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Optical Properties and Quasiparticle Band Gaps of Transition-Metal Atoms Encapsulated by Silicon Cages

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ABSTRACT: Semiconductors assembled upon nano-templates consisting of metal-encapsulating Si cage clusters ($M@Si_n$) have been proposed as prospective materials for nano-devices. To make an accurate and systematic prediction of the optical properties of such $M@Si_n$ clusters, which represent a new type of metal-silicon hybrid material for components in nanoelectronics, we have performed first-principles calculations of the electronic properties and quasiparticle band gaps for a variety of $M@Si_{12}$ ($M = Ti, Cr, Zr, Mo, Ru, Pd, Hf, \text{ and } Os$) and $M@Si_{16}$ ($M = Ti, Zr, \text{ and } Hf$) clusters. At first stage, the electronic structure calculations have been performed within plane-wave density functional theory in order to predict equilibrium geometries, polarizabilities, and optical absorption spectra of these endohedral cage-like clusters. The quasiparticle calculations were performed within the *GW* approximation, which predict that all these systems are semiconductors exhibiting large band gaps. The present results have demonstrated that the independent-particle absorption spectra of $M@Si_n$, calculated within the local density or generalized gradient approximations to density-functional theory, are dramatically influenced by many-body effects. On average, the quasiparticle band gaps were significantly increased, in comparison with the independent-particle gaps, giving values in the 2.45–5.64 eV range. Consequently, the inclusion of many-body effects in the electron-electron interaction, and going beyond the mean-field approximation of independent particles, might be essential to realistically describe the optical spectra of isolated $M@Si_n$ clusters, as well as their cluster-assembled materials.

1. INTRODUCTION

Electronic and structural properties of transition metal atoms encapsulated in cage-like silicon clusters have been extensively studied, due to the possibility of these systems being employed as building blocks for cluster-assembled semiconducting materials.¹⁻⁷ Early studies on the formation of these cluster-metal atom compounds in a supersonic molecular beam has been reported by Beck.⁸ From the technological viewpoint, as in the case of most cluster-assembled materials⁹, the cage-like silicon-metal nano-templates are expected to exhibit distinct optical properties from those of pure silicon clusters¹⁰ or metals. Currently, silicon is the chemical element which is most widely used in microelectronics. In turn, the incorporation of metal atoms into endohedral Si clusters stabilizes them and makes the corresponding condensed phases semiconductors feasible and efficient for several applications, such as light-emitting diodes, photovoltaic solar cells, thin-film transistors and other photoelectronic devices^{11,12}. Actually, these systems have been considered ideal candidates for the next generation of silicon-based nanoelectronics. The stability exhibited by endohedral Si cages, when their internal dangling bonds are recombined with *d* orbitals by the incorporation of a transition-metal atom (M) at its geometric center, as first shown by Hiura *et al.*¹³, is an important motivation for further studies dedicated to these systems.

Systematic studies about the dependency on size (number of silicon atoms, *n*) as well as on the transition metal element indicate that clusters with *n* = 7, 10, 12 exhibit high cohesive energies, independently of the metal species involved^{2,4}. In contrast to the emblematic clusters with twelve silicon atoms, which exhibit the characteristic conformation of a hexagonal prism (a cluster that, in its undistorted shape, belongs to the *D*_{6h} point group symmetry) for all M species, most of the other energetically favorable M@Si_{*n*} (*n* < 12) clusters do not exhibit any special symmetry.^{2,4,14} However, in their “as synthesized” form, many of the M@Si₁₂ clusters are slightly distorted from the ideal *D*_{6h} symmetry.¹³ More interestingly, the M@Si₁₂ clusters synthesized in the gas phase have been successfully deposited on Si-substrates.¹⁵ Also, as a stable Si-based alternative of the carbon nanotubes, nanowires with metallic properties built up from M@Si₁₂ clusters have been predicted.¹⁶

Another class of interesting M@Si_{*n*} systems, which has received special attention in the recent years, is that of the M@Si₁₆ clusters (M = Ti, Zr and Hf).¹⁷⁻¹⁸ Similarly to the case of M@Si₁₂, these systems have been considered as promising units for assembling optoelectronic devices.¹⁹⁻²⁰ The strong covalent bond between the metal-center (e.g., Ti, Zr and Hf) and the Si₁₆ cage leads to larger gaps, exhibiting absorption in the visible region.^{21,22} As widely accepted in the literature, these features of M@Si₁₆ emphasize their generally

higher stability when compared to $M@Si_{12}$,^{5,7,17-22} making $M@Si_{16}$ possibly more eligible than $M@Si_{12}$ for viable applications. Thus, the structural stability of these clusters is a significant advantage for possible applications of $M@Si_{16}$ in optical devices. Furthermore, the oligomerization of two fullerene-like $Zr@Si_{16}$ and two Frank-Kasper-like $Ti@Si_{16}$ clusters has demonstrated that the dimers keep the cage-structures of the clusters intact, which confirms the possibility of self-organized assemblies of these superatoms.²³

In general, one may expect that the silicon cage clusters doped with transition metal atoms also exhibit some similarities with endohedral fullerenes encapsulating metal atoms. Particularly, studies on the polarizability of these clusters may reveal a closer relationship with their photophysical properties. For instance, in the context of endohedral fullerenes, Sabirov and Bulgakov²⁴ have investigated the polarizability magnification attributed to the encapsulation effect. Also, interesting electronic properties of small alkali-based metallofullerenes, e.g., $M@C_{20}$, have been studied through ab initio methods.^{25,26} Recently, theoretical predictions of metallofullerenes containing transition metal atoms have indicated that their electronic and optical properties can be properly tuned.^{27,28} All these features also deserve to be carefully evaluated in the context of the silicon cage clusters containing transition metal atoms.

Although the stable and synthesizable metal-encapsulating Si clusters have been considered and discussed as potential candidates for optical nanodevices, their excited state properties have been scarcely addressed.²⁹ In contrast, the optical properties of silicon quantum dots,³⁰ silicon nanocrystals³¹ and small silicon clusters^{32,33} have been extensively described by using different levels of theory. These theoretical methods range from the independent-particle model up to more accurate approaches employed in the optical spectrum calculations, such as the *GW* approximation (GWA).³⁴ Hence, in addition to determining the ground-state properties of some important $M@Si_n$ clusters, within at a high level of theory, our main purpose here is to understand the role of many-body effects in the optical properties of these potential building blocks for cluster-assembled semiconducting materials.

In the present work, we report accurate results on the polarizabilities, absorption spectra, and quasiparticle band gaps of stable $M@Si_{12}$ ($M = Ti, Cr, Zr, Mo, Ru, Pd, Hf$, and Os) and $M@Si_{16}$ ($M = Ti, Zr$, and Hf) clusters, obtained from first-principles density-functional theory (DFT) calculations. Adopting a more sophisticated theoretical approach to realistically describe the quasiparticle (QP) spectra of different $M@Si_n$ systems, we have employed the many-body Green's function perturbation formalism within GWA. Starting from the local density approximation (LDA)³⁵ to DFT, the total energies have been

evaluated by employing the scheme based on the projector augmented wave basis sets³⁶ method. Our results are discussed here in comparison with the ground state properties of these systems (also calculated in this work), and compared to recent results for correlated systems obtained from the literature.

2 METHODOLOGY AND COMPUTATIONAL DETAILS

2.1. Gradient Optimizations and Ground-State Description. Geometry optimizations and electronic-structure calculations of the $M@Si_{12}$ ($M = Ti, Cr, Zr, Mo, Ru, Pd, Hf, \text{ and } Os$) and $M@Si_{16}$ ($M = Ti, Zr, \text{ and } Hf$) clusters were carried out by employing plane-wave DFT calculations, as implemented in the VASP code.³⁶⁻³⁸ The starting point geometries of $M@Si_{12}$ were considered within the D_{6h} symmetry and those of $M@Si_{16}$ were considered within the C_{3v} symmetry³⁹ (Frank-Kasper type structure). The exchange-correlation potential was approximated by the generalized gradient approximation (GGA), using the Perdew-Wang (PW91) scheme⁴⁰ with the full-potential projector augmented wave (PAW) method^{41,42} and 380 eV as plane wave cutoff. Hence, all cluster geometries were fully optimized at the PW91/PAW level of theory. For the gradient optimizations, an automatic mesh to sample only the Γ point of the Brillouin zone was employed. Cubic boxes with side of 15 Å for $M@Si_{12}$ and 20 Å for $M@Si_{16}$ were employed to avoid interactions with adjacent images. The atomic positions were optimized within 0.01 eV/Å for the atomic forces and the convergence criterion for the total electronic energy calculations was set to 10^{-5} eV. The choice of the VASP code to optimize the $M@Si_n$ clusters reported in this work was due to the high accuracy of the PAW method (especially when dealing with metal atoms and even when the atomic core wave functions are included⁴²). Furthermore, to evaluate spin effects on the electronic properties of these systems, spin-polarized calculations have been performed within this same level of theory.

2.2. Bader Charge Analysis, Finite Field Method and Random Phase Approximation. In order to characterize the electric properties of the $M@Si_n$ clusters, as well as to accurately predict their optical properties, we have calculated charge distributions, dipole moments, and static polarizabilities. This information is of great value for further experimental studies of such systems, as reported by Broyer *et al.*⁴³ in the context of other metal-cage clusters. The charge analysis was performed within the Bader method⁴⁴ considering a charge density grid in the VASP CHGCAR format. From this analysis, we have obtained the charge

transfer direction between the metal and silicon cage in each $M@Si_n$ cluster. The dipole moments and static polarizability tensors were calculated within the finite field method^{45,46} in the approximation of small electric fields applied in the three Cartesian directions. Furthermore, the dynamic polarizabilities were calculated within the random-phase approximation (RPA), as implemented in the VASP code, taking into account 300 bands in the frequency dependent polarizability, which was evaluated up to 10 eV. In this scheme, the frequency dependent dielectric matrix was calculated from the electronic ground state. The imaginary part was determined by a summation over empty Kohn-Sham states, while the real part of the dielectric tensor was obtained by the usual Kramers-Kronig transformation.^{37,38}

2.3. Quasiparticle Calculations within the Frequency-Dependent GW Approximation. The quasiparticle (QP) band gaps of the $M@Si_n$ cages were calculated starting from DFT calculations within LDA to obtain the Kohn-Sham (KS) eigenvalues and eigenvectors, which provide the independent-particle absorption spectrum. In this case, we have considered the same optimization criteria (with a plane wave kinetic energy cutoff of 340 eV) as described above. The treatment of semicore states in these calculations was considered, which is especially important in the cases of Ti and Ru. For the QP calculations, we have employed the frequency-dependent GW method within the PAW framework, as implemented in the VASP code.^{37,38,47} Using this approach, the vertex corrections were not taken into account and the self-energy Σ operator was reduced to a single direct product of one-particle Green's function G and the screened Coulomb interaction W . The iterative procedure constructs $\Sigma = iGW$ from the KS eigenvalues and eigenfunctions. To correct the band gap values obtained with LDA, we have started the calculations from a single shot G_0W_0 . Then, the set of QP shifts were iterated four times whereas the screened Coulomb potential W was fixed to the initial DFT W_0 , and only the eigenvalues for the one-particle Green's function were updated (usually called GW_0).^{47,48} As it is well known, fully self-consistent calculations deteriorate the QP spectrum and yield overestimated gaps.⁴² During the frequency-dependent GWA calculations, we have employed 300 bands, 80 frequency points, and an energy cutoff of 80 eV for the response function in the case of both $M@Si_{12}$ and $M@Si_{16}$ clusters. These criteria have been chosen in order to equally describe the electronic states of the systems.⁴⁹

3. RESULTS AND DISCUSSION

3.1. Structure, Electric and Magnetic Properties. As expected for all $M@Si_{12}$ clusters (see Fig. 1a), after geometry relaxation the Si–Si and M–Si bonds undergo specific distortions with respect to the symmetric cages, forming, thus, strongly bound covalent systems (see the values of relative distortion listed in Table 1). On average, the largest relative distortions with respect to the perfect D_{6h} symmetry were found for $Ti@Si_{12}$ (2.0%), $Pd@Si_{12}$ (3.4%), $Zr@Si_{12}$ (7.5%), and $Hf@Si_{12}$ (5.0%). These results agree with previous calculations,^{4,50} indicating that among all the $M@Si_{12}$ clusters studied here, those belonging to group-4 of the periodic table (Ti, Zr, Hf), together with Pd, give raise to the most distorted structures. Moreover, a rather distorted structure of $Ti@Si_{12}$ was found by He *et al.*²⁹ as its lowest-energy configuration, which is also in agreement with calculations conducted by Guo *et al.*⁵¹ The clusters belonging to group-6 were moderately distorted, i.e., $Cr@Si_{12}$ (0.9%) and $Mo@Si_{12}$ (0.5%), while the clusters of group-8, i.e., $Ru@Si_{12}$ and $Os@Si_{12}$ became almost perfectly symmetric. The average optimized Si–Si and M–Si bond lengths for these clusters are listed in Table 1. In general, these distances are in very good agreement with those obtained from calculations in other works.^{4,52}

Following the same optimization procedure discussed in the methodology section, we have obtained relaxed configurations of the $M@Si_{16}$ clusters ($M = Ti, Zr, \text{ and } Hf$). In these cases, the C_{3v} symmetry (Frank-Kasper type structure) has been used as starting point for the optimization procedure (see Fig. 1b). After relaxation, the initial atomic positions did not undergo significant displacements, maintaining the symmetric Frank-Kasper shape. This result is in good agreement with recent theoretical calculations by Reis and Pacheco.³⁹ They also reported the parameters characterizing the bond lengths as well as the bond angles of these three clusters (see Ref.³⁹). The $M@Si_{16}$ clusters have been successfully synthesized by experimental techniques such as laser ablation.¹⁹ and magnetron sputtering.⁵³ Additionally, vibrational spectra calculations⁷ have confirmed the remarkable and higher stability of the $M@Si_{16}$ cages than the stability of $M@Si_{12}$. In contrast to the $M@Si_{12}$ ($M = Ti, Zr, \text{ and } Hf$) clusters that, as mentioned above, possess significantly distorted equilibrium geometries, the corresponding $M@Si_{16}$ for the same metals belonging to group-4 exhibit more symmetric shapes. As we will discuss later, the higher stability of $M@Si_{16}$ also implies larger and more similar energy gaps (when these systems are compared among themselves) than in the case of the $M@Si_{12}$ clusters (again, when the systems are compared within their own class).

Considering now the calculated electric properties, among all the $M@Si_{12}$ clusters analyzed here, only $Zr@Si_{12}$, $Pd@Si_{12}$ and $Hf@Si_{12}$ exhibited appreciable dipole moments; i.e., 1.0, 1.2, and 0.8 D, as listed in Table 2. Interestingly, these clusters form the most distorted geometries in this series. As discussed by Wang and Han,⁵⁰ the dipole moment of

these clusters is generally related to symmetry breaking of the perfect geometry. In agreement with this assumption, our calculated dipole moment of Zr@Si_{12} (the most distorted structure) is 1.002 D, which is consistent with the corresponding values (1.021 D) calculated in Ref.⁵⁰. Accordingly also, all the M@Si_{16} clusters (the least distorted structures) exhibit small dipole moments of order of 0.1 D. Note that the existence of a dipole moment in some of these clusters may be a useful feature to characterize specific clusters in the presence of an external electric field. To evaluate the amount of charge transfer (CT) between the transition metal atoms and silicon cages we have employed the Bader analysis (see Table 2). Indeed, CT is strongly dependent on the method employed to estimate the charge distribution, as well as the size and shape of the cluster, as it has long been discussed in the literature.^{50,54,55,56} However, the amount of CT is useful to understand the bonding character of the clusters. As can be seen in Table 2, the interaction between the transition metal and the Si_n cage is characterized by substantial ionic admixtures due to CT between the two cluster subsystems (transition metal atom and silicon cage).

As a complement to the calculation of the dipole moment for these systems, we have also calculated their dipole polarizability, which is a valuable molecular electric property for understanding the linear optical response. Furthermore, the polarizability is closely related to the size, shape, and electronic structure of the clusters.²⁹ Table 2 displays the calculated mean polarizabilities^{45,46} for all the systems studied here. Our results, as calculated within the finite field method at the PW91/PAW level of theory, have indicated that for M@Si_{12} the mean polarizabilities preserve an approximate relationship with the atomic size of each encapsulated transition metal element. For example, Ti@Si_{12} , Cr@Si_{12} , and Pd@Si_{12} (in which each one of the metal atoms has similar Slater atomic radius of 140 pm) give mean polarizabilities of 396.20, 373.57, and 398.95 a.u., respectively. Obeying this relation, Zr@Si_{12} (Zr atomic radius is of 185 pm) and Hf@Si_{12} (Hf atomic radius is of 155 pm) give mean polarizabilities of 418.72 and 415.23 a.u., respectively. In contrast, for the M@Si_{16} clusters such a dependence of the polarizability on the size of the encapsulated metal atom is not observed; i.e., the calculated mean polarizabilities are almost constant regardless the metal atom involved (see Table 2). This analysis shows that for larger clusters, such as M@Si_{16} , the mean polarizability depends much more on the volume of the silicon cage. A similar behavior for the polarizability was found by Sabirov and Bulgakov²⁴ for distinct endofullerenes. For example, considering a C_{20} cage, the mean polarizability of the endofullerene increased with the increasing size of the encapsulated atom, whereas in the case of C_{60} , the polarizability was essentially constant, regardless of the size of the encapsulated atom.²⁴

In addition to the electric properties, we can analyze the caging effects on the magnetic moment of the transition metals by means of spin-polarized DFT calculations. Because of their ground state electron configurations, most of the transition metal atoms considered here exhibit net spin polarization when isolated. For example, the calculated magnetic moments of the Ti, Zr and Hf atoms belonging to group-4 are 3.1, 2.0 and 2.0 μ_B , respectively. For both Cr and Mo (group-6), the magnetic moment is 6.0 μ_B ; for both Ru and Os (group-8), the magnetic moment is 4.0 μ_B ; and for Pd (group-10), the magnetic moment vanishes, as can be expected for its closed-shell electronic structure. Within the context of the caging effects introduced by the Si atoms, it is interesting to analyze the magnetic moments of these transition metals when encapsulated by the silicon cages (see Table 3). Upon formation of the $M@Si_n$ clusters, their magnetic moments are completely quenched (except in the case of $Ti@Si_{12}$ that still retains a magnetic moment of 2.0 μ_B). These results confirm that the Si cages significantly reduce or entirely cancel the intrinsic magnetic moment of the corresponding transition metal atoms.^{3,57,58} In the case of $Ti@Si_{12}$, our spin-polarized calculations have predicted the system is a spin triplet. As pointed out by Sen and Mitas⁵⁹ and also by Guo *et al.*⁶⁰, the spin triplet ground state of the cluster has a total energy lower than its singlet state. However, He *et al.*²⁹ have found a distorted spin singlet structure of $Ti@Si_{12}$ with a total energy lower than the triplet state. In addition, we have found that the magnetic moment of the Si-encapsulated Ti atom is completely quenched when the size of its Si cage increases, as obtained in the case of $Ti@Si_{16}$. This may be explained by a stronger hybridization between Ti 3d and Si 3p states in the $Ti@Si_{16}$ than in the distorted $Ti@Si_{12}$ cluster.

3.2 Electronic States and Optical Absorption. Here, as a first estimate of the absorption gaps of these systems, we have calculated the difference between the KS eigenvalues of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of their ground-state electronic structure. The values that we have obtained for the HOMO-LUMO gaps are listed in Table 3. These independent-particle gaps are in agreement with previous DFT calculations.^{2,56} In Figures 2 and 3, we display the calculated density of states (DOS) for the $M@Si_{12}$ clusters. In order to understand the distorting effect on the electronic structure of these systems, we have separated the DOS of the most distorted clusters in Figure 2, while the DOS of the less distorted clusters are displayed in Figure 3. The charge densities of the frontier orbitals of the clusters are also displayed in their respective DOS. $Ti@Si_{12}$, $Zr@Si_{12}$, and $Hf@Si_{12}$ exhibit HOMOs that are less symmetric and more distributed, from the metal to the silicon bonds, than the charge densities of other

more symmetric $M@Si_{12}$ clusters (see Figure 2). Regarding the LUMOs of $Ti@Si_{12}$, $Zr@Si_{12}$, and $Hf@Si_{12}$, a significant delocalization over the silicon bonds is observed; only $Ti@Si_{12}$'s LUMO exhibits an additional density around the metal-center, leading to possible low-lying transitions mostly located at this site. In the case of $Pd@Si_{12}$, which is another cluster exhibiting a large distortion, the HOMO and LUMO are more similar among themselves, which allows low-lying transitions in this system. This feature may be responsible for the small HOMO-LUMO gap calculated for this cluster (Table 3).

The more symmetric clusters $Cr@Si_{12}$ and $Mo@Si_{12}$ exhibit HOMO charge densities that are less localized at the metal-center, whereas their LUMOs are highly localized at the metal. In the particular case of $Mo@Si_{12}$, the electronic transitions should occur from an orbital of Si to an orbital of the metal, leading to a large energy gap value. Indeed, as listed in Table 3, this system exhibits the largest HOMO-LUMO gap of all the $M@Si_{12}$ clusters investigated here. This has also been confirmed by experimental measurements of the optical gap (1.05 eV) of the $Mo@Si_{12}$ film, made possible by the fact that $Mo@Si_{12}$ is one of the clusters which has been synthesized and successfully deposited as an amorphous film onto silica substrates by Uchida and coworkers.⁶¹ In agreement with these results, also Sen and Mitas⁴⁷ have calculated a large HOMO-LUMO gap for $Mo@Si_{12}$ (singlet state) by employing DFT schemes. Among all the $M@Si_{12}$ systems considered in the present study, only $Ru@Si_{12}$ and $Os@Si_{12}$ exhibit HOMOs more definitely localized at the metal center and LUMOs delocalized towards the silicon bonds, indicating possible specific metal-silicon electronic transitions.

In Figure 4, the DOS and the charge densities near the Fermi level of the $M@Si_{16}$ ($M = Ti, Zr, \text{ and } Hf$) systems are displayed. As discussed above, these systems maintain their stable Frank-Kasper shape, in contrast to the corresponding $M@Si_{12}$ which undergo large structural distortions. In fact, when the number of silicon atoms around the transition metal atom increases, the energy gaps of the clusters become enlarged, as reported in Table 3. As displayed in Figure 3, the HOMO charge densities of the $M@Si_{16}$ are much more localized at the metal center, exhibiting a d_{z^2} -like charge density typical for the transition metal atoms belonging to group-4. In general, the LUMOs of these systems are delocalized at the silicon atoms, allowing electronic transitions from an orbital belonging to the metal to an orbital of Si. The major difference in the electronic structure of these clusters occurs in the case of $Ti@Si_{16}$, for which the LUMO also exhibits an appreciable charge density at the metal atom, which may give rise to $d-d$ intrashell transitions. Such a behavior is also present for $Ti@Si_{12}$ which was discussed above. Because of the stability and characteristic features of the frontier orbitals of the $M@Si_{16}$ clusters, their HOMO-LUMO gaps are more similar

among themselves, with energies at the 2.35–2.58 eV range. These values are in good agreement with the previous calculations by Reis and Pacheco.³⁹

From the KS electronic states and within the RPA method, the optical absorption spectra of the $M@Si_n$ clusters were simulated in the 0-10 eV range (which includes the UV-visible region), as displayed in Figures 5-7. The calculated spectra for the less symmetric $M@Si_{12}$ clusters (i.e., those including Ti, Zr, Hf, and Pd) are displayed in Figure 5. As can be seen, these spectra exhibit small absorptions at energies between 0.5 and 2 eV, while relatively intense absorptions appear between 2 and 4 eV. When compared to some available data in other works²⁹, our results for $Ti@Si_{12}$ are in a reasonable agreement, although we also determine here a far absorption region at higher energies (between 4 and 8 eV). Similarly, we have found intense absorption regions between 4 and 8 eV for $Zr@Si_{12}$, $Hf@Si_{12}$, and $Pd@Si_{12}$. Figure 6 displays the calculated spectra for the more symmetric $M@Si_{12}$ clusters (i.e., those encapsulating Cr, Mo, Ru, and Os). The spectra of these systems exhibit absorptions starting from approximately at 2 eV, featuring reduced absorptions at 4 eV, while exhibiting more intense absorption between 4 and 8 eV. Finally, considering the absorption spectra of the $M@Si_{16}$ clusters (Figure 7), we stress that their absorption profiles are typically more concentrated at the energies between 2 and 6 eV. As discussed above, this is a result of the band gap enlargement in the larger $M@Si_{16}$ clusters.

Despite the qualitative interpretation of the probability densities of the frontier KS orbitals and the features of the absorption spectra calculated within the RPA for $M@Si_n$ clusters, it is well known that the independent-particle energy gap is only a first estimate of the excitation energies. Of course, it is difficult to address the effect of electronic excitations in the optical gaps of such complex systems by employing effective single particle DFT orbitals; especially because most correlation density functionals are designed specifically for the electronic ground state. Following this line of arguments, below we report more accurate estimates for the absorption gaps of the $M@Si_n$ clusters calculated by correcting the KS energies through the *GW* approximation.

3.3. Quasiparticle Band Gaps within GW_0 . As a more accurate method to calculate the absorption gaps of these clusters, we have adopted the *GW* approximation. To describe the optical gaps of the $M@Si_n$ cages, we have considered the frequency-dependent scheme based on the PAW basis sets up to the GW_0 level of approximation. An advantage of this method is that it allows treating *d* and *f* orbitals with a relatively modest computational effort. The corrected HOMO-LUMO gaps within the GWA are reported in Table 3 for all the $M@Si_n$ clusters. In Figure 8, we display the DFT and GW_0 gaps as a function of the

atomic number of the encapsulated transition element. It is noteworthy that the GW_0 calculations widen the energy gap independently of the spatial distortion of the cluster and the atomic number of the metal atom in the cluster center. Actually, the GWA provides systematically larger values for the HOMO-LUMO gaps of all these systems.

In the case of Ti@Si_{12} , Zr@Si_{12} , and Hf@Si_{12} , the GW_0 gaps are increased by 3.05, 2.78, and 3.15 eV, respectively, when compared to the corresponding DFT/GGA values. For the next group, Cr@Si_{12} and Mo@Si_{12} , the increase is of 3.11 and 3.46 eV, respectively, whereas for Ru@Si_{12} and Os@Si_{12} the increase is of 3.23 and 2.84 eV, respectively. For Pd@Si_{12} this increase is of 2.32 eV, while its HOMO-LUMO gap is strongly underestimated via DFT calculations (0.13 eV with GGA, as discussed in the previous section). Among all M@Si_{12} clusters considered here, after corrections at the GWA level, Pd@Si_{12} underwent the largest relative gap variation with respect to its DFT value. In turn, the smallest relative gap variation due to the inclusion of many-body effects was observed for Ru@Si_{12} . This increase is clearer in Figure 8, where we plot the energy gap as a function of the atomic number of the transition-metal center in each M@Si_{12} cluster.

At this point, it is also instructive to consider the size and many-body effects on the energy gap increase for the M@Si_{16} systems. In general, the GWA corrections lead to increased HOMO-LUMO gaps of these systems. As listed in Table 3, the increment in the GWA gaps of the M@Si_{16} clusters is of 2.76–3.32 eV from the corresponding GGA values. Notice that such increment range was similar to the calculated for the corresponding M@Si_{12} systems. However, it is also possible here to notice the size effect in the energy gaps of these systems. For example, whereas the GGA gaps of Ti@Si_{12} , Zr@Si_{12} , and Hf@Si_{12} were respectively 0.74, 0.78, and 0.82 eV, they increase by an amount of approximately 1.5 eV (see Table 3) for the corresponding M@Si_{16} , i.e., Ti@Si_{16} , Zr@Si_{16} , and Hf@Si_{16} . This already implies a formation of semiconducting clusters with larger gaps. If the GW_0 corrections to the DFT gaps of M@Si_{16} are taken into account, their energy gaps increase further by 2.76, 3.32, and 3.15 eV, respectively, thus becoming 4.99, 5.64, and 5.48 eV, respectively. Only in the case of Hf@Si_{16} , we have found an energy gap increment due to the GW_0 correction, which is of the same magnitude as that calculated for Hf@Si_{12} . However, for Zr@Si_{16} there is a relative increase in the gap variation (due to the GW_0 correction) of 20%, compared to Zr@Si_{12} . On the contrary, for Ti@Si_{16} there is a reduction of 15% in the relative increase of the gap variation (due to the GW_0 correction), as compared to Ti@Si_{12} . This effect is, however, expected due to mainly distinct QP effects in each group.

The differences in the magnitude of the QP corrections for all these systems reveal subtle differences in the nature of their optical gaps. In Table 4, we provide the specific corrections to the HOMO and LUMO energy levels calculated with LDA. The corrected results for the HOMO-LUMO gaps can be better understood by analyzing explicitly the *GW* corrections to the KS energy levels, i.e., $\Delta\epsilon_n^{\text{QP}} = \Delta\langle n | \Sigma - V_{xc}^{\text{DFT}} | n \rangle$. In fact, the calculation of the screened Coulomb interaction for the M@Si_n clusters depends strongly on the type of the encapsulated metal. One may expect that if the spatial distribution of an occupied orbital is modified for each cluster, the region of strong screening would be also changed in the same direction. Thus, taking into account the spatial geometry of the Si cages in these clusters, the *GW* corrections should be relatively stable with respect to changing the silicon distribution around the metal-center for each cluster. However, because of the distinct behavior of the electronic structure of each encapsulated transition metal and the specific hybridization between orbitals of *M* and Si, such regularity is not observed in the case of the M@Si_n clusters.

This effect can be clarified if the difference between the LDA and *GW* energies, i.e., $\Delta GW = \epsilon_n^{\text{QP}} - \epsilon_n^{\text{DFT}}$ is analyzed. In Table 4, we list the *GW* corrections to the HOMO, LUMO, and ΔGW . As can be seen, there are appreciable changes in these quantities depending on the cluster examined. For example, whereas ΔGW HOMO in Ti@Si_{12} and Ti@Si_{16} are essentially of the same magnitude (−0.20 and −0.23 eV, respectively), in the case of Zr@Si_{12} ΔGW HOMO reads −0.64 eV, while in the case of Zr@Si_{16} this quantity is −0.29 eV. These variations indicate that the number of encapsulating Si atoms may dramatically affect a specific energy level for a given metal-center in the cluster. For this reason, generally, it should not be expected a similar absorption pattern in the optical spectra of different-size clusters encapsulating the same metal. In this sense, the optical properties of the M@Si_n clusters are dominated by many-body effects.

4. CONCLUSIONS

In the present work, we have theoretically determined reference values for the static dipole polarizabilities and optical linear response of M@Si_{12} (*M* = Ti, Cr, Zr, Mo, Ru, Pd, Hf, and Os) and M@Si_{16} (*M* = Ti, Zr, and Hf) clusters, within *ab initio* plane-wave DFT calculations. The calculations of the optical gaps were performed by employing the frequency-dependent *GW* approximation as a post-DFT scheme. This level of theory allows the treatment of *d* and *f* orbitals of the M@Si_n clusters with a relatively low computational

cost. The semicore states of the transition-metal atoms were also considered in the GWA. It is well-known that the electronic properties calculated at this level of theory ensure better accuracy of the predicted static screening properties if the local-density approximation is used. Our results demonstrate that including the QP effects in the one-electron Green's function results in higher energies than the density-functional one-electron energies, even when taking into account the screening properties within DFT approximations. Therefore, the *GW* corrections predict that Ti@Si_{12} , Cr@Si_{12} , Zr@Si_{12} , Mo@Si_{12} , Ru@Si_{12} , Pd@Si_{12} , Hf@Si_{12} , and Os@Si_{12} are semiconducting clusters exhibiting large energy gaps.

Caging effects on the electronic properties were also examined for these clusters. Our results have indicated that for M@Si_{12} the mean polarizabilities preserve an approximate relationship with the atomic size of each encapsulated transition metal element. In contrast, for M@Si_{16} such a dependence of the polarizability on the size of the encapsulated metal atom was not observed. This analysis shows that for larger clusters, such as M@Si_{16} , the mean polarizability depends much more on the volume of the silicon cage. As a consequence of the increased electronic stability of M@Si_{16} , their HOMO-LUMO gaps are more similar among themselves than the corresponding gaps in M@Si_{12} . Also, the increase of the polarizability for the largest clusters, such as Ti@Si_{16} , Zr@Si_{16} , and Hf@Si_{16} , leads to an additional increase in their QP energy gaps by 1.20, 2.08, and 1.51 eV, respectively, as compared to the corresponding values of M@Si_{12} . These results for the gas-phase M@Si_{12} and M@Si_{16} nano-templates suggest that extended phases assembled upon them may possibly form semiconductor films with tunable optical properties, which may find applications in a new generation of optoelectronic nanodevices.

ASSOCIATED CONTENT

Supporting Information

Additional information on the optimized geometries of the clusters is provided in a separate document. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Tables

Table 1. Average Bond Lengths (in Å) and Relative Distortion (in %) Calculated for the M@Si₁₂ Clusters.

System	Si-Si ^a	Si-Si ^b	M-Si	Distortion ^c
Ti@Si ₁₂	2.40	2.41	2.68	2.0
Cr@Si ₁₂	2.33	2.37	2.61	0.9
Zr@Si ₁₂	2.74	2.40	2.86	7.5
Mo@Si ₁₂	2.37	2.40	2.66	0.5
Ru@Si ₁₂	2.35	2.38	2.63	0.02
Pd@Si ₁₂	2.42	2.36	2.62	3.4
Hf@Si ₁₂	2.58	2.41	2.78	5.0
Os@Si ₁₂	2.35	2.38	2.63	0.02

^a Si-Si bond lengths within the hexagonal planes; ^b Inter-hexagonal Si-Si bond lengths. ^c Average relative distortion with respect to the perfect *D*_{6h} symmetry.

Table 2. Dipole moments (in D), Mean Polarizability (in a.u.), and Charge Transfer (in |e|) Calculated for the M@Si_n Clusters.

System	Dipole moment	Mean polarizability	Charge transfer ^a
Ti@Si ₁₂	0.000	396.20	-1.203
Cr@Si ₁₂	0.000	373.57	-0.487
Zr@Si ₁₂	1.002	418.72	-1.207
Mo@Si ₁₂	0.002	381.79	-0.343
Ru@Si ₁₂	0.005	376.38	0.451
Pd@Si ₁₂	1.199	398.95	0.533
Hf@Si ₁₂	0.844	415.23	-1.241
Os@Si ₁₂	0.000	375.58	0.789
Ti@Si ₁₆	0.097	458.51	-1.141
Zr@Si ₁₆	0.149	455.47	-1.103
Hf@Si ₁₆	0.132	453.32	-1.120

^a Negative signs indicate electron transfer from the transition metal to the silicon cage.

Table 3. GGA HOMO-LUMO Gaps, QP-Corrected Gaps (in eV), and Spin Effect (in μ_B) Calculated for the $M@Si_n$ Clusters.

System	GGA gap	GW_0 gap	Magnetic moment
Ti@Si ₁₂	0.74	3.79	2.0
Cr@Si ₁₂	0.86	3.97	0.0
Zr@Si ₁₂	0.78	3.56	0.0
Mo@Si ₁₂	1.04	4.50	0.0
Ru@Si ₁₂	1.00	4.23	0.0
Pd@Si ₁₂	0.13	2.45	0.0
Hf@Si ₁₂	0.82	3.97	0.0
Os@Si ₁₂	0.92	3.76	0.0
Ti@Si ₁₆	2.23	4.99	0.0
Zr@Si ₁₆	2.32	5.64	0.0
Hf@Si ₁₆	2.33	5.48	0.0

Table 4. GWA Corrections to the HOMO and LUMO Energy Levels and to the LDA Electronic Gaps (in eV) for the $M@Si_n$ Clusters.

System	LDA gap	ΔGW HOMO	ΔGW LUMO	ΔGW gap
Ti@Si ₁₂	0.77	-0.20	2.81	3.02
Cr@Si ₁₂	0.79	-0.43	2.75	3.18
Zr@Si ₁₂	0.75	-0.64	2.16	2.81
Mo@Si ₁₂	0.99	-0.55	2.96	3.51
Ru@Si ₁₂	1.04	-0.13	3.06	3.20
Pd@Si ₁₂	0.12	-0.53	1.80	2.34
Hf@Si ₁₂	0.85	-0.55	2.57	3.12
Os@Si ₁₂	0.93	-0.48	2.34	2.82
Ti@Si ₁₆	2.36	-0.23	2.70	2.93
Zr@Si ₁₆	2.43	-0.29	2.90	3.20
Hf@Si ₁₆	2.43	-0.21	2.83	3.05

Figure Captions

Figure 1. (a) The hexagonal cage-like prism shape (D_{6h}) of the $M@Si_{12}$ clusters. (b) The Frank-Kasper type structure (C_{3v}) of the $M@Si_{16}$ clusters.

Figure 2. Density of states (DOS) of $Ti@Si_{12}$, $Zr@Si_{12}$, $Hf@Si_{12}$, and $Pd@Si_{12}$. Isosurfaces of the probability densities for the Kohn-Sham eigenstates near the Fermi level calculated at the Gpoint are displayed on the DOS.

Figure 3. Density of states (DOS) of $Cr@Si_{12}$, $Mo@Si_{12}$, $Ru@Si_{12}$, and $Os@Si_{12}$. Isosurfaces of the probability densities for the Kohn-Sham eigenstates near the Fermi level calculated at the Gpoint are displayed on the DOS.

Figure 4. Density of states (DOS) of $Ti@Si_{16}$, $Zr@Si_{16}$, and $Hf@Si_{16}$. Isosurfaces of the probability densities for the Kohn-Sham eigenstates near the Fermi level calculated at the Gpoint are displayed on the DOS.

Figure 5. Absorption spectra of $Ti@Si_{12}$, $Zr@Si_{12}$, $Hf@Si_{12}$, and $Pd@Si_{12}$, calculated within RPA. Dynamic polarizabilities are given in arbitrary units.

Figure 6. Absorption spectra of $Cr@Si_{12}$, $Mo@Si_{12}$, $Ru@Si_{12}$, and $Os@Si_{12}$, calculated within RPA. Dynamic polarizabilities are given in arbitrary units.

Figure 7. Absorption spectra of $Ti@Si_{16}$, $Zr@Si_{16}$, and $Hf@Si_{16}$, calculated within RPA. Dynamic polarizabilities are given in arbitrary units.

Figure 8. Energy gap variation as a function of the atomic number (Z) of the transition-metal center in each $M@Si_{12}$ cluster. Blue circles correspond to DFT and black triangles correspond to GW_0 .

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

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