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2004 J. Phys.: Condens. Matter 16 1769

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## Helium-like donors in semiconductor quantum dots

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Received 12 November 2003

Published 27 February 2004

Online at [stacks.iop.org/JPhysCM/16/1769](http://stacks.iop.org/JPhysCM/16/1769) (DOI: 10.1088/0953-8984/16/10/009)

### Abstract

We carry out detailed studies of charged ( $D^+$ ) and neutral ( $D^0$ ) impurity states of helium-like donors in spherical semiconductor quantum dots using both the density functional-effective mass and tight-binding formalisms. We find the two sets of results to be consistent with each other down to very small size quantum dots. We vary the shape of the confining potential, taking it to be square, harmonic and triangular. Independent of the confining potential, we observe a shallow to deep transition of the donor level as the dot size is reduced. However, on further reduction of the size the donor level tends to become shallow again. This suggests that carrier ‘freeze out’ is a distinct possibility for both  $D^+$  and  $D^0$ . Further, optical gaps also show similar behaviour with the size of the dot.

Impurities play a central role in semiconductor devices. Shallow hydrogenic donors raise the conductivity of a semiconductor by several orders of magnitude. Helium-like donors do not have as central a role to play as hydrogenic donors in semiconductors. Nevertheless they are of great academic interest. Oxygen in Si forms the very well known A-centre [1]. The other group VI donors such as S, Se and Te form relatively deep donors in Si. The effective mass theory (EMT) for helium-like donors in bulk semiconductors was first carried out by Glodeanu [2] way back in 1967. Various experimental studies were carried out by Grimmeiss *et al* [3, 4]. A detailed theoretical work on group VI donors in bulk Si within a complete local density approximation (LDA) approach was carried out by Singh *et al* [5]. In the present study of helium-like impurities in semiconductor quantum dots (QDs) we report an intriguing non-monotonic behaviour of binding energy with size.

Semiconductor QDs have been studied over the past decade and a half. While the role of hydrogen-like donors in these systems has received some attention, studies of the helium-like donors have been very few [6, 7]. For hydrogenic donors we have predicted an interesting phenomenon, namely a shallow to deep transition of the binding energy as the dot size is reduced [8, 9]; on further reduction the donor level once again becomes shallow. We have termed this non-monotonic shallow–deep behaviour as SHADES. The deepening of the donor level implies carrier ‘freeze out’. In the present work we investigate the binding energies and the optical gaps of ionized and neutral helium-like donors and show a similar phenomena for

these systems. This, we show, is a result of quantum confinement. The motivation for the work is to see if electron–electron interaction makes any difference in such a behaviour. We use two distinct methodologies, density functional-effective mass theory (DF-EMT) [10] and non-orthogonal tight-binding (TB) [11].

Our present study of helium-like donors is intimately connected to the work of Bhargava *et al* [12] on optical properties of Mn doped ZnS. They found that incorporating Mn impurities in ZnS nanocrystallites results in a spectacular enhancement of the luminescence efficiency (up to 18%) with a corresponding decrease of lifetime from milliseconds to nanoseconds. The deep defect levels in QD act as efficient traps for photo-excited carriers. Enhanced luminescence results when these carriers undergo radiative recombination. These observations are further supported by some other experimental work in this direction [13, 14]. Thus high luminescence is perhaps partly related to the deepening of impurity levels.

We employ DF-EMT using the Harbola–Sahni (HS) exchange potential [15]. Note that the HS scheme accounts for self-interaction correction while the LDA does not. This formalism has been employed earlier [16] to study the Coulomb blockade and the quantum capacitance of quantum dots. For the atomic case, the method essentially reproduces Hartree–Fock results for all the elements in the periodic table [17].

In the work presented below, we have used effective atomic units in which the unit of energy is  $27.2m^*/\epsilon^2$  eV and that of length is  $0.53\epsilon/m^* \text{ \AA}$ , where  $m^*$  is taken to be the effective mass of the electron in units of  $m_e$  (the free electron mass) and  $\epsilon$  is the relative dielectric constant of the bulk material. For example in bulk Si,  $m^* = 0.2$ ,  $\epsilon = 11.7$  so that the unit of energy is 39.7 meV and unit of length is 31  $\text{\AA}$ . The Hamiltonian of the system is

$$H = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \frac{1}{2} \sum_{j \neq i, i=1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} + V_{\text{ext}}(r) - \frac{Z}{r} \quad (1)$$

where  $V_{\text{ext}}$  is the confinement potential and  $-Z/r$  is the potential due to the impurity at the centre of the dot. For a helium-like impurity,  $Z = 2$ . We model the external potential as [16, 18]:

$$V_{\text{ext}}(r) = \begin{cases} (V_0/R^k)r^k - V_0 & r \leq R \\ 0 & r > R \end{cases} \quad (2)$$

where  $V_0$  is the depth of the potential. This is related to the conduction band offset (valence band offset) between the QD and the surrounding layer for the electron (hole).  $R$  is the radius of the QD and  $k$  assumes positive integral values. Changing the value of  $k$  results in the change of the shape of the potential. In particular  $k = 1$  is quasi-triangular,  $k = 2$  is the quasi-harmonic confinement and  $k \geq 10$  is the quasi-square well confinement. We solve the Schrödinger equation under the central field approximation. To obtain the radial component of the wavefunction, we employ the Herman–Skillman code [19] modified to incorporate the HS exchange potential in it.

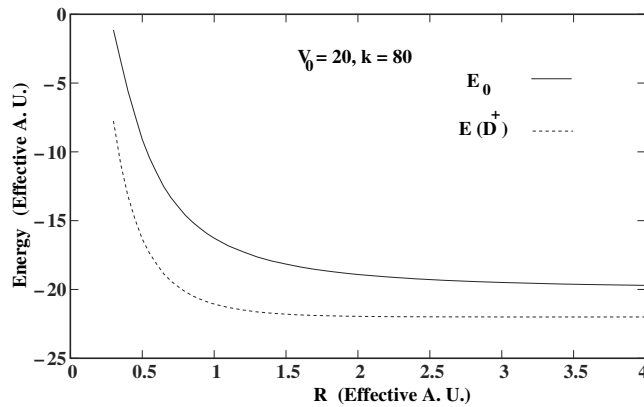
Since we are studying a helium-like impurity, it can exist in either the neutral or positively charged state. The binding energy of a positive donor can be written as

$$E_B(D^+) = E_0 - E(D^+) \quad (3)$$

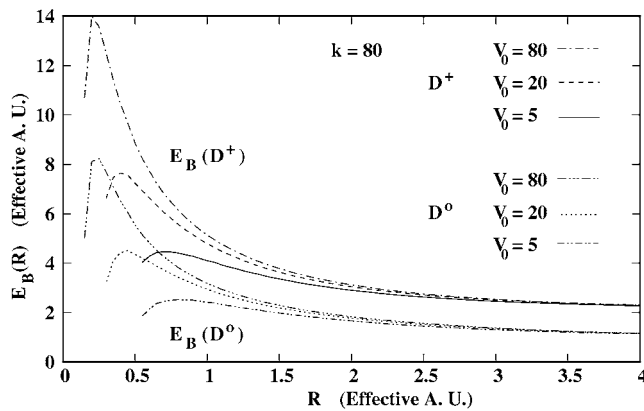
where  $E_0$  is the ground state energy of an electron in the conduction band and  $E(D^+)$  is the ground state energy of positive donor state ( $D^+$ ). The binding energy of a neutral donor is defined as

$$E_B(D^0) = E(D^+) + E_0 - E(D^0) \quad (4)$$

where  $E(D^0)$  is the ground state energy of a neutral donor.



**Figure 1.** The conduction band minimum (CBM) or LUMO (solid curve) and the donor level (dashed curve) are depicted as a function of QD size for  $V_0 = 20$  and  $k = 80$ . Effective atomic units are employed.



**Figure 2.** The binding energy  $E_B(R)$  is plotted as a function of the size  $R$  of the quantum dot for both charged ( $D^+$ ) and neutral ( $D^0$ ) donors. The shape chosen is a quasi-square well ( $k = 80$ ). The depths of the potential well are taken to be  $V_0 = 80, 20$  and  $5$ . The figure shows a non-monotonic shallow to deep (SHADES) transition as the dot size is reduced. Effective atomic units are employed.

Figure 1 depicts the conduction band minimum (CBM) or lowest unoccupied molecular orbital (LUMO) (solid curve) and the positive donor level (dashed curve) as a function of QD size for  $V_0 = 20$  and  $k = 80$ . As the dot size is decreased the CBM rises monotonically as  $1/R^\gamma$ , where  $\gamma \in [1.2:2.0]$  [20]. On the other hand, initially the impurity energy remains relatively constant in value as  $R$  is decreased and then it increases rapidly. This is because the impurity wavefunction is localized and consequently the impurity charge density is highly confined. This charge density does not sense the boundary initially. A visual examination of the figure indicates that the binding energy, which is the difference between the two levels, becomes large as  $R$  is decreased and then becomes small on further decrease. In other words, the donor level appears to undergo a SHADES transition.

Binding energies of the positively charged ( $E_B(D^+)$ ) and neutral ( $E_B(D^0)$ ) donors are depicted in figure 2. The shape of the potential is taken to be a quasi-square well ( $k = 80$ ).

**Table 1.** The table shows the maximum binding energy of the  $D^+$  and  $D^0$  states and the critical size ( $R_{\text{SHADES}}$ ) at which the SHADES transition takes place with varied depth of the confinement potential ( $V_0$ ). The shape of the confinement potential chosen is a quasi-square well ( $k = 80$ ). Effective atomic units are employed.

$V_0$	$R_{\text{SHADES}}(D^+)$	$V_0 R_{\text{SHADES}}^2(D^+)$	$E_B(D^+)$	$R_{\text{SHADES}}(D^0)$	$V_0 R_{\text{SHADES}}^2(D^0)$	$E_B(D^0)$
80	0.20	3.20	13.99	0.25	5.00	8.243
40	0.30	3.60	10.24	0.30	3.60	6.001
20	0.40	3.20	7.642	0.45	4.05	4.504
10	0.50	2.50	5.754	0.60	3.60	3.300
5	0.70	2.45	4.462	0.80	3.20	2.525
1	1.35	1.82	2.814	1.55	2.40	1.481

We vary the depths of the confining potential,  $V_0 = 5, 20$  and  $80$ . As is clearly seen from the plots, the binding energy exhibits a non-monotonic shallow to deep transition (SHADES): the binding energy increases as the dot size is reduced, on further reduction of the dot size the binding energy becomes shallow again. We observe that the binding energy depends on the depth of the confining potential and is large for large values of  $V_0$ . This is on account of the large confinement of the charge carrier. Binding energies of the neutral donor ( $D^0$ ) are smaller than those of the positive donor ( $D^+$ ). This is expected due to the Coulomb interaction between electrons in a neutral donor in a confined space.

We term the size at which binding energy is maximum as  $R_{\text{SHADES}}$ . From figure 2 we observe that  $R_{\text{SHADES}}$  increases monotonically with decrease in the depth of the well. These observations are recorded in table 1. We note that over a large range of confining potential ( $V_0 = 1-80$ ) the strength of confinement ( $V_0 R^2$ ) at  $R_{\text{SHADES}}$  remains relatively unchanged (column III and VI). This shows that the size at which SHADES occurs scales roughly as

$$R_{\text{SHADES}} \sim \frac{1}{\sqrt{V_0}}. \quad (5)$$

Why the SHADES transition occurs can be understood on the basis of following qualitative arguments. The expectation value of the potential seen by the electron becomes more negative as  $R$  shrinks. As a result the energy level of the electron gets deeper. However, as we decrease the size further (below  $R_{\text{SHADES}}$ ), the kinetic energy expectation value rises due to the well confinement and the electron wavefunction starts leaking out of the well. Consequently, in addition to the kinetic energy becoming larger, the potential energy expectation value also becomes relatively less negative with decreasing  $R$ . Thus the defect energy level starts rising up. At the same time the conduction band minimum also goes up but not as fast as the defect level. This results in SHADES. The qualitative arguments given above are also supported by the scaling of these levels with respect to the size of the dot. The scaling law for the conduction band minimum (CBM) is [20]

$$E_0(R) = -V_0 + \frac{C}{R^\gamma} \quad (6)$$

where  $\gamma$  is about 1.5 for quasi-square confinement ( $k = 80$ ) and  $V_0 = 10$ . For quasi-harmonic ( $k = 2$ ) and quasi-triangular ( $k = 1$ ) confinements with  $V_0 = 10$ ,  $\gamma$  is found to be 0.98 and 0.60 respectively.  $C$  is a constant. The impurity ground state energy  $E_i(R)$  is found to scale with size as [8]

$$E_i(R) = -E_\infty + \frac{C_1}{R^2} - \frac{C_2}{R} \quad (7)$$

where  $E_\infty$  is the bulk binding energy.  $C_1$  and  $C_2$  are constants. The binding energy, which is the difference between equations (6) and (7), yields a maximum and hence a non-monotonic

**Table 2.** The table shows the maximum binding energy of  $D^+$  and  $D^0$  along with  $R_{\text{SHADES}}$ . The shape ( $k$ ) of the confinement potential is varied. The depth of the confinement potential chosen is  $V_0 = 10$ . Effective atomic units are employed.

$k$	$R_{\text{SHADES}}(D^+)$	$E_B(D^+)$	$R_{\text{SHADES}}(D^0)$	$E_B(D^0)$
80	0.50	5.754	0.60	3.300
10	0.55	5.877	0.65	3.441
4	0.65	5.902	0.70	3.498
2	0.75	5.711	0.80	3.433
1	0.90	5.272	1.00	3.172

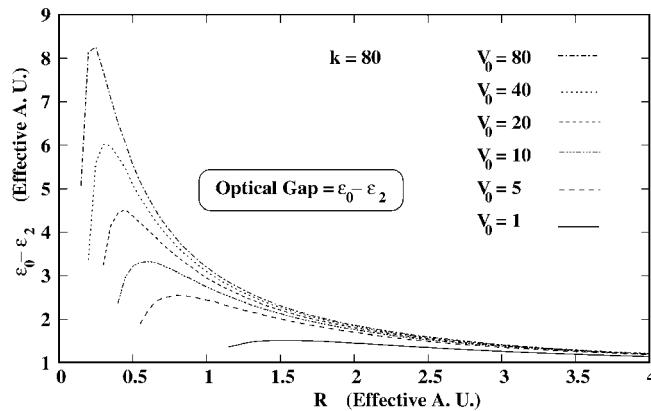
SHADES transition. Although these scaling arguments are based on our previous EMT calculations [8, 20], we find that they are also supported by the TB calculations reported here.

Table 2 summarizes the binding energies of  $D^+$  and  $D^0$  along with  $R_{\text{SHADES}}$  and their dependence on the shape of the confinement. Note that the values of  $R_{\text{SHADES}}$  for  $D^+$  and  $D^0$  and corresponding binding energies  $E_B(D^+)$  and  $E_B(D^0)$  are relatively insensitive to the shape of the confinement chosen. Further, the dependence of the binding energy maximum on the shape parameter ( $k$ ) is non-monotonic. Thus the shape of the confinement has little effect on the SHADES behaviour.

As we have mentioned earlier, the HS scheme is self-interaction free and gives good eigenvalues for a dot with a small number of electrons [16, 18]. We have calculated the ground state eigenvalue differences for both the positive and neutral donors,  $\epsilon_0 - \epsilon_1$  and  $\epsilon_0 - \epsilon_2$ . Here,  $\epsilon_0$  ( $=E_0$ ) is the eigenvalue of an electron in the conduction band minimum,  $\epsilon_1$  is the eigenvalue of the  $D^+$  state and  $\epsilon_2$  is the eigenvalue of the  $D^0$  state. These eigenvalue differences are representative of the optical gaps of the system [21]. Small corrections to it are provided by the time dependent density functional method [22, 23]. We have not incorporated these corrections here since our main motivation is to see the qualitative behaviour of the optical gap with the size of the QD. As expected, the eigenvalue difference,  $\epsilon_0 - \epsilon_1$  is exactly equal to the binding energy of the positive donor (equation (3)). Interestingly, in helium-like impurities  $\epsilon_0 - \epsilon_2$  is also found to be nearly equal to the binding energy of the neutral donor. The behaviour of the optical gap for a neutral donor is depicted in figure 3. The plot is for varied depth of the potential well ( $V_0 = 1-80$ ). From figure 3 it is clearly seen that the optical gap also shows a non-monotonic SHADES transition almost tracking the binding energy of the neutral donor (figure 2).

The physical significance of the SHADES transition is that a nominally shallow donor becomes deep and may act as a trap centre for the charge carriers. Thus carrier ‘freeze out’ is a distinct possibility in such systems. We also note from figure 2 and equation (5) that the binding energy has a systematic dependence on the well depth  $V_0$ . The well depth  $V_0$  is related to the band offsets between the dot and its dielectric coating. In fact as table 1 suggests,  $V_0 R^2$  at  $R_{\text{SHADES}}$  is approximately constant. This suggests the so-called ‘synthetic tailorability’ [24] of binding energy by selecting a suitable dot size or dielectric coating.

The observations reported above are based on the DF-EMT approach. We now ask if the same results are obtained by non-EMT based methods such as the tight-binding approach. The effective mass approximation is generally applied to large clusters and shallow levels. It is therefore important to learn how the results change when small size clusters and deep-levels are treated in EMT. We therefore also check the EMT results using the TB approach. In previous studies using a non-orthogonal tight-binding (TB) frame work, Ranjan *et al* [7] found that the binding energy of a neutral sulfur (S) donor in a Si QD was relatively insensitive to the dot

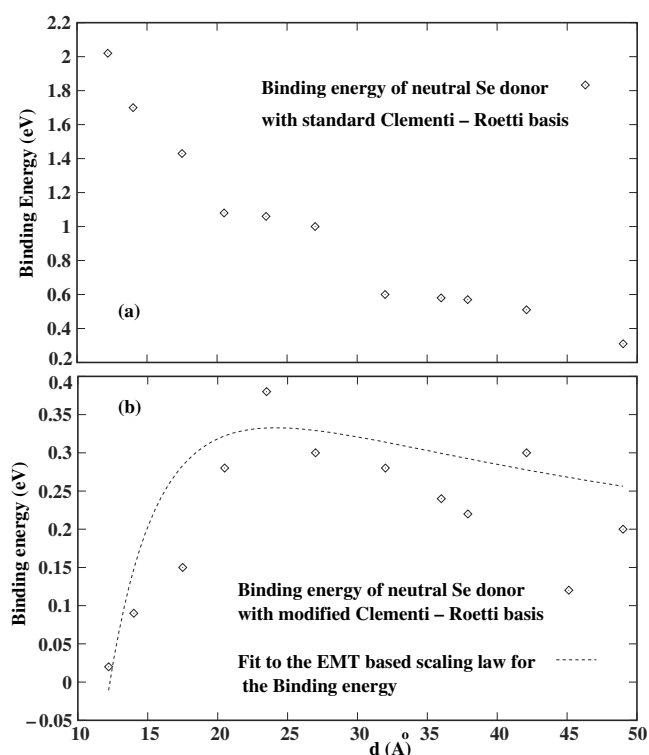


**Figure 3.** The eigenvalue difference of an electron in the conduction band minimum and the neutral donor ( $\epsilon_0 - \epsilon_2$ ) is depicted as a function of the size  $R$  of the QD. We call it the optical gap. The shape chosen is a quasi-square well ( $k = 80$ ). The depth of the potential well is varied,  $V_0 = 80, 40, 20, 10, 5$  and  $1$ . Effective atomic units are used.

size. Song *et al* [6] studied neutral and positive donors of chalcogen impurities in Si QDs, using the nearest neighbour orthogonal tight-binding model and the fixed cluster shape of the host. An examination of their results reveals that the chalcogen impurity levels are relatively insensitive to the dot size. Our investigation of both studies indicates that although the donor level becomes deep with decreasing dot size, the non-monotonic behaviour of the binding energy with size is not evident. On the other hand, our EMT based results definitively indicate a SHADES transition both in the binding energy and the optical gaps. Thus there appears to be an inconsistency between the two sets of results.

In order to understand the apparent disagreement between the DF-EMT results and the TB results, we have done calculations for a selenium (Se) impurity, using the tight-binding Clementi–Roetti (CR) [25] orbitals and the orbitals for an atom confined in the Si QD of the order of  $20 \text{ \AA}$  size. The latter have been obtained by solving the Kohn–Sham equation in a model potential (equation (2)). The results are shown in figure 4. We see that whereas the standard CR orbitals do not give SHADES (upper plot), the modified orbitals do (lower plot). This is because whereas CR orbitals fail to sense the boundary of the QD, the latter orbitals do and hence show its effect. For larger sizes, the two results are similar. This shows that when we use the CR orbitals with the boundary effects built-in, we observe a trend similar to our EMT results. Interestingly the EMT based scaling law for the binding energy, i.e. the difference between equations (6) and (7), fits well with the TB result (dashed curve in the lower plot of figure 4), with  $\gamma = 1.4$ . For the TB calculation, the Se atom was placed centrally at the substitutional site and the atoms of the Si QD were arranged around it up to a size of  $50 \text{ \AA}$ . We used  $4s$  and  $4p$  non-orthogonal orbitals which overlap up to six neighbours. This methodology was developed three decades ago and was termed as the ‘defect molecule’ method [26, 27]. A number of defects in silicon and carbon were studied including hydrogen in silicon [11].

We point out that EMT and TB both substantiate the quantum confinement model. Simply stated, this model implies that as the size of the QD is reduced, the conduction (valence) band minimum (maximum) upshifts (downshifts). This scenario has been validated by a wide variety of EMT, TB and even first principles LDA calculations [28]. It has been confirmed by diverse experimental methods [29, 30]. While detailed agreement between theory and experiment is



**Figure 4.** The binding energy of a neutral selenium donor in a silicon quantum dot is shown as a function of diameter ( $d = 2R$ , where  $R$  is the radius of quantum dot). The results are obtained using a non-orthogonal tight-binding framework. In the upper plot (a) the standard Clementi–Roetti basis is used, whereas in the lower plot (b) a modified basis which takes into account the boundary effects is used.

lacking [31], the basic fact of inverse dependence on size is not in doubt. It is thus heartening to note that we find a similar agreement between EMT and TB for an impurity in a QD.

An important question is how we may verify SHADES. Several properties have been studied as a function of nanostructure size. For example the band edges have been extensively investigated by a variety of experimental techniques [29, 30]. Their size can be controlled by chemical means during preparation so that the band gap of the particles can easily be selected [13, 32]. So, imprecise as it might be, progress is being made towards measuring energy related parameters. There are reports on deep level transient spectroscopy (DLTS) measurements of defect energies [33]. Similar techniques can be employed to study variation of defect energies with size of a quantum dot.

In conclusion SHADES implies carrier ‘freeze out’. However, further studies with off-centred impurities and alternative methodologies should be carried out. We note that our results are relevant to the experimental investigations of Bhargava *et al* [12]. In their work, they proposed that deep levels in materials such as Mn doped ZnS would act as efficient traps for photo-excited carriers. This leads to enhanced luminescence when these carriers undergo radiative recombination. The quantum efficiency increases with decreasing size of the particles (see their figure 4). This suggests that a suitably tailored ‘deep’ dopant may act as a luminescent centre. These statements are supported by some further experimental investigations [13, 14]. Finally, experimental validation of SHADES and associated scaling laws would be heartening.



## Acknowledgment

This work was supported by the Department of Atomic Energy through the Board of Research in Nuclear Sciences, India (Grant No 2001/37/16/BRNS).

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