Impurities in covalent crystals: Exchange-correlation and local-field effects

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A many-body investigation is presented for the screening of a pointlike impurity at a substitutional and at an interstitial site in diamond and silicon. Along the lines of previous work on the optical response and on the quasiparticle properties, the induced electronic charge density is obtained within the linear-response theory by adopting successively improved approximations for the polarizability matrix, namely, the random-phase approximation without (RPA) and with (RPA) the inclusion of local-field effects, and the time-dependent screened—Hartree-Fock approximation (TDSHF) with the inclusion of excitonic and local-field effects. It is shown that for diamond, both excitonic and local-field corrections introduce changes in the density profile comparable in magnitude to the commonly used zeroth-order (RPA) screening result. Thus, both many-body corrections are indispensable in a realistic description of impurity screening in a covalent insulator. For silicon the combined corrections are still of comparable size as the RPA, with the dominance of RPA local-field corrections. The charge flux towards the impurity in diamond is preferentially directed along the bonds; in silicon this asymmetry is less pronounced, in agreement with empirical bond-charge models. Changing the impurity position from a substitutional to an interstitial site shows that the screening is more efficient for the substitutional than for the interstitial case. Our findings should strongly influence binding-energy calculations of shallow impurities and should also be important for interpretations of experiments where charged particles such as muons and positrons probe the electronic many-particle system.

I. INTRODUCTION

The major part of the work on the electronic properties of defects has been devoted to the development and application of efficient methods for extracting new localized quasiparticle states, which appear in the presence of a defect. The effective-mass approximation (shallow impurities) and the one-particle Green's-function method (deep impurities) have both been quite successful in quantitatively explaining experimental data, especially for the idealization of point defects.1–5 A central quantity for the application of both methods is the effective impurity potential, which includes the screening effect of the electrons of the crystal. In the effective-mass approximation the self-consistent screening of the impurity potential is treated on an empirical basis.1 On the other hand, in the application of the Green's-function method,3–5 the effective impurity potential is determined self-consistently. However, here interaction effects of the valence electrons of the host are only taken into account in the single-particle states of the Green's function, and thus the induced charge density is still given by an effective one-particle density.

In this paper we investigate many-body effects in the screening of point defects in the covalent crystals diamond (C) and silicon (Si). Our work rests on an a priori treatment of the dielectric function within linear response and includes for the first time electron-hole interaction as well as local-field effects. The quantities calculated are the induced charge density and the induced potential. Besides the different many-body approximations [random-phase approximation with (RPA) and without (RPA) local-field effects and time-dependent screened—Hartree-Fock approximation (TDSHF)], we analyze the dependence of the screening on the impurity position (substitutional or interstitial) in the lattice.

For internal consistency of the calculation, an improved version of the optical spectrum for Si including the same many-body corrections is also reported. Previous investigations of impurity screening in covalent materials have mostly rested on model treatments such as the Thomas-Fermi theory6–8 and the
Penn model. There exists also work where a pseudopotential band structure is used for the calculation of the dielectric function, but here as well as in the model calculations local-field effects or the Bragg reflections of the induced charge density on the periodic ions are neglected. Recently, model investigations of the screening of pointlike impurities in the framework of the RPA have appeared, which already point to the importance of local-field effects.

Our paper is organized as follows: In Sec. II the wave-vector- and energy-dependent two-particle Green’s functions are constructed for diamond and Si including local-field and excitonic many-body effects, and then checked against optical data. Sections III and IV give the theoretical formulation of the impurity screening and the results for substitutional and interstitial impurities in C and Si. Section V contains our conclusions which are centered around our main findings, i.e., that (a) an a priori study demonstrates that in C both excitonic and local-field effects introduce in the induced charge-density changes comparable to the diagonal \([\tilde{Q}=\tilde{Q}’] in the polarizability matrix \(\epsilon(\tilde{Q},\tilde{Q}’)\) screening result, (b) for Si the nondiagonal screening contribution again is comparable to the diagonal one but with the dominance of the RPA local-field effect, and (c) the combined many-body effects give rise to a screening pattern (quasi-one-dimensional in C) which justifies empirical bond-charge models.

II. DIELECTRIC FUNCTION OF DIAMOND AND SILICON

As already mentioned in the Introduction, we need a reliable and accurate theoretical description of the wave-vector dependence of the dielectric function of the density-density component of the two-particle Green’s function. For this purpose we use the method of Hanke and Sham and their results for C and Si, which we improve and extend to the inclusion of the wave-vector dependence. As a criterion for the quality of the dielectric function we take its agreement with the optical experiment in the long-wavelength limit \((q\to0)\).

To introduce notations needed in the following discourse, we first summarize the results for the local-orbital representation of the two-particle Green’s function \(G\). The starting point is to expand the electronic Bloch wave function \(\psi\) into a set of local orbitals \(\phi\):

\[
\psi_n(\vec{r}) = N^{-1/2} \sum_{\nu,\ell} e^{i\vec{k} \cdot \vec{R}_\nu} \phi_{\nu,\ell}(\vec{r} - \vec{R}_\nu).
\]

Here \(n\) and \(\vec{k}\) denote the band index and the wave vector, respectively, \(N\) is the number of Wigner-Seitz cells, \(\vec{R}_\nu\) are the positions of the lattice sites, and \(\nu\) identifies the different local orbitals. The choice of the local orbitals allows for a transformation of the Bethe-Salpeter equation into an equivalent matrix equation the dimension of which is determined by overlap and which can be solved by inversion for the two-particle Green’s function

\[
G = G^0[1 - (V - \frac{1}{2} V_\psi)G^0]^{-1}.
\]

In this equation \(G^0\) is the propagator of a noninteracting electron-hole pair, \(-\frac{1}{2} V_\psi\) is the electron-hole attraction, and \(V\) is the exchange between electron-hole pairs. One finds for the electron-hole propagator

\[
G^0_{n,n'}(\vec{q},\omega) = N^{-1} \sum_{n,n',\vec{k}} c_{n,\vec{k}}^* c_{n',\vec{k}+\vec{q}} \frac{f_{n}(\vec{k}) - f_{n}(\vec{k} + \vec{q})}{E_n(\vec{k} + \vec{q}) - E_{n}(\vec{k}) - \omega - i\eta} \times \exp[-i(\vec{k} + \vec{q}) \cdot \vec{r}] c_{n',\vec{k}}^* c_{n,\vec{k}+\vec{q}} c_{n,\vec{k}},
\]

where \(f_{n}(\vec{k})\) is the occupation number and \(E_{n}(\vec{k})\) the energy of the one-particle state \((n,\vec{k})\). \(\eta\to0^+\) is a positive convergence factor and \(s\) stands for the set \((\nu,\mu,\vec{R}_\nu)\) of indices. The electron-hole attraction is given by

\[
V_{\nu\mu}(\vec{q}) = \sum_{m} e^{-i\vec{q} \cdot \vec{R}_m} \int d^3r \int d^3r' \phi_{\nu}^*(\vec{r} - \vec{R}_\nu) \phi_{\mu}^*(\vec{r'} - \vec{R}_\mu) V_{\nu\mu}(\vec{r} - \vec{r}') \phi_{\mu}(\vec{r'}),
\]

where \(V_{\nu\mu}(\vec{r} - \vec{r}')\) is the statically screened Coulomb potential. Finally, the local-orbital formulation of the electron-hole exchange can be written in the form

\[
V_{\nu\mu}(\vec{q}) = \sum_{m} e^{-i\vec{q} \cdot \vec{R}_m} \int d^3r \int d^3r' \phi_{\nu}^*(\vec{r} - \vec{R}_\nu) \phi_{\mu}^*(\vec{r'} - \vec{R}_\mu) V(\vec{r} - \vec{r}') \phi_{\mu}(\vec{r'}),
\]

where

\[
\sum_{\vec{q} \neq 0} A_{\nu\mu}(q) \psi(\vec{q} + \vec{Q}) A_{\mu\nu}(q) = \sum_{\vec{q} \neq 0} A_{\nu\mu}(q) \psi(\vec{q} + \vec{Q}) A_{\mu\nu}(q).
\]
What is needed for the screening problem is the inverse dielectric function, which is connected to the density-density component of the two-particle Green’s function,

\[ e^{-1} \tilde{q} + \tilde{Q}, \tilde{q} + \tilde{Q} \rightarrow (\omega) = \delta_{\tilde{q}} \cdot \tilde{q} \cdot + V(\tilde{q} + \tilde{Q}) \sum_{ss'} A_s(\tilde{q} + \tilde{Q}) G_{ss'}(\tilde{q}, \omega) A_{s'}^*(\tilde{q} + \tilde{Q}). \]  

(6)

Here

\[ A_s(\tilde{q} + \tilde{Q}) = \int d^3 r \phi^*_s(r)e^{-i(\tilde{q} + \tilde{Q}) \cdot r} \phi_s(r - \tilde{R}_s) \]  

(7)

are density form factors.

We are now in a position to explain the meaning of the different many-body approximations which we are going to use in this paper:

(a) The time-dependent Hartree approximation without local-field effects (RPA) means neglecting the electron-hole attraction \(-\frac{1}{2} V_x\) and taking \(e^{-1}\) diagonal in the reciprocal-lattice vectors (\(\tilde{Q} \equiv \tilde{Q}'\)).

(b) The time-dependent Hartree approximation with local-field effects (RPA) includes the nondiagonal elements (\(\tilde{Q} \neq \tilde{Q}'\)) in the wave-vector representation of the dielectric function but still neglects the electron-hole attraction.

(c) The TDSHF approximation with local-field effects takes into account both the screened electron-hole attraction \(-\frac{1}{2} V_x\) and also the nondiagonal elements of the dielectric function (\(\tilde{Q} \neq \tilde{Q}'\)).

A. Diamond

The calculation of the dielectric function of C in the long-wavelength limit (\(\tilde{q} \rightarrow 0\)) closely follows the work of Hanke and Sham.\(^{13}\) We use a Slater-Koster representation\(^{14}\) of the Xα band structure of Painter et al.\(^{15}\) as an approximation to the quasiparticle states of C needed for determination of the electron-hole propagator \(G^0(\tilde{q} \equiv 0)\) in the long-wavelength limit. The direct gap of this Xα work is 6.3 eV instead of the experimental 7.3 eV.\(^{13}\)

Bonding and antibonding tetrahedral orbitals in a Gaussian representation are taken as the local-orbital basis of the valence- and conduction-band wave functions, respectively. Main criteria for the determination of the local orbitals are the fulfillment of current conservation (Ward identities\(^{13,16}\)) and the reproduction of the valence charge density.

In principle, we should have used a quasiparticle band structure including nonlocal exchange-correlation and energy-dependent self-energy corrections. Such a single-particle excitation spectrum has been calculated by us most recently for C from first principles,\(^{16}\) employing the same many-body features for the two-particle Green’s function, as discussed in this paper. The resulting band structure (real part of the complex single-particle energy) is in excellent agreement with optical and photoemission experiments both with respect to band gaps and bandwidths. Its influence on the present impurity screening work has been investigated in preliminary fashion for C. It introduces changes of typically 5–10% in the induced charge-density profiles of Figs. 7–10, to be discussed later.

Thus our procedure is to get as close as possible an approximation to the actual quasiparticle band structure and then to improve step by step the irreducible vertex \([V - \frac{1}{2} V_x]\) in Eq. (2)], i.e., the many-body effects in the two-particle Green’s function \(G\). This may be considered a practical approach to approximately fulfilling a Ward identity, which relates the self-energy to the irreducible vertex (see also Ref. 16).

We consider the overlap between bonding and antibonding orbitals up to nearest neighbors in the fcc sublattice, an approximation which has been justified in Ref. 13. This, of course, includes second-nearest neighbors in the \(sp^3\) hybrids and leads for \(G^0, -\frac{1}{2} V_x\), and \(V\) to matrices of dimension 28 \(\times\) 28. We found it necessary to use a statically screened Coulomb potential in the electron-hole attraction \(-\frac{1}{2} V_x\) for which we use a Gaussian fit to the Penn-model\(^{17}\) results of Srinivasan.\(^{18}\)

The results for the frequency dependence of the dielectric function are slightly improved in comparison to Ref. 13. The sum rules\(^{19}\) for the imaginary part of the dielectric function and the inverse dielectric function are fulfilled to within 10%. The static dielectric constant is found to be 4.8 in the RPA, 4.3 in the TDSHF, and 6.1 in the TDSHF. The experimental value\(^{20}\) is \(\varepsilon_0 = 5.85\).

For the calculation of the impurity screening we need an extension of these results to the wave-vector dependence of the dielectric function.\(^{16}\) This means that we must calculate the wave-vector dependence of the density form factors \(A\) [Eq. (7)] and of the two-particle Green’s function \(G\) [Eq. (2)]. It is relatively easy to do this exactly for the density form factors, but for the two-particle Green’s function we must make some approximations. The wave-vector-dependent terms in the two-particle Green’s function are the electron-hole propagator \(G^0\), the electron-hole attraction \(-\frac{1}{2} V_x\), and the exchange between electron-hole pairs \(V\). The electron-hole exchange \(V\) can be calculated exactly from the density form factors \(A\) [Eq. (5)]. For the electron-hole attraction \(-\frac{1}{2} V_x\) and the electron-hole propagator \(G^0\) we take a wave-vector-independent approximation.
This approximation is readily justified for the electron-hole attraction, where the \( \mathbf{q} \)-dependent terms \( \mathbf{R}_m \neq 0 \) in the sum over lattice vectors [Eq. (4)] become rapidly small, and thus only the \( \mathbf{q} \)-independent terms \( \mathbf{R}_m = 0 \) need be retained. The justification of a wave-vector-independent approximation for the electron-hole propagator cannot be seen so easily. To extract a justification for it, we calculate the static dielectric function in the RPA for a special direction\(^{21} \) in the irreducible Brillouin zone

\[
(k_x, k_y, k_z) = \frac{2\pi}{a_0} (0.835 39, 0.407 47, 0.257 74) \xi, \\
0 \leq \xi \leq 1
\]  

(8)

later used for \( \mathbf{k} \) summations (see Sec. III), according to the relation

\[
\varepsilon(\mathbf{q}) = 1 - \frac{\mathbf{v}(\mathbf{q})}{\Omega_0} \sum_{s,s'} A_s(\mathbf{q}) G^{0}(\mathbf{q} = 0; \omega = 0) \times A_{s'}(\mathbf{q}'). \tag{9}
\]

Here \( \Omega_0 \) is the volume of the Wigner-Seitz cell. In Eq. (9) the density form factors \( A_s(\mathbf{q}) \) [besides the Coulomb potential \( \mathbf{v}(\mathbf{q}) \)] are the only quantities depending on the wave vector.

Figure 1 shows the result in comparison to the interpolation formula of Penn,\(^9 \) normalized to the value 4.8 of Eq. (9) for \( \mathbf{q} = 0 \). The good agreement confirms the assumption that the wave-vector dependence of the electron-hole propagator, Eq. (3), can indeed be safely neglected.

**B. Silicon**

As in the work of Hanke and Sham\(^{13} \) we use a Slater-Koster representation\(^{14} \) of the self-consistent orthogonalized plane-wave band structure of Ortenburger and Rudge\(^{22} \) as an approximation to the quasiparticle states of Si. This band structure contains adjusted pseudopotential parameters and is very close to what one would expect from experiment for the actual quasiparticle bands in Si (see also Ref. 13). To calculate the frequency dependence of the dielectric function, we follow the same procedure as in the case of C. However, here one must include, in addition, (parallel) second-nearest neighbors in the fcc sublattice in the matrix formalism. This implies that \( G^0, V_x, \) and \( V \) become \( 52 \times 52 \) matrices with 35 independent elements for \( G^0 \) and 47 independent elements for \( V_x \) and \( V \). Remaining second-nearest neighbor and third-nearest-neighbor overlaps introduce changes less than 5% in the induced density profiles in Si. In addition, the orthogonalization of valence on conduction-band states gains importance for Si, since the band gap is significantly smaller than that in C. We improve the orthogonalization between conduction- and valence-band functions or antibonding and bonding orbitals with the aid of Schmid's orthogonalization procedure.\(^{23} \) As a consequence, we must consider correction terms for the density form factors \( A_s \), the electron-hole attraction \( -\frac{1}{2} V_x \), and the electron-hole pair exchange \( V \).

When calculating the dielectric function in the described manner, systematic changes for the dielectric function of Si emerge, different from the results of Hanke and Sham\(^{13} \) who took only nearest neighbors into account. In particular, the differences between the various theoretical approximations (RPA, RPA, TDSHF) become smaller, and the agreement of the final result with experiment becomes better. Figures 2 and 3 show a comparison of the three theoretical approximations for the imaginary and the real parts of the dielectric function of Si in the

![FIG. 1. Wave-vector dependence of the dielectric function of C for \( \omega = 0 \), \( q_{\text{max}} \) denotes the edge of the Brillouin zone in the special direction. Displayed are the Penn-model results (circles) and the symmetrized RPA (+).](image)

![FIG. 2. Comparison of the theoretical results for the imaginary part of the dielectric function in Si.](image)
region of the $E_1$ and $E_2$ structures of the optical spectrum. The inclusion of the many-body effects leads to corrections which are completely analogous to those in the case of C. However, in Si they are smaller because of the more extended nature of the wave functions. Figures 4 and 5 show the imaginary and the real parts of the experimental dielectric functions of Si (Ref. 24) together with the TDSHF calculation. The agreement between theory and experiment is quite good in the region of the $E_1$ and $E_2$ structures. The $E_2$ structure is somewhat too small, the reason for this fact probably being related to the origin of the $E_2$ structure: It is due to transitions between a lower conduction and an upper valence band which are parallel over a large part of the Brillouin zone. This parallelness is very difficult to accurately reproduce in a Slater-Koster—fitted band structure. For the static dielectric constant we get 10.9 in the RPA, 10.3 in the RPA, and 10.6 in the TDSHF. The experimental value is $\varepsilon_0 = 11.7$.

The extension to the wave-vector dependence of the dielectric function for Si is accomplished, as in the case of C, by taking a wave-vector—dependent approximation for the electron-hole attraction $-\frac{1}{2} V_x$ and the electron-hole propagator $G_0$. This approximation seems to be less justified for $-\frac{1}{2} V_x$, since the terms with $\mathbf{K} = 0$ are larger in Si than in C. To confirm again the central approximation of a wave-vector—dependent $G_0$, we calculate as in C the static dielectric function $\varepsilon(\mathbf{q})$ [Eq. (9)] in the RPA approximation along the special line [Eq. (8)] in the irreducible Brillouin zone (BZ) and average over the corresponding star. Figure 6 shows the result in comparison with the interpolation formula of Penn, fitted to the same value 10.9 for $\mathbf{q} = 0$. The good agreement between the two results is a strong indication that the wave-vector dependence of the
electron-hole propagator $G^0$ can, in fact, also be neglected in Si.

III. THEORETICAL TREATMENT OF THE IMPURITY SCREENING

In the following investigations (Secs. IV and V) we calculate the induced potential $V_{\text{ind}}$ and the induced charge density $\rho_{\text{ind}}$, where $\bar{u}$ denotes the position of the impurity relative to a lattice point. In linear-response theory both quantities are directly connected via the static inverse dielectric function $\varepsilon^{-1}$. For instance,

$$V_{\text{ind}}(\bar{r}, \bar{u}) = \int d^{3}r' \rho_{\text{ind}}(\bar{r}', \bar{u}) \frac{1}{|\bar{r} - \bar{r}'|}$$

$$= \int d^{3}r'[\varepsilon^{-1}(|\bar{r} + \bar{u}, \bar{r}' + \bar{u}; \omega = 0) - \delta(\bar{r} - \bar{r}')] V_{\text{imp}}(\bar{r}') .$$

(10)

Here $V_{\text{imp}}(\bar{r})$ denotes the unscreened potential of the defect. As discussed in Sec. II, the inverse dielectric function implies a restriction of the self-consistent response to the contribution of the valence electrons only which, as well as the application of a linear theory, is certainly justified for shallow impurities. The contribution of core electrons will modify the screening mainly near the nucleus. However, it is not our aim to obtain absolute numerical accuracy in this special region, but rather to ascertain the importance of local-field effects and excitonic effects in general. For this reason, we also make use of a very simple (pointlike) form of the defect potential $V_{\text{imp}}$.

Employing the wave-vector representation of the inverse dielectric function

$$\varepsilon^{-1}(\bar{q}, \bar{r}; \omega = 0) = V_0^{-1} \sum_{\bar{Q}} \sum_{\bar{Q}} e^{i(\bar{q} + \bar{Q}) \cdot \bar{r}} e^{-1}(\bar{q} + \bar{Q}, \bar{r} + \bar{Q}; \omega = 0) e^{-i(\bar{q} + \bar{Q}) \cdot \bar{r}} ,$$

(11)

with $V_0$ being the crystal volume one obtains

$$V_{\text{ind}}(\bar{r}, \bar{u}) = N^{-1} \sum_{\bar{q}} \sum_{\bar{q}} \bar{F}_{\text{ind}}^{(0)}(\bar{q}, \bar{r}, \bar{u}) G_{\text{pr}}(\bar{q}; \omega = 0) F_{\text{pr}}(\bar{q}, \bar{u})$$

(12)

for the induced impurity potential, where $G$ is the two-particle Green's function [Eqs. (2)-(5)]. The quantities $\bar{F}_{\text{ind}}^{(0)}$ and $F_{\text{pr}}$ are defined by the relations

$$\bar{F}_{\text{ind}}^{(0)}(\bar{q}, \bar{r}, \bar{u}) = 8\pi \Omega_0^{-1} \sum_{\bar{Q}} e^{i(\bar{q} + \bar{Q}) \cdot \bar{r} + \bar{Q} \cdot \bar{u}}$$

$$\times A_{\text{pr}}(\bar{q} + \bar{Q})$$

(13)

$$|\bar{q} + \bar{Q}|^2$$

and

$$F_{\text{pr}}(\bar{q}, \bar{u}) = \Omega_0^{-1} \sum_{\bar{Q}} e^{-i \bar{q} \cdot \bar{u}} A_{\text{pr}}^*(\bar{q} + \bar{Q}) V_{\text{imp}}(\bar{q} + \bar{Q}) ,$$

(14)

where $\Omega_0$ is the volume of the Wigner-Seitz cell and $V_{\text{imp}}(\bar{q} + \bar{Q})$ is the Fourier representation of the unscreened impurity potential.

The local representation of the induced charge density $\rho_{\text{ind}}(\bar{r}, \bar{u})$ can also be cast into the form of Eq. (12). The only difference is that the term $\bar{F}_{\text{ind}}^{(0)}$ must be replaced by

$$\bar{F}_{\text{ind}}^{(1)}(\bar{q}, \bar{r}, \bar{u}) = 2\Omega_0 \sum_{\bar{Q}} e^{i(\bar{q} + \bar{Q}) \cdot \bar{r} + \bar{Q} \cdot \bar{u}} A_{\text{pr}}(\bar{q} + \bar{Q}) .$$

(15)

In Eq. (12) the induced potential is written as a sum over form factors $\bar{F}$ and $F$ multiplied by matrix elements of the two-particle Green's function. The form factors alone contain the information about the position of the impurity relative to the crystal lattice ($\bar{u}$) and the position $\bar{r}$ (measured from the impurity) at which the induced charge density and the induced potential are to be calculated.

From Eqs. (12)-(15) we obtain the TDSHF approximation if we consider the two-particle
Green's function [Eq. (2)] the electron-hole exchange $V$ as well as the electron-hole attraction $-V_x$. If we neglect the electron-hole attraction, we obtain instead the RPA result. The RPA, on the other hand, cannot be written in the form of Eq. (12). In this case we find the following representation for the induced potential:

$$V_{\text{ind}}(\vec{r})=N^{-1} \sum_{q} \sum_{Q} H^{(0)}(\vec{q}+\vec{Q}, \vec{r}) \chi(\vec{q}+\vec{Q}).$$

(16)

Here the density-density correlation function $\chi$ is related to the irreducible polarization $\tilde{\chi}$ by

$$\chi(\vec{q}+\vec{Q}) = \frac{\chi(\vec{q}+\vec{Q})}{1-V(\vec{q}+\vec{Q})\tilde{\chi}(\vec{q}+\vec{Q})},$$

(17)

which is valid only within the RPA,

$$V(\vec{q}+\vec{Q}) = 8\pi \Omega_0^{-1} |\vec{q}+\vec{Q}|^{-2}$$

is the Fourier representation of the Coulomb potential $V(r) = 2/r$. The irreducible polarization $\tilde{\chi}$ is defined through

$$\tilde{\chi}(\vec{q}+\vec{Q}) = \sum_{x,s} A_x(\vec{q}+\vec{Q}) G_{x,0}^0(\vec{q}; \omega = 0) \times A_s^*(\vec{q}+\vec{Q})$$

(18)

The form factors $H^{(0)}$, appearing in Eq. (16), are given by

$$H^{(0)}(\vec{q}+\vec{Q}, \vec{r}) = 8\pi \Omega_0^{-1} |\vec{q}+\vec{Q}|^{-2} \times e^{i(\vec{q}+\vec{Q}) \cdot \vec{r}} V_{\text{imp}}(\vec{q}+\vec{Q}).$$

(19)

The induced charge density $\rho_{\text{ind}}(\vec{r})$ can be calculated in the RPA with an equation which is formally equivalent to Eq. (16) with the form factor $H^{(0)}$ being replaced by

$$H^{(1)}(\vec{q}+\vec{Q}, \vec{r}) = 2\Omega_0^{-1} e^{i(\vec{q}+\vec{Q}) \cdot \vec{r}} V_{\text{imp}}(\vec{q}+\vec{Q}).$$

(20)

Note at this point that the induced potential and the induced charge density in the RPA do not depend on the impurity position relative to a lattice site. This fundamental deficiency of the RPA is a consequence of the neglect of local-field effects. Since we are mainly interested in the screening properties of the electronic system, a simple model for the unscreened impurity, i.e., a positive point charge, $V_{\text{imp}}(\vec{r}) = V/|\vec{r}|$, is chosen.

For the evaluation of the sums over the Brillouin zone appearing in Eqs. (12) and (16), we use the special direction method of Bansil.\textsuperscript{21} This method allows, under certain restrictions, the replacement of a three-dimensional integral over the Brillouin zone by a sum over one-dimensional integrals along suitably chosen directions in the Brillouin zone. The angular dependence of the integrand, which might be singular at the $\Gamma$ point, is assumed to be not too pronounced. The special directions are determined by the condition that an appropriate number of cubic harmonics, up to a given angular momentum $l_{\text{max}}$, vanishes. For our calculation we use the minimum set of special directions, which consists of the line given by Eq. (8) and the corresponding star (48 lines). Thus angular dependence up to totally symmetric cubic harmonics with $l = 6$ is included exactly.

IV. RESULTS FOR THE SCREENING IN DIAMOND AND SILICON

We now apply the results of Sec. III to the calculation of the static screening of point charges in the covalent insulator C and the covalent semiconductors Si. Considered are the cases of a substitutional and interstitial impurity position. A comparison between the RPA, RPA, and TDSHF calculations will clarify the importance of the corresponding improvements in the theoretical description of the inverse dielectric function for the impurity screening. The determination of the induced charge density in the (110) plane through the impurity position will provide a two-dimensional view over the charge rearrangement about the impurity. Also the site dependence of the screening, substitutional versus interstitial, will clearly show the important influence of many-body effects.

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FIG. 7. Induced charge density of a positive substitutional point defect in diamond. Results of various theoretical approximations (RPA, RPA, TDSHF) are shown along the [111] and [100] directions. Arrows on the horizontal axis characterize the positions of neighboring atoms.
A. Diamond

The two-particle Green's function $G$ and the density form factors $A$ are taken from Sec. II. Eleven equidistant points are chosen along the special line to perform the integration over the Brillouin zone.

1. Substitutional impurity

A substitutional impurity corresponds to setting $\bar{u} = 0$ in the equations of Sec. III. Figure 7 shows the induced charge density for a positive substitutional point charge along two specially chosen directions, which are the diagonal [111] and the edge [100] direction of the cubic unit cell. Arrows on the horizontal axis denote the positions of neighboring atoms. As can be seen in Fig. 7, the results for the different theoretical approximations deviate strongly from one another, particularly in the region of the tetrahedral bonds and near the atomic positions. The drastic corrections which are found in the RPA (as compared to the RPA), as well as in the TDSHF (as compared to the RPA), make it clear that both local-field effects and excitonic effects, being of comparable magnitude, must be considered in a realistic description of the impurity screening in C. Especially interesting is the form of the induced charge-density profile along the tetrahedral bond to the next-nearest neighbor ([111] direction). Here an induced dipole appears which is not present in the RPA. The inclusion of local-field effects and excitonic effects in the TDSHF is necessary to produce this polarization dipole (see Fig. 7). We note that the induced charge density is appreciably different from zero only in the regions of the atomic positions and the tetrahedral bonds. There are the high-density regions where the many-body effects are also dominant.

Figure 8 displays the induced potential along the same two directions as the induced charge density. Again the three theoretical approximations are compared. The corrections in the RPA and TDSHF are less pronounced than before, as can be expected from the weighted integration over the induced charge density [Eq. (10)]. Nevertheless, we see that local-field and electron-hole effects lead to indispensable corrections for a quantitative calculation of the induced potential. These corrections increase as one approaches the impurity and are not isotropic.

Figure 9 gives a two-dimensional plot of the induced charge density in the (110) plane through the impurity position, which contains tetrahedral bonds to the neighboring atoms. The semicircle at the left edge gives the impurity position. Crosses denote the

![Diagram](attachment:image_url)
locations of neighboring atoms in the plane. Areas of negative or positive induced charge density are encircled by solid or dashed lines, respectively. The left edge is a symmetry line of the (100) plane. Figure 9 shows again very clearly the strong anisotropy of the induced charge density. In the regions far from atomic positions or tetrahedral bonds the induced charge density vanishes within numerical errors. Along the bonding orbitals between the atoms (bond-charge positions) one finds polarization dipoles, which are ordered in such a way that the impurity is screened as effectively as possible. Furthermore, one finds that the polarizability of the electronic charge density of the bonds perpendicular to the bond direction is small. This result is in agreement with a semiempirical analysis of the Raman and infrared spectra of C (Ref. 26) in the framework of the bond-charge model.27 There a negligible polarizability of the bond charge perpendicular to the bond direction is found. From the results of Fig. 9 we can conclude, moreover, that the movements of the electrons in the process of screening are practically restricted to quasi-one-dimensional channels along the bond directions. This effective reduction of the motional degrees of freedom for the electrons can also be regarded as an explanation for the unexpected importance of the many-particle effects for the impurity screening in C.

2. Interstitial impurity

We shall now investigate the static screening of a positive point charge at the interstitial position \( \vec{u} = -(a_0/4)(1,1,1) \). This position (with respect to the lattice point) is located in the opposite direction of a tetrahedral bond at a next-nearest-neighbor distance.

FIG. 11. Induced charge density of a positive interstitial point defect at \(- (a_0/4) \) (1,1,1) in diamond in the (110) plane. Otherwise as in Fig. 9.

Figure 10 gives the induced charge density starting from the impurity position along the diagonal ([111] direction) an the parallel to an edge ([100] direction) of the cubic unit cell. The results for the RPA, RPA, and TDSHF approximations display distinct differences. As in the substitutional case, there are qualitative differences in the sense that new structures appear between the RPA on the one hand, and the RPA and TDSHF on the other hand. These structural changes can be attributed to the local-field effects. Going from the RPA to the TDSHF (or including electron-hole attraction effects) leads then to more quantitative corrections. Especially striking are the sizable differences in comparison to the induced charge density of a substitutional impurity, which are induced by the many-body effects. While we still have identical results in the RPA, which is not dependent on the impurity position \( \vec{u} \), the inclusion of local-field and excitonic effects leads to corrections in different directions about the impurity. For a substitutional impurity one finds a large increase, whereas for an in-

FIG. 12. Induced potential of a positive interstitial point charge at \(- (a_0/4) \) (1,1,1) in diamond. Otherwise as in Fig. 7.
terstitial impurity a large decrease results in the induced charge density. Moreover, the negative induced charge density of an interstitial impurity has its maximum not at the impurity position but at a distance of about 0.275 lattice constants in both directions and therefore nearer to neighboring atoms and bonds of the host lattice.

These results support the qualitative picture from the substitutional case, i.e., the strong coupling of the charge response to the quasi-one-dimensional channels formed by the ions and the bonds. For the further elucidation of this point, Fig. 11 gives the induced charge density in the (110) plane through the impurity position. One sees that the polarization of the charge concentrated at the ions and the bonds is indeed rather weak. Absolute numbers are much smaller than those for a substitutional impurity, and the maximum of the induced negative charge density are near to the neighboring atoms and bonds.

From the smaller induced charge density a smaller induced potential results. As can be seen from the TDHF results of Fig. 12, the induced potential of an interstitial point charge is reduced by about a factor of 2 in comparison to the substitutional case. This implies that interstitial impurities are not so effectively screened and are therefore expected to have larger binding energies (Ref. 12 and 28).

B. Silicon

Again we take the results of Sec. II for the two-particle Green's function $G$ and the density form factors $A$. For the Brillouin-zone integration 15 equidistant points are chosen along the special line.

1. Substitutional impurity

Figure 13 displays the induced charge density of a substitutional positive point charge along the [111] and [100] directions. Between the various theoretical approximations (RPA, RPA, TDHF) we find also important differences in Si. In quantitative comparison to C, however, local-field and electron-hole effects are less pronounced. In particular, the difference between the RPA and TDHF is evidently smaller in Si. Remarkable, in addition, is a qualitative difference with respect to C: The minimum of the induced charge density in Si is not at the impurity position, but (in the RPA and TDHF) about 0.15 lattice constants away. This points to a difference in the polarizability of the charges contributing to the tetrahedral bonds. To elaborate further on this point, we show in Fig. 14 the induced charge density in the (110) plane through the impurity position. The most prominent differences in comparison to the equivalent figure 9 for C are in the region of the bonding orbital to the next-nearest neighbor. The impurity is not capable of polarizing the bond charges strongly enough in the bond directions so as to create a maximum of induced negative charge density at the impurity position. This favors a greater symmetry in the screening of the impurity in

![Image](image_url)
FIG. 15. Induced potential of a positive substitutional point defect in Si. Otherwise as in Fig. 7.

the sense that the bond charges are also strongly polarized perpendicular to the bond directions. As a result an induced quadrupole in the region of the bond to the first neighbor develops. The polarizabilities of the bond charges parallel and perpendicular to the bond direction are of about comparable magnitude in Si. This result may again be considered as an a priori confirmation of a semiempirical analysis of the Raman and infrared spectra of Si with the use of the bond-charge model.29

Figure 15 gives the induced potential along the same two directions as the induced charge density. In Si the differences between the theoretical approximations (RPA, RPA, TDSHF) appear to be rather small in comparison to C. Of the strong differences in the induced charge density (Fig. 13) between the RPA on the one hand and the RPA and TDSHF on the other hand, not much is left because of the averaging effect in the weighted integration of Eq.

FIG. 16. Induced charge density of a positive interstitial point defect at $-(a_0/4) (1,1,1)$ in Si. Otherwise as in Fig. 7.

(10). As in C, the correction of the RPA via the local-field effects and the electron-hole attraction becomes greater as one is approaching the impurity.

2. Interstitial impurity

Figure 16 gives the induced charge density of a positive interstitial impurity at $u=-(a_0/4)(1,1,1)$. Displayed are the [111] and the [100] directions. Again note that the differences between the RPA and the TDSHF are rather small in Si, while in comparison to the RPA large qualitative and quantitative changes appear. In contrast to C, the quantitative differences between the induced charge densities of substitutional and interstitial impurities are much smaller. Moreover, the maximum of the induced negative charge density is practically at the impurity position and not, as in C, a distance of 0.275 lattice constants displaced. This result points to an easier polarizable electronic charge density in Si.

Figure 17 gives the induced potential of a positive interstitial point charge along the same two directions as in Fig. 16. The local-field effects and the electron-hole attraction decrease the strength of the induced potential (near to the impurity) in comparison in the RPA. The electron-hole attraction has clearly a smaller influence than local-field effects. In comparison to substitutional impurities (Fig. 15), Si interstitial impurities are also less effectively screened.

Finally, Fig. 18 gives the induced charge density in the (110) plane through the impurity position and reinforces our previous conclusion about the comparatively large polarizability of the electronic charge. Charge-density rearrangements over rela-
tively large distances are necessary to have the maximum of the induced negative charge density at the impurity position.

V. CONCLUSIONS

The aim of this paper is to present a quantitative study of the role of many-body effects of local-field and electron-hole attraction character in the screening of impurities in covalent crystals. The density-density component of the two-particle Green’s function, together with a material-adapted local-orbital description of the single-particle electronic states, supplies the appropriate tool for this task. The prototype materials for our investigation are the insulator C and the semiconductor Si.

The basis for the calculation of the impurity screening is a detailed theoretical description of the frequency— and wave-vector—dependent dielectric function or the two-particle Green’s function of the respective crystals. This subject is covered in Sec. II, where previous results of Hanke and Sham are summarized and extended in several points. New results are an improvement in the frequency dependence of the optical response in Si through the inclusion of higher-order neighbors and orthogonalization corrections in the local orbitals. For the wave-vector dependence of the dielectric function one gets already satisfactory results with a wave-vector—dependent approximation for the electron-hole propagator $G^0$, which is stripped from its matrix elements. These in turn entirely give rise to the $\mathbf{q}$ dependence. This last finding has important practical consequences for many-body calculations of elementary excitations in realistic insulators and semiconductors, because we can deal in a satisfactory manner simultaneously with $\mathbf{q}$ and $\omega$ dependences.

In our detailed analysis of C and Si we find that also in the screening problem the consideration of local-field and electron-hole effects is a necessary ingredient for a quantitative analysis. Especially important are the local-field effects because they introduce a complete change in even the qualitative screening pattern. Thus the strong influence of the lattice structure due to the Bragg reflections on the periodic ions emerges. On the other hand, the electron-hole attraction introduces no new structures in the induced charge density. However, in particular, in C it gives rise to corrections, which are of comparable magnitude to the zeroth-order diagonal screening result. A few important differences in the screening of impurities are found for C and Si. In C the polarizability of the electronic charge density is tied very much to the quasi-one-dimensional bonding channels. Bond charges are practically only polarizable parallel to these channels. In Si the polarizabilities of the bond charges parallel and perpendicular to the bond directions are of comparable magnitude. These differences between C and Si become, in particular, obvious in the comparison of the screening pattern of substitutional and interstitial impurities. In both C and Si substitutional impurities are better screened, because they are embedded in the channels of preferred electronic charge response. The more pronounced restriction in the motional degrees of freedom for the electrons in C leads also to much stronger electron-hole attraction effects than those in Si.

Finally, our detailed screening study emphasizes again the close relationship between the importance of many-particle effects and the degree of localization of the electronic density, which has already become evident in recent studies of single-particle and two-particle excitation spectra. An interesting continuation of the investigation of the impurity screening would be the calculation of bound electronic states, where rough preliminary estimates for the binding energies give 30% changes in C and 20% changes in Si due to the combined local-field (see also Ref. 12) and excitonic many-body effects. Our findings should also significantly affect the theoretical interpretation of experimental results which make use of probes, such as muons or positrons, acting as a (weak) external perturbation on the electronic many-particle system.
IMPURITIES IN COVALENT CRYSTALS: EXCHANGE...