

## Defects in semiconductor nanostructures

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**Abstract.** Impurities play a pivotal role in semiconductors. One part in a million of phosphorous in silicon alters the conductivity of the latter by several orders of magnitude. Indeed, the information age is possible only because of the unique role of shallow impurities in semiconductors. Although work in semiconductor nanostructures (SN) has been in progress for the past two decades, the role of impurities in them has been only sketchily studied. We outline theoretical approaches to the electronic structure of shallow impurities in SN and discuss their limitations. We find that shallow levels undergo a SHADES (SHAllow–DEep–Shallow) transition as the SN size is decreased. This occurs because of the combined effect of quantum confinement and reduced dielectric constant in SN. Level splitting is pronounced and this can perhaps be probed by ESR and ENDOR techniques. Finally, we suggest that a perusal of literature on (semiconductor) cluster calculations carried out 30 years ago would be useful.

**Keywords.** Dopants; semiconductor; defects; nanostructures; effective mass theory; density functional theory; tight binding.

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### 1. Introduction

Semiconductor nanostructures (SNs), more popularly known as quantum dots (QDs), have been extensively studied in the past two decades. The system is interesting from the point of view of basic physics, with the carriers being confined to an essentially ‘zero’-dimensional structure. The efficient luminescence observed in some of these crystallites makes them promising candidates for opto-electronic devices. Further, the inexorable drive towards device miniaturization makes them technologically significant.

The study of impurity states in low-dimensional heterostructures is an important aspect to which many theoretical and experimental works have been devoted. Experimental work in connection with impurities in semiconductor nanostructures is in the initial stage and is of recent origin [1–3]. Bastard [4] reported the first calculation for binding energies of hydrogenic impurities in quantum wells. He reported that the binding energy of an impurity depends both on the position of the impurity and the thickness of the well. This work was followed by several others [5,6].

Over the last ten years many developments in the synthesis of quantum dots (QD) attracted the attention of some workers towards hydrogenic impurities in them. Porrás-Montenegro and Pérez-Merchancano [7] studied the hydrogenic impurity in QDs. Theirs was a variational calculation for impurities in GaAs/Ga<sub>1-x</sub>Al<sub>x</sub>As. The same group later calculated the density of states of the impurity [8]. Ribeiro and Latgé [9] calculated the same for the cubic dots and compared it to the effect of dimensionality and shape of quantum dots. Fanyao and co-workers [10] studied the intense field effect on hydrogenic impurities in QDs. The effect of intense field, they found, was to effectively shift the impurity from the center of QD to some off-center position. In this work we review our work on dopants in semiconductor nanostructures (SN) which has been carried out using a variety of theoretical methodologies [11].

## 2. EMT model

In the simplest version of effective mass theory (EMT) the Hamiltonian of the system is (Hartree's atomic units are used, unit of energy is 27.2 eV and that of length is 0.53 Å) [12]

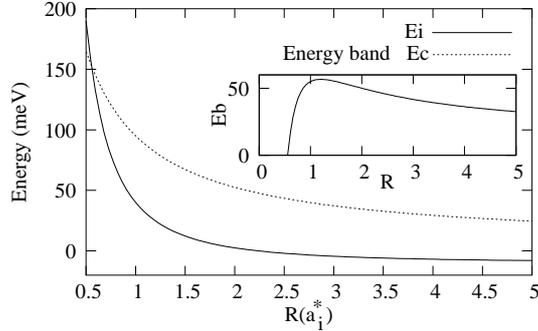
$$H = - \sum_{i=1}^N \frac{\nabla_i^2}{2m^*} + \frac{1}{2} \sum_{j \neq i, i=1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{i=1}^N \left( V_{\text{ext}}(r_i) - \frac{Z}{r_i} \right), \quad (1)$$

where  $V_{\text{ext}}$  is the confinement potential and  $-Z/r$  is the potential due to the impurity at the center of the dot. For a hydrogenic impurity,  $Z = 1$ ,  $m^*$  is the effective mass of the electron inside the QD in units of  $m_e$ , the free electron mass. We model the external potential as [13,14]

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

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 quasi-harmonic confinement and  $k \geq 10$  is quasi-square well confinement.

The hydrogenic donor impurity exhibits a spectrum of behaviour going from shallow to deep and then to shallow. We term this behaviour SHADES (SHAllow-DEep-Shallow). In figure 1 we have shown the conduction band minima (CBM) for GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As, based on our calculation mentioned above, and the hydrogenic impurity level for different sizes of QD. The conduction band upshifts infra-quadratically for all sizes of QD. When the size of the QD is much larger than the extend of the impurity wave function, then the impurity level remains insensitive, i.e. it remains unchanged as the dot size is decreased. When the dot size is reduced further, wave function starts sensing the QD boundary. Consequently, wave function shows confinement effect. This is the region where the impurity level



**Figure 1.** Plot of the variation of the conduction band minimum  $E_c$  and the impurity level  $E_i$  with size. The difference is the binding energy  $E_b$  which is depicted in the inset. Note that  $E_b$  undergoes a SHADES transition. The size is in units of the impurity Bohr radius  $a_i^*$ .

rises very steeply. This accounts for SHADES. The SHADES behaviour has been noticed in a variety of systems: GaAs, GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , CdS, ZnS, in other words in III–V and II–VI semiconductors (see figures 3–5 of [12]).

### 3. DF-EMT model

We have also studied helium-like and charged hydrogenic donors. The latter study is relevant to chalcogen (S, Se, Te) impurities in silicon and they can exist in either neutral or positively charged state. Electron–electron interaction needs to be taken into account in this case. We employ the density functional methodology within EMT (DF-EMT) using the Harbola–Sahni (HS) exchange potential [15]. Note that the HS scheme accounts for self-interaction correction while the local density approximation (LDA) does not. This formalism has been employed earlier [13] to study the Coulomb blockade and the quantum capacitance of quantum dots. In this scheme the binding energy of a positive donor can be written as

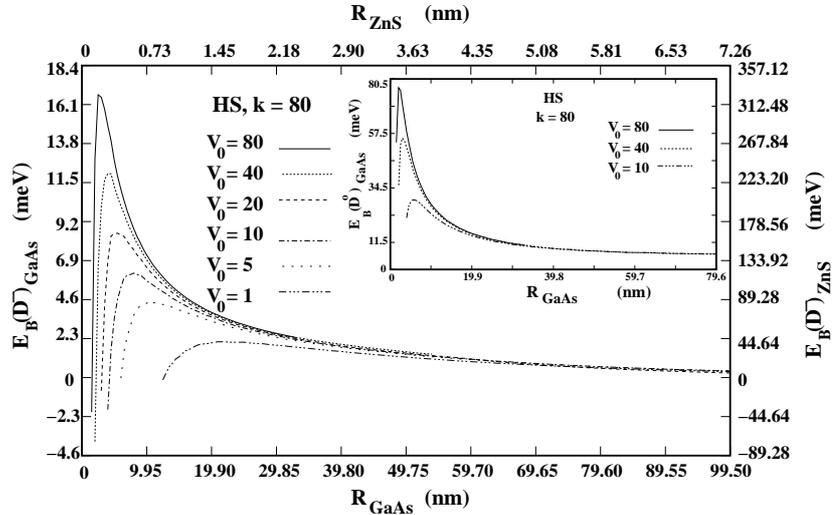
$$E_b(D^+) = E_0 - E(D^+) \quad (3)$$

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.

This scenario is presented for the technologically relevant case GaAs and ZnS QDs in figure 2. Figure 2 is for a negatively charged donor where many-body effects are relevant. The inset is for neutral donor. Both  $D^0$  and  $D^-$  show similar behaviour. SHADES is once again observed. As we have mentioned earlier, the HS scheme has self-interaction correction built-in, hence it calculates very good eigenvalues for small number of electrons. This enables us to study optical transition energies

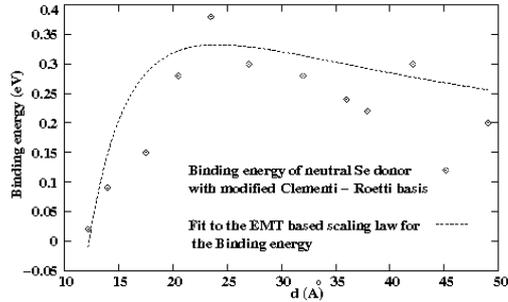


**Figure 2.** This plot shows the dependence of the binding energy of the negative donor (meV) on the size  $R$  (nm) and the depth  $V_0$ . The materials chosen are GaAs and ZnS (adapted from ref. [16]).

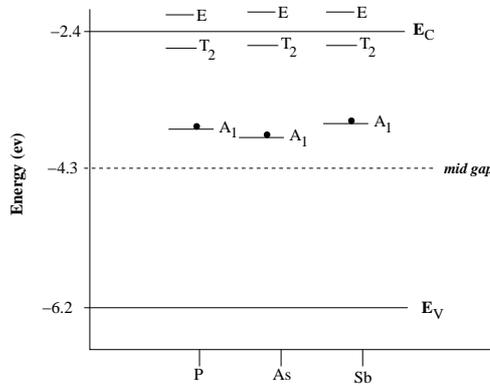
as well (see figures 3 and 4 of [16] and figure 3 of [17]). We have also observed SHADES behaviour for the helium-like double donor in SN (see figure 2 of [17]). The helium-like double donor case will be discussed critically in §4. We will discuss the implications of SHADES behaviour in §6.

#### 4. Tight binding (TB) methodology

The observation reported above are based on DF-EMT approach. We now ask if the same results are obtained by non-EMT based methods such as tight-binding approach. We have done calculations for selenium (Se) impurity, using orbitals for the Se atom confined in the Si QD of the order of 20 Å size. The latter has been obtained by solving the Kohn-Sham equation in a model potential (eq. (2)). The results are shown in figure 3. We note that whereas the standard Clementi–Roetti (CR) [18] orbitals do not give SHADES, the modified orbitals do. This is because CR orbitals are generated for the free case and fail to sense the boundary of the QD but the modified orbitals do and hence show its effect. For larger sizes, the two results are similar. Interestingly, the EMT-based scaling law for the binding energy, i.e. the difference between eqs (6) and (7) (see §6.1) fits well with the TB result 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 upto a size of 50 Å. We used 4s and 4p non-orthogonal orbitals which overlap up to six neighbours [19].



**Figure 3.** The binding energy of neutral selenium donor in a silicon quantum dot is shown. The results are obtained using a non-orthogonal tight-binding framework. Instead of the standard Clementi–Roetti basis we employ a modified basis which takes into account the boundary effects.



**Figure 4.** First principles Si cluster calculations for the Group V dopants in  $\text{Si}_{71}\text{XH}_{47}$  where  $X = \text{P}, \text{As}, \text{Sb}$ .

## 5. First principles cluster calculation

We have carried out cluster calculations using first principles methodology. The calculations are based on LDA. Hamann, Schlter, and Chiang Pseudopotentials [20] was employed so that we can deal with relatively large clusters. Preliminary results for centrally located substitutional Group V donors (P, As, Sb) in an 71 atom hydrogen terminated Si cluster are displayed in figure 4. The ‘band gap’ of the cluster is enhanced (3.8 eV) as is to be expected from quantum confinement considerations. All three donors are deep with  $E_b \approx 1.0$  eV. An examination of the charge density suggests that the donors are deep due to the reduction of screening. The large splittings ( $A_1 - E - T_2$ ) suggest that local field effects are important and can be probed by EPR and ENDOR experiments. On account of computational limitations we cannot go to larger clusters and probe the possibility of SHADES. We have also carried out similar calculations for the Mn impurity in GaAs [21].

## 6. Discussion

### 6.1 Scaling laws

We now discuss some scaling laws which hold for the neutral, the charged, and the double donor. We term the size at which binding energy is maximum as  $R_{\text{SHADES}}$ . We observe from the figures described above that  $R_{\text{SHADES}}$  increases monotonically with decrease in the depth of the well. We find that the size at which SHADES occurs scales roughly as

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

Another interesting observation is the increase in the binding energy with increasing  $V_0$ .

The SHADES behaviour is supported by the following scaling arguments. The scaling law for the conduction band minimum (CBM) is

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

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

$$E_i(R) = -E_b^{\text{bulk}} + \frac{C_1}{R^2} - \frac{C_2}{R}, \quad (7)$$

where  $E_b^{\text{bulk}}$  is the bulk binding energy and,  $C_1$  and  $C_2$  are constants. The binding energy which is the difference between eqs (6) and (7) yields a maximum and hence a non-monotonic SHADES transition.

### 6.2 Implications of the scaling laws

The increase in binding energy in SN suggests that carriers will ‘freeze out’. We also find that the binding energy and its maxima depend on the well depth  $V_0$ . The latter is a surface-related property depending on surface termination of dangling bonds, the dielectric coating, etc. Thus, with experience, it may be possible to engineer the magnitude of the binding energy, making it shallow, intermediate or deep depending on one’s needs. This suggests the so-called ‘synthetic tailorability’ of binding energy by selecting a suitable dot size or dielectric coating. It could usher in the era of ‘defect engineering’ in QDs. To repeat, it is clear from figure 2 that the doped GaAs QDs of size  $R \leq 20$  nm will be susceptible to carrier ‘freeze out’. Similarly, the doped ZnS QDs of size  $R \leq 2$  nm will be susceptible to carrier ‘freeze out’.

### 6.3 Historical observations

The tight binding methodology described in §4 was developed three decades ago and was termed as the ‘defect molecule’ method. A number of defects in silicon and carbon was studied including hydrogen [19] and lithium (the shallowest donor) [22] in silicon. These studies covered a wide canvas: electronic levels, structural relaxation, migration pathways, vibrational modes, frequencies etc. The largest cluster sizes were less than 100 Si atoms due to computational limitations. An interesting parallel is that current first principles calculations alluded to in §5 are size hampered for similar reasons. These ‘defect molecule’ calculations were probably the first studies in SN. We believe that a perusal of this ‘ancient’ scientific literature would provide valuable insights even today.

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