Self-Consistent Green's-Function Calculation of the Ideal Si Vacancy

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We have developed a method for solving the Green's-function equations describing an isolated localized defect in an otherwise perfect crystal. It yields a charge density in sufficient detail to allow recalculation of the potential and iteration to self-consistency. The method is applied to the ideal (unrelaxed) vacancy in silicon, in the ionic-pseudopotential, local—exchange-correlation approximation.

The need for a Green's-function method to study the electronic structure of localized defects is, if anything, greater today than it was when the method was first proposed.[1] The limitations of effective-mass theory preclude its use where the bound-state wave function is too localized.[2] Cluster and defect-molecule calculations do not give band edges relative to which the bound-state energy can be referred, nor can they yield the width or energy of resonances should these occur.[2] Periodically repeated large unit cells, each containing one defect,[3] introduce a spurious "defect band structure" with rather uncertain bound-state energies and also discard the possibility of obtaining resonance widths. On the other hand, Green's-function formulations suffer from none of these drawbacks, and have recently again become popular.[4,5]

Green's-function calculations have heretofore emphasized energies. The work being reported here represents significant progress in that we have devised a scheme that yields a *charge density* sufficiently precise to allow construction of an impurity potential, and have used it to carry out a fully converged self-consistent calculation. The example chosen to illustrate the method is the ideal, unreconstructed silicon vacancy. The importance of this example is not that the results are new: Indeed, the essential qualitative behavior of the phase shifts $\varphi(E)$ [see below] and the correct physical interpretation of their meaning can be found in Ref. 5, while a self-consistent charge and potential, using well-trusted pseudopotential and bulk-band-structure techniques, has been given in Ref. 3. The importance is rather as a demonstration that this new method, which is both more practical and of greater utility than the bulk-band-structure technique, is of comparable accuracy in those matters for which the band-structure technique can be trusted.

A point defect is represented by a potential $U(\vec{r})$ which tends to zero at large distance and is described by $[H_0+U]\psi(r)=E\psi(r)$, where $H_0=-\frac{1}{2}\nabla^2+V_c$ denotes the Hamiltonian of the perfect crystal. Eigenfunctions of H_0 are Bloch waves and the Green's function for the perfect crystal is

$$G_E(r,r')\equiv\sum_n\int d^3k\,\frac{\psi_n(k,r)\psi_n{}^*(k,r')}{E-E_n(k)}. \tag{1}$$

The Schrödinger equation can be transformed into well-known integral equations[1] for bound states of energy E,

$$\psi(r)=\int G_E(r,r')U(r')\psi(r')d^3r', \tag{2a}$$

and for scattering states[6] (with $E\equiv E_{n_0}(k_0)+i0^+$),

$$\psi(r)=\psi_{n_0}(k_0,r)+\int G_E(r,r')U(r')\psi(r')d^3r'. \tag{2b}$$

To solve (2), we approximate $\psi(r)$ as a linear combination of atomic orbitals (LCAO), each orbital to be centered on an occupied atomic position, and each occupied atomic position supporting a number of orbitals:

$$\psi(r)\approx\textstyle\sum_i C_i\phi_i(r). \tag{3}$$

The number and types of orbitals at each site are to be chosen by convergence studies or by quantum-chemical intuition, the intent being to satisfy

$$U(r')\psi(r')\approx U(r')\textstyle\sum C_i\phi_i(r'). \tag{4}$$

No orbital lying totally beyond the range of the potential is thus needed, however, maximum orbital flexibility should be permitted where the overlap between U and ψ is expected to be large.

Consider a variational principle[7] for Eq. (2a), namely,

$$\delta\Lambda[\phi,\epsilon]/\delta\phi(r)=0, \tag{5a}$$

$$\Lambda[\phi,E]\equiv N[\phi]/D[\phi,E]=1, \tag{5b}$$

$$N[\psi]\equiv\int\psi^*(r)U(r)\psi(r)\,dr, \tag{6a}$$

$$D[\psi,E]$$
$$\equiv\int\psi^*(r)U(r)G_E(r,r')U(r')\psi(r')\,dr\,dr'. \tag{6b}$$

The conditions (5) are satisfied when $U(r)\psi(r)=U(r)\phi(r)$ [cf. Eq. (4)]. By choosing (3) as the trial function ϕ we obtain

$$\textstyle\sum_j [N_{ij} - D_{ij}(E)]C_j = 0, \tag{7}$$

$$N_{ij} = \int \phi_i^*(r)U(r)\phi_j(r)\,dr, \tag{8a}$$

$$D_{ij}(E) \equiv \int \phi_i^*(r)U(r)G_E(r,r')U(r')\phi_j(r')\,dr\,dr'. \tag{8b}$$

Equation (7) has no solution unless

$$\det[N_{ij} - D_{ij}(E)] = 0. \tag{9}$$

which determines the energy E to second-order accuracy in the wave-function error. No first-order error occurs because our matrices N and D each contain an additional factor of $U(r)$ which has not been heretofore employed.

To normalize the C_i, we write Eq. (2a) in the symbolic form $\psi = G_E U\psi$. The normalization of the bound state is then $(\psi,\psi) = (\psi U G_E, G_E U\psi) = 1$. But since $G_E G_E = -dG_E/dE$, and since $U\psi$ is given by Eq. (4), the normalization condition is

$$\textstyle\sum_{ij} C_i^*[dD_{ij}(E)/dE]C_j = -1. \tag{10}$$

Correct normalization of bound states extending beyond the range of the potential is absolutely essential for a self-consistent treatment.

For Eq. (2b), the functional to be varied is

$$J[\phi] = 2F[\phi] - N[\phi] + D[\phi, E], \tag{11}$$

$$F[\phi] \equiv \int \phi^*(r)U(r)\psi_{n_0}(k_0, r)\,dr. \tag{12}$$

The determinant of the matrix of the coefficients,

$$\det|N - D(E)| \equiv R(E)e^{i\varphi(E)},$$

describes the change in the energy density of states via $\Delta n(E) = -(1/\pi)d\varphi(E)/dE$.

To this point, $U\psi$, rather than ψ, has been the unknown. But ψ can be evaluated, once $U\psi$ is known, via Eq. (2). To do so, we introduce a second set of localized orbitals, infinite, periodic, and complete enough in every unit cell to expand each of the Bloch waves used in the Green's function [Eq. (1)] and in Eq. (2b) as

$$\psi_n(k,r) = \textstyle\sum B_m(n,k)\Phi_m(r).$$

The coefficients B_m are fixed by a least-squares fit, constrained to satisfy strict normalization. Using this local representation of the $\psi_n(k,r)$, the Green's function takes the form

$$G_E(r,r') = \sum_{mm'} \Phi_m(r)G_{mm'}(E)\Phi_{m'}^*(r'). \tag{13}$$

The matrix $G_{mm'}(E)$ is evaluated, using the B coefficients and the band energies $E_n(k)$, via the Gilat-Raubenheimer-Kam technique for the imaginary part and a Kramers-Kronig transformation for the real part. Although costly, calculation of this matrix is a one-time expense, and it can be stored and used for a variety of defect calculations.

By using (13) in (2), we obtain each state ψ_j in the form $\psi_j(r) = \sum C_m(j)\Phi_m(r)$. Coefficients $C_m(j)$ involve the elements $G_{mm'}(E)$, the LCAO coefficients, and also matrix elements of $U(r)$ taken between states $\Phi_m(r)$ and $\phi_i(r)$, in a straightforward manner.

It is necessary to sum the states so as to obtain a charge density

$$\rho(r) = \sum_{j\ \text{occupied}} |\psi_j(r)|^2 = \sum_{mm'} \Phi_m^*(r)\rho_{mm'}\Phi_{m'}(r),$$

where

$$\rho_{mm'} = \sum_{j\ \text{occupied}} C_m^*(j)C_{m'}(j). \tag{14}$$

For the scattering-state contribution, the sum in (14) is recast as an energy integral by inserting $\int\delta[E - E_n(k)]\,dE$ and then substituting, for the LCAO coefficients, their algebraic solution which introduces $[N - D(E)]^{-1}$. This latter factor contains all of the resonant behavior, but can be integrated analytically whenever this behavior threatens numerical difficulty. The matrix $\rho_{mm'}$ calculated via Eqs. (7)–(14) can be shown to satisfy the Kohn-Majumdar[8] theorem: It is continuous as a function of impurity potential even if a bound state is split off from, or returns to, a band edge as the potential varies. This too is essential for a self-consistent treatment.

The impurity potential $U(r)$ is evaluated numerically using the same ionic pseudopotential and the same Slater $X\alpha$ ($\alpha = 0.79$) form[3] as was used in the self-consistent band-structure calculations for $\psi_n(k,r)$. The electrostatic potential was obtained from $\rho(r)$ via Poisson's equation. Spatial integrals involving the Green's function are performed analytically, using s-, p-, and d-type Gaussians (up to 18 per atom)[9] for orbitals $\phi_i(r)$ and $\Phi_m(r)$ and fitting $U(r)$ by a linear combination of about twenty s- and p-type Gaussians. We have experimented with up to twenty bands in the Green's function, and up to four shells of atoms centered about the vacancy. The results presented here were obtained with fifteen bands, two shells of atoms, and 204 k points in each irreducible $\frac{1}{48}$ of the Brillouin zone. After iteration, input and output potentials agree on average to 0.14 eV. Full use is made of the defect-crystal point-group symmetry, T_d, as described, for example, in Ref. 6. Each complete iteration involves only evaluating matrix elements of $U(r)$, multiplications to produce $D(E)$, and inversions of $N-D(E)$. This can typically be done at a small fraction one-fifth of the cost of a supercell calculation.[3]

Let us now describe the results and compare them with those of other calculations of the ideal neutral Si vacancy. In Fig. 1, we exhibit the Si bulk density of states and the A_1 and T_2 phase shifts, from which changes in the density of states can be inferred. Our phase shifts are qualitatively similar to those calculated non-self-consistently in Ref. 5 to which we refer the reader for a more detailed discussion. Quantitatively, however, our energies agree rather better with those obtained in the supercell calculation.[3] In our calculation, a sharp A_1 resonance at -8.4 eV has a strength of 0.4 states and a width of 0.1 eV. A broader A_1 resonance, having a strength of about 0.6 states and a width of about 0.6 eV, is located at about -1.1 eV. Our T_2 bound state appears as the abrupt drop in the T_2 phase shift at 0.7 eV, slightly higher than the 0.5 eV extracted by Louie *et al.*[3] from the defect band. Scattering does change the spatial density associated with the other representations and, while these changes have been included in our self-consistent charge density, the phase shifts are small and uninteresting.

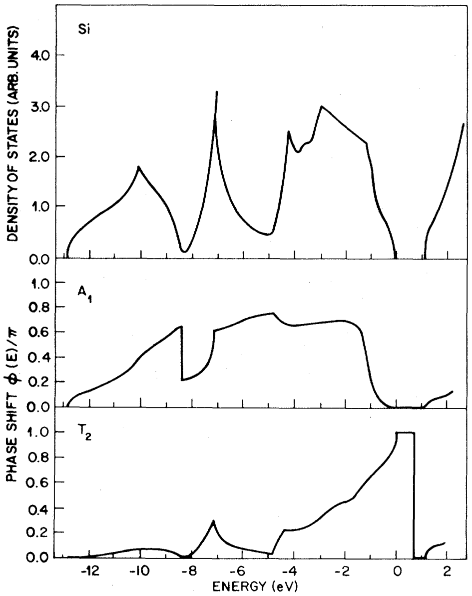

FIG. 1. Bulk density of states of Si and the A_1 and T_2 phase shifts induced by a neutral vacancy.

The spatial charge density here has been evaluated by filling each of the threefold-degenerate T_2 states in the gap to one-third occupancy, resulting in a system which is both electrically neutral and invariant under T_d. Such occupancy is unstable with respect to symmetry-lowering Jahn-Teller distortions,[10] and so direct comparison with experiment is not yet appropriate. This self-consistent charge density for the ideal neutral vacancy is displayed in Fig. 2. The display has been prepared by expanding the Bloch waves in an infinite set of orbitals Φ_m and retaining only those orbitals which influence the density in the neighborhood of the impurity. No information is lost in this way but the display lacks the translational periodicity one would expect to see.

The calculated densities agree closely with those calculated in Ref. 3. It is clear to us that the supercells chosen in that work were large enough to isolate the periodic defect potentials but not large enough to remove the overlap of the T_2 bound states, which are more extended

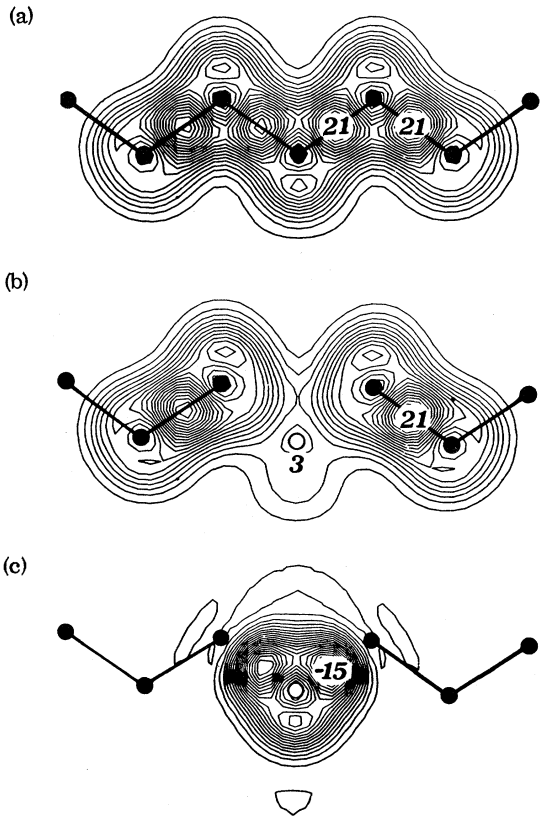

FIG. 2. (a) Unperturbed, (b) perturbed, and (c) change of charge density displayed in a (110) plane of atoms containing the vacancy. The values are given in units of electrons per Si bulk unit cell.

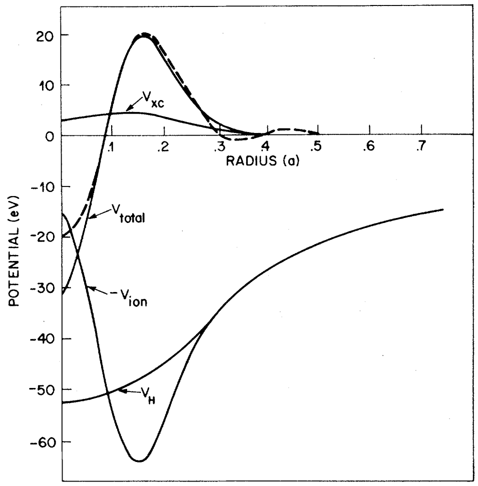

FIG. 3. Spherical average of components of the self-consistent vacancy potential and the total potential of Ref. 3 (dashed line). Angular anisotropy of the potentials is generally smaller than ± 10%.

than the potential.

In Fig. 3, we present the spherical average of various components of the defect potential. The total potential of Ref. 3 (dashed line) was evaluated using a relatively low cutoff of Fourier components which introduced spurious oscillations into the "supercell" ionic potential. We believe that this accounts for the difference between the two calculated defect potentials.

In summary, this Green's-function technique yields self-consistent *densities* and *potentials* which agree with those calculated self-consistently via a bulk-band-structure calculation of a periodic vacancy array. Its real strength, however, is that it produces bound-state energies, resonance energies, and resonance widths that are more reliable than, or inaccessible to, the periodic-array technique and at less cost. The type of information and the degree of accuracy made available by this new technique will be needed to study the effects of lattice distortions and their coupling to the electronic system.

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Self-Consistent Method for Point Defects in Semiconductors: Application to the Vacancy in Silicon

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We report the development of a method to calculate self-consistently the electronic structure of neutral point defects in semiconductors. The method is an adaptation of the original Koster-Slater idea. Calculations become feasible, practical, and accurate at the level of current band-structure and surface calculations when an LCAO basis set is used instead of Wannier functions. A detailed study of the isolated vacancy is Si is used to illustrate the method.

Point defects (vacancies, interstitials, etc.) and impurities in semiconductors are known to introduce localized states with energy levels in the fundamental gap. While shallow levels and some moderately deep levels are adequately described by effective-mass theory,[1] the theoretical description of most deep levels, which play a dominant role in determining many properties of electronic devices, has been one of the major outstanding problems of semiconductor physics. A large number of methods have been introduced and used for a variety of defects and impurities.[2]