Electronic structure and ground states of transition metals encapsulated in a Si_{12} hexagonal prism cage

Prasenjit Sen and Lubos Mitas
Department of Physics, North Carolina State University, Raleigh, North Carolina 27695, USA
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We report on a computational study of the electronic structure of recently discovered clusters with an encapsulated transition metal (TM) atom in a Si_{12} hexagonal prism cage. The cage geometry is remarkably stable regardless of the type of doping TM atom from $3d$, $4d$, and $5d$ series. We predict and quantify the stability for several other TM dopings besides the experimentally observed ones. The multiplicity of the ground states can be ''tuned'' between singlets and triplets by varying the type of TM atom (even number of electrons), while they are doublets for odd number of electrons. We also explore the possibility of forming solids with hexagonal structure from selected clusters.

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In nature, the most prevalent building blocks of materials are either atoms or molecules. Clusters, which are metastable assemblies of ≈10–1000 atoms, provide an alternate building block with the fullerene C_{60} solid and its superconducting derivatives as prime examples.[1] Clusters are particularly interesting because the property of the materials can be designed by exploring the enormous variability in the size, shape, and composition of the constituent clusters. Since silicon is the most widely used material in the microelectronic industry, Si clusters have attracted extensive theoretical and experimental attention.[2–7] Unlike carbon, however, silicon does not spontaneously form stable fullerene structures, since sp^2 hybridization is highly unfavorable in Si as opposed to C.[8] This has motivated a search for other ways to stabilize Si cage clusters such as doping, in particular, by transition metal (TM) atoms. Beck was able to produce $TM@Si_n$ clusters that were more stable towards photofragmentation than bare Si clusters of similar size, using a laser vaporization supersonic expansion technique.[5] Very recently, Ohara *et al.* produced Ti, Hf, Mo, and W embedded Si clusters.[9] Hiura *et al.* produced $TM@Si_nH_x$ (TM=Hf, Ta, W, Re, Ir, Nb, Mo, Co, Ni) clusters in an external quadrupole static attraction ion trap.[6] The maximum value of n depends on the particular transition metal atom, for which completely dehydrogenated clusters were found. A simple electron counting shows that the most stable clusters observed appear to fulfill the ''18-electron rule'' originating in a simplified model of the cluster as a sphere with TM being at the center (''Ar-like atom''). They also found that for $W@Si_{12}$, a regular hexagonal prism Si_{12} cage with a W atom at the center has the lowest energy. In a related development, a recent calculation[10] shows that embedded $Al_{12}X$ (X=Si, Ge, Sn, Pb) stabilizes Si_{60} cage clusters.

The six-fold symmetry prism structure was quite unexpected since Si clusters usually show very different structural patterns in this range of sizes.[3,4] The goal of this paper is to understand the electronic and structural properties of Si clusters doped with a variety of TM atoms including ones not tested in experiment, to investigate the nature of the ground states and possibilities of various spin multiplicities, and to elucidate the character of the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) levels and their filling with an increasing number of d electrons. Our calculations show that the structural frame of the hexagonal prism cage [Fig. 1(a)] is remarkably stable regardless of the type of the central transition metal atom. An analysis of the one-electron states indicates a varying degree of p-d hybridization with corresponding changes in the stability and character of ground and lowest excited states. For example, the energy differences between singlet and triplet states depend on the type of the TM atom and, in fact, for Ti, the triplet is the lowest energy state. Finally, we attempt to construct a three-dimensional periodic solid using the clusters as building blocks in a hexagonal structure which is different from the one investigated in a previous study.[11]

We have carried out electronic structure calculations of $TM@Si_{12}$ with TM=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Mo, W, Re, Os, Pt, and Au. Although our main focus was on systems with $n=12$, we also investigated clusters with $n=10$ and 11 such as $Fe@Si_{10}$ and $Re@Si_{11}$ to understand the changes in stability with different numbers of Si cage atoms. The atomic structures were determined by geometry optimization for each spin state separately using density functional theory (DFT) approach. Mostly B3LYP and PW91 functionals were used along with effective core potentials on TM atoms and a basis set which is qualitatively similar to the

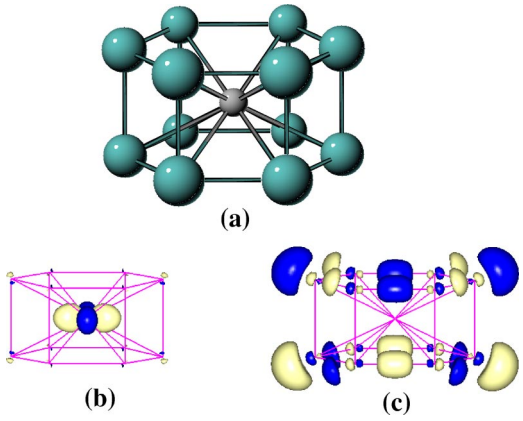

FIG. 1. (Color online) (a) The hexagonal prism cage structure of 12 Si atoms with D_{6h} symmetry with a TM atom at the center. (b) The singly occupied state in the majority spin channel for $V@Si_{12}$ localized on the TM atom. (c) The LUMO level for the same cluster.

6-311G* basis in all-electron calculations. For some clusters the electronic structure was further analyzed by Hartree-Fock and quantum Monte Carlo (QMC) approaches. For calculations of solids, we used the local density approximation (LDA) and plane waves. Geometry optimizations have led to small bond adjustments and relaxations for various doping TMs. However, the distortions from the perfect D_{6h} symmetry were rather small. In a few cases the distortions were found to be more pronounced with the deviations of the order of ~ 0.15 Å.

Qualitatively, one expects the TM *d* states to hybridize with the *p* states of the Si atoms and the resulting spins to be smaller than those of highly spin-polarized TM atoms in the middle of the *d* series. This was indeed the case for TM atoms with an odd number of electrons. We found that ground states are doublets for all such elements we studied, namely Sc, V, Mn, Co, Cu, Re and Au. One of the interesting features is the character of the singly occupied electronic state in the majority spin channel. We found that this level is invariably and predominantly *d* like, localized on the TM atom, and almost completely enclosed in the cage [Fig. 1(b)]. In case of $Co@Si_{12}$ and $Re@Si_{12}$ this state is the HOMO level. In rest of the doublet systems, this state is slightly lower in energy than the HOMO, which happens to be a bonding state of the Si cage consisting of Si *p* states. It is interesting that the LUMO has eigenvalues relatively high in energy, leading to pronounced effective HOMO-LUMO gaps. This can be understood from the large on-site Coulomb interaction typical of *d* states. In the case of $Mn@Si_{12}$ and $V@Si_{12}$, we also tested the spin quartet states which turned out to be higher than the doublets by significant amounts (more than 1.5 eV).

For transition metal atoms with an even number of electrons, the picture which emerged was more varying and complex than one would expect. For TM=Mo, Os, and W the singlet states have lower energy with a singlet-triplet splitting of about 1 eV or more. For TM=Cr, Fe, Ni, Zr, and Hf the singlet is lower in energy; however, the energy difference between the two spin states is less than 1 eV. $Pt@Si_{12}$ clusters have singlet and triplet spin states which are within 0.06 eV in energy. Remarkably, for Ti, the triplet is lower and in fact, it appears that Ti *d* states do not form strong covalent bonds with the Si cage. Isosurface plots of the singly occupied states of the $Ti@Si_{12}$ triplet [Figs. 2(b) and 2(c)] show that they essentially derive from the Ti atom/ion *d* levels which couple into triplet. The Ti_{2+} ion is known to be small in size, which leads to a weaker *p*-*d* hybridization. Since $Ti@Si_{12}$ was the only system with a triplet energy significantly lower than the singlet, we carried out more systematic and accurate investigations of the singlet-triplet energy difference. An all-electron calculation using HF led to a triplet state lower in energy by 0.65 eV. Similar calculation using B3LYP gave a triplet state lower by 0.49 eV compared to the singlet. Since HF and B3LYP can bias towards high spin states, we repeated the calculation with the PW91 gradient corrected exchange-correlation functional. This also gave a triplet state that is lower in energy than the singlet by 0.49 eV. Given the approximate way in which these methods treat the exchange and correlation effects, we decided to study the

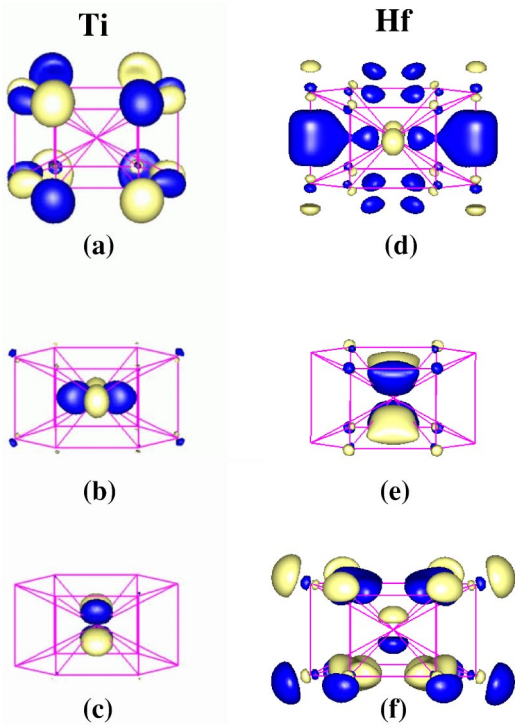

FIG. 2. (Color online) Isosurface plots of a few representative molecular orbitals for $Ti@Si_{12}$ (triplet) and $Hf@Si_{12}$ (singlet) clusters showing the different amounts of hybridization between *p* and *d* states in the two systems: (a) $Ti@Si_{12}$ LUMO. (b) and (c) The two singly occupied MOs for $Ti@Si_{12}$ triplet. (d) LUMO for $Hf@Si_{12}$. (e) HOMO for $Hf@Si_{12}$. (f) The MO below the HOMO in $Hf@Si_{12}$. A simple electron counting and symmetry implies that (b) corresponds to (d), while (c) corresponds to (e), respectively. The more pronounced *p*-*d* hybridization in both HOMO and LUMO levels of $Hf@Si_{12}$ contrasts with atomic character of the singly occupied HOMO levels and Si *p* character of the LUMO level in $Ti@Si_{12}$.

system with more accurate QMC methods. The QMC method captures the electron correlation accurately using correlated wave functions and stochastic solution of the Schrödinger equation within the fixed-node approximation as described in detail elsewhere.[4,12] Our QMC calculations show the triplet being lower by 0.7(1) eV and thus confirm the result obtained by the DFT approaches. We therefore conclude that triplet is indeed the ground state of $Ti@Si_{12}$.

An analysis of clusters with other TM atoms having an even number of electrons shows that the HOMO level can be either of *p* character extended over the cage Si atoms, or of *d* character localized on the TM depending on the number of *d* electrons. While Cr, Mo, and W singlets have *p*-like HOMO levels,[13] Fe and Os have *d*-like ones. The LUMO levels in all these cases are of *d* like character. Obviously, one can expect that the type of the actual HOMO state is important since it will likely affect the behavior of these clusters in forming larger aggregates, surface depositions, or solids.

The character of states and hybridization changes depending on TM atoms, in particular, going down the group ($3d \rightarrow 4d \rightarrow 5d$), brings about a stronger covalent bonding that leads to a more effective quenching of the spin on the TM

TABLE I. Formation energies (FE) and HOMO-LUMO gaps (in eV) of T@Si_n ($n=10$, 11, or 12) clusters in a hexagonal (pentagonal) prism structure as obtained with the B3LYP functional. ($\uparrow\downarrow$), ($\uparrow$), ($\uparrow\uparrow$), and ($\uparrow\uparrow\uparrow$) indicate a spin singlet, doublet, triplet, and quartet, respectively. The triplet ground state of $Ti@Si_{12}$ was also confirmed by QMC calculations.

	$ScSi_{12}$	$TiSi_{12}$	$TiSi_{12}$	VSi_{12}	VSi_{12}	$CrSi_{12}$	$CrSi_{12}$	$MnSi_{12}$	$MnSi_{12}$	$FeSi_{12}$	$FeSi_{12}$	$CoSi_{12}$	$NiSi_{12}$	$NiSi_{12}$	$CuSi_{12}$	$ZrSi_{12}$
spin	($\uparrow$)	($\uparrow\downarrow$)	($\uparrow\uparrow$)	($\uparrow$)	($\uparrow\uparrow\uparrow$)	($\uparrow\downarrow$)	($\uparrow\uparrow$)	($\uparrow$)	($\uparrow\uparrow\uparrow$)	($\uparrow\downarrow$)	($\uparrow\uparrow$)	($\uparrow$)	($\uparrow\downarrow$)	($\uparrow\uparrow$)	($\uparrow$)	($\uparrow\downarrow$)
FE	1.49	3.43	3.92	4.46	2.52	2.99	2.45	2.68	0.99	3.42	2.55	2.60	3.90	3.32	0.62	4.30
Gap	0.83	0.88	2.74	3.06	1.17	3.04	3.05	2.97	1.93	2.79	1.05	1.07	1.03	0.57	0.44	1.24
	$ZrSi_{12}$	$MoSi_{12}$	$MoSi_{12}$	$HfSi_{12}$	$HfSi_{12}$	WSi_{12}	WSi_{12}	$ReSi_{12}$	$OsSi_{12}$	$OsSi_{12}$	$PtSi_{12}$	$PtSi_{12}$	$AuSi_{12}$	$ReSi_{11}$	$FeSi_{10}$	$FeSi_{10}$
spin	($\uparrow\uparrow$)	($\uparrow\downarrow$)	($\uparrow\uparrow$)	($\uparrow\downarrow$)	($\uparrow\uparrow$)	($\uparrow\downarrow$)	($\uparrow\uparrow$)	($\uparrow$)	($\uparrow\downarrow$)	($\uparrow\uparrow$)	($\uparrow\downarrow$)	($\uparrow\uparrow$)	($\uparrow$)	($\uparrow$)	($\uparrow\downarrow$)	($\uparrow\uparrow$)
FE	4.04	6.10	4.89	4.70	4.51	8.44	6.93	7.44	8.13	7.18	5.07	5.13	0.68	6.34	1.07	0.14
Gap	2.43	2.40	2.14	1.22	2.57	2.78	1.70	2.83	2.25	1.07	0.99	1.37	1.33	1.88	0.93	0.79

atom. This is supported by the observation that the singlet-triplet energy difference increases from Cr to Mo to W and from Fe to Os. A comparison of the molecular orbitals (MOs) of $Ti@Si_{12}$ and $Hf@Si_{12}$ more clearly brings out this point. By examining a few MOs around the HOMO level we have found that the amount of overlap between TM *d* and Si *p* is much stronger in $Hf@Si_{12}$ than in $Ti@Si_{12}$ (see Fig. 2). This leads to $Ti@Si_{12}$ having a triplet ground state and $Hf@Si_{12}$ having a singlet ground state. The enhanced bonding with an increasing number of filled *d* shells is not difficult to understand. First, the size of the atoms is increasing and the larger size fits the hexagonal cavity better. Second, the atomic levels are more shallow and energetically closer to the *p* levels of silicon, resulting in a better hybridization as we have observed.

A measure of the relative stabilities of various clusters is the energy gain in forming T@Si_n starting with the lowest known Si_n cluster isomer and an isolated TM atom. This formation energy (FE) is given by

$$\mathrm{FE} = E(\mathrm{Si}_{n,\ \text{lowest isomer}}) + E(\mathrm{T}) - E(\mathrm{T@Si}_n) \qquad (1)$$

where *E* denotes the calculated ground state total energy of a given system. A summary of our estimations of FEs within B3LYP are shown in Table I. For the lowest isomer of Si_{12} cluster (structurally very different from the hexagonal cage) we used the geometry obtained by Ho *et al.*[3] which was further optimized within the DFT methods we used. For Si_{11} and Si_{10} clusters, we used the lowest energy structures obtained previously.[4] Perhaps the most surprising fact is that *all* TM atoms we have studied form stable $TM@Si_{12}$ clusters. However, the amount of formation energy varies considerably. While the TM atoms at the beginning or end of a series (Sc, Cu, Au) lead to a marginal stability, those towards the middle are clearly more stable.

In the 3*d* series, $Cr@Si_{12}$ does not have the highest FE, showing that electron shell filling (''18-electron rule'') is just one of the aspects which determine the cluster stability. Another feature that becomes obvious is that the FE increases as one goes down a group. $Hf@Si_{12}$ has a higher FE than $Zr@Si_{12}$, which has a higher FE than $Ti@Si_{12}$. Things are similar for $W@Si_{12}$, $Mo@Si_{12}$, and $Cr@Si_{12}$. This is again related to the better *p*-*d* hybridization and larger atom size with an increased filling of the *d* shells, as explained above. This also shows that the center of the 5*d* series is a ''sweet spot'' with corresponding TM atoms leading to the highest stability. Out of these, $W@Si_{12}$ has the largest FE. This explains why $W@Si_{12}$ clusters were readily observed in the experiments. It is interesting that in the 3*d* row we predict the highest stability for $V@Si_{12}$ which has the largest FE and also a remarkably large HOMO-LUMO gap.

In order to test the ''18-electron rule'' further we calculated electronic structures of $Fe@Si_{10}$ and $Re@Si_{11}$ clusters, which also satisfy the rule. In $Fe@Si_{10}$, a Fe atom is placed between two Si pentagons, while in $Re@Si_{11}$ a Re atom is sandwiched between a Si pentagon and a hexagon. Clearly, $Fe@Si_{10}$ clusters, particularly the triplet, are only marginally bound (Table I). The $Re@Si_{11}$ cluster is also less stable than a $Re@Si_{12}$ cluster showing a less favorable character of the binding. Nevertheless, both of them have reasonably large formation energies. That the ''18-electron rule'' is not quite general is also clear from the fact that Beck[5] produced $TM@Si_{15}^{+}$ and $TM@Si_{16}^{+}$ clusters with TM=Mo and W while Ohara *et al.*[9] produced $TM@Si_n^{-}$ for TM=Ti, Mo, Hf, and W of which $n=15$ and 16 were found to be the most stable.

Since the ultimate aim is to use these clusters as building blocks for condensed phases of matter, we studied the cluster-cluster binding properties. We calculated the binding energy (BE) of a dimer of $Nb@Si_{12}$ clusters in a geometry such that one Si-Si bond in the upper hexagon of the first cluster is parallel to a Si-Si bond in the lower hexagon of the second cluster, since this was suggested as the lowest energy structure.[11] With a B3LYP functional, the binding between the clusters is small, albeit nonzero. The maximum binding occurs at a Nb-Nb distance of $\sim$7.25 Å and the BE is 0.37 eV. The calculation with the LDA functional[14] leads to larger binding (1.53 eV), and the Nb-Nb distance decreases to 6.75 Å. This is not surprising since the LDA is known to produce overbinding for the cases of van der Waals or weak covalent bonds. On the other hand, B3LYP tends to underestimate the binding in such cases and therefore we conjecture that the actual binding is bracketed by these two estimators.

Similar to the study of Pacheco *et al.*,[11] we explored the possibility of forming periodic solids from these clusters. We chose $Nb@Si_{12}$ and $Ti@Si_{12}$ as our test clusters for the purpose, in particular to study the possibilities of magnetically ordered phases of the solid. For these calculations we used the LDA functional[14] and the VASP code[15] with ultrasoft pseudopotentials[16] and a plane-wave basis set. We calculated the cohesive energies of solids of $Nb@Si_{12}$ and $Ti@Si_{12}$ clusters in hexagonal close packed (hcp) structures. The choice of hcp was motivated by maximizing the clusters' edge-edge neighboring, which leads to the highest binding for pairs. The minimum energy for such a solid of $Nb@Si_{12}$ is found for an in-plane lattice constant of $a \approx 6.75$ Å. The c/a ratio for the hcp structures is fixed at 1.6. In this structure, the cohesive energy is calculated to be 4.96 eV per $Nb@Si_{12}$ cluster. For a solid of $Ti@Si_{12}$ clusters, the in-plane lattice constant for the minimum energy structure is also found to be $a \approx 6.75$ Å. The cohesive energy for this system is 1.08 eV per cluster. These numbers suggest that the $Nb@Si_{12}$ solid probably has a combination of covalent and van der Waals bindings, whereas, in the case of $Ti@Si_{12}$, it is only a weak van der Waals binding. An interesting point to note is that both solids appear to have paramagnetic ground states. Our conclusions, of course, apply only to zero temperature and to the hcp type of structure. We do not rule out possibilities of other types of structures, in particular, with lower symmetries. Similarly, finite temperature effects,[11] which are beyond the scope of the present study, would become relevant once all promising crystalline structures are identified.

In conclusion, our results can be summarized as follows: (i) essentially all $3d$, $4d$ and $5d$ transition metal atoms can act as nucleation centers to form $TM@Si_{12}$ hexagonal prism cage clusters; (ii) the character of the states at the Fermi level depends on the type of atom, its size, and its number of d electrons which results in a varying and ''tunable'' difference between close spin states; (iii) the formation energy of $TM@Si_{12}$ increases as one goes from $3d$ to $4d$ to $5d$ groups and we predict the (meta)stability of several other systems beyond the experimentally observed ones; (iv) the ''18-electron rule'' has a limited applicability since we found that stability depends on other factors as well (size of TM atom, etc); (v) we tested the suggestion of Martins *et al.*[11] for forming extended solids of clusters, and propose a particular crystalline structure which may be stable. Our study shows the exceptional flexibility of the d-p hybridization which leads to structural robustness of the hexagonal prism cage structure and to a tunable character of electronic states by a proper choice of the TM atom. We believe that information about the relaxed structures would be valuable for the research community and therefore can be found at http://altair.physics.ncsu.edu/data/structures/clusters/.

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[1] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, and D.R. Huffman, Nature (London) **347**, 354 (1990); R.C. Haddon, *ibid.* **388**, 31 (1991).

[2] K. Raghavachari and V. Logovinsky, Phys. Rev. Lett. **55**, 2853 (1985); U. Röthlisberger, W. Andreoni, and P. Gianozzi, J. Chem. Phys. **96**, 1248 (1992); M.F. Jarrold, J. Phys. Chem. **99**, 11 (1995); E. Kaxiras and K. Jackson, Phys. Rev. Lett. **71**, 727 (1993); S. Wei, R.N. Barnett, and U. Landman, Phys. Rev. B **55**, 7935 (1997); J. Müller, B. Liu, A.A. Shvartsburg, S. Ogut, J. Chelikowsky, K.W.M. Siu, K-M. Ho, and G. Gantefor, Phys. Rev. Lett. **85**, 1666 (2000); V. Kumar and Y. Kawazoe, *ibid.* **87**, 045503 (2001); **88**, 235504 (2002); T. Nagano, K. Tsumuraya, H. Eguchi, and D.J. Singh, Phys. Rev. B **64**, 155403 (2001); D. Tománek and M.A. Schlüter, *ibid.* **36**, 1208 (1987); J.R. Chelikowsky, K.M. Glassford, and J.C. Phillips, *ibid.* **44**, 1538 (1991); M.R. Pederson, K. Jackson, D.V. Porezag, Z. Hajnal, and Th. Frauenheim, *ibid.* **54**, 2863 (1996).

[3] K.-M. Ho, A.A. Shvartsburg, B. Pan, Z-Y. Lu, C-Z. Wang, J.G. Wacker, J.L. Fye, and M.F. Jarrold, Nature (London) **392**, 582 (1998).

[4] J.C. Grossman and L. Mitas, Phys. Rev. Lett. **74**, 1323 (1995).

[5] S.M. Beck, J. Chem. Phys. **90**, 6306 (1989).

[6] H. Hiura, T. Miyazaki, and T. Kanayama, Phys. Rev. Lett. **86**, 1733 (2001).

[7] S.N. Khanna, B.K. Rao, and P. Jena, Phys. Rev. Lett. **89**, 016803 (2002).

[8] M. Broyer, M. Pellarin, B. Baguenard, J. Lermé, J.L. Vialle, P. Melinon, J. Tuaillon, V. Dupuis, B. Prevel, and A. Perez, in *Cluster Assembled Materials*, edited by K. Sattler [Mater. Sci. Forum **232**, 27 (1996)].

[9] M. Ohara, K. Koyasu, A. Nakajima, and K. Kaya, Chem. Phys. Lett. **371**, 490 (2003).

[10] Q. Sun, Q. Wang, P. Jena, B.K. Rao, and Y. Kawazoe, Phys. Rev. Lett. **90**, 135503 (2003).

[11] J.M. Pacheco, G.K. Gueorguiev, and J.L. Martins, Phys. Rev. B **66**, 033401 (2002).

[12] W.M.C. Foulkes, L. Mitas, R.J. Needs, and G. Rajagopal, Rev. Mod. Phys. **73**, 33 (2001), and references therein.

[13] HOMO and LUMO for $W@Si_{12}$ were also studied by T. Miyazaki, H. Hiura, and T. Kanayama, cond-mat/0208217 (unpublished) and presented at the 26-th International Conference on the Physics of Semiconductors, Edinburgh, UK.

[14] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[15] G. Kresse and J. Hafner, Phys. Rev. B **47**, R558 (1993); G. Kresse and J. Furthmüller, *ibid.* **54**, 11 169 (1996).

[16] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).