Atomistic Description of Shallow Levels in Semiconductors

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Abstract

The wave function and binding energy for shallow donors in GaAs are calculated within the tight binding (TB) approach, for supercells containing up to two million atoms. The resulting solutions, coupled with a scaling law, allow extrapolation to the bulk limit. A sharp shallow-deep transition is obtained as the impurity perturbation increases. The model allows investigating the quantitative consistency between the effective mass theory and the TB formalism. Although the calculated binding energies are in excellent agreement, anisotropies and the overall decay obtained in the TB envelope function can not be afforded by the hydrogenlike effective mass prediction.

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Electronic states in condensed matter systems may exist in either localized atomic-like states or in delocalized running-wave states [1]. Such dualistic behavior has led naturally to two well-established frameworks in which to describe the electronic behavior of solids: Real space pictures privilege the atomic aspects of electronic behavior, whereas Bloch states provide a foundation to describe the wave-like properties. For an ideal periodic crystal, these two views were reconciled several decades ago, when Wannier [2] showed that a set of orthogonal “atomic” functions localized at the crystal’s atomic sites may be obtained from the Bloch eigenfunctions, and that either may be taken as the basis set for the general description of electrons in solids. Any electronic theory which adopts a basis set localized in real space is generally referred to as following the tight-binding (TB) approach. In some practical cases, it is also possible to utilize a basis set localized in reciprocal space about an appropriate point in the Brillouin zone. Such an approach then gives rise to the so-called Effective Mass Theory (EMT) [3]. EMT is the most successful comprehensive approach for the description of electronic excitations in insulators, of transport and optical properties in semiconductors, of dynamics of electrons in metals [4].

A crowning achievement, dating as far back as the 1950’s, of the EMT is undoubtedly the quantitative understanding obtained of shallow impurity states in semiconductors [5–7]. A complementary TB theory for deep impurities was presented later by Hjalmarson et al, [8]. The choice of approach in each case is defined naturally, given the extended nature of the shallow levels described within EMT versus the localized nature of the deep states considered in the TB scheme. A basic limitation of the EMT, however, is that the approximation (i.e., a single dominant k-point) breaks down as the impurity state becomes increasingly delocalized throughout the Brillouin zone, such as the case for deep levels. Similarly, a practical limitation of the TB approach is that until now it could not be extended to the shallow impurity limit due to the slow decay of the defect wave function which requires extremely large supercells for meaningful calculations. As a result, for decades a gap has existed between two of the most widely used theories for impurities in semiconductors: The TB approach was confined to deep states, whereas the EMT was used for shallow states.
In the present work we demonstrate that the gap between shallow and deep levels may be bridged via the TB formalism in conjunction with extrapolation schemes for the binding energies and for the envelope functions. Our proposed atomistic description provides a flexible way to explore and test key predictions of EMT for shallow levels. In particular, the following points are addressed and explained: (a) The values of ionization energies, (b) the independence of these ionization energies on the impurity species, and (c) the shape of the envelope function for the defect state. We show that wave functions may substantially deviate from the hydrogen-like predictions of EMT. Besides the obvious academic interest of unifying shallow and deep impurity level descriptions within a single theoretical approach, problems of current interest in nanostructured materials demand an atomistic description for which the TB approach coupled to the theoretical tools adopted herein may provide a reliable alternative to EMT and to ab-initio treatments based in the local density approximation.

In the EMT, it is assumed that the impurity wave function is highly delocalized in real space, which in turn implies a strong localization in \( k \)-space. The electronic properties of the host material are thus described by a few parameters related to the energy bands near the set of \( k \)-points in consideration. In particular, effective masses are defined from the bands’ curvatures at these points. The simplest case is that of a nondegenerate conduction band with an extremum at \( \Gamma (k = 0) \), corresponding to the Bloch eigenstate \( \psi_{C}(r) \) and eigenvalue \( E_{C} (\Gamma) \). The cubic symmetry of the lattice implies that the nondegenerate band is isotropic around this extremum, leading to a single effective mass \( m^* \): \( E_{C}(k \approx 0) = E_{C}(\Gamma) + \hbar^{2}k^{2}/2m^* \). Following the original EMT formulation, the perturbation potential for donor impurities is

\[
U(r) = -e^{2}/\varepsilon r,
\]  

where \( \varepsilon \) is the static dielectric constant of the host. Within a set of additional approximations, the impurity wave function is written as \( \Psi(r) = F(r)\psi_{C}^{\Gamma}(r) \), and the eigenvalue problem for the one-electron Hamiltonian \( H = H_{0} + U(r) \), where \( H_{0} \) describes the perfect host material, maps into an hydrogenic equation.
\[ [-\hbar^2 \nabla^2 /2m^* + U(r)]F(r) = [E - E_C(\Gamma)]F(r) \]  

leading to the ground state envelope function \( F(r) = (1/\sqrt{\pi a^*}) \exp(-r/a^*) \), where \( a^* = a_0 \varepsilon (m_0/m^*) \) is the effective Bohr radius, \( a_0 = 0.53 \text{ Å} \) is the Bohr radius of the hydrogen atom and \( m_0 \) is the free electron mass. The EMT basic assumptions are fulfilled if \( a^* \) is much larger than the host lattice parameter. In this case, the donor binding energy for a single impurity is \( E^*_d = E_H [m^*/(\varepsilon^2 m_0)] \), where \( E_H = 13.6 \text{ eV} \) is the hydrogen ionization energy.

For donor levels in semiconductors with a conduction-band minimum at \( \Gamma \), the above model combines simplicity and physical intuition and moreover leads to a good agreement with experimental results. In the case of GaAs, \( \varepsilon = 12.56 \) and \( m^*/m_0 = 0.068 \), leading to \( a^* = 97.7 \text{ Å} \) (which is indeed much larger than the host lattice parameter \( a_{\text{GaAs}} = 5.65 \text{ Å} \)), and to \( E^*_d = 5.86 \text{ meV} \), which is in remarkable agreement with the experimental data for donor binding energies in this material [13]. It is intriguing that most donor levels in GaAs are essentially independent of the substitutional species, e.g. 5.91, 5.84 and 5.88 meV respectively for C, Si and Ge replacing Ga, while acceptor levels vary by almost a factor of two for these same species substituting As [12]. We choose this extreme situation of very shallow donor levels, for which EMT predictions for the binding energy work remarkably well, to explore the limits and capabilities of the TB formalism within a recently proposed scheme [12].

We consider a single impurity placed in a large cubic supercell containing \( N = 8(L/a_{\text{GaAs}})^3 \) atoms arranged in the zincblende structure, where \( L \) is the supercell edge length. Periodic boundary conditions are imposed, and supercells containing up to 2 million atoms \( (L = 64 \times a_{\text{GaAs}} = 361.6 \text{ Å}) \) are considered. We use the \( sp^3s^* \) basis for the TB description of the electronic structure, with the bulk GaAs Hamiltonian taken from Boykin’s parametrization [10], which includes first and second neighbor interactions and leads to an accurate value for the conduction band effective mass at \( \Gamma \). Due to the \( s \)-character of the GaAs conduction band edge, spin-orbit corrections may be neglected in our calculations. The TB Hamiltonian is written as [12].
\[ H = \sum_{ij\mu\nu} h_{ij\mu\nu} c_{i\mu}^{\dagger} c_{j\nu} + \sum_{i\mu} U(r_i) c_{i\mu}^{\dagger} c_{i\mu} \]

where \( i \) and \( j \) denote the sites in the zincblende structure, \( \mu \) and \( \nu \) denote the atomic orbitals and \( r_i \) is the distance from site \( i \) to the impurity site. The \( h_{ij\mu\nu} \) define all the on-site energies and first and second neighbor hoppings for the bulk material. The perturbation potential \( U(r_i) \) is described by Eq.(1), except at the impurity site \( (r_i = 0) \), where it is assigned the value \( U_0 \), describing central cell effects according to the substitutional species. In the present calculations, \( U_0 \) is kept as a free parameter. Estimates for this parameter are of the order of one to a few eV. Note that the impurity potential in (3) incorporates both the long-range component of the original EMT formulation and the short-range perturbation \( U_0 \) restricted to the impurity site) of the original TB formulation.

The exact ground state wave function and binding energy \( E_L \) for a donor level within a supercell of size \( L \) was obtained by minimizing the expectation value of \( \langle \Psi | (H - \varepsilon_{\text{ref}})^2 | \Psi \rangle \), where \( \varepsilon_{\text{ref}} \) is a reference energy chosen below the conduction band minimum, with the TB wave function expansion coefficients \( \{ C_{i\mu} \} \) taken as independent variational parameters. This procedure is equivalent to the exact diagonalization of \( H \) for the eigenvalue and eigenfunction closest to \( \varepsilon_{\text{ref}} \). The calculated binding energies as a function of \( U_0 \) are given in Fig. 1(a). It is clear that there is a range of the values of \( U_0 \) for which \( E_L(U_0) \) is constant, indicating that the binding energy does not depend on the impurity species, in agreement with the EMT and with experiments. A well defined shallow-to-deep transition occurs for \( U_0 \approx 1.8 \) eV, above which the binding energy increases approximately linearly with \( U_0 \). Aiming at a better characterization of this transition, we calculate the orbital averaged spectral weight of the donor state,

\[ W(k) = \frac{2}{N} \sum_{\mu,i,j} e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} C_{i\mu}^{*} C_{j\mu}, \]

where \( \mathbf{R}_i \) and \( \mathbf{R}_j \) denote the position vectors of the \( i \) and \( j \) atomic sites. The calculated \( W(k) \) for \( k = \Gamma, X \) and \( L \) points in the fcc Brillouin zone are given in Fig. 1(b). We visualize in this Figure the \( k \)-space counterpart of the shallow-to-deep transition around \( U_0 = 1.8 \) eV. For \( U_0 \approx 1.8 \) eV, the wave function has an almost pure \( \Gamma \) character, since \( W(\Gamma) \) is very
close to 1. This extreme localization in k-space is consistent with the EMT assumptions, and indicates a highly delocalized wave function in real space. Increasing \( U_0 \) beyond 1.8 eV, the dominant \( \Gamma \) character breaks down and the impurity state must be described in terms of the several \( k \)-point components, indicating delocalization in \( k \)-space, localization in real space. This is consistent with the deeper character of the state obtained in Fig. 1(a) in this range of \( U_0 \).

In their original TB study, Hjalmarson et al. [8] noted that shallow levels are unbound by the central cell potential alone, and thus could not be obtained there. Our calculations are in complete agreement with this interpretation: We find that, in the whole range of \( U_0 \) for which \( E_L(U_0) \) is constant, no bound state is obtained if the Coulomb potential is not included in the impurity perturbation. This result confirms a simple physical criterion characterizing shallow levels, and the reason why they do not depend on the substitutional impurity species, i.e. on \( U_0 \), since the binding is entirely due to the Coulomb attraction part of the perturbation potential. On the other hand, when deeper levels are obtained, \( U_0 \) alone also leads to a bound state, and therefore the binding energy is sensitive to the impurity species.

In the following we focus on shallow donors. Given that the binding energy is independent of \( U_0 \) in this regime, we arbitrarily take \( U_0 = 1.0 \) eV in the model calculations. This is a reasonable choice given the value of the Coulombic potential at the nearest-neighbor distance. Fig. 2(a) gives the donor ionization energy calculated at increasing supercell sizes. Results for \( E_L \) presented there, even for the largest sizes, are still decreasing with \( L \). This difficulty was overcome in Ref. [12] by assuming that, asymptotically, the convergence of \( E_L \) to the isolated-impurity limit (\( L \to \infty \)) should be exponential, namely

\[
E_L = E_\infty + \tilde{E} e^{-L/\lambda}.
\]

where \( \tilde{E} \), \( \lambda \) and the donor ionization energy for infinite cells \( E_\infty \) are taken as adjustable parameters. The validity of Eq.(5) implies a linear dependence of \( \ln[(E_L - E_\infty)/E_\infty] \) on the system size \( L \). These are the circles in Fig. 2(b). As indicated by the straight solid
line, a linear behavior is obtained for $L/a^* \gtrsim 1.5$ with the extrapolated bulk donor binding energy $E_\infty = 6.7 \text{ meV}$ and $\lambda = 1.25a^*$. We note a much slower convergence of the donor shallow level with $L$ as compared to previous calculations for acceptors [12]. Similar fits were obtained for $E_\infty = 6.7 \pm 0.7 \text{ meV}$, while values of $E_\infty$ outside this range lead to systematic deviations of the calculated data points from a linear behavior. The extrapolated binding energy $E_\infty$ is indicated in Fig. 2(a). Although the EMT value is slightly off the lower limit estimated numerically, our results do not indicate any significant discrepancy between the binding energies determined by the two approaches [13].

We now focus on the analysis of the donor wave function. Fig. 3 gives the TB envelope function squared (expansion coefficients squared, summed over the five orbitals for the cation sublattice), calculated for $L = 48a_{\text{GaAs}} \approx 270\text{ Å}$, as a function of distance from the impurity along the [100], [110] and [111] directions. At long distances, the wave function shows no angular dependence, as predicted by EMT. However, in the vicinity of the impurity there are noticeable anisotropies, which are highlighted in the inset. This is an effect of the crystalline environment that is automatically captured in an atomistic method such as TB. A more important discrepancy with respect to EMT is that the donor-state wave functions cannot be described by a simple exponentially decaying behavior. In fact, the line in Fig. 3 is a sum of exponential functions centered at each supercell-periodic replica of the impurity, decaying with the EMT Bohr radius of 97.7 Å. The agreement is not good, and it cannot be improved by varying the Bohr radius.

It is not surprising that EMT works well for the binding energies but not so well for wave functions. This can be seen as a manifestation of the variational principle: Small variations in the ground-state wave functions do not affect the ground-state energies in linear order. We test this hypothesis through a set of variational calculations in which trial wave functions are constructed by rescaling the TB expansion coefficients of the true wave function in such a way that they are constrained to an envelope composed of summing exponential functions centered at each periodic replica of the impurity. In other words, in these test calculations, the TB wave function expansion coefficients $\{C_{\mu\nu}\}$ are not independent.
variational parameters, but follow an exponential-decay behavior, corrected for the periodic boundary conditions. The decay length is now the sole variational parameter and it is then varied to minimize energy. We name these calculations “hydrogenic tight-binding” (HTB). The binding energies resulting from these constrained variational calculations also scale with supercell size as in Eq. (5), as shown by the triangles in Fig. 2(b). The extrapolated value, $E_{\infty}^{HTB} = 6.4 \pm 0.6$ meV, is for all practical purposes indistinguishable from the full TB value. We also calculate, for different supercell sizes $L$, the optimum decay length $a_L$, as illustrated in Fig. 4. We find that the calculated lengths also converge exponentially:

$$a_L = a_\infty + \bar{a} e^{-L/\lambda}.$$  \(6\)

The extrapolated Bohr radius is $a_\infty = (93 \pm 5)$ Å, entirely consistent with the EMT prediction! Therefore, even though the true wave function is not exponentially decaying, if such a constraint is imposed (as in EMT), the optimum Bohr radius agrees with EMT predictions and the binding energy is essentially correct.

In conclusion, we study the problem of shallow donors in GaAs within the TB formalism. The use of large supercells (up to $L = 361.6$ Å), together with a finite-size scaling procedure, allows an unprecedented test of EMT for shallow levels in semiconductors. We find good agreement between TB and EMT in the determination of the binding energy, but hydrogenlike wave functions do not provide an accurate description of the impurity state. In addition, by varying the central cell corrections to the potential, we confirm the EMT predictions that the binding energy is independent on atomic impurity species for shallow levels. Our results are inconsistent with the commonly accepted idea that it is straightforward to describe bound states within atomistic approaches if the supercell is large compared to the Bohr radius (or typical localization lengths). For the binding energy, the value obtained for a cell at least 3 times the EMT Bohr radius is about 30% above the converged value. An extrapolation scheme is required to reach reliable results. Description of the wave function is even more subtle, due to the adopted boundary conditions. Periodic boundary conditions requires careful consideration of contributions from the impurity periodic images.
We demonstrate these inconsistencies and propose general and original ways to overcome them, applicable to any atomistic approach.

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[15] Note the large energy scales involved in the problem, e.g. in Figs. 1(a) and 2(a), from which differences of tens of a meV may well be due to some degree of arbitrariness in the fitting procedures or small inaccuracies in our numerical variational scheme.
FIG. 1. (a) Binding energy of the impurity level as a function of the central cell perturbation potential $U_0$ for different supercell sizes $L$. (b) Calculated spectral weights for the $\Gamma$, $X$ and $L$ $k$-points as a function of $U_0$. The solid lines are guides for the eye. Both (a) and (b) reveal a clear shallow-to-deep level transition around $U_0 = 1.8$ eV.
FIG. 2. (a) Tight-binding results for the binding energy of a single donor substitutional impurity in GaAs as function of supercell size $L$, with a central cell correction $U_0 = 1.0$ eV. The dotted line represents the EMT value ($E^*_d = 5.86$ meV), which is in good agreement with experimental data. The circle at the lower left gives our extrapolated value for $L \rightarrow \infty$, $E_\infty = 6.7 \pm 0.7$ meV. (b) Exponential convergence of the donor binding energy for both TB and HTB calculations described in the text. The line is an exponential fit to the TB results (see text) with $E_\infty = 6.7$ meV.
FIG. 3. TB envelope function squared along the indicated lattice directions. The solid line is a sum of exponential functions centered at each periodic replica of the impurity, decaying with the EMT Bohr radius of 97.7 Å. The inset illustrates the anisotropy of the TB wave function around the impurity site.
FIG. 4. Exponential convergence of the Bohr radius with the supercell size $L$ in the HTB model. The dotted line corresponds to $a_\infty = 93 \, \text{Å}$. 