

# Multireference perturbation theory can predict a false ground state†

Cristopher Camacho,<sup>a</sup> Renzo Cimiraglia<sup>b</sup> and Henryk A. Witek<sup>\*a</sup>

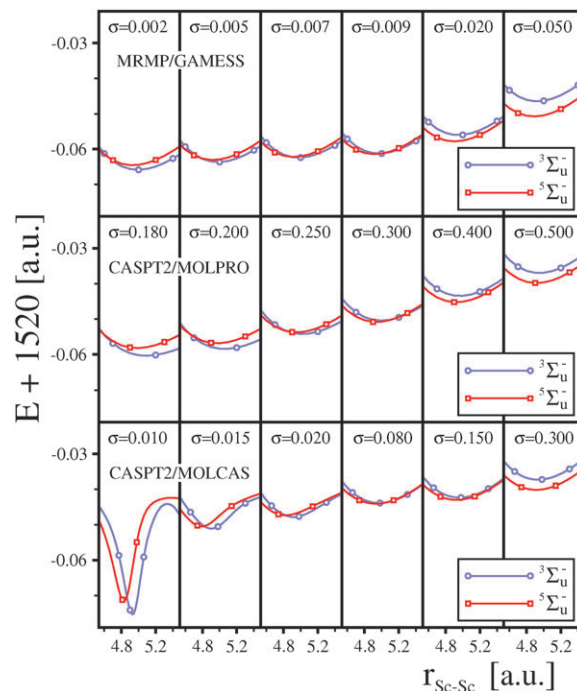
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**Prediction of a false ground state with popular variants of multireference perturbation theory (CASPT2 and MRMP) is reported for a remarkably simple chemical system: the Sc<sub>2</sub> molecule.**

In a recent publication, Matxain *et al.*<sup>1</sup> used quantum diffusion Monte Carlo (DMC) and second-order multireference Møller–Plesset perturbation theory<sup>2,3</sup> (MRMP) to show that the ground state of Sc<sub>2</sub> is <sup>3</sup>Σ<sub>u</sub><sup>-</sup> instead of the previously predicted <sup>5</sup>Σ<sub>u</sub><sup>-</sup>. Their finding was rather surprising, because the consensus concerning the symmetry of the ground state of the scandium dimer dates back to 30 years ago. This result motivated us to reinvestigate the same problem using popular variants of multireference perturbation theory. It has been found that the multireference perturbation theory (MRPT) ground state calculations (either for <sup>3</sup>Σ<sub>u</sub><sup>-</sup> or <sup>5</sup>Σ<sub>u</sub><sup>-</sup>) suffer severely from the intruder state problem. In order to obtain smooth potential energy surfaces (PESs) it has been necessary to employ intruder state removal techniques. The resultant curves—shown in Fig. 1 for various magnitudes of the shift parameter—are continuous and closely spaced. Surprisingly enough, the energy ordering of the <sup>3</sup>Σ<sub>u</sub><sup>-</sup> and <sup>5</sup>Σ<sub>u</sub><sup>-</sup> states depends on the magnitude of the shift parameter,  $\sigma$ . The energy separation between the two curves is not large, but clearly smaller values of the shift parameter,  $\sigma$ , promote the <sup>3</sup>Σ<sub>u</sub><sup>-</sup> state as the ground state, while larger values of  $\sigma$  produce similar order like at the CASSCF level. A discussion of this behavior is presented below. At present, MRPT is routinely used for finding the energetics and properties of a wide spectrum of chemical systems in their ground and excited states. Often these calculations are plagued by intruder states and the intruder state removal technique is a standard tool to deal with such problems. It was found previously that the choice of the shift parameter can influence significantly the values of spectroscopic properties of the ground state of Mn<sub>2</sub>.<sup>4,5</sup> The present study raises further doubts as to the appropriateness of using the shift techniques in MRPT. A choice of too small a value of the shift parameter can produce false assignment of the ground state and consequently distort the energy spectrum of a given molecule in a considerable manner. We stress again that the MRPT calculations employing the intruder state removal techniques should be performed at least twice



**Fig. 1** Potential energy curves for the <sup>5</sup>Σ<sub>u</sub><sup>-</sup> and <sup>3</sup>Σ<sub>u</sub><sup>-</sup> states obtained from the MRMP/GAMESS, CASPT2/MOLPRO, and CASPT2/MOLCAS calculations using different values of shift parameter,  $\sigma$ .

(with different values of  $\sigma$ ) to verify the independence of the results on the shift magnitude.

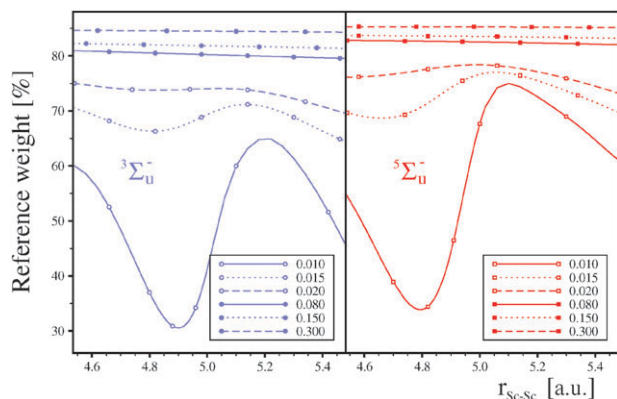
The present calculations have adopted the same, moderate-size basis set as used previously by Matxain *et al.*<sup>1</sup> A detailed specification of this basis is given in the ESI.† The (reduced valence) active space consists of the molecular orbitals derived from the 4s and 3d AOs of scandium. The orbitals are optimized state-specifically. The MRPT calculations correlate the inner 3s and 3p orbitals. The CASPT2<sup>6,7</sup> calculations have been performed using the MOLCAS<sup>8</sup> and MOLPRO<sup>9</sup> quantum chemistry programs whereas the MRMP<sup>2,3</sup> calculations used the GAMESS<sup>10</sup> program. The CASPT2/MOLCAS employed the IPEA shift<sup>11</sup> of 0.25 a.u. in conjunction with the imaginary shift technique,<sup>12</sup> the CASPT2/MOLPRO used the real shift technique,<sup>13</sup> and MRMP used the intruder state avoidance (ISA) technique.<sup>14</sup> All calculations were performed with the standard, unmodified zeroth-order Hamiltonian. Dissociation energies,  $D_e$ , have been computed using the MRPT energy of the <sup>5</sup>Σ<sub>u</sub><sup>-</sup> at 40.00 a.u., which corresponds to the <sup>2</sup>D<sub>g</sub> + <sup>4</sup>F<sub>g</sub> atomic asymptote.

At the CASSCF level, the <sup>5</sup>Σ<sub>u</sub><sup>-</sup> state lies 0.335 eV lower than the <sup>3</sup>Σ<sub>u</sub><sup>-</sup> state. The experimentally determined spectroscopic parameters of the ground state are  $\omega_e = 238.9 \text{ cm}^{-1}$

<sup>a</sup> Institute of Molecular Science and Department of Applied Chemistry, National Chiao Tung University, 1001 Ta-Hsueh Road, Hsinchu 30010, Taiwan. E-mail: hwitek@mail.nctu.edu.tw

<sup>b</sup> Dipartimento di Chimica, Università di Ferrara, Via Borsari 46, I-44100 Ferrara, Italy

† Electronic supplementary information (ESI) available: Potential energy curves for the <sup>5</sup>Σ<sub>u</sub><sup>-</sup> and <sup>3</sup>Σ<sub>u</sub><sup>-</sup> states obtained with the NEVPT2 method; basis set used. See DOI: 10.1039/c000196a



**Fig. 2** Reference weights for the  ${}^5\Sigma_u^-$  and  ${}^3\Sigma_u^-$  states in CASPT2/MOLCAS calculations for different values of imaginary shift,  $\sigma$ .

and  $D_0 = 1.05 \pm 0.2$  eV; no accurate estimate of  $r_e$  is available. Accounting for dynamical correlation using MRPT leads to highly perturbed potential energy curves caused by numerous intruder states. Using intruder state removal techniques improves the situation considerably; the resultant curves—shown in Fig. 1—are smooth. For small values of the shift parameter,  ${}^3\Sigma_u^-$  is lower in energy, while for larger values of the shift parameter, the situation is opposite. A possible explanation of this behavior can be given by taking into account the following facts. In the limit of an infinitely large shift, the second-order perturbation energy contribution is equal to zero, and the reproduced energy order is exactly the same as the CASSCF level (*i.e.*  ${}^3\Sigma_u^-$  is the ground state). On the other hand, for small values of the shift parameter, the intruder states' influence can be expected to be larger for the triplet

state, since the number of intermediate states appearing in the perturbation expansion is much larger for the triplet than for the quintet space (7 295 672 and 3 506 188, respectively). Consequently, the number of intermediate states with quasi-degenerated zeroth-order energy is statistically larger for the triplet state, causing much stronger defects and artificial energy lowering than for the quintet state. This behavior is most visible in the CASPT2/MOLCAS curve with  $\sigma = 0.01$  and  $\sigma = 0.015$ . Analogous information can be inferred from the CASSCF reference weight plotted for the CASPT2/MOLCAS wavefunctions in Fig. 2 for various values of  $\sigma$ . The CASSCF reference weight in the  ${}^3\Sigma_u^-$  wavefunction is almost constantly lower than for  ${}^5\Sigma_u^-$  over the whole studied range of distances.

This analysis allows us to conclude that the energy order found by Matxain *et al.*<sup>1</sup> in their MRPT calculations—*i.e.* with  ${}^3\Sigma_u^-$  being the ground state and  ${}^5\Sigma_u^-$  the first excited state—is merely an artifact produced by the intruder state removal technique. In the previously studied case of the manganese dimer,<sup>5</sup> we showed that the spectroscopic parameters of this molecule depend strongly on the magnitude of the shift parameter. A similar situation occurs for both of the investigated states of  $\text{Sc}_2$ . The spectroscopic parameters obtained from the CASPT2/MOLCAS, CASPT2/MOLPRO, and MRMP/GAMESS calculations with various values of the shift parameter are tabulated in Table 1. As can be seen, the change is largest for small values of the shift parameter, while for larger values of  $\sigma$ , the spectroscopic parameters tend toward those of CASSCF.

Intruder states appearing in MRPT originate from a poor choice of the zeroth-order Hamiltonian. In all the studied cases, the zeroth-order Hamiltonian is chosen as a multi-reference generalization of one-electron Møller–Plesset

**Table 1** Spectroscopic parameters of the  ${}^5\Sigma_u^-$  and  ${}^3\Sigma_u^-$  states of  $\text{Sc}_2$  computed using CASPT2 and MRMP with different values of the shift parameter,  $\sigma$ . For details, see text. Equilibrium distances ( $r_e$ ) are given in Å, harmonic frequencies ( $\omega_e$ ) in  $\text{cm}^{-1}$  and dissociation energies ( $D_e$ ) in eV

Method	$\sigma$	${}^5\Sigma_u^-$			${}^3\Sigma_u^-$			$\Delta E({}^5\Sigma_u^- \rightarrow {}^3\Sigma_u^-)$
		$r_e$	$\omega_e$	$D_e$	$r_e$	$\omega_e$	$D_e$	
MRMP/GAMESS	0.002	2.610	237.1	1.51	2.641	240.0	1.54	-0.035
	0.005	2.605	237.7	1.51	2.636	241.1	1.52	-0.017
	0.007	2.603	238.0	1.50	2.633	241.6	1.51	-0.006
	0.009	2.600	238.4	1.50	2.631	242.0	1.50	0.005
	0.020	2.593	239.8	1.48	2.622	245.6	1.43	0.049
	0.050	2.586	242.4	1.43	2.605	248.8	1.32	0.116
	$\infty$	2.665	256.2	1.20	2.644	268.5	0.87	0.335
CASPT2/MOLPRO	0.180	2.637	221.4	— <sup>a</sup>	2.691	208.0	— <sup>a</sup>	-0.059
	0.200	2.632	226.2	— <sup>a</sup>	2.678	218.0	— <sup>a</sup>	-0.043
	0.250	2.623	232.3	— <sup>a</sup>	2.654	229.8	— <sup>a</sup>	-0.013
	0.300	2.616	235.7	1.65	2.641	236.5	1.64	0.011
	0.400	2.607	239.7	1.63	2.629	242.9	1.58	0.048
	0.500	2.601	242.3	1.61	2.619	247.7	1.53	0.077
	$\infty$	2.665	256.2	1.20	2.644	268.5	0.87	0.335
CASPT2/MOLCAS	0.010	2.555	1528.0	2.45	2.609	1767.2	2.55	-0.102
	0.015	2.535	439.6	1.87	2.596	436.6	1.89	-0.016
	0.020	2.550	301.6	1.78	2.604	318.6	1.80	-0.013
	0.080	2.609	238.8	1.69	2.631	249.5	1.69	0.005
	0.150	2.607	240.0	1.69	2.626	249.2	1.67	0.018
	0.300	2.599	243.6	1.67	2.611	252.5	1.60	0.078
	$\infty$	2.665	256.2	1.20	2.644	268.5	0.87	0.335

<sup>a</sup> At 40.00 a.u. the calculation is affected by strong intruder states.

Hamiltonian. This choice often produces a large number of quasi-degeneracies in the zeroth-order energy spectrum as there is no guarantee that the energy order in the zeroth-order Hamiltonian spectrum would be the same as for the original two-electron operator. Consequently, the zeroth-order energy of the reference state can be embedded in the zeroth-order spectrum of the intermediate states, which brings about the appearance of the intruder states in the perturbation calculations. We want to stress here that these problems are purely artificial and have very little connection to the physical reality of a given system. Nor does the inclusion of additional orbitals in the active space provide a viable way to the solution of the intruder state problem. The intruder state removal techniques discussed here, due to the arbitrariness in choosing the magnitude of the energy shift, result in a corresponding arbitrariness in the final MRPT results. As discussed by Dyll, <sup>15</sup> the definition of a partially bielectronic zeroth-order Hamiltonian can be effective in removing the intruder states. A recent variant of MRPT, NEVPT, <sup>16</sup> which makes use of such a Hamiltonian, is shown to be free from the problem of quasi-degeneracies in the zeroth-order spectrum. Preliminary results obtained with NEVPT2 for the two states of Sc<sub>2</sub> studied here and given in the ESI† show that the ground state of this system is <sup>5</sup>Σ<sub>u</sub><sup>-</sup>. An extensive study of low-lying states of the scandium dimer using the NEVPT method will be published shortly.

In this communication, we have shown that the calculations recently published by Matxain *et al.*<sup>1</sup> are affected by a serious intruder state problem. The energy order of the two low-lying states of the scandium dimer, <sup>5</sup>Σ<sub>u</sub><sup>-</sup> and <sup>3</sup>Σ<sub>u</sub><sup>-</sup>, depends strongly on the magnitude of the shift parameter used to remove the intruder states from the perturbation expansion. For small shift values, multireference perturbation theory predicts <sup>3</sup>Σ<sub>u</sub><sup>-</sup> to be the ground state, while for larger values, <sup>5</sup>Σ<sub>u</sub><sup>-</sup> is lower in

energy. The strong shift-dependence of the computed results cast serious doubts on the validity of the shift techniques in multireference perturbation theory.

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