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Total-energy gradients and lattice distortions at point defects in semiconductors

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A parameter-free, self-consistent method for calculating the gradient of the total energy (i.e., forces on atoms) of point defects in semiconductors is described. It is shown that under two conditions, (i) the pseudopotential approach and (ii) the inclusion of basis-set derivatives, the Hellmann-Feynman theorem can be applied. The convergence properties of the force calculation are examined, and the method is used to study the breathing distortions of the vacancy in silicon. The results, such as the direction and amplitude of the distortions and the force constants, are compared to other calculations and to available experimental data.

I. INTRODUCTION

Many properties of point defects (i.e., vacancies, substitutional impurities, and interstitial atoms) in semiconductors depend on the positions of the nearby atoms.[1–6] For the example of deep centers, which represent a well-localized perturbation of the crystal, the knowledge of the atomic geometry can be essential for an understanding of the electronic properties. On the other hand, the electronic structure, or more precisely the defect induced *change* in the electronic charge density, locally alters the perfect crystal's chemical bonds, the lattice stability, and the atomic geometry. Thus there is a close interdependence of the electronic and the atomic structure of a defect. The equilibrium atomic geometry is determined by the minimum of the total energy or by the zero of the forces on the atoms (i.e., the gradient of the total energy) with respect to the atomic positions. A theory which allows one to calculate either the total energy or the forces is therefore of paramount importance. Such a theory is required for a detailed understanding of the defect's electronic properties and it is also needed for calculations of force constants and vibrational frequencies. Furthermore, we note that deep-level defects can usually exist in different charge states. The Franck-Condon shift and the stability of the defect are again determined by the total energy or the forces. Recent examples which demonstrate the important implications of the charge-state dependence of the defect stability are the "negative *U*" behavior of the vacancy in Si,[2] and the diffusion of defects.[7–9]

Little is known about the local geometry at defects, as for example interatomic distances. Experimental studies (e.g., optical and infrared absorption) give information on the symmetry of the defect. However, it is not clear whether these methods can be developed to a state which allows the determination of distances between atoms. Extended x-ray absorption fine structure experiments or related techniques are the most promising methods to provide such detailed geometric informations.[10,11] Also electron-spin resonance, if combined with a quantitative theory to calculate spin densities, might evolve into a tool to determine the atomic positions at a paramagnetic defect.[12] So far, such analyses have, however, not been performed systematically.

With respect to the theory,[13] the development of the self-consistent Green's-function method[14–16] is a milestone in the investigations of electronic properties of localized defects (for recent reviews on these calculations see, e.g., Refs. 17 and 18). This approach allows a parameter-free, self-consistent calculation of the electronic structure of a defect system once its atomic geometry is known. The current status of experiments is such that they cannot fully determine the local atomic geometry around deep defects. Therefore the early calculations used to take the local lattice geometry as an input parameter. Only in some cases the geometry was varied to check its influence on the final theoretical results.[19–21] Such calculations have shown that a change of calculated ionization energies up to half an electron volt (over a typical semiconductor gap of about one electron volt) is in fact possible as a consequence of modest lattice distortions. For the case of the vacancy in silicon Baraff, Kane, and Schlüter combined the results of self-consistent Green's-function calculations with those of a semiempirical valence-force model.[2] This allowed them to deduce the amount of the Jahn-Teller distortion. The breathing distortion, however, could not be determined that way, and had to be fixed by analogy with the amount of the relaxation of a free silicon surface. Lindefelt[22] has recently determined the direction of this breathing distortion using the Hellmann-Feynman theorem. He also gave a semiempirical estimate of the distortion amplitude.

Parameter-free, self-consistent calculations of the lattice distortion around a defect have only been attempted very recently. Three main routes are currently followed: the supercell,[23,8] the Green's-function total energy,[5,7,9] and the Green's-function force method.[3-5] The supercell technique is a particular form of a cluster approximation, where the cluster is repeated periodically. This allows to apply standard band-structure programs for the calculation of the electronic structure and the total energy. One disadvantage of this technique is that it is limited to small unit cells (8—16 atoms is a typical number) and usually to quite small distortions: The interaction between the different cells implies that the impurity induces a band within the gap rather than a discrete level; independent of that, one also accepts an artificial elastic interaction between neighboring defects. As a consequence, the method usually breaks down for distortions where either the impurity band enters the valence band, or the elastic deformation clearly propagates from one cell to the next. Nevertheless, excellent results have been obtained in cases of interest (see, for example, Ref. 8). The Green's-function total energy and force methods consider an isolated point defect in an otherwise perfect, infinite crystal. They allow an accurate calculation of the electronic charge density, which then is used to evaluate the total energy[5,7,9] or its gradient, i.e., the force.[3-5] A possible advantage of a force method arises, because, as will be shown below, it is possible to recover the Hellmann-Feynman theorem.[24-26] Then the calculated force becomes particularly transparent because it can be interpreted in a purely electrostatic picture. Such analysis is obscured in the total energy, because of double counting and exchange-correlation terms.

In this paper we give a more detailed description of the Green's-function force method of Ref. 3. Section II deals with the basic theoretical arguments. In particular we mention two independent tests which can be used to check the accuracy of the results. In Sec. III we apply the method to the doubly positive and neutral charge states of the vacancy in silicon. We demonstrate the convergence properties of the method and compare the results to those of earlier semiempirical calculations.

II. HELLMANN-FEYNMAN THEOREM FOR FORCE CALCULATIONS

In this section we derive the Hellmann-Feynman theorem from density-functional theory.[27] In particular we discuss the problems of an application of this theorem to localized systems and we describe how these problems can be solved. Rydberg units are used.

A. Gradient of the total energy

The electronic energy of an interacting many-electron system with charge density $n(\mathbf{r})$ in an external potential $v(\mathbf{r})$ is given by[27,28]

$$E_v[n]=\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'+T_s[n]+E_{\mathrm{xc}}[n]\ . \quad (1)$$

The functional T_s is the kinetic energy of noninteracting electrons. E_{xc} is the exchange-correlation energy and thus contains the whole complexity of the quantum-mechanical many-electron problem. We note that the following discussion does not depend on the actual form of this functional. Therefore the discussion is valid in general but also for the local-density or the $X\alpha$ approach. The external potential $v(\mathbf{r})$ might be the potential of the nuclei, or, in a frozen-core approximation, the potential of the ions. In a pseudopotential approach, it is given by the ionic pseudopotentials. Below we refer to $v(\mathbf{r})$ as the potential of the ions. The ground-state total energy is a minimum for the correct electron density. Taking into account that the total number of electrons is conserved, this minimization can be expressed as

$$\delta E_v[n]=\int\left[\frac{\delta E_v}{\delta n}-\mu\right]\delta n\,d\mathbf{r}=0\ , \quad (2)$$

where μ is a Lagrange parameter. Thus, Eq. (2) determines the electron density of the electronic ground state, for a given external potential $v(\mathbf{r})$. If $E_v[n]$ is stationary, $\delta E_v/\delta n$ is constant and equals μ. Let us now consider that the external potential depends on a set of parameters Q_i (hereafter collected in a vector $\mathbf{Q}$) which determine the atomic geometry. Obviously, each $\mathbf{Q}$ represents a different external potential $v(\mathbf{r},\mathbf{Q})$, giving rise to a different electron density $n(\mathbf{r},\mathbf{Q})$. From Eq. (1) it follows that the gradient of the ground-state energy is given by

$$-\frac{\partial E_v}{\partial Q_i}=-\int\frac{\partial v(\mathbf{r},\mathbf{Q})}{\partial Q_i}n(\mathbf{r},\mathbf{Q})d\mathbf{r}-\int\frac{\delta E_v}{\delta n}\frac{\partial n(\mathbf{r},\mathbf{Q})}{\partial Q_i}d\mathbf{r}\ . \quad (3)$$

The first term in Eq. (3) is the Hellmann-Feynman force,

$$F_i^{\mathrm{HF}}[n]=-\int\frac{\partial v(\mathbf{r},\mathbf{Q})}{\partial Q_i}n(\mathbf{r},\mathbf{Q})d\mathbf{r}\ . \quad (4)$$

This term describes the pure electrostatic interaction of the electron charge density $n(\mathbf{r},\mathbf{Q})$ and the potential of the ions, $v(\mathbf{r},\mathbf{Q})$. As noted already above, $\delta E_v/\delta n$ is constant if the variational problem [Eq. (2)] has been solved exactly. If this is the case, the second integral in Eq. (3) vanishes because the number of particles does not depend on $\mathbf{Q}$. Unfortunately, as will be discussed in Sec. II B below, the variational problem of Eq. (2) is not solved exactly in actual calculations, and therefore the use of the Hellmann-Feynman theorem [i.e., the neglect of the second term in Eq. (3)] is usually not justified. In other words, the Hellmann-Feynman theorem does not usually work in actual calculations. We recall that the total energy is variational [Eq. (2)] and thus insensitive to small changes in $n(\mathbf{r},\mathbf{Q})$. However, the two integrals in Eq. (3) depend linearly on little density changes[29,30] and small errors in $n(\mathbf{r})$ might have significant effect on each of them, even if their sum is nearly unaffected. As a consequence, the use of the Hellmann-Feynman theorem requires a more accurate charge density than a total-energy calculation. The second term of Eq. (3) is due to inaccuracies in the calculated electron density, i.e., to inaccuracies in solving the variational problem of Eq. (2).[31,32] We therefore refer to the second term of Eq. (3) as the variational force,

$$F_i^V[n] = -\int \frac{\delta E_v}{\delta n} \frac{\partial n(\mathbf{r},\mathbf{Q})}{\partial Q_i} d\mathbf{r} \ . \tag{5}$$

It is clear from Eqs. (3)—(5) that, when the Hellmann-Feynman theorem is used, it is crucial to keep careful control on the variational force, either to show that it is negligible, or to include it, if necessary. These two possibilities are the two routes being used for force calculations in quantum chemistry.[33]

So far, the discussion dealt only with the electronic part of the total energy. The atomic geometry is, however, determined by both the electronic and the internuclear (or ion-ion) interactions. Consequently, the ith component of the force is given by

$$F_i[n] = F_i^{\mathrm{HF}}[n] + F_i^V[n] + F_i^{\mathrm{ion}} \ . \tag{6}$$

The ion-ion interaction is of pure electrostatic origin. If the ionic potentials are spherically symmetric, and their central-cell (non-Coulombic) parts do not overlap, $\mathbf{F}^{\mathrm{ion}}$ can be evaluated in a point-charge model. Further details are presented in Appendixes A and B.

B. Recovery of the Hellmann-Feynman theorem

The calculation of the variational force $\mathbf{F}^V[n]$, is not particularly complicated [see Eq. (10) below]. However, $\mathbf{F}^V$ does not describe any physical interaction, but is only due to inaccuracies in the solution of Eq. (2). Therefore, the occurrence of this force obscures the transparency of the Hellmann-Feynman theorem and thus the mechanism which drives the atomic rearrangement. Obviously, an approach which allows to neglect the term $\mathbf{F}^V$ would be important. This is discussed in this subsection. We first analyze the origin of the variational force and then describe the conditions which make it negligible.

In order to analyze the force $\mathbf{F}^V$ we note that the charge density is usually determined from a self-consistent calculation of the Kohn-Sham equations:[28]

$$\{-\nabla^2 + V_{\mathrm{eff}}[n(\mathbf{r});\mathbf{r}]\}\phi_k(\mathbf{r}) = \epsilon_k \phi_k(\mathbf{r}) \ , \tag{7}$$

with

$$V_{\mathrm{eff}}[n(\mathbf{r});\mathbf{r}] = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\mathrm{xc}}}{\delta n} \ , \tag{8}$$

and

$$n(r) = \sum_{k=1}^{N} |\phi_k(\mathbf{r})|^2 \ , \tag{9}$$

where the sum runs over all occupied states.

With these equations, $\mathbf{F}^V$ is written as

$$F_i^V[n] = -2\,\mathrm{Re} \sum_{k=1}^{N} \int \frac{\partial \phi_k^*}{\partial Q_i} \frac{\delta E_v}{\delta n} \phi_k d\mathbf{r} \tag{10a}$$

$$= -2\,\mathrm{Re} \sum_{k=1}^{N} \int \frac{\partial \phi_k^*}{\partial Q_i} \{-\nabla^2 + V_{\mathrm{eff}}[n(\mathbf{r});\mathbf{r}] - \epsilon_k\}\phi_k d\mathbf{r} \ . \tag{10b}$$

Here the normalization conditions,

$$\frac{\partial}{\partial Q_i} \int \phi_k(\mathbf{r})\phi_k^*(\mathbf{r}) d\mathbf{r} = 0 \ ,$$

have been added for convenience of the later discussion. Equation (10b) allows to calculate the $\mathbf{F}^V$ directly from the single-particle results. Furthermore, it allows a detailed analysis of its origin. We emphasize again that Eq. (10b) would be zero if Eq. (2) or Eqs. (7) to (9) had been solved exactly, i.e., if the calculated wave functions ϕ_k were *exact* eigenfunctions of $\{-\nabla^2 + V_{\mathrm{eff}}[n(\mathbf{r});\mathbf{r}]\}$. We will show below that this is never achieved in actual calculations. Equation (10b) has been discussed recently by Satoko[34] in the framework of the $X\alpha$ approximation and was applied by him to cluster calculations. Bendt and Zunger[35] studied this equation in the context of their suggestion to simultaneously relax the nuclei and the electrons.

We have so far stated that the force $\mathbf{F}^V$ should be considered because the charge density $n(\mathbf{r},\mathbf{Q})$ is usually not an exact solution of Eq. (2). One reason for this is that the consistency between the effective potential [Eq. (8)] and the charge density [Eq. (9)] after a finite number of self-consistent iterations might be excellent for many purposes, but is never exact. The potential in Eq. (10b) should be obtained from a charge density [Eq. (9)], which is constructed with the wave functions of the last iteration. However, if the calculation is not completely self-consistent, these wave functions are calculated for a different potential, say $V_{\mathrm{eff}}[\tilde{n}]$, related to the previous iteration. We therefore add and subtract this potential inside the brackets of Eq. (10b), and obtain

$$F_i^V[n] = -2\,\mathrm{Re} \sum_{k=1}^{N} \int \frac{\partial \phi_k^*}{\partial Q_i} \{-\nabla^2 + V_{\mathrm{eff}}[\tilde{n}] - \epsilon_k\}\phi_k d\mathbf{r} - 2\,\mathrm{Re} \sum_{k=1}^{N} \int \frac{\partial \phi_k^*}{\partial Q_i} \{V_{\mathrm{eff}}[n] - V_{\mathrm{eff}}[\tilde{n}]\}\phi_k d\mathbf{r} \ . \tag{11}$$

The first term contains the eigenvalue problem which one should have solved in the last iteration. Let us assume for a moment that this has been achieved without the need of any approximation. Then this term is zero and the force $\mathbf{F}^V$ is only due to the difference between the input potential $V_{\mathrm{eff}}[\tilde{n}]$, which was used for the last iteration, and the new (output) potential $V_{\mathrm{eff}}[n]$. Thus, in order to neglect the force $\mathbf{F}^V$ it is important to bring the calculation very close to self-consistency. Part of the problems in all-electron calculations arose from this difficulty. In this respect a frozen-core approximation provides an important advantage: It is well known that the influence of a little rearrangement of the highly localized core charge density on the potential can be quite significant. Nevertheless, such a rearrangement is usually unimportant for the chemical binding, which is determined by the valence electrons. Therefore the calculation gets more stable if the core electrons are kept fixed.[36] A further step toward a stabilization of self-consistent electronic structure calculations is provided by the pseudopotential approach, where the core is frozen and the valence charge density is smoothened in the region of the core. As a consequence, a high degree of self-consistency can be reached and the self-consistency part of the variational force [last term of Eq. (11)] can be made arbitrarily small.

We now come back to the first term on the right side of Eq. (11). This term includes the single-particle equations which should have been solved in the last but one iteration. However, this solution is usually not exact, because a finite (M dimensional) basis set is introduced. The wave functions are then expanded as

$$\phi_k(\mathbf{r},\mathbf{Q})=\sum_{l=1}^{M} C_{kl}(\mathbf{Q})\chi_l(\mathbf{r},\mathbf{Q}) \ , \tag{12}$$

and the first term in Eq. (11) reads

$$-2\,\mathrm{Re}\sum_{k=1}^{N}\sum_{l=1}^{M}\sum_{m=1}^{M} C_{kl}^{*}C_{km}\int \frac{\partial\chi_l^{*}(\mathbf{Q})}{\partial Q_i} \times\{-\nabla^2+V_{\mathrm{eff}}[\tilde{n}]-\epsilon_k\}\chi_m(\mathbf{Q})d\mathbf{r}=\sum_{l=1}^{M} F_{\mathrm{basis}}^{l} \ , \tag{13}$$

with

$$F_{\mathrm{basis}}^{l}=-2\,\mathrm{Re}\sum_{k=1}^{N}\sum_{m=1}^{M} C_{kl}^{*}C_{km}\int \frac{\partial\chi_l^{*}(\mathbf{Q})}{\partial Q_i} \times\{-\nabla^2+V_{\mathrm{eff}}[\tilde{n}]-\epsilon_k\}\chi_m(\mathbf{Q})d\mathbf{r} \ . \tag{14}$$

We note that the terms (13) and (14) are usually different from zero, because the matrix equation of Eq. (7), which is studied in an actual calculation, is

$$\sum_{m=1}^{M}\int \chi_l^{*}\{-\nabla^2+V_{\mathrm{eff}}[\tilde{n}]\}\chi_m d\mathbf{r}\, C_{km} -\epsilon_k\sum_{m=1}^{M} C_{km}\int \chi_l^{*}\chi_m d\mathbf{r}=0 \ .$$

But

$$\sum_{m=1}^{M}\int \frac{\partial\chi_l^{*}}{\partial Q_i}\{-\nabla^2+V_{\mathrm{eff}}[\tilde{n}]\}\chi_m d\mathbf{r}\, C_{km} -\epsilon_k\sum_{m=1}^{M} C_{km}\int \frac{\partial\chi_l^{*}}{\partial Q_i}\chi_m d\mathbf{r}$$

is usually different from zero.

The derivatives of the expansion coefficients C_{kl} do not appear in Eq. (14) because of the normalization condition. In Eqs. (13) and (14) the variational force $\mathbf{F}^{V}$ is decomposed into M contributions, where each is associated to one basis function χ_l. The corresponding equation in Hartree-Fock theory was recently discussed by Nakatsuji and co-workers.[37,38] They also showed that F_{basis}^{l} vanishes if the derivative $\partial\chi_l(\mathbf{Q})/Q_i$ lies entirely in the Hilbert space spanned by the basis. In other words, the part of the variational force associated to a given orbital can be eliminated just by including its derivative in the basis set. This scheme provides a systematic way for improving the basis set and to reduce the value of $\mathbf{F}^{V}$. In fact, it has been shown for molecular calculations that the variational force can be made arbitrarily small.[37]

At this point it may be of interest to apply our method to two types of basis sets which are particularly useful. First, Gaussian orbitals $x^iy^jz^ke^{-\alpha r^2}$ have the advantage that their derivatives are also Gaussian orbitals with the same decay.[39] Therefore the variational force due to an s function will be eliminated just by including the corresponding p Gaussian. In general, the force F_{basis}^{l}, where l is now the angular momentum quantum number, is canceled by the $l+1$ Gaussian orbitals. An even better basis set, appropriate for calculations of phonon modes,[40,41] surface structure (with the repeated slab method), and defects (with the supercell method), is plane waves. As they are independent of the positions of atoms, all forces F_{basis}^{l} vanish exactly. To be precise, the variational force vanishes if the Hilbert space spanned by the basis is independent of the atomic distortions (see also Ref. 39). Thus, the variational force would vanish if the plane-wave basis is defined by an energy cutoff, but it would not vanish if the basis set were defined by a fixed number of reciprocal-lattice vectors. It is remarkable that $\mathbf{F}^{V}$ can be reduced significantly or even eliminated even if the basis set is not complete.

The above discussion shows that the accuracy of an application of the Hellmann-Feynman theorem can be tested by improving the basis set in a systematic way. Another independent test is possible for localized systems like defects or molecules, by comparing the results of different charge states. Let us define the difference Δ_i as

$$\begin{aligned}\Delta_i(N\rightarrow N+m\,;\mathbf{Q}) &= F_i[n^{N+m}(\mathbf{r},\mathbf{Q})]-F_i[n^{N}(\mathbf{r},\mathbf{Q})]\\ &= -\frac{\partial}{\partial Q_i}\{E_v[n^{N+m}(\mathbf{r},\mathbf{Q})]-E_v[n^{N}(\mathbf{r},\mathbf{Q})]\} \ .\end{aligned} \tag{15}$$

The indices $N+m$ and N indicate the number of electrons. Following the concept of transition state[42,43] it follows that

$$\Delta_i(N\rightarrow N+m\,;\mathbf{Q})\simeq-\frac{m}{2}\frac{\partial}{\partial Q_i}\{\epsilon(\mathbf{Q},N+m)+\epsilon(\mathbf{Q},N)\} \tag{16a}$$

$$\simeq-m\frac{\partial}{\partial Q_i}\epsilon(\mathbf{Q},N+m/2) \ . \tag{16b}$$

Here $\epsilon(\mathbf{Q},n)$, $\epsilon(\mathbf{Q},N+m)$, $\epsilon(\mathbf{Q},N+m/2)$ are the highest occupied single-particle energies of the Kohn-Sham equation of the N- and $(N+m)$-particle systems and of the transition state. It is well known that the replacement of the total-energy difference in Eq. (15) by single-particle energies[42,43] is a very good approximation. Therefore Eqs.

(16a) and (16b) allow us to compare the results of the force calculation with those of a total-energy calculation. Below in Sec. III, we give an example of this test for the vacancy in silicon. We note that Eqs. (16a) and (16b) are in principle only valid if the total energy is a continuous function of the electron number, which holds for the local density and the $X\alpha$ approach.

We summarize that the variational force [Eq. (11)] can be made arbitrarily small if a pseudopotential approach is used and if an appropriate basis set is chosen. This means that the basis set should include all basis functions necessary for a total-energy calculation plus their derivatives with respect to the parameter of the distortion. This approach allows to neglect the force $\mathbf{F}^V$, i.e., to use the Hellmann-Feynman theorem with its great advantage in the interpretation of theoretical results. We also note that it can be more accurate to calculate the equilibrium geometry and force constants with this method than from a numerical derivative of a finite (and often quite small) number of total-energy points. Further, our method allows for a tractable test of the numerical accuracy (see for example the discussion of Fig. 1) whereas a corresponding test for total-energy calculations is significantly more complicated.

C. Application to point defects

Because of the localized nature of point defects, it is convenient to distinguish two groups of atoms. The atoms in the immediate neighborhood of the defect are labeled by an index A and all the other atoms by an index B. The configuration vector $\mathbf{Q}$ may then be written as $\mathbf{Q}=\{\mathbf{Q}_A,\mathbf{Q}_B\}$. The total elastic and electronic energy is

$$\Phi(\mathbf{Q}_A)=\tilde{\Phi}(\mathbf{Q}_A,\mathbf{Q}_B^0)-\Delta\Phi(\mathbf{Q}_A)\ , \tag{17}$$

with

$$\tilde{\Phi}(\mathbf{Q}_A,\mathbf{Q}_B^0)=E_{v(\mathbf{Q}_A,\mathbf{Q}_B^0)}[n(\mathbf{r},\mathbf{Q}_A,\mathbf{Q}_B^0)]+E^{\text{ion-ion}}(\mathbf{Q}_A,\mathbf{Q}_B^0)\ . \tag{18}$$

Here $E_{v(\mathbf{Q}_A,\mathbf{Q}_B^0)}[n(\mathbf{r},\mathbf{Q}_A,\mathbf{Q}_B^0)]$ is the total electronic energy of Eq. (1), calculated for different distortions of the A atoms, but keeping the other atoms at their perfect crystal positions $\mathbf{Q}_B^0$. $E^{\text{ion-ion}}$ is the electrostatic interaction of the ions. $\Delta\Phi(\mathbf{Q}_A)$ is the correction term due to the fact that $\tilde{\Phi}(\mathbf{Q}_A,\mathbf{Q}_B^0)$ was calculated with the constraint of keeping the B atoms fixed. Thus $\Delta\Phi(\mathbf{Q}_A)$ is the energy released when the B atoms are allowed to relax. Because of the variational principle this contribution is alway positive. It will lower the total energy of the system and soften its force constant. For a sufficiently large region A, this long-range correction is of purely elastic origin, it is a property of the unperturbed crystal and can therefore be calculated with a semiempirical method. On the other hand, the energy $\tilde{\Phi}(\mathbf{Q}_A,\mathbf{Q}_B^0)$ depends sensitively on the particular defect and should be calculated self-consistently.

Because we are concerned in this paper with calculations of the total-energy gradient, we rewrite Eq. (17) in terms of the force on the A atoms:

$$\begin{aligned}\mathbf{F}_A[n]&=-\frac{\partial\tilde{\Phi}(\mathbf{Q}_A,\mathbf{Q}_B^0)}{\partial\mathbf{Q}_A}+\frac{\partial}{\partial\mathbf{Q}_A}\Delta\Phi(\mathbf{Q}_A)\\&=\mathbf{F}_A[n]\,|_{\mathbf{Q}_B^0}+\frac{\partial}{\partial\mathbf{Q}_A}\Delta\Phi(\mathbf{Q}_A)\ .\end{aligned} \tag{19}$$

Here the force $\mathbf{F}_A[n]\,|_{\mathbf{Q}_B^0}$ is given by Eq. (6), which should be calculated under the constraint of unrelaxed B atoms. The prerequisite for a calculation of $\mathbf{F}_A[n]\,|_{\mathbf{Q}_B^0}$ is, of course, a method which allows an accurate calculation of the charge density $n(\mathbf{r},\mathbf{Q})$ of a macroscopic solid with a localized defect. This method is the self-consistent Green's-function method,[14–18] shortly summarized below.

Let $H^0[n^0]$ be the Hamiltonian in the Kohn-Sham equations of a perfect crystal [charge density $n^0(\mathbf{r})$]. It can be calculated using standard band-structure methods. $n(\mathbf{r},\mathbf{Q})$ is the, at first unknown, density of the crystal containing a defect. The defect-induced density change,

$$\Delta n(\mathbf{r},\mathbf{Q})=n(\mathbf{r},\mathbf{Q})-n^0(\mathbf{r}) \tag{20}$$

is then determined by

$$\begin{aligned}\Delta n(\mathbf{Q})=-\frac{2}{\pi}\text{Im}\int_{\text{occ}}&G^0(E)U[n^0,\Delta n]\\&\times\{1-G^0(E)U[n^0,\Delta n]\}^{-1}G^0(E)dE\ .\end{aligned} \tag{21}$$

The integral is over all occupied states. The perturbation $U[n^0,\Delta n]$ is defined as the difference between the Hamiltonians of the perfect and the perturbed crystal,

$$U[n,\Delta n]=H[n]-H^0[n^0]\ , \tag{22}$$

and the Green's function $G^0(E)$ is

$$G^0(E)=\lim_{\eta\to 0}\{E-H^0[n^0]+i\eta\}^{-1}\ . \tag{23}$$

The advantage of the Green's-function approach for defects is due to the fact that for such systems both $\Delta n(\mathbf{r},\mathbf{Q})$ and $U[n,\Delta n]$ are well localized in real space. Equations (21) and (22) can be solved self-consistently to a very high degree of accuracy if a localized basis is used.

As shown above, the Green's-function method splits the problem into the perfect crystal [charge density $n^0(\mathbf{r})$] and the defect-induced change [$\Delta n(\mathbf{r},\mathbf{Q})$]. When we introduce this splitting also in the calculation of the Hellmann-Feynman force, we get

$$F_i^{\text{HF}}[n]=F_i^{\text{HF}}[\Delta n]+F_i^{\text{HF}}[n^0]\ . \tag{24}$$

The first term on the right side of Eq. (24),

$$F_i^{\text{HF}}[\Delta n]=-\int\frac{\partial v(\mathbf{r},\mathbf{Q})}{\partial Q_i}\Delta n(\mathbf{r},\mathbf{Q})d\mathbf{r}\ , \tag{25}$$

is just the integral of a well-localized function. It can be computed by standard numerical procedures. The second term arises from the electron density of the perfect crystal:

$$F_i^{\text{HF}}[n^0]=-\int\frac{\partial v(\mathbf{r},\mathbf{Q})}{\partial Q_i}n^0(\mathbf{r})d\mathbf{r}\ . \tag{26}$$

Because the external potential can be easily obtained in analytic form and because the charge density $n^0(\mathbf{r})$ is periodic, this term is evaluated in reciprocal space. Details for a breathing distortion are given in Appendix B.

We emphasize that Eq. (26) does not have its counterpart variational force. Because of the splitting defined by Eq. (20), $n^0(\mathbf{r})$ is independent of the atomic rearrangement. Thus only $F^{\mathrm{HF}}[\Delta n]$ is sensitive to inaccuracies in the charge density. Following the ideas of the preceding paragraph it is then straightforward to estimate and to reduce the inaccuracies by systematically improving the basis set used for solving Eqs. (21) and (22).

III. VACANCY IN SILICON

The above described method has already been applied to study the breathing distortion at Ga-site single donors in GaP,[3] the As antisite in GaAs,[4] and chalcogens in Si.[5] In this section we discuss its application to the vacancy in silicon. We use the self-consistent Green's-function method in the formulation described in Ref. 20. It is well known that the undistorted Si vacancy has a threefold degenerate (without spin) level in the band gap (see for example Refs. 14 and 15). The corresponding wave functions are built from those sp^3 hybrids of the four neighbor atoms, which point toward the vacant site. In p-doped material, the level is empty and the vacancy is in its doubly positive charge state, V^{2+}. Only a breathing distortion is expected for this charge state.[44] If the Fermi energy moves up in the band gap, the next possible charge states are the singly positive and the neutral state. Here the deep level is filled with one and two electrons, respectively. As the level is orbitally degenerate and only partially filled, the system will reduce its energy by going to a lower symmetry, which lifts the degeneracy of the level (Jahn-Teller effect). This Jahn-Teller distortion was studied by Baraff, Kane, and Schlüter[2] by combining a self-consistent Green's-function calculation of the single-particle energies with a semiempirical valence-force model to describe the elastic restoring forces of the crystal. They found that the first donor level $\epsilon(0/+)$ lies *below* the second donor level $\epsilon(+/2+)$, due to different lattice distortions of the different charge states. Thus, the silicon vacancy forms a "negative U" system and the V^+ charge state is not stable. Independently of this symmetry lowering distortion, a breathing distortion exists. This breathing distortion was not calculated from the valence-force model. More recently, DeLeo, Fowler, and Watkins[6] have shown that models which are based on a valence-force treatment can give completely unreasonable results for the breathing distortion. It is not clear to us if this conclusion is really a failure of the valence-force model, or if it arose because of additional approximations.

It might be argued that breathing distortions at defects can be estimated from the covalent radii of the atoms. However, it is well known that such arguments can be quite misleading for predicting the distortion: Such an approach should take into account that the "radius of an atom" depends on the type of chemical bonds that are formed with the adjacent atoms. But for deep-level defects these bonds can be significantly different from those known from perfect crystals or molecules. In turn, it appears that breathing distortions are often even less understood than Jahn-Teller driven distortions. Below we discuss only the breathing of the Si vacancy and not its Jahn-Teller distortions. In subsection A we discuss the convergence properties of the force calculation. Subsection B deals with the discussion of the results, with the comparison to experimental data and to semiempirical calculations.

A. Convergence properties of the Hellmann-Feynman force

For silicon we use the ionic pseudopotential of Schlüter *et al.*[45] The exchange-correlation potential is treated in the $X\alpha$ form with $\alpha=0.8$. This potential was used by Ihm and Cohen[46] to study the equilibrium properties of bulk Si and of the unreconstructed (111) surface. The equilibrium lattice constant and the crystal energy were in good agreement with experiment. However, the calculated bulk modulus was clearly overly high. Nevertheless, the calculated equilibrium relaxation for the Si(111) surface was in excellent agreement with measurements.

In Sec. II B we discussed the problems related to a Hellmann-Feynman study. We noted that the accuracy of the force calculation should be tested by improving the basis set in a systematic way. We therefore performed self-consistent calculations with four different basis sets. Each set contains s, p, d, and f_0 functions at the vacant site. The sets differ with respect to the angular momentum functions at the four neighbor atoms: set 1 has only s functions, set 2 has s and p functions, set 3 has s, p, and d functions and set 4 has s, p, d, and f_0 functions. For each angular momentum three Gaussian radial functions are used $(r^l e^{-\alpha_i r^2})$ with the decays $\alpha_1=0.2$ a.u.$^{-2}$, $\alpha_2=0.4$ a.u.$^{-2}$, and $\alpha_3=0.6$ a.u.$^{-2}$.

Figure 1 shows the results of the force calculations with these four different basis sets. Only the four nearest neighbors of the vacancy are moved. The long-range distortion [compare Eq. (19)] will be included later. We note that each calculation is carried to self-consistency. This implies that the difference between different calculations arises from two sources: In part the difference is due to the variational force $\mathbf{F}^V$ and in part it is due to the difference in the variational flexibility. The latter aspect would also affect a total-energy calculation. Thus Fig. 1 represents a *complete* test of the accuracy of the calculation. We see that at the undistorted geometry the basis set 2 already gives a sufficiently accurate result. However, in order to predict the amplitude of the distortion with an accuracy[47] of ±0.2% of the perfect-crystal Si—Si bond length, one needs to include at least d orbitals at the neighbors. Figure 1 thus also indicates the possible difficulty with this approach. For systems with larger distortions the amount of the required basis functions might increase significantly. Then it might be preferable to calculate the variational force [Eq. (11)] and to include it in the calculations explicitly. Figure 1 also displays the single particle eigenvalues of the four calculations. Clearly, the results of the smallest basis set (only s orbitals at neighbors) are worse than those of the other calculations. However, even this calculation differs by less than ±0.1 eV from the better ones.

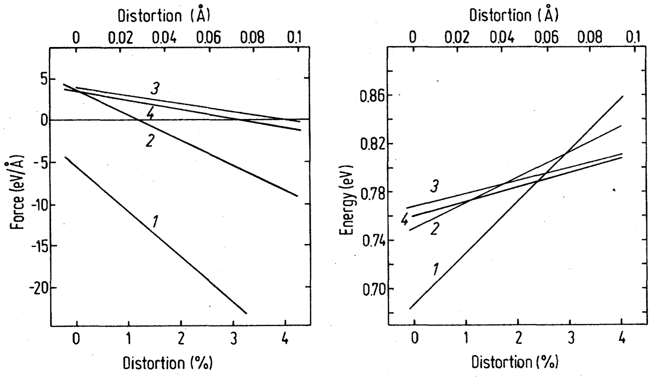

FIG. 1. Convergence test for the calculation of the breathing distortion of the neutral vacancy in Si moving only the four nearest neighbors. Zero distortion refers to the geometry of the perfect Si lattice. The distortion is defined positive if the nearest neighbors of the vacancy move away from the vacant site. Four different basis sets are used. The most complete one is 4 (see text). Left: Calculated force on the four nearest neighbors. Right: Single particle energy of the t_2 level in the gap; the zero of energy is at the top of the valence band.

We now turn to the other test of the force calculation, i.e., to the comparison of the force differences of different charge states to eigenvalue derivatives [compare Eqs. (16)]. As noted above in Sec. II B, this comparison reflects the differences between the Hellmann-Feynman force and the derivative of the total energy. Table I displays the results. The numerical accuracy of these calculations is about ±0.1 eV/Å. Thus it is clear that the basis set 3, which contains *s*, *p*, and *d* functions at the neighbors is already sufficiently complete in order to neglect the errors due to Eq. (11).

B. Results and comparison to other calculations and to experiment

In this section we analyze our results and we compare them to those of other calculations. We will now also include the long-range (elastic) distortions [compare Eq. (17)], which are calculated from

$$\Delta\Phi(\mathbf{Q}_A) = -\Phi^D(\mathbf{Q}_A) + \tilde{\Phi}^D(\mathbf{Q}_A,\mathbf{Q}_B^0) \ . \tag{27}$$

Here $\Phi^D(\mathbf{Q}_A)$ is the deformation energy of a vacancy in a fully relaxed lattice. It is calculated using the semiempirical model and the parameters of Baraff, Kane, and Schlüter[2] (see also Ref. 22). The atoms of region A are the four nearest neighbors of the vacancy. $\tilde{\Phi}^D(\mathbf{Q}_A,\mathbf{Q}_B^0)$ is calculated in the same model, but freezing the B atoms into their undistorted crystal positions. This approach is particularly suited for covalent systems, like Si, where the elastic properties are well described using only short-range interatomic forces. We emphasize that the function $\Delta\Phi(\mathbf{Q}_A)$ does not depend on the particular defect, as it only accounts for the (elastic) relaxation of more distant atoms. The inclusion of this term softens the force constant of the nearest neighbors and it also affects their equilibrium geometry.

TABLE I. Convergence test of the force calculation for the Si vacancy for four different basis sets (see text). The difference of the energy gradient for the neutral and the doubly positive charge state as directly derived from the force calculation $[\Delta^{\text{force}}(0\rightarrow 2+) = F(2+) - F(0)]$ is compared to the same quantity as obtained from the numerical derivative of the energy $(\Delta^{\text{energy}}(0\rightarrow 2+) = +(\partial/\partial Q)[\epsilon(2+)+\epsilon(0)])$. The distortion is taken as +2%.

Basis	Δ^{force} (eV/Å)	Δ^{energy} (eV/Å)	Difference (eV/Å)
1 (s)	3.73	2.99	+0.74
2 (s,p)	1.39	1.71	−0.32
3 (s,p,d)	1.01	0.95	+0.06
4 (s,p,d,f_0)	1.04	0.98	+0.06

We start with the doubly positive charge state of the vacancy (V^{2+}), which has tetrahedral symmetry.[2,44] Figure 2 shows the calculated force on the nearest neighbors: These atoms move away from the vacant site by 0.15 Å, thus increasing the distance from the center by 6.5% compared to the perfect-crystal Si-Si distance. Because we are dealing with a breathing distortion, we omit in the following the vector notation. The vector $\mathbf{Q}_A$ which describes the positions of the four neighbors of the vacancy, is replaced by the distance qR_{Si} between the center and its neighbors. R_{Si} is the perfect-crystal Si—Si bond length. In the distortion range of interest the force is found to be approximately linear:

$$F(q) = -K(qR_{\text{Si}} - q^* R_{\text{Si}}) \ . \tag{28}$$

Here q^* is the equilibrium geometry. The force constant K is calculated as 29 eV/Å^2. This value depends sensitively on the accuracy of the calculation. The numerical accuracy[47] of K is estimated as ±12 eV/Å^2. It is an im-

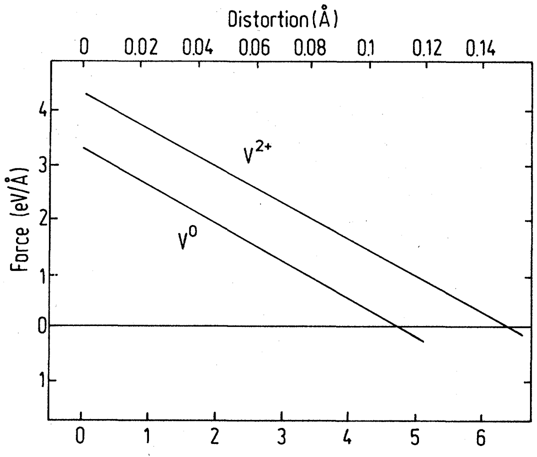

FIG. 2. Force on the four nearest neighbors of the Si vacancy as a function of a breathing distortion for two different charge states (neutral: V^0; doubly positive: V^{2+}). The long-range elastic distortions are included via a semiempirical model (see text). Zero distortion refers to the geometry of the perfect Si lattice. The distortion is defined as positive if the nearest neighbors of the vacancy move away from the vacant site.

portant advantage of the force method that a test as in Fig. 1 is tractable and an estimate of the numerical accuracy is possible. A corresponding estimate of the force-constant accuracy from a total-energy calculation is significantly more costly and complicated.

For comparison, Fig. 2 also shows the results of the breathing distortion of the neutral charge state of the vacancy. We see that the force constant is nearly unchanged. However, for V^0, the nearest neighbors move less than for V^{2+}, i.e., by 0.11 Å (i.e., + 5% of the perfect crystal Si—Si bond length).

These results can be understood as follows. For the doubly positive charge state the vacancy-induced deep level is empty. The direct interaction between the four atoms around the vacancy is weak. Because of the absence of the central atom for each of the neighbors, the symmetry is broken, and their electronic structure is no longer required to form sp^3 bonds. In fact, the geometry might be expected to favor sp^2 bonds with the next shell of atoms. As a consequence, each of the four neighbors moves away from the vacant site, toward the center of the three atoms of the second shell to strengthen its bonds with them. However, a perfect sp^2 bond is hard to realize, because it would require that the atoms move by 0.8 Å, which is by far too large, as it would induce a significant long-range distortion. Nevertheless, it seems that the tendency to form a more sp^2-type bonding drives the atoms away from the vacant site, giving rise to an outward distortion of 0.15 Å and 0.11 Å, respectively. The comparison of the results for the two charge states shows that the force of the neutral-charge state is higher than that of the doubly positive one. This comes about because the neutral state has two electrons in the t_2 dangling bonds. Because the center of gravity of the electronic charge of these dangling bonds is inside the cage of the four Si neighbors, the neutral-charge state has more negative charge in this cage than the doubly positive charge state. As a consequence, this higher negative charge pulls the nearest ions (positive charges) closer to the center. We note, however, that this effect is not very dramatic, and that the neutral charge state also shows a slight outward distortion.

The above results show that (close to the equilibrium geometry) the force for the neutral charge state is smaller than that for the positive one. According to Eq. (16) this just reflects the fact that the deep-level wave function of the vacancy is nonbonding in character and that its orbital energy increases with an outward breathing distortion. Therefore we can qualitatively expect the same behavior for all acceptors (bonding deep-level wave function) and the reverse for deep donors (antibonding deep-level wave function) (see also Ref. 5).

We now compare our results to those of other calculations. The slope of the single particle energies is calculated as 0.48 eV/Å. This quantity was previously calculated by Jaros *et al.*,[21] Lipari *et al.*,[19] and Baraff *et al.*[2] All these authors attain nearly the same result. Baraff *et al.*[2] have also calculated the force constants of the vacancy distortions from a semiempirical valence-force model. For the breathing distortion, they obtained $K=7.5$ eV/Å^2. This result is significantly smaller (i.e., by about a factor of 4) than our value. In fact, using only the semiempirical model, i.e., $\Phi^D(\mathbf{Q}_A)$ of Eq. (27), we obtain the same number as Baraff *et al.* In such a model the interaction between the four neighbors of the vacancy is assumed to be zero. However, this assumption is not confirmed by the self-consistent calculations: In the case of the vacancy there is an a_1 resonance at the top of the valence band which is due to a *bonding* combination of sp^3 dangling orbitals. This resonance is filled with two electrons and thus implies a weak attraction between the four neighbors and therefore an increase of the breathing-mode force constant if compared to a model which neglects this interaction. In Table II we compare the results of Baraff *et al.* to those of a similar semiempirical calculation of Larkins and Stoneham[1] and to recent experimental estimates given by DeLeo, Fowler, and Watkins.[4] We see that DeLeo *et al.* estimated values which are significantly higher than those derived from the valence force treatments. In fact, these experimental estimates lie within the range of accuracy of our result. Furthermore, we note that the calculated direction and the amount of the calculated distortion of the four neighbor atoms of the vacancy are consistent with the experimental results of the unreconstructed Si(111) surface.[48] Such a comparison is meaningful, because locally the Si vacancy looks like the Si-vacuum interface. The only difference is due to the fact that the dangling orbitals of the vacancy can interact, which gives rise to the above mentioned increase in the force constant. Neither the direction nor the amount of the breathing distortion could be determined by Baraff *et al.* from the valence-force model. Therefore these authors estimated the breathing distortion of the neutral vacancy from the analogy to the unreconstructed (impurity-stabilized) Si(111) surface.[48] They obtained an outward distortion of 0.1 Å for the neutral vacancy and of 0.23 Å for the doubly positive-charge state. Their value for the neutral vacancy is practically equivalent to our number. However, as a consequence of their small force constant, their value for the double positive vacancy is somewhat higher than our result. The important point is the energy gain due to the breathing relaxation occurring if one goes from the V^0 to the V^{2+} charge state. From Fig. 2 we derive that this energy is quite small, i.e., about 0.03 eV. Therefore we conclude that our calculations roughly confirm the breathing distortion which was used by Baraff,

TABLE II. Comparison of the breathing mode force constants of the Si vacancy. The results of Baraff, Kane, and Schlüter (Ref. 2) and of Larkins and Stoneham (Ref. 1) are obtained from a semiempirical valence-force model. The experimental estimates are from DeLeo, Fowler, and Watkins (Ref. 6). They are derived from an analogy to the vacancy in diamond using two different models. (To be consistent with our definition of the force constants, the values given in Ref. 6 simply had to be multiplied by 4.)

	K (eV/Å^2)
This work	29±12
Baraff *et al.*	7.5
Larkins and Stoneham	∼4
Experimental estimates	20.4,27.2

Kane, and Schlüter for their suggestion and analysis of the negative-U properties of the Si vacancy.

IV. SUMMARY

We discussed a parameter-free method for calculating the gradient of the total energy and lattice distortions at defects in semiconductors. The approach is based on the self-consistent Green's-function method,[14,15,20] which allows a highly accurate calculation of the electronic charge density at a defect. From this charge density we calculated the gradient of the total energy using the Hellmann-Feynman theorem. We have considered that the Hellmann-Feynman force is linear in little inaccuracies in the electronic charge density and therefore usually not very accurate. The origin of this problem is analyzed and it is shown how it can be overcome by taking two conditions into account, i.e., (i) the pseudopotential approach and (ii) the inclusion of basis set derivatives. It is shown that then the Hellmann-Feynman force gives results at the same level of accuracy as a corresponding total-energy calculation. Two tests of the accuracy are proposed and they are demonstrated for the breathing distortions of the vacancy in silicon. This investigation shows that the proposed Green's-function force method works and that a test of the numerical accuracy[47] is tractable.

Furthermore, the results for the Si vacancy are analyzed and compared to previous (semiempirical) calculations as well as to available experimental estimates. We find that the nearest neighbors of the vacancy move away from the center by about 0.11 Å for the neutral charge state and by 0.15 Å for the double positive charge state. The direction and the amount of this calculated breathing distortion agree with those experimentally known for a somewhat similar system, namely the relaxation of the unreconstructed Si(111) surface.[48] The vacancy force constant is calculated as $K=29\pm12$ eV/Å^2 which is significantly different to that of the semiempirical methods, but it is consistent with the experimental estimates by DeLeo, Fowler, and Watkins.[6]

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APPENDIX A: ION-ION INTERACTION

This appendix deals with the evaluation of the ion-ion force for a defect of tetrahedral symmetry and a breathing distortion. We assume a frozen-core approximation where the core is sufficiently localized such that there is no core-core overlap. The ion-ion interaction is then purely Coulombic, which implies that ions can be treated as point charges. Taking the origin of the coordinate system at the center of the defect, the positions of the four nearest-neighbor atoms at the *undistorted* geometry are $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$, $\mathbf{R}_4$. For a breathing distortion their positions are $q\mathbf{R}_1$, $q\mathbf{R}_2$, $q\mathbf{R}_3$, $q\mathbf{R}_4$. The charges of the perfect-crystal ions at the center and at the four nearest neighbors are Z_k, with $k=0,1,2,3,4$. The ionic charge of the impurity is Z_{imp} which for a vacancy is zero. The ion-ion interaction is then

$$\begin{aligned}F^{\text{ion}}=&-\sum_{\mathbf{G}}\frac{4\pi}{G^2}e^{-G^2/4g^2}(1/V_c)\sum_l Z_l e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_l}\sum_{k=1}^{4}Z_k i\mathbf{G}\cdot\mathbf{R}_k e^{iq\mathbf{G}\cdot\mathbf{R}_k}\\&-g^2\sum_{k=1}^{4}\sum_{\substack{i=1\\(i\neq k)}}^{4}Z_iZ_kp(g\,|q\mathbf{R}_k-\mathbf{R}_i|)\frac{qR_k^2-\mathbf{R}_1\cdot\mathbf{R}_k}{|q\mathbf{R}_k-\mathbf{R}_i|}+g^3\sum_{k=1}^{4}Z_k^2h(g\,|q-1|\,|\mathbf{R}_k|)(q-1)R_k^2\\&+\frac{1}{q^2}\left[\frac{1}{2}\sum_{k=1}^{4}\sum_{\substack{k'=1\\(k\neq k')}}^{4}\frac{Z_kZ_{k'}}{|\mathbf{R}_k-\mathbf{R}_{k'}|}+\sum_{k=1}^{4}\frac{(Z_{\text{imp}}-Z_0)Z_k}{|\mathbf{R}_k|}\right]-\sum_{k=1}^{4}\sum_{\substack{k'=1\\(k\neq k')}}^{4}Z_kZ_{k'}\mathbf{R}_k\cdot\frac{q\mathbf{R}_k-\mathbf{R}_{k'}}{|q\mathbf{R}_k-\mathbf{R}_{k'}|^3}\;.\end{aligned}\tag{A1}$$

In this expression, $\boldsymbol{\tau}_l$ is the position of the lth atom in the unit cell and the sum over l runs over all atoms within one cell. V_c is the unit cell volume, g is the Ewald G-space cutoff, and the functions p and h are

$$p(x)=-\frac{2}{\sqrt{\pi}}\frac{e^{-x^2}}{x}\left[1+\frac{\sqrt{\pi}e^{x^2}\text{erf}(x)}{2x}\right],\tag{A2}$$

and

$$h(x)=-\frac{2}{\sqrt{\pi}x^3}[xe^{-x^2}-(\sqrt{\pi}/2)\text{erf}(x)]\;.\tag{A3}$$

The $\mathbf{G}=\mathbf{0}$ contribution of this expression is divergent due to the long-range nature of the Coulomb interaction. However, this particular term, which reads

$$F^{\text{ion}}_{\mathbf{G}=0}=-\frac{1}{V_c}\left[\sum_l Z_l\right]\left[\sum_{k=1}^{4}i\mathbf{G}\cdot\mathbf{R}_k\frac{4\pi Z_k}{G^2}\right]_{\mathbf{G}=0},\tag{A4}$$

is exactly canceled out by a corresponding divergence in the electronic contribution to the force (see Appendix B), because of the charge neutrality of the perfect crystal.

APPENDIX B: FORCE $\mathbf{F}^{\text{HF}}[n^0]$

Here we examine the contribution of the perfect-crystal charge density to the total force. Again we discuss the breathing distortion of a tetrahedral defect. The notations are the same as in Appendix A. According to Eq. (26), the perfect-crystal charge density gives rise to the contribution

$$F^{\mathrm{HF}}[n^0] = -\int \frac{\partial v(\mathbf{r},q)}{\partial q} n^0(\mathbf{r}) d\mathbf{r} \ . \tag{B1}$$

Here $v(\mathbf{r},q)$ is the sum of the ionic pseudopotentials of the four neighbors of the defect, i.e.,

$$v(\mathbf{r},q) = \sum_{k=1}^{4} v_k(\mathbf{r} - q\mathbf{R}_k) \ . \tag{B2}$$

The use of a Fourier expansion of the perfect-crystal electron density in this equation immediately leads to the following reciprocal space summation:

$$F^{\mathrm{HF}}[n^0] = -\sum_{\mathbf{G}} C_{\mathbf{G}} \sum_{k=1}^{4} S_{\mathbf{G}}^{k} V_{\mathbf{G}}^{k} \ , \tag{B3}$$

with

$$S_{\mathbf{G}}^{k} = i\mathbf{G}\cdot\mathbf{R}_k e^{i\mathbf{G}\cdot\mathbf{R}_k} \tag{B4}$$

and

$$V_{\mathbf{G}}^{k} = \int v_k(\mathbf{r}) e^{i\mathbf{G}\cdot\mathbf{r}} d\mathbf{r} \ . \tag{B5}$$

For a local pseudopotential given in the analytic form,

$$v_x(\mathbf{r}) = -\frac{Z_k}{r}\mathrm{erf}(\sqrt{\beta_k}\, r) + \sum_{j=1}^{s} a_j^k e^{-\alpha_j^k r^2} \ , \tag{B6}$$

the ionic potential is spherically symmetric, and its Fourier transform only depends on the modulus of **G**:

$$V_{\mathbf{G}}^{k} = -\frac{4\pi Z_k}{G^2} e^{-G^2/4\beta_k} + \sum_{j=1}^{s} a_j^k \left[\frac{\pi}{\alpha_j^k} \right]^{3/2} e^{-G^2/4\alpha_j^k} \ . \tag{B7}$$

The expression (B3) contains a diverging part which reads

$$F_{\mathbf{G}=0}^{\mathrm{HF}}[n^0] = \left[C_{\mathbf{G}} \sum_{k=1}^{4} i\mathbf{G}\cdot\mathbf{R}_k \frac{4\pi Z_k}{G^2} \right]_{\mathbf{G}=0} \ . \tag{B8}$$

$C_{\mathbf{G}=0}$ is the mean particle density in the crystal and thus is given by

$$C_{\mathbf{G}=0} = \frac{1}{V_c} \sum_{l} Z_l \ , \tag{B9}$$

where the sum extends over all atoms in the unit cell (volume V_c). It is thus obvious that Eqs. (B9) and (A4) cancel each other.

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