

Scaling hypothesis for corrections to total energy and stress in plane-wave-based *ab initio* calculations

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We present a technique aimed at preventing plane-wave-based total energy and stress calculations from the effect of abrupt changes in basis set size. This scheme relies on the interpolation of energy as a function of the number of plane waves and on a scaling hypothesis that allows us to perform the interpolation for a unique reference volume. From a theoretical point of view, the method is compared to those already proposed in the literature, and its more rigorous derivation is emphasized. From a practical point of view, we illustrate the importance of the correction on different materials (Si, BaTiO₃, and He) corresponding to different types of bonding, and to different *k*-point samplings and cutoff energies. Then, we compare the different approaches for the calculation of a_0 , B_0 , and B'_0 in bulk silicon.

INTRODUCTION

Since the early eighties, the local density approximation (LDA) (Ref. 1) to density functional theory (Ref. 2) has proven to be a choice tool to obtain reliable total energies of solids. Application of the total energy method to a solid of a given (or assumed) crystal structure usually begins by the determination of the static equilibrium properties, like the lattice constant a_0 , the bulk modulus B_0 , and possibly its pressure derivative B'_0 . This determination is carried out before evaluation of other properties such as phonon spectra. Considerable help in this task arises from the stress theorem, derived by Nielsen and Martin,³⁻⁵ that complements a calculation of the total energy, by giving the six components of the macroscopic stress tensor $\sigma_{\alpha\beta}$, at practically no cost.

For simplicity, we first consider a cubic structure (for which there is only one lattice constant). The hydrostatic pressure is related to the total energy and the volume V by

$$P = P(V) = -\frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3} = -\frac{\partial E_{\text{tot}}}{\partial V}. \quad (1)$$

In this case, the static equilibrium properties can easily be determined either from the curve of energy E_{tot} versus lattice constant a (or, in an equivalent way, versus volume V) or from that of pressure P versus lattice constant a . These curves can be obtained by fitting a polynomial to the values of E_{tot} and P calculated for several values of the lattice constant.

We now describe the problems that arise when a plane-wave-based method is used for total energy and pressure calculation. Considering a periodic cell, the electronic wave functions should be expanded in terms of an *infinite* set of plane waves (Fourier series) at each of an *infinite* set of *k* points in the Brillouin zone. The following two approximations are introduced. First, a small number

of carefully chosen *k* points (special points) are used to sample the Brillouin zone.⁶ Second, the wave functions at each *k* point are expanded in terms of a *finite* basis set of plane waves $e^{i(k+G)r}$, such that their kinetic energy is smaller than a fixed cutoff energy E_{cut} (Hartree atomic units are used throughout the paper):

$$\frac{1}{2} |k + G|^2 < E_{\text{cut}}. \quad (2)$$

In principle, it is possible to approach energy convergence by augmenting the number of special *k* points and the cutoff energy (which corresponds to increasing the size of the basis set). However, working with large number of special points and plane waves requires a huge amount of CPU time. In order to perform calculations on larger and more complex systems, one aims at using smaller plane-wave basis sets at each *k* point without reducing the accuracy of the calculation.

Differences in the total energy of systems with the same unit cell are known to be accurately calculated for a number of plane waves and special *k* points smaller than those required to ensure convergence of the energy, provided that *identical* plane-wave basis sets are used for each calculation.⁷ The error due to the truncation of the Fourier series is systematic and cancels out. One could expect a_0 , B_0 , and B'_0 to have similar properties: part of the systematic error in E_{tot} should cancel. However, when computing energy differences between systems of varying size, it is impossible to use *identical* plane-wave basis sets, due to the periodic boundary conditions imposed on the edge of the cell whose dimensions change with the volume. Instead, we must choose either to use a constant number of plane waves $\bar{N}_{\text{PW}}$ (Ref. 8) in the basis set with E_{cut} depending upon the volume, or a constant cutoff energy for determining the plane-wave basis set.

The E_{tot} curve for constant $\bar{N}_{\text{PW}}$ is always very

smooth since the set of plane waves scales smoothly with the lattice constant. Unfortunately, relying on this curve leads to a systematic underestimation of the lattice constant, as discussed in previous papers.⁹ On the other hand, constant E_{cut} corresponds to a constant resolution in real space, which gives less biased results;⁹ but, the curve for constant E_{cut} is ragged. One gets a set of disconnected microcurves (a microcurve being a continuous segment of E_{tot} or P) as shown in Fig. 1, whereas the experimental curves are perfectly continuous. This stairlike variation is due to the discontinuous increase of the number of plane waves accompanying the unit cell volume changes. Every time new $(k + G)$ vectors are added to the basis set, E_{tot} discontinuously decreases, due to the added variational freedom in the wave function. The P curve also presents discontinuities for the same reasons. Moreover, at the approximate minimum of the E_{tot} curve, the pressure does not vanish.

The purpose of this paper is to analyze how these systematic discontinuities and associated errors in the total energy and the pressure can be dealt with. In Sec. I, we introduce the definitions that will be used all along the paper, including the basic concept of interpolation of energy. In Sec. II, we present accurate, but CPU time-consuming, formulas for corrections to energy and pressure. In Secs. III and IV, approximations that make it simpler to use are examined. Section III is dedicated to a

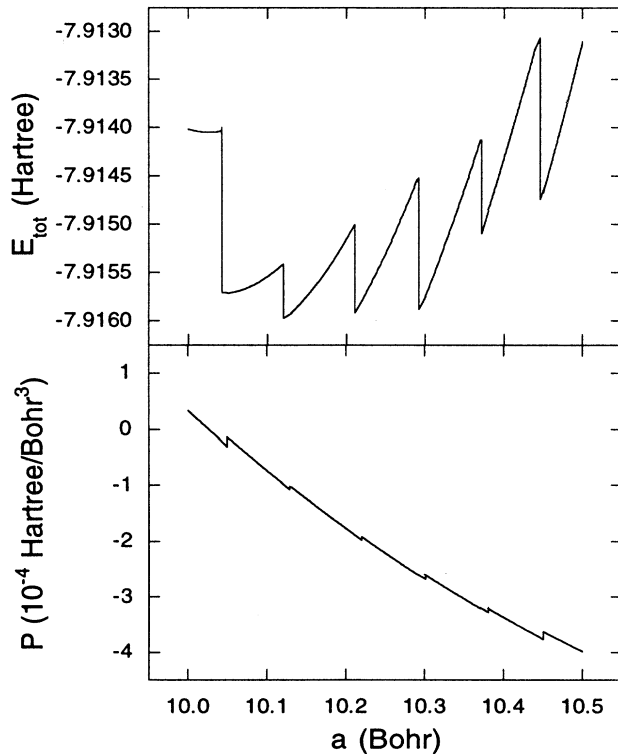


FIG. 1. Total energy (top) and pressure (bottom) of Si calculated at constant cutoff energy [$E_{\text{cut}}=6$ Hartree with two special k points in the irreducible Brillouin zone (IBZ)]. The graph highlights the presence of “microcurves” (see text).

technique based on a scaling hypothesis (S.H.), allowing us to compute the energy curve for a unique reference volume, whereas Sec. IV treats, with the same notations, the corrections proposed by Froyen and Cohen¹⁰ to pressure and by Francis and Payne¹¹ to energy. We emphasize the theoretical differences between these techniques. In Sec. V, we present the results obtained using the scaling hypothesis for silicon, barium titanate, and helium. In Sec. VI, we compare the different techniques by their effect on the calculation of a_0 , B_0 , and B'_0 in bulk silicon. In Sec. VII, we present a generalization to anisotropic deformations. We introduce a correction to the stress tensor and apply it in the case of bulk silicon. Finally, we present our conclusions in the last section.

I. DEFINITIONS

Let $\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V)$ be the mean number of plane waves in the basis set [see Appendix A) and (Ref. 12)] for a given value of the cutoff energy E_{cut} and of the volume V . The subscript “d” stands for “discontinuous.” As the reciprocal lattice is discrete, $\bar{N}_{\text{PW}}$ can stay constant for a range of cutoff energies, or for different volumes. On the other hand, it will change abruptly for some values

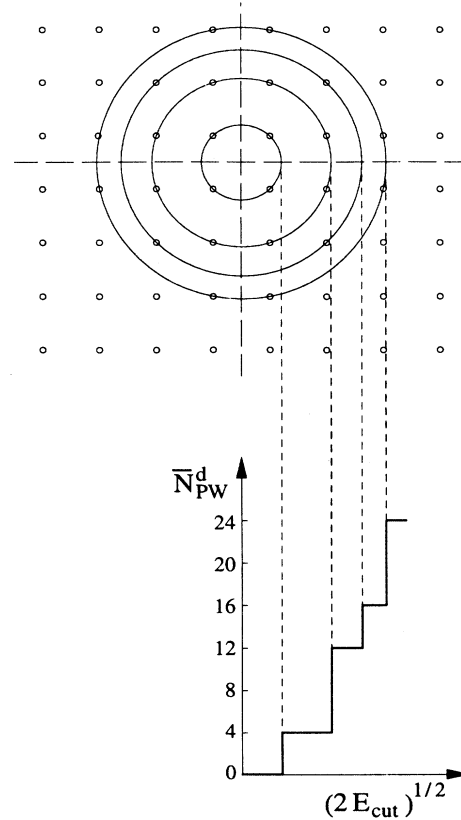


FIG. 2. Number of plane waves $\bar{N}_{\text{PW}}^d$ in a basis set defined by Eq. (2) in a two-dimensional case. The upper graph illustrates how these k points are enclosed in a circle of radius $(2E_{\text{cut}})^{1/2}$. The lower graph illustrates the stairlike evolution of $\bar{N}_{\text{PW}}^d$ as a function of E_{cut} .

of E_{cut} , at fixed volume, or for some values of V , at fixed E_{cut} . So, $\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V)$ is a stairlike function (see Fig. 2).

Let $\bar{N}_{\text{PW}}^c(E_{\text{cut}}, V)$ be the fictitious number of plane waves in the basis set for a given value of the cutoff energy E_{cut} and of the volume V , if it were determined by the product of the density of state in the reciprocal lattice by the volume of a sphere of radius $(2E_{\text{cut}})^{1/2}$:

$$\begin{aligned}\bar{N}_{\text{PW}}^c(E_{\text{cut}}, V) &= \left(\frac{V}{8\pi^3}\right) \frac{4}{3}\pi((2E_{\text{cut}})^{1/2})^3 \\ &= \frac{V}{6\pi^2}(2E_{\text{cut}})^{3/2},\end{aligned}\quad (3)$$

where the subscript "c" stands for "continuous."

Let $E_{\text{cut}}^c(\bar{N}_{\text{PW}}, V)$ and $E_{\text{cut}}^d(\bar{N}_{\text{PW}}, V)$ be the inverse of $\bar{N}_{\text{PW}}^c(E_{\text{cut}}, V)$ and $\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V)$, respectively. The first can trivially be obtained from Eq. (3):

$$E_{\text{cut}}^c(\bar{N}_{\text{PW}}, V) = \frac{1}{2} \left(\frac{6\pi^2 \bar{N}_{\text{PW}}}{V} \right)^{2/3}, \quad (4)$$

whereas the second is defined for certain values of $\bar{N}_{\text{PW}}$ for a given volume V , and links these values to a semiopened interval $[E_{\text{cut}}^1, E_{\text{cut}}^2[$. Let $E_{\text{tot}}[\bar{N}_{\text{PW}}, V]$ be the total energy that is calculated when the number of plane waves used in an actual calculation, at volume V , is $\bar{N}_{\text{PW}}$.

For a given volume, this function is defined only for $\bar{N}_{\text{PW}} = \bar{N}_{\text{PW}}^d(E_{\text{cut}}, V)$. In order to obtain a continuous curve, we interpolate through these points, so that $E_{\text{tot}}[\bar{N}_{\text{PW}}, V]$ can be obtained at any value of $\bar{N}_{\text{PW}}$. At the present stage of the discussion, the choice of the interpolation scheme is not relevant (see Sec. V). The introduction of such an interpolating energy curve was also performed in other papers treating the problem.^{10,11}

We also define the function $E_{\text{tot}}^d\{E_{\text{cut}}, V\}$, which gives the total energy obtained when the basis set is determined by E_{cut} through Eq. (2). This function is connected to $E_{\text{tot}}[\bar{N}_{\text{PW}}, V]$ by

$$E_{\text{tot}}^d\{E_{\text{cut}}, V\} = E_{\text{tot}}[\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V), V]. \quad (5)$$

Since $\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V)$ changes by abrupt jumps, this function is not the smooth desired one, but a set of microcurves that correspond to a fixed $\bar{N}_{\text{PW}}$ (see Fig. 1).

We finally introduce an ideal continuous function $E_{\text{tot}}^c\{E_{\text{cut}}, V\}$ that corresponds to the energy of a hypothetical calculation, at volume V , with $\bar{N}_{\text{PW}}^c(E_{\text{cut}}, V)$ plane waves. It is connected to $E_{\text{tot}}[\bar{N}_{\text{PW}}, V]$ by the following equation:

$$E_{\text{tot}}^c\{E_{\text{cut}}, V\} = E_{\text{tot}}[\bar{N}_{\text{PW}}^c(E_{\text{cut}}, V), V]. \quad (6)$$

The function $E_{\text{tot}}^c\{E_{\text{cut}}, V\}$ is the smooth function that should be used for the determination of material properties, whereas the one we get from a usual calculation is $E_{\text{tot}}^d\{E_{\text{cut}}, V\}$. Thus, the correction to energy aims at determining the function $E_{\text{tot}}^c\{E_{\text{cut}}, V\}$, starting from

$E_{\text{tot}}^d\{E_{\text{cut}}, V\}$.

Using the same type of notations, we can now introduce the definitions related to pressure. Let $P[\bar{N}_{\text{PW}}, V]$ be the pressure that is calculated by using the stress theorem³⁻⁵ when the number of plane waves used in the calculation, at volume V , is $\bar{N}_{\text{PW}}$. This function is connected to $E_{\text{tot}}[\bar{N}_{\text{PW}}, V]$ by

$$P[\bar{N}_{\text{PW}}^1, V_1] = - \left(\frac{\partial E_{\text{tot}}[\bar{N}_{\text{PW}}, V]}{\partial V} \right)_{\bar{N}_{\text{PW}}} \bigg|_{\substack{V=V_1 \\ \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^1}}, \quad (7)$$

where the subscript $\bar{N}_{\text{PW}}$ to the parentheses indicates that the derivative of the total energy versus the volume is taken at a constant number of plane waves, and the subscripts $V = V_1$ and $\bar{N}_{\text{PW}} = \bar{N}_{\text{PW}}^1$ to the vertical bar indicate where the previous expression is evaluated. Let $P^d\{E_{\text{cut}}, V\}$ be the pressure that is calculated with E_{cut} and the volume V as inputs. This function is connected to $E_{\text{tot}}^d\{E_{\text{cut}}, V\}$ by

$$P^d\{E_{\text{cut}}^1, V_1\} = - \left(\frac{\partial E_{\text{tot}}^d\{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V \bigg|_{\substack{V=V_1 \\ E_{\text{cut}}=E_{\text{cut}}^1}}. \quad (8)$$

In fact, this function is a set of microcurves, each of which corresponds to fixed $\bar{N}_{\text{PW}}$ (see Fig. 1). So let $P^c\{E_{\text{cut}}, V\}$ be the ideal continuous pressure curve. This function is connected to $E_{\text{tot}}^c\{E_{\text{cut}}, V\}$ by

$$P^c\{E_{\text{cut}}^1, V_1\} = - \left(\frac{\partial E_{\text{tot}}^c\{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V \bigg|_{\substack{V=V_1 \\ E_{\text{cut}}=E_{\text{cut}}^1}}. \quad (9)$$

The function $P^c\{E_{\text{cut}}, V\}$ is the function that should be used for the determination of material properties, whereas the one we get from a usual calculation is $P^d\{E_{\text{cut}}, V\}$. Thus, the correction to pressure aims at determining the function $P^c\{E_{\text{cut}}, V\}$, starting from $P^d\{E_{\text{cut}}, V\}$.

II. ACCURATE CORRECTIONS TO ENERGY AND PRESSURE

The correction to energy at $E_{\text{cut}} = E_{\text{cut}}^1$ and $V = V_1$, needed to connect the output of a computer run $E_{\text{tot}}^d\{E_{\text{cut}}^1, V_1\}$ with the ideal value $E_{\text{tot}}^c\{E_{\text{cut}}^1, V_1\}$ is obtained by combining Eqs. (5) and (6):

$$E_{\text{tot}}^c \{E_{\text{cut}}^1, V_1\} = E_{\text{tot}}^d \{E_{\text{cut}}^1, V_1\} + \left\{ E_{\text{tot}} \left[\bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1), V_1 \right] - E_{\text{tot}} \left[\bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1), V_1 \right] \right\}. \quad (10)$$

A schematic representation of this expression is given in Fig. 3. Indeed, Eq. (10) can be rewritten $E_{\text{tot}}(B) = E_{\text{tot}}(C) + \{E_{\text{tot}}(D) - E_{\text{tot}}(E)\}$, following the notations of the figure. The idea is that going from point C to B is equivalent to going from point E to D , as suggested by the arrows in Fig. 3.

The correction to pressure (the correcting term is called Pulay stress¹¹ by analogy with the Pulay force¹³) at $E_{\text{cut}} = E_{\text{cut}}^1$ and $V = V_1$ is obtained by deriving Eq. (10) with respect to the volume at fixed cutoff energy:

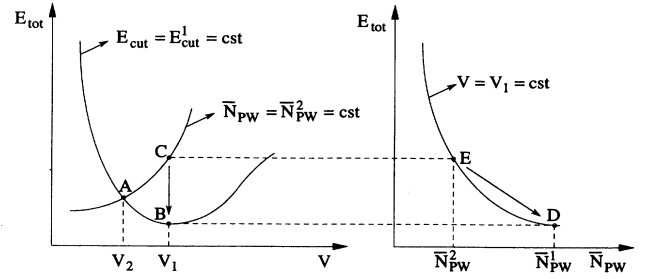


FIG. 3. Schematic representation of energy correction. The desired curve $E_{\text{tot}}^c \{E_{\text{cut}}^1, V\}$ is the one going through points A and B . The calculated curve $E_{\text{tot}}^d \{E_{\text{cut}}^1, V\}$ is the one going through points A and C . The correction at volume V_1 moves point C , obtained by a calculation with $\bar{N}_{\text{PW}}^2 = \bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1)$, to point B , obtained by a hypothetic calculation with $\bar{N}_{\text{PW}}^1 = \bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1)$. This operation is equivalent to moving point E to point D . This is easily done if the curve $E_{\text{tot}} [\bar{N}_{\text{PW}}, V_1]$ is known [see Eq. (10)].

$$P^c \{E_{\text{cut}}^1, V_1\} = P^d \{E_{\text{cut}}^1, V_1\} + P \left[\bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1), V_1 \right] - P \left[\bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1), V_1 \right] - \frac{\bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1)}{V_1} \left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}} V]}{\partial \bar{N}_{\text{PW}}} \right)_V \bigg|_{V=V_1, \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1)}. \quad (11)$$

This result was obtained by using the chain rule and the following derivatives:

$$\left(\frac{\partial \bar{N}_{\text{PW}}^c (E_{\text{cut}}, V)}{\partial V} \right)_{E_{\text{cut}}} = \frac{\bar{N}_{\text{PW}}^c (E_{\text{cut}}, V)}{V}, \quad (12)$$

from Eq. (3), and

$$\left(\frac{\partial \bar{N}_{\text{PW}}^d (E_{\text{cut}}, V)}{\partial V} \right)_{E_{\text{cut}}} = 0, \quad (13)$$

since $\bar{N}_{\text{PW}}^d (E_{\text{cut}}, V)$ is a stair function.

The validity of Eqs. (10) and (11) rests only on the choice of an interpolation scheme for $E_{\text{tot}} [\bar{N}_{\text{PW}}, V]$. At this stage, in order to find $E_{\text{tot}}^c \{E_{\text{cut}}, V\}$ or $P^c \{E_{\text{cut}}, V\}$, as a function of the volume using Eq. (10) or Eq. (11), one should consider a few values of V , then for each V , choose a few basis sets, and interpolate the energy to get $E_{\text{tot}} [\bar{N}_{\text{PW}}, V]$. Unfortunately, this procedure is time consuming.

III. SCALING HYPOTHESIS

We now introduce a technique that allows us to make the interpolation effort only for one given reference volume V_0 . It is different from the technique proposed by Francis and Payne for correcting the energy,¹¹ or by Froyen and Cohen for correcting the pressure¹⁰ (see Sec. IV).

We make a realistic hypothesis that for the purpose of the calculation of the correction to energy and pressure, the difference between energy at V and at V_0 at constant E_{cut} does not depend on E_{cut} :

$$E_{\text{tot}}^c \{E_{\text{cut}}, V\} \approx E_{\text{tot}}^c \{E_{\text{cut}}, V_0\} + f(V - V_0), \quad \forall E_{\text{cut}}. \quad (14)$$

This is the mathematical expression of the principle of cancellation of errors between similar geometries, already mentioned in the Introduction.

By deriving this equation with respect to E_{cut} at constant V , we get

$$\left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V \bigg|_{\substack{V=V_1 \\ E_{\text{cut}}=E_{\text{cut}}^1}} \approx \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V \bigg|_{\substack{V=V_0 \\ E_{\text{cut}}=E_{\text{cut}}^1}}, \quad (15)$$

which means that the successive derivatives of $E_{\text{tot}}^c \{E_{\text{cut}}, V\}$, with respect to the cutoff energy at constant volume, do not depend on V .¹⁴ This last equation can be developed by means of Eq. (6). Deriving the latter with respect to E_{cut} at constant V and using the chain rule, we get

$$\left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V = \left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right)_V \bigg|_{\bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^c(E_{\text{cut}}, V)} \left(\frac{\partial \bar{N}_{\text{PW}}^c(E_{\text{cut}}, V)}{\partial E_{\text{cut}}} \right)_V, \quad (16)$$

where the last term can be obtained from Eq. (3):

$$\left(\frac{\partial \bar{N}_{\text{PW}}^c(E_{\text{cut}}, V)}{\partial E_{\text{cut}}} \right)_V = \frac{V}{2\pi^2} (2E_{\text{cut}})^{1/2}. \quad (17)$$

When introducing these results in Eq. (15), we get

$$\left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right)_V \bigg|_{\substack{V=V_1 \\ \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^1}} \approx \frac{V_0}{V_1} \left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right)_V \bigg|_{\substack{V=V_0 \\ \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^0}}, \quad (18)$$

where $\bar{N}_{\text{PW}}^1 = \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)$ and $\bar{N}_{\text{PW}}^0 = \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_0) = \frac{V_0}{V_1} \bar{N}_{\text{PW}}^1$. The relation expressed in Eq. (18) is valid for any $\bar{N}_{\text{PW}}^1$ and $\bar{N}_{\text{PW}}^0$ connected by

$$\bar{N}_{\text{PW}}^0 = \frac{V_0}{V_1} \bar{N}_{\text{PW}}^1. \quad (19)$$

Let us now consider the correction to energy. We can rewrite Eq. (10) in the following way:

$$E_{\text{tot}}^c \{E_{\text{cut}}, V_1\} = E_{\text{tot}}^d \{E_{\text{cut}}, V_1\} + \int_{\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V_1)}^{\bar{N}_{\text{PW}}^c(E_{\text{cut}}, V_1)} \left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right)_V \bigg|_{\substack{V=V_1 \\ \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^1}} d\bar{N}_{\text{PW}}. \quad (20)$$

Inserting Eq. (18) in this expression, we get

$$E_{\text{tot}}^c \{E_{\text{cut}}, V_1\} \approx E_{\text{tot}}^d \{E_{\text{cut}}, V_1\} + \int_{\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V_1)}^{\bar{N}_{\text{PW}}^c(E_{\text{cut}}, V_1)} \frac{V_0}{V_1} \left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right)_V \bigg|_{\substack{V=V_0 \\ \bar{N}_{\text{PW}}=\frac{V_0}{V_1} \bar{N}_{\text{PW}}^1}} d\bar{N}_{\text{PW}}. \quad (21)$$

By introducing the change of variables given by Eq. (19), we get

$$E_{\text{tot}}^c \{E_{\text{cut}}, V_1\} \approx E_{\text{tot}}^d \{E_{\text{cut}}, V_1\} + \int_{\frac{V_0}{V_1} \bar{N}_{\text{PW}}^d(E_{\text{cut}}, V_1)}^{\frac{V_0}{V_1} \bar{N}_{\text{PW}}^c(E_{\text{cut}}, V_1)} \left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right)_V \bigg|_{\substack{V=V_0 \\ \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^0}} d\bar{N}_{\text{PW}}. \quad (22)$$

Finally, we have

$$E_{\text{tot}}^c \{E_{\text{cut}}, V_1\} \approx E_{\text{tot}}^d \{E_{\text{cut}}, V_1\} + E_{\text{tot}} \left[\frac{V_0}{V_1} \bar{N}_{\text{PW}}^c(E_{\text{cut}}, V_1), V_0 \right] - E_{\text{tot}} \left[\frac{V_0}{V_1} \bar{N}_{\text{PW}}^d(E_{\text{cut}}, V_1), V_0 \right]. \quad (23)$$

This expression allows us to correct the value of energy obtained at V_1 by using the interpolating curve $E_{\text{tot}} [\bar{N}_{\text{PW}}, V]$

calculated at V_0 .

Let us finally consider the correction to pressure. We can get different expressions depending on the way we work starting from Eq. (10). We can either use the scaling approximation and then differentiate with respect to the volume, or vice versa. In the first case, we start from Eq. (23) and differentiate it with respect to the volume at fixed cutoff energy. This leads to

$$P^c \{E_{\text{cut}}^1, V_1\} \approx P^d \{E_{\text{cut}}^1, V_1\} - \frac{V_0}{V_1^2} \bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1) \left(\frac{\partial E_{\text{tot}}[\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right) \bigg|_V \bigg|_{\substack{V=V_0 \\ \bar{N}_{\text{PW}} = \frac{V_0}{V_1} \bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1)}}. \quad (24)$$

Using Eq. (18), this can be rewritten:

$$P^c \{E_{\text{cut}}^1, V_1\} \approx P^d \{E_{\text{cut}}^1, V_1\} - \frac{\bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1)}{V_1} \left(\frac{\partial E_{\text{tot}}[\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right) \bigg|_V \bigg|_{\substack{V=V_1 \\ \bar{N}_{\text{PW}} = \bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1)}}. \quad (25)$$

On the other side, we can start from Eq. (11) and use the approximation Eq. (15) and its consequences. This leads to

$$P^c \{E_{\text{cut}}^1, V_1\} \approx P^d \{E_{\text{cut}}^1, V_1\} + \frac{V_1}{V_0} \left(P \left[\frac{V_0}{V_1} \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1), V_0 \right] - P \left[\frac{V_0}{V_1} \bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1), V_0 \right] \right) - \frac{V_0}{V_1^2} \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1) \left(\frac{\partial E_{\text{tot}}[\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right) \bigg|_V \bigg|_{\substack{V=V_0 \\ \bar{N}_{\text{PW}} = \frac{V_0}{V_1} \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)}}. \quad (26)$$

Between these different, but equivalent, expressions of the correction to pressure Eq. (24) is the most convenient, because it simply needs the interpolation of E_{tot} as a function of $\bar{N}_{\text{PW}}$ for a given reference volume V_0 .

IV. COMPARISON WITH OTHER TECHNIQUES

While the S.H., presented in the preceding section, starts from the correction to energy and proceeds by derivation to obtain the correction to pressure, Francis and Payne¹¹ have proposed a technique for the correction to energy that starts from the correction to pressure proposed by Froyen and Cohen¹⁰ and proceeds by integration. Let us recall their results.

A. Froyen-Cohen correction to pressure

The expression proposed by Froyen and Cohen for the correction to pressure is the following:

$$P_{\text{FC}}^c \{E_{\text{cut}}^1, V_1\} = P^d \{E_{\text{cut}}^1, V_1\} - \frac{2}{3} \frac{E_{\text{cut}}^1}{V_1} \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right) \bigg|_V \bigg|_{\substack{V=V_1 \\ E_{\text{cut}} = E_{\text{cut}}^1}}. \quad (27)$$

The definition of an interpolating energy curve is also central in this approach.

Let us develop Eq. (27) to compare it with the accurate correction to pressure Eq. (11) and our approximations Eqs. (24) and (26). By using the chain rule in Eq. (27), we easily get

$$P_{\text{FC}}^c \{E_{\text{cut}}^1, V_1\} = P^d \{E_{\text{cut}}^1, V_1\} - \frac{\bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)}{V_1} \left(\frac{\partial E_{\text{tot}}[\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right) \bigg|_V \bigg|_{\substack{V=V_1 \\ \bar{N}_{\text{PW}} = \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)}}, \quad (28)$$

where one term is missing compared to Eq. (11).

Let us continue the analysis. By using the scaling hypothesis in the form of Eq. (15) and Eq. (18), respectively, in Eq. (27) and Eq. (28), we get

$$P_{\text{FC}}^c \{E_{\text{cut}}^1, V_1\} = P^d \{E_{\text{cut}}^1, V_1\} - \frac{2}{3} \frac{E_{\text{cut}}^1}{V_1} \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V \bigg|_{\substack{V=V_0 \\ E_{\text{cut}}=E_{\text{cut}}^1}}, \quad (29)$$

$$= P^d \{E_{\text{cut}}^1, V_1\} - \frac{V_0}{V_1^2} \bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1) \left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right)_V \bigg|_{\substack{V=V_0 \\ \bar{N}_{\text{PW}} = \frac{V_0}{V_1} \bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1)}}, \quad (30)$$

where clearly one term is missing in regard to Eq. (26). When this equation is compared to Eq. (24), we see that $\bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1)$ is changed into $\bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1)$. This is due to an inaccurate definition of the Pulay stress (as shown in Appendix B).

Between these different expressions of the correction to pressure, Eq. (30) is the most convenient, because it just needs an interpolation of E_{tot} as a function of $\bar{N}_{\text{PW}}$ for a given reference volume V_0 .

Before going further, we illustrate the two proposed stress correction techniques in Fig. 4. We draw the output of a computer run $P^d \{E_{\text{cut}}^1, V_1\}$ and the curves $P^c \{E_{\text{cut}}^1, V_1\}$ obtained, respectively, by applying to it either the correction given by Eq. (24) or the Froyen-Cohen correction given by Eq. (30). We also draw the curve obtained by applying the following pressure correction:

$$P^* \{E_{\text{cut}}^1, V_1\} = P^d \{E_{\text{cut}}^1, V_1\} + \frac{V_1}{V_0} \left(P \left[\frac{V_0}{V_1} \bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1), V_0 \right] - P \left[\frac{V_0}{V_1} \bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1), V_0 \right] \right), \quad (31)$$

which consists of adding to $P^d \{E_{\text{cut}}^1, V_1\}$ the missing term in Eq. (30) in regard to Eq. (26) [which is equivalent to Eq. (24)]. The graph clearly shows the importance of each term of the proposed corrections. The correction of Froyen and Cohen given by Eq. (30) is responsible for a shift of the uncorrected curve, whereas the correction given by Eq. (31) is responsible for the cancellation of the jumps between the microcurves. The S.H. correction includes these two effects as can be seen from Eq. (26) and Fig. 4. The first is definitely the most important, but the second is not negligible. Moreover, Eq. (24) or Eq. (30) is equally easy to use, so that the more accurate Eq. (24) should always be preferred.

B. Francis-Payne correction to energy

The expression proposed by Francis and Payne for the correction to energy is the following (see Appendix C):

$$E_{\text{tot,FP}}^c \{E_{\text{cut}}^1, V_1\} = E_{\text{tot}}^d \{E_{\text{cut}}^1, V_1\} - \frac{2E_{\text{cut}}^1}{3} \ln \left(\frac{\bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1)}{\bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1)} \right) \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V \bigg|_{\substack{V=V_1 \\ E_{\text{cut}}=E_{\text{cut}}^1}}. \quad (32)$$

It can be shown (see Appendix C) that the derivation of this expression implies the use of the approximation given by Eq. (15). Moreover, it is obtained by integrating the Pulay stress expression proposed by Froyen and Cohen, which is inaccurate (see Appendix B). By using the chain rule in Eq. (32), we get

$$E_{\text{tot,FP}}^c \{E_{\text{cut}}^1, V_1\} = E_{\text{tot}}^d \{E_{\text{cut}}^1, V_1\} - \bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1) \ln \left(\frac{\bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1)}{\bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1)} \right) \times \left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right)_V \bigg|_{\substack{V=V_1 \\ \bar{N}_{\text{PW}} = \bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1)}}. \quad (33)$$

By using our approximation in the form of Eq. (15) in Eq. (32), we get

$$E_{\text{tot,FP}}^c \{E_{\text{cut}}^1, V_1\} = E_{\text{tot}}^d \{E_{\text{cut}}^1, V_1\} - \frac{2E_{\text{cut}}^1}{3} \ln \left(\frac{\bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1)}{\bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1)} \right) \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V \bigg|_{\substack{V=V_0 \\ E_{\text{cut}}=E_{\text{cut}}^1}}. \quad (34)$$

By using our approximation in the form of Eq. (18) in Eq. (33), we get

$$E_{\text{tot,FP}}^c \{E_{\text{cut}}^1, V_1\} = E_{\text{tot}}^d \{E_{\text{cut}}^1, V_1\} - \frac{V_0}{V_1} \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1) \ln \left(\frac{\bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1)}{\bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)} \right) \times \left(\frac{\partial E_{\text{tot}}[\bar{N}_{\text{PW}}, V]}{\partial \bar{N}_{\text{PW}}} \right) \bigg|_{V=V_0, \bar{N}_{\text{PW}} = \frac{V_0}{V_1} \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)} \quad (35)$$

This last expression of the correction to energy is the most convenient, because it just needs an interpolation of E_{tot} as a function of $\bar{N}_{\text{PW}}$ for a given reference volume V_0 .

The comparison with the S.H. technique is not as straightforward as for the correction to pressure. But

it is clear that the inaccuracy in the definition of the Pulay stress, from which Eq. (35) is derived, is a source of error.

V. APPLICATIONS

The importance of the correction is now investigated for silicon, barium titanate, and helium, various materials presenting different types of bonding.

Our calculations, performed within the LDA,¹ use a preconditioned conjugate gradient algorithm.^{15,16} We use a rational polynomial parametrization of the exchange-correlation energy functional,¹⁷ which is based on the Ceperley-Alder gas data.¹⁸ The Brillouin zone is sampled with different Monkhorst-Pack⁶ meshes of special k points. The “all-electron” potentials are replaced by *ab initio*, separable, norm-conserving pseudopotentials, as described below.

Then, we apply Eqs. (23) and (24) to correct the results. The interpolating scheme for obtaining $E_{\text{tot}}[\bar{N}_{\text{PW}}, V_0]$ is the following. We first calculate the total energy for three different values of $\bar{N}_{\text{PW}}$:

$$\begin{aligned} &\bar{N}_{\text{PW}}^d(E_{\text{cut}} - 3\%, V_0), \bar{N}_{\text{PW}}^d(E_{\text{cut}}, V_0), \\ &\bar{N}_{\text{PW}}^d(E_{\text{cut}} + 3\%, V_0). \end{aligned} \quad (36)$$

Then, we interpolate between these values by an exponential fit of the form:

$$E_{\text{tot}}[\bar{N}_{\text{PW}}, V_0] = E_{\text{tot}}^{\text{inf}} + \exp(a_0 + a_1 \bar{N}_{\text{PW}}). \quad (37)$$

First, we apply this correction to bulk silicon, with covalent bonding. The corresponding pseudopotential was built following the scheme proposed in Ref. 19. The atomic positions in the unit cell are completely determined by symmetry: the only free parameter is the lattice parameter a . We compute simultaneously the total energy $E_{\text{tot}}(a)$ and the pressure $P(a)$ as we vary the lattice parameter a at a constant energy cutoff ($E_{\text{cut}}=6$ Hartree with two special k points in the irreducible Brillouin zone). Then, we apply the S.H. correction. The effect of correction to energy in Fig. 5 is obvious: it cancels out the jumps between microcurves. The effect of correction to pressure in Fig. 4 has already been commented on. First, the jumps between microcurves are suppressed. Second, the whole curve is shifted towards larger pressure. These results will be commented on with more details in Sec. VI. The lattice parameter value is found to be 10.23 Bohr.

Then, we consider barium titanate (BaTiO_3), for which we used extended norm-conserving pseudopoten-

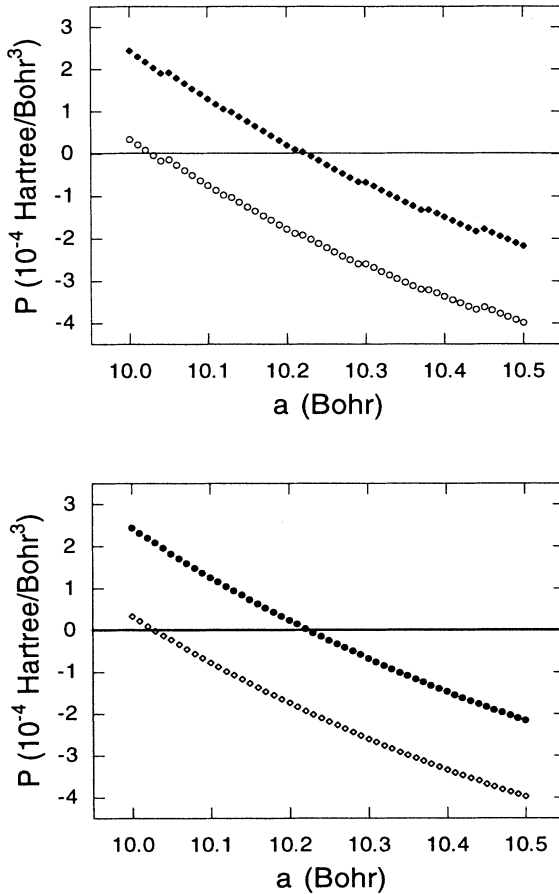


FIG. 4. Pressure in Si calculated at constant cutoff energy ($E_{\text{cut}}=6$ Hartree with two special k points in the IBZ) for 51 lattice constants. (a) The open circles ($\circ$) represent the uncorrected values of pressure, whereas the solid diamonds ($\blacklozenge$) illustrate the values corrected by the Froyen-Cohen technique. (b) The open diamonds ($\diamond$) represent partially corrected values of pressure [see P^* defined by Eq. (31) in the text], whereas the solid circles ($\bullet$) are the values corrected by the S.H. technique. The graphs (a) and (b) point out that the S.H. correction technique ($\bullet$) has two effects. The first is a shift of the uncorrected curve ($\circ$), also included in Froyen-Cohen technique ($\blacklozenge$), whereas the second is the cancellation of microcurve jumps that is also present in the partial correction ($\diamond$).

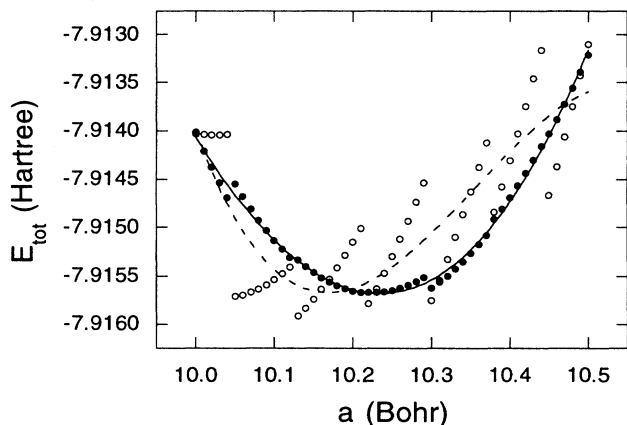


FIG. 5. Total energy of Si calculated at constant cutoff energy ($E_{\text{cut}}=6$ Hartree with two special k points in the IBZ) for 51 lattice constants. The open circles (o) represent the uncorrected values of total energy, whereas the solid circles (●) illustrate the values corrected by the S.H. technique. The solid curve and (respectively) the broken curve are obtained by a least-squares third-order fit to the corrected and (respectively) uncorrected data. The solid curve yields a lattice parameter of 10.23 Bohr, whereas the broken curve yields 10.17 Bohr.

tials given in Ref. 20. This material is sometimes classified as an ionic compound. As pointed out recently, it also presents a partial covalent character.^{21,22} Its structure is cubic perovskite at high temperature (above about 120 °C), while it undergoes three successive ferroelectric phase transitions as the temperature goes down. In this study, we will focus on the cubic, high symmetry phase in

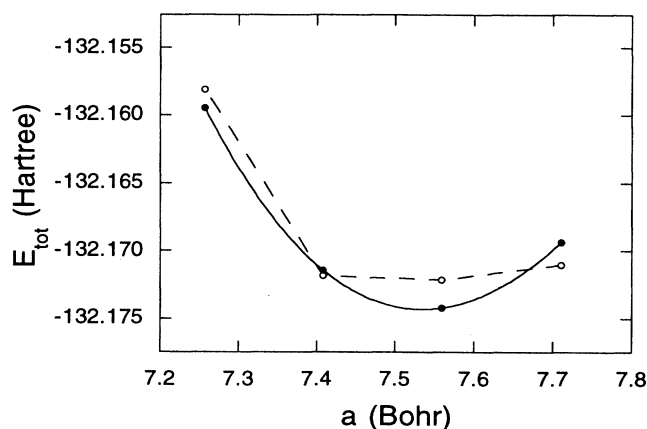


FIG. 6. Total energy of cubic BaTiO₃ calculated at constant cutoff energy ($E_{\text{cut}}=20$ Hartree with four special k points in the IBZ) for four lattice constants. The open circles (o) represent the uncorrected values of total energy, whereas the solid circles (●) are the values corrected by the S.H. technique. The corrected values of energy are joined by a least-squares third-order fit (solid curve). Without correction, the residual noise leads to incorrect values of the static equilibrium properties, as there are not enough data. The lattice parameter value is found to be 7.53 Bohr from the solid line.

which the atoms are at symmetric positions, so that the only structural degree of freedom is the lattice parameter a . When using the S.H. correction, a first estimation of a_0 at 7.53 Bohr is already possible on the basis of only four points at a 20 Hartree cutoff with four points in the irreducible Brillouin zone (see Fig. 6). For BaTiO₃, an accurate investigation of some properties (as, for example, the phonon frequencies) requires it nevertheless to work at a 45 Hartree energy cutoff on a $6 \times 6 \times 6$ mesh of k points. At this high cutoff, the total energy is well converged ($\frac{\partial E_{\text{tot}}}{\partial N_{\text{PW}}}$ is very small), so that the correction on E_{tot} becomes negligible (Fig. 7). We predict a lattice parameter of 7.45 Bohr in good agreement with other LDA calculations. By contrast, even for this case, the error on the pressure remains critical. As illustrated in Fig. 7, it can be efficiently corrected when using the S.H. technique. This correct estimation of the pressure proves

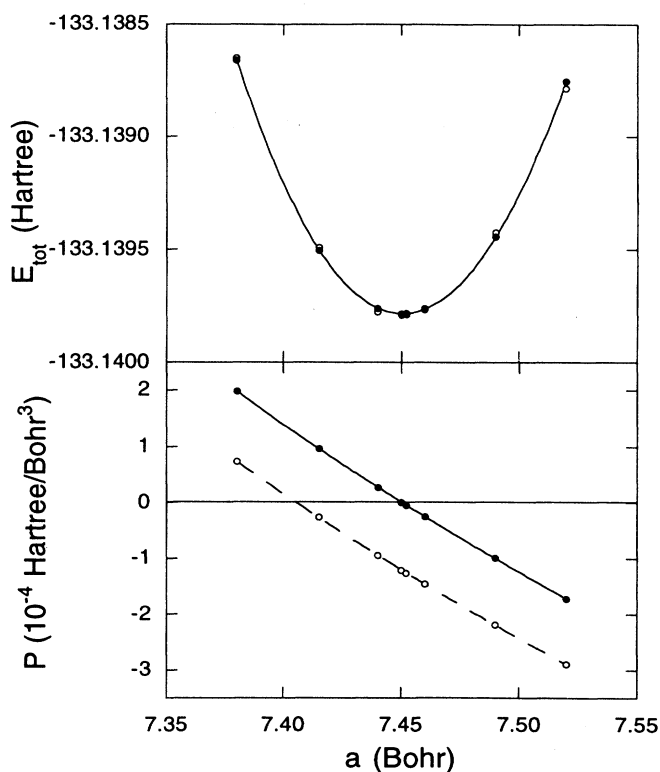


FIG. 7. Total energy and pressure of cubic BaTiO₃ calculated at constant cutoff energy ($E_{\text{cut}}=45$ Hartree with ten special k points in the IBZ) for eight lattice constants. The open circles (o) represent the uncorrected values (joined by a scattered dashed line), whereas the solid circles (●) illustrate the values corrected by the S.H. technique. The corrected values of energy and pressure are joined by a least-squares third-order fit (solid curves). For total energy, the values obtained with or without correction are nearly the same (a high energy cutoff has been used, which leads to well converged values of total energy). For pressure, instead, the values obtained with or without correction differ despite the high energy cutoff. The lattice parameter value is found to be 7.45 Bohr from the solid lines.

essential for the investigation of the energy surface of the low symmetry phases.

Finally, we perform an energetic calculation for fcc helium. Once again, we observe the cancellation of the scattering in the total energy data and the shift of the pressure curve, showing that the correction is independent of this type of bonding, and applicable to a large range of materials. These results will be published in a future paper.²³

VI. COMPARISON OF THE TECHNIQUES

It has been shown in the previous section that corrections to energy and stresses can be rather important. Now, we analyze in more detail their importance, and we compare more quantitatively the two possible correction techniques in the case of silicon [Eqs. (23) and (24) for the scaling hypothesis technique, Eqs. (30) and (35) for the Froyen-Cohen technique and Francis-Payne technique]. We investigate different aspects of this correction, more specifically, we analyze its effect on the calculation of the lattice constant a_0 , the bulk modulus B_0 , and its pressure derivative B'_0 . These properties can easily be determined either from the curve of energy E_{tot} versus lattice constant a (or, in an equivalent way, versus volume as $V \propto a^3$) or from that of pressure P versus lattice constant a . In order to obtain the $E_{\text{tot}}(a)$ and $P(a)$ curves, we calculate the total energy and the pressure for a set of lattice constants at a given cutoff energy.

As we mentioned above, the result is a set of microcurves: $E_{\text{tot}}^d\{E_{\text{cut}}, a\}$ and $P^d\{E_{\text{cut}}, a\}$. By fitting a polynomial to these values, we get continuous curves $E_{\text{tot}}(a)$ and $P(a)$. Depending on its degree, the polynomial fit matches more or less accurately the data. We measure the matching by the standard deviation χ of the data (x_i, y_i) from the polynomial $g(x)$:

$$\chi = \sqrt{\frac{\sum_{i=1}^N [y_i - g(x_i)]^2}{N - 1}}, \quad (38)$$

where N is the number of data. For example, from Fig. 5, we have calculated the value of χ for, respectively, uncorrected data (open circles) and those obtained with the S.H. correction (solid circles), with respect to their corresponding polynomial fit (respectively, the broken curve and the solid one). We illustrate in Fig. 8 the evolution of χ as a function of the degree of the polynomial. On one side, it is evident that the higher the degree of the polynomial is, the better the matching with the data will be. On the other side, the aim of the fitting is to get rid of the noise,²⁴ due to jumps between microcurves. The higher the degree, the greater the part of this noise included in the fit. So, a compromise has to be reached. We will consider that the separation between trustworthy data and the noise has been accomplished as soon as the standard deviation reaches a plateau (called residual noise) as a function of the degree of the polynomial. Going to a higher-order polynomial would mean beginning

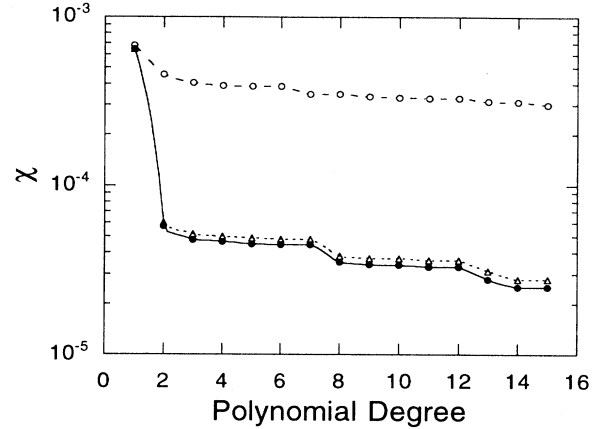


FIG. 8. Semilogarithmic plot of standard deviation χ of the data, as a function of the degree of the polynomial (obtained by least-squares fit). The standard deviation χ , which is defined by Eq. (38) in the text, is a measure of the matching of a polynomial to the total energies of Si calculated at constant cutoff energy ($E_{\text{cut}}=6$ Hartree with two special k points in the IBZ) for 51 lattice constants, see Fig. 5. The open circles ($\circ$) represent χ calculated from uncorrected values of total energy, the open triangle (Δ) represents that calculated from the values corrected by the Froyen-Cohen technique, whereas the solid circles ($\bullet$) represent that calculated from the values corrected by the S.H. technique. The graph clearly illustrates the reduction of χ with the correction.

to include the residual noise in the fit. So, the degree of the polynomial is chosen by detection of a plateau in the standard deviation of the data from the polynomial. In Fig. 8, this plateau is already reached for a polynomial of the third degree.

We apply the different techniques presented in the previous sections to correct the calculated values. By fitting a polynomial to these values, we get two different expressions of $E_{\text{tot}}^c\{E_{\text{cut}}, a\}$ and of $P^c\{E_{\text{cut}}, a\}$, corresponding to the Froyen-Cohen-Francis-Payne correction or to the scaling hypothesis. So, finally, we have three different expressions of the $E_{\text{tot}}(a)$ and $P(a)$ curves.

However, if there are not enough data, statistical fluctuations occur on the static equilibrium properties (a_0 , B_0 , and B'_0), due to the noise²⁴ present when the correction is not used (see Figs. 5–7 of Sec. V, especially for BaTiO₃). So, from now on, we will work with a large number of data points in order to suppress these fluctuations, and concentrate on the techniques.

A. Scale analysis

In order to analyze quantitatively the reduction of noise, we consider different sets of a lattice parameter, each set being characterized by a given scale, which is defined as the distance between two successive points of the set. We consider six different scales: 0.01, 0.025,

TABLE I. List of the different sets of lattice constants (expressed in atomic units) and the corresponding degree of the polynomial used to fit the data.

Scale	Points of the set	Number of points	Degree of the polynomial
0.01	10.00 – 10.50	51	3
0.025	10.00 – 10.50	21	3
0.05	9.90 – 10.60	15	3
0.1	9.50 – 11.00	16	3
0.2	9.00 – 11.60	14	4
0.5	7.00 – 13.00	13	8

0.05, 0.1, 0.2, and 0.5 Bohr (see Table I). We generate the three different $E_{\text{tot}}(a)$ curves and of the three $P(a)$ ones for all these sets. From these curves, we determine the lattice constant a_0 , the bulk modulus B_0 , and its pressure derivative B'_0 .

Many observations occur. The residual noise in the

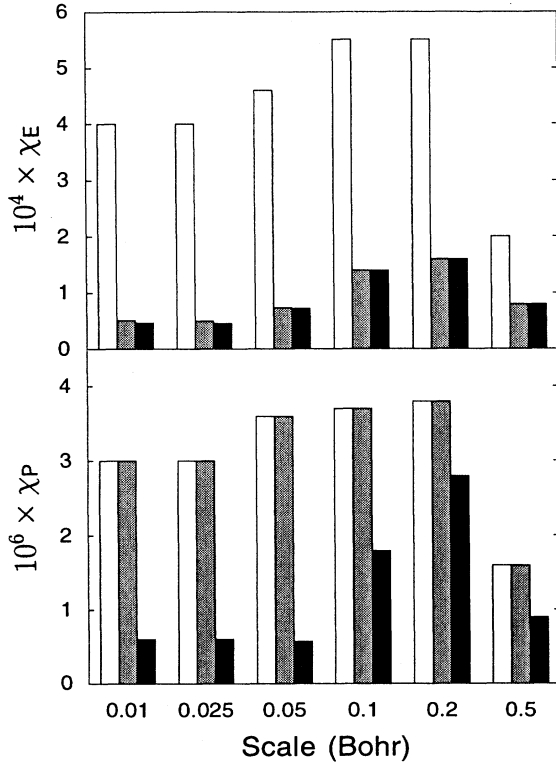


FIG. 9. Plot of standard deviations χ_E (top) and χ_P (bottom) of the energy and pressure data calculated at different scales at constant cutoff energy ($E_{\text{cut}}=6$ Hartree with two special k points in the IBZ) for 51 lattice constants. The white bars represent the standard deviation χ calculated from uncorrected data, the gray bars illustrate the one calculated from the values corrected by the Froyen-Cohen technique for pressure and by the Francis-Payne technique for energy, whereas the black bars represent that calculated from the values corrected by the S.H. technique. The graph illustrates that the reduction of χ is more important for small scales than large ones. Note also that the Froyen-Cohen technique does not reduce the noise in the pressure data.

energy and pressure data is decreased by the correction. This noise reduction is more important for small scales than large ones (see Fig. 9). This is due to the fact that the presence of microcurves is much more apparent at small than at large scales. So, for the *energy* curve, the results obtained at large scales with and without correction do not differ significantly. Whereas, for the *pressure* curve, the correction also includes a shift of the uncorrected curve: whatever the scale, the correction is always important. So, from now on, we just discuss the results obtained with the corrected values of energy and pressure. Regarding the lattice constant, it can be seen (see Table II) that there is a quite good agreement between the values obtained at the different scales and between those obtained starting from the $E_{\text{tot}}(a)$ curve and those calculated from the $P(a)$ one. Regarding the bulk modulus, there is still a very good agreement between the values obtained at the different scales from the pressure curve, but not between those calculated from the energy one (see Table III). Moreover, the values obtained starting from the $E_{\text{tot}}(a)$ curve and those calculated from the $P(a)$ curve agree only at large scale. Regarding the derivative of the bulk modulus versus pressure, the agreement is worse (these data are not reproduced here). As a general rule for the calculation of static equilibrium properties (a_0 , B_0 , and B'_0), we can state that first, calculations based on the pressure data are more accurate than those based on energy data, and second, the accuracy decreases with the number of derivatives taken from the starting curve.

Regarding the different proposed techniques, it can be noticed that their results are nearly the same. This is due to the fitting operation that eliminates the residual noise. Note, nevertheless, that it is always lower with the S.H. technique, especially for the pressure curve (see Fig. 4).

B. Microcurve analysis

When studying the small scales, in the previous section, microcurves corresponding to a constant number of plane waves have been detected. The analysis of these microcurves separately will emphasize the efficiency of the different corrections.

For this purpose, we consider the scale 0.01 Bohr with the following sets of points for each microcurve (see open circles in Fig. 5): from 10.00 to 10.04, from 10.05 to

TABLE II. Equilibrium lattice constant calculated at different scales ($E_{\text{cut}}=6$ Hartree with two special k points in the IBZ) from the energy curve before (before) and after the correction with the Francis-Payne technique (F.-P.) or scaling hypothesis technique (S.H.), and from the pressure curve before (before) and after the correction with the Froyen-Cohen technique (F.-C.) or scaling hypothesis technique (S.H.). The values are expressed in Bohr. σ is the standard deviation between the results obtained for the different scales.

Scale	From energy			From pressure		
	Before	F.-P.	S.H.	Before	F.-C.	S.H.
0.01	10.1672	10.2340	10.2341	10.0301	10.2234	10.2245
0.025	10.1678	10.2349	10.2351	10.0312	10.2236	10.2243
0.05	10.1997	10.2241	10.2239	10.0308	10.2241	10.2245
0.1	10.2136	10.2266	10.2262	10.0295	10.2236	10.2224
0.2	10.2196	10.2243	10.2241	10.0272	10.2241	10.2249
0.5	10.2287	10.2188	10.2188	10.0280	10.2256	10.2241
μ	10.1994	10.2271	10.2270	10.0294	10.2241	10.2241
σ	2.6×10^{-2}	6.2×10^{-3}	6.3×10^{-3}	1.6×10^{-3}	8.1×10^{-4}	8.8×10^{-4}

TABLE III. Equilibrium bulk modulus calculated at different scales ($E_{\text{cut}}=6$ Hartree with two special k points in the IBZ) from the energy curve before (before) and after the correction with the Francis-Payne technique (F.-P.) or scaling hypothesis technique (S.H.), and from the pressure curve before (before) and after the correction with the Froyen-Cohen technique (F.-C.) or scaling hypothesis technique (S.H.). The values are expressed in Mbar. σ is the standard deviation between the results obtained for the different scales.

Scale	From energy			From pressure		
	Before	F.-P.	S.H.	Before	F.-C.	S.H.
0.01	1.181	0.8243	0.8233	1.071	0.9849	0.9419
0.025	1.079	0.8390	0.8368	1.088	0.9823	0.9417
0.05	0.8326	0.8860	0.8859	1.123	0.9560	0.9426
0.1	1.0030	0.9709	0.9710	1.127	0.9482	0.9412
0.2	0.9546	0.9630	0.9601	1.115	0.9333	0.9285
0.5	0.9539	0.9485	0.9481	1.108	0.9321	0.9411
μ	1.0007	0.9053	0.9042	1.1053	0.9561	0.9395
σ	1.2×10^{-1}	6.5×10^{-2}	6.5×10^{-2}	2.2×10^{-2}	2.3×10^{-2}	5.4×10^{-3}

TABLE IV. Equilibrium lattice constant calculated for the different microcurves ($E_{\text{cut}}=6$ Hartree with two special k points in the IBZ) from the energy curve before (before) and after the correction with the Francis-Payne technique (F.-P.) or scaling hypothesis technique (S.H.), and from the pressure curve before (before) and after the correction with the Froyen-Cohen technique (F.-C.) or scaling hypothesis technique (S.H.). The values are expressed in Bohr. σ is the standard deviation between the results obtained for the different scales.

Microcurve	From energy			From pressure		
	Before	F.-P.	S.H.	Before	F.-C.	S.H.
1	10.0263	10.2000	10.2287	10.0263	10.1996	10.2279
2	10.0380	10.2138	10.2262	10.0380	10.2135	10.2258
3	10.0423	10.2188	10.2260	10.0425	10.2188	10.2260
4	10.0537	10.2247	10.2241	10.0473	10.2245	10.2241
5	10.0529	10.2328	10.2224	10.0544	10.2328	10.2226
6	10.0577	10.2400	10.2216	10.0605	10.2404	10.2222
7	10.0671	10.2527	10.2200	10.0711	10.2534	10.2213
μ	10.0482	10.2261	10.2241	10.0485	10.2261	10.2241
σ	1.4×10^{-2}	1.7×10^{-2}	3.1×10^{-3}	1.5×10^{-2}	1.8×10^{-2}	2.4×10^{-3}

TABLE V. Equilibrium bulk modulus calculated for the different microcurves ($E_{\text{cut}}=6$ Hartree with two special k points in the IBZ) from the energy curve before (before) and after the correction with the Francis-Payne technique (F.-P.) or scaling hypothesis technique (S.H.), and from the pressure curve before (before) and after the correction with the Froyen-Cohen technique (F.-C.) or scaling hypothesis technique (S.H.). The values are expressed in Mbar. σ is the standard deviation between the results obtained for the different scales.

Microcurve	From energy			From pressure		
	Before	F.-P.	S.H.	Before	F.-C.	S.H.
1	1.244	1.080	0.9178	1.244	1.087	0.9294
2	1.226	1.063	0.9203	1.227	1.069	0.9278
3	1.215	1.062	0.9253	1.220	1.062	0.9261
4	1.278	1.071	0.9428	1.211	1.056	0.9281
5	1.125	1.044	0.9260	1.201	1.047	0.9295
6	1.165	1.031	0.9201	1.189	1.037	0.9285
7	1.142	1.012	0.9143	1.171	1.022	0.9276
μ	1.1993	1.0518	0.9238	1.2090	1.0543	0.9281
σ	5×10^{-2}	2×10^{-2}	1×10^{-2}	2×10^{-2}	2×10^{-2}	1×10^{-3}

10.12, from 10.13 to 10.21, from 10.22 to 10.29, from 10.30 to 10.37, from 10.38 to 10.44, and from 10.45 to 10.50. We generate for each of these microcurves the three different $E_{\text{tot}}(a)$ curves and the three $P(a)$ ones. From these curves, we also determine the lattice constant a_0 , the bulk modulus B_0 , and its pressure derivative B'_0 .

Regarding the lattice constant, the agreement between the values obtained for the different microcurves (see mean value μ and standard deviation σ in Table IV) is much better with the S.H. technique than with the Froyen-Cohen or Francis-Payne technique. Note also that there is a very good consistency between the values obtained starting from the $E_{\text{tot}}(a)$ curve and those calculated from the $P(a)$ one.

Regarding the bulk modulus, there is still a very good accordance between the values obtained for the different microcurves from the pressure curve, but it is a little bit worse for those calculated from the energy one (see mean value μ and standard deviation σ in Table V). Moreover, the values obtained starting from the $E_{\text{tot}}(a)$ curve and those calculated from the $P(a)$ one agree very well.

Regarding the derivative of the bulk modulus versus pressure, the agreement is worse, except for results obtained by calculations based on the pressure curve with the S.H. technique (these data are not reproduced here). The conclusions, regarding the calculation of static equilibrium properties (a_0 , B_0 , and B'_0), drawn in the scale analysis still apply for microcurve analysis.

Regarding the different techniques, the results are generally not the same. This is due to the fact these techniques transform the original microcurve into different microcurves. The agreement of the results between the microcurves is a measure of the effectiveness of the correction method. In this case, it clearly shows that the S.H. is the best. When looking at Fig. 5, we see that there are still discontinuities (this should be analyzed by further studies) in $E_{\text{tot}}(a)$ curve though there is a good agreement of the slopes between the microcurves. This means that the microcurves are parallel, which is confirmed by the fact that there are no discontinuities in the

$P(a)$ curve.

We have also tested the validity of the approximation given by Eq. (15). The first test consists of using a reference volume different for each microcurve. In doing so, the difference between V and V_0 is smaller and, thus, the influence of the approximation should be reduced. It appears that the results obtained (not reproduced here) are almost not affected, in favor of the scaling hypothesis Eq. (15). The second test consists of not introducing the approximation. This can only be done for a reduced set of lattice constants, for example a microcurve, because it makes it necessary to calculate $E_{\text{tot}}[\bar{N}_{\text{PW}}, V]$ for each of the lattice constants. Unfortunately, this increases the residual noise so that no comparison can be made, and this second test is inconclusive.

C. Convergence analysis

We finally analyze the effect of the correction on the convergence of the calculated values of a_0 , B_0 , and B'_0 in cutoff energy (working successively at 3, 6, 10, and 15 Hartree, the latter considered as giving completely converged values) and number of special k points (working successively with two, six, and ten special points, the latter considered as giving completely converged values) for three different scales (0.01, 0.1, and 0.5). We see that working at $E_{\text{cut}}=10$ Hartree with two special k points can be considered as converged enough (it leads to a relative error of 0.1% on a_0 , 1% on B_0 and B'_0). From Tables VI and VII, we see that the convergence is not really improved by the correction, except for the result obtained from the pressure curve. This can be explained by the fact that the fitting operation acts as a correction by eliminating the residual noise on the energy curve, so that the results with and without correction are nearly the same. In the limit of a very large number of data points, this implicit correction is sufficient. However, in practical applications, very few points are used, and the correction is needed to avoid the statistical fluctuations

TABLE VI. Equilibrium lattice constant calculated with a different cutoff energy at scale 0.1 (with two special k points in the IBZ) from the energy curve before (before) and after the correction with the Francis-Payne technique (F.-P.) or scaling hypothesis technique (S.H.), and from the pressure curve before (before) and after the correction with the Froyen-Cohen technique (F.-C.) or scaling hypothesis technique (S.H.). The values are expressed in Bohr. The values in parentheses indicate the relative error with respect to the fully converged value at 15 Hartree, for the same technique.

E_{cut}	From energy			From pressure		
	Before	F.-P.	S.H.	Before	F.-C.	S.H.
3	10.1121 (0.8%)	10.0935 (0.9%)	10.0935 (0.9%)	9.6899 (5%)	10.0856 (1%)	10.0854 (1%)
6	10.2135 (0.2%)	10.2266 (0.4%)	10.2262 (0.4%)	10.0295 (2%)	10.2236 (0.4%)	10.224 (0.4%)
10	10.1897 ($\ll 0.1\%$)	10.1894 ($\ll 0.1\%$)	10.1894 ($\ll 0.1\%$)	10.1771 ($\ll 0.1\%$)	10.1867 ($\ll 0.1\%$)	10.1869 ($\ll 0.1\%$)
15	10.1886	10.1888	10.1888	10.1716	10.1856	10.1856

mentioned above. In this sense, it can be said to improve the convergence. For the pressure, the correction also includes a shift of the uncorrected curve; this explains why the correction is always important whatever the degree of convergence.

VII. ANISOTROPIC DEFORMATIONS

We now consider anisotropic deformations and generalize our technique for stress correction. In this case, the total energy does not only depend on the volume of the unit cell, but also on its shape. In order to be as general as possible, we consider that E_{tot} depends on the matrix $\underline{A}$ formed by the components of unit cell vectors. So that the energy correction given by Eq. (10) becomes, in the case of isotropic deformations,

$$E_{\text{tot}}^c \{E_{\text{cut}}^1, \underline{A}^1\} = E_{\text{tot}}^d \{E_{\text{cut}}^1, \underline{A}^1\} + E_{\text{tot}} \left[\bar{N}_{\text{PW}}^c (E_{\text{cut}}^1, V_1), \underline{A}^1 \right] - E_{\text{tot}} \left[\bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1), \underline{A}^1 \right], \quad (39)$$

where $V_1 = \det \underline{A}^1$ is the volume of the unit cell. We now make the approximation that the difference between energy at $\underline{A}$ and at $\underline{A}^0$ at constant E_{cut} does not depend on E_{cut} :

$$E_{\text{tot}}^c \{E_{\text{cut}}, \underline{A}\} \approx E_{\text{tot}}^c \{E_{\text{cut}}, \underline{A}^0\} + f(\underline{A} \rightarrow \underline{A}^0), \quad \forall E_{\text{cut}}, \quad (40)$$

which is a generalization of Eq. (14). This leads to the generalized forms of Eq. (15):

$$\left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, \underline{A}\}}{\partial E_{\text{cut}}} \right)_{\underline{A}} \bigg|_{\substack{\underline{A}=\underline{A}^1 \\ E_{\text{cut}}=E_{\text{cut}}^1}} \approx \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, \underline{A}\}}{\partial E_{\text{cut}}} \right)_{\underline{A}} \bigg|_{\substack{\underline{A}=\underline{A}^0 \\ E_{\text{cut}}=E_{\text{cut}}^1}} \quad (41)$$

and of Eq. (18),

TABLE VII. Equilibrium bulk modulus calculated with a different cutoff energy at scale 0.1 (with two special k points in the IBZ) from the energy curve before (before) and after the correction with the Francis-Payne technique (F.-P.) or scaling hypothesis technique (S.H.), and from the pressure curve before (before) and after the correction with the Froyen-Cohen technique (F.-C.) or scaling hypothesis technique (S.H.). The values are expressed in Mbar. The values in parentheses indicate the relative error with respect to the fully converged value at 15 Hartree, for the same technique.

E_{cut}	From energy			From pressure		
	Before	F.-P.	S.H.	Before	F.-C.	S.H.
3	1.126 (14%)	1.169 (18%)	1.169 (18%)	1.620 (64%)	1.154 (19%)	1.154 (19%)
6	1.003 (2%)	0.9709 (2%)	0.9710 (2%)	1.1270 (15%)	0.9482 (2%)	0.9412 (3%)
10	0.9889 (0.2%)	0.9902 (0.3%)	0.9902 (0.3%)	0.9805 (0.2%)	0.9712 (0.2%)	0.9714 (0.2%)
15	0.9875	0.9872	0.9872	0.9826	0.9692	0.9692

$$\left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, \underline{A}]}{\partial \bar{N}_{\text{PW}}} \right)_{\underline{A}} \bigg|_{\substack{\underline{A}=\underline{A}^1 \\ \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^1}} \approx \frac{V_0}{V_1} \left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, \underline{A}]}{\partial \bar{N}_{\text{PW}}} \right)_{\underline{A}} \bigg|_{\substack{\underline{A}=\underline{A}^0 \\ \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^0}}, \quad (42)$$

where

$$\bar{N}_{\text{PW}}^0 = \frac{V_0}{V_1} \bar{N}_{\text{PW}}^1 = \frac{\det \underline{A}^0}{\det \underline{A}^1} \bar{N}_{\text{PW}}^1. \quad (43)$$

Finally, the generalized energy correction follows:

$$E_{\text{tot}}^c \{E_{\text{cut}}, \underline{A}^1\} \approx E_{\text{tot}}^d \{E_{\text{cut}}, \underline{A}^1\} + E_{\text{tot}} \left[\frac{V_0}{V_1} \bar{N}_{\text{PW}}^c (E_{\text{cut}}, V_1), \underline{A}^0 \right] - E_{\text{tot}} \left[\frac{V_0}{V_1} \bar{N}_{\text{PW}}^d (E_{\text{cut}}, V_1), \underline{A}^0 \right]. \quad (44)$$

Deriving this expression with respect to the strain $\epsilon_{\alpha\beta}$ at fixed cutoff energy, we get the stress correction,

$$\sigma_{\alpha\beta}^c \{E_{\text{cut}}^1, \underline{A}^1\} \approx \sigma_{\alpha\beta}^d \{E_{\text{cut}}^1, \underline{A}^1\} + \delta_{\alpha\beta} \frac{V_0}{V_1^2} \bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1) \left(\frac{\partial E_{\text{tot}} [\bar{N}_{\text{PW}}, \underline{A}]}{\partial \bar{N}_{\text{PW}}} \right)_{\underline{A}} \bigg|_{\substack{\underline{A}=\underline{A}^0 \\ \bar{N}_{\text{PW}}=\frac{V_0}{V_1} \bar{N}_{\text{PW}}^d (E_{\text{cut}}^1, V_1)}}, \quad (45)$$

where we have used the following definitions:

$$\sigma_{\alpha\beta}^d \{E_{\text{cut}}^1, \underline{A}^1\} = \left(\frac{\partial E_{\text{tot}}^d \{E_{\text{cut}}, \underline{A}\}}{\partial \epsilon_{\alpha\beta}} \right)_{E_{\text{cut}}} \bigg|_{\substack{\underline{\epsilon}=0 \\ \underline{A}=\underline{A}^1 \\ E_{\text{cut}}=E_{\text{cut}}^1}}, \quad (46)$$

and

$$\sigma_{\alpha\beta}^c \{E_{\text{cut}}^1, \underline{A}^1\} = \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, \underline{A}\}}{\partial \epsilon_{\alpha\beta}} \right)_{E_{\text{cut}}} \bigg|_{\substack{\underline{\epsilon}=0 \\ \underline{A}=\underline{A}^1 \\ E_{\text{cut}}=E_{\text{cut}}^1}}. \quad (47)$$

We have also used the following result:

$$\frac{1}{V_1} \frac{\partial V}{\partial \epsilon_{\alpha\beta}} \bigg|_{\substack{\underline{\epsilon}=0 \\ V=V_1}} = \delta_{\alpha\beta}, \quad (48)$$

which is obtained by deriving the expression of the volume V of a unit cell defined by matrix $\underline{A}$ in terms of the strain tensor $\underline{\epsilon}$, with respect to the unit cell defined by matrix $\underline{A}^1$:

$$\begin{aligned} V = \det \underline{A} &= V_1 \det(\underline{\delta} + \underline{\epsilon}) \\ &= \frac{1}{6} V_1 \epsilon_{ijk} \epsilon_{lmn} (\delta_{il} + \epsilon_{il}) \\ &\quad \times (\delta_{jm} + \epsilon_{jm}) (\delta_{kn} + \epsilon_{kn}). \end{aligned} \quad (49)$$

The third-rank tensor $\underline{\epsilon}$ is defined in order that ϵ_{ijk} is equal to +1 if $\{i, j, k\}$ corresponds to any even permutation of $\{1, 2, 3\}$, to -1 if $\{i, j, k\}$ corresponds to any odd permutation of $\{1, 2, 3\}$, to 0 in every other case.

It can be shown from Eq. (45) that the stress correction only concerns the diagonal part of the stress tensor $\sigma_{\alpha\beta}$.

This result had already been mentioned by Vanderbilt,²⁵ but in a form similar to that proposed by Froyen and Cohen.¹⁰ More precisely, the stress tensor $\sigma_{\alpha\beta}$ can be decomposed into an isotropic contribution $\sigma_{\alpha\beta}^h$ (where the h superscript stands for “hydrostatic”) and an anisotropic one $\sigma_{\alpha\beta}^d$ (where the d superscript stands for “deviatory”):

$$\sigma_{\alpha\beta}^h = -P \delta_{\alpha\beta} \quad (50)$$

and

$$\sigma_{\alpha\beta}^d = \sigma_{\alpha\beta} - \sigma_{\alpha\beta}^h, \quad (51)$$

where P is the pressure defined by Eq. (1). From this decomposition, it appears that only the isotropic part $\sigma_{\alpha\beta}^h$ of the stress tensor has to be corrected. So, we come back to the case of isotropic deformations and the correction to pressure is given by Eq. (24).

We apply this correction in the case of silicon. The chosen anisotropic deformation corresponds to a compression (or expansion) of the unit cell along the [001] direction, with concurrent expansion (or compression) of the unit cell along the [100] and [010] directions, such that the length of the three cubic directions is changed to $a = b$ and c , while the volume V is unchanged. The energy and the pressure are functions of the ratio $y = b/c$. $\sigma_{11} = \sigma_{22}$ and σ_{33} stresses are present, while nondiagonal stresses vanish. Note that the atomic positions in the unit cell are no longer completely determined by symmetry. The results obtained are shown in Fig. 10. The minimum of the total energy and the zero of stresses nearly correspond to the expected value of $y = 1$ (the relative error is 0.3% for the value obtained from the energy curve and 0.03% for the values obtained from stress curves). The effect of energy correction in Fig. 10 is obvious. In the stress graph, first, there is a suppression of jumps between microcurves. Though it is not visible on the graph, it can be detected by the residual noise reduction (it is approximatively divided by 3). Second, there is a shift of the uncorrected curve. It is the only effect included

in the Froyen-Cohen technique. In this particular case, it is a shift by a constant due to the fact that the deformation is at constant volume. Indeed, $\bar{N}_{PW}^C(E_{cut}, V)$ is

constant in Eq. (30) for the Froyen-Cohen technique and in Eq. (24) for the S.H. technique.

CONCLUSIONS

In this paper, a different means of correcting total energy and stress calculations performed using a fixed cutoff energy plane-wave basis set has been presented. This technique relies on the interpolation of the energy as a function of the number of plane wave, and a scaling hypothesis (S.H.) that allows us to work with a unique reference volume. It has been compared to that of Froyen and Cohen for stress correction and that of Francis and Payne for energy correction, both presented using the same notations. From a theoretical point of view, the approximations used in the different approaches have been contrasted, showing that the scaling hypothesis technique is more rigorous. From a practical point of view, we have shown the importance of the correction by presenting its effects on different materials (Si, BaTiO₃, and He) corresponding to different types of bonding.

Then, we have compared the different methods by analyzing their effect on the calculation of a_0 , B_0 , and B'_0 in bulk silicon starting from both the energy curve and the pressure one. As a general rule, calculations based on the pressure data are more accurate than those based on the energy data. Also, the accuracy reduces with the number of derivatives taken from the starting curve (i.e., pressure derivative of the bulk modulus is more difficult to correct than the bulk modulus). The results of a scale analysis shows that if we do not focus on one microcurve, the benefits of the different correction techniques are rather similar. This is due to the final fitting operation that cancels the residual noise, although the latter is always obtained lower with the S.H. technique. By contrast, the results obtained when working at the microcurve level show that the S.H. is the best, though there are still discontinuities in the $E_{tot}(a)$ curve.

Regarding the convergence with respect to the cutoff energy and to the number of special k points, we see that it is not really improved by the corrections, except for the results obtained by the pressure curve. For the energy curve, in the limit of a very large number of data points, the fitting operation acts as a correction by eliminating the residual noise, and the results with and without correction are nearly the same. However, when working with a small number of data, the correction is needed to avoid statistical fluctuations. For the stress curve, the correction also includes a shift of the uncorrected curve; this explains why the correction is always important whatever the degree of convergence.

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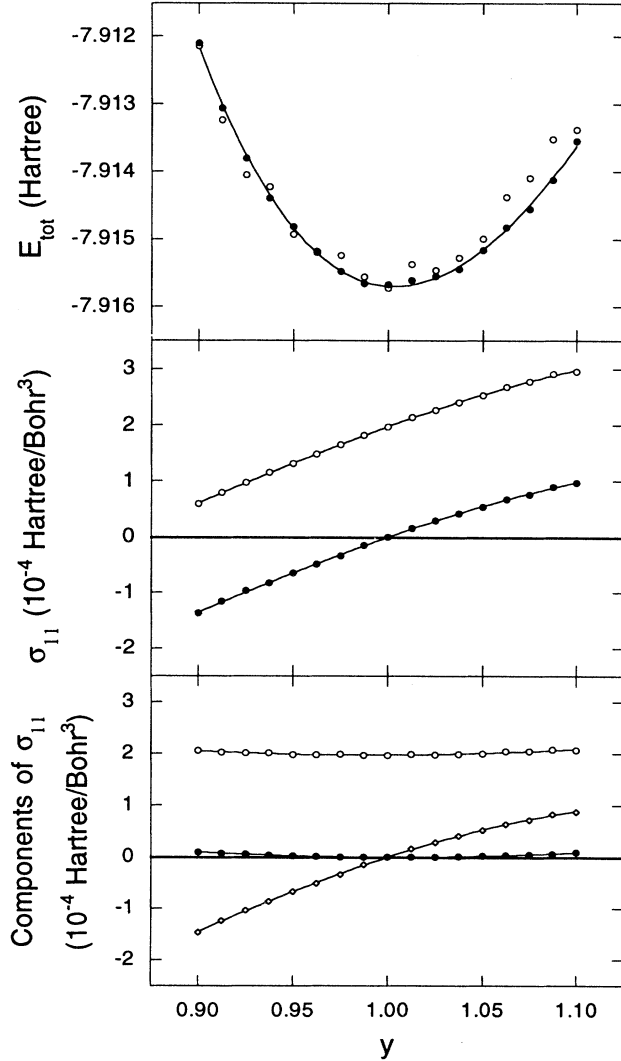


FIG. 10. Total energy (top) and σ_{11} (middle) of Si calculated at constant cutoff energy ($E_{cut}=6$ Hartree with two special k points in the IBZ) for 17 values of the ratio $y = b/c$ in the case of an anisotropic deformation, which consists in compressing (or expanding) the unit cell along the [001] direction in order that the length of the three cubic directions is changed to $a = b$ and c , keeping the volume V unchanged. The open circles ($\circ$) represent the uncorrected values, whereas the solid circles ($\bullet$) are the values corrected by the S.H. technique. The solid curves are obtained by the least-squares third-order fit. The graph points out the effect of the correction, namely, the cancellation of the jumps between the microcurves for energy, and a shift of the curve for stress. A decomposition of σ_{11} into its different components is also presented (bottom). The open circles ($\circ$) represent the uncorrected values of the isotropic part of σ_{11} , whereas the solid circles ($\bullet$) are the values corrected by the S.H. technique. The open diamonds ($\diamond$) illustrate the values of the anisotropic part of σ_{11} that are not affected by the correction.

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APPENDIX A: MEAN NUMBER OF PLANE WAVES

Since the number of plane waves differs at each k point, while the techniques exposed in this paper use a single number to characterize this set, we decide to work with an average number of plane waves. It is not clear how this average should be calculated on the different k points. We can think to an arithmetic mean,

$$\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V) = \sum_k f_k N_{\text{PW},k}^d(E_{\text{cut}}, V), \quad (\text{A1})$$

or to a geometric mean (as suggested by Francis and Payne¹¹),

$$\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V) = \prod_k (N_{\text{PW},k}^d(E_{\text{cut}}, V))^{f_k}, \quad (\text{A2})$$

where f_k are weights defined in order that

$$\sum_k f_k = 1. \quad (\text{A3})$$

An interesting starting point for our reflection would be the expression of the total energy as a function of its value at the different k points. Such an expression is known for some of its components. For example, the kinetic energy is the arithmetic mean of its value $E_{\text{kin},k}$ at the different k points:

$$E_{\text{kin}} = \sum_k f_k E_{\text{kin},k}, \quad (\text{A4})$$

where f_k are the weights of the different k points. On the other hand, the exchange-correlation contribution to total energy is global; it cannot be physically divided in a sum of contributions of each k point. However, we can suppose that Eq. (A4) can be generalized for total energy, so that we can write

$$E_{\text{tot}}^d\{E_{\text{cut}}, V\} = \sum_k f_k E_{\text{tot},k}^d\{E_{\text{cut}}, V\}. \quad (\text{A5})$$

By using Eq. (5) to develop Eq. (A5), we get

$$\begin{aligned} E_{\text{tot}} \left[\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V), V \right] \\ = \sum_k f_k E_{\text{tot},k} \left[N_{\text{PW},k}^d(E_{\text{cut}}, V), V \right]. \end{aligned} \quad (\text{A6})$$

This expression can be considered as a definition of the average number of plane waves.

Unfortunately, it is not very useful as $E_{\text{tot},k}$ is not known as a function of N_{PW} at each different k point. To say something about the definition of $\bar{N}_{\text{PW}}$, we have to consider cases where the total energy at each different k point and the total energy E_{tot} are the same function of N_{PW} [it corresponds to deleting the k subscript of E_{tot} in the right-hand side of Eq. (A6)]. This is precisely the case where the bands are dispersionless, which is the case, e.g., when studying an isolated molecule in a supercell. Let us analyze two of these simple cases. If all these functions were the same linear function of N_{PW} , the definition of $\bar{N}_{\text{PW}}$ given by Eq. (A6) would correspond to an arithmetic mean. Whereas, if all these functions were the same logarithmic function of N_{PW} , the definition of $\bar{N}_{\text{PW}}$ given by Eq. (A6) would correspond to a geometric mean.

In our calculations, we decide to use the geometric mean for defining $\bar{N}_{\text{PW}}$. This choice seems more physical than the arithmetic mean, because the latter is supposed to be a linear dependence of E_{tot} versus N_{PW} . But it is clear that the problem should be investigated further, and that it is a source of error on the corrected values.

APPENDIX B: FROYEN-COHEN TECHNIQUE FOR PRESSURE CORRECTION

The starting point of this technique is the definition of the Pulay stress. It is the quantity to be added to the pressure that is obtained using E_{cut} and V for the definition of the plane-wave basis set, to get the pressure that effectively corresponds to these given values of E_{cut} and V :

$$\begin{aligned} \sigma_{\text{Pulay}}(E_{\text{cut}}^1, V_1) &= P^c\{E_{\text{cut}}^1, V_1\} - P^d\{E_{\text{cut}}^1, V_1\} \\ &= P^c\{E_{\text{cut}}^1, V_1\} \\ &\quad - P \left[\bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1), V_1 \right]. \end{aligned} \quad (\text{B1})$$

Froyen and Cohen, in their paper,¹⁰ propose

$$\begin{aligned} \sigma_{\text{Pulay,FC}}(E_{\text{cut}}^1, V_1) \\ = -\frac{2}{3} \frac{E_{\text{cut}}^1}{V_1} \left(\frac{\partial E_{\text{tot}}^c\{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V \bigg|_{\substack{V=V_1 \\ E_{\text{cut}}=E_{\text{cut}}^1}}. \end{aligned} \quad (\text{B2})$$

We now show that this expression corresponds to an inaccurate definition the Pulay stress. Using the definition of $E_{\text{cut}}^c(\bar{N}_{\text{PW}}, V)$ given by Eq. (4), we get that

$$\begin{aligned} \left(\frac{\partial E_{\text{cut}}^c(\bar{N}_{\text{PW}}, V)}{\partial V} \right)_{\bar{N}_{\text{PW}}} &= -\frac{1}{3} (6\pi^2 \bar{N}_{\text{PW}})^{2/3} (V)^{-5/3} \\ &= -\frac{2}{3} \frac{E_{\text{cut}}^c(\bar{N}_{\text{PW}}, V)}{V}. \end{aligned} \quad (\text{B3})$$

The Pulay stress, as given by Eq. (B2) can thus be rewritten as

$$\sigma_{\text{Pulay,FC}}(E_{\text{cut}}^1, V_1) = \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V \bigg|_{\substack{V=V_1 \\ E_{\text{cut}}=E_{\text{cut}}^1}}^{\substack{V=V_1 \\ \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)}} \left(\frac{\partial E_{\text{cut}}^c(\bar{N}_{\text{PW}}, V)}{\partial V} \right)_{\bar{N}_{\text{PW}}} \bigg|_{\substack{V=V_1 \\ \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)}}. \quad (\text{B4})$$

Finally, the expression of the Pulay stress given by Eq. (B4) can be worked out, using the chain rule and the definitions Eqs. (7) and (9) of $P[\bar{N}_{\text{PW}}, V]$ and $P^c\{E_{\text{cut}}, V\}$, in order to give

$$\sigma_{\text{Pulay,FC}}(E_{\text{cut}}^1, V_1) = P^c\{E_{\text{cut}}^1, V_1\} - P[\bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1), V_1]. \quad (\text{B5})$$

This expression does not correspond to the accurate definition of the Pulay stress given by Eq. (B1), since $\bar{N}_{\text{PW}}^d(E_{\text{cut}}, V)$ has been replaced by $\bar{N}_{\text{PW}}^c(E_{\text{cut}}, V)$ in the last term of the right side of this expression.

APPENDIX C: FRANCIS-PAYNE TECHNIQUE FOR ENERGY CORRECTION

The technique proposed by Francis and Payne consists of integrating the Pulay stress in the form of Eq. (B5) and Eq. (B2) between V_2 and V_1 defined in Fig. 3, i.e., by the following relations: let V_1 be the volume at which energy has to be calculated, $\bar{N}_{\text{PW}}^1 = \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)$, $\bar{N}_{\text{PW}}^2 = \bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1)$, and V_2 be the volume such that $\bar{N}_{\text{PW}}^2 = \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_2)$.

Let us now consider each term of this integration. The first term of the right side of Eq. (B5) is quite easy to integrate:

$$\begin{aligned} \int_{V_2}^{V_1} P^c\{E_{\text{cut}}^1, V'\} dV' &= \int_{V_2}^{V_1} - \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial V} \right)_{E_{\text{cut}}} \bigg|_{\substack{V=V' \\ E_{\text{cut}}=E_{\text{cut}}^1}} dV' \\ &= E_{\text{tot}}^c\{E_{\text{cut}}^1, V_2\} - E_{\text{tot}}^c\{E_{\text{cut}}^1, V_1\} \\ &= E_{\text{tot}}[\bar{N}_{\text{PW}}^2, V_2] - E_{\text{tot}}[\bar{N}_{\text{PW}}^1, V_1]. \end{aligned} \quad (\text{C1})$$

It corresponds to $E_{\text{tot}}(A) - E_{\text{tot}}(B)$ in Fig. 3.

The integration of the right side of Eq. (B2) necessitates the use of the approximation given by Eq. (15):

$$\int_{V_2}^{V_1} - \frac{2}{3} \frac{E_{\text{cut}}^1}{V'} \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial V} \right)_{E_{\text{cut}}} \bigg|_{\substack{V=V' \\ E_{\text{cut}}=E_{\text{cut}}^1}}^{\substack{V=V' \\ E_{\text{cut}}=E_{\text{cut}}^1}} dV' = \frac{2E_{\text{cut}}^1}{3} \ln\left(\frac{V_2}{V_1}\right) \left(\frac{\partial E_{\text{tot}}^c \{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}} \right)_V \bigg|_{\substack{V=V_1 \\ E_{\text{cut}}=E_{\text{cut}}^1}}. \quad (\text{C2})$$

Using the definition of V_1 and V_2 with Eq. (3), we get

$$\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{\bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_2)}{\bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)}\right) = \ln\left(\frac{\bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1)}{\bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)}\right) = \ln\left(\frac{\bar{N}_{\text{PW}}^2}{\bar{N}_{\text{PW}}^1}\right). \quad (\text{C3})$$

An approximation is needed to integrate the second term of the right side of Eq. (B5), because it is impossible to solve analytically:

$$\int_{V_2}^{V_1} P[\bar{N}_{\text{PW}}, V'] dV' = \int_{V_2}^{V_1} - \left(\frac{\partial E_{\text{tot}}[\bar{N}_{\text{PW}}, V]}{\partial V} \right)_{\bar{N}_{\text{PW}}} \bigg|_{\substack{V=V' \\ \bar{N}_{\text{PW}}=\bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V')}} dV'. \quad (\text{C4})$$

Indeed, the derivative in this integral has to be taken on a curve at a constant number of plane waves $\bar{N}_{\text{PW}} = \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V')$, but the latter varies while integrating (because of the variation of V'). Graphically, it means that this derivative has to be evaluated on each of the curves at constant $\bar{N}_{\text{PW}}$ situated between the points A and B in Fig. 3.

On the other side, if we accept that the number of plane waves is kept constant to $\bar{N}_{\text{PW}} = \bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_2) =$

$\bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1) = \bar{N}_{\text{PW}}^2$ while integrating, we get quite easily

$$\int_{V_2}^{V_1} P[\bar{N}_{\text{PW}}, V'] dV' = E_{\text{tot}}[\bar{N}_{\text{PW}}^2, V_2] - E_{\text{tot}}[\bar{N}_{\text{PW}}^2, V_1]. \quad (\text{C5})$$

It corresponds to $E_{\text{tot}}(A) - E_{\text{tot}}(C)$ in Fig. 3. It should be noted that making this approximation leads to a result equivalent to the one that would be obtained by integrating the Pulay stress in the form of Eq. (B1) [instead of Eq. (B5)] and Eq. (B2).

Globally, the integration of the right side of Eq. (B2) gives $E_{\text{tot}}(B) - E_{\text{tot}}(C)$, which is the correction for energy

$$E_{\text{tot}}[\bar{N}_{\text{PW}}^1, V_1] = E_{\text{tot}}[\bar{N}_{\text{PW}}^2, V_1] - \frac{2E_{\text{cut}}^1}{3} \ln\left(\frac{\bar{N}_{\text{PW}}^2}{\bar{N}_{\text{PW}}^1}\right) \left(\frac{\partial E_{\text{tot}}^c\{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}}\right)_V \bigg|_{V=V_1, E_{\text{cut}}=E_{\text{cut}}^1}. \quad (\text{C6})$$

This can be rewritten as

$$E_{\text{tot}}^c\{E_{\text{cut}}^1, V_1\} = E_{\text{tot}}^d\{E_{\text{cut}}^1, V_1\} - \frac{2E_{\text{cut}}^1}{3} \ln\left(\frac{\bar{N}_{\text{PW}}^d(E_{\text{cut}}^1, V_1)}{\bar{N}_{\text{PW}}^c(E_{\text{cut}}^1, V_1)}\right) \left(\frac{\partial E_{\text{tot}}^c\{E_{\text{cut}}, V\}}{\partial E_{\text{cut}}}\right)_V \bigg|_{V=V_1, E_{\text{cut}}=E_{\text{cut}}^1}, \quad (\text{C7})$$

which is the final result presented by Francis and Payne.

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