] shows that the serious intruder-state problem in the CASPT2 calculations on Sc_2 can be solved by expanding the reduced valence active space (12o, 6e) to the full valence active space (18o, 6e). The approach employed by Soto *et al.*[11] is in line with the strategy[12] advocated by Roos for dealing with CASPT2 calculations plagued by intruder states: enlarge the active space with low-lying external orbitals to avoid the quasi-degeneracies.

Soto *et al.*[11] state that in the full valence active space the CASSCF reference weight in the $^3\Sigma_u^-$ and $^5\Sigma_u^-$ CASPT2 wave functions is higher than 0.8 for the whole potential energy curve and there is no need to employ the intruder-state removal techniques. We completely agree with the appropriateness of this approach and its advantage over using the intruder state removal techniques. Unfortunately, this approach has very limited applicability, as usually the intruder states originate from a large number of low-lying external orbitals; an inclusion of all of them in the active space is in most situations not feasible. A very good illustration of such situation can be found in our recent study of the intruder state problem in the manganese dimer,[13] where the reduced valence (4s + 3d) active space should be augmented with the atomic 4p, 5s, and 5p orbitals, resulting in a completely intractable (26o, 14e) CASSCF/MRPT problem.[14] Note that for Sc_2, the extension to the full valence (18o, 6e) active space could be performed only thanks to the small number (six) of active electrons. We point out, in passing, that the intruder-state removal techniques[7–9] have been introduced just as a remedy to this limitation. Our work on Sc_2 and Mn_2 casts serious doubts on the validity of the shift techniques in the framework of multireference perturbation theory and shows that this direction of development can be a dead-end street.

While we agree in principle with the main conclusions of the comment by Soto *et al.*,[11] we feel that it is necessary to rectify some incorrect or misleading statements appearing there.

We never predicted in our communication[1] that the ground state of Sc_2 is $^3\Sigma_u^-$! On the contrary, the potential energy curves shown in the ESI[15] accompanying our communication as well as the actual reading of the text show clearly that the real ground state of Sc_2 is $^5\Sigma_u^-$. In fact, our work was motivated by recent dubious conclusions of Matxain *et al.*,[16] who used MRMP to show that the ground state of Sc_2 is $^3\Sigma_u^-$ instead of the well established $^5\Sigma_u^-$. In the course of our investigation it

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turned out that the results of Matxain *et al.*[16] are plagued by serious procedural faults and should be treated with caution; our worries were soon confirmed by an erratum published by Matxain *et al.*[17]

It is relatively difficult, but *not impossible*, to obtain clean 4s + 3d molecular orbitals from CASSCF over the whole range of interatomic distances. In fact, the MRMP and CASPT2 calculations presented in our communication use a set of such orbitals, which can be made available upon request from the authors. Note that the NEVPT2 calculations performed with a set of such orbitals correctly predict $^5\Sigma_u^-$ as the ground state. We want to stress here once again that the strong shift-dependence of the computed MRMP and CASPT2 results is not a consequence of using a *wrong* active space, but stems from a serious intruder-state problem inherently connected to the one-electron character of the zeroth-order Hamiltonian used by these methods.

Adding a pair of $4p_z$ orbitals or a sextet of 4p orbitals to the reduced valence (12o, 6e) active space does not modify strongly the description of the $^3\Sigma_u^-$ and $^5\Sigma_u^-$ wave functions. We have analyzed carefully the behavior of low-lying states of Sc_2 in connection with the reduction of the full valence (18o, 6e) active space in a recent publication,[18] which has been apparently disregarded by Soto *et al.*[11]

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