Comparison between a sp^3d^5 tight-binding and an effective-mass description of silicon quantum dots

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This paper presents a tight-binding approach to the calculation of the electronic structure of small silicon nanocrystals. It is based on a nearest-neighbor sp^3d^5 Hamiltonian. This Hamiltonian is designed to give accurate results in the limit of a bulk Si crystal and more exactly to reproduce as much as possible the Si band structure. This method is then compared with an effective-mass calculation in order to apprehend the limit of this simplified technique widely used to study the electrical properties of devices based on silicon quantum dots.

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I. INTRODUCTION

The current fields of research in semiconductor nanostructure fabrication allow the emergence of innovative device concepts based on quantum mechanics as alternative to conventional transistors or memories. Among other things, the Coulomb blockade devices such as single-electron transistors offer one of the most promising prospects. To operate at room temperature these devices must be composed of quantum dots of a few nanometers, which ensures the charging energy to be much greater than the thermal energy. Recent works have demonstrated the feasibility of such devices and proved that, for instance, silicon- or germanium-nanocrystal-based memories are no longer a dream.[1–3] The study of silicon quantum dots is thus of first importance and the number of papers concerning the subject keeps growing.[4–7]

The determination of the electronic structure of silicon quantum dots is mainly grounded today on the effective-mass approximation due to its effectiveness in the treatment of a many-electron system.[4–7] However for quantum dots reaching the size of a few nanometers it becomes crucial to evaluate the limits of this method. From this point of view, it may be interesting to compare an effective-mass simulation with a more accurate chemical description of nanocrystals using semiempirical methods such as pseudopotential[8] or linear combination of atomic orbital[9,10] (LCAO) calculations.

The purpose of this paper lies then in the comparison between an effective-mass and a LCAO treatment of Si nanocrystals. In order to link both approaches, the effective masses employed in the first method are deduced from the bulk Si band-structure calculation using a sp^3d^5 tight-binding Hamiltonian, and the same sp^3d^5 basis is then used for the LCAO calculation. Moreover the parameters deduced from the tight-binding method when fitting the band structure at some critical points are used as interaction parameters in the LCAO method.

II. TIGHT-BINDING sp^3d^5 BAND STRUCTURE

The choice of the model used for describing bulk Si must take into account two important features.

• It must describe with sufficient accuracy the first conduction band of silicon. Indeed the longitudinal and transverse masses taken from this band structure will be employed as parameters for the effective-mass method.

• When applied to the nanocrystal structure, it must be as simple as possible to be able to treat large size quantum dots, i.e., of more than 5000 atoms.

The semiempirical tight-binding approach, and especially the sp^3d^5 tight-binding Hamiltonian given by Ren, Chen, and Don in Ref. 11, seems to be a good compromise. Thus, with nine basis orbitals (s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, $d_{z^2-r^2/3}$) and considering only the nearest-neighbor interactions, this Hamiltonian gives a convenient description of the first conduction band as shown in Fig. 1. The use of a more complete $sp^3d^5s^*$ basis[12] would make drastically heavier the calculation without significant improvement of this description. Table I presents some of the main characteristics deduced from this band structure. The density of states (DOS) of bulk Si is also calculated and plotted in Fig. 1 with the aim of comparing with the density of states of a Si nanocrystal.

III. APPLICATION TO Si NANOSTRUCTURES

A. Nanocrystal structure

In order to calculate the electronic properties of quantum dots whose radii range from 5 to 35 Å, we set up the Si

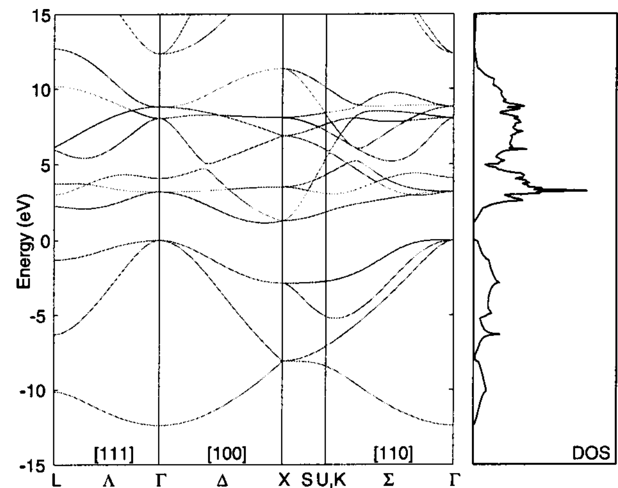

FIG. 1. Band structure and density of states of bulk silicon using the sp^3d^5 model and the interaction parameters given in Ref. 11.

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TABLE I. Main results derived from the sp^3d^5 tight-binding calculation of Si band structure.

Position of conduction-band minima	85.6% Γ-X
Band-gap energy	$E_{gap} \approx 1.14$ eV
Longitudinal mass	$m_l \approx 0.74$
Transverse mass	$m_t \approx 0.15$

atoms at diamond lattice sites as in bulk Si. Of course it is well known that small Si clusters neither crystallize in a diamond lattice[13] nor keep the same Si—Si bond length. However, to avoid the complication of studying real Si clusters, whose structure determination is a problem in itself, and to make relevant the comparison with bulk effective-mass calculation, we assume that the Si atoms occupy diamond lattice sites with a crystal Si—Si bond length and that the surface dangling bonds are saturated with H atoms. The Si—H bond length is taken equal to the Si—H bond length of a SiH_4 molecule, i.e., 1.480 Å.[14] In practice, the clusters are artificially created by starting from a SiH_4 molecule and replacing all Si—H bonds by Si—Si bonds, the surface dangling bonds being then saturated with H atoms. By iterating this procedure step by step, clusters of various sizes are built. The silicon nanocrystals studied have then the general shape presented in Fig. 2.

We are thus able to study systematically the influence of the cluster size on the electronic properties expecting that for quite large clusters these properties are similar to those of real structures. Although the quantum dot shape cannot be approximated by a sphere, we will talk in this paper of the "quantum dot radius": this value refers to the radius of the sphere whose volume is equivalent to the quantum dot volume.

B. Effective-mass method

A first common way to calculate the electronic properties of such Si clusters consists of solving for one electron the three-dimensional Schrödinger equation in the envelope approximation:

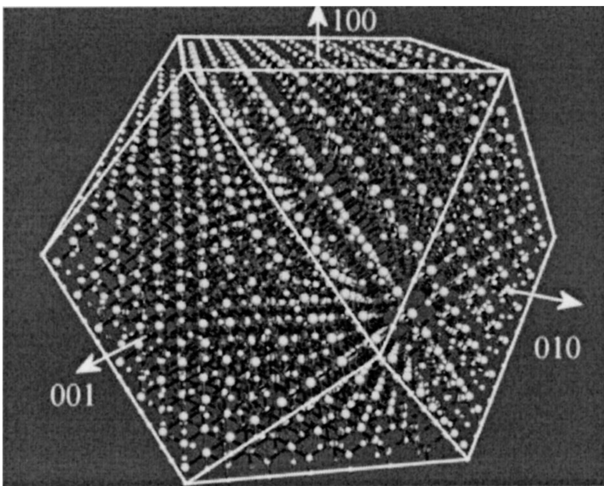

FIG. 2. Structure of a nanocrystal containing 3127 Si atoms and 1188 H atoms. The global shape (a cuboctahedron) and some crystallographic directions are indicated.

$$-\frac{\hbar^2}{2}\vec{\nabla}[M^{-1}\vec{\nabla}\Psi_n(\vec{r})]+V(\vec{r})\Psi_n(\vec{r})=E_n\Psi_n(\vec{r}). \quad (1)$$

In this equation, $V(\vec{r})$ is the confining potential and M is the electron effective-mass tensor. In our case, we consider a square-well potential of depth V_0 whose shape is given in Fig. 2. We take $V(\vec{r})=0$ at the bottom of the conduction band of silicon and $V_0=4$ eV outside the cluster, which corresponds to the Si vacuum energy level. As to the effective-mass tensor M, the parabolic band approximation is assumed, which gives

$$M^{-1}=\begin{bmatrix} 1/m_l & 0 & 0 \\ 0 & 1/m_t & 0 \\ 0 & 0 & 1/m_t \end{bmatrix}. \quad (2)$$

The numerical values of the longitudinal and transverse masses of Eq. (2) are chosen equal to the values of Table I in order to make relevant the comparison with a LCAO treatment. Moreover, we must keep in mind that each electron state is 12-fold degenerate due to the spin and silicon six-valleys degeneracies.

To perform the calculations, the differential Eq. (1) is discretized using a finite differences technique. Solving the Schrödinger equation turns then into a linear algebra eigenvalue problem. To achieve this computation, an implicitly restarted Arnoldi method[15,16] is used because of its effectiveness for large-scale eigenvalue problems.

C. Tight-binding method

In view of the very small size of quantum dots studied (up to 10 Å), it is legitimate to wonder up to what extent the effective mass remains valid. In this way, the interaction parameters calculated for the bulk Si band structure are now used to construct the Hamiltonian of the Si cluster. Each Si atom is then described by nine orbitals (s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, $d_{z^2-r^2/3}$) and only the self-interaction and the nearest-neighbor matrices are nonzero. For H atoms, we consider only a single s orbital. The self-interaction matrix parameter for H atoms (E_s) is taken identical to that used in a Si self-interaction matrix, since the energy level of the silicon s orbital [−13.55 eV (Ref. 17)] is very close to that of a hydrogen atom (−13.6 eV). To estimate the interaction matrix between H and Si, the same matrix as the nearest-neighbor Si/Si interaction is used but with Harrison's rule to adjust the parameters,[17,18]

$$V_{Si/H}=V_{Si/Si}\left(\frac{d_{Si—Si}}{d_{Si—H}}\right)^2, \quad (3)$$

where $d_{Si—Si}$ and $d_{Si—H}$ represent Si—Si and Si—H bond lengths, respectively. Moreover, the interaction between the H s orbital and Si d orbitals is neglected.

The construction of this cluster Hamiltonian leads us to the calculation of some eigenvalues around 1.14 eV, i.e., near the first conduction band of bulk Si. To perform such a calculation we still use the Arnoldi method taking into account the large size of the matrices (for instance, a cluster with

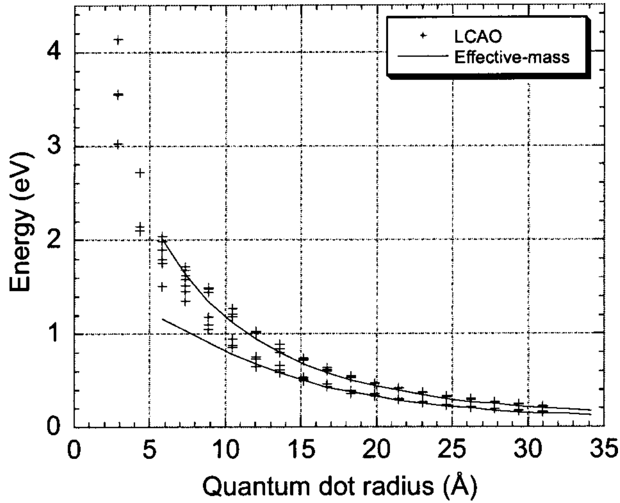

FIG. 3. Energy versus quantum dot radius calculated via an LCAO and an effective-mass method. Solid line, first and second energy levels of Si cluster calculated via effective mass; each level is 12-fold degenerate (spin and Si six-valleys degeneracy). Crosses, 12 first energy levels (some of them are superimposed) of the cluster via LCAO treatment; each level is twofold degenerate (spin degeneracy).

6209 Si atoms and 1884 H atoms requires determination of a few eigenvalues of a $57\,765\times 57\,765$ matrix).

The tight-binding method offers the additional advantage of making possible the calculation of the cluster density of states. This feature allows us to study the evolution of the DOS with the cluster size and to compare with the bulk Si DOS. To calculate the density of states, let us call H the tight-binding Hamiltonian of the cluster, and $|\Psi_n\rangle$ the wave function associated with eigenvalue $\mathcal{E}_n$, so that $H|\Psi_n\rangle = \mathcal{E}_n|\Psi_n\rangle$. We can decompose the tight-binding wave function $|\Psi_n\rangle$ as

$$|\Psi_n\rangle = \sum_{i=1}^{N_{\mathrm{Si}}} \sum_{k=1}^{9} \langle \phi^{\mathrm{Si}_i,k}|\Psi_n\rangle |\phi^{\mathrm{Si}_i,k}\rangle + \sum_{j=1}^{N_{\mathrm{H}}} \langle \phi^{\mathrm{H}_j}|\Psi_n\rangle |\phi^{\mathrm{H}_j}\rangle, \tag{4}$$

where i and j run over all Si and H atoms, respectively, and k refers to the nine Si basis orbitals. For any atom i of orbital k the local DOS may be written as

$$d_{i,k}(\mathcal{E}) = \sum_{n=0}^{9N_{\mathrm{Si}}+N_{\mathrm{H}}} |\langle \phi^{i,k}|\Psi_n\rangle|^2 \delta(\mathcal{E}-\mathcal{E}_n). \tag{5}$$

We can then calculate different types of densities of states:

• the total DOS $[D_{\mathrm{tot}}(\mathcal{E})]$ by summing the local DOS over all atoms and orbitals,

• the silicon DOS $[D_{\mathrm{Si}}(\mathcal{E})]$ by summing the local DOS over all Si atoms and orbitals only, and

• the hydrogen DOS $[D_{\mathrm{H}}(\mathcal{E})]$ by summing the local DOS over all H atoms only.

In this case the knowledge of all eigenvalues and eigenvectors is required. A classical Householder and QL (Ref. 19) algorithm are then used to perform the computation.

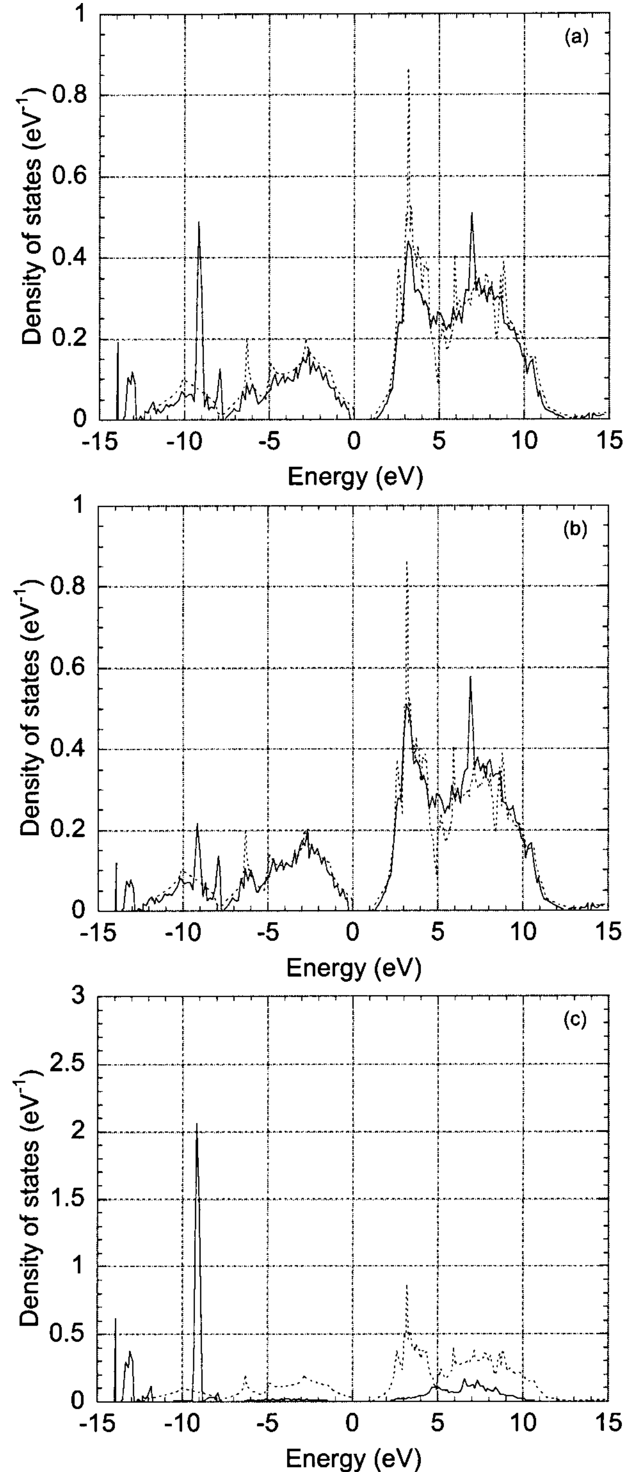

FIG. 4. For a cluster of radius 18.3 Å containing 1285 Si atoms and 652 H atoms: (a) Normalized total DOS, (b) normalized DOS associated to Si atoms only, and (c) normalized DOS associated to H atoms only. The dashed curves represent the normalized DOS of bulk Si calculated in Sec. II and plotted in Fig. 1.

IV. RESULTS

Figure 3 presents, as functions of the cluster radius, on the one hand the first two energy levels of the Si quantum dot calculated with the effective-mass method and, on the other

hand, the first 12 unoccupied energy levels of the cluster treated as a molecule via the LCAO method. The reference of energy is taken at the bottom of the Si conduction band. We must not forget that the energy levels computed using the effective-mass method are 12-fold degenerate due to the Si six valleys and spin degeneracies and that LCAO energy levels are only twofold degenerate due to spin degeneracy.

First, this graph shows that the two methods are in good agreement regarding the determination of the first energy level, even for a cluster radius as small as 12 Å. This agreement is all the more striking since the methods of calculation are completely different and almost independent. Of course, for large cluster sizes the first energy level tends towards the position of the first conduction band of bulk silicon. Another interesting conclusion lies in the fact that for both methods, the same degree of degeneracy is approximately found for cluster radii greater than 15 Å. Thus, the 12 LCAO levels of large clusters are clearly separated into two groups of six levels (each one twofold degenerate). For a radius greater than 15 Å the sublevels inside a given group are partially but weakly split. They are very well approximated by the corresponding effective-mass energy level. As an example, for a radius of 20 Å the maximum energy shift between sublevels in each group is 23 and 12 meV, respectively. It becomes less than 5 meV for a dot radius of 30 Å. In consideration of the uncertainty about the exact shape and the physical parameters of a real cluster, such results lead us to think that, in most cases, the "classical" effective-mass computation of energy states is sufficiently accurate to be used in the case of dot radii greater than 15 Å. However, this fast computation method does not allow us to describe the fine structure of sublevels and cannot be applied for quantum dots of smaller radii in which the energy splitting between sublevels become strong, as shown in Fig. 3. We even observe a mixing of the two groups of sublevels for very small nanocrystals.

Typical total densities of states, Si DOS, and H DOS of a 18.3 Å radius quantum dot are plotted in Fig. 4. All these densities of states are normalized, i.e., they are multiplied by a factor so that the sum of the density of states over all occupied states is equal to 1, i.e.,

$$\int_{-\infty}^{0} D(\mathcal{E})\,d\mathcal{E} = 1. \tag{6}$$

In each graph, the bulk Si DOS is also represented as dashed lines. In this relatively large cluster the cluster DOS tends to have the same shape as the bulk Si DOS. This feature already observed in Ref. 9 with a sp^3s^* Hamiltonian is still present here as well as effects of H surface atoms near −9 and 6 eV.

V. CONCLUSION

We have used an approach based on the linear combination of atomic orbitals to calculate the electronic properties of small Si clusters. This model is compared to an effective-mass calculation of the quantum dot energy levels. The goal is to determine the limitation of this simple and fast effective-mass method when decreasing the cluster size. It first appears that even for clusters as small as 15 Å both methods give the same results. Moreover, they are in agreement not only on the value of first energy levels but also on the degree of degeneracy of these levels. Of course, the effective-mass method is unable to give access to the sublevel fine structure of the cluster, but the gap between these sublevels is so small that this simple method is sufficiently accurate to correctly describe Si quantum dots of radii greater than 15 Å.

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