PHYSICAL REVIEW B VOLUME 20, NUMBER 12 15 DECEMBER 1979

Theory of the hydrogen interstitial impurity in germanium

Warren E. Pickett* and Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720
and Molecular and Materials Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

C. Kittel
Department of Physics, University of California, Berkeley, California 94720

(Received 20 April 1979)

The self-consistent pseudopotential method is used to study the electronic structure of the hydrogen interstitial impurity in Ge. The impurity is considered to be at the site of tetrahedral symmetry and strong intra-atomic correlation effects are included. It is found that a singly occupied H-1*s* deep donor state exists, a result consistent with positive muon spin rotation (μ^+SR) experiments. This state lies at least 1 eV, and perhaps as much as 6 eV, below the Ge valence-band maximum. An examination of the charge density suggests only a small tendency of H to bond with the neighboring Ge atoms. It is tentatively concluded that this deep donor state is the one probed by μ^+SR experiments but that H migrates to impurity- or defect-related complexes or forms of molecular hydrogen rather than remaining as an isolated interstitial impurity.

I. INTRODUCTION

Hydrogen is likely the most common impurity in nominally pure crystals of Si and Ge. Unfortunately almost no direct experimental information is available, as the H impurity is "electrically inactive"[1] (unionized) even at room temperature and above. Indirect indication of a deep donor state associated with H in Si and Ge is provided by positive muon spin rotation (μ^+SR) spectroscopy.[2-4] This technique makes use of the μ^+ decay to measure the contact hyperfine interaction, interpreted as providing a measurement of the ratio $A(S)=|\Psi(0)|_S^2/|\psi(0)|_{\text{vac}}$ of the electron density at the μ^+ (or proton) site in semiconductor S ($S=\text{Si},\text{Ge}$) to that in a vacuum. The values for Ge (Ref. 2) and Si (Ref. 3)

$$A(\text{Ge})=0.58\pm 0.04\,,$$

$$A(\text{Si})=0.444\pm 0.20$$

are interpreted as due to a relaxed hydrogenic 1*s* "deep donor" state confined to a region of <3 a.u. for the simple reason that estimates assuming a shallow level lead to ratios $A(S)\sim 10^{-5}-10^{-7}$. (Actually, very recently shallow H-related states have been detected in Ge by Haller,[5] who suggests these may arise from complexes of hydrogen and other electrically inactive impurities.)

Theoretically it was recognized early on that the 1*s* level of interstitial H in Si or Ge could not be described by the effective-mass approximation used for shallow levels. A study by Reiss[6] and by Kaus[7] of cavity models, in which the potential V takes the form

$$V(r)=\begin{cases} e^2/\epsilon r\,, & r\gg R \\ e^2/r+k\,, & r\ll R \end{cases} \tag{1}$$

in which ϵ is the dielectric constant of the semiconductor, R is the cavity radius, and k is a constant, indicated a deep (very localized) donor 1*s* state for cavities the size of those in Si or Ge. The variational procedure of Reiss suggested an ionization (or binding) energy E_i of 1–3 eV, while Kaus's calculations suggested $E_i\simeq 4-5$ eV. The uncertainty arises from the lack of a precise way of fixing R; however, both calculations account for the experimentally observed lack of ionization at room temperature.

Wang and Kittel[8] applied the cavity model to determine $|\psi(0)|_S^2$, the quantity determined by μ^+SR experiments, and found quite reasonable results $[A(S)\sim 0.5]$, considering the simplicity of the model. They also investigated the effects of including a radial dependence of the effective mass and/or the dielectric constant, concluding that the most realistic estimates of their generalized cavity model were $A(\text{Si})\cong 0.43$, $A(\text{Ge})\cong 0.46$, $E_i^{\text{Si}}=1.55$ eV, and $E_i^{\text{Ge}}=1.65$ eV. (The results we have quoted for Reiss, Kaus, and Wang and Kittel were all obtained from calculations utilizing a free-electron mass.)

The cavity models of course treat the host semiconductor as nothing more than a dielectric medium in which H is immersed. A recent calculation of Coker, Lee, and Das[9] (CLD) has gone beyond this approximation by the application of their "self-consistent-charge extended Hückel" approach to a cluster of one H plus 30 Si or Ge atoms. The resulting ionization energy was found to be of the order of 0.7 eV in both materials, significantly smaller than the previous estimates, while the nuclear density ratios [$A(\mathrm{Si}) = 0.74, A(\mathrm{Ge}) = 0.64$] showed the reverse trend as compared to experiment. Singh *et al.*[9] have also done extended Hückel calculations on the interstitial hydrogen impurity in Si, finding a similar ionization energy for the donor.

In this paper we give a self-consistent microscopic treatment of interstitial H (or μ^+) in Ge. In addition to providing theoretical estimates of the known hyperfine splitting ratio A(Ge) and the measurable ionization energy E_i (so far unmeasured), the self-consistent pseudopotential approach we use allows a study of H-Ge bonding and of the H spectral density throughout the bulk Ge valence-band region. A knowledge of these properties is necessary before the interstitial hydrogen impurity can be understood.

The outline of the paper is as follows. In Sec. II we describe an application of the pseudopotential method (in the *spirit* of the empirical pseudopotential method) to describe a small supercell containing one H and eight Ge atoms. An oversimplified, but physically transparent, picture is given of the main effects of an interstitial H impurity. This picture leads to a consideration of the important part intra-atomic electron-electron correlations will play in this system. Both correlation (beyond any local density approximation) and self-consistency are included in a large supercell (H plus 54 Ge atoms) calculation described in Sec. III. It is found that a well-defined H-associated deep donor state in the upper *valence-band region* is present in the self-consistent results. This state does not exhaust the H spectral density, however, and the hydrogen local density of states remains nonzero (though small) nearly to the bottom of the valence-band region. It is found that minor bonding occurs between H and its nearest-neighbor Ge atoms.

In Sec. IV we extrapolate beyond the supercell results to consider an *isolated* H impurity in a semiconductor. We emphasize the corrections which may be needed to interpret excited-state spectra when strong intra-atomic correlation is important. We also point out a generalization which is important in the interpretation of the μ^+SR results, namely, that the spin density at the proton which is measured need not arise entirely from a single H-1s-like state. The main conclusions of this study are summarized in Sec. V.

II. AN UNSCREENED PROTON IN Ge

In this section we describe the characteristic band structure of a simple model system consisting of an unscreened proton in Ge. This system provides a simple picture of the important changes which occur when an H impurity is introduced into a semiconductor. The input to the calculation consists of the H and Ge potentials and their atomic positions.

A. Description of heuristic study

In the diamond lattice of Ge there are two high-symmetry interstitial positions at which an impurity is likely to reside. One is the "antibond" site of tetrahedral local symmetry, exactly one Ge-Ge bond length away from the four Ge nearest neighbors. The other is a site of hexagonal local symmetry, which lies at the center of a nearly planar hexagon of Ge nearest neighbors. Both sites have been considered by Wang and Kittel,[8] who note that the mean radius of the tetrahedral site is some 15% larger than that of the hexagonal site. Throughout this paper only the tetrahedral site will be considered. The higher symmetry makes the calculations less expensive, and the larger interstitial cavity results in more clearly drawn physical effects (e.g., a more localized donor level). Ge was chosen rather than Si because of its higher dielectric constant and larger lattice parameter.

In this initial heuristic calculation we utilize a screened atomic Ge potential[10] which gives a good description of the bulk band structure. The potential due to the proton is rigorously $-e^2/r$; it has been found,[11] however, that both the eigenvalues E_n and the radial charge density $r^2|\psi_n(r)|^2$ for $n = 1s$, $2s$, and $2p$ can be described quite well by a "pseudopotential" $V_H(r)$ which converges much more quickly in a plane-wave expansion. The Fourier transform of V_H for convenience has been fitted to an expression of the form

$$V_H(q) = -(4\pi e^2/\Omega q^2)a_1(\cos a_2 q + a_3)\exp(a_4 q^4) , \qquad (2)$$

where Ω represents the unit-cell volume. The parameters a_i are given in Table I. This potential has been used in other applications[11] which have given confidence in its reliability. The unit cell used in this calculation is a cube with a side of length $a_c = 5.658$ Å $= 10.696$ a.u., equal to the dia-

TABLE I. Ionic potential parameters of H^+ and Ge^{4+} corresponding to the form of Eq. (2). a_1 and a_3 are dimensionless; a_2 and a_4 are in a.u.

	H^+	Ge^{4+}
a_1	1.856	14.69
a_2	0.280	2.415
a_3	−1.538	0.584
a_4	−0.007	−3.440

mond structure lattice constant of Ge. This unit cell contains eight Ge atoms.

The band structure of Ge along the Γ-X direction, assuming this unit cell, is shown as the solid lines in Fig. 1. The energy zero is fixed at the valence-band maximum. There are 16 valence bands to accommodate the 32 electrons/(unit cell). Also shown in Fig. 1, as dashed lines, is the band structure which results when the unscreened proton is introduced. In addition to the 16 Ge bands, which are perturbed but easily recognizable, an additional band appears in the region −7.5 to −6 eV. An analysis of the charge density at Γ shows this extra band to be strongly associated with the proton. Approximately 60% of the charge of this "H band" very closely resembles that of the 1s state of H, and another ~30% lies in an s-like (symmetric) configuration of similar size centered on the Ge atom midway between protons. The remaining 10% of an electron is distributed throughout the unit cell. These figures are undoubtedly sensitive to the size of supercell chosen. In particular, the charge on the Ge atom midway between protons would be expected to decrease rapidly as the supercell size is increased. The Ge states at Γ below −3 eV contain small but significant amounts of charge within 2–3 a.u. of the proton, while those in the range −3 to 0 eV have very little charge in this region.

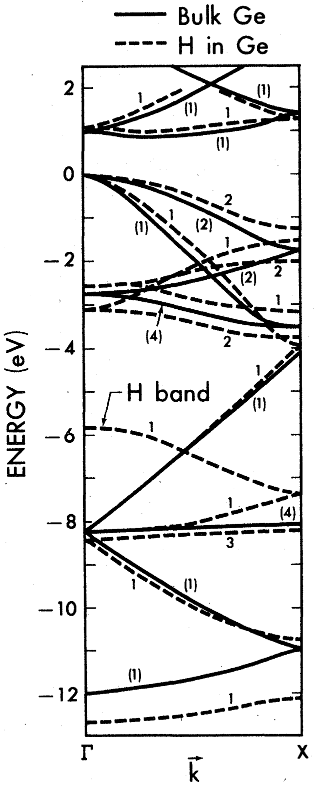

FIG. 1. Band structure of Ge in a simple cubic unit supercell containing eight atoms is denoted by solid lines, with degeneracies given in parentheses. The dashed lines show the band structure when an unscreened proton is introduced into a tetrahedral interstitial site. The numbers denote the band degeneracies

An impression of what can be expected from an isolated unscreened proton in Ge can be obtained from Fig. 1 as follows. Suppose we double the dimension of the unit supercell which still contains a single proton impurity. One effect is to reduce the Γ-X length by half; a second effect (which can be ignored for a qualitative discussion) is to reduce the magnitude of the perturbation felt by the Ge bands. The main effect can be accounted for roughly by folding the bands from $\Delta_0 = (\frac{1}{2}, 0, 0)(2\pi/a_c)$ to X, back to $\Gamma - \Delta_0$. Actually bands from elsewhere in the Brillouin zone (BZ) are also folded back. This results in $16 \times 2^3 = 128$ Ge valence bands and still a single proton-related state (with smaller dispersion due to a reduced H-H interaction). This process can then be repeated. In the limit of a single impurity, however, all states are folded back to Γ (there being no periodicity, the BZ degenerates to a point). Bulk Ge states lie arbitrarily close to the proton 1s level. The apparent result will be a more or less sharp resonant proton 1s state in the midst of the Ge density of states at ~6 eV. Small but perhaps significant amounts of spectral density (i.e., local density of states) associated with the proton will be spread throughout the valence-band region.

There are various reasons why this calculation, which would suggest $E_i^{\mathrm{Ge}} \simeq 7$ eV and $A(\mathrm{Ge}) \simeq 0.6$, should not be taken literally. The most obvious shortcoming is the use of an unscreened proton potential, which would be expected to overestimate both E_i and A. However, even if a screened potential were used, the lack of self-consistency of this calculation makes its predictions questionable. The importance of, and difficulty in, attaining self-consistency must now be addressed.

The system we are considering, i.e., a single H impurity in a supercell, is known to be semiconducting and electrically neutral. A single neutral H impurity atom in a supercell configuration inevitably leads to an odd number of electrons/(unit cell), which an automatic application of the usual (paramagnetic) band theory would predict to be metallic. Obviously this approach is wrong, since it is the nonzero electron *spin polarization* at the proton (actually, the muon) which is observed in μ^+SR spectroscopy. Evidently the H band in Fig. 1 should be occupied by a single spin-up (say) electron, with the corresponding spin-down state pushed into, or more likely above, the gap by a large correlation energy, thus leading to a net spin polarization as observed experimentally. (These conclusions tacitly assume that the tetrahedral interstitial site is one of those observed to μ^+SR experiments.)

Simple estimates suggest that a correlation energy of the necessary magnitude (say, of the order of 0.5 Ry) is likely to occur for the H-1*s* deep donor state, even in its relaxed form which is believed to occur in Ge and Si. Consider first the H-1*s* state, with an eigenvalue of −1 Ry. One (spin-up) electron in this state is bound by 1 Ry, but putting a second (spin-down) electron into the 1*s* state does *not* result in a total binding energy of 2 Ry. Rather, the second electron in H^- is known to be only weakly bound (by ~0.75 eV). This specifies a correlation energy of nearly 1 Ry for the H-1*s* state. Relaxation of the 1*s* state outward, induced by the host semiconductor lattice, will reduce the correlation energy somewhat, but it is not difficult to imagine an actual correlation energy of ~0.5 Ry for the deep donor state. For the cavity model, estimates[12] give a correlation energy of almost three times greater than the deep donor ionization energy of ~1.5 eV.

It is apparent now that a rigorous description of the H impurity in Ge requires a spin-polarized treatment. It can be expected that the result of a self-consistent local spin-density calculation would be as follows. The spin-up potential $V_\uparrow$ would be strongly attractive in the interstitial cavity containing the proton, closely approximating $-e^2/r$ and strong enough to bind a state of primarily H-1*s* character. The spin-down potential $V_\downarrow$ would have a strongly screened (by the spin-up electron) $-e^2/r$ potential which is unable to bind an electron. The difference $V_\uparrow - V_\downarrow$ should be of short range, however, as no disruption of the Ge lattice and its bulk properties by interstitial H has yet been detected.

However, there is a method *for this system*, short of a full spin-polarized treatment, that can be expected to yield an approximate solution containing the important physical effects. *As long as there is a single identifiable band* (or state at Γ in a larger supercell) *of primarily* H-1*s character*, one can in a self-consistent procedure occupy this state singly and all other states doubly. This will give an approximate account of both the intra-atomic correlation and the local-field corrections due to the host lattice. The results of an implementation of this program are described in Sec. III.

B. A digression on supercell effects

It is instructive to note on a quantitative level the effect of the impurity on the Ge supercell band structure. As mentioned above, the reference band structure, shown as solid lines in Fig. 1, is that of Ge, but considering the unit cell is considered to be a cube containing 8 Ge atoms. Consequently the Brillouin zone is simple cubic (sc) with $\frac{1}{4}$ the volume of the fcc BZ. The fcc BZ can be considered to be "folded down" into the sc BZ in an appropriate manner. Specifically, the fcc symmetry points Γ, *X*, *L*, *W*, and *K* are folded back to the sc symmetry points Γ, *R*, *X*, and *M*, respectively. The folding back of the fcc bands along Γ-*X* is evident in Fig. 1.

In addition there are two fourfold bands, which arise from the two rather flat Ge bands along *X*-*W* and become folded back to Γ-*X* in the sc BZ. The degeneracy must be doubled since there are 12 *inequivalent* *X*-*W* directions and only six Γ-*X* directions. This fourfold degeneracy does not occur in the true band structures of cubic crystals and can probably be traced to space-group operations which leave the crystal, but not the unit cell, invariant; i.e., symmetries which are ignored when using a nonprimitive unit cell.

It is the two fourfold bands which arise from the zone-boundary *X*-*W* bands which are perturbed by the proton potential. (The lowest valence band is lowered by the *average* perturbation; this vanishes for an isolated impurity and therefore is of no importance.) Thus in some sense it is the zone-boundary states which are more important in determining the deep donor energy and localization. This is in contrast to the case of shallow-impurity states, which can be constructed efficiently from near-band-edge crystal eigenstates. It is fairly evident that very localized states can not be easily built up from smooth (wave vector $k \simeq 0$) states. This observation is also consistent with further results discussed in Sec. IV.

III. THE SELF-CONSISTENT INTERSTITIAL HYDROGEN IMPURITY

In this section we describe the results of a self-consistent investigation of the electronic structure of interstitial H in Ge. As in Sec. II, the proton is positioned in a high-symmetry tetrahedral site, and a supercell configuration is used. To decrease the interaction between H atoms in the H superlattice, we take as the unit cell a rhombohedral cell with each linear dimension three times that of the primitive diamond cell (which contains two Ge atoms). The unit cell therefore contains $2 \times 3^3 = 54$ Ge atoms and one H atom. The BZ volume conversely is reduced by a factor of 27. The self-consistent procedure (described below) will be carried out using a single *k* point (Γ), which will be roughly equivalent to using 27 k points in bulk Ge.

The Ge ions are described by an ionic pseudopotential of the form given in Eq. (2), with the corresponding constants listed in Table I. This potential gives a reliable bulk band structure and has been used in surface and interface calculations with good results.[13] To begin the self-consistent procedure, the screened Ge potential referred to in Sec. II was used. In addition, the H ionic pseudopotential [Eq. (2)] was screened by the Walter-Cohen[14] dielectric function $\epsilon(q)$ for Ge, as fitted to an analytic expression by Wang and Kittel.[8] Of course it is desirable to begin as near to the self-consistent solution as possible. The dielectric function $\epsilon(q)$ contains no local-field effects and in some sense describes a spatially averaged Ge crystal. The H pseudopotential, which is placed in a comparatively large empty cavity, is therefore somewhat overscreened at the beginning, but this starting point represents an improvement over an unscreened H potential.

With this as a starting point, the Hamiltonian is diagonalized in a plane-wave representation. A matrix size of the order of 650 × 650, corresponding to an energy cutoff of 2.6 Ry, is necessary for reasonable covergence of the wave functions. An additional ~700 plane waves are included via Löwdin's perturbation scheme to improve the accuracy of the eigenvalues. The group symmetry at Γ is used to reduce the size of the secular matrix. A complete description of the procedure is given elsewhere.[15]

From an inspection of the charge densities of the eigenstates, the state which is primarily H-1s can be located. To account for the large correlation energy, the charge density $\rho(r)$ is calculated assuming this state to be *singly occupied* and the lowest 108 states elsewhere to be doubly occupied. From this charge density a direct Coulomb potential and exchange-correlation potential [proportional to $\rho^{1/3}$, $\alpha = 0.79$ (Ref. 15)] are determined. The sum of these potentials gives an "output" screening potential which is mixed with the "input" screening potential to define a new input potential which is used to screen the ionic (H + 54 Ge) pseudopotentials. The secular equation is then re-solved. The procedure is repeated until the desired criterion for self-consistency is attained. The H-related 1s state was easily located in each iteration, and six iterations produced eigenvalues which were stable to within ±0.1 eV.

In Fig. 2 a contour plot of the self-consistent pseudocharge density in the (110) plane containing the H atom is shown. A small tendency of the H to form bonds with both the nearest-neighbor Ge atoms (two of which are shown) and second-neighbor Ge atoms (one shown) is evident. However, this bonding tendency does not seem to affect appreciably the nearby Ge-Ge bonds, which retain a structure typical of the bulk bonds (when calculated in the same supercell procedure). The Ge-Ge bonds near the edges of the supercell are somewhat distorted; this is an artifact of the calculation which will be discussed below.

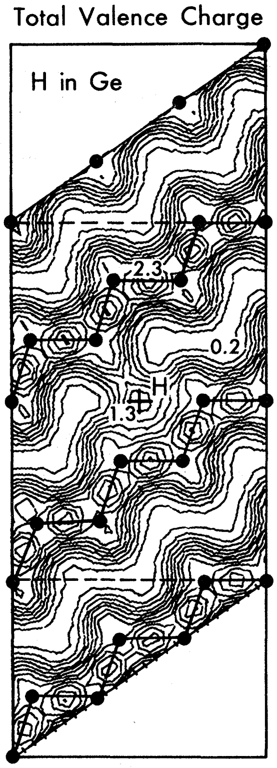

FIG. 2. Contour plot in a (110) plane of the self-consistent valence electron pseudocharge density for an interstitial H impurity in a supercell containing 54 Ge atoms. The solid lines denote Ge-Ge bonds, the hydrogen is denoted by the cross. A cross section of a single unit cell is shown. The charge is normalized to unity over the unit cell.

In Fig. 3 the contributions to the charge density from various parts of the energy spectrum are presented. From Figs. 3(a) and 3(b) it can be seen that there is a small amount of charge in the H-occupied interstices contributed by the lower half of the spectrum (−7 to −12 eV). A considerably large amount of charge in the H-occupied cavity results from states in range −4 to −6 eV, as shown in Figs. 3(c) and 3(d). In band theory jargon, this represents part of the H-s-Ge-p hybridization. This hybridization persists to some extent to the top of the valence band. However, there exists a single state, with an energy eigenvalue of −0.8 eV, which is much more strongly associated with the H impurity than any other state. The charge density of this state L_1, which

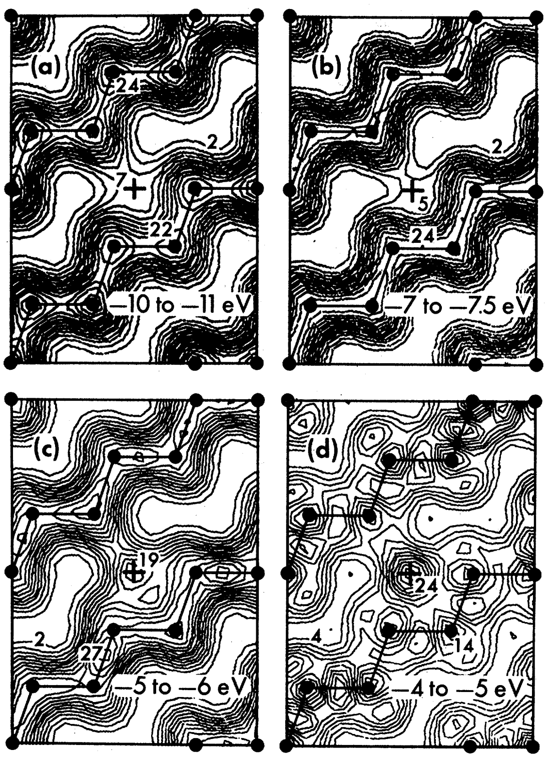

FIG. 3. Contour plots of the relative charge density arising from selected energy "windows" in the valence-band region. Only the region between the dotted lines in Fig. 2 is pictured. Note than even the Ge s states at low energy feel the hydrogen impurity.

will be referred to also as the deep donor state, is shown in Fig. 4(a). The deep donor characterization will be qualified somewhat in Sec. IV.

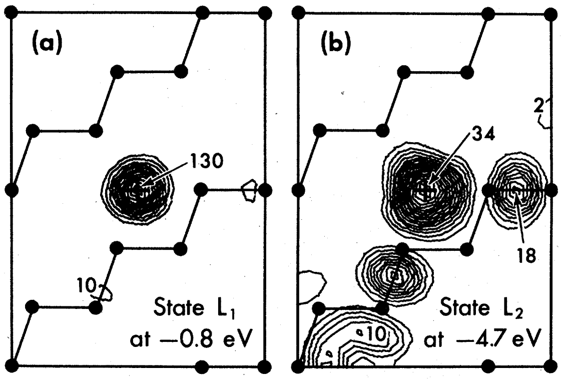

FIG. 4. Charge density of (a) the "deep donor" state L_1 and (b) the more tightly bound state L_2 which is also hydrogen related. The region shown is the same as in Fig. 3.

The effect of self-consistency on the deep donor state was to give a higher degree of localization and to bind it somewhat more strongly, i.e., to counteract the aforementioned overscreening due to the neglect of local-field corrections in the dielectric function. The charge density of the deep donor state is *not* as strongly localized as is suggested by Fig. 4(a). In Fig. 5 we have plotted the charge $Q(R)$, given by

$$Q(R)=4\pi\int_0^R r^2\rho_{L_1}(r)\,dr\ , \qquad (3)$$

versus the radius R for this state. For comparison, the analogous quantity is plotted for the total self-consistent charge density ρ_{tot} as well as for the self-consistent H atom charge density ρ_{H} resulting from a single H atom in the supercell. [The short dotted line indicates the *exact* result for a hydrogen atom; the oscillations in $Q_{\text{H}}(R)$ at large R could have been eliminated by using a larger number of reciprocal-lattice vectors in the expansion of ρ_{H}.] Only 35% of the charge of the deep donor state lies in the region of space occupied by the H-1s charge. The remaining 65% is spread throughout the large supercell, but particularly on the Ge-Ge bonding chains which most directly connect the H atom to another H atom in the neighboring cell. Occupying this state singly during the self-consistency procedure therefore somewhat disrupts the Ge-Ge bonds near the edges of the unit cell as well as some of the Ge states near the gap, the artifact referred to earlier. This disruption is small and should produce only a small perturbation in the region of the H atom.

Other than the L_1 deep donor state, there is only one other state with a significant amount

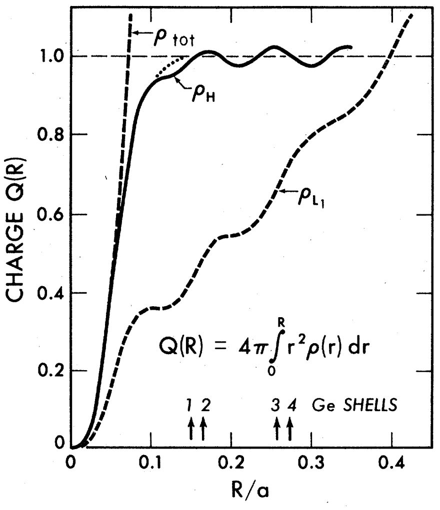

FIG. 5. Integrated charge $Q(R)$ vs radius R for the L_1 state (ρ_{L_1}), the total charge density (ρ_{tot}, shown in Fig. 2), and the hydrogen atom in a supercell (ρ_{H}). The dotted line gives the exact result for a hydrogen atom. The radius scale a is three times the Ge lattice constant.

(>2%) of its charge in the H-occupied cavity. This state is the L_2 state shown in Fig. 4(b); approximately 5–10% of the charge of this state can be attributed to the H atom. The correlation energy should be small compared to its binding energy of ~5 eV, justifying its treatment as a band state. The L_2 charge density is included in that shown in Figure 3(d).

To complete this section we consider the predictions of the deep donor ionization energy and hyperfine splitting ratio. *Assuming* the eigenvalue difference $E_c - E_{L_1}$ between the conduction-band minimum E_c and the L_1 eigenvalue can be associated with the ionization energy E_i, the prediction is $E_i^{\mathrm{Ge}} \simeq 1.6$ eV (the Ge gap is 0.8 eV). The hyperfine ratio cannot be expected to be given accurately in a pseudopotential calculation, since the potential at the proton, and thus $|\psi_{L_1}(0)|^2$ is somewhat arbitrary. However, the ratio can be estimated from the related ratio

$$A'(\mathrm{Ge}) = |\psi_{L_1}(r_m)|^2 / |\psi_{\mathrm{vac}}(r_m)|^2 , \qquad (4)$$

where r_m is the position of the maximum in the radial charge density $4\pi r^2 \rho_{\mathrm{H}}(r)$ of the free H atom ($r_m = 2$ a.u.). This ratio is given accurately in a pseudopotential treatment and is found to be $A'(\mathrm{Ge}) \simeq 0.4$, about 30% smaller than the measured value of $A(\mathrm{Ge})$. These predictions are somewhat oversimplified and will be discussed further in Sec. IV, in which the isolated H impurity is discussed.

IV. IMPLICATIONS FOR THE ISOLATED HYDROGEN IMPURITY

The calculations of Secs. II and III suggest a localized state associated with H lying in the Ge valence-band region. However, it is impossible for a perfectly sharp and strictly localized state to exist in a continuum of delocalized states, since mixing with continuum states of the same energy can always occur. The situation is reminescent of the classic treatment by Anderson[16] of localized magnetic states in metals. However, the presence of a gap between occupied and empty states in Ge precludes spin compensation by continuum states. Thus an isolated hydrogen impurity will be accompanied by a net spin of one Bohr magneton, and the Anderson model does not apply directly. An extension of the Anderson model to transition-metal impurities in semiconductors has been given by Haldane and Anderson,[17] but for transition-metal impurities the multiple charge states in the gap are of primary interest. Since H^- is almost certainly unbound in a semiconductor and neutral hydrogen appears to lead to polarized state(s) only below the valence-band maximum, states in the gap (which would be more readily identifiable experimentally) are not present to obscure the new physics occurring at lower energies.

The calculational results we have presented are based on the self-consistent density functional formalism,[18] which generates the ground-state energy and charge density but guarantees nothing regarding excited-state spectra and one-electron wave functions. In practice, however, the intermediately generated one-electron-like eigenvalues and eigenfunctions have been found to be very useful in interpreting excited state properties as long as the one-electron states which are involved are not too localized. Thus the binding energy of a very localized state, such as the deep donor state of Sec. III, is not necessarily given by the difference in eigenvalues $E_c - E_{L_1}$.

To estimate the corrections to the deep donor binding energy E_b, we consider the corresponding results[19] for the (spin-polarized) neutral H atom, assuming an exchange-correlation potential coefficient $\alpha = 0.79$ as in Sec. III. The total energy, which is the negative of the binding energy, is reproduced rather well, $E_{\mathrm{H}} = -13.7$ eV (compared to the exact value of -13.6 eV), but it is *not* given by the 1*s* eigenvalue $\epsilon_{1s} = -8.1$ eV. Both E_{H} and ϵ_{1s} can vary by ~1 eV depending on the exchange-correlation functional which is used, but our point here is that the binding energy E_b of the 1*s*-like deep donor state may be several eV greater than the eigenvalue difference $E_c - E_{L_1}$. An upper limit of 5.5 eV to the correction of E_b is given by the hydrogen atom calculation described above, so we can conclude $1.6\ \mathrm{eV} < E_b < 7$ eV.

It is possible to anticipate some features of a spin-polarized study of this system. The present treatment of correlation, i.e., occupying the deep donor state only once (with spin up, say), results in the correct charge in the vicinity of the proton and a correct Coulomb potential. The exchange-correlation potential is assumed to be the same for spin up and spin down, however, and this would be corrected in a spin-polarized study. The correct exchange-correlation potential will result in the spin-up electrons seeing a relatively unscreened proton, with a resulting E_{L_1} eigenvalue which is lower than found here and a spectral density which is perhaps strongly perturbed at other energies. The spin-down electrons, however, will "see" a proton which is well screened by the "localized" spin-up electron and will be relatively less affected. As a result the spin density at the proton (taken to be at the origin) $\rho^{\uparrow}(0) - \rho^{\downarrow}(0)$, which is measured by μ^+SR, may not result entirely from a single 1*s*-like state, but rather from a continuum of states of both spins. In Sec. III, it was found that the predicted spin-density ratio from the deep donor state only is 30% smaller than the measured value. It is likely that the continuum corrections, which would be available in a spin-polarized treatment, would result in a much closer agreement with the experimental ratio.

V. DISCUSSION AND CONCLUSIONS

The primary result of this study is that a self-consistent calculation of interstitial H in Ge, including the effects of strong correlation at the H site, indicates a singly occupied deep-donor-like state *in the valence-band region.* This result is consistent with positive muon spin rotation measurements. The binding energy of the deep donor state is bounded by the relation $1.6\ \mathrm{eV} < E_b < 7\ \mathrm{eV}$. The resulting moment of one Bohr magneton is free to rotate and should contribute to the susceptibility.

The present study goes beyond previous studies of hydrogen impurities in semiconductors by considering both the local environment of the impurity (i.e., local-field corrections) and the strong intra-atomic correlation which must be present, and by including both of these in a self-consistent manner. Still, this treatment is only approximate, since the strong correlation is not treated in a rigorous procedure. A self-consistent spin-polarized calculation, which we have not yet attempted, would provide a more rigorous basis for studying this system.

In this study, we have treated the case where the proton (or muon) occupies the tetrahedral interstitial position, and we have ignored any possible effects of thermal or zero-point motion. Although the deep donor muonium state is often interpreted in terms of this position,[20] there is no previous evidence of the position(s) the proton is likely to occupy. The extended Hückel calculations of Singh *et al.*[9] suggest the tetrahedral position as the most stable, however.

The results we have presented lead to the tentative conclusion that *hydrogen impurities in* Ge *do not occupy the tetrahedral interstitial position,* for if they did they would show a hyperfine spitting as does the positive muon. The splitting, which is just that seen in μ^+SR experiments, would show up in electron spin resonance and nuclear magnetic resonance experiments, in contradiction with the findings to date.[21] Possibilities for diamagnetic configurations of hydrogen in Ge include molecular hydrogen and formation of a H-Ge bond at a vacancy, as well as more involved H-related complexes. This difference between the proton and muon sites can be accounted for by noting that the muon does not have time to migrate to defects, etc., before decaying, whereas the proton has essentially an infinite time to find the most stable configuration. We consider it unlikely that the difference in zero-point motion plays any important role in the site determination.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (Grant No. DMR 7822465) and the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Department of Energy (Grant No. W-7405-ENG-48). M.L.C. was a recipient of a Guggenheim fellowship (1978–79). W. E. P. appreciates the hospitality of Northwestern University where the manuscript was prepared.

---

*Permanent address: Code 6684, Naval Research Laboratory, Washington, D. C. 20375.

[1] A. G. Milnes and D. L. Feucht, *Heterojunctions and Metal-Semiconductor Junctions* (Academic, New York, 1972).

[2] I. I. Gurevich *et al.*, Phys. Lett. B 29, 387 (1969); I. I. Gurevich *et al.*, Zh. Eksp. Teor. Fiz. 60, 471 (1971) [Sov. Phys.—JETP 33, 253 (1971)].

[3] K. M. Crowe *et al.*, Bull. Am. Phys. Soc. 17, 594 (1972).

[4] Reviews of μ^+SR experiments in semiconductors have been given by J. H. Brewer, K. M. Crowe, F. N. Gynax, and A. Schenck, in *Muon Physics*, edited by V. W. Hughes, and C. S. Wu (Academic, New York, 1975), Vol. III, and by J. H. Brewer *et al.*, Phys. Scr. 11, 144 (1975).

[5] E. E. Haller, Phys. Rev. Lett. 40, 584 (1978).

[6] H. Reiss, J. Chem. Phys. 25, 681 (1956).

[7] P. E. Kaus, Phys. Rev. 109, 1944 (1958).

[8] J. S.-Y. Wang and C. Kittel, Phys. Rev. B 7, 713 (1973).

[9] A. Coker, T. Lee, and T. P. Das, Hyper. Int. 4, 84 (1978); V. A. Singh, C. Weigel, J. W. Corbett, and L. M. Roth, Phys. Status Solidi B 81, 637 (1977).

[10] The screened Ge potential used in this calculation is discussed in Ref. 13.

[11] K. M. Ho, M. L. Cohen, and M. Schlüter, Phys. Rev. B 15, 3888 (1977).

[12] A. Manoliu (private communication).

[13] W. E. Pickett, S. G. Louie, and M. L. Cohen, Phys. Rev. B 17, 815 (1978).

[14] J. P. Walter and M. L. Cohen, Phys. Rev. B 2, 1821 (1970).

[15] S. G. Louie, M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1654 (1976).

[16] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[17] F. D. M. Haldane and P. W. Anderson, Phys. Rev. B 13, 2553 (1976).

[18] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, *ibid.* 140, 1133 (1965).

[19] W. E. Pickett and D. E. Ellis (unpublished). A related treatment has been published by O. Gunnarsson, B. I. Lundqvist, and J. W. Wilkins, Phys. Rev. B 10, 1319 (1974).

[20] B. D. Patterson *et al.*, Phys. Rev. Lett. 40, 1347 (1978).

[21] See Ref. 4 in Wang and Kittel (Ref. 8).