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COMMENT

Comment on “Multiconfigurational perturbation theory can predict a false ground state” by C. Camacho, R. Cimiraglia and H. A. Witek, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5058†

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Prediction of the true ground state of Sc_2 with multiconfigurational perturbation theory requires a balanced active space in building the reference wave function.

In a recent communication, Camacho *et al.*¹ have questioned the reliability of multiconfigurational perturbation theory (MCPT). The authors arrive at this conclusion by studying the behavior of the potential energy surfaces of Sc_2 . To be specific, they found that MCPT as implemented in the CASPT2 method^{2,3} of MOLCAS and MOLPRO as well as the MCPT calculations done with GAMESS predicts that the ground state of Sc_2 is a triplet (${}^3\Sigma_u^-$), which is in contradiction with the accepted symmetry of the lowest energy state that is a quintet (${}^5\Sigma_u^-$). They argue that this erroneous prediction of the calculations is due to the presence of the intruder state problem.

This comment shows that a suitable active space for the CASSCF reference wave function predicts correctly the ${}^5\Sigma_u^-$ ground state of Sc_2 with the CASPT2 method. The ground state of the Sc atom has a $4s^23d^1$ configuration. Therefore, to study Sc_2 , a reasonable choice of the active space should include six electrons ($4s^23d^1 \times 2$) distributed in twelve molecular orbitals [$1(4s) + 5(3d) \times 2$]. This is the active space chosen in ref. 1. However, we have found a very remarkable difficulty concerning such an active space: it is impossible to span the ten d-type orbitals given that two unoccupied $4p_z$ type orbitals replace the two $d_{x^2-y^2}$ type orbitals. As a consequence, the multiconfigurational perturbation treatment of the problem predicts that the triplet state is lower in energy than the quintet state. In contrast, if we enlarge the active space by including $[3(4p)] \times 2$ orbitals, that is, six electrons distributed in eighteen orbitals, ${}^5\Sigma_u^-$ is computed as the ground state at the MCPT level.

The wave function is converged under D_{2h} symmetry constraints. The multi-state extension of the second-order multiconfigurational perturbation theory (MS-CASPT2) has been applied to all of our calculations, which have been performed with the MOLCAS program.⁴ The standard IPEA shift has been applied. The inner 3s and 3p orbitals have been

correlated in the perturbation calculation. The basis set consisted of atomic natural orbital type, in particular, the ANO-RCC basis set⁵ with the $\text{Sc}(5s\ 4p\ 3d\ 2f\ 1g)$ contraction scheme. In addition, the scalar relativistic effect is included by adding the corresponding terms of the Douglas–Kroll–Hess Hamiltonian.^{6,7} It must be remarked that the weight of the reference wave function was higher than 0.8 along the whole path and for the three states shown in Fig. 1; consequently, the application of imaginary or real shift techniques, to avoid the intruder state problem, was unnecessary.

Fig. 1 shows the potential energy curves obtained with the six electrons–eighteen orbitals active space for the ${}^3\Sigma_u^-$ and ${}^5\Sigma_u^-$ states (3A_u and 5A_u under D_{2h} symmetry). Three states were optimized in each symmetry block. The quintet state has the lowest energy and its minimum is 0.14 eV under the minimum of the triplet state. Moreover, the calculations with the reduced six electrons twelve orbitals active space predict

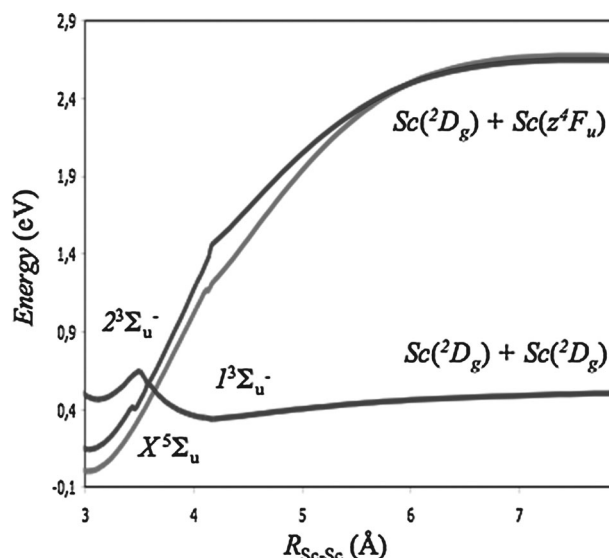


Fig. 1 MS-CASPT2/CAS(6,18) potential energy surfaces of the $X^5\Sigma_u^-$, $I^3\Sigma_u^-$ and $2^3\Sigma_u^-$ states of Sc_2 .

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that the triplet is the ground state (0.12 eV under the quintet minimum). The computed MS-CASPT2 harmonic frequency of ${}^5\Sigma_u^-$ amounts to 226 cm^{-1} which compares well with the experimentally determined⁸ harmonic frequency of 238.9 cm^{-1} . The calculated equilibrium internuclear distance is 2.624 \AA . The dissociation energy E_d of ${}^5\Sigma_u^-$ is 2.63 eV, computed at an internuclear separation of 66 \AA and leading to $\text{Sc}({}^2D_g) + \text{Sc}({}^4F_g)$. Our results agree completely with the multireference configuration interaction (MRCI) calculations applied to Sc_2 by Kalemios *et al.*,⁹ which used the same active space as this comment.

In summary, to properly apply multiconfigurational perturbation theory to the Sc_2 molecule, an active space of six electrons distributed in eighteen orbitals is required. Otherwise, reduced active spaces lead to false conclusions.

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