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Nearly-free-electron gas in a silicon cage

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A systematic study of the ground state geometries, electronic structure, and stability of the metal (M) encapsulated $M\mathrm{Si}_{12}$ ($M=\mathrm{Sc}$, Ti, V, Cr, Mn, Fe, Co, Ni) clusters has been carried out within a gradient-corrected density functional formalism. It is shown that the ground state of most $M\mathrm{Si}_{12}$ clusters has the lowest spin multiplicity as opposed to the high spin multiplicity in free transition metal atoms. Consequently, a proper inclusion of the spin conservation rules is needed to understand the variation of the binding energy of M to Si_{12} clusters. Using such rules, CrSi_{12} and FeSi_{12} are found to exhibit the highest binding energy across the neutral while VSi_{12}^- has the highest binding energy across the anionic $M\mathrm{Si}_{12}^-$ series. It is shown that the variations in binding energy, electron affinity, and ionization potential can be rationalized within an 18-electron sum rule commonly used to understand the stability of chemical complexes and shell filling in a confined free-electron gas.

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I. INTRODUCTION

One of the most exciting objectives of the research on clusters is to identify motifs that could serve as the building blocks for extended units or bulk materials. Since the properties of clusters can be tailored by changing the size and composition, this can lead to the formation of materials with desirable collective traits. The realization of this interesting and promising concept, however, relies on our ability to identify the stable building blocks that would retain their identity upon growth. Finding electronic and geometrical principles that can help identify the suitable units is therefore an important goal of the research on clusters.[1] For simple metal clusters, it has been shown that a model based on a confined free-electron gas can provide a useful guide to their stability.[2] For example, the magic numbers in $\mathrm{Li_n}$, $\mathrm{Na_n}$, or $\mathrm{K_n}$ clusters have been understood within a simple Jellium model where valence electrons respond to a uniform positive background formed by the ionic cores. The more stable clusters correspond to sizes containing enough electrons to fill the electronic shells.[2] Such a model has been used to understand the stability and electronic properties of numerous metal clusters and was recently[3,4] used to demonstrate the superhalogen behavior of Al_{13}^-. Another class of stable clusters are the fullerenes,[5] e.g., C_{60} and bigger cages. Here, it is the sp^2 bonding and the special geometry (number of hexagons and pentagons and their arrangement) that provide the guiding principle. Some time ago, it was proposed that endohedral metal atoms could stabilize the silicon cages.[6] This raises the question whether electronic or geometric rules that can help guide the search of stable metal-silicon clusters could be formulated.

A few years ago, Hiura *et al.*[7] reported generating metal (M)-containing hydrogenated silicon clusters ($M\mathrm{Si_nH_m^+}$) by reacting transition metal ions M^+ with $\mathrm{SiH_4}$ that acts as the source of Si. By comparing the abundance of $M\mathrm{Si_n^+}$ amongst $M\mathrm{Si_nH_x^+}$ clusters, they identified WSi_{12} to be an exceptionally stable cluster. They further suggested that its stability could be reconciled within an octet (18 electrons) rule,[8] assuming that each Si contributes one electron to the valence manifold. Since a W atom has six valence electrons, the total of 18 valence electrons would result in a closed electronic shell as in the case of rare gas atoms. Further, the shape of the cluster was a regular hexagonal prism of 12 Si atoms with a W at the center and thus had a compact geometrical shape in addition to the electronic shell closure. Apart from octet rule used for rare gas atoms, a shell filling at 18 electrons also occurs in a Jellium model. This initial proposition, therefore, started a flurry of activities and Khanna *et al.*[9] examined the 18-electron rule in $\mathrm{CrSi_n}$ ($n=11-14$) clusters since Cr also has six valence electrons. They showed that the gain in binding energy in adding a Si atom to the CrSi_{n-1} was indeed large for CrSi_{11}. This along with vertical detachment energy (VDE) and the adiabatic electron affinity (AEA) supported the proposition. While the above studies provided some evidence for the octet rule, a more critical investigation would be to examine the binding of transition metal atoms in $M\mathrm{Si}_{12}$ across the entire transition metal series. If the octet rule were to hold, one would expect CrSi_{12} to have the highest binding energy of all the $3d$ elements.

Recently, Sen and Mitas[10] carried out total energy calculations on $M\mathrm{Si}_{12}$ clusters for all M belonging to the $3d$, and part of the $4d$ and $5d$ series. They found that the cage geometries were more stable than other arrangements, irrespective of the type of doping. Further, the $M\mathrm{Si}_{12}$ clusters had the lowest spin multiplicity (except for TiSi_{12}), indicating that the magnetic moment on the free-transition metal atoms is quenched by the silicon cage. To examine the stability across the various series, they calculated the dissociation energy (D.E.) for the process $M\mathrm{Si}_{12} \rightarrow M + \mathrm{Si}_{12}$ via the equation

$$\mathrm{D.E.} = E(\mathrm{Si}_{12}) + E(M) - E(M\mathrm{Si}_{12}), \tag{1}$$

where $E(\mathrm{Si}_{12})$, $E(M)$, and $E(M\mathrm{Si}_{12})$ are the total ground state energies of a Si_{12} cluster, isolated metal atom, and the $M\mathrm{Si}_{12}$ cluster respectively. Using their calculated total energy for the ground state of the free $M\mathrm{Si}_{12}$, M, and Si_{12} clusters, they

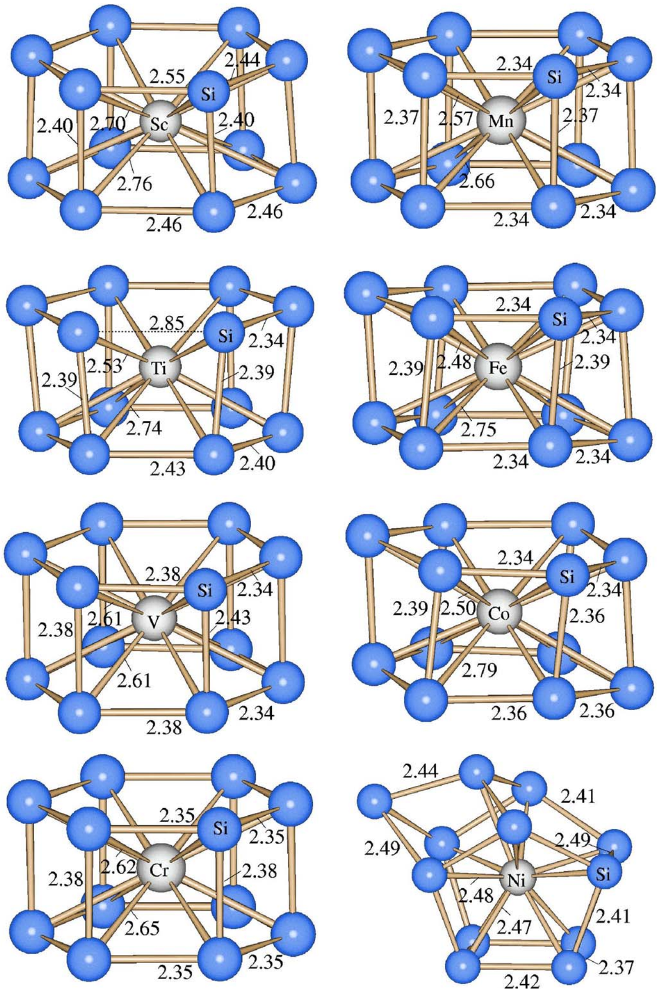


FIG. 1. (Color online) The ground state geometries of neutral $M\mathrm{Si}_{12}$ clusters. The bond lengths are in Å.

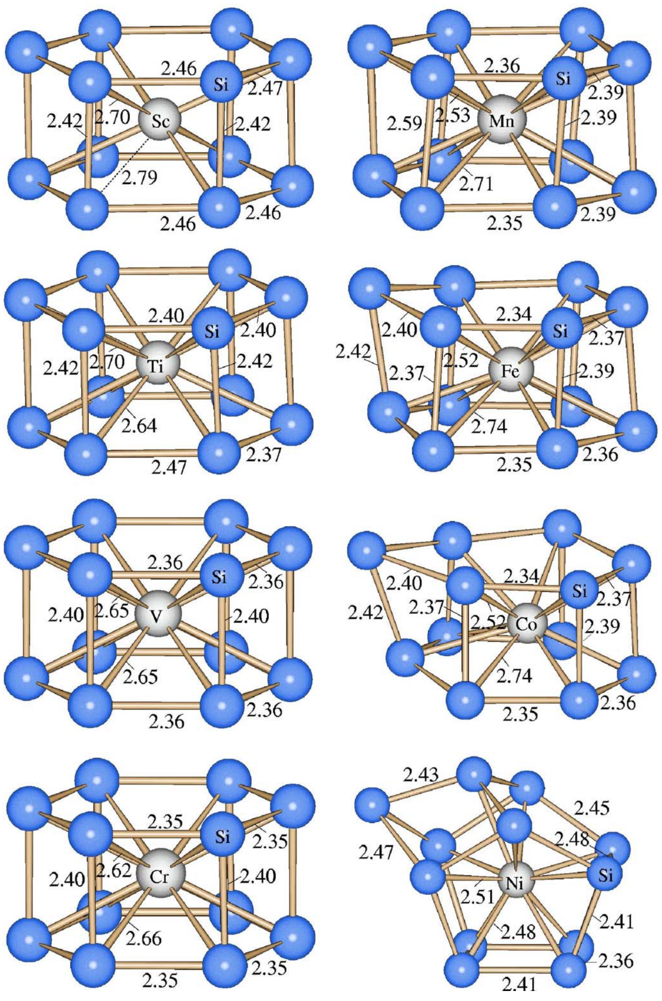


FIG. 2. (Color online) The ground state geometries of anionic $M\mathrm{Si}_{12}^-$ clusters. The bond lengths are in Å.

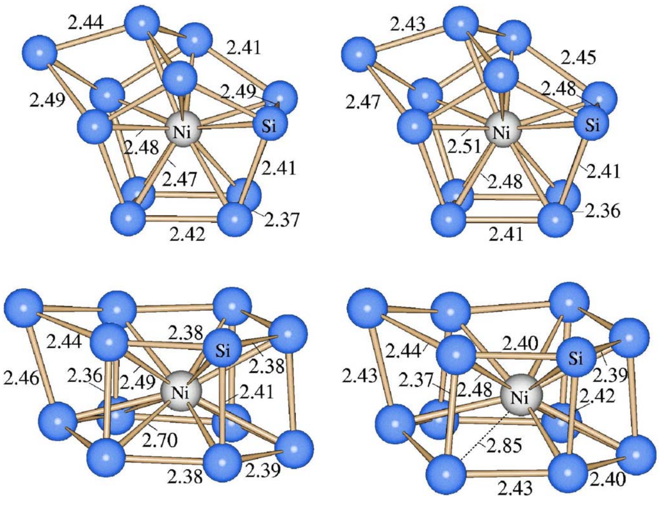
found that amongst the 3*d* series, VSi_{12} had the highest dissociation energy, thus negating the octet rule. Their findings were also supported by the later work by Kumar who reached similar conclusions.[11]

The calculation of D.E. in Eq. (1) using the ground state energy for free *M* atoms, however, violates the Wigner-Witmer spin conservation rule[12] since the spin moments of the free M atoms are quenched in the formation of $M\mathrm{Si}_{12}$. Consider the case of a Cr atom that has the highest spin multiplicity in the 3*d* series. As already noted by Khanna *et al.*, the ground state of CrSi_{12} is a spin singlet.[9] For the dissociation process, $\mathrm{CrSi}_{12} \rightarrow \mathrm{Cr} + \mathrm{Si}_{12}$, according to the Wigner-Witmer rule, both the reactant and product in the reaction should have the same spin multiplicity. One should therefore deduce the dissociation energies for the most favorable process using the reaction ${}^1\mathrm{CrSi}_{12} \rightarrow {}^1\mathrm{Cr} + {}^1\mathrm{Si}_{12}$. Since the excitation energies to the lowest multiplicity vary considerably across the 3*d* series, the D.E. incorporating the spin conservation rules could exhibit different trends. It is interesting to note that similar violations have previously been known to lead to erroneous conclusions in the binding of Cr to benzene clusters.[13]

The purpose of this paper is to reexamine the validity of the electron counting rules enforcing the spin conservation. We show that while the numerical computations by Sen and Mitas[10] are correct, the enforcing of spin conservation leads to different conclusions. We show that when analyzed with spin conservation, the binding energy of CrSi_{12} and FeSi_{12} are indeed the highest amongst the 3*d* series. The enhanced stability of FeSi_{12} provides some evidence to extend the octet rule to include shell closure at 20 found in a confined free-electron gas. To further substantiate the role of the number of electrons in stability, the studies were extended to anionic clusters. Interestingly, the presence of an extra electron shifted the shell closing and the stability patterns by one electron, making VSi_{12}^- as most stable. In Sec. II, we present the details of the calculations, while in Sec. III we present our results and their discussion. Section IV outlines our main conclusions.

II. DETAILS OF CALCULATIONS

The theoretical calculations are carried out within a density functional formalism[14] that incorporates exchange and correlation effects within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof.[15] In par-



(a) ΔE = 0.25 (b) ΔE = 0.22

FIG. 3. (Color online) (a) The isomers for neutral and (b) anionic $NiSi_{12}$ cluster. ΔE is the relative energy in eV.

ticular, the Gaussian basis sets are employed to construct atomic wave function while the cluster wave function is formed from a linear combination of atomic orbitals. All calculations were performed using the deMon software.[16] Here, an auxiliary basis set is used for the variational fitting of the Coulomb and exchange-correlation potential.[17] The numerical integration of the exchange-correlation energy and potential were performed on an adaptive grid.[18] The minimum structures were fully optimized in delocalized internal coordinates without constraints using the rational function optimization (RFO) method and the Broyden, Fletcher, Goldfarb and Shanno (BFGS) update.[19] The double zeta valence polarized (DZVP) basis set was employed.[20] We also repeated our calculations using the Naval Research Laboratory Molecular Orbital Library (NRLMOL) set of codes developed by Pederson and co-workers[21–23] in order to eliminate any uncertainty from the basis set or the numerical procedure. For the NRLMOL set of calculations, we used a 6*s*, 5*p*, and 3d basis set for Si and 7*s*, 5*p*, and 4*d* basis for transition metal atoms.[23] In each case, the basis set was supplemented by a diffuse Gaussian. For details, the reader is referred to original papers.[21–23]

III. RESULTS AND DISCUSSION OF RESULTS

The previous studies on $M\mathrm{Si}_{12}$ clusters indicate that the ground state has an hexagonal prism structure with an endohedral M atom. For $Si_{12}Ni$, Kumar[11] also proposes a structure that could be regarded a fragment of the Frank-Casper phases as an isomer to the hexagonal prism. In this work, we optimized the structures for all the $M\mathrm{Si}_{12}$ (M=Sc, Ti, V, Cr, Mn, Fe, Co, Ni) clusters by starting from the previous suggested structures and optimizing the geometry without any symmetry constraint. In addition, we tried various spin multiplicities to obtain the lowest spin state. The studies were extended to anionic clusters to examine the extensibility of the electronic and geometric rules. As in case of neutrals, the anionic ground states were obtained by optimizing the geometry and the spin states.

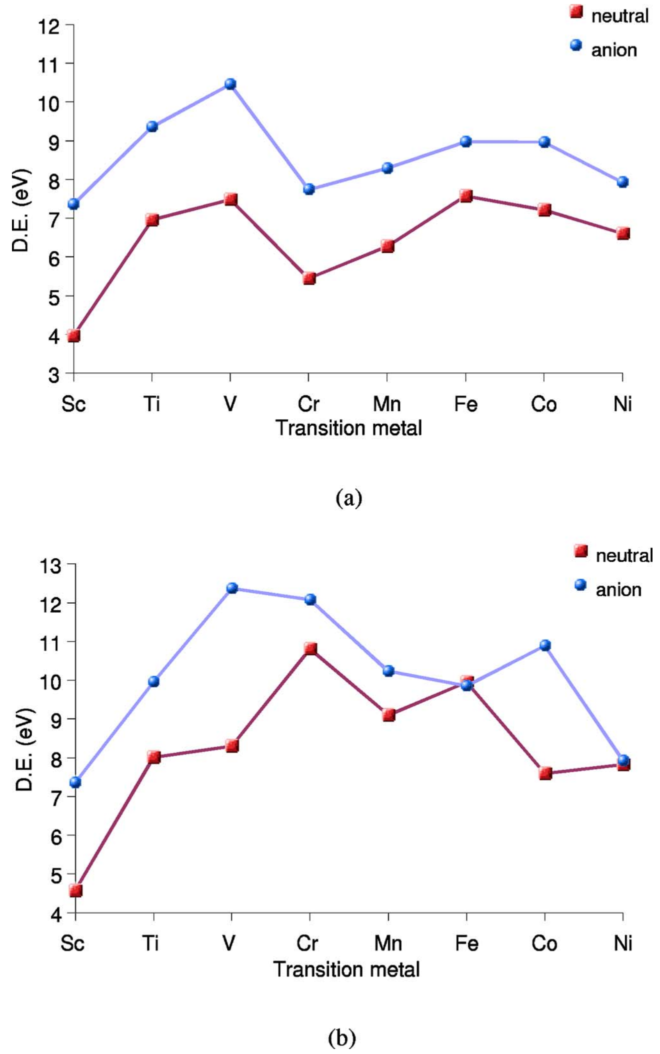


FIG. 4. (Color online) (a) Variation of the D.E. calculated using Eq. (1) across the transition metal series. All energies are in eV. (b) Variation of the $\mathrm{D.E.}^{\mathrm{W\text{-}W}}$ calculated using Eq. (2) across the transition metal series. All energies are in eV.

In Figs. 1 and 2 we show the ground state geometries of neutral and anionic $M\mathrm{Si}_{12}$ (M=Sc, Ti, V, Cr, Mn, Fe, Co, Ni) clusters. Also marked are the bond lengths in angstroms. In Table I, we give the relative stability of the various spin states. For $NiSi_{12}$, the pentagon based structure[11] and the distorted hexagonal prism are almost degenerate in energy. In Fig. 3 we also show the relative stability of these two isomers for both the neutral and anion clusters. We first focus on the progression in geometry and spin states of neutral clusters. The previous work on simple metal clusters indicates that clusters with filled electronic and geometric shells generally have compact symmetric structures. These studies[24] also indicate that clusters with unfilled electronic shells can lower their energy either through geometrical distortions leading to Jahn-Teller distortions or through spin

TABLE I. Relative energies for different spin multiplicities M_s $(2s+1)$ for the $M\mathrm{Si}_{12}$ clusters

Transition Metal	M_s	M_s (eV)
Sc	4	2 (0.06)
Ti	1	3 (0.06)
V	2	4 (1.09)
Cr	1	3 (0.75)
Mn	2	4 (1.57)
Fe	1	3 (0.51)
Co	2	4 (0.85)
Ni	1	3 (0.01)

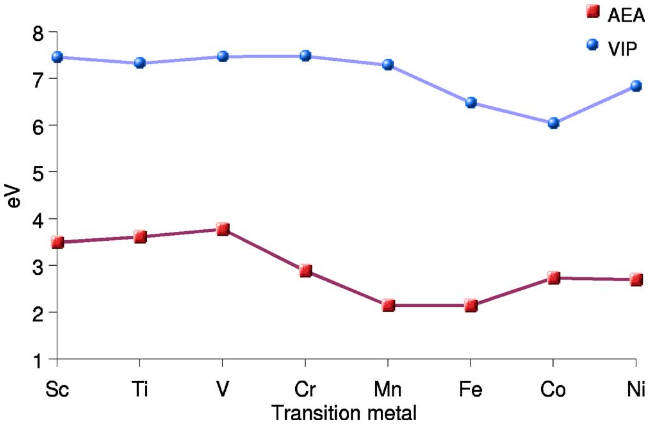


FIG. 5. (Color online) Adiabatic electron affinity (AEA) and vertical ionization potential (VIP) for the $M\mathrm{Si}_{12}$ clusters. All energies are in eV.

unpairing resulting in Hund's coupling. In an earlier work, we had demonstrated such an interplay for the case of Na_4 clusters.[24] It was shown that the ground state is a Jahn-Teller distorted singlet rhombus structure. However, the ground state for a spin triplet is a symmetric square structure. This competition between the Jahn-Teller and the Hund's coupling is also seen in the free-electron gas in the silicon cage, examined in this work. To illustrate this, consider the progressions in geometry. The hexagonal cage in case of Sc is really distorted but the ground state is a spin quartet. The distortion increases as one goes to Ti and then decreases as one approaches the middle of the $3d$ series. Further, the ground state of CrSi_{12} is an undistorted hexagonal cage. The distortions again increase as one approach the end of the series, and the ground state of NiSi_{12} is a pentagon based structure or the severely distorted hexagonal cage. In addition to the geometrical structure, we examined various spin multiplicities. In Table I we report the ground state spin multiplicities and the relative energies for the next spin state. Note that the doublet multiplicity in case of Sc is only 0.06 eV higher in energy. We found that the geometrical structure for the doublet (not shown in Fig. 1) is more distorted than that for the quartet shown in Fig. 1. For Ni and Ti, the triplet states are only 0.01 and 0.06 eV above the corresponding ground states. We will come to a discussion of these results later. The geometrical structures for the anions shown in Fig. 2 also exhibit distortions as a function of the transition metal atom. Note, however, that unlike the case of neutral clusters, it is VSi_{12}^- that now has the most symmetric structure. In Table II we report the ground state spin multiplicities and the relative energies for the next spin state for the anionic clusters. In this case, for Sc and Mn the triplet states are only 0.08 eV above the corresponding singlet ground states.

The central objective of the current work is to examine if the stability of the $M\mathrm{Si}_{12}$ units can be linked to the number of valence electrons. To this end, we first calculated D.E. defined in Eq. (1) ignoring the Wigner-Witmer rules, as carried out by Sen and Mitas[10] and Kumar.[11] For Si_{12}, we used the ground state geometry obtained by Jackson *et al.*[25] which was further optimized within our density functional theory (DFT) method. The calculated values are given in Table III while Fig. 4(a) shows the variation of D.E. as a function of the total number of electrons. Note that D.E. varies nonmonotonically with the number of valence electrons. It is highest for VSi_{12} and FeSi_{12} as opposed to CrSi_{12}. Assuming that each Si contributes one valence electron, VSi_{12} and FeSi_{12} would contain 17 and 20 electrons respectively. The CrSi_{12}, which satisfies the 18 electron rule, in fact appears as the least magic cluster. These trends do not suggest any electronic counting rule. Table IV and Fig. 4(a) show the similar calculation for the case of anions. Here, VSi_{12}^- does exhibit special stability. Is the octet rule invalid in neutrals?

It is proposed that the key to the puzzle lies in the fact that except for Sc, the ground states of all the MSi_{12} clusters have the lowest spin multiplicity. On the other hand, the ground states of isolated transition metal atoms are marked by high spin multiplicity arising due to Hund's coupling of the electrons in the open d shell. Further, the exchange energies can be fairly high so that the energy required to promote an atom from a high spin multiplicity to the lowest spin multiplicity can be large and varies with the atom. As mentioned above, the Wigner-Witmer (W-W) rule[11] requires that the reaction

TABLE II. Relative energies for different spin multiplicities M_s $(2s+1)$ for the anionic $M\mathrm{Si}_{12}$ clusters

Transition Metal	M_s	M_s (eV)
Sc	3	1 (0.08)
Ti	2	4 (1.41)
V	1	3 (1.43)
Cr	2	4 (1.49)
Mn	3	1 (0.08)
Fe	2	4 (0.11)
Co	1	3 (0.22)
Ni	2	4 (0.75)

TABLE III. The dissociation energy for various $M\mathrm{Si}_{12}$ clusters obtained by using Eqs. (1) and (2). All energies are in eV

	ScSi_{12}	TiSi_{12}	VSi_{12}	CrSi_{12}	MnSi_{12}	FeSi_{12}	CoSi_{12}	NiSi_{12}
D.E.	3.96	6.95	7.48	5.44	6.27	7.57	7.21	6.60
$\mathrm{D.E.}^{\mathrm{W\text{-}W}}$	4.57	8.01	8.30	10.81	9.10	9.95	7.59	7.82

products have the same spin multiplicity as the reactants. One should therefore calculate $\mathrm{D.E.}^{\mathrm{W\text{-}W}}$ defined by

$$\mathrm{D.E.}^{\mathrm{W\text{-}W}} = E(\mathrm{Si}_{12}) + E_s^M(M) - E_s^M(M\mathrm{Si}_{12}) \tag{2}$$

by using, for the energy of the transition metal atom, the same spin multiplicity M_s as for the $M\mathrm{Si}_{12}$ cluster. In Fig. 4(b) we also show $\mathrm{D.E.}^{\mathrm{W\text{-}W}}$ as a function of the transition element. Note that, as opposed to D.E., $\mathrm{D.E.}^{\mathrm{W\text{-}W}}$ does exhibit a maximum at Cr. In addition, there is a second peak at Fe reminiscent of the shell filling at 20 electrons in a Jellium model.[2] To further examine the validity of such a picture we examined the one-electron energy levels. The energy level structure for a confined electron gas presents[2] the sequence $1s^2\ 1p^6\ 1d^{10}\ 2s^2$. For FeSi_{12}, the electron energy levels consisted of a set of degenerate states followed by a separate single highest occupied molecular orbital (HOMO) occupied by two electrons, reminiscent of a s-like HOMO. For CrSi_{12}, while the HOMO had several almost degenerate states expected in case of d-like states, they also contained states emerging out of bonding between Si atoms (and consequently with no Cr content). It was therefore difficult to uniquely identify a d-like HOMO. The single well separated HOMO in FeSi_{12} and degenerate HOMO in CrSi_{12} do, however, provide some validity to the electronic counting rules. As pointed out earlier, the Si_{12} cage undergoes distortion in the beginning and end of the series, again reminiscent of the geometrical distortions seen in simple metal clusters with unfilled electronic shells again supporting shell closures.

Additional justification for the electronic rules and geometrical features obtained above comes from our studies on the anionic clusters. The electron counting rule would now predict that VSi_{12}^- should have the maximum binding. Again, we used the atomic reference energy for the correct multiplicity of the anion for each M determined by the multiplicity of the $M\mathrm{Si}_{12}^-$ cluster. In Fig. 4(b), we show the variation in $\mathrm{D.E.}^{\mathrm{W\text{-}W}}$ for the anionic clusters calculated using Eq. (2) for the anions and in Table IV we provide the actual values. Note that the maximum occurs at VSi_{12}^-. Also, the small structural distortion in the neutral cluster now disappears for the anion. The maximum at 20 electrons (MnSi_{12}^-) is not as marked. This could be due to the fact that the extra electron does not reside completely inside the cage. One, however, again notices the geometrical distortions in the beginning and end of the series.

To even further examine the applicability of the electronic counting rules, we calculated the adiabatic electron affinity (AEA) of the anions and the vertical ionization potential (VIP) of the neutral clusters. The former (AEA) corresponds to the energy difference between the ground state of the anion and neutral cluster while the latter (VIP) corresponds to the energy required to remove an electron from the neutral cluster without relaxing the geometry. These are shown in Fig. 5. Note that the VIP is maximum for CrSi_{12} as it represents a transition from 18 to a less stable 17 electron system while it is minimum for CoSi_{12} as it represents a transition from a 21 electron system to a more stable 20 electron system. The trends in AEA are similar. AEA is highest for VSi_{12}^- as it corresponds to going from a very stable 18 electron system to a less stable 17 electron system.

Since the original experiments by Hiura *et al.*[7] identified $\mathrm{Si}_{12}\mathrm{W}$ to be a stable motif, we extended our studies to $5d$ transition metals to examine the behavior of D.E. and $\mathrm{D.E.}^{\mathrm{W\text{-}W}}$. For the neutral clusters, both D.E. and $\mathrm{D.E.}^{\mathrm{W\text{-}W}}$ exhibit maxima for W and Os in agreement with experiment and previous calculations.[10] For the anionic species, the maxima changed to $\mathrm{Si}_{12}\mathrm{Ta}^-$, again indicative of the shell closing at 18. These results along with the investigations on the $4d$ series will be published in a later publication.

The above calculations were carried out using the deMon set of codes. To further ensure any uncertainties due to use of basis sets or numerical procedure, we repeated the above studies using the NRLMOL set of codes. While the numerical binding energies were slightly different the main results about the stability of CrSi_{12} and FeSi_{12} in neutral clusters and VSi_{12}^- in anions were the same.

IV. CONCLUSIONS

The present studies support the earlier proposition[7] that the stability of $M\mathrm{Si}_{12}$ cages can be understood within an electron counting rule where clusters with 18 valence electrons exhibit enhanced stability. For neutral clusters, the present work also shows stability for 20 valence electrons. Realizing that the Si atoms in these cage clusters have four-

TABLE IV. The dissociation energy for various anionic $M\mathrm{Si}_{12}$ clusters obtained by using the Eqs. (1) and (2). All energies are in eV

	ScSi_{12}^-	TiSi_{12}^-	VSi_{12}^-	CrSi_{12}^-	MnSi_{12}^-	FeSi_{12}^-	CoSi_{12}^-	NiSi_{12}^-
D.E.	7.35	9.36	10.45	7.73	8.29	8.97	8.95	7.92
$\mathrm{D.E.}^{\mathrm{W\text{-}W}}$	7.35	9.96	12.37	12.08	10.23	9.85	10.89	7.92

fold coordination, it would seem that the fourfold coordination of Si and the electron shell filling around metal both govern the stability. It will be interesting to examine if these rules can be extended to clusters containing different number of metal and Si atoms. Such calculations are in progress and will be reported in a coming paper.

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