

Many-body effects in the screening of substitutional impurities in covalent crystals

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A many-body description for the screening of impurities, including both local-field and electron-hole effects, is applied to diamond (C) and silicon (Si). *A priori* studies demonstrate the following: (a) For C, both of these many-body effects introduce in the induced-charge-density profiles changes comparable to the zeroth-order diagonal screening result; (b) for Si, the nondiagonal screening is again comparable to the diagonal one with the dominance of the random-phase-approximation local-field effect; and (c) the screening pattern (being preferentially along the bonds in C) justifies empirical bond-charge models.

Recently considerable effort has been directed towards a quantitative understanding of the electronic structure in the presence of point defects (impurities, vacancies) in semiconductors and insulators.^{1,2} Most of the work has been concerned with constructing efficient methods for solving the associated quasiparticle equation within the effective-mass² (shallow states) and the one-particle Green's function²⁻⁵ (deep states) schemes. In the effective-mass treatment the starting point is an assumed *ad hoc* form of the impurity potential, whereas in the Green's-function treatment the impurity potential is self-consistently determined. However, this treatment takes into account electron-interaction effects only in the single-particle spectrum, thereby implying that the induced charge density is calculated to within an effective single-particle picture.

In this Communication we present a first-principles study of the charge density induced by a positive substitutional point charge in the covalent crystals diamond (C) and silicon (Si) as prototypes for insulators and semiconductors, respectively. Previous investigations of impurity screening in various covalent materials either rest on model treatments, like Thomas-Fermi screening^{6,7} and the Penn model,⁸ or pseudopotential band-structure treatments,^{9,10} all of which neglect local-field and exchange-correlation, i.e., electron-hole interaction effects. In a recent Letter, studies based on a model dielectric function were presented, which indicated the importance of random-phase-approximation (RPA) local-field effects.¹¹ On the other hand, our work is based on an *a priori* density-response function, taking electron-hole interaction effects into account in addition to the local-field effects. For diamond, it is demonstrated that excitonic as well as RPA local-field effects represent corrections which are both of similar magnitude as the zeroth order and commonly used diago-

nal screening results. In Si, with its more spread out charge distribution, the excitonic or exchange-correlation effects are somewhat less pronounced. The induced charge density is highly anisotropic, with the amount of anisotropy strongly increasing if, in addition to the local field, the excitonic effects are taken into account. Again, the anisotropy is more pronounced in C, where the screening pattern is quasi one dimensional along the tetrahedral bonds and thus justifies much-used empirical models.

The evaluation of the density-response function is restricted to the contribution of the valence electrons. This, as well as the application of a linear-response theory, is certainly justified for shallow impurities. Contributions from the core electrons will modify the screening mainly near the nucleus.

Going to a Fourier-space formulation and expanding the quasiparticle wave functions into a set of orbitals $\phi_\nu(\vec{r} - \vec{l})$, localized around the N lattice sites \vec{l} , we arrive at the expression (atomic units)

$$\rho_{\text{ind}}(\vec{r}) = N^{-1} \sum_{\vec{q}} \sum_{ss'}^{\text{BZ}} \bar{F}_s^{(0)}(\vec{q}, \vec{r}) G_{ss'}(\vec{q}; \omega=0) F_{s'}(\vec{q}) . \quad (1)$$

Here

$$\bar{F}_s^{(0)}(\vec{q}, \vec{r}) = e^2 \Omega_{\text{wsz}}^{-1} \sum_{\vec{Q}} \exp[i(\vec{q} + \vec{Q}) \cdot \vec{r}] A_s(\vec{q} + \vec{Q}) , \quad (2a)$$

$$F_s(\vec{q}) = \Omega_{\text{wsz}}^{-1} \sum_{\vec{Q}} V_{\text{imp}}(\vec{q} + \vec{Q}) A_s^*(\vec{q} + \vec{Q}) , \quad (2b)$$

where \vec{Q} is a reciprocal-lattice vector, Ω_{wsz} is the volume of the Wigner-Seitz cell, $V_{\text{imp}}(\vec{q} + \vec{Q})$ is the Fourier transform of the unscreened impurity poten-

tial, and

$$A_s(\vec{q} + \vec{Q}) = \int \phi_\nu^*(\vec{r}) \exp[-i(\vec{q} + \vec{Q}) \cdot \vec{r}] \times \phi_\mu(\vec{r} - \vec{l}) d\vec{r} \quad (3)$$

are density form factors.¹² The index s stands for the set of indices \vec{l}, ν, μ . The local-orbital representation of the two-particle Green's function G , used in (1), is obtained by inverting the respective matrix representation of the Bethe-Salpeter equation¹²

$$G = G^{(0)}[1 - (V - V_{\text{exc}})G^{(0)}]^{-1} \quad (4)$$

The theoretical description [Eqs. (1)–(4)] of the electronic response involves essentially a two-step process, which also illustrates the physical role of the many-particle effects. In a first step the external impurity potential creates noninteracting electron-hole pairs ($G^{(0)}$) at all lattice sites, which may be alternatively viewed as a change in charge density. In a second microscopic step the induced charge densities of the electrons and holes interact. These interactions have a typical length scale of the order of the lattice parameter and consist of two types of terms. The first term (V) gives the interaction between electron-hole pairs, leading to the RPA local-field effect. The second term (V_{exc}) corresponds to the excitonic or electron-hole interaction.

Focusing mainly on the screening properties, we chose the simplest model for the bare impurity potential, i.e., a positive point-charge scaling with e . The one-electron states for our examples C and Si,

which enter the evaluation of the two-particle Green's function, are based on a $X\alpha$ band calculation¹³ for C and a self-consistent orthogonalized plane-wave OPW band calculation¹⁴ for Si. Results for optical data based on these band determinations have been found in good agreement with experiment.^{12,15} A quasiparticle band structure based on a nonlocal and energy-dependent self-energy, which we have recently determined for C,¹⁶ and which is in very good accord with experiment, gives rise to negligible corrections on the scale of Figs. 1 and 4. As in our previous work on optical response¹² and single-particle excitations,¹⁶ the matrices $G^{(0)}$, V , and V_{exc} are taken as 28×28 in C and 52×52 in Si. Brillouin-zone integrations are performed by employing the special direction method.^{15,16} Further calculational details will be given elsewhere.¹⁵

Figure 1 displays the induced charge density of a positive substitutional point charge in C along the [100] and the [111] direction. The arrows at the bottom give the positions of neighboring atoms. We have studied three different approximations to the dielectric function: $\bar{\text{RPA}}$ is without local-field effects [$\epsilon^{-1}(\vec{q} + \vec{Q}, \vec{q} + \vec{Q}')$ diagonal in \vec{Q} and \vec{Q}'], RPA is with local-field effects ($\vec{Q} \neq \vec{Q}'$), and time-dependent screened Hartree-Fock TDSHF includes, in addition, the electron-hole attraction or excitonic effects [V_{exc} in Eq. (4)]. The results demonstrate that, in C, both local-field and excitonic effects introduce corrections of comparable magnitude. Since they are of the same magnitude as the zeroth-order isotropic screening (RPA), they both are crucial for a microscopic

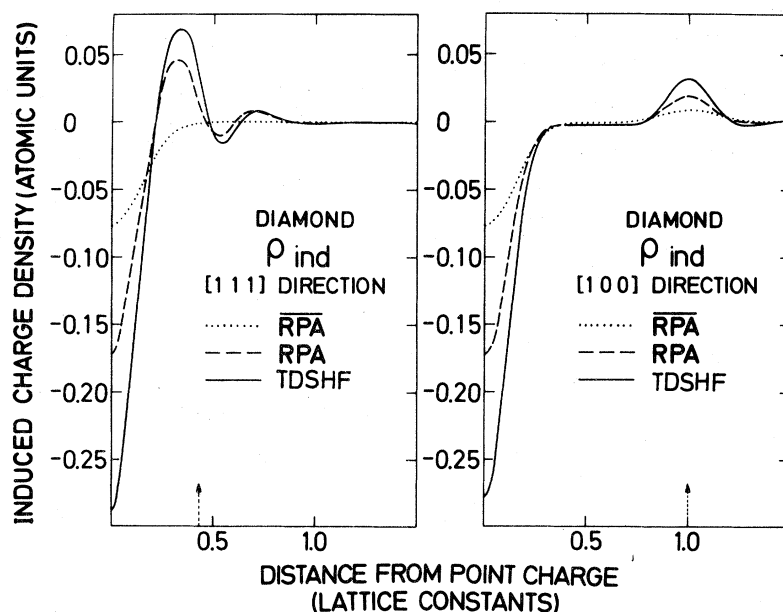


FIG. 1. Induced charge density of a substitutional impurity (positive point charge) in C along the [111] and [100] direction. The comparison of the $\bar{\text{RPA}}$, RPA, and TDSHF approximations is shown. The arrows at the bottom denote the positions of neighboring atoms.

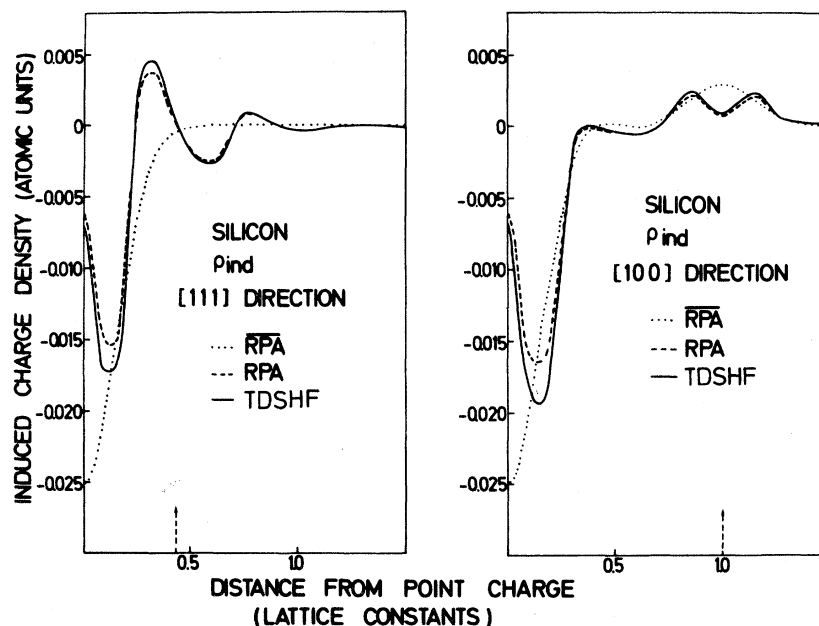


FIG. 2. Induced charge density of a substitutional impurity in Si. Otherwise like Fig. 1.

description of the impurity screening. Along the bond direction to the first neighbor ([111] direction) a polarization dipole is present. As evidenced in Fig. 1, it is not possible to get this polarization dipole without including many-body effects.

In Si, on the other hand, as evidenced in Fig. 2, the magnitude of local-field and excitonic corrections is reduced in comparison to C. In particular, we have a smaller difference between the RPA and TDSHF approximation. We also note an interesting qualitative difference in comparison to C, in that the maximum pileup of negative induced charge density is not at the impurity position but 0.15 lattice constants away from it. This points to a change in the polarizabilities of the tetrahedral bonds, which will be discussed below.

We have calculated the induced charge density in

the [110] plane through the impurity position, which contains the bonds to the neighboring atoms.

Figures 3 and 4 show the results of the full calculation (TDSHF) including local-field and excitonic effects for C and Si, respectively. The dot on the left edge of the figure gives the impurity position. Crosses represent positions of neighboring atoms. Full lines enclose negative- and dashed lines positive-induced charges. Both figures demonstrate again clearly the strong anisotropy of the screening charge distribution, which is more pronounced in C than in Si. Along the different bonds polarization multipoles are formed. In C we find an induced dipole along the bond direction, whereas in Si an induced quadrupole is formed.¹⁵ These results can be interpreted in terms of the bond-charge polarizability which, from our results for C, we can extract to be

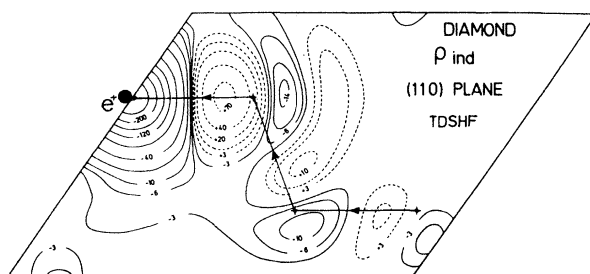


FIG. 3. Induced charge density in the [110] plane through the impurity position (positive, substitutional point charge) for C, calculated with the TSDHF approximation (see text). Numbers have to be multiplied by 10^{-3} to get atomic units.

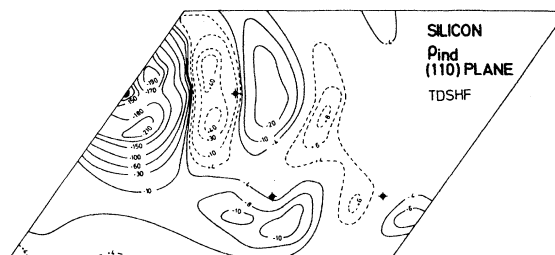


FIG. 4. Induced charge density in the [110] plane through the impurity position for Si. Numbers to be multiplied by 10^{-4} to get atomic units. Otherwise like Fig. 3.

essentially parallel to the bond directions. In Si, on the other hand, the polarizabilities parallel and perpendicular to the bonds are of comparable magnitude.¹⁵ Our results on the polarizability confirm on a microscopic basis a semiempirical analysis of the Raman and IR spectra of C and Si,¹⁷ using the bond-charge model.¹⁸

Summarizing, we have studied the screening of impurities in the prototype covalent materials C and Si on the basis of an accurate determination of the two-particle Green's function.^{12,15} The strong influence of many-body effects of electron-hole attraction and

local-field nature, both of which are of comparable magnitude to the zeroth-order screening result (in C), has been demonstrated. The relation of their strength to the degree of localization of the electronic charge has been clarified. From our work we conclude that the inclusion of both many-body effects is a necessary ingredient in an accurate determination of self-consistent impurity potentials and therefore also in the determination of the binding energies. Rough preliminary estimates let us expect a binding-energy reduction of 30% in C and 20% in Si as a consequence of the combined many-body effects.

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¹M. Altarelli and F. Bassani, in *Handbook of Semiconductors*, edited by W. Paul (North-Holland, Amsterdam, 1982), Vol. 1; F. Bassani, G. Iadonisi, and B. Preziosi, *Rep. Prog. Phys.* **37**, 1099 (1974).

²S. T. Pantelides, *Rev. Mod. Phys.* **50**, 797 (1978).

³M. Jaros, in *Proceedings of the Fourteenth International Conference on Semiconductors, Edinburgh, Scotland, 1978*, edited by B. L. H. Wilson, *Inst. Phys. Conf. Proc. No. 43* (IOP, Bristol and London, 1979), p. 281.

⁴G. A. Baraff and M. Schlüter, *Phys. Rev. Lett.* **41**, 892 (1978).

⁵J. Bernholc, N. O. Lipari, and S. T. Pantelides, *Phys. Rev. Lett.* **41**, 895 (1978).

⁶R. Resta, *Phys. Rev. B* **16**, 2717 (1977); F. Cornolti and R. Resta, *ibid.* **17**, 3239 (1978).

⁷M. Lannoo and G. Allan, *Solid State Commun.* **33**, 293 (1980).

⁸D. Penn, *Phys. Rev.* **128**, 2093 (1962); G. Srinivasan, *ibid.* **178**, 1244 (1969).

⁹H. Nara, *J. Phys. Soc. Jpn.* **20**, 778 (1965).

¹⁰J. P. Walter and M. L. Cohen, *Phys. Rev. B* **2**, 1821 (1970).

¹¹R. Car and A. Selloni, *Phys. Rev. Lett.* **42**, 1365 (1979); R. Car, A. Selloni, and M. Altarelli, *Solid State Commun.* **39**, 1013 (1981).

¹²W. Hanke and L. J. Sham, *Phys. Rev. B* **12**, 4501 (1975); **21**, 4656 (1980).

¹³G. S. Painter, D. E. Ellis, and E. R. Lubinsky, *Phys. Rev. B* **4**, 3610 (1971).

¹⁴B. Ortenburger and W. E. Rudge (unpublished).

¹⁵H. J. Mattausch, W. Hanke, and G. Strinati, *Phys. Rev. B* (in press).

¹⁶G. Strinati, H. J. Mattausch, and W. Hanke, *Phys. Rev. Lett.* **45**, 290 (1980); *Phys. Rev. B* **25**, 2867 (1982).

¹⁷S. Go, H. Bilz, and M. Cardona, *Phys. Rev. Lett.* **34**, 580 (1975).

¹⁸J. C. Phillips, *Phys. Rev.* **166**, 832 (1968).