Electronic structure and chemical bonding of 3d-metal dimers ScX, X=Sc–Zn

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The electronic and geometrical structures of the ground and excited states of the homonuclear Sc2, mixed ScTi, ScV, ScCr, ScMn, ScFe, ScCo, ScNi, ScCu, and ScZn 3d-metal dimers and their anions have been calculated using the density functional theory with generalized gradient approximation for the exchange-correlation potential. The ground states of the neutral dimers are found to be 3Σu− (Sc2), 6Σ+ (ScTi), 7Σ+ (ScV), 4Σ+ (ScCr), 3Σ+ (ScMn), 2Δ(ScFe), 1Σ+ (ScCo), 2Σ+ (ScNi), 3Δ(ScCu), and 4Σ+ (ScZn). A natural bond analysis reveals an antiferromagnetic spin coupling in the ground states of ScCr, ScMn, and ScFe. This is due to the electron transfer from Sc to the opposite atom and specific bond formations. While each dimer has a unique chemical bonding pattern, most curious is the localization of two 4s electrons at both atomic sites in the ground 5Σu− state of Sc2, which leads to formation of two lone pairs and the bonding scheme: (3d + 3d)½(4s + 4s)½. No appreciable sd hybridization is found for the ground states of the ScX dimers except ScNi. Even though the electron affinities of the ScX dimers are relatively low and do not exceed 1 eV, each ScX− (except ScCo−) possesses at least two states stable towards detachment of an extra electron. © 2001 American Institute of Physics. [DOI: 10.1063/1.1373693]

I. INTRODUCTION

Elemental (also named as monoatomic or homonuclear) 3d-metal dimers have received a considerable attention in theoretical and experimental studies.1,2 Most recent theoretical papers3–6 have addressed the applicability of a number of contemporary density-functional theory (DFT) and hybrid DFT methods by means of comparison between computed and experimental properties of the dimers from Sc2 to Cu2. It has been shown3,4 that the results obtained with the use of a generalized gradient approximation for the exchange-correlation functional that consists of Becke’s exchange5 and Perdew–Wang6 correlation (referred to as BPW91) are, generally, in better agreement with the experiment than those obtained with other DFT or hybrid DFT methods.

The ground-state spin multiplicities do change irregularly along the series of 3d dimers from Sc2 to Cu2, but no reasonable explanation for such a behavior as well as trends in chemical bonding of the dimers seem to have been suggested in the literature. A common practice is to relate7 properties of the dimers with sd-transfer energies \( \Delta_{sd} = E(4s^13d^{n-1}) - E(4s^23d^{n-2}) \) of the constituent 3d atoms. However, Ti2, V2, and Ni2 have the same ground-state spin multiplicity of three while their \( \Delta_{sd} \)’s are very different (0.81, 0.25, and −0.03 eV, respectively).8 A similar disparity is observed for Sc2 and Co2, which have quintet ground states.

Formal D_{sh} symmetry of nuclei in homonuclear dimers could not be the symmetry of electronic states if the latter are antiferromagnetic, i.e., when local magnetic moments at the nuclei have opposite signs. Therefore, it seems to be reason-

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pable for a fair reproduction of experimental data such as spectroscopic parameters of 3d-metal dimers,\textsuperscript{3,4} 3d-metal monoxides,\textsuperscript{15} and dioxides,\textsuperscript{16} as well as electron affinities of 3d-metal monoxides and dioxides,\textsuperscript{5,16} FeO\textsubscript{3}, FeO\textsubscript{4},\textsuperscript{17,18} MnO\textsubscript{2}, MnO\textsubscript{2},\textsuperscript{19,20} and pure metal clusters Fe\textsubscript{2} and Fe\textsubscript{3}.\textsuperscript{9} In addition, we have performed computations of Sc\textsubscript{2}, since this dimer opens the ScX series and a number of experimental\textsuperscript{21–27} and theoretical\textsuperscript{28–40} data are available for comparison. Besides, the Sc\textsubscript{2} anion has been calculated\textsuperscript{41} by a configuration interaction method with singles and doubles.

In order to get an insight into the nature of chemical bonding in homonuclear and mixed d-metal dimers, we have applied a natural bond orbital (NBO) analysis.\textsuperscript{42} Our results obtained for the ScX series are believed to be helpful in understanding general trends in formation of mixed and homonuclear d-metal dimers as well as the nature of their chemical bonding.

II. COMPUTATIONAL DETAILS

Our computations are performed using a usual approach when linear combinations of atomic orbitals centered at dimer atomic sites constitute Kohn–Sham one-electron (or molecular) orbitals. For the atomic orbitals we have used a [15s11p4d1f/10s7p4d1f] basis due to Wachters\textsuperscript{43} and Hay\textsuperscript{44} referred as to 6-311+G* in the GAUSSIAN 94 software.\textsuperscript{45} Optimizations were performed for each permitted spin multplicity for both neutral and anionic 3d-metal dimers until further increasing the spin multiplicity would result in a dimer state whose total energy is above the energy of dissociation to the corresponding ground-state atoms. In each case, the geometry optimization was carried out by examining the gradient forces at atomic sites until the maximum force was below 3×10^{-4}.

Kohn and Sham\textsuperscript{46} have formulated the DF theory for the ground states. This theory has been extended later\textsuperscript{47–49} to excited states comprising the lowest energy states in each particular symmetry (spatial and spin) channel. This is important for justification of the DFT application in the present case because transition metal dimers may possess a number of closely spaced states of various orbital spin and angular momenta, thus making determination of the ground states to be a nontrivial problem.

The operator of the spin momentum is not defined in a conventional density functional theory applied here, where only the densities \( \rho^\alpha \) and \( \rho^\beta \) of electrons with \( \alpha \) and \( \beta \) spins are available. However, having assumed that the total electron density \( \rho(\mathbf{r}) = \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}) \) corresponds to some wave function \( \Psi \) satisfying conditions \( \hat{S}^z\Psi = (S + 1)/2\Psi \) and \( \hat{S}_+\Psi = S\Psi \), one can relate the spin multiplicity \( M = 2S + 1 \) and the number of electrons in the spin-up \( (n_\alpha) \) and spin-down \( (n_\beta) \) representations as

\[
2S + 1 = \int [\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})]d\mathbf{r} = n_\alpha - n_\beta + 1.
\]

Spatial symmetry of an electronic state obtained from optimizations with a fixed number of ‘‘spin-up’’ \( (\alpha, \text{majority}) \) and ‘‘spin-down’’ \( (\beta, \text{minority}) \) electrons is defined by a direct product of symmetries of partially occupied Kohn–Sham molecular orbitals (MOs) as in conventional Hartree–Fock theory.

The orbital and spin angular momenta each have a magnetic moment associated with them,\textsuperscript{50} and the total magnetic moment may be defined as \( \mu = -\mu_B(\hat{L} + 2\hat{S}) \),\textsuperscript{50} where \( \mu_B \) is the Bohr magneton. Within the Heisenberg model, one omits the total angular momentum operator \( \hat{L} \) and defines \( \mu = g\mu_B\hat{S} \), where \( g \) is close to the ‘‘spin-only’’ value of 2.

In order to determine spin densities at atoms which are responsible for the local magnetic moments, one can use conventional Mulliken population analysis.\textsuperscript{51} However, a recently developed approach called a NBO analysis provides a more convenient scheme for partitioning the electronic density of a system into atomic contributions by constructing localized (Lewis) bonding MOs. Inspection of such bonding MOs would allow one to get an insight into the nature of chemical bonding in a transition-metal compound. Advantages of the NBO analysis are following: (i) it is less sensitive than the Mulliken analysis to basis sets used, (ii) it never results in negative charge values in neutral systems, (iii) it describes more reasonably atomic configurations and bonding in ionic compounds.\textsuperscript{52}

The NBO analysis is based on the use of special orthogonal sets of orbitals constructed by the method of an ‘‘occupancy-weighted symmetric orthogonilization’’ from an initial \( \{ \phi_i \} \) MOs. This orthogonalization differs from a conventional symmetric Löwdin’s procedure\textsuperscript{54} which searches for such a set of orbitals \( \{ \phi_i^\prime \} \) that

\[
\sum_i \|\phi_i^\prime - \phi_i\|^2 = \min
\]

by using a weighted search for localized orbitals

\[
\sum_i w_i\|\phi_i^\prime - \phi_i\|^2 = \min,
\]

where the weighting factor \( w_i \) is the occupancy of the orbital \( \phi_i \).

\[
w_i = \int \int \phi_i^\prime(1)\Gamma(1|1^\prime)\phi_i(1^\prime)d\tau_1d\tau_1^\prime
\]

and \( \Gamma(1|1^\prime) \) is the one-particle density operator

\[
\Gamma(1|1^\prime) = N\int \Psi^*(1,2,...,N)\Psi^*(1^\prime,2,...,N)d\tau_2\cdots d\tau_N.
\]

Since no explicit wavefunction corresponding to optimized DFT electronic densities is available, a reasonable choice appears to be the use of Slater determinants built on Kohn–Sham molecular orbitals in Eq. (5) in the same way as in conventional unrestricted Hartree–Fock approximation.

The bond rupture energy of a ScX dimer is computed as the difference in the ground-state total energies of the dimer and its constituent atoms:

\[
D_{b}(\text{ScX}) = E_{\text{tot}}(\text{Sc}) + E_{\text{tot}}(\text{X}) - E_{\text{tot}}(\text{ScX})
\]

neglecting the zero-point vibrational energy of the ScX dimer, which is smaller than 0.05 eV.
TABLE I. Composition of bonding orbitals (BO) and lone pairs (LP) in the ground states of Sc² and Sc²⁻.

<table>
<thead>
<tr>
<th></th>
<th>α spin Sc(4s⁰⁹d⁰³p⁰⁴⁻⁰⁴)</th>
<th>β spin Sc(4s⁰⁹d⁰³p⁰¹⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sc₁</td>
<td>Sc₂</td>
</tr>
<tr>
<td>Sc²⁻</td>
<td>ε₁</td>
<td>4s % 3d%</td>
</tr>
<tr>
<td>LP</td>
<td>-4.77</td>
<td>100 0 0</td>
</tr>
<tr>
<td>BO</td>
<td>-4.89</td>
<td>0 48 0</td>
</tr>
<tr>
<td></td>
<td>+0.50</td>
<td>0 47 0</td>
</tr>
<tr>
<td></td>
<td>+0.75</td>
<td>0 49.5 0</td>
</tr>
<tr>
<td></td>
<td>+0.88</td>
<td>0 49 0</td>
</tr>
</tbody>
</table>

III. RESULTS AND DISCUSSIONS

A. Sc₂ dimer

An ESR study²⁶ has predicted the ground state of Sc₂ to be ⁵Σ⁻ while resonance Raman spectra of Sc₂ trapped in argon matrices have shown³⁷ its vibrational constant to be 239.9 cm⁻¹. No experimental data are available for the equilibrium bond length of the dimer. Theoretical predictions of the Sc₂ ground-state symmetry have broadly varied from ¹Σ⁺₂ to triplet and quintet states with various spatial symmetries.²⁸–⁴⁰ At present, there seems to be a consensus with respect to the ground state symmetry of Sc₂: ⁵Σ⁻. However, different methods provide different equilibrium bond lengths of the dimer in this state. For example, a CASSCF calculation⁴⁰ performed using a basis of Slater-type atomic functions (double-zeta + 4p, 4d, and two 4f) has resulted in Rₑ = 2.70 Å, while another CASSCF calculation¹² carried out with the use of a conventional Gaussian-type basis of a rather good quality—(14s11p6d3f) /[8s7p4d2f]—has arrived at a value of 2.79 Å. The computed vibrational frequencies differ by 48 cm⁻¹. DFT methods provide more consistent values of Rₑ within a shorter range, 2.63 ± 0.02 Å.³⁴,³⁹

Because calculations performed by various methods lead to different ground state electronic configurations of Sc₂, it is interesting to consider the states of Sc₂ of several spin multiplicities at the BPW91 level of theory. According to our computations, at least three states of Sc₂, namely, ¹Σ⁺ (Rₑ = 2.27 Å, ωₑ = 287 cm⁻¹, Tₑ = 0.35 eV), ³Σ⁻ (Rₑ = 2.61 Å, ωₑ = 256 cm⁻¹, Tₑ = 0.18 eV), and ⁵Σ⁻ (Rₑ = 2.50 Å, ωₑ = 240 cm⁻¹, Tₑ = 0.49 eV) are thermodynamically stable, and the spectroscopic parameters of the two latter states are rather close to those of the ground ⁵Σ⁻ state (Rₑ = 2.63 Å, ωₑ = 241 cm⁻¹, Tₑ = 0.0 eV). Thus, it is not surprising that less accurate methods used in earlier studies found any of the earlier states.

Pápai and Castro³⁹ have obtained larger total energy separations between the ¹Σ⁺, ³Σ⁻, and ⁵Σ⁻ states using the BP86 approach which is similar to the BPW91. This is probably due to the fact that they have used a smaller (63321/5211/41) basis set. Akeby and Petterson³⁷ have obtained many more closely spaced states of Sc₂ for singlet, triplet, and quintet spin multiplicities at a CASSCF level; however, their calculations failed to predict ⁵Σ⁻ to be the ground state of Sc₂, and the calculated Rₑ of 2.51 Å in this state appears to be too short.

Our early calculations³⁴ performed by an Xα method with a numerical basis have favored ¹Σ⁺ as the ground state with Rₑ = 2.21 Å and a triple bond. The present NBO analysis confirm Sc₂ to possess a classic triple bond in its ¹Σ⁺ state, and the effective electronic configurations of Sc atoms in this state are 4s⁰⁹³d⁰³p⁰⁷. Now a question arises: What kind of bonding is realized in the Sc₂ dimer in its ground ⁵Σ⁻ state? Let us examine the results of the NBO analysis presented in Table I. First, note that the MOs have no appreciable sd mixing. The MOs are almost pure sd ones and may contain a small admixture of sp and higher atomic orbitals. One could also see from Fig. 1 a rather unusual type of chemical bonding in the ground state of Sc₂: There are two lone pairs, each occupied by one electron, which are entirely composed of 4s atomic orbitals localized at Sc sites. That is, instead of an energetically unfavorable promotion of two 4s electrons which would approximately cost 2Δₑ(Sc) = 2.86 eV, the two 4s electrons prefer to form lone pairs at the corresponding two atom sites. There are one 4s + 4s and three 3d + 3d single bonding orbitals. Since a (4s + 4s) β bonding orbital can accommodate only one elec-
spin multiplicities are six and seven, respectively and ScV continue to favor high-spin ground states whose corresponding atomic computations performed at the same thermodynamic stability of this state.

Figure 1 presents bonding patterns in all four low-lying states of Sc$_2$. Except the ‘classically’ bonded $1\Sigma_g^+$ state, all other three states contain 4s lone pairs. To indicate a promotion of a single 4s electron from both Sc sites, we use an $\Sigma_e$ designation at each site. Atomic energy levels (eigenvalues to the Kohn–Sham equations) are taken from the corresponding atomic computations performed at the same BPW91/6-311+G$^*$ level. Formally, all three $3\Sigma_u^-$, $5\Sigma_u^-$, and $7\Delta_g$ states possess four bonding orbitals, but the topmost $7\Delta_g$ state has no 4s+4s bonding orbital. This state is higher in total energy than the $1\Sigma_g^+$ state by 0.15 eV only, even though the latter has six bonding orbitals. Thus, the number and type of bonding orbitals in a particular electronic state of a 3d dimer does not seem to be related directly with the thermodynamic stability of this state.

**B. Mixed ScX dimers**

The results of our computations for the ScX and ScX$^-$ series are presented in Tables II and III. Following Sc$_2$, ScTi and ScV continue to favor high-spin ground states whose spin multiplicities are six and seven, respectively (see Table II). However, the low spin multiplicity states of ScTi and ScV, which could be considered as following the $1\Sigma_g^+$ state of Sc$_2$, are rather close in total energy to their ground high spin multiplicity states. ScCr prefers to form a low spin multiplicity ground state $3\Sigma^+$ which is below its high-spin $8\Sigma^*$ state by 0.23 eV. ScMn decreases its ground-state spin multiplicity with respect to ScCr by one (see Table II); ScFe and ScCo continue the trend of decreasing ground-state spin multiplicities. Beginning with ScNi, the spin multiplicity increases to four at ScZn. The anion series shows a similar behavior.

Effective electronic configurations of Sc in the ground-state ScX dimers are rather different. They are close to 4s$^1$3d$^{1.5}$ in Sc$_2$ and 4s$^1$3d$^2$ in ScTi, ScV, and ScZn, while they are closer to 4s$^3$3d$^{1.5}$ in ScMn–ScCu. Therefore, one needs additional data in order to understand the peculiarities of the internal structure of various states. The number and content of bonding orbitals and lone pairs appears to be rather helpful in understanding the chemical bonding in the ScX dimers.

First, let us get an insight in the structure of high and low spin multiplicity states of ScTi, ScV, and ScCr. Figure 2 presents the bonding scheme for the two lowest-energy states of ScTi. In both cases, one can see a promotion of 4s electrons into the 3d* manifolds and formation of a doubly occupied 4s+4s orbital. Flipping-up the spins of two electrons occupying the $(3d+3d)_g$ MOs, which is required formally to obtain the 6\Sigma$^+$ state from the $\Sigma^+$ state, does not change the number of bonding orbitals but brings a 0.16 eV gain in total energy.

Compared to ScTi, ScV shows a rather different bonding behavior in both high and low spin multiplicity states (see Fig. 3). Its ground $7\Sigma^+$ state has a 4s-lone pair at Sc, a 3d-lone pair at V, a 4s+4s bond and two 3d+3d bonds. Note that we preserve the term ‘lone pair’ for a molecular orbital consisting of a localized atomic orbital which is occupied by one electron and the term ‘bond’ for a molecular orbital occupied by two electrons with coupled spins, in order to be consistent with the terminology developed for sp compounds. In this state, a 4s electron of V is promoted into a 3d$^*$ orbital. The $3\Delta$ state, which is higher in total energy by 0.1 eV, has a 3d-lone pair at V, while a 4s electron of Sc is promoted into an excited 3d$^*$ orbital of Sc. Formation of an additional 3d+3d bonding orbital appears to be not sufficient for compensating the promotional energy at the Sc site.

The high-spin $8\Pi$ state of ScCr possesses two lone pairs (4s and 3d) at the Sc site and five 3d lone pairs at the Cr site (see Fig. 4). It has a 4s+4s bond and no 3d+3d bonds. The ground $4\Sigma^+$ state has an interesting bonding scheme which is different from those found previously in the ground states of Sc$_2$, ScTi, and ScV. A 4s electron of Sc is partially promoted to an excited 3d$^*$ orbital at Sc and partially transferred into 3d$^*$ manifold of Cr in order to form a (3d+3d)$_g$ bonding orbital. Thus, the formal effective configurations of Sc and Cr are close to 4s$^1$3d$^{1.75}$ and 4s$^1$3d$^{2.25}$, respectively. There is a double lone 3d pair at Cr, two 4s+4s bonding orbitals, and five 3d+3d bonding orbitals. Note that the formation of five 3d+3d bonding orbitals compensates the 4s promotion at the Sc site and the 3d promotion at the Cr site and provides a 0.23 eV gain in total energy with respect to the promotionless $8\Pi$ state, which has only one doubly occupied (4s+4s) bonding orbital. As shown in Fig. 5, the ground states of ScMn and ScFe have rather similar chemical bonding patterns. In both of these states, there are 3d-lone pairs at Mn and Fe sites, and the lowering in the the spin multiplicity when going from ScCr...
TABLE II. Equilibrium bond lengths ($R_j$, in Å), harmonic vibrational frequencies ($\omega_j$, in cm$^{-1}$), bond dissociation energies ($D_{0j}$, in eV), dipole moments (DM, in Debye), magnetic moments on atoms ($\mu_M$, in Bohr magneton), effective atomic electronic configurations, and number of bonding orbitals in $\alpha$ and $\beta$ spin representations (NBO) of the neutral 3$d$-metal dimers ScX, X=Sc, Ti, V, Cr, and their anions. $\Delta E_{\text{tot}}$ (in eV) denote relative positions of the corresponding dimer states.

<table>
<thead>
<tr>
<th></th>
<th>Sc$^2$</th>
<th>ScTi</th>
<th>ScV</th>
<th>ScCr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5\Sigma^-$</td>
<td>$\Sigma^+$</td>
<td>$6\Sigma^+$</td>
<td>$\Delta$</td>
<td>$7\Sigma^+$</td>
</tr>
<tr>
<td>$R_j$</td>
<td>2.630</td>
<td>2.065</td>
<td>2.290</td>
<td>2.001</td>
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<tr>
<td>$\omega_j$</td>
<td>241</td>
<td>382</td>
<td>272</td>
<td>342</td>
</tr>
<tr>
<td>DM</td>
<td>0.0</td>
<td>1.07</td>
<td>0.57</td>
<td>1.54</td>
</tr>
<tr>
<td>$\mu_{Sc}$</td>
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<td>0.30</td>
<td>1.50</td>
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</tr>
<tr>
<td>$\mu_X$</td>
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<td>0.70</td>
<td>3.50</td>
<td>2.13</td>
</tr>
<tr>
<td>NBO</td>
<td>3(\alpha 1(\beta)</td>
<td>4(\alpha 3(\beta)</td>
<td>6(\alpha 1(\beta)</td>
<td>4(\alpha 3(\beta)</td>
</tr>
<tr>
<td>$\Delta E_{\text{tot}}$</td>
<td>0.0</td>
<td>+0.16</td>
<td>0.0</td>
<td>+0.10</td>
</tr>
</tbody>
</table>

$\alpha$ Experimental $\omega_j = 239.9$ (see Ref. 27).

TABLE III. Equilibrium bond lengths ($R_j$, in Å), harmonic vibrational frequencies ($\omega_j$, in cm$^{-1}$), bond rupture energies ($D_{0j}$, in eV), dipole moments (DM, in Debye), magnetic moments on atoms ($\mu_M$, in Bohr magneton), effective atomic electronic configurations, and number of bonding orbitals (NBO) of the neutral 3$d$-metal dimers ScX, X=Mn–Zn, along with their anions.

<table>
<thead>
<tr>
<th></th>
<th>ScTo</th>
<th>ScFe</th>
<th>ScCo</th>
<th>ScNi$^a$</th>
<th>ScCu</th>
<th>ScZn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3\Sigma^+$</td>
<td>$9\Sigma^+$</td>
<td>$2\Delta$</td>
<td>$1\Sigma^+$</td>
<td>$2\Delta$</td>
<td>$3\Delta$</td>
<td>$4\Sigma^+$</td>
</tr>
<tr>
<td>$R_j$</td>
<td>1.935</td>
<td>2.859</td>
<td>1.849</td>
<td>1.799</td>
<td>2.047</td>
<td>2.497</td>
</tr>
<tr>
<td>$\omega_j$</td>
<td>382</td>
<td>186</td>
<td>474</td>
<td>513</td>
<td>349</td>
<td>215</td>
</tr>
<tr>
<td>DM</td>
<td>1.74</td>
<td>1.16</td>
<td>2.33</td>
<td>2.65</td>
<td>1.82</td>
<td>1.96</td>
</tr>
<tr>
<td>$\mu_{Sc}$</td>
<td>-1.21</td>
<td>2.35</td>
<td>-0.68</td>
<td>0.0</td>
<td>0.84</td>
<td>1.91</td>
</tr>
<tr>
<td>$\mu_X$</td>
<td>3.21</td>
<td>5.65</td>
<td>1.68</td>
<td>0.0</td>
<td>0.16</td>
<td>0.09</td>
</tr>
<tr>
<td>NBO</td>
<td>4(\alpha 4(\beta)</td>
<td>0(\alpha 1(\beta)</td>
<td>4(\alpha 5(\beta)</td>
<td>4(\alpha 4(\beta)</td>
<td>3(\alpha 4(\beta)</td>
<td>1(\alpha 1(\beta)</td>
</tr>
</tbody>
</table>

$\alpha$ The ground state vibrational interval $\Delta G_{10}$ is 334.5±1 cm$^{-1}$ (see Ref. 14).
$\beta$ The ground state is the $3\Sigma^+$ state and $9\Sigma^+$ is -1.45 eV above.
to ScFe is due to increasing the number of \((3d + 3d)_\beta\) bonding orbitals.

According to Tables II and III, ScCr, ScMn, and ScFe have antiferromagnetically coupled magnetic moments at nuclear sites. As one could see from Figs. 4 and 5, there is no local magnetic moment related to a lone pair at the Sc sites which is antiferromagnetically coupled to a lone pair at the opposite site. That is, this antiferromagnetic coupling is entirely different from couplings in typical antiferromagnetic 3d-metal dimers such as CrMn. Antiferromagnetic couplings in ScCr, ScMn, and ScFe is due to a partial promotion of a \(4s\) electron into a 3d* vacant AOs of Cr, Mn, and Fe.

Electron promotions in ScCo are similar to those in ScCr, ScMn, and ScFe. The ground \(1\Sigma^+\) state of ScCo has one \(4s + 4s\) bond, three \(3d + 3d\) bonds, and two double lone pairs at Co. This dimer is thermodynamically most stable in the ScX series (see Table IV). ScNi has the \(3\Delta\) ground state, there is a \(4s\)-lone pair at Sc and five \(3d\)-lone pairs at Co, four of which are coupled to each other. This state has a similar bonding pattern as the ground state of ScCo, except a more noticeable mixture of \(4s\) and \(3d\) orbitals in the bonding MOs.

The bonding pattern in the ground \(3\Delta\) state of ScCu is similar to that in the \(8\Pi\) state of ScCr. The main difference is the electron transfer \(4s_{Sc} \rightarrow 4s^*_{Cu}\), which is feasible because the latter atomic orbital (AO) is not populated in the ground-state Cu atom. It is shown in Fig. 7 as a half-of-electron transfer from the Sc site to the Cu site. Two lone pairs at Sc are formed in the \(\alpha\) spin representation and ten \(3d\) electrons of Cu form five coupled \(3d\)-lone pairs, whose energies are shifted downward with respect to one-electron energy levels of the Cu atom. There is one \(4s + 4s\) bond with larger contributions from Cu \(4s\) AOs. ScZn possesses formally one bonding orbital which can be represented as \(0.12\times4s_{Sc} + 0.88\times4s_{Zn}\). As is seen from Table IV, this bonding is very weak and the dissociation channel ScZn \(\rightarrow \text{Sc} + \text{Zn}\) has an energy of 0.16 eV (3.7 kcal/mol) only. Rather, ScZn has to be considered as a van der Waals system.

Attachment of an extra electron increases the population of \(4s\) AOs (see Tables II and III), which exceeds the population in reactive states \(4s^13d^{n-1}\). Since \(4s\) states can only form bonding \(4s + 4s\) and antibonding \(4s - 4s\) molecular orbitals, it might be anticipated that an antibonding \(4s - 4s\) MO is filled by an extra electron in the anion states. However, the NBO analysis shows that \(4s\) electrons prefer to form lone pairs at both sites. Thus, the gain in total energy is due mainly to lacking promotions of \(4s\) electrons into \(3d^*\) manifolds. A special case is presented by ScZn\(^-\), where \(4s\) electrons at both sites are partially promoted into \(4p\) AOs. In the lowest \(3\Sigma^+\) state, there is two bonding orbitals: a \((4s + 4s)\) one as in the neutral ground state plus \((4p + 4p)\) one.

FIG. 2. Bonding patterns in the high and low spin multiplicity states of ScTi.

FIG. 3. Bonding patterns in two states of ScV.
Despite the relatively low binding energies of an extra electrons, all the ScX\(^-\) anions except ScCo\(^-\) possess at least two states which are stable towards detachment of an extra electron. The relative positions of different spin-multiplicity states in the ScX and ScX\(^-\) series are presented in Fig. 8. There are plenty of closely spaced states in the beginning of the series, while electron-rich ScFe, ScCo, ScNi, and especially ScCu possess states well separated in total energy.

**Table IV.** Bond rupture energies (\(D_0\)), atomic inter-configurational splitting energies \(\Delta_{sd} = E(4s^13d^{n-1}) - E(4s^23d^{n-2})\), adiabatic electron affinities (\(A_{ad}\)), and vertical detachment energies (\(E_{vd}\)) for the ground-state ScX dimers, along with experimental atomic inter-configurational splitting energies \(\Delta_{sd} = E(4s^13d^{n-1}) - E(4s^23d^{n-2})\), as well as the experimental electron affinities \(A\) and first ionization potentials (IP) of the constituent ground-state atoms. All values are in electron volts.

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>ScTi</th>
<th>ScV</th>
<th>ScCr</th>
<th>ScMn</th>
<th>ScFe</th>
<th>ScCo</th>
<th>ScNi</th>
<th>ScCu</th>
<th>ScZn</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_0) (eV)</td>
<td>1.53</td>
<td>2.22</td>
<td>2.57</td>
<td>1.07</td>
<td>1.98</td>
<td>3.19</td>
<td>3.91</td>
<td>3.30</td>
<td>1.74</td>
<td>0.16</td>
</tr>
<tr>
<td>(\Delta_{sd}(X))</td>
<td>1.43</td>
<td>0.81</td>
<td>0.25</td>
<td>-1.00</td>
<td>2.15</td>
<td>0.87</td>
<td>0.42</td>
<td>-0.03</td>
<td>-1.49</td>
<td>...</td>
</tr>
<tr>
<td>(A_{ad}) (eV)</td>
<td>0.86</td>
<td>0.88</td>
<td>0.74</td>
<td>0.66</td>
<td>0.52</td>
<td>0.51</td>
<td>0.52</td>
<td>0.80</td>
<td>0.86</td>
<td>0.89</td>
</tr>
<tr>
<td>(A(X)) (eV)</td>
<td>0.18</td>
<td>0.079</td>
<td>0.525</td>
<td>0.666</td>
<td>0.0</td>
<td>0.163</td>
<td>0.661</td>
<td>1.156</td>
<td>1.228</td>
<td>0.0</td>
</tr>
<tr>
<td>(E_{vd}, M-1)</td>
<td>5.14</td>
<td>5.50</td>
<td>6.18</td>
<td>6.55</td>
<td>6.56</td>
<td>6.86</td>
<td>...</td>
<td>5.67</td>
<td>5.72</td>
<td>5.73</td>
</tr>
<tr>
<td>(E_{vd}, M+1)</td>
<td>5.48</td>
<td>5.36</td>
<td>6.32</td>
<td>6.00</td>
<td>6.20</td>
<td>6.40</td>
<td>6.57</td>
<td>7.21</td>
<td>7.36</td>
<td>8.47</td>
</tr>
<tr>
<td>IP(X) (eV)</td>
<td>6.56</td>
<td>6.83</td>
<td>6.74</td>
<td>6.77</td>
<td>7.44</td>
<td>7.90</td>
<td>7.86</td>
<td>7.64</td>
<td>7.73</td>
<td>9.39</td>
</tr>
</tbody>
</table>

\(a\)Experimental \(D_0\) = 1.12±0.22 (see Ref. 21), 1.65±0.22 (see Refs. 22–25).

\(b\)Negative values mean that a \(4s^13d^{n-1}\) configuration is the ground state configuration. The lowest excited configuration of Zn is \(4s^14p^13d^1\).

\(c\)See Ref. 56.

\(d\)\(M\) is the spin multiplicity of the neutral ground state and \(M+1\) are the spin multiplicities of the corresponding cations.

\(e\)See Ref. 8.
C. Adiabatic electron affinities

The adiabatic electron affinity \( A_{\text{ad}} \) of a neutral dimer is defined as the difference in the ground-state total energies of the dimer and its anion. Within the Born–Oppenheimer approximation, one could evaluate the \( A_{\text{ad}} \) as:

\[
A_{\text{ad}} = E_{\text{tot}}(\text{ScX}, R_e) - E_{\text{tot}}(\text{ScX}^-, R_e^-) = \frac{1}{2} \omega_a(\text{ScX}) + \frac{1}{2} \omega_a(\text{ScX}^-),
\]

where \( R_e \) and \( R_e^- \) denote equilibrium bond lengths of a neutral AB dimer and its AB\(^{-}\) anion, respectively. Since the differences in zero-point vibrational energies, computed within the harmonic approximation, were found to be less than 100 cm\(^{-1}\) (0.01 eV), they were neglected.

Our computed values of the \( A_{\text{ad}} \)s in the ScX series are:

- Sc 2 0.86 eV
- ScTi 0.88 eV
- ScV 0.74 eV
- ScCr 0.66 eV
- ScMn 0.52 eV
- ScFe 0.51 eV
- ScCo 0.52 eV
- ScNi 0.80 eV
- ScCu 0.86 eV
- ScZn 0.89 eV

These \( A_{\text{ad}} \)s have the largest and nearly same values in the beginning and at the end of the series and reach the minimum value of about 0.5 eV at ScMn, ScFe, and ScCo. The estimated full configuration interaction (CI) value\(^{41}\) of Sc 2 is 0.91 eV, which is in agreement with our value of 0.86 eV. Comparison of the dimer \( A_{\text{ad}} \)s with atomic electron affinities\(^{56}\) does not show any simple correlation (see Fig. 9).

Experimental electron affinities are available for homonuclear dimers Cr 2 (0.505 ± 0.005 eV),\(^{57,58}\) Fe 2 (0.902 ± 0.008 eV),\(^{59,60}\) Co 2 (1.110 ± 0.008 eV),\(^{59}\) and Ni 2 (0.926 ± 0.010 eV),\(^{61}\) as well as the mixed NiCu dimer (0.979 ± 0.010 eV).\(^{62}\) These values have to be compared to our BPW91/6-311 + G\(^{*}\) results on the \( A_{\text{ad}} \) computations of the above dimers: Cr 2: 0.43 eV;\(^64\) Fe 2: 0.94 eV;\(^9\) Co 2: 0.91 eV;\(^63\) Ni 2: 0.79 eV;\(^{64}\) and NiCu: 0.85 eV.\(^{64}\) As is seen, the largest difference between experimental and theoretical values does not exceed 0.2 eV. Such an accuracy has been achieved in \( A_{\text{ad}} \) computations\(^5\) of typical sp compounds performed by an infinite-order coupled-cluster method with all
singles and doubles and noniterative inclusion of triple excitations [CCSD(T)] and a 6-311+ + G(2d,2p) basis set.

D. Vertical detachment energies

Because detachment of an electron of from a neutral dimer state with the spin multiplicity of $M$ could result in final cationic states with the spin multiplicities of $M \pm 1$, we have computed the vertical detachment energies as

$$E_{vd}, M \pm 1 = E_{vd}(\text{ScX}^+, R_v, M \pm 1) - E_{vd}(\text{ScX}, R_v, M).$$

Our computed $E_{vd}$ for the ground state dimers are given in Table IV. As is seen, the vertical detachment energies to high- and low-spin multiplicity states are similar for the dimers from Sc$_2$ to ScFe, while they are splitted at the end of the ScC series. The dimer’s $E_{vd}$ are lower than the lowest detachment energies of an electron [also called the first ionization potentials (FIP)] from the constituent atoms. In fact, only detachment from ScCo$^-$ to the singlet closed-shell ScCo provides the energy of 6.57 eV which matches the Sc FIP of 6.56 eV.

This is rather surprising, because electrons are detached from bonding orbitals. Note that adiabatic detachment energies should be even smaller. In order to get some insight in the nature of such an unusual trend in the $E_{vd}$ values of the ScX dimers, we have optimized the lowest $^4\Sigma^+$ and $^6\Delta_g$ states of Sc$_2$ as well as $^5\Delta$ and $^7\Sigma^+$ of ScTi$^+$. Adiabatic detachment energies from the ground $^5\Sigma_u^-$ state of Sc$_2$ are found to be 5.13 and 5.37 eV, which are indeed somewhat lower than the $E_{vd}$ of 5.14 and 5.48 eV, respectively (see Table IV). Our value of 5.13 eV for the adiabatic detachment energy of an electron in Sc$_2$ is in fair agreement with the value of 4.82 eV obtained at the CI level.$^{41}$

According to the data of the NBO analysis, effective electronic configurations of Sc atoms in the $^4\Sigma^+_g$ ($R_e = 2.57$ Å, $\omega_e = 268$ cm$^{-1}$) and $^6\Delta_g$ ($R_e = 2.42$ Å, $\omega_e = 270$ cm$^{-1}$) states of Sc$_2$ are $\alpha^7\beta^4\gamma^0\delta^2\epsilon^0\zeta^0$, respectively. Both states have no lone pairs; the number of bonding orbitals is 8 ($\alpha/1\beta$ and $5(\alpha)$/0$\beta$

in these states, respectively. The bonding pattern in the $^4\Sigma^+_g$ state is similar to that in $^5\Sigma^-_u$ state of Sc$_2$ (see Fig. 1) if two lone pairs are replaced by a (4s + 4s)$_\beta$ bonding orbital. To arrive at this state, an electron should be detached from a (3d + 3d) MO. However, if to compare the bonding pattern in the $^4\Sigma^+_g$ state (one 4s + 4s bond and three 3d + 3d bonding orbitals), one would rather infer that the electron is removed from a combination 4s(LP) + 4s(LP), while another half of 4s(LP) + 4s(LP) forms a bonding orbital. The bonding pattern in the $^6\Delta_g$ state [one (4s + 4s)$_\alpha$ and four (3d − 3d)$_\beta$ bonding orbitals] would be the same as in $^5\Delta_g$ state of Sc$_2$ (see Fig. 1) if consider again that the electron is removed from a combination 4s(LP) + 4s(LP), while another electron of the combination has filled a bonding orbital. If such an analogy is pertinent, then one could reasonably explain why the $E_{vd}$ of Sc$_2$ are lower than the FIP of Sc. In both cases, the electron leaves a 4s-lone pair with a subsequent reconstruction of bonding patterns in the cation.

However, such an explanation is not satisfactory for the next ScTi dimer whose ground state possesses no lone pairs. The optimized $^5\Delta$ ($R_e = 2.50$ Å, $\omega_e = 274$ cm$^{-1}$) and $^7\Sigma^+_u$ ($R_e = 2.27$ Å, $\omega_e = 295$ cm$^{-1}$) states of ScTi$^+$ provide the adiabatic electron detachment energies of 5.32 and 5.34 eV, respectively. One can see a slight decrease with respect to the corresponding vertical values of 5.50 and 5.36 eV, respectively (see Table IV). Effective electronic configurations are: Sc $[4s^{0.98}3d^{1.37}4p^{0.03}]$ and Ti $[4s^{0.80}3d^{2.72}4p^{0.03}]$ in $^5\Delta$, Sc $[4s^{0.46}3d^{1.84}4p^{0.03}]$ and Ti $[4s^{0.53}3d^{3.14}4p^{0.04}]$ in $^7\Delta$. This indicates that an electron is detached from a 3d + 3d MO during transition $^6\Sigma^+ \rightarrow ^5\Delta$, while it is detached from a 4s + 4s MO in $^5\Sigma^- \rightarrow ^7\Delta$. Correspondingly, the number of bonding orbitals is $5(\alpha)/1(\beta)$ in the $^5\Delta$ state and $6(\alpha)/0(\beta)$ in the $^7\Sigma^+_u$ state, i.e., by one less than in the ScTi ground state ($6(\alpha)/1(\beta)$, see Table II). Both these cationic states have no lone pairs. Thus one could surmise that a relative lowering of total energies in (Sc + X)$^+$ with respect to (Sc + X) could be due to lacking unfavorable promotions in the cation states.

The observation that the molecular ionization energies are less than the ionization energy of either of the constituent atom means that the 3d-metal dimer cations are more strongly bound than their neutral parents. Computations of dissociation energies show the channel Sc$_2$($^4\Sigma^+_g$) → Sc$^+$ + Sc$^+$ to have the energy of 2.55 eV, while the channels ScTi$^+$(^7\Sigma^+)$\rightarrow$ Sc$^+$ + Ti$^+$ and ScTi$^+$(^7\Sigma^+)$\rightarrow$ Sc$^+$ + Ti$^+$ have the energies of 3.39 and 3.00 eV, respectively. Comparing these values to $D_0$ values of Sc$_2$ and ScTi given in Table IV, we see that the cations Sc$_2^+$ and ScTi$^+$ are more stable than their neutral parents Sc$_2$ and ScTi, respectively, by about 1 eV.

E. Ground-state spin-multiplicity rules

Our assignment of ground state spin multiplicities of the ScX dimers is consistent with the “±1 rule,” which states that the spin multiplicity of a neutral ground state has to differ by ±1 from the ground state spin multiplicity of the corresponding anion, as is seen from the following chart.

FIG. 9. Comparison of the electron affinities of the ScX dimers and their X constituents.
According to a common point of view, the effective electronic configuration of a 3d-metal atom is $4s^13d^{n+1}$ in a dimer, that formally allows the two remaining $4s$ electrons to form a $(4s + 4s)$ bond (or two bonding orbitals in $\alpha$ and $\beta$ spin representations). Thus, one could construct ground state multiplicities of XY dimers in two extreme limits: coupling or decoupling of $3d$-electron spins in $X\,4s^13d^{n+1}$ and $Y\,4s^13d^{m+1}$ effective electronic configurations. More formally, one might anticipate that the ground state multiplicity $(2S+1)G.S.$ could be expressed as

$$\frac{2S+1}{G.S.} = |\text{mod}(n+1) - \text{mod}(m+1)| + 1,$$

where the mod function is defined as $N \text{mod} (N/5) \times 5 \left(\frac{1}{11}\right)$. Note that in Zn-containing dimers, an effective electronic configuration could be considered as $4s^13d^{10}p^1$.

Let us check if this rule works in the ScX series. Sc has a $4s^23d^1$ configuration, thus the Sc$_2$ dimer should have the ground state spin multiplicity of 1 or 5 in dependence how spins of 3$d$ electrons of two effective electronic configurations $4s^13d^2$ are coupled, i.e., $2S+1 = 1$ or 5. Indeed, the ground state spin multiplicity is 5. Let us consider the other ScX dimers.

(1) ScTi: Sc($4s^13d^2$) + Ti($4s^13d^3$) should result in $2S+1 = 2$ or 6. The ground state has 6.

(2) ScV: Sc($4s^13d^3$) + V($4s^13d^4$) should result in $2S+1 = 3$ or 7. The ground state has 7.

(3) ScCr: Sc($4s^13d^4$) + Cr($4s^13d^5$) should result in $2S+1 = 4$ or 8. The ground state has 4.

(4) ScMn: Sc($4s^13d^5$) + Mn($4s^13d^6$) should result in $2S+1 = 3$ or 7. The ground state has 3.

(5) ScFe: Sc($4s^13d^6$) + Fe($4s^13d^7$) should result in $2S+1 = 2$ or 6. The ground state has 2.

(6) ScCo: Sc($4s^13d^7$) + Co($4s^13d^8$) should result in $2S+1 = 1$ or 5. The ground state has 1.

(7) ScNi: Sc($4s^13d^8$) + Ni($4s^13d^9$) should result in $2S+1 = 2$ or 4. The ground state has 2.

(8) ScCu: Sc($4s^13d^9$) + Cu($4s^13d^{10}$) should result in $2S+1 = 3$. The ground state has 3.

(9) ScZn: Sc($4s^13d^{10}$) + Zn($4s^14p^33d^{10}$) should result in $2S+1 = 2$ or 4. The ground state has 4.

The rule (9) for determining the ground state spin multiplicity of a homonuclear or mixed d-metal dimer is so simple, that it hardly believable that is valid for all the d-metal dimers. Indeed, the ground-state spin multiplicities of Ti$_2$ and V$_2$ should be 1 or 7 and 1 or 9, respectively, according to this rule. However, the ground spin multiplicity of the both dimers equals three which is in agreement with rule (9) predictions for isoelectronic ScV and ScMn. None the less, such violations are occasional and this simple rule could be very useful when guessing the ground state spin multiplicities of transition metal dimers.

### IV. SUMMARY

The results of our density functional theory computations of Sc$_2$ and Sc$_2$ compare well with the results obtained for Sc$_2$ and Sc$_2$ at most advanced levels of theory and experimental data. Our computed vibrational frequencies of Sc$_2$ and ScNi, 241 and 349 cm$^{-1}$, respectively, are in good agreement with experimental values of 239.9 cm$^{-1}$ and 334 ± 1.0 cm$^{-1}$, respectively, that allows one to anticipate a similar accuracy for other mixed dimers ScX.

This first systematic investigation on the electronic structure and chemical bonding of the 3d-metal ScX and ScX$^-$ dimers (X=Sc–Zn) has revealed a number of interesting features.

(i) Each dimer has a specific bonding pattern which is guided by different promotion schemes inside electronic configurations of the constituent atoms.

(ii) Local magnetic moments are coupled antiferromagnetically in the ScCr, ScMn, and ScFe dimers.

(iii) The ground state multiplicity of a ScX dimer is described by a simple relation (9) between the number of 3$d$ electrons in effective electronic configurations of the constituent atoms.

(iv) Even though the electron affinities of the ScX dimers are within a narrow range (0.5 eV $< \Delta E_{\text{ad}} <$ 0.9 eV), each dimer except closed-shell ScCo possesses at least two states stable towards detachment of an extra electron. In particular, ScTi$^-$, ScV$^-$, and ScCr$^-$ possess at least four stable states.

(v) The 3$d$-electron poor dimers Sc$_2$, ScTi, ScV, ScCr, and ScMn possess several states of different spin multiplicities which are close in total energy to the corresponding ground states, while excited states of the 3$d$-electron rich dimers ScFe, ScCo, ScNi are well separated in total energy from their ground states.

(vi) Vertical electron detachment energies for a ground-state ScX dimer are smaller than detachment energies of an electron in the ground-state Sc and X atoms.

### ACKNOWLEDGMENT

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