THE EUROPEAN
PHYSICAL JOURNAL D

Regular Article

The nature of binding in the ground state of the scandium dimer

U. Miranda and I.G. Kaplan[a]

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apdo. Postal 70-360,
04510, México D.F., México

Abstract. For the study of the nature of binding in the Sc_2 dimer, the ground state, $X^5\Sigma_u^-$, was calculated by the valence multireference configuration interaction method with single and double excitations plus Davidson correction, MRCISD (+Q), at the complete basis set (CBS) limit. The employment of the C_{2v} symmetry group, allowed us to obtain the Sc atoms in different states at the dissociation limit. From the Mulliken population analysis and comparison with atomic energies follows that in the ground state Sc_2 dissociates on one Sc in the ground state and the other in the second excited quartet state, ^4F_u. The spectroscopic parameters of the ground potential curve, obtained at the valence MRCISD (+Q)/CBS level, are: $R_e = 5.20$ bohr, $D_e = 50.37$ kcal/mol, and $\omega_e = 234.5$ cm^{-1}. The obtained value for the harmonic frequency agrees very well with the experimental one, $\omega_e = 239.9$ cm^{-1}. The dissociation energy with reference to the dissociation on two Sc in the ground states was estimated as $D_e = 9.98$ kcal/mol. In contrast with many other studied transition-metal dimers, which are attributed to the van der Waals bonded molecules, the Sc_2 dimer is stabilized by the covalent bonding on the hybrid atomic orbitals.

1 Introduction

Already many years ago, due to their catalytic and magnetic properties, the transition-metal clusters with $3d$ electrons have attracted a great interest both experimentally and theoretically [1]. It is worth-while to mention that ab initio calculations of $3d$-clusters (even dimers) are still a challenge to theorists. The main reason is that they cannot be treated by single-reference approaches, on which the modern standard methods: configuration interaction (CI), coupled cluster (CC), and Møller-Plesset perturbation theory (MPPT) are based.

As was shown by Roos et al. [2], a reliable potential curve for the ground state of the Cr_2 dimer can be obtained only by multireference (MR) methods. Bauschlicher [3] demonstrated that in the case of Mn_2, the ground state wave function found at the complete active space (CASSCF) level has a pronounced multireference character. In its configuration expansion the Hartree-Fock configuration appears with the coefficient $c_o = 0.08$, while among other configurations more than 130 configurations have coefficients $c_i > 0.05$. Thus, instead of one base configuration in the CI procedure, a large number of reference configurations must be treated equally.

In spite of only one electron in the $3d$-shell, the Sc_2 dimer also presents a complex computational problem. The existence of a very large number of degenerate and quasi-degenerate terms makes the precise calculation of Sc_2 potential curve extremely complicated.

The ground state of the Sc atom is ^2D_g $(4s^23d)$ with the first three excited states ^4F_g $(4s3d^2)$, ^2F_g $(4s3d^2)$ and ^4F_u $(4s3d4p)$, which are located 1.43, 1.85, and 1.96 eV above [4]. The relatively small excitation energy makes quite probable the existence of several asymptotic dissociation limits for the lowest potential curves; the symmetric $Sc(^2D_g) + Sc(^2D_g)$ and the three asymmetric: $Sc(^2D_g) + Sc^*(^4F_g)$, $Sc(^2D_g) + Sc^*(^2F_g)$, and $Sc(^2D_g) + Sc^*(^4F_u)$. In the second and fourth limits the maximum total spin of the dimer is $S = 2$. Thus, for these asymptotes the Sc_2 dimer can possess $S = 0, 1$, and 2. The total number of the lowest terms having these four dissociation limits is very high and equals 270. In Table 1 we represent the 160 possible triplet and quintet terms arising in the second and fourth dissociation limits.

In the ESR experiments by Knight et al. [5], the ground state of Sc_2 was assigned as $^5\Sigma_u^-$. Let us stress that it was not obtained in a direct measurement. Processing their experimental data, the authors [5] made some assumptions. Several years before, the quintet ground state, $^5\Sigma_u^-$, was predicted in the DFT calculations by Harris and Jones [6]. They employed a rough (but the best at that time) local spin density approximation (LSDA). So it is surprising that Harris and Jones were able to predict by their method such exotic ground state, corresponding to an asymmetric dissociation. They mentioned that the triplet state, $^3\Sigma_g^-$, can also be a candidate for the ground state.

It is interesting to mention that in all published, to the best of our knowledge, DFT calculations of Sc_2 [6–13], the quintet state, $^5\Sigma_u^-$, was claimed as the ground state.

a e-mail: kaplan@iim.unam.mx

Table 1. Molecular states stemming from the interaction of one Sc atom in the ground ^2D_g state and one Sc atom in the excited ^4F state.

Sc($3d4s^2$; ^{2}D) + a Sc*($3d^24s$; ^4F_g)		Sc($3d4s^2$; ^{2}D) + z Sc*($3d4s4p$; ^4F_u)	
Triplets	Quintets	Triplets	Quintets
$^3\Sigma_g^+$ (2), $^3\Sigma_u^+$ (2)	$^5\Sigma_g^+$ (2), $^5\Sigma_u^+$ (2)	$^3\Sigma_g^+$ (3), $^3\Sigma_u^+$ (3)	$^5\Sigma_g^+$ (3), $^5\Sigma_u^+$ (3)
$^3\Sigma_g^-$ (3), $^3\Sigma_u^-$ (3)	$^5\Sigma_g^-$ (3), $^5\Sigma_u^-$ (3)	$^3\Sigma_g^-$ (2), $^3\Sigma_u^-$ (2)	$^5\Sigma_g^-$ (2), $^5\Sigma_u^-$ (2)
$^3\Pi_g$ (5), $^3\Pi_u$ (5)	$^5\Pi_g$ (5), $^5\Pi_u$ (5)	$^3\Pi_g$ (5), $^3\Pi_u$ (5)	$^5\Pi_g$ (5), $^5\Pi_u$ (5)
$^3\Delta_g$ (4), $^3\Delta_u$ (4)	$^5\Delta_g$ (4), $^5\Delta_u$ (4)	$^3\Delta_g$ (4), $^3\Delta_u$ (4)	$^5\Delta_g$ (4), $^5\Delta_u$ (4)
$^3\Phi_g$ (3), $^3\Phi_u$ (3)	$^5\Phi_g$ (3), $^5\Phi_u$ (3)	$^3\Phi_g$ (3), $^3\Phi_u$ (3)	$^5\Phi_g$ (3), $^5\Phi_u$ (3)
$^3\Gamma_g$ (2), $^3\Gamma_u$ (2)	$^5\Gamma_g$ (2), $^5\Gamma_u$ (2)	$^3\Gamma_g$ (2), $^3\Gamma_u$ (2)	$^5\Gamma_g$ (2), $^5\Gamma_u$ (2)
^3H_g, ^3H_u	^5H_g, ^5H_u	^3H_g, ^3H_u	^5H_g, ^5H_u

This consensus is in a sharp contrast with the DFT calculations of other transition-metal dimers, e.g. for Mn_2 the DFT results are quite conflicting, see discussion in reference [14]. Although it should be noted that only in limited DFT studies [6,7,9,10], the different spin states of Sc_2 were comparatively studied; in other published DFT calculations only $^5\Sigma_u^-$ state was selected and authors studied the dependence of obtained results on functionals used.

As in the case of other transition-metal dimers, precise computational results for Sc_2 can be obtained by ab initio multireference (MR) methods with large basis sets. Among widely applied MR methods are the MR CISD method [15–19] often used in conjunction with the Davidson quadruple correction [20,21], denoted as MRCISD (+Q), and the multireference average coupled functional pair (ACPF) approach [22,23].

Till recent time, the most precise ab initio calculations of Sc_2 were performed by Åkeby et al. [24] using a multireference treatment at the ACPF level and by Suzuki et al. [25] at the MRCISD (+Q) level. After these publications it became widely accepted that the ground state of Sc_2 is the quintet $^5\Sigma_u^-$ state.

In 2008 Matxain et al. [26] revised the problem of the Sc_2 ground state. They stressed that at a high level only the $^5\Sigma_u^-$ quintet was studied [24,25], whereas the triplet terms were calculated in reference [27] using not very precise the CASSCF approach. Matxain et al. [26], applying the quantum diffusion Monte Carlo (DMC) method [28], have calculated at the same level of theory ten low-lying states of the scandium dimer, including the $^5\Sigma_u$ and $^3\Sigma_u$ terms (the upper index in the Σ terms was not specified). According to their calculations, the triplet $^3\Sigma_u$ state is more stable than the $^5\Sigma_u$ state by 0.17 eV. The authors [26] claimed that the correct ground state of scandium dimer is the triplet $^3\Sigma_u$ state, but not the quintet $^5\Sigma_u^-$ state, as was accepted in all previous investigations.

However, the calculations by Matxain et al. [26] did not have a sufficient level to be safe. The authors [26] used a relatively small basis set and checked the DMC results comparing it with CASPT2 calculation (the latter was taken as a final criteria). It should be mentioned that for transition metals the CASPT2 approach often predicts an artificial stability [29]. CASPT2 and connected with it the MRMP2 approach [30] are very sensitive to the choice

of the active space. The use of non-closed active space can lead to large errors [29]. This is what happened in the calculation [26], as was noted by the authors in erratum [31]. They noted that the use of 10 active orbitals instead of erroneously reported 12 "doubts on the reliability of the reported MRPT calculations, which might yield meaningless results". It is also important to mention that the CASPT2 and MRMP2 methods suffer from the intruder state problem [32]. Thus, the conclusion of Matxain et al. [26] had to be verified in a more precise calculation. This has been done in the recent publications [33,34].

In the study by Kalemos et al. [33], the MRCISD (+Q)/cc-pVQZ calculations were carried out for the two competitive terms $^5\Sigma_u^-$ and $^3\Sigma_u^-$. It was established that the quintet state $^5\Sigma_u^-$ is really the ground state and the triplet state $^3\Sigma_u^-$ is located just 1 kcal/mol (0.04 eV) above. These results were qualitatively confirmed in the study by Camacho et al. [34] where the multireference n-electron valence state perturbation theory (NEVPT) method [35,36] was employed. The authors found that the triplet $^3\Sigma_u^-$ state is located by 0.10 eV above the ground; $^5\Sigma_u^-$ state.

In the present work we performed a detailed study of the nature of binding in the ground state of the Sc_2 dimer using the valence MRCISD (+Q) method at the complete basis set (CBS) limit. Special attention was paid to study the dissociation limit. For the possibility to obtain the two Sc atoms in different states, we used the C_{2v} symmetry restriction (in all previous studies of Sc_2, including reference [33], the D_{2h} symmetry group was used). From the Mulliken population analysis and energy calculations follows that the dimer Sc_2 dissociates on one Sc in its ground state and the other in the second excited quartet state ^4F_u ($4s^13d^14p^1$).

2 Methodology

2.1 Computational method

The wave functions were optimized by means of the CASSCF method [37,38]; the active space was defined by the $3d$, $4s$ and $4p$ orbitals, making a set of 18 active orbitals and 6 active electrons, 3 from the atomic valence

shells of each atom. As was discussed in Introduction, the total spin $S = 2$ in the ground state of the scandium dimer, the $^5\Sigma_u^-$ state, stems from the interaction between one ground state Sc atom and other in an excited state, therefore the calculations were done under C_{2v} symmetry constraints. The C_{2v} calculation is more time consuming than D_{2h} one, but it allows to obtain at the dissociation limit the two Sc atoms in different states, as it takes place in the $^5\Sigma_u^-$ state. The C_{2v} or D_{2h} symmetry groups are used instead of $C_{\infty v}$ or $D_{\infty h}$, because in the MOL-PRO suite of programs only the Abelian groups can be exploited. As follows from the studies in reference [39], for some molecules (e.g. FeO$^+$) the change of symmetry group used in the calculations can lead to a change of the energy, while for the Fe$_2$ dimer it does not change. The same is valid for the Sc$_2$ dimer. The binding energy and equilibrium distance obtained under C_{2v} and D_{2h} restrictions are the same.

The energy results were obtained by the valence multireference internally contracted configuration interaction (MRCISD) method, see references [18,19]. The size-inconsistency error was corrected only through the Davidson (+Q) approach [20,21], since this error in the case of Sc$_2$ is small; according to our results, the quadruple Davidson corrections lead to small changes, e.g. the difference in D_e is about 0.04 eV. For the cc-pV5Z basis set, the number of configuration functions (CFs) in the reference wave functions was approximately 34 000, their corresponding valence MRCI expansions are about 1.65×10^8 CFs, which are internally contracted to 6.7×10^6 CFs according to a procedure described in references [18,19]. For all calculations the MOLPRO 2009 suite of programs [40] was used.

We employed the Dunning-type basis sets, see reference [41], presented in the Pacific Northwest National Laboratory basis set website[1]. To study the dependence of calculation results on the basis set size and finding the complete basis set (CBS) limit, we performed calculations with three basis sets, cc-pVXZ with $X = 3$, 4, and 5. The largest basis set, cc-pV5Z, is constructed with $[28s20p12d4f3g2h1i]$ functions, which are contracted to $[9s8p6d4f3g2h1i]$, and comprises 153 contracted spherical gaussian functions. The scalar relativistic calculations were obtained at both calculated levels, CASSCF and MRCI, by means of the Douglas-Kroll-Hess approach in the second order scheme [42], which is corrected in reference [43], and with the relativistic basis set cc-pV5Z-DK [41].

2.2 Complete basis set limit

After the development by Dunning [44] of the correlation-consistent cc-pVXZ basis sets, it was recognized that the sequence of results obtained with different XZ allows an extrapolation to the CBS limit [45–47]. Calculation of E_X with different values of X makes possible to find the CBS limit, E_∞, using some analytical function of X connecting

---

[1] https://bse.pnl.gov/bse/portal

E_X and E_∞. At present, several asymptotic formulae for finding the CBS limit at the HF, CASSCF, and MRCI levels have been developed, see reference [48] and references therein.

In this study we applied the procedure for obtaining the CBS limit at the MRCI level, based on the presentation of E^{MRCI} as two terms,

$$E^{MRCI} = E^{CAS} + E^{dc}, \tag{1}$$

and finding the CBS limit for each term separately [48]; see also previous publications [49,50].

As we see from equation (1), the energy obtained at the MRCI level includes some additional electron correlation energy, E^{dc}, in comparison with the CASSCF energy. This energy is named the *external* or *dynamical correlation energy* [48,51]; it arises from the non-specific instantaneous correlation motion of electrons and was introduced by Sinanoglu et al. [52,53].

The studies by Sinanoglu et al. [52–54] showed that the correlation energy can be roughly divided into two types: dynamical correlations, which are transferable from system to system, and non-dynamical correlations, which are not. Usually non-dynamical correlations are responsible for a correct description of the dissociation products and in some papers is named *left-right correlation* [55]. Sinanoglu stressed that a good example of the transferable correlation energy is the closed $1s^2$ shell for the first-row atoms. At that time the MRCI approach was not created. Brown and Truhlar [51] divided the dynamical correlations into core and valence contributions. The latter corresponds to the dynamical correlation energy defined by equation (1).

3 Results and discussion

3.1 Calculations at the complete basis set limit

As we discuss in Section 2, at the MRCI level the CBS limit can be found separately for each term in the presentation of MRCI energy according to equation (1).

For energy at the CASSCF level we used the Karton-Martin [56] extrapolation formula. The equation employed is

$$E_X^{CAS} = E_\infty^{CAS} + A(X+1)e^{-b\sqrt{X}}, \tag{2}$$

in which A and b are parameters found after solving equations and E_∞^{CAS} is the quantity sought for. Inserting in equation (2) the energy E_X^{CAS} calculated for $X = 3$, 4, and 5, we obtain three equations for three unknowns: A, b, and E_∞^{CAS}, which can be precisely solved.

First we determined a proper value for parameter b. With the energies obtained at the CASSCF level and the basic equation (2), it is easy to set the three-equation system:

$$E_3^{CAS} = E_\infty^{CAS} + 4A\exp\left(-b\sqrt{3}\right),$$
$$E_4^{CAS} = E_\infty^{CAS} + 5A\exp\left(-2b\right), \tag{3}$$
$$E_5^{CAS} = E_\infty^{CAS} + 6A\exp\left(-b\sqrt{5}\right).$$

Table 2. Parameter A and CASSCF total energy (in hartree) at the CBS limit obtained by setting parameter $b = 5.925$, see equation (3) and the text below.

	(a) k_{34}	(b) k_{45}
Parameter A	8.5881973960	8.5870548880
	(a) using A from k_{34}	(b) using A from k_{45}
$E_\infty^{CAS}(X = 3)$	−1519.5339605170	−1519.5339603570
$E_\infty^{CAS}(X = 4)$	−1519.5339605160	−1519.5339604750
$E_\infty^{CAS}(X = 5)$	−1519.5339604870	−1519.5339604750

If we subtract E_4^{CAS} from E_3^{CAS} denoting the result as k_{34}, and then subtract E_5^{CAS} from E_4^{CAS} denoting this result k_{45}, and divide k_{34} on k_{45}, we obtain the equation

$$\frac{k_{34}}{k_{45}} = \frac{4e^{-b\sqrt{3}} - 5e^{-2b}}{5e^{-2b} - 6e^{-b\sqrt{5}}}, \tag{4}$$

from which we can find parameter b by trial and error method. It should be mentioned that in the original work by Karton-Martin [56] the parameter b was optimized on a great number of simple molecules with light atoms. They recommended $b = 9$. Since our dimer is formed of $3d$ transition-metal atoms, we put b as a free parameter. We found that $b = 5.925$ gives better results than $b = 9$. At this point we could determine the value of parameter A through the equation

$$A = \frac{k_{34}}{4e^{-b\sqrt{3}} - 5e^{-2b}} = \frac{k_{45}}{5e^{-2b} - 6e^{-b\sqrt{5}}}. \tag{5}$$

As parameter b was not determined analytically, and k_{34} and k_{45} have different values, it follows from equation (5) that parameter A will have two values. Nevertheless, the differences in the final values of E_∞^{CAS} are negligible, see Table 2.

The CBS limit for the dynamical correlation energy, E_∞^{dc}, was found using the Varandas USTE scheme [48]. The employed equation has the following form:

$$E_X^{dc} = E_\infty^{dc} + \frac{A_3}{(X - 3/8)^3}\left[1 + \frac{1}{(X - 3/8)^2}\left(\frac{a}{A_3} + cA_3^{1/4}\right)\right] \tag{6}$$

where a and c are fixed numerical coefficients and A_3 is a parameter that has to be found. Thus equation (6) has two unknowns, E_∞^{dc} and A_3. They were found using a code, which is based on the least-squares method, and was kindly presented to us by Varandas. The best results were obtained for the basis set pair with the highest XZ, $X = 4$ and 5, which produces two equations:

$$E_4^{cor} = E_\infty^{cor} + \frac{A_3}{(4 + \alpha)^3}\left[1 + \frac{1}{(4 + \alpha)^2}\left(\frac{A_5^0}{A_3} - cA_3^{1/4}\right)\right], \tag{7}$$

$$E_5^{cor} = E_\infty^{cor} + \frac{A_3}{(5 + \alpha)^3}\left[1 + \frac{1}{(5 + \alpha)^2}\left(\frac{A_5^0}{A_3} - cA_3^{1/4}\right)\right]. \tag{8}$$
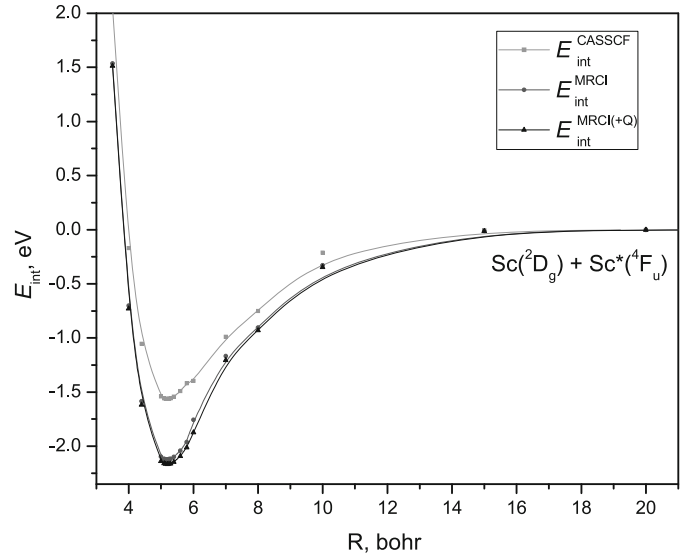

Fig. 1. Potential energy curves for the ground state of Sc_2 at the CASSCF, MRCISD, and MRCISD (+Q) levels calculated with cc-pV5Z basis set.

They were solved by the least-squares method. The obtained values are the following $A_3 = 0.087390$ hartree and $E_\infty^{cor} = -0.040620$ hartree.

The dependence of obtained results on the basis set is presented in Table 3. The CBS limit data are also included. The final results at the valence MRCISD (+Q)/CBS level were obtained as a sum of the CBS estimations of E_∞^{CAS} and E_∞^{dc}. We also calculated at the CBS limit the harmonic part of the ground state potential curve and found all spectroscopic parameters by the Dunham analysis [57].

According to Table 3, the larger is the basis set the stronger is the bonding. The dissociation energy D_e at the CBS limit is equal to 2.183 eV (50.3 kcal/mol). The obtained equilibrium distance R_e at the MRCISD (+Q)/CBS level is equal to $R_e = 5.2$ bohr (2.752 Å). The account of the $3s3p$ correlation effects in our previous study [33] does not change D_e, but reduced R_e on 0.2 bohr. Thus, the corrected value of R_e should be 5.0 bohr (2.65 Å). The harmonic frequency ω_e, at the MRCISD (+Q)/CBS level, is equal to 234.5 cm^{-1}, which is in a very good agreement with the experimental value 239.9 cm^{-1} [58].

The potential energy curves of Sc_2 in the ground state $^5\Sigma_u^-$, calculated at the CASSCF, MRCISD, and MRCISD (+Q) levels with the largest basis set cc-pV5Z, are represented in Figure 1. The last two curves almost coincide (in the hartree scale). This fact and the data in Table 3 for the equilibrium distance indicate that in the case of Sc_2 the size-inconsistency error is small, in contrary to the Mn_2 dimer case [14]. Thus, the MRCISD (+Q) approach can be considered as a quite satisfactory approximation for the study of the Sc_2 dimer.

In Table 4 the scalar relativistic calculations with cc-pV5Z-DK basis set are compared with nonrelativistic MR-CISD (+Q) calculations with cc-pV5Z basis set at the

Table 3. The dependence of the equilibrium distance, R_e (a_0), total energy, E (hartree), dissociation energy, D_e (eV), and the harmonic frequency, ω_e (cm^{-1}), on the basis set cc-pVXZ and the CBS limit for Sc$_2$ in the ground state, $^5\Sigma_u^-$.

Basis set	MRCI				MRCI (+Q)			
	R_e	E	D_e	ω_e	R_e	E	D_e	ω_e
TZ	5.202	−1519.567779	2.073	222.6	5.214	−1519.569566	2.111	223.6
QZ	5.195	−1519.570613	2.107	224.5	5.206	−1519.572522	2.150	224.8
5Z	5.193	−1519.571661	2.122	226.3	5.204	−1519.573631	2.166	229.2
CBS					5.200	−1519.574560	2.183	234.5

Table 4. Comparison of the dissociation energy, D_e, and harmonic frequency, ω_e, for the Sc$_2$ ground state potential curves calculated at the scalar relativistic level with cc-pV5Z-DK basis set and the nonrelativistic MRCISD (+Q) level with the basis set cc-pV5Z; energies are in eV (kcal/mol), frequencies are in cm^{-1}.

Basis set	CASSCF		MRCISD		MRCISD (+Q)	
	D_e	ω_e	D_e	ω_e	D_e	ω_e
5Z	1.563 (36.01)	217.1	2.122 (48.90)	226.3	2.166 (49.91)	229.2
5Z-DK	1.578 (36.37)	223.9	2.127 (49.01)	229.0	2.169 (49.98)	229.1

Table 5. Mulliken population in Sc$_2$ at the equilibrium and dissociation limit distances at different levels of theory.

(a) MRCISD	
R_e:	$4s^{1.22}3d^{1.29}4p^{0.46}$: $4s^{1.22}3d_{z^2}^{0.49}3d_{x^2-y^2}^{0.01}3d_{xz}^{0.39}3d_{yz}^{0.39}3d_{xy}^{0.01}4p_z^{0.22}4p_x^{0.12}4p_y^{0.12}$
$R = 50a_0$:	Sc$\left(4s^23d^1\right)$: $4s^{1.82}3d_{z^2}^{0.01}3d_{x^2-y^2}^{0.00}3d_{xz}^{0.01}3d_{yz}^{0.01}3d_{xy}^{0.98}4p_z^{0.05}4p_x^{0.05}4p_y^{0.05}$
	Sc$\left(4s^13d^14p^1\right)$: $4s^{0.95}3d_{z^2}^{0.02}3d_{x^2-y^2}^{0.99}3d_{xz}^{0.01}3d_{yz}^{0.01}3d_{xy}^{0.00}4p_z^{0.98}4p_x^{0.01}4p_y^{0.01}$

(b) CASSCF	
R_e:	$4s^{1.22}3d^{1.26}4p^{0.47}$: $4s^{1.22}3d_{z^2}^{0.48}3d_{x^2-y^2}^{0.01}3d_{xz}^{0.38}3d_{yz}^{0.38}3d_{xy}^{0.01}4p_z^{0.23}4p_x^{0.12}4p_y^{0.12}$
$R = 50a_0$:	Sc$\left(4s^23d^1\right)$: $4s^{1.82}3d_{z^2}^{0.00}3d_{x^2-y^2}^{0.50}3d_{xz}^{0.00}3d_{yz}^{0.00}3d_{xy}^{0.49}4p_z^{0.06}4p_x^{0.05}4p_y^{0.05}$
	Sc$\left(4s^13d^14p^1\right)$: $4s^{0.96}3d_{z^2}^{0.02}3d_{x^2-y^2}^{0.50}3d_{xz}^{0.01}3d_{yz}^{0.01}3d_{xy}^{0.50}4p_z^{0.98}4p_x^{0.01}4p_y^{0.01}$

same equilibrium distance, R_e, which is not changed at the relativistic level. As follows from Table 4, the difference in the dissociation energy, D_e, in comparison with the value obtained at the nonrelativistic level, is very small; at the CASSCF level it equals 0.36 kcal/mol and at the MR-CISD (+Q) level it is only 0.07 kcal/mol. The change of the harmonic frequency, ω_e, is also small; at the CASSCF level it equals 6.8 cm^{-1} and at the MRCISD (+Q) level it is reduced up to 0.1 cm^{-1}. The small values of the relativistic corrections for the 3d-transition metals can be expected [41,59]. This is the reason why we did not take into account the spin-orbit effects and other relativistic corrections.

3.2 Dissociation limit

The determination of the dissociation limit of the Sc$_2$ ground state potential curve is a rather delicate problem. From the experiment [5] and precise calculations, see discussion in Introduction, it follows that the Sc$_2$ ground state corresponds to the $^5\Sigma_u^-$ term, which can be obtained if one of Sc is created in an excited quartet state. Only in this case the total spin S of Sc$_2$ can be equal 2. But according to Table 1, the quintet term $^5\Sigma_u^-$ can have the two dissociation limits: Sc(^{2}D$_g$) + Sc*(^{4}F$_g$) and Sc(^{2}D$_g$)

+ Sc*(^{4}F$_u$). In both limits Sc$_2$ dissociates on one Sc in the ground state and another in an excited state. In the D$_{2h}$ symmetry restrictions, applied in previous studies [33,34], one cannot distinguish Sc atoms because of the inversion symmetry. For obtaining two Sc in different state we employed the C$_{2v}$ symmetry restrictions. Although, in the wave function, describing the dissociation limit, both scandium atoms should have the same population, see discussion below.

In Table 5 the Mulliken atomic valence orbital populations at the equilibrium, R_e, and dissociation limit, $R = 50$ bohr, distances are represented. From it follows that at the MRCISD (+Q) level, Sc$_2$ dissociates on one Sc in the ground state, Sc ($4s^23d^1$; ^{2}D$_g$), and another in the second excited quartet state, Sc* ($4s^13d^14p^1$; ^{4}F$_u$). The same dissociation limit is obtained at the CASSCF level.

Thus, the Mulliken population indicates that the ground state potential energy curve of Sc$_2$ has the asymmetric Sc(^{2}D$_g$) + Sc*(^{4}F$_u$) dissociation limit. On the other hand, both Sc atoms are identical and each of them can be excited. So, at the dissociation limit the wave function of the dimer must be a linear combination of the wave function, in which the one Sc atom is in the ground state and another Sc atom is in an excited state, and the wave

Table 6. Comparison of the dissociation limit energy of Sc_2 in the ground state and energies of the Sc atom in the ground and excited states calculated with the basis set cc-pV5Z at different levels of theory; energies are in hartree, Δ is in kcal/mol.

	CASSCF	MRCISD	MRCISD+Q
$Sc_2(R = 50a_0)$	−1519.476420	−1519.493675	−1519.494029
$Sc(^2D_g) + Sc^*(^4F_g)$	−1519.465245	−1519.498898	−1519.508093
$Sc(^2D_g) + Sc^{**}(^4F_u)$	−1519.467668	−1519.493072	−1519.494483
$\Delta(^4F_g)^a$	7.01	3.27	8.82
$\Delta(^4F_u)^b$	5.5	0.38	0.28

$^a\Delta(^4F_g) = Sc_2(R = 50a_0) - [Sc(^2D_g) + Sc^*(^4F_g)]$
$^b\Delta(^4F_u) = Sc_2(R = 50a_0) - [Sc(^2D_g) + Sc^{**}(^4F_u)]$

function describing the opposite possibility:

$$\Psi(Sc_2, R \to \infty) = \frac{1}{\sqrt{2}}$$
$$\times [\Psi_0(Sc_a) \Psi_n(Sc_b^*) + \Psi_n(Sc_a^*) \Psi_0(Sc_b)]. \quad (9)$$

Thus, both Sc atoms have an equal population: $4s^{1.5}3d^14p^{0.5}$.

The dissociation on one of the atoms in the second, but not in the first, excited quartet state seems quite unusual. For verifying this result we have compared the dimer energy at $R = 50$ bohr with the sum of atomic energies in different excited quartet states calculated at the same level of theory. As follows from Table 6, the energy of Sc_2 at $R = 50$ bohr corresponds to the sum of energies $Sc(^2D_g) + Sc^*(^4F_u)$. The dissociation level $Sc(^2D_g) + Sc^*(^4F_g)$ is located on 0.0141 hartree (or 8.82 kcal/mol) below, which is much larger than the calculation error. At the CASSCF level we cannot arrive to definite conclusions using the atomic energy calculations.

We would like to note that in our recent study [33] of $^5\Sigma_u^-$ state with the D_{2h} symmetry restriction, the $Sc(^2D_g) + Sc^*(^4F_u)$ dissociation limit was obtained. Nevertheless, it was rejected as a wrong asymptote and the creation of one of Sc in ^4F_g state was postulated. Camacho et al. [34], basing on an almost negligible $4p$ population obtained in their studies, also made erroneous conclusion that at the dissociation limit Sc does not appear in the ^4F_u state. On the one hand, a negligible $4p$ population obtained in Camacho et al. studies [34] indicates that the NEVPT method does not give a reliable Mulliken population. On the other hand, from the population of excited orbitals at the equilibrium distance it may not be done any conclusions about the population at the dissociation limit. The interatomic interactions at the equilibrium distance can populate excited orbitals, although this does not prevent atoms to dissociate in their ground states. Just this takes place in the case of the alkaline-earth dimers [60].

Thus, more detailed analysis performed in the present study demonstrates that the conclusions about the dissociation limit of the Sc_2 ground state potential curve made in references [33,34] were not properly substantiated.

The values of the dissociation energy, D_e, obtained at the CBS limit and corrected on the scalar relativistic effects are presented in Table 7. For obtaining D_e

Table 7. CBS D_e values with relativistic corrections for two dissociation limits; energies are in eV (kcal/mol).

Method	D_e	D_e
	$^2D_g + ^4F_u$	$^2D_g + ^2D_g$
CASSCF	1.58 (36.40)	−0.196 (−4.52)
MRCISD (+Q)	2.186 (50.37)	0.433 (9.98)

at the symmetric dissociation limit $Sc(^2D_g) + Sc(^2D_g)$, the calculated atomic excitation energy $E[Sc^*(^4F_u)] - E[Sc(^2D_g)]$ was subtracted from D_e obtained in the dissociation limit $Sc(^2D_g) + Sc^*(^4F_u)$. At the CASSCF level the negative value of D_e for the symmetric dissociation limit was obtained. This is connected with a lack of precision for calculating the atomic excited states at this level.

3.3 The nature of bonding

According to the Mulliken population and energy calculations, at the dissociation limit one of the Sc atoms is formed in the second excited quartet state (it has the populated $4p$-shell). When atoms are approaching, the atomic orbital population is redistributed between atoms. The Mulliken analysis (even at the C_{2v} symmetry restrictions) gives at the equilibrium distance the same orbital population for both atoms. As follows from Table 5, the MRCISD orbital population on each atom is equal to $4s^{1.22}3d^{1.29}4p^{0.46}$. A part of the $4s$ electron density is transferred to $3d$ orbitals and the $4p$ orbital has as it is at infinity about 0.5 electron.

The main references configurations obtained in our CASSCF calculations are the following:

$$\left|^5\Sigma_u^-\right\rangle = 0.826 \left|4s\sigma^24s\sigma^13d_{z^2}\sigma^13d_{xz}\pi_x^13d_{yz}\pi_y^1\right\rangle$$

$$- 0.237 \left|4s\sigma^24s\sigma^14p_z\sigma^13d_{xz}\pi_x^14p_y\pi_y^1\right\rangle$$

$$- 0.237 \left|4s\sigma^24s\sigma^14p_z\sigma^14p_x\pi_x^13d_{yz}\pi_y^1\right\rangle. \quad (10)$$

In their early study of Sc_2, Walch and Bauschlicher [61] analyzed only the dominant configuration, which does not contain the $4p$ orbitals. They did not consider the participation of the $4p$-orbitals in bonding and stressed the important role of the one-electron $3d\pi$ bonds. But if we

take into account that the mean radius of $3d$ shell is $\langle r_{3d}\rangle = 1.68$ bohr [62], which is much smaller than the equilibrium distance $R_e = 5.2$ bohr, it became evident that the $3d$-overlap integrals are very small and in reality the one-electron $3d$-bonds do not contribute to the bonding. It is also worth-while to mention that the $4s$ shell has a much larger mean radius, $\langle r_{4s}\rangle = 3.96$ bohr [62] and $\langle r_{4s}\rangle/\langle r_{3d}\rangle = 2.36$, meaning that $3d$ electrons are deeply inside the $4s$ electron shell.

The second and third configurations in expansion (10) contain molecular orbitals built of $4p$ atomic orbitals. So, the $4p$ orbitals are involved in the bonding process. The latter also can be concluded from the Mulliken population at the equilibrium distance: $4s^{1.22}3d^{1.29}4p^{0.46}$. This population is favorable for the atomic hybridization [63]. The hybridized orbitals enhance the overlap in the bond region increasing the strength of the bond. The most probable is the creation of three hybrid orbitals on each Sc

$$h_1 = a_1 4s + a_2 4p_z,$$
$$h_2 = b_1 3d_{xz} + b_2 4p_x,$$
$$h_3 = c_1 3d_{yz} + c_2 4p_y. \tag{11}$$

It can be concluded that the dimer is stabilized by the formation of one two-electron $h_1\sigma_g$-bond and two one-electron $h_2\pi_{xu}$- and $h_3\pi_{yu}$-bonds. These hybridized orbitals should make the bonds stronger. Thus, in the Sc_2 dimer there is a covalent chemical bonding in contrast with the Mn_2 dimer [14].

4 Conclusions

The study of the Sc_2 dimer was carried out at the valence MRCISD (+Q)/CBS level. The calculations were performed under the C_{2v} symmetry restrictions. The latter allowed to obtain at the dissociation limit the different Mulliken population on Sc atoms. Namely, it has been demonstrated that the ground state potential curve, $^5\Sigma_u^-$, has the asymmetric dissociation limit, $Sc(^2D_g) + Sc^*(^4F_u)$ with one of the Sc atoms in the second excited quartet state. While in the wave function describing the dissociation limit both scandium atoms have the same population.

The ground state dissociation energy at the valence MRCISD (+Q)/CBS level is equal to 2.186 eV (50.37 kcal/mol) and in respect to the thermodynamically stable dissociation limit with both Sc atoms in their ground states it is equal to 9.98 kcal/mol. The harmonic frequency $\omega_e = 234.5$ cm^{-1} is in an excellent agreement with the experimental value 239.9 cm^{-1} [59].

In all $3d$ transition-metal atoms, the $3d$-shell has a small mean radius and is located deeply inside the $4s$-shell. The unpaired $3d$-electrons densities practically are not overlapped, so the contribution of the one-electron $3d$-bonds should be very small. Usually the atoms with the closed valence $4s$-shell are bound by the weak van der Waals dispersion forces; but the Sc_2 dimer is an exception from this tendency. At the equilibrium distance a strong atom-atom interaction populates the $4p$ atomic orbitals, which remained populated at infinity; it transfers 0.29e on $3d$ orbitals and makes the closed $4s$ shell partly open. This favors the atomic hybridization. The dimer is stabilized by the formation of one two-electron $(4s4p_z)\sigma_g$ bond and two one-electron bonds: $(3d_{xz}4p_x)\pi_{xu}$ and $(3d_{yz}4p_y)\pi_{yu}$. As a result, the Sc_2 dimer has a chemical covalent bonding.

References

1. J.R. Lombardi, B. Davids, Chem. Rev. **102**, 2431 (2002)
2. B.O. Roos, P.R. Taylor, P.E.M. Siegbhan, Chem. Phys. **48**, 157 (1980)
3. C.W. Bauschlicher Jr., Chem. Phys. Lett. **156**, 95 (1989)
4. Y. Ralchenko, A.E. Kramida, J. Reader, *NIST ASD Team*, *NIST Atomic Spectra Database* (version 3.1.5), (2008) [Online]. Available: http://physics.nist.gov/asd3, National Institute of Standards and Technology (Gaithersburg, MD, 2009)
5. L.B. Knight, J.R. Van Zee, W. Weltner, Chem. Phys. Lett. **94**, 296 (1983)
6. J. Harris, R.O. Jones, J. Chem. Phys. **70**, 830 (1979)
7. I. Pápai, M. Castro, Chem. Phys. Lett. **267**, 551 (1997)
8. C.J. Barden, J.C. Rienstra-Kiracofe, H.F. Schaefer III, J. Chem. Phys. **113**, 690 (2000)
9. G.L. Gutsev, P. Jena, B.K. Rao, S.N. Khanna, J. Chem. Phys. **114**, 10738 (2001)
10. M. Valiev, E.J. Bylaska, J.H. Weare, J. Chem. Phys. **119**, 5955 (2003)
11. G.L. Gutsev, C.W. Bauschlicher Jr., J. Phys. Chem. A **107**, 4755 (2003)
12. F. Furche, J.P. Perdew, J. Chem. Phys. **124**, 044103 (2006)
13. Y. Zhao, D.G. Truhlar, J. Chem. Phys. **124**, 224105 (2006)
14. D. Tzeli, U. Miranda, I.G. Kaplan, A. Mavridis, J. Chem. Phys. **129**, 154310 (2008)
15. R.J. Buenker, S.D. Peyerimhoff, Theor. Chim. Acta **35**, 33 (1974)
16. P.E.M. Siegbahn, Int. J. Quantum Chem. **18**, 1229 (1980)
17. H. Lischka, R. Shepard, F.B. Brown, I. Shavitt, Int. J. Quantum Chem. **15**, 91 (1981)
18. H.-J. Werner, P.J. Knowles, J. Chem. Phys. **89**, 5803 (1988)
19. P.J. Knowles, H.-J. Werner, Chem. Phys. Lett. **145**, 514 (1988)
20. S.R. Langhoff, E.R. Davidson, Int. J. Quantum Chem. **8**, 61 (1974)

21. E.R. Davidson, D.W. Silver, Chem. Phys. Lett. **52**, 403 (1977)
22. R.J. Gdanitz, R. Ahlrichs, Chem. Phys. Lett. **143**, 413 (1988)
23. H.-J. Werner, P.J. Knowles, Theor. Chim. Acta **78**, 175 (1990)
24. H. Åkeby, L.G.M. Peterson, P.E.M. Siegbahn, J. Chem. Phys. **97**, 1850 (1992)
25. Y. Suzuki, S. Asai, K. Kobayashi, T. Noro, F. Sasaki, H. Tatewaki, Chem. Phys. Lett. **268**, 213 (1997)
26. J.L. Matxain, E. Rezabal, X. Lopez, J.M. Ugalde, L. Gagliardi, J. Chem. Phys. **128**, 194315 (2008)
27. H. Åkeby, L.G.M. Peterson, J. Mol. Spectrosc. **159**, 17 (1993)
28. W.M.C. Foulkes, L. Mitas, R.J. Needs, G. Rajagopal, Rev. Mod. Phys. **73**, 33 (2001)
29. A.A. Buchachenko, G. Chalasinski, M. Szszesnyak, J. Chem. Phys. **132**, 024312 (2010)
30. K. Nakano, J. Chem. Phys. **99**, 7983 (1993)
31. J.L. Matxain, E. Rezabal, X. Lopez, J.M. Ugalde, L. Gagliardi, J. Chem. Phys. **132**, 139901 (2010)
32. C. Camacho, H.A. Witek, S. Yamamoto, J. Comput. Chem. **30**, 468 (2009)
33. A. Kalemos, I.G. Kaplan, A. Mavridis, J. Chem. Phys. **132**, 024309 (2010)
34. C. Camacho, R. Cimiraglia, H.A. Witek, J. Chem. Phys. **132**, 244306 (2010)
35. C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, J.-P. Malrieu, J. Chem. Phys. **114**, 10252 (2001)
36. C. Angeli, M. Pastore, R. Cimiraglia, Theor. Chem. Acc. **117**, 743 (2007)
37. H.-J. Werner, P.J. Knowles, J. Chem. Phys. **82**, 5053 (1985)
38. P.J. Knowles, H.-J. Werner, Chem. Phys. Lett. **115**, 259 (1985)
39. A. Sorkin, M.A. Iron, D.G. Truhlar, J. Chem. Theory Comput. **4**, 307 (2008)
40. MOLPRO 2009.1, *A package of ab initio programs*, edited by H.-J. Werner, P.J. Knowles, R. Lindh, F.R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T.B. Adler, R.D. Amos, A. Bernhardsson, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, E. Goll, C. Hampel, G. Hetzer, T. Hrenar, G. Knizia, C. Köppl, Y. Liu, A.W. Lloyd, R.A. Mata, A.J. May, S.J. McNicholas, W. Meyer, M.E. Mura, A. Nicklaß, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, U. Schumann, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, A. Wolf
41. N.B. Balabanov, K.A. Peterson, J. Chem. Phys. **123**, 064107 (2005)
42. M. Douglas, N.M. Kroll, Ann. Phys. (NY) **82**, 89 (1974)
43. G. Jansen, B.A. Hess, Phys. Rev. A **39**, 6016 (1989)
44. T.H. Dunning Jr., J. Chem. Phys. **90**, 1007 (1989)
45. D. Feller, J. Chem. Phys. **96**, 6104 (1992)
46. S.S. Xantheas, T.H. Dunning Jr., J. Phys. Chem. **97**, 18 (1993)
47. D. Feller, J.A. Sordo, J. Chem. Phys. **113**, 485 (2000)
48. A.J.C. Varandas, J. Chem. Phys. **126**, 244105 (2007)
49. D.G. Truhlar, Chem. Phys. Lett. **294**, 45 (1998)
50. A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A.K. Wilson, Chem. Phys. Lett. **286**, 243 (1998)
51. F.R. Brown, D.G. Truhlar, Chem. Phys. Lett. **117**, 307 (1985)
52. V. McKoy, O. Sinanoglu, J. Chem. Phys. **41**, 2689 (1964)
53. C. Hollister, O. Sinanoglu, J. Am. Chem. Soc. **88**, 13 (1966)
54. O. Sinanoglu, K.A. Brueckner, in *Three approaches to electron correlation in atoms* (Yale University Press, New Haven, 1970), Chap. 5
55. A.D. Becke, J. Chem. Phys. **119**, 2972 (2003)
56. A. Karton, J.M.L. Martin, Theor. Chem. Acc. **115**, 330 (2006)
57. J.L. Dunham, Phys. Rev. **41**, 721 (1932)
58. M. Moskovits, D.P. Di Lella, W. Limm, J. Chem. Phys. **80**, 626 (1984)
59. N.E. Schultz, Y. Zhao, D.G. Truhlar, J. Comput. Chem. **29**, 185 (2008)
60. I.G. Kaplan, S. Roszak, J. Leszczinski, J. Chem. Phys. **113**, 6245 (2000)
61. S.P. Walch, C.W. Bauschlicher Jr., J. Chem. Phys. **79**, 3590 (1983)
62. C.F. Bunge, J.A. Barrientos, A. Bunge, At. Data Nucl. Data Tables **53**, 113 (1993)
63. R. McWeeny, *Coulson's Valence*, 3th edn. (Oxford University Press, Oxford, 1979)