Ab Initio Calculation of Hyperfine and Superhyperfine Interactions for Shallow Donors in Semiconductors

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For the shallow group V donors in Si we show that the hyperfine interaction for the donor nucleus and the superhyperfine interactions for the first five shells of Si ligands can be quite accurately calculated using the local spin-density approximation of the density-functional theory. We treat the impurity problem in a Green's function approach. Since we have to truncate the long-ranged part of the defect potential, we do not obtain a localized gap state. Instead we identify the resonance above the conduction band with the paramagnetic defect state. We show that the hf and shf interactions thus obtained are at least as accurate as those obtained from one-electron theories with fitting parameters. Application of this first principles method to other shallow donors could be an essential help in defect identification.

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Theoretical methods to treat point defects in semiconductors are divided into methods for deep defects and methods for shallow defects: the former defect class is treated by *ab initio* methods, usually based on the local spin-density approximation (LSDA) of the density-functional theory (DFT) (see, e.g., Ref. [1]), while for the latter class approximate one-electron theories like the effective mass theory (EMT) [2–4] or many-band extensions thereof are used. The reason for this distinction is related to the different spatial extent of the defect-induced electronic states.

Deep point defects seriously disturb the crystal in a small region centered at the defect site. The additional long-range perturbations as, e.g., a Coulomb potential tail for charged defects or the strain field are either ignored or treated as a correction. A self-consistent treatment of the deep defect is possible because it can be restricted to a small region in space, a cluster, a supercell, or the perturbed region in a Green's function approach.

For shallow defects the defect-induced gap state typically extends over several hundred or even thousand unit cells and, therefore, cannot be treated directly with *ab initio* methods. Instead, the defect-induced change of the crystal potential is replaced by a model potential and the defect state is treated in a one-electron approximation [2–4]. In the simplest EMT for a substitutional donor, the defect state is expanded into the Bloch states close to the minimum of the lowest conduction band, for which the dispersion of the band can be approximated by a parabola. For semiconductors like Si with several equivalent minima of the lowest conduction band, the donor state is expanded into Bloch states of all equivalent minima [3]. The contributions from the different minima give rise to rather complicated interferences of the defect wave function.

These are readily detected in the superhyperfine (shf) interactions with paramagnetic ligand nuclei. A well-known example is the electron nuclear double resonance (ENDOR) data for group V donors in Si by Feher [5] and by Hale and Mieher [6]. The interferences have been interpreted by a theoretical many-valley EMT that includes the anisotropy of the effective mass. Later Ivey and Mieher [7] showed that a many-*band* Hamiltonian is required in order to correlate the experimentally resolved shf data with ligand shells of the Si lattice. The many-band approach also removes the spurious inversion symmetry of the EMT envelope function. Unfortunately, this approach is quite complicated, which may be the reason that it has not been extended to similar defects like shallow donors in diamond or in SiC. For the latter donors, a plain EMT treatment similar to that of Hale and Mieher has been presented, with limited success [8].

In this Letter, we show that with an *ab initio* Green's function approach the hyperfine (hf) and shf interactions for the group V donors can be calculated directly without invoking a one-electron approximation. Since we treat a rather small perturbed region, we obtain the hf interaction with the donor nucleus and the shf interactions with the nuclei of five ligand shells only, much less than the 27 shells reported by Ivey and Mieher. For the donor nucleus and for the three shells included in our perturbed region for which experimental shf interactions are available, the difference between our calculated data and the experimental data is comparable to that of Ivey and Mieher. For the two shells in our perturbed region for which there are no experimentally resolved and identified shf data we obtain theoretical shf data that are below the 600 kHz "continuum" limit of the experiment.

We calculate the electronic structure of the donors in Si using the self-consistent linear muffin-tin orbital method in the atomic-spheres approximation (LMTO-ASA) [9]. Many-body effects are treated in the local spin-density approximation of the density-functional theory (LSDA-DFT). In a Green's function approach the problem

separates into two parts. First, the Green's function $g^0(E)$ of the perfect crystal is constructed from the band structure of the perfect crystal. Second, the Green's function $g(E)$ is obtained as a solution of Dyson's equation

$$\{1 + g^0(E)[\Delta P(E) - \Delta S]\}g(E) = g^0(E). \quad (1)$$

Here $\Delta P = P - P^0$ is the perturbation of the so-called potential function describing the electronic structure, and $\Delta S = S - S^0$ is the relaxation-induced change of the LMTO-ASA structure constants. Since the LSDA underestimates the fundamental band gap of semiconductors, we use a scissors operator technique to obtain the experimental band gap in $g^0(E)$.

We solve Dyson's equation within a "perturbed region" that contains the donor and five shells of ligands (47 atoms in total) and six shells with 42 "empty" spheres to reduce the overlap of the ASA spheres. Minimizing the total energy by a symmetry-conserving relaxation of the nearest neighbor distances we find a minimum for a nearest neighbor distance that is increased by 1.7% for P^0_{Si}, by 3.2% for As^0_{Si}, and by 6% for Sb^0_{Si}, respectively, with respect to the distance in a perfect Si crystal. In the ENDOR experiments for group V donors in Si no symmetry-lowering lattice distortions have been resolved.

Since in our approach we ignore the long-range tail of the Coulomb potential for that part of the induced density that is not contained within the perturbed region, we do not find a shallow gap state but rather a resonance just above the onset of the conduction band. Thus we cannot hope to obtain meaningful donor energies by this approach. Figure 1 shows the change of the density of states (DOS) introduced by the defect (the "induced" DOS) for the three group V donors in comparison with the DOS of the unperturbed crystal. In our approach we separate densities that arise from states transforming according to the different irreducible representation of the group T_d. In Fig. 1 we display the a_1-like densities only, suppressing the t_2 and e-like resonances that are ascribed to excited states.

The induced DOS for P^0_{Si} and As^0_{Si} show a relatively well-defined minimum near 1.6 eV above the valence band edge. We consider the induced DOS below this minimum as a substitute for the shallow gap state (for Sb^0_{Si} the resonance is much less pronounced). It contains about 0.15 of an electron within the perturbed region for P^0_{Si} and As^0_{Si}, while for Sb^0_{Si} we find as little as 0.05 of an electron. We occupy the resonance below the minimum with one spin-up electron and calculate the spin polarization of all electrons within the LSDA.

A contour plot of the density of this state for As^0_{Si} is plotted in Fig. 2 for a $(1, \bar{1}, 0)$ plane. The left part of the figure displays the induced density that is caused by the conduction band resonance, while in the right part the magnetization density caused by the spin polarization of the valence band is also included. Although the difference is hardly visible in the figure, we see below that it has some consequences. Our magnetization density is qualitatively different from the EMT result which had been displayed in Fig. 2 of Ref. [6] in that it does not show the spurious inversion symmetry characteristic for the

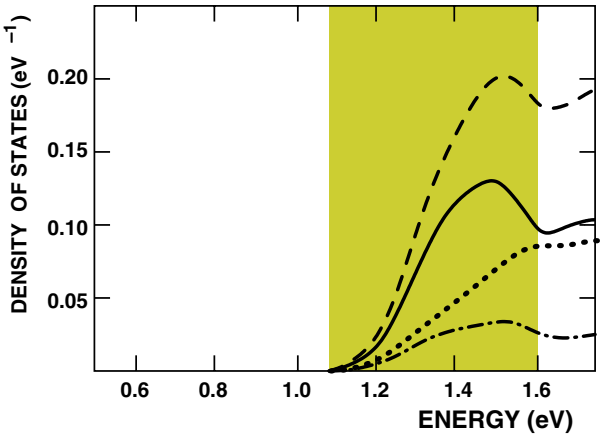

FIG. 1 (color online). Density distribution of states that transform according to the a_1 irreducible representation of the point group T_d for group V donors in silicon. The full line denotes the induced density of the As^0_{Si}, the dashed line is for P^0_{Si}, and the dash-dotted line is for the Sb^0_{Si} donors. The dotted line represents the a_1 density of the unperturbed Si crystal for comparison. The grey area denotes the energy interval of the a_1 resonance for P^0_{Si} and As^0_{Si}.

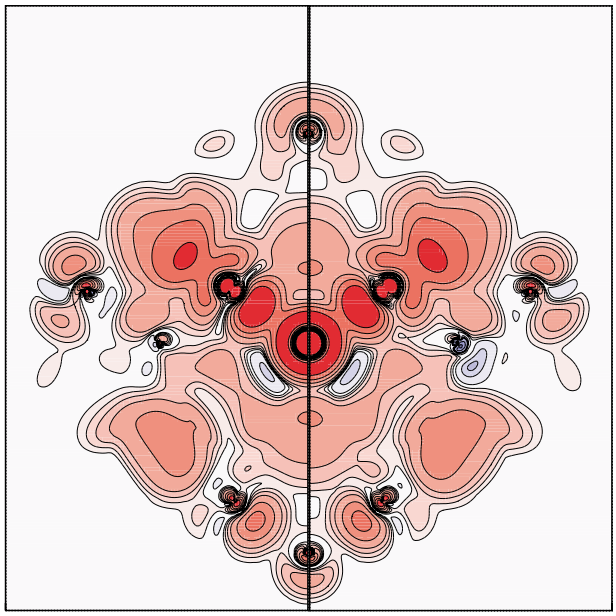

FIG. 2 (color online). Contour plot of the electron density in the $(1, \bar{1}, 0)$ plane for As^0_{Si} in Si. The induced density of the conduction band resonance that transforms according to the a_1 irreducible representation is shown in the left part; the total density is depicted in the right part.

EMT. Instead it has some similarities with the envelope function obtained by Ivey and Mieher (Fig. 15 of Ref. [7]), with the clear distinction that there is no well-defined minimum at the nearest neighbor. A direct comparison is, however, difficult because we present the spin density with all its oscillations rather than some envelope function. An indirect comparison of the different approaches is, however, possible from a comparison of the calculated hf and shf data with ENDOR data.

Table I lists the isotropic hf interaction data and the shf data for the interaction with the first five shells of ligands. Experimental data are displayed in comparison with the results of our present approach, with results of the earlier treatment of Ivey and Mieher (IM) [7], and also with their EMT results. Since the nuclear gyromagnetic factor of ^{29}Si is negative, all shf data shown have a negative sign. A comparison of the hf interactions with the donor nuclei shows that our present approach, except for the Sb^0_{Si} defect, is superior to the IM and EMT methods. The failure of our present approach to describe the Sb^0_{Si} donor is comparable to the similar failure to properly describe the Te_{Si} double donor [10]. We do not have a convincing explanation for the fact that for Sb^0_{Si} the resonance is that much more hybridized with the conduction band states if compared with the other two group V donors.

TABLE I. Isotropic hf and modulus of the shf interactions (in MHz) for group V donors in Si. Experimental values are compared with theoretical results of our present calculation, the pseudopotential approach from Ivey and Mieher, and a EMT approach. All shf data shown have a negative sign.

Shell		Donor	Exp.	This work	IM	EMT
Donor	(0, 0, 0)	^{31}P	117.53	121.4	71.2	448.0
		^{75}As	198.35	198.6	120.0	850.0
		^{121}Sb	186.80	66.8	89.4	548.0
E	(1, 1, 1)	P	0.540	0.518	0.036	1.524
		As	1.284	1.168	0.006	2.424
		Sb	0.586	2.053	0.090	1.232
	(2, 2, 0)	P	···	0.115	0.608	0.861
			···	0.193	0.788	1.216
		Sb	···	0.587	0.532	0.734
	(1, 1, $\bar{3}$)	P	···	0.053	···	···
		As	···	0.179	···	···
		Sb	···	0.001	···	···
A	(0, 0, 4)	P	5.962	2.963	5.848	8.414
		As	7.720	3.160	7.606	11.400
		Sb	6.202	2.923	5.168	7.324
F	(3, 3, 1)	P	1.680	1.461	1.5776	0.988
		As	2.242	2.351	2.590	1.290
		Sb	1.008	0.848	1.212	0.872

For the nearest neighbor shell denoted by E (1, 1, 1) the isotropic shf interactions of our resonance states compare favorably (again with the exception of Sb^0_{Si}) with the experimental data. The agreement is, in fact, much closer than for the IM and EMT results for this shell. The shf interaction is only to a small part due to the conduction band resonance: more than 75% of the isotropic shf is caused by the spin polarization of the valence band states (which in turn is caused by the proximity of the donor with its relatively high spin density). Unfortunately, the polarization is not observable in Fig. 2: the isotropic hf interactions arise from the magnetization density *at* the ligand nuclei, and the resolution of Fig. 2 is not sufficient there. Such polarizations are not included in the one-electron approach of IM, which may explain in part the striking discrepancy between the experimental data and the results of the one-electron theories. Ivey and Mieher [7] have suggested that the discrepancy is due to their neglect of the lattice relaxations, an explanation that is not supported by our results, that are rather insensitive to lattice relaxations.

The next two neighbor shells have not been identified experimentally, presumably because the isotropic shf constant is below about 600 kHz, the continuum of many overlapping ENDOR results. This explanation is in line with our results. Note that for the (2, 2, 0) shell both IM and EMT predict hf interactions that should be readily observed [the (1, 1, $\bar{3}$) shell is not mentioned in [7]].

For shell A (0, 0, 4) the isotropic shf data are too small by a factor of 2 if compared with the experimental data. This rather poor result is somewhat surprising if we compare with shell F (3, 3, 1). For this outermost shell in our perturbed region our results compare quite well with the experimental data and with the results of IM. We do not have an explanation why the results for the A (0, 0, 4) shell should so much poorer than for the more distant F (3, 3, 1) shell.

The anisotropic shf interactions are compared in Table II with experimental data and with the results of IM. The anisotropic shf interactions form a traceless tensor which can be described by two constants, the axial component b and the nonaxial parameter b' (see, e.g., [1]). Except for the E (1, 1, 1) nearest neighbor shell, the calculated anisotropic shf parameters are quite small and compare reasonably well with the experimental data.

In many respects the shf data for the group V donors in Si constitute the most difficult test case for a theoretical treatment of shallow donors. According to all one-electron theories the donor wave function is composed from six equivalent minima and the interferences of this superposition give rise to the oscillatory behavior of the magnetization density. One may wonder whether these interferences can be found in an approach where the Coulomb potential that extends outside of the perturbed region has to be cut, and where the gap state is represented by a resonance in the conduction band which contains

TABLE II. Anisotropic hf and shf interactions (in MHz) for group V donors in Si. Experimental values are compared with theoretical results of our present calculation, and of the pseudopotential approach from Ivey and Mieher. All shf data shown have a negative sign.

			Exp.		This work		IM	
Shell		Donor	b	b'	b	b'	b	b'
E	(1, 1, 1)	P	0.700	0	0.661	0	0.492	0
		As	1.258	0	1.140	0	0.932	0
		Sb	0.522	0	0.250	0	0.346	0
	(2, 2, 0)	P	···	···	0.012	0.010	0.0309	0.0286
		As	···	···	0.018	0.011	0.0251	0.0222
		Sb	···	···	0.058	0.007	0.0222	0.0197
A	(0, 0, 4)	P	0.0207	0.0413	0.015	0.012	0.0195	0.0191
		As	0.0285	0.0557	0.021	0.017	0.0192	0.0248
		Sb	0.023	0.034	0.047	0.013	0.0230	0.0342
F	(3, 3, 1)	P	0.0588	0.0290	0.053	0.014	0.0414	0.0036
		As	0.0756	0.0412	0.086	0.024	0.0749	0.0025
		Sb	0.0301	0.0115	0.028	0.011	0.0294	0.0057

only 15% of one electron in the perturbed region. In order to check that our shf results do not suffer from termination errors we have calculated Green's functions with different perturbed regions. When decreasing the size of the perturbed region, the maximum of the resonance slightly shifts to higher energies, thereby decreasing the moduli of all hf and shf data monotonously. This decrease is not dramatic and amounts to less than 10% if we come down to a perturbed region that consists of the donor and two shells of ligands.

The agreement between theoretical and experimental hf and shf data confirms that the resonance is a valid representative of the ground state of the shallow defect state. According to the EMT, there is a full hydrogenic series of bound states that transform according to the A_1 irreducible representation of T_d. Since these states are much less localized than the ground state, the truncation of the defect potential can be expected to shift these states to higher energies. Apparently there is no visible influence of these states.

From our results we speculate that the "simpler" shallow defects in diamond and SiC (simpler because these have larger binding energies and are more localized) should be tractable in the same way. This would open the way towards an understanding of many interesting defect systems for which the atomistic defect model is still unknown because the experimentally known hf and shf data could not be interpreted theoretically. The *ab initio* calculations, although considerably more complex, are much more flexible, and furthermore their application requires considerably less manpower than one of the more involved one-electron methods for shallow defects. Furthermore, these *ab initio* methods can easily incorporate lattice relaxations. Most probably this method cannot be extended to supercells containing a few hundred atoms because here the periodic images of the defect superlattice are superimposed into each cell, but it is not unlikely that for cluster calculations a similar extension will hold. However, in a Green's function approach the *ab initio* calculation results in hf and shf interactions that for the center region of the defect are considerably more accurate than those obtained from the best empirical approaches.

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