

Chemical-shift enhancement for strongly confined electrons in silicon nanocrystals

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Abstract

Theoretical study of the chemical shift and ground level splitting in spherical silicon quantum dot with a shallow donor has been carried out within the framework of the $\mathbf{k-p}$ method. We have found the great value of the chemical shift compared to the one in bulk. It is shown that the level splitting strongly depends on the dot radius and the donor position inside the nanocrystal.

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Modification of electronic structure and optical properties of silicon quantum dots has been the subject of great attention last years. As a method, doping of the dots with shallow donors has been proposing. In this connection various aspects of the problem, such as the screening of impurity fields [1,2], formation of impurity atoms inside nanocrystals from the energy point of view [3], spatial charge distribution in a dot [4], intervalley scattering [5], optical gap and hyperfine splitting [6] have been studied theoretically.

Calculation of the energy splitting caused by V-group donors or III-group acceptors has been carried out in the work [7] for silicon nanocrystal $\text{Si}_{86}\text{XH}_{76}$ with X being the chemical element of V- or III-group. Using local-density approximation for V-group donors the authors have found an anomalously great level splitting (about 1 eV) in the “conduction band” compared to that in bulk. As is known, the latter is of the order of 10–20 meV for various dopants. Unfortunately, in Ref. [7] the only structural configuration has been considered. This configuration is characterized by the central donor position in the nanocrystal and the nanocrystal size equal to 1.6 nm in accordance with the authors’ estimations. Meanwhile, some interesting questions, such as the energy-splitting dependence on the dot size, remain beyond the frames of the paper [7].

Perhaps, the envelope-function approximation is more convenient for this purpose. We use it in our calculations and find the size-dependence of the level splitting and chemical shift for the conduction electron states in 2–5 nm silicon quantum dots with substitutional V-group donor. Moreover, we have obtained the electron energies as functions of the donor displacement from the dot center. At the same time, similarly to [7], we will show that the chemical shift is very large in small nanocrystals. In this case the valley-orbit interaction [8,9], intensified by a quantum confinement effect, plays a crucial role in the level splitting.

Within the framework of the envelope-function method the lowest energy level in undoped spherical silicon quantum dots is sixfold degenerate (not including spin variables) [10,11]. The first-principles calculations based on the pseudopotential [12], tight binding [13,14], or density-functional [15] approaches exhibit some weak splitting (from ~ 20 meV to ~ 5 meV for 2–5 nm

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nanocrystals) of the ground electron state even in undoped spherical dots. This is due to the point group T_d symmetry of the structure, which makes the ground state split into a singlet, doublet, and triplet.

The presence of a donor in some arbitrary position inside the dot destroys the T_d -symmetry, completely removes the degeneracy, and increases the level splitting. However, the main reason of the strong splitting lies not only in the system asymmetry but the so-called central-cell effect. It is caused by a strong electron–ion interaction that remains, in fact, unscreened in the vicinity (less than the Bohr radius) of the donor nucleus. This interaction is described with the potential-energy function that quickly varies in space. Such a fast potential leads to the valley–orbit coupling [8,9] and enhances the level splitting because of the strong quantum confinement in the system.

The quantum confinement is the main factor determining the electron spectrum of small nanocrystals. However, the electron–ion interaction also strongly influences the electron states as will be shown below.

In bulk silicon the Coulomb interaction of electron and donor ion can be separated into two parts with two different typical scales [16]: $U_{bulk}(\mathbf{r}) = W(\mathbf{r}) + V_{bulk}(\mathbf{r})$. The first part $W(\mathbf{r})$ is the central-cell potential leading to the valley–orbit coupling. It can be written as (see Eq. (4.24) in Ref. [16]):

$$W(\mathbf{r}) = -\frac{e^2}{r} \left(A e^{-\alpha r} + (1-A) e^{-\beta r} - \frac{e^{-\gamma r}}{\varepsilon_s} \right) + W_{nl}. \quad (1)$$

Here $\varepsilon_s \approx 12$ is silicon permittivity, the numerical parameters α , β , γ equal 0.7572, 0.3123, 2.044 of the reciprocal Bohr radius, respectively, $A = 1.175$. W_{nl} is some non-local part that is different for various chemical elements. Its typical scale is similar to the one for the local part.

It is seen that the function $W(\mathbf{r})$ is of the short-range type and drops quickly in the distance of a few Bohr radii from the donor nucleus. This length is the scale of screening of the unit positive charge (the donor ion) that is screened by a cloud of the valence electrons surrounding the donor.

However, the valence electrons are incapable to screen the donor ion completely. The remaining part of the Coulomb field can be described by the weakened ε_s -times hydrogen-like potential energy

$$V_{bulk}(\mathbf{r}) = -\frac{e^2}{\varepsilon_s r}. \quad (2)$$

At r greater than the Bohr radius the total potential energy $U_{bulk}(\mathbf{r})$ almost coincides with the field (2). The weakening of the donor-ion field is explained by the effective reduction of the donor charge due to the presence of the negatively charged cloud in the nearest vicinity of the ion. Evidently, a test electron, being outside the cloud, “feels” the common charge of the donor ion and electron cloud. Naturally, this charge is less than the donor’s one. Its value aspires to e/ε_s at large r .

The second part (2) slowly varies in space. As usual, for Coulomb-like fields, its typical scale may be estimated as the effective Bohr radius. The latter is much greater than the one for the field $W(\mathbf{r})$ because of the smaller effective mass in bulk silicon and high value of the permittivity.

In the quantum dot the fast part $W(\mathbf{r})$ does not change presumably its form due to the short-range character. It is clear that the potential $W(\mathbf{r})$ differs from zero on the scale of the Bohr radius around the nucleus and close to zero elsewhere. Consequently, even at the boundary of the unit cell containing the donor, we may already treat $W(\mathbf{r})$ as negligible small. It means that the field $W(\mathbf{r})$ certainly vanishes at the boundary of the quantum dot independently of the donor position inside the dot. As a result, the fast part of the electron–ion interaction in the dot is described by the bulk-like expression (1) in which we should substitute \mathbf{r} by $\mathbf{r} - \mathbf{h}$, where \mathbf{h} is the donor position-vector.

In contrast to the central-cell interaction (1), the second “slow” part (2) of the Coulomb field undergoes significant changes due to appearance of the polarized surface charges at the dot boundary. It becomes the sum of two terms: $V(\mathbf{h}, \mathbf{r}) = V_{ie}(\mathbf{h}, \mathbf{r}) + V_{sp}(r)$, where

$$V_{sp}(r) = \frac{e^2(\varepsilon_s - \varepsilon_d)}{2\varepsilon_s R} \sum_{l=0}^{\infty} \frac{l+1}{l\varepsilon_s + (l+1)\varepsilon_d} \frac{r^{2l}}{R^{2l}} \quad (3)$$

is the self-polarization potential energy (see, e.g., Ref. [17, p. 279]) that originates from the interaction between the electron and its own image. The term $V_{ie}(\mathbf{h}, \mathbf{r})$ describes the direct electron–ion interaction, as well as the interaction of the electron with the ion image [2]:

$$V_{ie}(\mathbf{h}, \mathbf{r}) = -\frac{e^2}{\varepsilon_s |\mathbf{r} - \mathbf{h}|} - \frac{e^2(\varepsilon_s - \varepsilon_d)}{\varepsilon_s R} \sum_{l=0}^{\infty} \frac{h^l r^l}{R^{2l}} \frac{l+1}{l\varepsilon_s + (l+1)\varepsilon_d} P_l(\cos \theta). \quad (4)$$

Here ε_d is the permittivity of the wide-band dielectric matrix surrounding the nanocrystal.

Because of the valley–orbit coupling and high values of size-quantization energies for small nanocrystals (from \sim eV to several tenths of eV for sizes \sim 2–5 nm) we use the generalized form of the Kopylov’s \mathbf{k} – \mathbf{p} Hamiltonian operator [18]. It is represented by the matrix 6×6 written in a basis of the Bloch states corresponding to the three X-points: $|X\rangle, |X'\rangle; |Y\rangle, |Y'\rangle; |Z\rangle, |Z'\rangle$. Each pair

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