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Binding energies of substitutional and interstitial donors in Si: Many-electron effects

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It is shown that the inclusion of both electron-hole correlations and local-field effects in the intervalley matrix elements for point-charge impurities is indispensable for the binding energies: For a substitutional donor these many-electron effects reduce the binding energy by as much as 35%, thus significantly strengthening the shallow character and introducing very good agreement with experiment (example Si:P). Combination of our quantitative calculations with recent muon-decay experiments allows for a prediction of the interstitial muonium site in Si.

The standard approximation in the description of the shallow impurity state in a semiconductor with a nondegenerate band minimum is the effective-mass theory (EMT).[1] In the EMT the impurity electron of a shallow donor can be depicted as orbiting around the donor ion with an effective mass m^* under the influence of the Coulomb potential due to the extra impurity charge, screened by the long-wavelength dielectric constant $\epsilon(q \rightarrow 0)$ of the crystal. This approximation has been derived by Kohn within the full context of the many-electron Hamiltonian for weakly bound and large orbits.[2]

The EMT can no longer be applied to a band structure with n equivalent minima (6 in Si) even if the impurity still has shallow character. In this case the intervalley coupling produces umklapp contributions ($\vec{G} \neq 0$) to the matrix element of the screened impurity potential U between Bloch functions $|\vec{k}\rangle$ and $|\vec{k}'\rangle$ belonging to different valleys[3-5]

$$\langle \vec{k}_i | U | \vec{k}_j \rangle = \sum_{\vec{G}} c(\vec{k}_i, \vec{k}_j; \vec{G}) \tilde{U}(\vec{k}_i - \vec{k}_j - \vec{G}) \ , \qquad (1)$$

where $c(\vec{k}_i, \vec{k}_j; \vec{G})$ are Fourier coefficients of the product of the periodic parts of $|\vec{k}_i\rangle$ and $|\vec{k}_j\rangle$, and $\tilde{U}(\vec{k}_i - \vec{k}_j - \vec{G})$ is the Fourier transform of $U(\vec{r})$. In addition to the fact that the EMT replacement of Bloch functions with simple plane waves leads to large errors in the evaluation of Eq. (1),[3-5] the consequences of the intervalley interactions can be quite dramatic: Through the umklapp wave vectors the intervalley interaction strongly puts emphasis on the short-range part of U and therefore on the microscopic details of the screening in the neighborhood of the impurity.

We have shown in previous work[6,7] for pointlike impurities in Si and C that this short-range part is significantly affected by many-body effects of local-field and excitonic nature. Figure 1 displays the induced charge density in the (110) plane through the position of a positive, substitutional point charge in Si. Here the density is determined within linear-response theory by adopting the time-dependent screened Hartree-Fock approximation (TDSHF) with the inclusion of both random-phase approximation (random-phase approximation without inclusion of local-field effects is denoted $\overline{\text{RPA}}$, with inclusion of local-field effects RPA) local-field and electron-hole interaction effects. Both of these many-body corrections are indispensable in a realistic description of impurity screening in a covalent semiconductor: the combined local-field and excitonic corrections introduce changes in the density profile comparable in magnitude to the commonly used zeroth-order $\overline{\text{RPA}}$ screening result.[7] They introduce a pronounced anisotropy (Fig. 1)

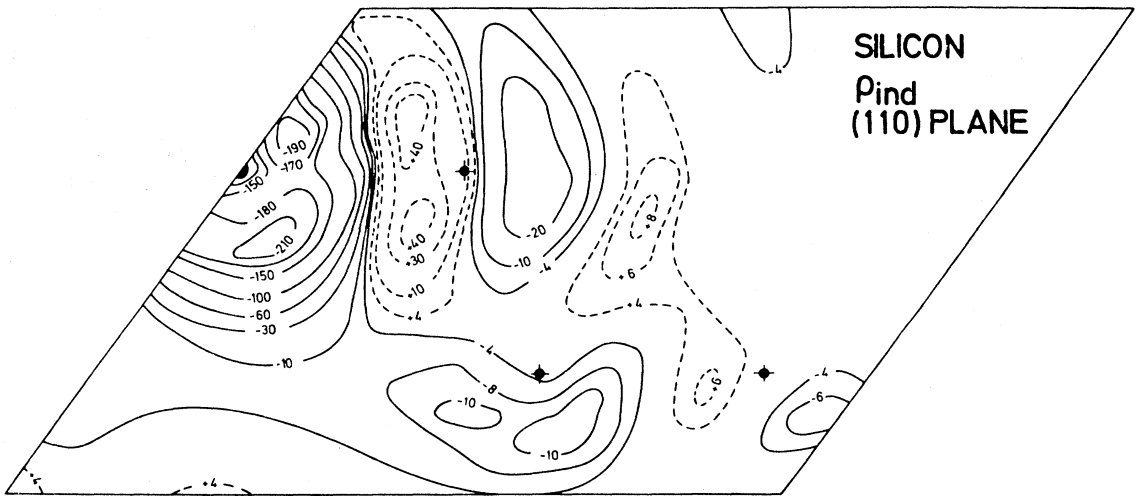

FIG. 1. Induced charge density in the (110) plane through the substitutional impurity position for Si. Numbers have to be multiplied by 10^{-4} to get atomic units.

TABLE I. Binding energies (in meV) of the ground-state multiplet components for substitutional isocoric donor Si:P in the three approximations $\overline{\text{RPA}}$, RPA, and TDSHF. Experimental results are from Ref. 17.

	$\overline{\text{RPA}}$	RPA	TDSHF	Experiment
λ	0.35	0.03	0.13	. . .
μ	0.45	0.40	0.37	. . .
(A_1)	75.3	48.5	46.6	45.3 meV
(T_2)	29.8	30.6	30.4	33.7 meV
(E)	28.8	28.7	28.9	32.3 meV

and a natural site dependence (interstitial versus substitutional) of the impurity potential.

In the present work we use the screened impurity potential, which is calculated from first principles, to extract the influence of the many-body effects on (a) the binding energy of a shallow pointlike substitutional donor (example P) in Si and (b) on the formation of the deep impurity character of interstitials[5] like positive muons or protons.[8,9] In particular, we find in the substitutional case the TDSHF approximation to result in very good agreement with experiment (46.6 meV for the A_1 ground state versus 45.3 meV in experiment, see Table I), whereas the commonly used screening $\overline{\text{RPA}}$ with a diagonal dielectric function

$$\epsilon(\vec{q}+\vec{G},\ \vec{q}+\vec{G}') \rightarrow \epsilon(\vec{q}+\vec{G})\delta_{\vec{G}\,\vec{G}'}$$

results in the much too large value of 75.3 meV. We would like to emphasize here that our $\overline{\text{RPA}}$ calculation is parameter free in contrast to the commonly used diagonal screening which is empirically fitted to experiment. The large reduction to 48.5 meV by the RPA local-field effects can be taken as a confirmation of a trend revealed already in an earlier study, where use has been made of a nondiagonal RPA model dielectric function.[10] Finally, our quantitative calculation of the impurity potential is used to resolve an open question which has been posed by recent positron blocking experiments from muon decay about the position of a low-symmetry muonium state in Si.

We start by rewriting Eq. (1) in the form

$$\langle \vec{k}_i|U|\vec{k}_j\rangle = \tilde{U}(\vec{k}_i-\vec{k}_j)\sum_{\vec{G}} c(\vec{k}_i,\vec{k}_j,\vec{G})\frac{\tilde{U}(\vec{k}_i-\vec{k}_j-\vec{G})}{\tilde{U}(\vec{k}_i-\vec{k}_j)}$$
$$= \tilde{U}(\vec{k}_i-\vec{k}_j)\lambda_{ij}\ , \qquad (2)$$

where $\tilde{U}$ is the impurity potential screened with a diagonal dielectric function. The correction factor λ_{ij} for each pair of equivalent minima renormalizes the strength of zeroth-order intervalley coupling by the umklapp terms $\vec{G}$ and the combined many-body effects. For example, for the tetrahedral site in Si, two different coefficients termed λ and μ in Table I exist, corresponding to the valleys on the same axis and on perpendicular axes, respectively.

The expansion coefficients $c(\vec{k}_i,\vec{k}_j;\vec{G})$ in Eq. (2) are extracted from pseudo wave functions, obtained with the local form factors of Chelikowsky and Cohen[11] with a basis of 88 plane waves. We take this empirical pseudopotential band structure both for the c coefficients and the electron hole or screening propagator as a (rather good) approximation to an actual quasiparticle band structure in Si,[12] which we should have ideally used. The Fourier coefficients $\tilde{U}(\vec{q}+\vec{G})$ of the effective impurity potential are related via the screening matrix ϵ^{-1} to the bare potential $\tilde{U}_0$

$$\tilde{U}(\vec{q}+\vec{G}) = \sum_{\vec{G}'}\epsilon^{-1}(\vec{q}+\vec{G},\vec{q}+\vec{G}')\,\tilde{U}_0(\vec{q}+\vec{G}')\ , \qquad (3)$$

ϵ^{-1} otherwise is calculated as described in detail in Refs. 7 and 13. The binding energies are then extracted, employing a variational procedure.[3,5]

Table I contains the λ and μ factors and the binding energies by adopting successively improved approximations for the polarizability matrix, namely, the random-phase approximation without and with inclusion of local-field effects, and finally the TDSHF approximation with the inclusion of excitonic and local-field effects.

The A_1 binding energy is lowered by as much as 30% when both these many-body effects are included. This is an explicit demonstration that the microscopic details of the short-range part of U, in particular the inhomogeneity of the induced density as displayed in Fig. 1, are crucial for even a qualitative description of the binding of a shallow donor in a prototype semiconductor like Si. The excited states of symmetry T_2 and E do not vary nearly as much as the A_1 ground state, when local-field effects and the electron-hole attraction are included. This is to be expected because of the less-localized nature of these excited states, which diminishes the importance of the many-body effects.[12,14]

We note that in particular the A_1 binding energy, when calculated within TDSHF, is in very good agreement with experiment. However, some cautious remarks are in order here: apart from the empirical pseudopotential bands and

TABLE II. Same as Table I, but for interstitial point charges in Si.

	$\overline{\text{RPA}}$	RPA	TDSHF
λ	1.35	1.27	1.19
μ	0.84	1.03	0.89
(A_1)	Deep	Deep	Deep
(T_2)	28.5	28.6	28.6 meV
(E)	28.7	28.2	28.4 meV

TABLE III. Umklapp renormalization factors for the two experimentally predicted muonium positions 0.9 Å along bonding and antibonding directions. a is the lattice constant.

	$\overline{\text{RPA}}$	RPA	TDSHF
	Bonding direction		
Coupled valleys $k_0=0.85\frac{2\pi}{a}$			
$(k_0,0,0)$, $(-k_0,0,0)$	0.54	0.58	0.45
$(k_0,0,0)$, $(0,k_0,0)$	0.17	0.09	0.11
$(k_0,0,0)$, $(0,-k_0,0)$	0.20	0.26	0.23
	Antibonding direction		
$(k_0,0,0)$, $(-k_0,0,0)$	0.79	0.82	0.72
$(k_0,0,0)$, $(0,k_0,0)$	0.69	0.70	0.63
$(k_0,0,0)$, $(0,-k_0,0)$	0.45	0.46	0.45

wave functions used in Eq. (1), one may also question the validity of the linear-response theory and the point-charge form of the impurity potential. The latter approximations should both be justified for the isocoric (i.e., from the same row of the periodic table) substitutional donor P in Si: an alternative form of an impurity pseudopotential for P has been tested and found to result in a negligible lowering of the binding energy of the A_1 level by about 1–2 meV. The point-charge potential is clearly justified for interstitial muons, but here the linear response can be questioned. The calculations in Ref. 10, which are based on an empirical model for the RPA local-field effect, yield a similar reduction in the μ values between $\overline{\text{RPA}}$ and RPA, but in contrast to our *a priori* screening result in an enhancement and not in a reduction in the corresponding λ values.[15]

Even for diagonal $\overline{\text{RPA}}$ screening, another site dependence of the intervalley matrix element in Eq. (1) stems from the fact that, when the impurity is changed to the position $\vec{\tau}$ in the unit cell, each term in Eq. (1) is multiplied by a factor $\exp(i\vec{G}\cdot\vec{\tau})$. This "diagonal" site dependence has been shown by Altarelli and Hsu[5] to lead already to a deep-level character of interstitial point-charge donor.

We want finally to investigate to what extent the deep-level character is reinforced or weakened by the many-body effects in the intervalley potential. Table II gives the λ and μ factors for the three different many-body descriptions in the case of a tetrahedral interstitial point charge in Si. In all three approximations, λ and μ are close to 1. This, therefore, corresponds to a deep impurity level.[3,5] We note that the RPA local-field effect results in a large enhancement of the μ factor and thus reinforces the deep-level character of the binding energy, in agreement with Ref. 9. However, the combined local-field and excitonic effects within TDSHF bring the μ factor essentially back to the diagonal $\overline{\text{RPA}}$ screening result.

A muon or proton resembles our theoretical picture of a point charge. Muon spin resonance experiments, although not giving directly the binding energy, indicate that the impurity state is indeed deep.[8,9] Very recently, positron blocking from muon decay in Si (Ref. 16) has been used to predict that the muonium state is 0.9 Å from a Si ion along [111] direction towards either the neighboring Si ion or the tetrahedral interstitial site. Table III gives the three independent umklapp renormalization factors for these two sites. We note, that clearly only the antibonding direction is capable of inducing a deep-level character, whereas the bonding direction would result in a shallow level.

In summary, the inclusion of many-body effects of both local-field and excitonic nature in intervalley umklapp matrix elements strongly reinforces the shallow character of a point-charge substitutional impurity (like P) in Si. They give rise to a 30% reduction of the binding energy. In combination with recent positron blocking experiments the quantitative determination of the impurity potential allows for a definite answer of the muonium site in Si, which is located 0.9 Å along [111] direction toward the tetrahedral interstitial site.

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