

Pressure, relaxation volume, and elastic interactions in charged simulation cells

Fabien Bruneval

CEA, DEN, Service de Recherches de Métallurgie Physique, F-91191 Gif-sur-Yvette, France

Céline Varvenne

Laboratory for Multiscale Mechanics Modeling, EPFL, CH-1015 Lausanne, Switzerland

Jean-Paul Crocombette and Emmanuel Clouet

CEA, DEN, Service de Recherches de Métallurgie Physique, F-91191 Gif-sur-Yvette, France

(Received 18 November 2014; published 21 January 2015)

The *ab initio* calculation of charged supercells within density-functional theory is a necessary step to access several important properties of matter. The relaxation volume of charged point defects or the partial molar volume of ions in solution are two such examples. However, the total energy and therefore the pressure of charged systems is not uniquely defined when periodic boundary conditions are employed. This problem is tightly related to the origin of the electrostatic potential in periodic systems. This effect can be easily observed by modifying the electrostatic convention or modifying the local ionic potential details. We propose an approach to uniquely define the pressures in charged supercells with the use of the absolute deformation potentials. Only with such a definition could the *ab initio* calculations provide meaningful values for the relaxation volumes and for the elastic interactions for charged defects in semiconductors or ions in solution. The proposed scheme allows one to calculate sensible data even when charge neutrality is not enforced, thus going beyond the classical force-field-based approaches.

DOI: [10.1103/PhysRevB.91.024107](https://doi.org/10.1103/PhysRevB.91.024107)

PACS number(s): 71.15.Mb, 61.72.Bb, 61.20.Ja

I. INTRODUCTION

The volume variation of a solid or a liquid upon the addition of a foreign specie is an important measure for several experimental situations. In material physics, the addition of defects (vacancies, self-interstitials, impurities) modifies the macroscopic volume of the sample. This situation is particularly relevant for the swelling of materials under irradiation [1], for the elastic interaction between impurities and dislocations [2–5], or for stress induced by implantation in thin films [6]. This is quantified by the relaxation volume of a defect. In the physics of liquids, the addition of ions in solution is to change the overall volume of the sample. Think of the change of density of salted water compared to fresh water [7]. In the context of liquids, this property is expressed in terms of partial molar volume, which is precisely a relaxation volume expressed in moles.

Some of the cited examples have a nonzero electric charge, such as the point defects in insulating or semiconducting solids or as ions in solution. Calculating the pressure, the relaxation volume, or the elastic energies for charged species would be a significant outcome of *ab initio* calculations.

Condensed matter systems, be they a crystal, a glass, or a liquid, are most generally handled with periodic boundary conditions, which allow one to get rid of the surface effects. Unfortunately, the combination of periodic boundary conditions and of nonzero charges poses a wide variety of problems.

First of all, the simulation cell needs to be maintained charge neutral in order to obtain a finite value for the total energy. This is generally enforced by the use of an homogeneous compensating background. For instance, this background is readily enforced in the reciprocal space term of the Ewald summation technique [8,9]. But even with a charge-neutralized

simulation cell, the electrostatic potential is only defined up to a constant. The constant is intrinsic to the long-range nature of the Coulomb interaction. The Ewald summation trick, for instance, transforms the mathematically conditionally convergent sum of Coulomb interactions into two absolutely convergent sums up to a constant. The impossibility to define an absolute electrostatic potential is not without consequences when we want to calculate the formation energy of a charged defect [10]. The formation energy as calculated from *ab initio* codes needs to be corrected with two terms: the so-called electrostatic energy and the potential alignment corrections [11–14].

As long as formation energies are concerned, the electrostatic energy correction is in general large and converges very slowly as $\Omega^{-1/3}$, where Ω is the supercell volume, whereas the potential alignment correction is small and converges quickly as Ω^{-1} . In a previous paper [15], we have demonstrated the surprising statement that when evaluating the relaxation volume of a charged defect, the potential alignment indeed prevails over the other correction. Furthermore, it yields a correction that converges to a finite value with the supercell size. In other words, the uncorrected relaxation volume does converge, but to a wrong value. The recent literature [14,16] has however shown that the potential alignment prescription we adopted in our previous study [15] was unfortunately not adequate. Some of our earlier conclusions need to be revised.

In the present article, we use the latest understanding in charge corrections [14,16] in order to explore the interplay between the electrostatic potential definition and the calculated pressure, relaxation volume, and elastic interaction energies in a charged simulation cell. We will demonstrate that these three mentioned physical properties can only be properly defined through the connection with a model for the variation

of the electrostatic potential as a function of the volume. This problem is equivalent to obtaining reliable absolute deformation potentials (ADPs), quantities that measure the variation of the absolute position of the electron energies with respect to the volume. The ADP can be calculated either with the simplistic model-solid theory introduced by van de Walle [17] in the 1980s or the more accurate strained superlattice calculations [18–20]. Another way to circumvent the problem would be to limit ourselves to groups of defects whose total charge would vanish, such as Frenkel or Schottky pairs [21]. However, this would leave many defect charge states not properly described.

The article is organized as follows. Section II is an introduction to the problem of the definition of pressure with the example of the free carriers in semiconductors. In Sec. III, we describe the general framework for the definition of absolute pressures. Section IV provides several applications to deep and shallow defects, gives an example for the connection with elasticity models, and sketches the consequences for ion solvation. Finally Sec. V gives some concluding remarks. Atomic units will be used throughout the text.

II. FREE CARRIER INDUCED PRESSURE IN SEMICONDUCTORS

In this section, we propose to examine a simple case in order to provide the first insights into the problem of defining the pressure in charged systems. Let us consider the calculation of the induced pressure by a free carrier in a semiconductor, that is, a hole in the valence band or an extra electron in the conduction band.

To approach this situation within a periodic *ab initio* framework, we propose to add or subtract a tiny part q of an electron to the system. In periodic calculations, which use the reciprocal space technique, the additional charge is automatically compensated by an opposite background density $-q/\Omega$, where Ω is the volume of the cell. The image charge error is expected to be vanishing for two independent reasons: (i) the leading monopole correction [11] scales as q^2 and therefore can be made very small when q is a percent of a charge; (ii) the small additional charge is mostly carried by the top valence wave functions or the bottom conduction wave functions that are delocalized all over the cell, which makes the charge correction vanishing.

An evaluation of the induced pressure in a charged unit cell of silicon is proposed in Fig. 1, as obtained from three different plane-wave codes ABINIT [22], QUANTUM ESPRESSO [23], and VASP [24]. Surprisingly, even though we employed the exact same convergence parameters and pseudopotentials for ABINIT and QUANTUM ESPRESSO the two results noticeably differ. The projector augmented wave [25,26] (PAW) results from VASP are also very different. This puzzling statement calls for more investigations.

The pressure of a system with charge q is defined as

$$P(q) = -\frac{\partial E(q)}{\partial \Omega}, \quad (1)$$

where $E(q)$ is the total energy of the system with charge q . As the values of q used here are relatively small, a first-order Taylor expansion of the total energy with respect to the charge

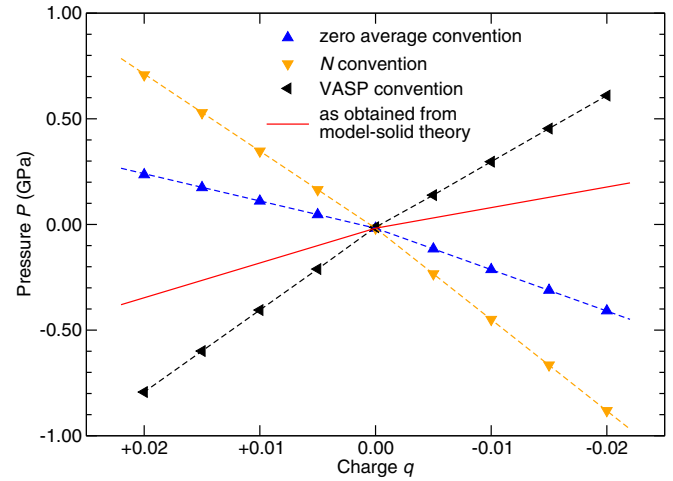


FIG. 1. (Color online) Pressure induced in a charged unit cell of silicon as obtained from different calculation conventions. ABINIT uses the zero average potential convention (blue up triangle symbols), QUANTUM ESPRESSO uses an other convention, named N convention in our previous study [16], (orange, down triangle symbols), VASP uses a zero average convention for the smooth potential (black, left triangle symbols). Absolute pressures as obtained from model-solid theory is shown with the red line.

is legitimate:

$$P(q) = -\frac{\partial E(0)}{\partial \Omega} - q \frac{\partial}{\partial \Omega} \left(\frac{\partial E}{\partial q} \right). \quad (2)$$

The first term in the right-hand side is just the pressure in the charge neutral cell $P(0)$, while the second term can be worked out with Janak's theorem [27].

Indeed, the charge $q = Z - N$ in the cell can be expressed as a function of the number of electrons N and of the number of positive charges from nuclei Z . Then, Janak's theorem implies that¹

$$\left. \frac{\partial E}{\partial N} \right|_{N^-} = \epsilon_v \quad (3)$$

$$\left. \frac{\partial E}{\partial N} \right|_{N^+} = \epsilon_c, \quad (4)$$

where ϵ_v stands for the top valence Kohn-Sham orbital energy and ϵ_c is the bottom conduction Kohn-Sham orbital energy. Note that this expression of the Janak's theorem assumes an exchange-correlation potential with no discontinuity [28] as it is the case of most of the practical approximations.

Finally, introducing these expressions into Eq. (2) yields

$$P(q) = P(0) + \frac{q}{\Omega} \frac{\partial \epsilon_v}{\partial \ln \Omega} \quad \text{when } q > 0 \quad (5)$$

$$P(q) = P(0) + \frac{q}{\Omega} \frac{\partial \epsilon_c}{\partial \ln \Omega} \quad \text{when } q < 0. \quad (6)$$

¹The Janak's theorem was originally derived for finite systems, but it can immediately be transposed to the infinite case, provided that the state index i is thought as a combined index on band and \mathbf{k} point. No assumption of locality nor of finite extension is actually needed in the derivation.

In these equations, one recognizes the so-called deformation potential of state i

$$a_i = \frac{\partial \epsilon_i}{\partial \ln \Omega}. \quad (7)$$

Owing to the impossibility of uniquely defining the electrostatic potential within periodic boundary condition, the origin of the energy scales for the eigenvalues is arbitrary. Its variation with respect to the volume is also arbitrary. As a consequence, the deformation potentials introduced in Eq. (7) are convention dependent. That is precisely why the different periodic codes have yielded different values for $P(q)$ in Fig. 1. The different conventions used in ABINIT, QUANTUM ESPRESSO, and VASP are studied in detail in Ref. [16]. This latter work is simply used to understand the connection between the different codes, but does not induce any correction.

In the natural band offset approach, authors have been able to define absolute values for the potential, eigenvalues, and as a consequence for the deformation potentials [17]. These are the so-called absolute deformation potential (ADP), labeled \bar{a}_i . The method for calculating the absolute quantities will be detailed later on in Secs. III C and III D. In the following, we will note with a bar all the physical quantities that are anchored to absolute references.

Knowing the ADP for a semiconductor hence provides well-defined expressions for the pressure whatever the charge q :

$$\bar{P}(q) = P(0) + \frac{q}{\Omega} \bar{a}_v \quad \text{when } q > 0 \quad (8)$$

$$\bar{P}(q) = P(0) + \frac{q}{\Omega} \bar{a}_c \quad \text{when } q < 0. \quad (9)$$

Note that $P(0)$ does not need a bar symbol, since the charge neutral pressure is (fortunately) a well-defined quantity.

We have calculated $\bar{a}_v = 2.37$ eV using the model-solid theory of van de Walle [17] (detailed in Sec. III C) for silicon, which agrees very well with the value 2.38 eV calculated in Ref. [20] with the strained superlattice technique (detailed in Sec. III D). We obtained $\bar{a}_c = 4.03$ eV under the same conditions. With these absolute values, we can now obtain the absolute pressure for charged silicon unit cells as shown in Fig. 1. Owing to the similarity of the numerical ADP values, the result using the strained superlattice evaluation would be indistinguishable from the model-solid lines.

A consequence of nonvanishing ADP in semiconductors is the finite value for the relaxation volume $\Delta\Omega$ induced by a free electron in conduction or a free hole in valence. If we limit the equation of state of the semiconductor to its bulk modulus dependence B , one obtains

$$\overline{\Delta\Omega}(h^+) \approx \frac{\bar{P}(+1)\Omega}{B} = \frac{\bar{a}_v}{B} \quad (10)$$

$$\overline{\Delta\Omega}(e^-) \approx \frac{\bar{P}(-1)\Omega}{B} = -\frac{\bar{a}_c}{B}. \quad (11)$$

An experimental value for silicon is available in the literature for the free electrons in silicon [29]. $-5.5 \pm 1.3 \text{ \AA}^3$, which is similar to our calculated value, -6.65 \AA^3 . As the experimental data had been obtained in heavily doped silicon

sample ($x_{\text{Ga}} = 0.1$), the comparison with our value can be considered as satisfactory.

III. DEFINING ABSOLUTE PRESSURES

A. Total energies and pressures of charged systems depend on the average electrostatic potential convention

Beyond the particular case of free carriers, the pressure of any charged cell is indeed ill defined. This uncertainty arises from a definition problem of the total energy itself for charged systems. This problem was addressed in great detail in our previous work [16], however, it is instructive to review here where the lack of an absolute definition enters in the total energy expression of the periodic *ab initio* framework.

The easiest way to appreciate the ill definition of the total energy of charged systems is to make use of the Janak's theorem again [27]. The same final result could be alternatively obtained by detailing each of the terms of the total energy of a charged system. The derivation would be, however, much less concise. Janak's theorem shows the link between total energies E_{tot} and electron eigenvalues:

$$E_{\text{tot}}(q) - E_{\text{tot}}(0) = \int_0^q dq \frac{\partial E_{\text{tot}}(q)}{\partial q} \quad (12)$$

$$= - \int_0^q dq \epsilon_f(q), \quad (13)$$

where $\epsilon_f(q)$ is the frontier orbital, either ϵ_v for positive q or ϵ_c for negative q .

As we already insisted on above, there is no way to calculate the absolute electrostatic potential and therefore the eigenvalues on an absolute scale within periodic boundary conditions. In order to track down the effect of the constant value, let us emphasize the zero-average convention with primed symbols:

$$\epsilon_f(q) = \epsilon'_f(q) + \langle v_H(\Omega) \rangle. \quad (14)$$

$\langle v_H(\Omega) \rangle$ is the average value of the Hartree potential, which incorporates both the electron density $n(\mathbf{r})$ and the nuclei density $\tilde{n}_{Zc}(\mathbf{r})$ following the notations of Ref. [16]. Note that the Hartree potential differs by the sign with the electrostatic potential, due to the conventional negative sign of electrons. The dependence of the average value on the cell shape and volume is outlined with our notation $\langle v_H(\Omega) \rangle$. However, in all the practical implementations we are aware of, $\langle v_H(\Omega) \rangle$ is independent from q . Then the integral in Eq. (12) can be calculated by introducing the total energy with zero-average convention E'_{tot} and noting that the neutral total energy does not depend on the convention $E_{\text{tot}}(0) = E'_{\text{tot}}(0)$:

$$E_{\text{tot}}(q) = E'_{\text{tot}}(q) - q \langle v_H(\Omega) \rangle, \quad (15)$$

which is the final result. This last equation highlights the difference between the zero-average total energy and the general expression. As a consequence, as soon as q is nonzero, the total energy shows a dependence on the arbitrary average value of the electrostatic potential.

As the convention used for $\langle v_H(\Omega) \rangle$ can be cell dependent, the pressure of charged system is also ill defined

$$P(q) = P'(q) + \frac{q}{\Omega} \frac{\partial \langle v_H(\Omega) \rangle}{\partial \ln \Omega}, \quad (16)$$

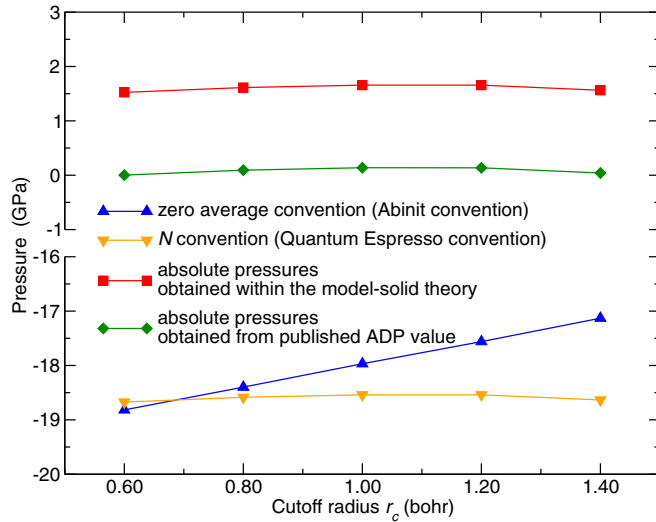


FIG. 2. (Color online) Pressure induced by a vacancy V_C^{2+} in diamond as calculated from a cubic 63-atom supercell as a function of the local pseudopotential cutoff radius r_c . The local pseudopotential is the d component and is expected to have little influence on the physical results in diamond (mainly sp electrons).

where the logarithm derivative has been readily introduced for consistency with the ADP definition.

As shown in Fig. 2, different codes with different electrostatic convention give different results for the pressure of a charged supercell containing a +2 vacancy in diamond. The norm conserving version of ABINIT uses a zero-average convention, QUANTUM ESPRESSO convention, named N convention in Ref. [16]. None of the mentioned conventions allow one to obtain physically sound pressures and therefore relaxation volumes. The zero-average convention pathologically depends on the details of the pseudopotential generation. The N convention is rather insensitive to the pseudopotential but yields nonphysically large pressures of about -18 GPa. The two corrected curves will be discussed later in the section.

B. Definition of absolute pressures

In the context of band offset calculations, i.e., the respective positioning of valence or conduction bands of two semiconductors in contact, several techniques have been developed to circumvent the issue of the unknown average electrostatic potential. These techniques can be sorted into two families: the strained superlattice calculations [18] and the electronic density modeling [17].

Let us postpone the connection with a specific technique and just allow us to assume that it is indeed possible to define a physically sound average potential $\langle \bar{v}_H(\Omega) \rangle$. Following the convention introduced in Sec. II, we wrote the physical potential with a bar. Using this assumption, the absolute eigenvalues $\bar{\epsilon}_i$ of any state i can be uniquely defined:

$$\bar{\epsilon}_i = \epsilon_i + \langle \bar{v}_H(\Omega) \rangle - \langle v_H(\Omega) \rangle, \quad (17)$$

where ϵ_i is the eigenvalue obtained from a periodic code having an average Hartree potential $\langle v_H(\Omega) \rangle$.

Hence, the total energy and most importantly for us the pressures can be obtained on an absolute scale. Writing

Eq. (16) for the absolute quantities yields

$$\bar{P}(q) = P(q) + \frac{q}{\Omega} \frac{\partial [\langle \bar{v}_H(\Omega) \rangle - \langle v_H(\Omega) \rangle]}{\partial \ln \Omega}, \quad (18)$$

which is our final expression for the absolute pressure $\bar{P}(q)$.

As a conclusion, provided that one could obtain the variation of the average electrostatic potential on an absolute scale, the pressure and hence all the derived quantities have a physical meaning now. Note that we only need to know the variation of the electrostatic potential and not its value. Our approach then relies on a weaker assumption than the one commonly used to build the so-called natural band offsets.

C. Absolute pressures with model-solid theory

With the model-solid theory [17], it is indeed possible to provide an approximate value for the average potential. Though approximate, this theory will be very insightful for our problem and its scaling properties.

The model-solid theory states that the average electrostatic potential in the crystal is identical to the average electrostatic potential of the superposition of independent neutral spherical atoms. These neutral spherical atoms are usually the configurations used for the pseudopotential generation and can be calculated easily for each atom a through

$$\alpha_a = \int dr 4\pi r^2 v_H[n^a + \tilde{n}_{Zc}^a](r), \quad (19)$$

where $v_H[n^a + \tilde{n}_{Zc}^a]$ is the Hartree potential generated by the neutral atom electron density n^a and the smooth charge \tilde{n}_{Zc}^a that would induce the local ionic potential of atom a . Then the model-solid theory simply supposes that the physical Hartree potential in the crystal is well approximated by

$$\langle \bar{v}_H(\Omega) \rangle \approx \frac{1}{\Omega} \sum_a \alpha_a, \quad (20)$$

where a runs over the atoms in the cell. The model-solid theory would be exact if there were no electronic relaxation in the crystal compared to the collection of the isolated atoms.

Hence, let us write down the correction to the pressures compared to a zero-average potential convention pressure $P'(q)$:

$$\bar{P}(q) = P'(q) - \frac{q}{\Omega^2} \sum_a \alpha_a. \quad (21)$$

In Fig. 2, the absolute pressure \bar{P} obtained with the formula in Eq. (21) is shown to deviate much from the bare data obtained from a straightforward calculation. The calculated pressure value is much more realistic and is almost independent from the pseudopotential details.

It is worth spending some time analyzing this formula for the correction and its asymptotic behavior when achieving the dilute limit. To approach the dilute limit for a defect in a matrix or for an ion in solution, one considers larger and larger supercells. Taking this limit, not only Ω increases but also the term $\sum_a \alpha_a$ since the summation includes more and more atoms.

Let us consider the case of a single substitutional impurity atom in order to fix the ideas. Let N_{bulk} be the number of bulk atoms in the supercell. The supercell volume is $N_{\text{bulk}}\Omega_0$ with

Ω_0 the volume per bulk atom and the sum over the atomic potentials reads

$$\sum_a \alpha_a = (N_{\text{bulk}} - 1)\alpha_{\text{bulk}} + \alpha_{\text{imp}}. \quad (22)$$

Hence the correction to the pressure for a single substitutional impurity is

$$\bar{P}(q) = P'(q) - \frac{q}{\Omega_0^2} \left(\frac{\alpha_{\text{bulk}}}{N_{\text{bulk}}} + \frac{\alpha_{\text{imp}} - \alpha_{\text{bulk}}}{N_{\text{bulk}}^2} \right). \quad (23)$$

The previous expression tells us two important facts: (i) The leading term of the error in the pressure of a charged supercell is $1/N_{\text{bulk}}$; (ii) The leading term depends on the bulk material quantities only. The details of the particular defect or impurity type induce some faster converging terms in $1/N_{\text{bulk}}^2$. We will neglect these terms from now on.

The slow convergence of the error has a huge consequence when evaluating the relaxation volume of a charged defect or of a solvated ion, as previously noticed in our earlier work [15]: the finite-size error in the relaxation volume converges to a nonzero value when achieving the dilute limit. Indeed, assuming the equation of state is limited to a second-order polynomial as in Sec. II, the error in the relaxation volume reads

$$\overline{\Delta\Omega} - \Delta\Omega' = -\frac{q}{B} \frac{\alpha_{\text{bulk}}}{\Omega_0} \quad (24)$$

$$= -\frac{q}{B} \langle \bar{v}_H(\Omega) \rangle. \quad (25)$$

This error is indeed independent from the supercell size.

D. Absolute pressures from published ADP

The model-solid theory allowed us to derive some interesting scaling behavior and general features of the absolute pressures and absolute relaxation volumes. However it is a simplistic model whose predictions can noticeably deviate from the higher accuracy strained superlattice calculations. The strained superlattice technique consists in monitoring the average potential change through an interface between a shrunken and a stretched region of the same material. The position of the atoms are fixed in the direction perpendicular to the interface, whereas the positions in the other two directions are allowed to relax. A strained superlattice calculation permits one to obtain the absolute deformation potential for one strained direction. Then the isotropic value is calculated thanks to an average over several superlattice stacking directions. The reader is referred to Ref. [30] for additional details.

We now show how the absolute pressure can alternatively be obtained from the knowledge of a material ADP value, previously calculated by any accurate technique. By combining Eq. (17) and Eq. (18), and introducing the definition of the deformation potential from Eq. (7), the absolute pressure becomes

$$\bar{P}(q) = P(q) + \frac{q}{\Omega} (\bar{a}_i - a_i). \quad (26)$$

In other words, the knowledge of the ADP for any state i is sufficient to reconstruct the absolute pressure. As shown in the previous section, the ADP of the bulk material is a fast converging approximation to the defective supercell ADP.

For instance, in Fig. 2 we evaluated Eq. (26) with the ADP value for the top valence band of diamond (2.16 eV) published by Li and coworkers [20]. Again, the calculated pressure has a realistic magnitude, but it differs somewhat from the model-solid evaluated pressure. The difference is to be ascribed to the limited predictive power of the model-solid theory.

Let us summarize here the practical way to obtain absolute pressures for a charged supercell representing a charged specie in a solid or liquid matrix:

(i) Find an ADP for any state of the bulk \bar{a}_i , either from the literature or from a new calculation (strained superlattice technique or model-solid theory).

(ii) Calculate the uncorrected deformation potential in a unit cell of the bulk a_i for the same state i . This value depends on the calculation scheme: details of the pseudopotential or PAW local potential, convention used for the average electrostatic potential, etc.

(iii) Calculate the pressure in the supercell containing the charged specie $P(q)$. This value also depends on the calculation scheme.

(iv) Evaluate the absolute pressure $\bar{P}(q)$ with the formula in Eq. (26). This value does not depend on the calculation technical details anymore.

IV. APPLICATIONS

A. Relaxation volume as a function of the charge state

Here we would like to illustrate the method with the silicon vacancy. The silicon vacancy case is interesting because of the Jahn-Teller distortion that appears for charge states $+1$, 0 , -1 , and -2 , but that is absent for charge state $+2$.

Figure 3 represents the relaxation volume of a single vacancy in silicon from different calculations. These data were obtained from a norm-conserving pseudopotential cal-

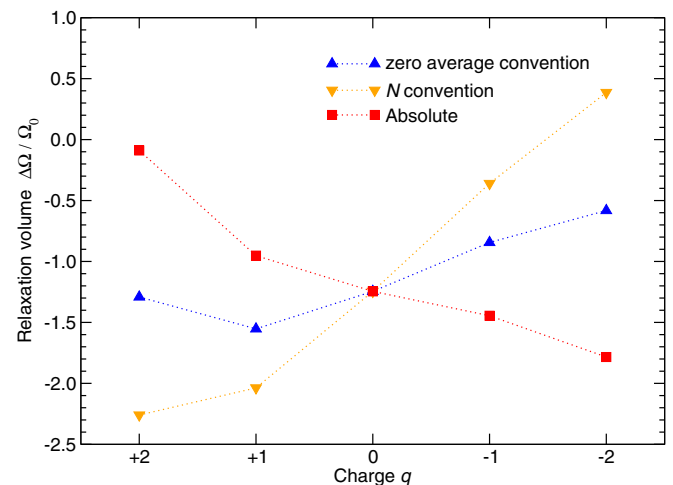


FIG. 3. (Color online) Relaxation volume of a single vacancy V_{Si} in silicon as a function of the charge state expressed in atomic volume Ω_0 . The charged pressures have been obtained in 215-atom supercells calculated with the zero-average potential convention (blue, up triangle symbols), with the N convention (orange, down triangle symbols), or corrected with the knowledge of the silicon ADP (red, square symbols).

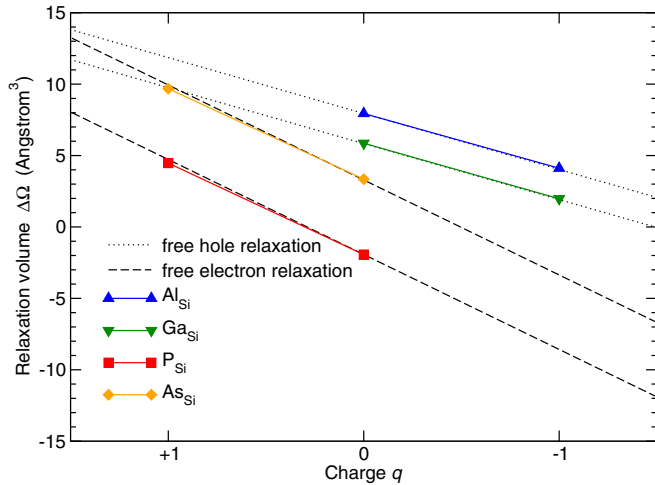


FIG. 4. (Color online) Absolute relaxation volume of shallow dopants in silicon as a function of the charge state. The charge state dependence of the relaxation volume of free hole and free electrons are a guide to the eyes.

calculation with ABINIT [22] using a 215-atom cubic supercell within the local-density approximation (LDA) within different conventions for the electrostatic potential. The pressure for the charged supercell was calculated for the supercells at the equilibrium lattice constant of the bulk. Then the relaxation volume is evaluated with $\Delta\Omega(q) = P(q)\Omega/B$ as mentioned earlier in the text. The different conventions (zero-average potential or N convention) again yield different values for the relaxation volume.

Using a published value [20] for the ADP of the top valence of silicon (2.38 eV), we were able to calculate absolute pressures through Eq. (26). The corresponding absolute relaxation volumes plotted in Fig. 3 show two interesting features: First, there is a discontinuity in the relaxation volume when the Jahn-Teller distortion disappears for charge state +2. Second, even for absolute relaxation volumes, an important charge state dependence can be observed. But this dependence strongly differs from the variations obtained with the naive conventions.

B. Defect relaxation volume compared to free carrier relaxation volume

At this stage, a legitimate question arises: Is it indeed necessary to calculate the relaxation volume of the charged defects? Could we evaluate the relaxation volume thanks to the combination of a neutral defect and free carriers?

The answer to that question depends on the defect type. Let us illustrate this with two examples.

The first example reported in Fig. 4 shows the relaxation volume dependence of shallow dopants in silicon. We considered two shallow acceptors (Al and Ga) and two shallow donors (P and As) in their relevant charge states. The data represented Fig. 4 are absolute relaxation volumes obtained from a published ADP value [20]. The shallow defect relaxation volumes were extracted from 216-atom supercell calculations. Even though this doping level is still far from the dilute limit, the relaxation volume appears as convergence with respect to the supercell size.

Once again the relaxation volume strongly depends on the charge state. However, the dependence can be easily rationalized for shallow defects. A shallow acceptor induces in principle a defect state very close to the valence band maximum. This delocalized defect state is very similar in nature to the top valence wave function. It is then expected that the relaxation volume difference between the occupied and the empty defect state is of the order of a free hole relaxation volume. The corresponding statement is valid for donors and free electrons relaxation volume. In other words, the relaxation volume of the charged shallow defects can be well approximated by

$$\overline{\Delta\Omega}(\text{Al}_{\text{Si}}^-) \approx \Delta\Omega(\text{Al}_{\text{Si}}^0) - \overline{\Delta\Omega}(h^+) \quad (27)$$

$$\overline{\Delta\Omega}(\text{P}_{\text{Si}}^+) \approx \Delta\Omega(\text{P}_{\text{Si}}^0) - \overline{\Delta\Omega}(e^-). \quad (28)$$

The quality of the approximation is demonstrated in Fig. 4 by the similarity between the thin black lines and the actual calculations of the charged supercells.

As a consequence, for shallow defects, there is not much interest in calculating the relaxation volume of the ionized dopant through an actual calculation. It could rather be obtained through Eqs. (27), (28).

The second example reported in Fig. 5 is the oxygen vacancy case in MgO in a 215-atom supercell. This example demonstrates that the rationale used for shallow defects is not valid for deep defects. We carry out the same analysis as previously and compare the calculated relaxation volume to those of the free carriers. The relaxation volume of V_{O} is linear with the charge state. However, the slope cannot be captured by the ADP of the top valence, nor bottom conduction. In other words, the ADP of the oxygen vacancy state does not match any of the band edges. In this case, a complete defect calculation for each of the charge state cannot be avoided.

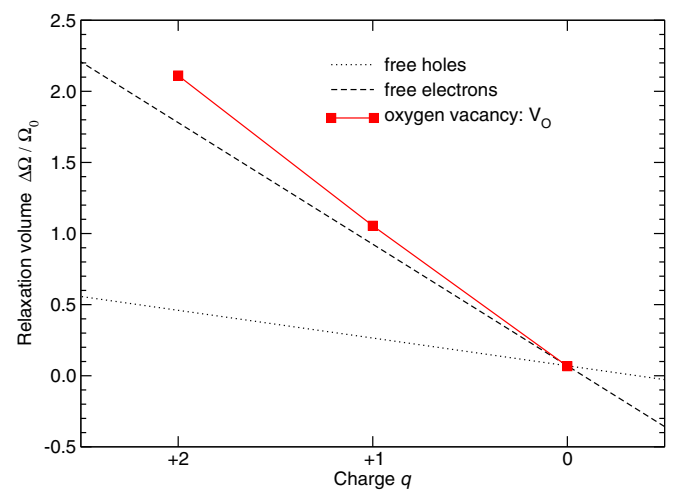


FIG. 5. (Color online) Relaxation volume of the oxygen vacancy in MgO as a function of the charge state, expressed in units of volume per atom Ω_0 . The relaxation volume of V_{O} (red, square symbols) is compared to that of free holes (dotted black line) and of free electrons (dashed black line).

C. Elastic interaction corrections in charged supercells

The definition of an absolute pressure is also beneficial in the context of finite-size effects corrections. Indeed, a point defect introduced in a host bulk material induces long-range elastic fields, which create spurious interactions as soon as the supercell technique is employed. In order to achieve the dilute limit, one should remove this spurious interaction energy between the defect periodic images.

In a previous study [31], we had developed a scheme that evaluates this interaction energy in the framework of the linear elasticity theory. The correction, labeled ΔE here, is subtracted to the direct *ab initio* calculation of the defective supercell energy. The dilute limit is then achieved with only few atoms, as long as only elastic interactions are concerned. The scheme we proposed is very handy in practical situations, since the only inputs required are the elastic constants of the host material and the stress tensor of the supercell with the defect.

We would like here to extend the original study that included only neutral point defects to the specific case of charged defects. As shown here, the pressure and then the stress tensor of a charged supercell are ill defined. The absolute stress tensor, instead of a potential convention-dependent stress tensor, should then be calculated to obtain the meaningful elastic corrections.

In Sec. II, we extensively used the model-solid theory to derive the general properties of the absolute pressures. Within the model-solid theory, the correction to the electrostatic potential is only a function of the volume Ω , as written in Eq. (20). Therefore only the trace of the stress tensor is affected by shifting from a given potential convention to the absolute values. Here, we thus only correct the isostatic pressure part of the stress tensor to obtain the absolute stress tensor. It should be however noted that the interface calculations as proposed by Li *et al.* [30] measure a directional dependence of the ADP. However this dependence is not huge, so the correction of the deviatoric part of the stress tensor should be of second order.

We illustrate this effect for a vacancy in silicon, with charge states +2, +1, 0, -1, and -2, using a 215-atom supercell. In Table I, we compare the evaluation of the elastic corrections $\Delta E'$ using the direct output of a zero-average convention code (such as the norm-conserving pseudopotential version of ABINIT), with the absolute evaluations of the elastic corrections

TABLE I. Pressure and spurious elastic interaction induced by a single vacancy in a 215-atom supercell of silicon in its different stable charge states. The zero-average pressures and the corresponding elastic corrections are provided with primed labels. The absolute pressures and the corresponding elastic corrections are provided with overlined labels.

V_{Si}	P' GPa	$\Delta E'$ meV	\bar{P} GPa	$\overline{\Delta E}$ meV
+2	-0.58	19	-0.04	0
+1	-0.70	38	-0.43	21
0	-0.56	44	-0.56	44
-1	-0.38	23	-0.65	39
-2	-0.26	17	-0.80	49

$\overline{\Delta E}$. Besides for the neutral case of course, the corrections largely deviate from the other convention evaluation. This part had the simple purpose of demonstrating the approach. We acknowledge that, for a single vacancy in a 215-atom supercell, the magnitude of the correction is rather small. However, larger defect clusters may induce much larger elastic interaction as we showed in Ref. [31].

D. Sketching the consequences for *ab initio* molecular dynamics simulations of ion solvation

Here we sketch the consequence of our developments for ion solvation. An actual calculation would be beyond our computational resources and beyond the scope of the paper.

The method of choice to determine the hydration properties of ions in solution is the *ab initio* molecular dynamics. Owing to the price of such calculations, the simulation cells are limited to few solvent molecules. For water, a simulation with 64 water molecules in a 12.44 Å edge cubic box is the most commonly used setup nowadays [32,33]. In such small cells, only one ion could be introduced: no counterion is present in the simulation box yielding a nonzero total charge. Therefore all the previous developments can be applied in the context of ions in solution too. Of course, the presence of ions in solution gives rise to the phenomenon of electrostriction. Some authors have ascribed the unusually large pressures they obtain in their simulations to this truly physical effect [34]. However, in the periodic cell calculation, there is an intrinsic error in the pressures. That is why most of the authors discard the pressures obtained in their calculation and rather assume a zero molar partial volume for the introduced ion [32,33]. While this approximation is certainly harmless for monoatomic ions, its consequences have never been controlled for larger molecular ions.

We have adapted the model-solid theory, for which the solid are considered as a sum of neutral atoms, to the specific case of liquid water. Let us approximate the potential in a liquid water simulation cell by a collection of neutral water molecules. With our norm-conserving pseudopotentials, we have evaluated that the error in the pressure for a 64 H₂O molecules box can be as large as 0.5 GPa per unit charge q when the zero-average convention is used. As the bulk modulus of liquid water is one or two orders of magnitude smaller than the one of solids, the consequences for the relaxation volume of the simulation box are catastrophic. Considering an experimental bulk modulus $B = 2.2\text{GPa}$, a monovalent ion would induce a 20% error of the simulation cell volume.

In the context of ions in solution, the change of volume induced by the ion (i.e., the relaxation volume) is named the partial volume. It is usually reported per mole. This is the so-called partial molar volume of the ionic species. If one wants to avoid any trouble, one could define the partial molar volume of pairs of ion and counterion. But this would preclude the use of small cells for the simulation and the experimentalists often desire to define an individual partial molar volume too [7,35].

In this context, it would be extremely useful to evaluate an accurate value of the ADP of liquid water from *ab initio* molecular dynamics. Such a value could be used with more confidence than the model-solid theory value we used here, however this evaluation is beyond the scope of the present article.

V. CONCLUSION

We have shown that the total energies, the pressures, the relaxation volume, and the elastic corrections are ill-defined in a charged supercell. The use of charged supercells is, however, crucial for point defects in semiconductors and for solvated ions for instance. We have proposed a general scheme to fix this definition problem. The solution requires the knowledge of the ADP of one single state of the bulk material. The calculation ADP requires some extra calculations or can be obtained from literature. In practice, ADPs are extracted either from density modeling (fast but sometimes inaccurate) [17] or from strained superlattice calculations (slow but more accurate) [18]. Once an ADP value is obtained, then the pressure, the relaxation volume, and the elastic corrections are uniquely defined. To first order, only bulk ADPs are indeed necessary to obtain absolute pressures for charged defects. Many bulk ADPs are readily available from literature [20].

In some cases, for shallow defects especially, the defect relaxation volume has the same charge state dependence as

the free carriers. However, in the vast majority of the cases, the defect relaxation volume has its own particular behavior with respect to the charge state. This specific behavior has two origins: Different structures may be stabilized for different charges states and there is no reason why the defect state ADP should be similar to the ADP of the band edges.

In all the practical cases considered in the present work, a supercell containing around 200 atoms was sufficient to converge the relaxation volume of a defect, even for shallow defects, which present delocalized defect wave functions. We do not exclude the possibility that some defects may experience a slower convergence. This work may pave the way towards the *ab initio* evaluation of the partial molar volume of ions in solution, which has been only sketched here.

ACKNOWLEDGMENTS

We acknowledge inspiring discussions with A. Pasquarello. This work was performed using HPC resources from GENCI-CCRT-TGCC (Grant No. 2014-096018).

-
- [1] G. Was, *Fundamentals of Radiation Materials Science: Metals and Alloys* (Springer, Berlin, 2007).
 - [2] A. H. Cottrell and B. A. Bilby, *Proc. Phys. Soc. London, Sect. A* **62**, 49 (1949).
 - [3] R. Bullough and R. C. Newman, *Rep. Prog. Phys.* **33**, 101 (1970).
 - [4] E. Clouet, *Acta Mater.* **54**, 3543 (2006).
 - [5] E. Clouet, S. Garruchet, H. Nguyen, M. Perez, and C. S. Becquart, *Acta Mater.* **56**, 3450 (2008).
 - [6] F. Rieutord, F. Mazen, S. Reboh, J. D. Penot, L. Billeau, J. P. Crocombette, V. Vales, V. Holy, and L. Capello, *J. Appl. Phys.* **113**, 153511 (2013).
 - [7] R. Wadi and P. Kathuria, *J. Solution Chem.* **21**, 361 (1992).
 - [8] P. P. Ewald, *Annalen der Physik* **369**, 253 (1921).
 - [9] R. M. Martin, *Electronic Structure: Basic Theory and Practical Methods*, Vol. 1 (Cambridge University Press, Cambridge, 2004).
 - [10] C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, *Rev. Mod. Phys.* **86**, 253 (2014).
 - [11] M. Leslie and M. J. Gillan, *J. Phys. C* **18**, 973 (1985).
 - [12] C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, *Phys. Rev. Lett.* **102**, 016402 (2009).
 - [13] S. E. Taylor and F. Bruneval, *Phys. Rev. B* **84**, 075155 (2011).
 - [14] H.-P. Komsa, T. T. Rantala, and A. Pasquarello, *Phys. Rev. B* **86**, 045112 (2012).
 - [15] F. Bruneval and J.-P. Crocombette, *Phys. Rev. B* **86**, 140103 (2012).
 - [16] F. Bruneval, J.-P. Crocombette, X. Gonze, B. Dorado, M. Torrent, and F. Jollet, *Phys. Rev. B* **89**, 045116 (2014).
 - [17] C. G. Van de Walle, *Phys. Rev. B* **39**, 1871 (1989).
 - [18] A. Baldereschi, S. Baroni, and R. Resta, *Phys. Rev. Lett.* **61**, 734 (1988).
 - [19] C. G. Van de Walle and R. M. Martin, *Phys. Rev. Lett.* **62**, 2028 (1989).
 - [20] Y.-H. Li, X. G. Gong, and S.-H. Wei, *Phys. Rev. B* **73**, 245206 (2006).
 - [21] M. J. Gillan, *Philos. Mag. A* **43**, 301 (1981).
 - [22] X. Gonze, B. Amadon, P. M. Anglade, J. M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Côté, T. Deutsch, L. Genovese, P. Ghosez, M. Giantomassi, S. Goedecker, D. R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S. Mazevet, M. J. T. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G. M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M. J. Verstraete, G. Zerah, and J. W. Zwanziger, *Comput. Phys. Commun.* **180**, 2582 (2009).
 - [23] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys. Condens. Matter* **21**, 395502 (2009).
 - [24] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
 - [25] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
 - [26] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
 - [27] J. F. Janak, *Phys. Rev. B* **18**, 7165 (1978).
 - [28] L. J. Sham and M. Schlüter, *Phys. Rev. Lett.* **51**, 1888 (1983).
 - [29] G. S. Cargill, J. Angilello, and K. L. Kavanagh, *Phys. Rev. Lett.* **61**, 1748 (1988).
 - [30] Y.-H. Li, X. G. Gong, and S.-H. Wei, *Appl. Phys. Lett.* **88**, 042104 (2006).
 - [31] C. Varvenne, F. Bruneval, M.-C. Marinica, and E. Clouet, *Phys. Rev. B* **88**, 134102 (2013).
 - [32] R. Atta-Fynn, E. J. Bylaska, G. K. Schenter, and W. A. de Jong, *J. Phys. Chem. A* **115**, 4665 (2011).
 - [33] R. Spezia, C. Beuchat, R. Vuilleumier, P. D' Angelo, and L. Gagliardi, *J. Phys. Chem. B* **116**, 6465 (2012).
 - [34] L. M. Ramaniah, M. Bernasconi, and M. Parrinello, *J. Chem. Phys.* **111**, 1587 (1999).
 - [35] J. K. Hovey, *J. Phys. Chem. B* **101**, 4321 (1997).