PHYSICAL REVIEW B VOLUME 59, NUMBER 3 15 JANUARY 1999-I

Size effect on chalcogen deep levels in Si quantum dots

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(Received 1 December 1997; revised manuscript received 21 April 1998)

The deep levels and electron spin resonance spectra associated with S, Se, and Te impurities at the centers of Si quantum dots are predicted as functions of dot size, for both the neutral and singly ionized states. [S0163-1829(98)01531-8]

I. INTRODUCTION

With the advent of experimental techniques for producing small semiconductor nanostructures having sizes ranging from a few atoms to bulk dimensions,[1–4] the physics of small quantum dots is assuming new importance. One area that has received little attention is the physics of impurities, especially ''deep'' levels. Historically, a deep level was originally defined as any level more than 0.1 eV from a band edge, in the fundamental gap—but it was soon realized that the proper definition was any level associated with the central-cell potential of an impurity.[5] This change of definition was necessitated by the realization that *every* impurity produces deep levels, but that most of these levels lie *outside* the fundamental gap, resonant with the host energy bands. For example, P in Si has, in addition to its shallow-donor Coulombic levels slightly below the conduction band minima, an *s*-like and a *p*-like deep level *above* the conduction-band edge, which can be uncovered by perturbing the Si so that its fundamental band gap is enlarged.[6–8] When this happens, the P impurity changes from an *n*-type donor to a semi-insulating trap. Similarly, size reduction of a quantum dot enlarges the fundamental gap, and should uncover many deep levels that were previously ignored, leading to interesting doping anomalies. For this reason, detailed investigations of deep levels in quantum dots *versus* dot size should be especially interesting.

In this paper, we study the chalcogen impurities S, Se, and Te and their deep levels in Si quantum dots, primarily because electron spin resonance (ESR) studies of these impurities in bulk Si have produced some of the best data[9–11] for comparison with theory,[12] making them prototypical deep levels. Therefore, studies of these deep levels in quantum dots with decreasing size can provide touchstones for comparison of deep-level charge densities with theory, and our theoretical predictions for chalcogen impurities in quantum dots should be tested against future measurements of charge-densities obtained with ESR.

II. APPROACH

We make three major approximations: (i) the quantum dot is assumed to retain tetrahedral shape (Fig. 1); (ii) the impurity is assumed to lie at the center of the cluster; and (iii) atomic relaxation around the impurity and in the dot itself is ignored, in the interest of exploring the general trends as a function of dot size.

These approximations are justified by our results for all but the smallest quantum-dot sizes. The deep levels in question, being of *s*-like symmetry and of radius <10 Å, will only be weakly perturbed by changes in the quantum dot more than ~ 10 Å distant from the impurity. (See Figs. 2, 3, and 4.) Atomic relaxation around an impurity will rarely change the deep energy level in the gap by as much as 0.3 eV. Only for the smallest quantum dots, consisting of only a few shells of atoms, do the approximations introduce significant errors, and in these small clusters the atoms often rearrange themselves in a manner that is best treated by a change of total energy method, such as the local density approximation.

In addition to the three major approximations, we also truncate the range of the defect potential at the central cell, as in the Hjalmarson *et al.* theory of deep levels in bulk semiconductors. Our general approach is based on the Hjalmarson *et al.* theory of deep levels in the bulk,[5] but draws as well on a long history of studies of impurities in clusters[13,14] and in the bulk.[15–23] The dangling Si bonds at the surface of the dot or cluster are terminated (theoretically) with H atoms, which we know do not produce deep levels in the fundamental gaps of any size cluster.[24] Each Si atom in a cluster is assumed to have an sp^3s* basis set.[25] Details of the calculations, which invoke group theory to simplify the evaluations of the electronic structures of rather large clusters, are included in the Appendix.

The quantities that we calculate are (i) the deep-level energies of S^0, Se^0, Te^0, S^{+1}, Se^{+1}, and Te^{+1}, and (ii) the wave functions $\langle A_1,\mathbf{R}=\mathbf{0},n=1|\psi\rangle$, $\langle A_1,\mathbf{R}_1,n=1|\psi\rangle$, and $\langle A_1,\mathbf{R}_1,n=2|\psi\rangle$, which are related to the hyperfine constants A, a, and b for the impurities S^+, Se^+, and Te^+, as

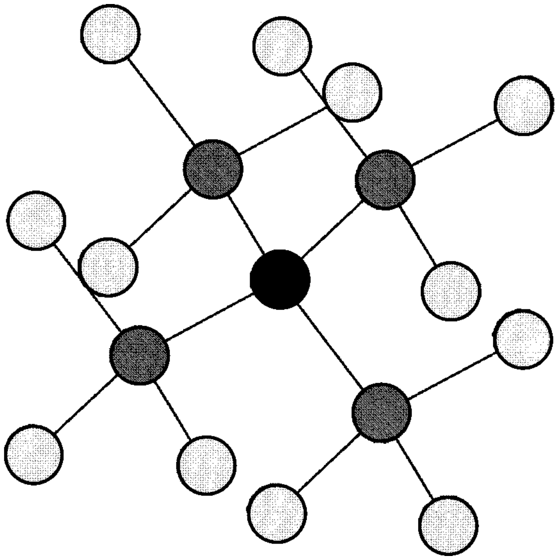

FIG. 1. Illustrating the diamond crystal structure of Si with a black atom at the center of the cluster, dark atoms as its nearest neighbors, and lighter atoms as second neighbors. The bonds to more distant neighbors, that would normally dangle, are deleted.

discussed in the Appendix.[26,27] More precisely, we do not actually compute deep-level energies in the bulk, but calculate the strengths of the bulk defect potentials that produce the *observed* energies, and then we use these potential strengths to predict the deep levels in the quantum dots.

III. RESULTS

Figure 2 displays the band edges and the S^0 deep level *versus* the quantum dot diameter d. Not unexpectedly, the band edges recede from the fundamental band gap of bulk Si as d decreases. The deep level varies in energy less than the band edges, reflecting its hostlike character, which is relatively insensitive to the detailed positions of either the conduction-band minima or the valence-band maximum.

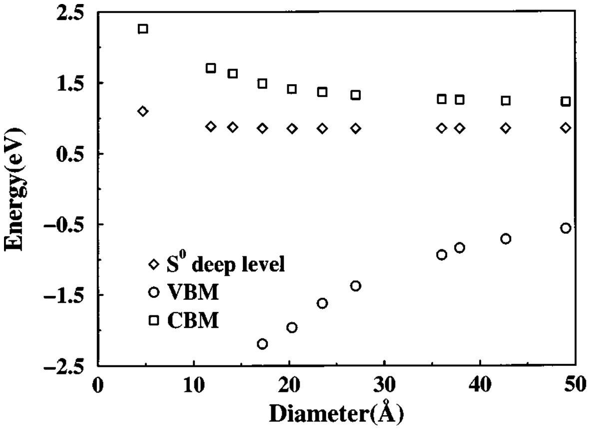

FIG. 2. The computed valence-band maxima (VBM; circles) and conduction-band minima (CBM; squares), and deep-level energies (in eV) of S^0 impurities (diamonds) located at the centers of Si quantum dots, against dot diameter d (in Å). The zero of energy is the VBM of bulk Si whose gap (Ref. 25) is 1.17 eV (Ref. 29).

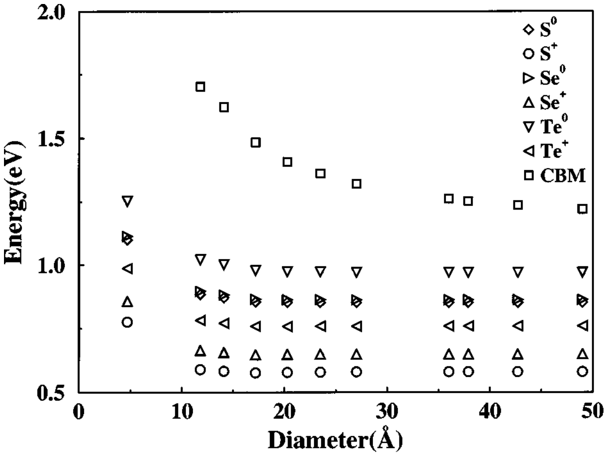

FIG. 3. Computed deep-level energies of S^+ (circles), Se^+ (upward-pointing triangles), Te^+ (left-pointing triangles), S^0 (diamonds), Se^0 (right-pointing triangles), and Te^0 (downward-pointing triangles) vs Si quantum dot diameter d (in Å). The corresponding bulk binding energies relative to the CBM are 0.59, 0.52, 0.41, 0.32, 0.31, and 0.20 eV, respectively.

The charge-state splitting of S, $E(S^+)-E(S^0)$ is relatively constant (to within 1%) as a function of dot size, as demonstrated in Fig. 3, and the differences in S, Se, and Te deep-level energies change very little as well (maximum of 1%), as shown in Fig. 3.

The electron-spin-resonance parameters A, a, and b (defined in the Appendix) are displayed in Fig. 4, and exhibit only a weak dependence on quantum dot size d. In particular, once the dot approaches the size of a five-atom cluster, the deep level (which has antibonding character, with much of its amplitude on the shell of first nearest neighbors) begins to show the effects of localization, and the amplitude of the wave function on the central site (and nearby) increases.

But a crude summary of our results is that the deep levels of S, Se, and Te in Si quantum dots are not affected much by quantum confinement, until the dots become quite small—only a few atoms in size.

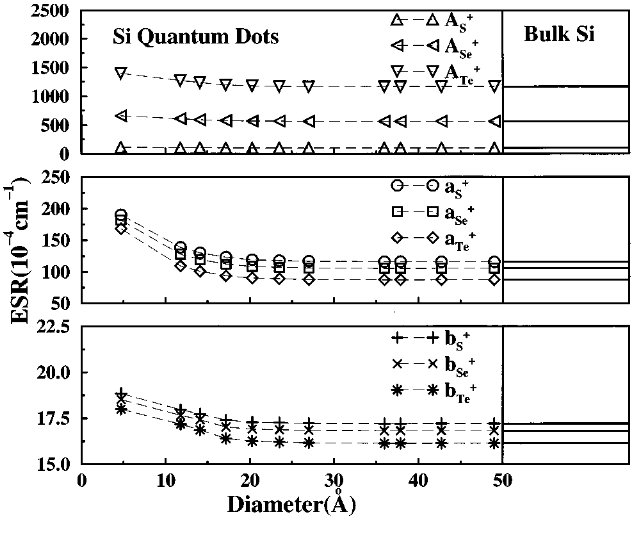

FIG. 4. Electron-spin-resonance hyperfine parameters (Ref. 27) (a) A, (b) a, and (c) b computed for S^+, Se^+, and Te^+, against quantum dot diameter d (in Å).

ACKNOWLEDGMENTS

J. S. and S. Y. R. thank the National Natural Science Foundation of China (Project Nos. 19574008 and 19774001), the National Climbing Program on the Science and Technology of Nanomaterials, and the National Laboratory of GaAs Integrated Circuits of China for their support. S.Y.R. and J.D.D. wish to thank the U.S. Army Research Office for their support (Contract No. DAAG55-97-1-0387). J.D.D. thanks Professor J. R. Schrieffer and Professor J. E. Crow of the National High Magnetic Field Laboratory for their hospitality during his visit.

APPENDIX: THEORY

1. General

We plan to compute the energy levels and wave functions of deep levels in the fundamental gaps of Si quantum dots, as a function of dot diameter. We shall employ the Hjalmarson *et al.* theory of deep levels,[5] modified to treat impurities in clusters in addition to defects in bulk semiconductors. The basis states will be localized linear combinations of sp^3 hybrids and an excited $s*$ orbital,[25] all centered on the same shell of atoms, that transform according to a specific irreducible representation of the tetrahedral group:

$$|l,\mathbf{R},n\rangle,$$

where l labels an irreducible representation: A_1 (s-like), T_2 (p-like), A_2, E, or T_1. Because we consider only s- and p-bonded impurities at the center of a Si cluster, only the A_1 and T_2 representations will be important in this work. The label n indexes the states transforming according to the lth irreducible representation at the $\mathbf{R}$th shell of neighbors. For example, for A_1-symmetric states, n may be as large as 6 for $\mathbf{R}$ within the first 12 shells of neighbors; for $\mathbf{R}=\mathbf{0}$, there is only the $n=1$ state at the impurity site:

$$|A_1,\mathbf{R}=\mathbf{0},1\rangle=\tfrac{1}{2}[|h_1,\mathbf{S}\rangle+|h_2,\mathbf{S}\rangle+|h_3,\mathbf{S}\rangle+|h_4,\mathbf{S}\rangle]=|s,\mathbf{S}\rangle \quad \text{for} \quad \mathbf{S}=\mathbf{0},$$

namely, the symmetric linear combination of the four sp^3 directed hybrids centered at the impurity site $\mathbf{S}=\mathbf{0}$, or $|s,\mathbf{S}=\mathbf{0}\rangle$.

Here the hybrid orbitals centered on site $\mathbf{S}$ are expressed in terms of the s and p orbitals at that site:

$$|h_1,\mathbf{S}\rangle=\tfrac{1}{2}[|s,\mathbf{S}\rangle+\lambda|p_x,\mathbf{S}\rangle+\lambda|p_y,\mathbf{S}\rangle+\lambda|p_z,\mathbf{S}\rangle],$$

$$|h_2,\mathbf{S}\rangle=\tfrac{1}{2}[|s,\mathbf{S}\rangle+\lambda|p_x,\mathbf{S}\rangle-\lambda|p_y,\mathbf{S}\rangle-\lambda|p_z,\mathbf{S}\rangle],$$

$$|h_3,\mathbf{S}\rangle=\tfrac{1}{2}[|s,\mathbf{S}\rangle-\lambda|p_x,\mathbf{S}\rangle+\lambda|p_y,\mathbf{S}\rangle-\lambda|p_z,\mathbf{S}\rangle],$$

and

$$|h_4,\mathbf{S}\rangle=\tfrac{1}{2}[|s,\mathbf{S}\rangle-\lambda|p_x,\mathbf{S}\rangle-\lambda|p_y,\mathbf{S}\rangle+\lambda|p_z,\mathbf{S}\rangle],$$

where we have $\lambda=+1$ (-1) for atoms at nominal anion (cation) sites, and the impurity is assumed to be at an anion site. Next we introduce the label $\nu=s^*$, h_1, h_2, h_3, or h_4, and our hybrid basis orbitals are $|\nu,\mathbf{S}\rangle$.

The $n=1$ state at the first shell of nearest neighbors is

$$|A_1,\mathbf{R}_1,1\rangle=\frac{1}{2}[+|h_1,\mathbf{S}_1\rangle+|h_2,\mathbf{S}_2\rangle+|h_3\mathbf{S}_3\rangle+|h_4,\mathbf{S}_4\rangle] \quad \text{for shell} \quad \mathbf{R}_1,$$

the linear combination of four sp^3 inward-directed hybrids, centered on the four nearest-neighbor sites $\mathbf{S}_i$, $i=1,2,3,4$ [in the (1,1,1), (1,−1,−1), (−1,1,−1), and (−1,−1,1) directions]; and we have, again for shell $\mathbf{R}_1$:

$$\begin{aligned}|A_1,\mathbf{R}_1,2\rangle=(12)^{-1/2}[&|h_2,\mathbf{S}_1\rangle+|h_3,\mathbf{S}_1\rangle+|h_4,\mathbf{S}_1\rangle+|h_1,\mathbf{S}_2\rangle\\&+|h_3,\mathbf{S}_2\rangle+|h_4,\mathbf{S}_2\rangle+|h_2,\mathbf{S}_3\rangle+|h_1,\mathbf{S}_3\rangle\\&+|h_4,\mathbf{S}_3\rangle+|h_2,\mathbf{S}_4\rangle+|h_3,\mathbf{S}_4\rangle+|h_1,\mathbf{S}_4\rangle],\end{aligned}$$

where this is the A_1 combination of twelve outward-directed hybrids centered on nearest-neighbor sites.

2. Si Hamiltonian and defect potential

The host Hamiltonian H_0 is the Vogl sp^3s* model[25] of the electronic structure of Si. To this is added a defect potential V, which, strictly speaking, is based on a mixed basis set of Löwdin orbitals,[5] but which we approximate using the defect potential

$$V=\Sigma_l|l,\mathbf{R}=\mathbf{0},n=1\rangle V(l)\langle l,\mathbf{R}=\mathbf{0},n=1|.$$

Its only nonzero matrix elements are the diagonal elements $V(l=s$ or $A_1)$ and $V(l=p,m$ or $T_2,m)$, where m runs over three values x, y, and z. It follows that $V(l)$ for the defect in the bulk crystal determines the deep energy level E of the impurity in the bulk, or conversely, by knowing the energies of the S^0 and Se^+ defects in the bulk, for example, we can determine two values of $V(A_1)$ that produce them, which in turn allows us to eliminate $V(A_1)$ as a parameter, in favor of the known deep levels.

For the clusters or quantum dots, the Hamiltonian matrix $H\equiv H_0+V$ is diagonalized, producing the eigenvectors $|\alpha\rangle$ and energy eigenvalues E_α.

3. ESR parameters

The parameters A, a, and b, which can be compared with ESR measurements are[26,27]

$$A=|\langle A_1,\mathbf{R}=\mathbf{0},n=1|\psi\rangle|^2A_0,$$

$$a=\tfrac{1}{16}|\langle l,\mathbf{R}_1,n=1|\psi\rangle+\sqrt{3}\langle l,\mathbf{R}_1,n=2|\psi\rangle|^2A_h,$$

and

$$b=\tfrac{1}{16}|\sqrt{3}\langle l,\mathbf{R}_1,n=1|\psi\rangle-\langle l,\mathbf{R}_1,n=2|\psi\rangle|^2B_h.$$

Here $|\psi\rangle$ is the defect state and A_0 is proportional to the *free atomic* hyperfine interaction (Fermi contact term) of the S, Se, or Te impurity:

$$A_0\propto|\psi_{s,\text{free atom}}(\mathbf{R}=\mathbf{0})|^2.$$

A_0 is also proportional to $(16\pi/3)(\mu_s/I_s)\beta$, where μ_s and I_s are the magnetic moment and nuclear spin of the S (or Se or Te), and β is the Bohr magneton. The hyperfine interaction parameter A_h for the neighboring host sites to the impurity (in shell $\mathbf{R}_1$) is

$$A_h=(16\pi/3)(\mu_{\mathrm{Si}}/I_{\mathrm{Si}})\beta|\psi_{\mathrm{Si;free\ atom\ 3}s}(0)|^2,$$

while we have the anisotropy parameter for the nearest-neighbors sites:

$$B_h=\tfrac{4}{5}(\mu_j/I_j)\beta\langle r_{3p}^{-3}\rangle,$$

where $\langle r_{3p}^{-3}\rangle$ represents an average of the dipole-dipole interaction over the electronic wave function.

We use the sign convention that $\langle A_1,\mathbf{R}=\mathbf{0},1|\psi\rangle$ is positive, which implies that $\langle A_1,\mathbf{R}_1,2|\psi\rangle$ is positive and $\langle A_1,\mathbf{R}_1,1|\psi\rangle$ is negative.

4. Alternative Green's-function approach

An alternative approach to directly computing the impurity energy levels and wave functions in a quantum dot is to employ the Green's-function approach. This approach is actually preferable in a bulk material.

The secular (operator) equation is

$$\det[1-G_0(E)V]=0,$$

where the unperturbed (impurity-free) quantum-dot or host-crystal Green's operator is

$$G_0(E)=(E-H_0)^{-1}=\Sigma_\alpha\frac{|\alpha\rangle\langle\alpha|}{E-E_\alpha},$$

and E is to be replaced by $E+i\eta$, where η is a positive infinitesimal, if E lies within a continuum of energy levels of the host Hamiltonian operator H_0. The eigenvalues of the host Hamiltonian H_0 are E_α, with eigenvectors $|\alpha\rangle$. The quantum dots with the chalcogen impurities at their centers are assumed to have tetrahedral symmetry. Therefore, by using projection operator techniques, and by selecting linear combinations of hybrid orbitals that transform according to the irreducible representations of the T_d or tetrahedral group, the Green's operator matrix $G_0(E)$ can be reduced to a direct sum of matrices associated with each irreducible representation. Only the A_1 representation has nontrivial solutions for the deep level's energy. Hence for either a host crystal or a quantum dot, the Green's-function secular equation for the impurity's energy level reduces to the scalar equation with $l=A_1$, for the deep level energy E:

$$\langle l,\mathbf{R}=\mathbf{0},1|G_0(E)|l,\mathbf{R}=\mathbf{0},1\rangle=V(l)^{-1}.$$

$G_0(E)$ is a matrix of considerable dimension in general, but it still can be reduced to a far more tractable dimension than the full matrix, which has not been reduced by symmetry. For example, here we treat clusters as large as 49 Å in diameter, involving 3108 Si atoms (with 5 orbitals each), one chalcogen atom (5 orbitals), and 852 hydrogen atoms (852 orbitals), yet the matrix to be diagonalized for A_1-symmetric states is only 834×834, not $16\,397\times 16\,397$.

The resulting deep impurity wave function $|\psi\rangle$ with energy E has components in this model:

$$\langle l,\mathbf{R},n|\psi\rangle=\langle l,\mathbf{R}=\mathbf{0},1|\psi\rangle\langle l,\mathbf{R},n|G_0(E)|l,\mathbf{R}=\mathbf{0},1\rangle \times\langle l,\mathbf{R}=\mathbf{0},1|G_0(E)|l,\mathbf{R}=\mathbf{0},1\rangle^{-1}.$$

5. Bulk crystal limit: Determination of $V(l=s$ or $A_1)$

In evaluating the band-edge energies and the deep levels of substitutional chalcogens in bulk Si, it is convenient to employ the Green's-function secular equation method, to invoke translational invariance, and to form the tight-binding orbitals for the bulk Si crystal from the hybrid orbitals centered on site $(\mathbf{L},\mathbf{v}_\beta)$:

$$|\nu,\mathbf{k},\mathbf{v}_\beta\rangle=N_s^{-1/2}\Sigma_L\exp(i\mathbf{k}\cdot\mathbf{L}+i\mathbf{k}\cdot\mathbf{v}_\beta)|\nu,\mathbf{L},\mathbf{v}_\beta\rangle,$$

where $\mathbf{k}$ is (in a reduced zone scheme) any wave vector of the first zinc-blende Brillouin zone. Here N_s is the number of unit cells and the site is $(\mathbf{L},\mathbf{v}_\beta)$, where $\mathbf{v}_a=\mathbf{0}$ for anion sites and $\mathbf{v}_c$ is the position of the closest cation relative to the central anion site.

Then the perfect Si crystal Hamiltonian H_0 is the one-electron tight-binding Hamiltonian of Vogl *et al.*,[25] and is given in terms of the tight-binding basis states $|\nu,\mathbf{k},\mathbf{v}_\beta\rangle$ obtained from localized orbitals $|\nu,\mathbf{S},\mathbf{v}_\beta\rangle$ centered on the βth site in the unit cell at $\mathbf{S}$

$$|\nu,\mathbf{k},\mathbf{v}_\beta\rangle=N_s^{-1/2}\Sigma_{\mathbf{S}}\exp(i\mathbf{k}\cdot\mathbf{S}+i\mathbf{k}\cdot\mathbf{v}_\beta)|\nu,\mathbf{S},\mathbf{v}_\beta\rangle.$$

The $\mathbf{k}$-space Hamiltonian is

$$H_0(\mathbf{k})=\Sigma_{\nu,\beta}|\nu,\mathbf{k},\mathbf{v}_\beta\rangle E(\nu,\beta)\langle\nu,\mathbf{k},\mathbf{v}_\beta| +\tfrac{1}{2}\Sigma_{\nu,\mu}[|\nu,\mathbf{k},\mathbf{v}_\alpha\rangle T(\nu a,\mu c)\langle\mu,\mathbf{k},\mathbf{v}_c|+\mathrm{H.c.}],$$

where H.c. means the Hermitian conjugate, ν and μ label the basis orbitals, s, p_x, p_y, p_z, and $s*$, and β is one of the two sites in the unit cell of Si ($\beta=a$ for the anion and $\beta=c$ for the cation). We distinguish between anion and cation sites even in diamond-structure Si to emphasize that the theory applies to zinc-blende semiconductors such as GaAs as well. The energies $E(\nu,\beta)$ and transfer integrals $T(\nu a,\mu c)$ are given in Ref. 25. The eigenstates of H_0 for bulk Si are the Bloch waves $|n,\mathbf{k}\rangle$, and the eigenvalues $E_n(\mathbf{k})$ are the band structure of bulk Si.

The advantage of employing the tight-binding orbitals and the Green's function secular equation method is that the diagonalization of the host Hamiltonian is reduced to a 10×10 matrix problem at each wave vector $\mathbf{k}$, and the eigenvalue equation for the deep level E is scalar and simple.

The evaluation of the matrix elements of the Green's-function operator for the bulk Si reduces to evaluations of

$$G_0(E)=\Sigma_{n,\mathbf{k}}|n,\mathbf{k}\rangle\langle n,\mathbf{k}|(E-E_{n,\mathbf{k}})^{-1},$$

where the sum extends over the band index n and over the first Brillouin zone of $\mathbf{k}$. The latter sum can be evaluated using 60 special points.[28]

Therefore the computation proceeds as follows: (i) The Green's function for bulk Si is first evaluated, using special points, and the experimental value of E is used to determine $V(s)$ for S, Se, or Te. This value of $V(s)$ is then employed in the Hamiltonians H_0+V for quantum dots of various sizes, each containing a single chalcogen impurity at its center. These Hamiltonians are directly diagonalized, producing the defect wave functions $|\psi\rangle$ and energy eigenvalues for the various quantum dots.

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[29] The total number of Si plus chalcogen atoms in each quantum dot, and its diameter, for the eleven dots treated here are (5,4.7 Å), (47,11.8 Å), (87,14.1 Å), (147,17.2 Å), (239,20.3 Å), (357,23.5 Å), (525,27.0 Å), (1231,36.0 Å), (1419,37.9 Å), (2059,42.7 Å), and (3109,49.1 Å).