

# Properties of hydrogen terminated silicon nanocrystals via a transferable tight-binding Hamiltonian, based on *ab-initio* results

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**Abstract** Tight-binding transferable parameters are created to reproduce *ab initio* energies of hydrogen-terminated Si-nanocrystals in order to extend the study of electronic and 0th order optical properties, through the HOMO–LUMO energy gap, to other larger or less symmetric silicon nanocrystals. For practical reasons the study is restricted to clusters where each Si atom has either three or no H neighbors. Results obtained so far are promising for future improvements and extensions to other systems.

**Keywords** Transferable tight-binding · Silicon nanocrystals · Si-nanoparticles · *Ab-initio* electronic properties

## 1 The scope

Accurate high-level *ab initio* calculations offer a very realistic description of the electronic and optical properties of silicon nanocrystals with diameters up to about 2.5 nm [1–3]. However, for larger sizes, which are usually the sizes suitable for most of the technological applications, calculations of this type are practically impossible with the present day computers. The common compromise for such cases is the use of phenomenological (empirical or semi-empirical) calculations such as tight-binding (TB) calculations with transferable adjustable parameters, which we use in this work. The underlying concept of the TB parameter transferability is that the total energy and

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eigenvalues, obtained by an accurate *ab-initio* method, can be adequately reproduced and also extrapolated to nearby stereochemical structures, within a non-orthogonal LCAO—or tight-binding—formalism, by appropriately fitting the TB Hamiltonian and overlap matrix elements, as integrals between non-orthogonal atomic orbitals. However, since, in order to reproduce the accurate *ab-initio* energy, only the values of the integrals are needed (fitted), the actual atomic orbitals are never used, making the TB description (after a successful fit) about three orders of magnitude faster than the *ab-initio* calculation with full orbital consideration. Of course, the Hamiltonian depends on the size of the cluster, and, for different structures, the values of the integrals depend on the bond length and on the angles, and, since the orbital functions should be the same in all similar atoms, their integrals also depend on the kind of the atoms forming the bond. The angle dependence has been known since the work of Slater and Koster [4]. For the bond-length dependence we use the polynomials (enveloped by exponential tails), introduced by Papaconstantopoulos et al. (cf. Ref. [5] and references therein) whose coefficients (and exponents) are treated as adjustable parameters, the so-called NRL parameters. Thus, for example, all Si–Si bond matrix elements are described with the same functions of the internuclear distance and bond angles, i.e., they depend on the local environment, independently of where in the cluster, how often, and in how large cluster, this environment occurs. Thus these parameters are transferable in the sense that, if successfully determined (fitted) from a local environment of a small cluster, they should in principle describe equally well the same environment in larger clusters as well (without fitting to a larger *ab initio* calculation). Since all electronic properties can be described in terms of the Hamiltonian, these parameters (describing energy and overlap matrix elements) are usually fitted to reproduce large scale band structure calculations for the corresponding infinite crystals and/or experimentally measured bulk properties. As has been explained elsewhere [1–3], fitting to bulk values is the larger source of error for small-size nanocrystal calculations, leading to significantly erroneous energy gap, due to the effects of quantum confinement. Therefore, in order to bridge the gap between zero (quantum dots) and infinite dimension nanocrystals, we have employed a transferable tight-binding Hamiltonian [5], which has been applied before (for a different system) very successfully [6–8].

The matrix elements of this transferable tight-binding Hamiltonian have been fitted to accurate high level density functional results for nanocrystals with diameters up to 2.5 nm [1–3,9].

## 2 Methodology

The transferable Tight-binding method was originally used as an energy interpolative scheme for solids [5], by fitting the energy of a collection of *ab initio* results, but since it primarily utilizes a (parametrized) Hamiltonian matrix, it can be also used to predict other relevant properties, not used in the fit, like surface energy, vacancy formation, thermal expansion, also lowest energy formation path and normal mode frequencies [6–8], optical properties (present work), etc. For this reason it should be rather considered as a reformulation of *ab initio* results in the tight binding language (rather than a specific energy interpolation method).

The tight binding Hamiltonian matrix elements are formed between on-site and/or neighboring  $s$ ,  $p$  and  $d$  orbitals for Si, and  $s$  orbitals for H. If  $\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \dots$  represent nuclear positions,  $\mathbf{r}$  represents the position of an electron,  $R$  represents an internuclear distance, e.g.,  $|\mathbf{X}_1 - \mathbf{X}_2|$ ,  $V(\mathbf{r} - \mathbf{X}_1)$  represents the electronic potential centered at  $\mathbf{X}_1$ , and  $\Psi(\mathbf{r} - \mathbf{X}_1)$  represents an atomic orbital centered at  $\mathbf{X}_1$ , then three-center integrals of the forms:

$$\begin{aligned} &< \Psi(\mathbf{r} - \mathbf{X}_1) | V(\mathbf{r} - \mathbf{X}_2) | \Psi_0(\mathbf{r} - \mathbf{X}_3) >, \\ &< \Psi(\mathbf{r} - \mathbf{X}_1) | V(\mathbf{r} - \mathbf{X}_2) | \Psi_0(\mathbf{r} - \mathbf{X}_1) >, \end{aligned}$$

are omitted, while the on-site and the hopping matrix elements, used, are of the form:

$$\begin{aligned} &< \Psi(\mathbf{r} - \mathbf{X}_1) | V(\mathbf{r} - \mathbf{X}_1) | \Psi_0(\mathbf{r} - \mathbf{X}_1) >, \\ &< \Psi(\mathbf{r} - \mathbf{X}_1) | V(\mathbf{r} - \mathbf{X}_1) | \Psi_0(\mathbf{r} - \mathbf{X}_2) >, \end{aligned}$$

respectively.

The hopping and overlap integrals are expressed as functions of the internuclear angles [4] and of the internuclear distance  $R$  [5–8] (usually extended to more than the first nearest neighbors): e.g.,

$$sp\sigma(R) = (R - a)(R - b)(R - c)e^{-ZR},$$

where  $a, b, c, Z$ , are the transferable (geometry independent—or bond-length dependent) adjustable parameters. Similar functions are used for all kinds of bonds,  $ss\sigma$ ,  $pp\sigma$ ,  $pp\pi$ , etc. with different values of  $a, b, c, Z$ , for each kind of bond. The on-site integrals, also expressed as functions of the neighboring atom distances, depend on the local environment. Further details are given in Refs. [5–8].

Since such functions are independent of any specific stereo-chemical structure, the adjustable parameters  $a, b, c, Z$ , are, in principle, transferable to any structure of the same material, i.e., to any intermediate or larger cluster. They are determined by a least square fit of the eigenvalues and total energy of a small collection of ab-initio results, serving as a data-base.

The ab-initio total energy of an  $N_e$  electron system is rigorously reduced to a simple sum of eigenvalues, suitable to tight-binding formalism, by absorbing the exchange and correlation energy  $F[n(r)]$ , known for each cluster in the ab-initio data-base collection, via a corresponding energy shift,  $F[n(r)]/N_e$ : If  $n(r)$  is the electronic density,  $E$  is the total energy,  $\varepsilon_i$  are the eigenvalues,  $\mu$  is the chemical potential (Fermi level, or HOMO level), and  $f[(\mu - \varepsilon)/T]$  is the Fermi (step) function with some temperature broadening  $T$ , then

$$\begin{aligned} E[n(r)] &= \sum_i \varepsilon_i f\left(\frac{\mu - \varepsilon_i}{T}\right) + F[n(r)] \sum_i f\left(\frac{\mu - \varepsilon_i}{T}\right) / N_e \\ &= \sum_i \left(\varepsilon_i + \frac{F[n(r)]}{N_e}\right) f\left(\frac{\left(\mu + \frac{F[n(r)]}{N_e}\right) - \left(\varepsilon_i + \frac{F[n(r)]}{N_e}\right)}{T}\right). \end{aligned}$$

Thus, the total energy can be treated as an independent particle problem:

$$E[n(r)] = \sum_i \tilde{\epsilon}_i f\left(\frac{\tilde{\mu} - \tilde{\epsilon}_i}{T}\right) = \sum_{i \in \text{core}} \tilde{\epsilon}_i + \sum_{i \in \text{valence}} \tilde{\epsilon}_i,$$

where  $N_e = \sum_i f\left(\frac{\mu - \epsilon_i}{T}\right)$  is the number of electrons and  $\tilde{\epsilon}_i = \epsilon_i + \frac{F[n(r)]}{N_e}$  are (fictitious independent-particle) shifted eigenvalues—to be fitted, thus avoiding the parametrization of the exchange and correlation energy  $F[n(r)]$ .

Since the TB Hamiltonian essentially describes bonds, the core levels are not fitted; only the valence levels, as well as the unoccupied states (which are known, but do not contribute to the total energy) are fitted by the TB Hamiltonian, allowing, in subsequent prediction, the computation of the HOMO–LUMO difference, relevant to the electronic and 0th order optical properties of other desired clusters.

### 3 Results

Despite the large difference in the size of the nanoparticles, indicated by the number of electrons in Table 1, the valence energy is fitted by the TB Hamiltonian, since it refers to the valence, and not the core, orbitals. Orthogonal orbitals were assumed in this fit, including only silicon nanocrystals with sizes ranging from 5 to 71 silicon atoms, in order to test the extrapolation of the model to larger nanocrystals. This extrapolation, although satisfactory up to a point, is not considered completely satisfactory.

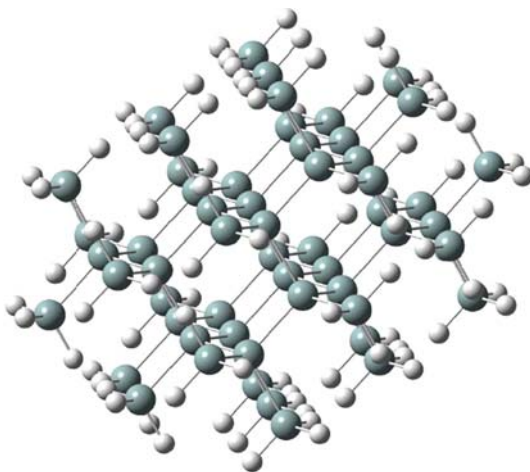
Conventional mathematical interpolation among clusters of significantly different sizes is obviously impossible. Tight-binding fitting of clusters of significantly different sizes is attempted here for the first time, the wide energy diversity being countered rigorously by the energy shift, and by focusing to the fit of the valence s and p eigenvalues; otherwise, energies ranging from 1,453 to 20,595 Hartree (Hy) cannot be fitted simultaneously. Fitting all of the above clusters was proven extremely time consuming, demanding large parallel computers that we do not possess. (In a Pentium-4 at 3 GHz 1 week of CPU time is needed for a single Tight-binding parameter optimization.)

Although it is impossible for us to perform a full parameter exhaustive search for the global minimum of the least square fit for all clusters, we suspect that the reason

**Table 1** Six DFT B3LYP-equilibrium H-terminated Si clusters of very different size and energy, transferably fitted by a Tight-binding Hamiltonian (in Hartree)

Structure	Number of valence electrons	Ab initio total energy	Ab initio valence energy	Fitted TB Hamiltonian
Si <sub>5</sub> – H <sub>12</sub>	32.000	–1,453.99	–253.92	–253.85
Si <sub>17</sub> – H <sub>36</sub>	104.00	–4,940.72	–838.40	–838.44
Si <sub>29</sub> – H <sub>36</sub>	152.00	–8,413.40	–1,290.3	–1,290.4
Si <sub>35</sub> – H <sub>36</sub>	176.00	–10,149.8	–1,513.7	–1,513.7
Si <sub>47</sub> – H <sub>60</sub>	248.00	–13,636.5	–2,100.7	–2,100.8
Si <sub>71</sub> – H <sub>84</sub>	368.00	–20,595.9	–3,134.8	–3,134.7

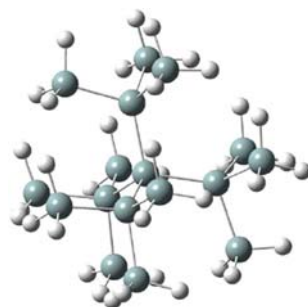
**Fig. 1** A  $\text{Si}_{26}\text{Si}_{30}\text{H}_{90}$  cluster.  
(A non-spherically shaped  
nanostructure)



of the aforementioned fit inaccuracy is that, computationally four kinds of Si atoms exists in these clusters, those binding with 0, 1, 2, and 3 H atoms, and that different tight binding parameters are needed for each kind. Thus, as a first choice, subsequently we concentrate in the study of clusters  $\text{SiSi}_4\text{H}_{12}$ ,  $\text{Si}_2\text{Si}_6\text{H}_{18}$ , (small size),  $\text{Si}_5\text{Si}_{12}\text{H}_{36}$ , (medium size), and  $\text{Si}_{26}\text{Si}_{30}\text{H}_{90}$ , (large), in all of which the Si atoms bind with either 0 or 3 H atoms. The atoms of the 1st and 3rd clusters above are spherically distributed around the center (in Td symmetry) whereas in the 2nd and 4th they are not.  $\text{Si}_{26}\text{Si}_{30}\text{H}_{90}$  is shown in Fig. 1. The first three belong to the linear-chain cluster family  $\text{Si}_n(\text{SiH}_3)_{2n+2}$  (with these two different kinds of Si–H coordination), a rather open structure; the third is more compact.

Then, three kinds of TB parameters are needed, those for  $\text{Si}_{-0\text{H}}$ ,  $\text{Si}_{-3\text{H}}$ , and those for H. In this latter approach we express the TB Hamiltonian in terms of non-orthogonal s and p orbitals for Si and s orbitals for H, forming all corresponding bond and overlap matrix elements among them, i.e., both hopping and overlap matrix elements with a total of 172 active NRL-parameters (e.g., H–H  $\text{pp}\sigma$  or H– $\text{Si}_{-0\text{H}}$   $\text{sp}\sigma$  parameters are inactive). This approximation seems more satisfactory: Although fitting the total valence energy is rather easy (because during the least square minimization, still incorrect TB Hamiltonian matrix elements may lead to incorrect degeneracies of the valence eigenvalues  $\varepsilon_i$ , but with almost the same total energy sum), fitting the eigenvalues in the correct order of degeneracy needs an exhaustive parameter search in the 172-dimensional parameter space. Ideally a large fitting data-base of ab-initio energies and eigenvalues should be used (i.e., from many clusters and many different bond lengths and angles). Within our limited computer power—but believing in the power of the Transferable Tight-binding interpolative method—we used only two structures in our ab-initio fitting data-base, the equilibrium  $\text{Si}_5\text{H}_{12}$  and the equilibrium  $\text{Si}_{17}\text{H}_{36}$  (Fig. 2), both computed within B3LYP DFT, and performed an exhaustive search demanding an accurate fit of not all ab-initio eigenvalues, but only caring to fit both the ab-initio bottom of the valence band and of the ab-initio HOMO and LUMO energy levels of these two clusters. At the least square minimum,

**Fig. 2** A  $\text{Si}_{17}\text{H}_{36}$  cluster at equilibrium. (A spherically shaped nanostructure)



the rest of the predicted TB levels agree automatically with the ab-initio ones within 0.005 Hy (0.14 eV), the same accuracy with that of the B3LYP DFT calculations, depending on polarization improvements of the basis set used (6-31G).

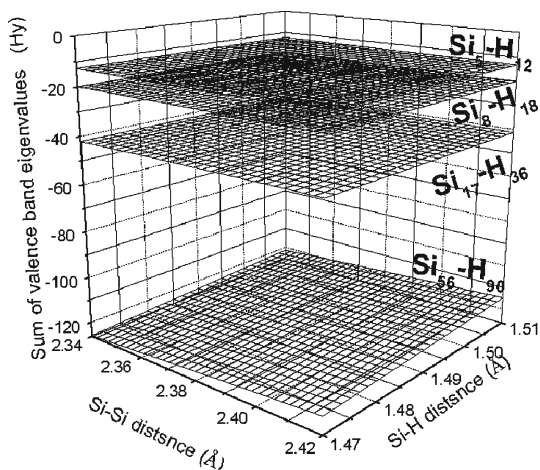
With the obtained TB parameters, from the above two rather small clusters, we computed the energies and in particular the HOMO–LUMO energy gap of 120 clusters in the same symmetry, 30 clusters of each kind, in a grid defined by assigning to the central Si–Si bond length the values 2.34, 2.35, 2.36, 2.38, 2.40, and 2.42 Å, and for each of them the Si–H bond length values 1.47, 1.48, 1.49, 1.50, and 1.51 Å. The bond lengths (2.34, 1.47) correspond to  $\text{Si}_2\text{H}_6$ , the default value of the Gaussian 03 [10] package, 2.35 corresponds to the Si crystalline lattice constant, while (2.36, 1.50) and (2.42, 1.50) correspond to the B3LYP DFT equilibrium structures of  $\text{Si}_5\text{H}_{12}$  (2.362, 1.498) and  $\text{Si}_{17}\text{H}_{36}$  (2.421, 1.494), respectively. The extrapolation to the TB prediction for  $\text{Si}_{56}\text{H}_{90}$ , a rather far extrapolation from our minimal ab initio data-base of  $\text{Si}_5\text{H}_{12}$  and  $\text{Si}_{17}\text{H}_{36}$  sometimes failed, because our data-base contained no information about long-range interaction (we did the fit within a range of 6.5 a.u., including interatomic interactions beyond the first nearest neighbors). Then we replaced in the fit  $\text{Si}_{17}\text{H}_{36}$  with a  $\text{Si}_{56}\text{H}_{90}$  cluster and extended the interaction range to 19.5 a.u. beyond the first nearest neighbors. This, however, resulted in a failure of some  $\text{Si}_{17}\text{H}_{36}$  clusters, while  $\text{Si}_8\text{H}_{18}$  did not fail with both fits. This apparent incompatibility of  $\text{Si}_{17}\text{H}_{36}$  with a  $\text{Si}_{56}\text{H}_{90}$  needs further investigation. So, for each structure we use the most accurate of the two available fits in order to explore the dependence on the Si–Si and the Si–H bond lengths.

Selected results are shown in Figs. 3–5. We observe that the HOMO–LUMO energy gap is largest (in the grid) near equilibrium, and it depends mainly on the Si–Si rather than the Si–H bond length. It also decreases with the cluster size.

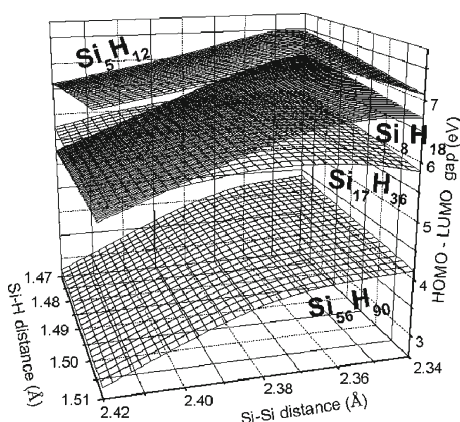
Furthermore, we deformed the  $\text{Si}_5\text{Si}_{12}\text{H}_{36}$  by up to  $\pm 5\%$  (a rather far extrapolation in view of our minimal ab initio data-base) along the (111) crystalline direction and along the perpendicular direction of (–110). The results are shown in Fig. 5. Again the HOMO–LUMO energy gap is largest near equilibrium.

Finally we show in Table 2 the largest (in the grid) HOMO–LUMO energy gap, as well as the one corresponding to the crystalline lattice constant with Si–H bond at 1.47 Å. We observe a general decreasing trend with increasing cluster size. The agreement between TB and DFT is good, with differences comparable to the DFT error bars.

**Fig. 3** The total energy (sum of shifted valence eigenvalues in Hy) of  $\text{SiSi}_4\text{H}_{12}$ ,  $\text{Si}_2\text{Si}_6\text{H}_{18}$ ,  $\text{Si}_5\text{Si}_{12}\text{H}_{36}$ , and  $\text{Si}_{26}\text{Si}_{30}\text{H}_{90}$ , for various central Si–Si bond lengths and various Si–H bond lengths, as predicted by the fitted Tight-binding Hamiltonian. All Si–Si bonds are varied proportionally to the central one. The energy changes slightly with the bond length



**Fig. 4** The HOMO–LUMO energy gap, in eV, of  $\text{SiSi}_4\text{H}_{12}$ ,  $\text{Si}_2\text{Si}_6\text{H}_{18}$ ,  $\text{Si}_5\text{Si}_{12}\text{H}_{36}$ , and  $\text{Si}_{26}\text{Si}_{30}\text{H}_{90}$ , for various Si–Si bond lengths and various Si–H bond lengths, as predicted by the fitted Tight-binding Hamiltonian. The gap of each cluster is maximum near equilibrium, it depends mainly on the Si–Si bond length, and decreases with the cluster size

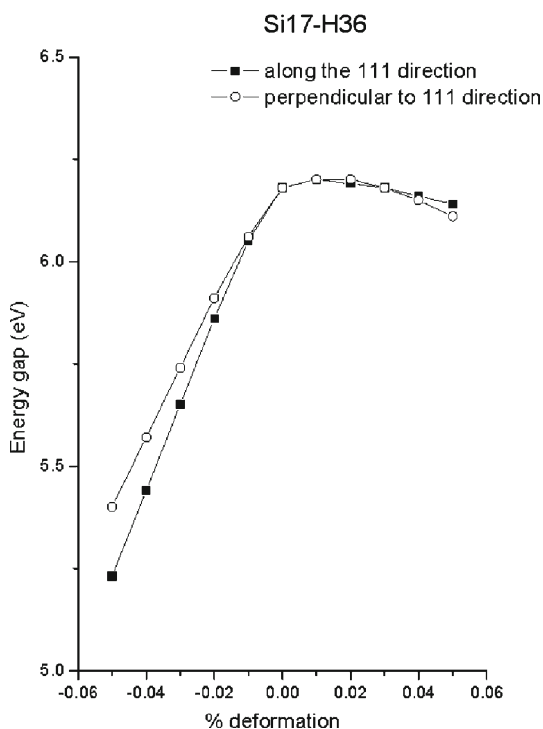


## 4 Conclusions

A conventional mathematical simultaneous interpolation of significantly different cluster nanostructures is impossible. However, this task, as well as an extrapolation to larger clusters, can be achieved via a transferable Tight-binding Hamiltonian, attempted here for the first time (as it concerns the wide diversity of the fitted systems). Present experience suggests that Si atoms, binding differently, should rather be treated differently. The results of this approach are promising, but further investigation is needed. Obtaining the transferable parameters is tedious due to non linear least square exhaustive search in large multidimensional parameter space, but we think it is worth pursuing this method, because, then, interpolating or extrapolating to any cluster of any shape would be reliable and trivial. Due to our minimal ab initio data-base (owing to our rather limited computer power) we only present general trends. We examined many (120) H-terminated Si clusters of small, medium and large size, differing in the bond length, in all of which the Si atoms bind to either three or no



**Fig. 5** The HOMO–LUMO energy gap, in eV, under linear deformation of  $\text{Si}_5\text{Si}_{12}\text{H}_{36}$ , as predicted by the fitted Tight-binding Hamiltonian. The gap is maximum near equilibrium



**Table 2** The HOMO–LUMO energy gap of various clusters predicted by the fitted Tight-binding Hamiltonian compared to B3LYP DFT values (all in eV)

Structure	Largest TB gap (in the grid used)	B3LYP DFT	TB gap at Si–H of 1.47 Å	B3LYP DFT at Si–H of 1.47 Å
$\text{SiSi}_4\text{H}_{12}$	7.56	7.60	7.47	7.64
$\text{Si}_2\text{Si}_6\text{H}_{18}$	6.96	6.88	6.86	6.85
$\text{Si}_5\text{Si}_{12}\text{H}_{36}$	5.68	5.72	6.22	5.95
$\text{Si}_{26}\text{Si}_{30}\text{H}_{90}$	4.59	4.43	4.39	4.35

H atom. The HOMO–LUMO energy gap is generally decreasing with the size, and for each kind of the examined species it is largest near equilibrium. The same trend is observed also in linearly deforming a cluster along a direction. The study is further continued by increasing the ab initio data-base and by proceeding to clusters with Si binding also to one and two H atoms.

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## References

1. A.D. Zdetsis, Optical properties of small size semiconductor nanocrystals and nanoclusters. *Rev. Adv. Mater. Sci.* **11**, 56–78 (2006)
2. A.D. Zdetsis, in *High-level Calculations of Electronic Optical and Structural Properties of Small Silicon Nanocrystals and Nanoclusters*, Lecture Series on Computer and Computational Sciences, vol. 3, eds by T. Simos, G. Maroulis (Brill Academic Publishers, Amsterdam, 2005), pp. 289–297
3. A.D. Zdetsis, C.S. Garoufalis, S. Grimme, in *Proceedings of NATO Advanced Research Workshop on “Quantum Dots: Fundamentals, Applications, and Frontiers” Crete, Greece* (Kluwer-Springer, Norwell, 2005), pp. 317–332
4. J.C. Slater, G.F. Koster, *Phys. Rev.* **94**, 1498 (1954)
5. D.A. Papaconstantopoulos, M.J. Mehl, *J. Phys. Condens. Matter* **15**, R413 (2003)
6. N.C. Bacalis, A. Metropoulos, D.A. Papaconstantopoulos, *Phys. Rev. A* **71**, 022707 (2005)
7. A. Gross, M. Scheffler, M.J. Mehl, D.A. Papaconstantopoulos, *Phys. Rev. Lett.* **82**, 1209 (1999)
8. A. Groß, A. Eichler, J. Hafner, M.J. Mehl, D.A. Papaconstantopoulos, *J. Chem. Phys.* **124**, 174713 (2006)
9. C.S. Garoufalis, A.D. Zdetsis, S. Grimme, *Phys. Rev. Lett.* **87**, 276402 (2001)
10. Gaussian 03, Revision C. 02, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, (Gaussian, Inc., Wallingford, CT, 2004)