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Screening of impurities in semiconductors: Muonium in germanium, silicon, and diamond

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With the use of the density-functional formalism and the pseudopotential description of the electronic structure of a semiconductor, a new simple theory is derived for calculating the ground-state impurity level for deep donors. It is shown that within well-defined approximations the wave function of the impurity level can be determined self-consistently from a set of equations involving the dielectric function and the pseudopotential of the host lattice. The model, which is further simplified by the replacement of the potential by its spherical average around the impurity, is applied to muonium in diamond, Si, and Ge, and it is shown that the muon zero-point motion is essentially important in calculating the hyperfine frequency. The calculated results are in a qualitative agreement with the experiments.

I. INTRODUCTION

Two different paramagnetic muon states have been observed[1] in diamond, silicon, and germanium. The hyperfine spectrum of the so-called normal muonium state (Mu) is analogous to that of vacuum muonium but with a reduced hyperfine frequency. The observed spectra of the anomalous muonium state (Mu*) are describable by an axially symmetric hyperfine interaction which is much smaller than the one for Mu and is strongly anisotropic.

Whereas no satisfactory model of the electronic structure of Mu* has been reported so far, various models have been proposed to explain at least qualitatively the observed reduction of the spin density of Mu which is given by

$$A=|\psi_I(0)|^2/|\psi_{\text{vac}}(0)|^2=\pi|\psi_I(0)|^2 .$$

Here $|\psi_I(0)|^2$ is the spin density at the μ^+ in the host and ψ_{vac} is the electron wave function of the 1*s* muonium state in vacuum which, except for a slightly enhanced effective mass, corresponds to the 1*s* hydrogen wave function. The measured values at low temperatures are[1]

$$A_{\text{C}}=0.831$$

for diamond,

$$A_{\text{Si}}=0.450$$

for silicon, and

$$A_{\text{Ge}}=0.529$$

for germanium.

An interstitial hydrogen or muon forms a deep-level impurity and the effective-mass theory used for shallow impurities is totally unable to describe its electronic structure. A qualitative understanding of the impurity level can be obtained by the use of an *r*-dependent dielectric function to screen the $1/r$ potential of the hydrogen. The simplest of these kind of models is the so-called cavity model[2] which assumes that the potential is $1/r$ inside the cavity radius and $1/\epsilon_0 r$ outside the cavity, ϵ_0 being the static dielectric constant. Wang and Kittel[3] obtained reasonable values for the hyperfine constants of Mu in Si and Ge both with a cavity model and with a space-dependent dielectric function, provided that the electron mass was taken as the free-electron mass. The latter assumption, however, cannot be justified, as has been discussed by Pantelides.[4] Moreover, new calculations[1] for diamond, Si, and Ge have shown that neither the cavity model nor other approaches using various *r*-dependent dielectric functions are able to reproduce the observed order of the contact interaction: $A_{\text{C}}>A_{\text{Ge}}>A_{\text{Si}}$. These simple models also neglect the actual lattice structure and do not take into account explicitly the site of the interstitial muonium in the lattice (except if the *ad hoc* assumption is made that the cavity radius is related to the size of the interstitial hole).

The Green's-function methods which have been developed[5–8] to calculate electronic states associated with deep impurities and localized defects in semiconductors have so far not been applied to study interstitial hydrogen. A self-consistent pseudopotential calculation of hydrogen in Ge has been reported by Pickett *et al.*,[9] who found that a singly occupied H 1*s* deep donor state exists in the valence band. Recently, Sahoo *et al.*[10] performed a Hartree-Fock cluster calculation for muonium in diamond where the simple models tend to underestimate the contact spin density. However, the Hartree-Fock method has not been applied to muonium in Si or Ge.

In the present paper we develop a new simple theory for calculating a deep impurity level. Starting from the density-functional formalism and a pseudopotential description of the semiconductor we derive within well-defined approximations a self-consistent equation for the impurity bound state. The host semiconductor is described by its dielectric function and a screened pseudopotential. The actual lattice structure is taken into account and thus the impurity level will depend on the site of the impurity.

As an application of the new model we have calculated the electronic state of normal muonium in diamond, Si, and Ge. The spin density at the muon was found to depend strongly on the muonium site. Thus the zero-point motion of the muon has a large effect on the experimentally observed precession frequencies.

II. THEORY

Our starting point is the density-functional formalism with the local spin-density approximation for the exchange and correlation energy. This method has proven to be successful in describing many of the electronic properties of impurities in metals.[11] The key idea of the density-functional theory is to write the ground-state density in terms of single-particle wave functions

$$n(\vec{r})=\sum_i |\psi_i(\vec{r})|^2 \tag{1}$$

which obey the Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2+V_{\text{eff}}(\vec{r})]\psi_i(\vec{r})=\epsilon_i\psi_i(\vec{r}) \ . \tag{2}$$

The effective potential $V_{\text{eff}}(\vec{r})$ is given by

$$V_{\text{eff}}(\vec{r})=-\frac{Z}{r}+\sum_{\vec{m}}V_{\text{ps}}(\vec{r}-\vec{R}_m)+\int d\vec{r}\,'\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+V_{\text{xc}}(n(\vec{r})) \ , \tag{3}$$

where the first two terms are the external potential provided by the impurity nucleus and the host lattice pseudopotential and V_{xc} is the local exchange-correlation potential. Assuming that there is a well localized impurity state the electron density can be split up as follows:

$$n(\vec{r})=n_I(\vec{r})+n_L(\vec{r})+n_P(\vec{r}) \ , \tag{4}$$

where $n_I(\vec{r})$ is the electron density of the impurity state, $n_L(\vec{r})$ is the density of the unperturbed lattice, and $n_P(\vec{r})$ is the charge density caused by the polarization of the lattice due to the impurity. With the help of Eq. (4) V_{eff} can be written as

$$V_{\text{eff}}(\vec{r})=V^L_{\text{eff}}(\vec{r})+V^I_{\text{eff}}(\vec{r}) \ , \tag{5}$$

where

$$V^L_{\text{eff}}(\vec{r})=\sum_m V_{\text{ps}}(\vec{r}-\vec{R}_m)+\int d\vec{r}\,'\frac{n_L(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+V^L_{\text{xc}}(\vec{r}) \tag{6}$$

is the effective potential of the unperturbed lattice and

$$V^I_{\text{eff}}(\vec{r})=-\frac{Z}{r}+\int d\vec{r}\,'\frac{n_I(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+\Delta V_{\text{xc}}(\vec{r})+\int d\vec{r}\,'\frac{n_P(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \ . \tag{7}$$

V^L_{eff} can be approximated by a sum over *screened* pseudopotentials as follows:

$$V^L_{\text{eff}}(\vec{r})=\sum_m \tilde{V}_{\text{ps}}(\vec{r}-\vec{R}_m) \ . \tag{8}$$

Since the impurity level $n_I(\vec{r})$ already provides a complete screening of the impurity potential $-Z/r$, the polarization charge $n_P(\vec{r})$ is a response to the weak (screened) potential given by the first three terms of Eq. (7). Therefore we approximate it within the linear-response theory and neglect the effect of the change in the exchange-correlation potential $\Delta V_{\text{xc}}(\vec{r})$ on $n_P(\vec{r})$. With help of the dielectric function $\epsilon(q)$ the Fourier transform of $n_P(\vec{r})$ is then given by

$$n_P(\vec{q})=\left[\frac{1}{\epsilon(q)}-1\right][-Z+n_I(\vec{q})] \ . \tag{9}$$

In studying a hydrogen impurity, $n_I(\vec{r})$ is caused by one wave function ψ_I. In that case the electrostatic self-energy, the second term in Eq. (7), approximately cancels the change in the exchange-correlation potential $\Delta V_{xc}(\vec{r})$. This cancellation roughly corresponds to the so-called self-interaction correction in the density-functional formalism.[12] The impurity bound state is now determined by the Schrödinger equation

$$-\tfrac{1}{2}\nabla^2\psi_I(\vec{r})+W_I(\vec{r})\psi_I(\vec{r})=\epsilon_I\psi_I(\vec{r}) \ , \tag{10}$$

where the effective potential W_I is given by

$$W_I(\vec{r})=-\frac{Z}{r}+\sum_m \widetilde{V}_{ps}(\vec{r}-\vec{R}_m)+\int d\vec{r}\,'\frac{n_P(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \ . \tag{11}$$

The impurity level ϵ_I and the corresponding wave function ψ_I can be determined by a self-consistent solution of Eqs. (9)–(11) once the screened pseudopotential and the dielectric function of the host are known.

With the standard definition of the r-dependent dielectric function

$$\frac{1}{r\epsilon(r)}=\int\frac{d\vec{q}}{(2\pi)^3}\frac{4\pi}{q^2\epsilon(q)}e^{i\vec{q}\cdot\vec{r}} \ , \tag{12}$$

the effective potential W_I can be written in the following form:

$$W_I(\vec{r})=-\frac{Z}{\epsilon(r)r}+\int d\vec{r}\,'\left[\frac{1}{\epsilon(\vec{r}-\vec{r}\,')}-1\right]\frac{n_I(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+\sum_m \widetilde{V}_{ps}(\vec{r}-\vec{R}_m) \ . \tag{13}$$

In earlier investigations[3,13,14] of the hydrogen impurity in semiconductors only the first term of Eq. (13) was included. In that case the total screening charge would be

$$\lim_{q\to 0}\left[n_I(q)-\left[\frac{1}{\epsilon(q)}-1\right]Z\right]=Z\left[1+\frac{\epsilon_0-1}{\epsilon_0}\right]>Z \ , \tag{14}$$

where $\epsilon_0=\epsilon(q=0)$ is the macroscopic dielectric constant. Thus the impurity would be overscreened. In our formulation the polarization charge is induced by a neutral impurity and no overscreening occurs. In addition to this correction [which leads to the second term in Eq. (13)], our calculation also includes the effect of the actual lattice potential [last term of Eq. (13)]. Note that in our formulation one always uses the bare mass of the electron; the effects of an effective mass are implicitly included due to the use of the lattice pseudopotential.

III. APPLICATION TO MUONIUM IN GERMANIUM, SILICON, AND DIAMOND

The theory developed in Sec. II is applied to calculate the wave function of an electron bound to a positive muon in semiconductors. Experimentally, the hyperfine frequency has been extracted from the observed transition frequencies in the low-field Zeeman region[1] or, more recently,[15] was directly observed in zero external field. The hyperfine frequency is proportional to the spin density at the muon site. In our theoretical model the spin density is solely determined by the singly occupied impurity state ψ_I and the wave-function amplitude at the muon, $|\psi_I(\vec{R}_\mu)|^2$, depends on the muon site in the lattice, $\vec{R}_\mu$, which is unknown. It should be noted that the muon spin-rotation (μSR) data obtained so far strongly indicate that normal muonium is diffusing very rapidly. This implies that the probable interstitial sites are not limited by symmetry considerations. For a static muonium at a site of low lattice symmetry, on the other hand, the crystal field could give rise to a nonspherically symmetric spin density.[16]

The solution of the self-consistent equations (9)–(11) for several muon sites $\vec{R}_\mu$ was further simplified by replacing the sum over lattice pseudopotentials by a spherical average around the muon site,

$$W_I(r)=-\frac{Z}{\epsilon(r)r}+\int d\vec{r}\,'\left[\frac{1}{\epsilon(|\vec{r}-\vec{r}\,'|)}-1\right]\frac{n_I(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+\int\frac{d\Omega}{4\pi}\sum_m \widetilde{W}_{ps}(\vec{r}-\vec{R}_m+\vec{R}_\mu) \ . \tag{15}$$

This so-called spherical solid model proposed by Almbladh and von Barth[17] has shown to be successful[18–20] in explaining the energetics and muon Knight-shift systematics in simple metals. Further, we neglect any lattice relaxation around the muon, which allows the summation over the lattice pseudopotentials in the reciprocal lattice. The pseudopotential parameters used for the three different lattices are given in Table I. For the dielectric func-

TABLE I. Parameter values used in the calculations. Pseudopotential form factors V (in Ry) for diamond are from Ref. 22; those for silicon and germanium are from Ref. 23. Q is the inverse screening length for the dielectric function, ϵ_0 the static dielectric constant, and a_L the lattice constant.

	a_L (Å)	$V(\sqrt{3})$	$V(\sqrt{8})$	$V(\sqrt{11})$	ϵ_0	Q (a.u.)
C	3.56	−0.514	−0.022	+0.186	5.7	1.15
Si	5.43	−0.211	+0.0403	+0.0805	11.9	0.92
Ge	5.65	−0.232	+0.0108	+0.0604	16.0	0.82

tion $\epsilon(q)$ we use the analytical formula of Hermanson,[21] which leads to a very convenient r-dependent function

$$\frac{1}{\epsilon(r)}=\frac{1}{\epsilon_0}+\frac{\epsilon_0-1}{\epsilon_0}e^{-Qr} . \tag{16}$$

The parameter Q is fitted[1] to give $\epsilon(q)$ in good agreement with the first-principles dielectric function. The values for ϵ_0 and Q are also given in Table I.

The self-consistent equations were solved by starting with an initial potential $W_I^{(0)}$ obtained by setting $n_I=0$. From the calculated impurity wavefunction amplitude a new potential $W_I^{(1)}$ was generated and the expression $0.75W_I^{(1)}+0.25W_I^{(0)}$ was used as a new input potential. This procedure was then iterated and good convergence in both n_I and W_I was achieved within typically 10 to 12 iterations.

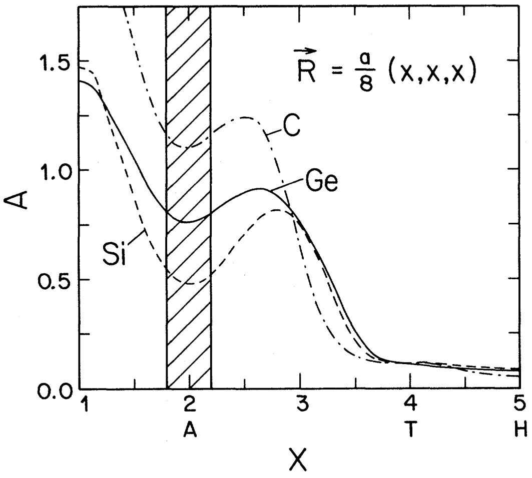

FIG. 1. Normalized spin densities at a muon in diamond, Si, and Ge vs the muon site $\vec{R}$ varying along the body diagonal of the cubic unit cell. Site A with coordinates $(2,2,2)a/8$ corresponds to an atom. T denotes the tetrahedral, H the hexagonal interstitial site, respectively.

In Fig. 1 the calculated normalized spin densities are given for $\vec{R}_\mu$ varying along the body-diagonal of the cubic lattice. The A values in all three host lattices are lowest (between 0.05 and 0.10) at the hexagonal interstitial site (H). They are slightly higher at the tetrahedral site (T) and strongly increase as R_μ is moved towards the host-atom position (A).

If the lattice potential is neglected, the self-consistent solution gives the following values: $A_C=0.67$, $A_{Si}=0.73$, and $A_{Ge}=0.77$. This shows that the lattice potential which includes the effects of the effective mass of the electron strongly influences the spin densities.

IV. INFLUENCES OF ZERO-POINT MOTION

Owing to the very light mass the muonium is expected to have a large zero-point vibration. The measured precession frequency is then an average

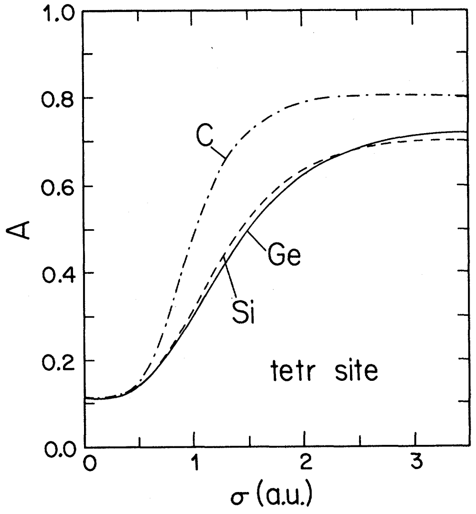

FIG. 2. Averaged normalized spin densities for muonium at the tetrahedral interstitial site vs the Gaussian width σ determining the zero-point vibration.

over the muonium zero-point motion. Assuming that the electron follows the muon adiabatically, the average spin density at the muon is given by

$$\langle\, |\psi_I(0)|^2 \rangle = \int d\vec{r}_\mu P(\vec{r}_\mu)\, |\psi_I(\vec{r}_\mu)|^2 \,, \qquad (17)$$

where $P(\vec{r}_\mu)$ is the probability that the muonium is at the point $\vec{r}_\mu$ and $|\psi_I(\vec{r}_\mu)|^2$ is the square of the wave function calculated for a fixed muon at the site $\vec{r}_\mu$.

To calculate the averaged spin densities the self-consistent calculations using Eqs. (10), (15), and (16) were repeated for several muon sites in the lattice (about 1600 altogether). The effect of the zero-point motion was estimated by assuming the muon distribution in Eq. (17) to be a Gaussian,

$$P(\vec{R}_\mu - \vec{r}_\mu) = \frac{1}{(2\pi\sigma^2)^{3/2}} e^{-(\vec{R}_\mu - \vec{r}_\mu)^2/2\sigma^2} \,, \qquad (18)$$

centered at the interstitial site $\vec{R}_\mu$. The results for the tetrahedral and hexagonal interstitial sites are shown in Figs. 2 and 3 as a function of the Gaussian width σ.

The values at the center of both of these sites are much smaller than the experimental results. Similar small A values were also found in earlier calculations[3] using an r-dependent dielectric function if the r-dependent effective mass was used. In our calculation this effective electron mass is accounted for by the use of the lattice pseudopotential.

As is evident from Figs. 2 and 3 the measured hyperfine frequencies may be drastically influenced by the zero-point motion. With a zero-point amplitude of 1.0 to 1.5 a.u., which is a reasonable guess for light impurity,[10,24] the theoretical values of A are enhanced and close to the experiments. In particular, the value for diamond stays well above those for Si and Ge.

The site of muonium is so far not known. There is some theoretical[10,25] and experimental[26] indication that the hydrogen site in these lattices is off center from the tetrahedral site towards the nearest atom (at about $x = 3.5$ in Fig. 1). We have repeated the calculations for a muon centered at this site and the results are qualitatively very similar to those at the hexagonal and tetrahedral sites (Figs. 2 and 3) showing the dominant role of zero-point motion.

V. SUMMARY AND CONCLUSIONS

A model has been developed for calculating the electronic structure of a deep-level impurity in semiconductors. It is based on the density-functional formalism and describes the host lattice by the dielectric function and a pseudopotential which accounts for the effective mass. With the use of various approximations, the wave function of the impurity level has been calculated from a set of self-consistent equations. The self-consistency of the theory guarantees the correct screening charge. The earlier simple models are found to be special limiting cases.

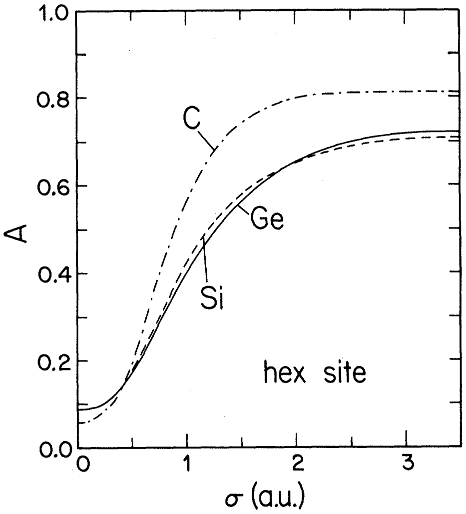

FIG. 3. Averaged normalized spin densities for muonium at the hexagonal interstitial site vs the Gaussian width σ determining the zero-point vibration.

The calculated spin density at the muon in Ge, Si, and diamond indicate the importance of the muon zero-point motion. The hyperfine frequency at the center of the hexagonal and tetrahedral interstitial sites is much smaller than the experimental value, but a zero-point amplitude of about 1 to 1.5 a.u. gives average values in reasonable agreement with experiments. An improvement of the model requires the neglect of the spherical approximation, calculation of the muon energy profiles in the lattice, and the actual three-dimensional muon distribution including the effects of the lattice relaxation around the muon.

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