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Real-space equation for single-donor impurities and core excitons in many-valley semiconductors

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We solve with high accuracy a previously derived equation in real space for single-donor impurities and core excitons in many-valley semiconductors. That includes, beyond the effective-mass theory, both effects due to the intervalley scattering and to the short-range behavior of the impurity potential. As we previously reported, we obtain in Si a shallow-deep instability for the A_1 singlets and the dispersively screened point-charge potential, at both the substitutional and the interstitial sites. Our prediction of such deep levels appears to be substantially confirmed by the most recent experimental data. We also introduce a direct test on the localization and convergence of the envelope function in $\vec{k}$ space. We show that in most cases there is no shallow-deep instability and the envelope function involves only a single band. In these cases this method should in fact provide accurate values for the binding energies.

I. INTRODUCTION

The problem of the donor levels in many-valley semiconductors is of fundamental importance in semiconductor physics. Very accurate and extensive experimental information has been gathered on the subject.[1,2] The theoretical effort to fully account for the experimental information has also been quite substantial.[2] However, basic questions remain unsolved.

Faulkner[3] has shown that the effective-mass theory (EMT) can predict very accurately all excited single-donor levels in Si and Ge. However, the structures of the corresponding ground states remain unexplained. We clearly understand from the experimental data that two basic effects beyond the EMT have to be included in order to explain these ground-state structures. The first effect is the intervalley scattering. It is indeed experimentally observed[1-3] that the donor ground states are split in multiplets which are composed of a number of states exactly equal to the number of equivalent minima of the conduction band (CB); this characteristic is revealed by performing optical experiments in samples under uniaxial stress. The second effect is the short-range behavior of the impurity potential. The experiments indeed show[1-3] the dependence of the donor ground-state structures on the chemical species with which the semiconductors are doped—this characteristic is called the chemical shift.

Another puzzling aspect of this problem originates from the experimental observation that the same kind of (single) donor impurities in the same kind of many-valley semiconductors may also exhibit deep levels.[4] Furthermore, it is observed that core excitons are deep.[5-7] These features very well may have been produced by a combination of the two effects that we have just indicated.

We have recently derived an equation in real space which generalizes the EMT and includes both these basic effects.[8,9] In the next section of this paper we provide accurate numerical solutions to that equation. As we previously reported, we show that an impurity potential, which diverges like r^{-1} at short distances, exhibits deep levels at

both interstitial and substitutional sites in Si because of the intervalley scattering among the lowest CB six equivalent minima along the [100] directions. Typically, effective-mass calculations do not predict deep levels.[5] Recently, a theory which includes the intervalley scattering predicted deep levels to occur only for interstitial donors.[10] However, deep substitutional donor levels in Si appear to have been recently detected,[11] and the experimental evidence that the core excitons can be deep is mounting.[6,7] This seems to be quite in agreement with our results.

As we previously remarked,[8,9] we can meaningfully predict the occurrence of a shallow-deep instability, even though the calculated binding energy cannot, of course, be directly related to the experimental value. The envelope function becomes of course quite localized in $\vec{r}$ space for a deep level, and therefore it involves several bands in $\vec{k}$ space. We can directly introduce within our formalism (Sec. III of this paper) a rigorous test on the localization and the convergence of the envelope function in $\vec{k}$ space. In most cases, there will be no shallow-deep instability, and this method should then provide accurate binding energies.

II. REAL-SPACE EQUATION BEYOND THE EFFECTIVE-MASS THEORY

The Schrödinger equation for the impurity-wave function $\psi(\vec{r})$ is

$$(H_0-E)\psi(\vec{r})+V(r)\psi(\vec{r})=0\ , \tag{1}$$

where H_0 is the Hamiltonian of the unperturbed crystal and $V(r)$ is the potential-energy difference introduced by the impurity. Following Refs. 8 and 9 we introduce the basis set

$$\Phi(\vec{\eta},\vec{r})=\sum_{\mu}\alpha_\mu\psi_c(\vec{k}_\mu+\vec{\eta},\vec{r})\ , \tag{2}$$

where ψ_c are the Bloch functions corresponding to the lowest CB around the equivalent minima $\vec{k}_\mu$, and the coefficients α_μ are solely determined by the symmetry around the impurity site. We then expand $\psi(\vec{r})$ as

$$\psi(\vec{r})=(2\pi)^{-3}\int d^3\eta\, c(\vec{\eta})\Phi(\vec{\eta},\vec{r})\ . \tag{3}$$

Assuming isotropy and parabolicity of the CB around the equivalent minima $\vec{k}_\mu$, Eq. (1) is transformed into

$$\left[\frac{\hbar^2\eta^2}{2m^*}-E\right]c(\vec{\eta})+(2\pi)^{-3}\int d^3\eta' c(\vec{\eta}\,')\int d^3r\,\Phi(\vec{\eta},\vec{r})^*V(r)\Phi(\vec{\eta}\,',\vec{r})=0\ . \tag{4}$$

That the effective-mass anistropy does not substantially influence the donor ground states (not even the wave functions) in Si has been shown by detailed calculations in connection with electron-nuclear double resonance (ENDOR) experiments.[12,13]

If we further assume in the potential-energy term that

$$\Phi(\vec{\eta},\vec{r})\simeq e^{i\vec{\eta}\cdot\vec{r}}\Phi(0,\vec{r})\ , \tag{5}$$

Eq. (4) reduces to

$$\left[\frac{\hbar^2\eta^2}{2m^*}-E\right]c(\vec{\eta})+(2\pi)^{-3}\int d^3\eta' c(\vec{\eta}\,')\int d^3r\, e^{i(\vec{\eta}\,'-\vec{\eta})\cdot\vec{r}}\,|\Phi(0,\vec{r})|^2V(r)=0\ . \tag{6}$$

Defining the impurity envelope function $F(\vec{r})$ as

$$F(\vec{r})=(2\pi)^{-3}\int d^3\eta\, e^{i\vec{\eta}\cdot\vec{r}}c(\vec{\eta})\ , \tag{7}$$

and Fourier antitransforming Eq. (6) in real space, we obtain[8,9]:

$$\left[-\frac{\hbar^2\nabla^2}{2m^*}-E\right]F(\vec{r})+|\Phi(0,\vec{r})|^2V(r)F(\vec{r})=0\ . \tag{8}$$

Isotropy implies that spherical averages must be taken. The spherical averages $|\Phi(r)|^2$ of the renormalization factors $|\Phi(0,\vec{r})|^2$ are[8,9,14]

$$|\Phi(r)|^2=1+\sum_{\mu,\nu,\vec{G}}{}' \alpha_\mu\alpha_\nu c_{\mu\nu}(\vec{G})\cos(\vec{G}\cdot\vec{\tau}_p)\frac{\sin|\vec{k}_\mu-\vec{k}_\nu-\vec{G}|r}{|\vec{k}_\mu-\vec{k}_\nu-\vec{G}|r} . \quad (9)$$

We have calculated $|\Phi(r)|^2$ in Si using form factors from pseudopotential band-structure calculations.[15] We display them in Figs. 1 and 2 for the singlets A_1 and the doublets E, respectively. The number n_G of plane waves (PW) used in the expansions are also indicated. Convergence, as a function of n_G, is sufficiently fast, except at very short distances; we show in Fig. 1 the situation in the substitutional case for the singlet A_1.

In this work we are still mostly concerned with the two basic cases of impurity potentials which we must study first in order to understand the whole nature of this problem. Namely,[8,9,16]

$$V_s(r)=-(\epsilon_0 r)^{-1} , \quad (10)$$

$$V_d(r)=-[\bar{\epsilon}(r)r]^{-1} . \quad (11)$$

In Eq. (10) $V_s(r)$ is the potential as in the EMT (Ref. 3). In Eq. (11) $V_d(r)$ should properly describe physical systems such as interstitial hydrogen and core excitons.[5] In order to calculate the actual chemical shift of the various donor ground states, suitable impurity pseudopotentials must be used, other than $V_s(r)$ or $V_d(r)$ (Refs. 8 and 9).

In Table I we show accurate solutions of Eq. (8) for the cases (10) and (11) in Si. Notice that if we consider either $V_s(r)$ or $|\Phi(r)|^2=1$, the deviations from the EMT are relatively small. However, if we consider $V_d(r)$ and $|\Phi(r)|^2\neq 1$, a shallow-deep instability occurs for the A_1 levels. Furthermore, the characteristics of the solutions do not substantially depend on whether we consider the interstitial or the substitutional cases. These characteristics do not substantially depend even on the number n_G of PW's used in the expansions of $|\Phi(r)|^2$. Notice, in fact, that a single PW in each minimum ($n_G=1$) already produces all the correct structures of the solutions, including the shallow-deep instability for the A_1 singlet with $V_d(r)$. The corresponding $|\Phi(r)|^2$ is simply (for both interstitial and substitutional cases):

$$|\Phi(r)|^2_{\mathrm{PW}}=1+\sum_{\mu,\nu}{}'\alpha_\mu\alpha_\nu\frac{\sin|\vec{k}_\mu-\vec{k}_\nu|r}{|\vec{k}_\mu-\vec{k}_\nu|r} . \quad (12)$$

We point out that this result does not imply that the present method may not differ too much from the traditional many-valley EMT, which neglects all terms with $\vec{G}\neq 0$ (Ref. 17). Actually, the same intervalley scattering effect is incorrectly present on both kinetic- and potential-energy terms in the

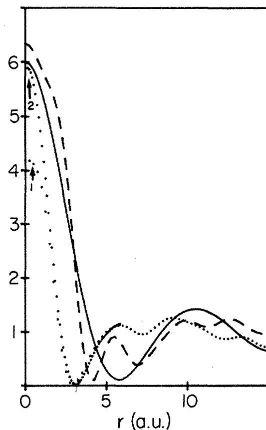

FIG. 1. Spherical $|\Phi(r)|^2$ in Si for the A_1 singlets ($\alpha_\mu=1/\sqrt{6}$). Form factors from Ref. 15. The dashed line represents interstitial ($n_G=137$). The solid line represents single PW ($n_G=1$). The dotted line represents substitutional (curves 1 and 2 are for $n_G=259$ and $n_G=59$, respectively).

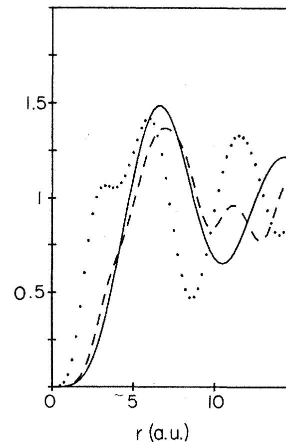

FIG. 2. Spherical $|\Phi(r)|^2$ in Si for the E doublets ($\alpha_1=\alpha_2=-\alpha_3=-\alpha_4=1/2$, $\alpha_5=\alpha_6=0$). Form factors from Ref. 15. The dashed line represents interstitial ($n_G=137$). The solid line represents single PW ($n_G=1$). The dotted line represents substitutional ($n_G=259$).

TABLE I. Solutions of Eq. (8) for various cases in Si. Binding energies (in meV) and effective principal quantum numbers n^* are reported. We use $m^*=0.2987$, which yields (first row) the EMT ground state calculated by Faulkner (Ref. 3).

$V(r)$	$\|\Phi(r)\|^2$	A_1 $-E$ (meV)	n^*	E $-E$ (meV)	n^*
V_s (EMT)	1	31.27 7.82	1.000 2.000	31.27 7.82	1.000 2.000
V_s	PW	34.15 8.17	0.957 1.957	30.88 7.77	1.006 2.006
V_s	sub	31.68 7.86	0.994 1.994	31.10 7.80	1.003 2.003
V_s	int	35.23 8.29	0.942 1.943	30.86 7.77	1.007 2.007
V_d	1	32.52 7.97	0.981 1.981	32.52 7.97	0.981 1.981
V_d	PW	28 351.52 27.02	0.033 1.076	30.90 7.77	1.006 2.006
V_d	sub	2220.93 22.81	0.119 1.171	31.30 7.80	0.999 2.003
V_d	int	36 502.57 27.46	0.029 1.067	30.90 7.77	1.006 2.006
V_d	AH-sub	59.59 10.43	0.724 1.732	31.76 7.88	0.992 1.992
V_d	AH-int	39 874.45 27.47	0.028 1.067	30.80 7.76	1.008 2.008

traditional many-valley EMT (Ref. 18).

In contrast with our results, Altarelli and Hsu (AH) have obtained a site dependence of the shallow-deep instability.[10] They claim that $V_d(r)$ exhibits deep levels only if centered at an interstitial site. We have shown[9] that the AH calculations involve an additional approximation with respect to ours, which is directly responsible for that anomalous result. In fact, by transforming the AH potential-energy term in real space,[9] we can see how that additional approximation produces a corresponding $|\Phi(r)|^2_{\mathrm{AH}}$ which is rather correct in the interstitial case [$|\Phi(0)|^2_{\mathrm{AH\text{-}int}}=6.512$], but strongly reduced at short distances in the substitutional case [$|\Phi(0)|^2_{\mathrm{AH\text{-}sub}}=2.78$]. If we multiply the summation in Eq. (12) by 5.512 and 1.78, respectively, we can see that the shallow-deep instability artificially disappears in the substitutional case only (ninth and tenth rows of Table I).

As a matter of fact, deep donor levels (~ 580 meV) of substitutional N in Si have been recently experimentally observed.[11] In that case, a substantial lattice distortion also takes place. We do not know at present how much that may contribute to the formation of the deep levels, in addition to the mechanism that we describe. On the other hand, no lattice relaxation occurs for core excitons, and yet they are experimentally found to be deep.[6–9]

III. CONSISTENCY CONDITIONS

Equation (8) contains various approximations, and we have to check their consistency. Essential-

ly, it is possible to expand $\psi(\vec{r})$ as in Eq. (3), including only the lowest CB, if and only if both the following conditions are satisfied: (a) the binding energy of the impurity level cannot exceed approximately half of the width E_c of the lowest CB corresponding to $\psi_c(\vec{k}_\mu+\vec{\eta},\vec{r})$; and (b) the value of η cannot exceed η_c, where[14]

$$\eta_c \le \tfrac{1}{2}\min' |\vec{k}_\mu-\vec{k}_\nu-\vec{G}| \; . \tag{13}$$

In Fig. 3 we sketch the situation for Si, where $E_c \sim 100$ MeV and $\eta_c \sim 0.09$ a.u. Clearly, if either one of conditions (a) and (b) is not satisfied, the expansion of $\psi(\vec{r})$ must also contain the contribution of higher conduction bands.

In all calculations in the literature so far, it has always been assumed that the $c(\vec{\eta})$'s in the expansion (3) are strongly peaked around the origin. However, condition (b) was never verified "*a posteriori.*" Within our framework we can satisfy concondition (b) "*a priori*" by simply limiting the expansion of $\psi(\vec{r})$ as

$$\psi(\vec{r})=(2\pi)^{-3}\int d^3\eta\, c(\vec{\eta})\Phi(\vec{\eta},\vec{r}) \times H(\eta_c-\eta) \; , \tag{14}$$

where $H(\eta_c-\eta)$ is the usual step function. If we proceed as in the preceding section, we arrive at the more complex integro-differential equation

$$\left[-\frac{\hbar^2\nabla^2}{2m^*}-E\right]G(\vec{r})+\int d^3r'\Delta_{\eta_c}(\vec{r}-\vec{r}\,') \times |\Phi(r')|^2 V(r')G(\vec{r}\,')=0 \; , \tag{15}$$

where

$$G(\vec{r})=(2\pi)^{-3}\int d^3\eta\, e^{i\vec{\eta}\cdot\vec{r}}c(\vec{\eta})H(\eta_c-\eta) \; , \tag{16}$$

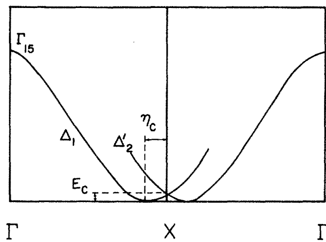

FIG. 3. Lowest conduction-band structure in Si along the [100] direction.

$$\Delta_{\eta_c}(\vec{r})=(2\pi)^{-3}\int d^3\eta\, e^{i\vec{\eta}\cdot\vec{r}}H(\eta_c-\eta) \; . \tag{17}$$

The function $\Delta_{\eta_c}(\vec{r})$ has been used in the past in connection with short-range interactions in exciton levels.[19] It represents a filter that eliminates (spatial) frequencies higher than the cutoff η_c. Clearly, in the limit $\eta_c \to \infty$, we have

$$\Delta_{\eta_c}(\vec{r}) \to \delta(\vec{r}) \; . \tag{18}$$

In that limit, Eqs. (15) and (16) reduce to Eq. (8).

It is instructive to study the limiting case of an arbitrary, large (negative) constant impurity potential. The problem with that potential is of course that it still has a great influence at infinity. Therefore, such a potential is certainly not a weak perturbation to H_0 in Eq. (1): Conditions (a) and (b) cannot be satisfied for Eq. (8), which indeed may exhibit unphysical arbitrary localized solutions. On the other hand, Eq. (15) satisfies conditions (a) and (b) by construction. It is easy to see that no irregular solutions appear in Eq. (15) even for such a potential. Notice in fact that

$$\int d^3r'\,\Delta_{\eta_c}(\vec{r}-\vec{r}\,')\,|\Phi(r')|^2=1 \tag{19}$$

holds exactly for all $\vec{r}$ because of Eq. (13).

Equation (15) can be solved iteratively. Actually, the first step

$$\left[-\frac{\hbar^2\nabla^2}{2m^*}-E\right]G(\vec{r})+G(\vec{r})\int d^3r'\,\Delta\eta_c(\vec{r}-\vec{r}\,') \times |\Phi(r')|^2 V(r')=0 \tag{20}$$

already produces a quite accurate solution.

It could be erroneously guessed that Eq. (20) should yield essentially the same results as the EMT because of Eq. (19). Not so, since high-frequency components in both $V(r)$ and $|\Phi(r)|^2$ can beat against each other and pass through the filter. A well-resolved structure for the ground state can thus be produced, due to the intervalley scattering and the short-range behavior of the impurity potential.

In Table II we show some solutions of Eq. (20) in Si. The numerical solution is time consuming and poses some problems with precision and round-off errors. These problems are essentially due to the slowly decaying oscillatory contributions produced by $\Delta_{\eta_c}(\vec{r})$. For practical reasons we have

TABLE II. Solutions of Eq. (20) for various cases in Si.

$V(r)$	$\lvert\Phi(r)\rvert^2$	A_1 $-E$ (meV)	n^*	E $-E$ (meV)	n^*
V_s	1	27.4 7.3	1.07 2.07	27.4 7.3	1.07 2.07
V_s	sub	27.5 7.3	1.07 2.07	27.4 7.3	1.07 2.07
V_s	int	27.8 7.4	1.06 2.06	27.6 7.3	1.06 2.07
V_d	1	27.6 7.3	1.06 2.07	27.6 7.3	1.06 2.07
V_d	sub	28.1 7.4	1.05 2.06	27.4 7.3	1.07 2.07
V_d	int	29.0 7.5	1.04 2.04	27.3 7.3	1.07 2.07
V_s ($\bar{r}=57.5$)	1	29.8 7.6	1.02 2.04	29.8 7.6	1.02 2.04

simplified our job by assuming that

$$\int d^3r'\,\Delta_{\eta_c}(\vec{r}-\vec{r}')\,|\Phi(r')|^2V(r')=V(r)\,, \tag{21}$$

exactly holds for $r\geq\bar{r}=28.5$. The first and the last row of Table II show that, for the EMT potential, if we increase the radius $\bar{r}$ beyond which Eq. (21) is assumed, the EMT results are better reproduced. The effect of increasing $\bar{r}$ from 28.5 to 57.5 should similarly be represented for all the other lowest levels by a rigid blue shift of $\sim$2 meV.

Actually, a better procedure for the numerical solution of Eq. (20) would have involved to obtain the Fourier transform $\mathscr{F}(\eta)$ of $|\Phi(r)|^2V(r)$ and then the Fourier antitransform of $H(\eta_c-\eta)\mathscr{F}(\eta)$. The superiority of the fast-Fourier-transform routines over the numerical integration routines in this kind of problems has been previously experimented.[20]

We notice from Table II that, within the numerical approximation (21), the results of Eq. (20) are close to the EMT for all levels, except for the A_1 singlets with $V_d(r)$ and $|\Phi(r)|^2\neq1$. It appears by comparison with Table I that in all cases in which the solutions are relatively close to the EMT values, Eqs. (8) and (20) substantially yield the same results [within the numerical approximations performed in solving Eq. (20)]. We thus conclude that Eq. (8) can describe reliably the doublets E and the triplets T_1, and that conditions (a) and (b) are satisfied in those cases.

The situation is quite different for the singlets A_1, with $V_d(r)$ and $|\Phi(r)|^2\neq1$. In those cases, Eqs. (8) and (20) yield totally different results. The strong dependence of the solutions on the cutoff η_c shows that the solutions do not intrinsically stabilize within η_c. If we let η_c increase continuously, we move continuously from the unstable solutions of Eq. (20) to the deep solutions of Eq. (8). As we remarked earlier,[8,9] the prediction of the shallow-deep instability by Eq. (8) remains quite valid. However, the calculated values of the binding energy are in fact much larger than the experimental values—the experimental value[6] corresponding to the singlet A_1 with $V_d(r)$ and $|\Phi(r)|^2_{\text{sub}}$ (core exciton) is $E^{\text{exp}}\sim300$ meV.

Except for interstitial hydrogen and core excitons,[5] $V_d(r)$ can hardly be an accurate potential in most cases (not even for isocoric single donors, say P in Si or As in Ge, as we also noticed earlier[8]). In general, the pseudopotential $V(r)$ in Eq. (1) will exhibit some cutoff around the origin.[8,9] There

should not be any shallow-deep instability in all those cases, and Eq. (8) should then provide accurate values for the binding energies.

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