

## Phonon dispersions: Performance of the generalized gradient approximation

Fabio Favot

*École Polytechnique Fédérale de Lausanne, Institut de Physique Appliquée, Laboratoire de Théorie du Solide,  
CH-1015 Lausanne, Switzerland*

Andrea Dal Corso

*SISSA, Via Beirut 2/4, 34014 Trieste, Italy and INFN Trieste, 34014 Trieste, Italy*

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By computing the phonon dispersions of a few selected solids (Si, C, Al, and Cu), within density-functional perturbation theory, we compare the performance of the local density approximation (LDA) with that of the generalized gradient approximations (GGA's) in the form recently proposed by Perdew, Burke, and Ernzerhof [Phys. Rev. Lett. **77**, 3865 (1996)]. We find that GGA systematically lowers the frequencies of phonon branches with positive Grüneisen parameters. This effect is correlated with the GGA's expansion of the lattice constant, since GGA phonon frequencies computed at the experimental lattice constants are higher than the corresponding LDA ones. In C, Al, and Cu, LDA and GGA phonon dispersions have similar accuracy with respect to the experimental data. Si is an exception since the LDA phonon dispersions are already in very good agreement with experiment and GGA worsens the comparison. [S0163-1829(99)03339-1]

In recent years, generalized gradient approximations<sup>1-3</sup> (GGA's) to density-functional theory have attracted a great deal of interest as one of the simplest approaches to improve upon the local density approximation (LDA) in first-principles calculations of material properties.<sup>4-12</sup> The success of GGA's derives from their ability to correct some LDA deficiencies with a modest computational overhead.

By now it has been established that GGA's give total energies of atoms and cohesive energies of solids, which are closer to experiment than the LDA ones.<sup>5,13-15</sup> Furthermore, GGA's are mandatory for systems containing "weak" or hydrogen bonds, such as molecular crystals, water, or ice. For these systems the intermolecular bond lengths are severely underestimated in LDA, but they can be appreciably improved in GGA.<sup>6,9</sup>

An interesting issue is to understand whether LDA always can be replaced by GGA's in electronic structure calculations. In fact, in many systems, several properties are already correctly described by LDA and it may happen that the introduction of GGA's worsens the good agreement between theory and experiment. The elastic and dynamical properties of Si are a paradigmatic case: the GGA values of the bulk modulus and of the vibrational phonon frequencies of Si are too low, and a sizable worsening of the LDA performance occurs.<sup>5,13-15</sup> However, the only data for Si are not sufficient to draw definitive conclusions about the usefulness of GGA's in *ab initio* phonon calculations. Up to now theoretical phonon spectra have been calculated only within LDA and no complete phonon dispersions, computed consistently within one of the GGA's, are available.

In this paper we present the GGA phonon dispersion spectra of two covalently bonded solids, Si and C, and two metals, Al and Cu. Si, C, and Al are three examples of *sp*-bonded materials, which have been extensively studied by *ab initio* methods and represent a useful benchmark for any new GGA approach. LDA calculations<sup>16-21</sup> well repro-

duce the experimental vibrational frequencies of these solids, and the introduction of GGA's should not spoil this agreement. As an example of noble metal, Cu needs an accurate description of *d* electrons to account for the cohesive properties and for the interatomic force constants. The LDA phonon dispersions of Cu overestimate the experimental frequencies,<sup>22,21</sup> and GGA's could provide an effective improvement.

We find that, in these four materials, GGA acts as a negative pressure. It increases the lattice constants, softens the frequencies of phonons with positive sign of the Grüneisen parameter and rises those with negative ones. In C, Al, and Cu, LDA and GGA phonon dispersions have similar accuracy when compared to experiment. Silicon is the only exception since the LDA phonon dispersions are in very good agreement with experiment whereas GGA worsens the results. We compare also LDA and GGA phonon calculations at the same experimental lattice constants and find that, in this case, GGA phonon frequencies are stiffer than the LDA ones. Therefore the observed phonon softening at the theoretical lattice constant is correlated with the GGA lattice expansion.

The dynamical matrices at arbitrary points of the Brillouin zone (BZ) have been computed within density-functional perturbation theory (DFPT),<sup>23</sup> using a plane-wave-basis set and pseudopotentials. DFPT, as implemented in our codes, has been extensively described elsewhere for both norm conserving<sup>16,20</sup> and ultrasoft<sup>22</sup> pseudopotentials. Here, we discuss only how GGA is included in the formalism. The first step beyond LDA is to assume that the exchange and correlation functional  $E_{xc}$  depends locally on both the local density  $n$  and the density gradient  $\nabla n$

$$E_{xc} = \int d\mathbf{r} n \varepsilon_{xc}(n, |\nabla n|). \quad (1)$$

The exchange and correlation term in the Kohn and Sham potential can be derived from Eq. (1) with standard calculus of variations

$$\begin{aligned} V_{xc} &= \frac{\partial F}{\partial n} - \sum_{\alpha=1}^3 \frac{\partial}{\partial r_{\alpha}} \left[ \frac{\partial F}{\partial (\partial_{\alpha} n)} \right] \\ &= \frac{\partial F}{\partial n} - \sum_{\alpha=1}^3 \frac{\partial}{\partial r_{\alpha}} [A(n, |\nabla n|) \partial_{\alpha} n], \end{aligned} \quad (2)$$

where the function  $F$  is defined as  $F = n \varepsilon_{xc}(n, |\nabla n|)$ ,  $\partial_{\alpha} n$  is the  $\alpha$  component of the density gradient and

$$A(n, |\nabla n|) = \frac{1}{|\nabla n|} \frac{\partial F}{\partial |\nabla n|}. \quad (3)$$

It is numerically convenient to calculate Eq. (2) as it is, without taking explicitly the derivatives of  $A(n, |\nabla n|) \partial_{\alpha} n$  since in this form  $V_{xc}$  is exactly the functional derivative of the exchange and correlation energy calculated with finite cutoff.<sup>24</sup> In order to evaluate the linear response, DFPT requires the  $f_{xc}$  operator,<sup>16</sup> i.e., the functional derivative of the exchange and correlation potential with respect to the density. The variation of the exchange and correlation potential due to a phonon perturbation is expressed as an explicit linear function of the induced charge density  $\Delta n$  and its  $\mathbf{r}$  derivatives:

$$\begin{aligned} \Delta V_{xc} &= \frac{\partial^2 F}{\partial n^2} \Delta n + \frac{\partial^2 F}{\partial |\nabla n| \partial n} \Delta |\nabla n| \\ &\quad - \sum_{\alpha=1}^3 \frac{\partial}{\partial r_{\alpha}} \left[ \left( \frac{\partial A}{\partial n} \Delta n + \frac{\partial A}{\partial |\nabla n|} \Delta |\nabla n| \right) \partial_{\alpha} n + A \partial_{\alpha} \Delta n \right], \end{aligned} \quad (4)$$

where

$$\Delta |\nabla n| = \frac{1}{|\nabla n|} \sum_{\beta=1}^3 \partial_{\beta} n \partial_{\beta} \Delta n. \quad (5)$$

Again this is the correct functional derivative even at finite cut off.<sup>25</sup> Within LDA  $F$  does not depend on the density gradient, thus only the first term in Eq. (4) is nonvanishing: in such case one recovers the standard LDA expression for  $f_{xc}$ .<sup>16</sup> To compute this general expression within any GGA's scheme it is necessary to evaluate the derivatives of  $F$ ,  $A$ , and  $\Delta n$ . In our implementation the derivatives of  $\Delta n$  are evaluated with Fourier techniques in reciprocal space, while the derivatives of the functions  $F$  and  $A$  are evaluated numerically.<sup>25</sup> In literature several GGA functionals have been proposed and compared to each other.<sup>13,14</sup> It has been shown that the differences among GGA's are very small for the systems discussed in the present paper, while the choice of GGA could be more critical for compounds containing hydrogen bonds.<sup>26</sup> In this paper we use the expression recently introduced by Perdew, Burke, and Ernzerhof (PBE).<sup>3</sup> This functional gives results similar to the best available GGA but is simpler to implement. Furthermore, PBE gives a

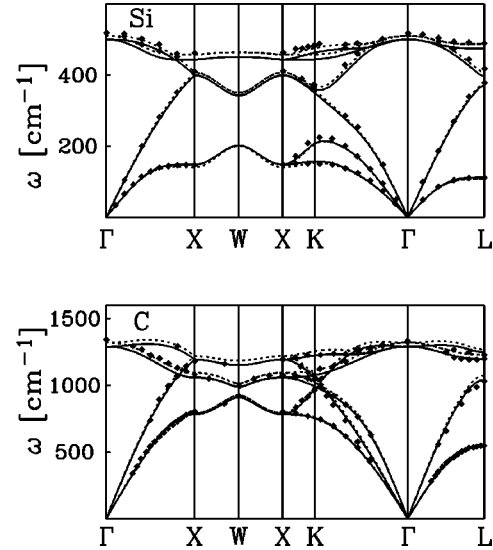


FIG. 1. Calculated PBE phonon dispersions (solid lines) for fcc Si and C compared to inelastic neutron scattering data (solid diamond) and to calculated LDA dispersions (dotted lines).

good description of the linear response of the uniform electron gas, which is an important feature for phonon calculations.

Ultrasoft pseudopotentials<sup>27</sup> are used for C and Cu, while norm-conserving pseudopotentials are used for Si and Al. Norm-conserving pseudopotentials have been generated according to a modified Rappe, Rabe, Kaxiras, and Joannopoulos (RRKJ) scheme where only 3 Bessel functions are used to describe the pseudowave functions before the core radii  $r_c$ .<sup>28,29</sup> The ultrasoft pseudopotentials have been generated using the approach of Ref. 28. All GGA's calculations have been performed with pseudopotentials generated consistently within the PBE scheme as recently recommended in Ref. 14. A kinetic-energy cut off of 24, 28, 20, and 30 Ry is used for Si, C, Al, and Cu, respectively. The augmentation charges of C and Cu are expanded up to 220 (C) and 300 Ry (Cu). For the BZ integration we use 28  $\mathbf{k}$  points in the irreducible BZ for the diamond structure of Si and C and 60  $\mathbf{k}$  points for the fcc structure of Al and Cu. For these metals, the integration up to the Fermi surface is done with the smearing technique of Ref. 30 with the smearing parameter  $\sigma=0.05$  Ry. The dynamical matrices have been computed on a  $4 \times 4 \times 4$   $\mathbf{q}$ -point mesh, and a Fourier interpolation has been used to obtain complete phonon dispersions.

In Fig. 1, we compare the computed PBE phonon dispersions of Si and C with experiment and, for reference, we plot also the LDA phonon dispersions. Both PBE and LDA calculations have been performed at the theoretical lattice constants reported in Table I. LDA results are in good agreement with previous works on Si (Refs. 16–18) and C.<sup>19</sup> They reproduce the experimental data within few wavenumbers. Only the optical frequencies of C along the  $\Gamma-L$  and  $X-W$  directions are slightly higher than the experiment. In order to test our PBE implementation we compare the PBE phonon frequencies of Si at  $\Gamma$  and  $X$  with those reported in Ref. 15. The differences are very small:  $1 \text{ cm}^{-1}$  for the optical mode at zone center [LTO( $\Gamma$ )],  $3 \text{ cm}^{-1}$  for the transverse optical mode at  $X$  [TO( $X$ )],  $5 \text{ cm}^{-1}$  for the two degenerate longitudinal acoustic and optical modes at

TABLE I. Calculated lattice constants ( $a_0$ ), bulk modulus ( $B_0$ ), and cohesive energy ( $E_c$ ) of the four systems studied in this paper. The latter includes LDA (GGA) spin corrections of 0.67 (0.79) eV for Si atom, 1.13 (1.26) eV for C atom, 0.15 (0.19) eV for Al atom and 0.20 (0.25) eV for Cu atom. Spin corrections are taken from Ref. 13. Experimental data are taken from Ref. 36.

|          | $a_0$ (a.u.) | $B_0$ (GPa) | $E_c$ (eV/atom) |
|----------|--------------|-------------|-----------------|
| Silicon  |              |             |                 |
| LDA      | 10.19        | 96          | 5.30            |
| GGA      | 10.35        | 87          | 4.60            |
| Expt.    | 10.26        | 99          | 4.63            |
| Carbon   |              |             |                 |
| LDA      | 6.67         | 460         | 9.02            |
| GGA      | 6.74         | 429         | 7.85            |
| Expt.    | 6.75         | 442         | 7.37            |
| Aluminum |              |             |                 |
| LDA      | 7.51         | 82          | 4.05            |
| GGA      | 7.67         | 75          | 3.52            |
| Expt.    | 7.65         | 77          | 3.39            |
| Copper   |              |             |                 |
| LDA      | 6.71         | 173         | 4.32            |
| GGA      | 6.94         | 129         | 3.30            |
| Expt.    | 6.80         | 138         | 3.50            |

$X[\text{LOA}(X)]$  and  $5 \text{ cm}^{-1}$  for the transverse acoustic mode at  $X[\text{TA}(X)]$ . On average<sup>31</sup> the difference between LDA and PBE is  $7 \text{ cm}^{-1}$  for Si and  $20 \text{ cm}^{-1}$  for C, with maximum deviations of 13 and  $34 \text{ cm}^{-1}$ , respectively. The acoustic modes are not significantly modified by PBE. The PBE frequencies of the transverse acoustic modes of Si are higher than the LDA ones consistently with the negative sign of the Grüneisen parameters of these branches. The main feature of the PBE phonon dispersions of both Si and C is the softening of the optical modes. This fact improves the agreement between theory and experiment along the  $\Gamma-L$  and  $X-W$  directions for C but it worsens the good LDA results for Si and those, along the  $\Gamma-X$  direction, for C. In order to quantify the difference between theory and experiment we have computed the average of this difference on the points of the BZ where experimental data are available [Refs. 32 (Si) and 33 (C)]. We find an average PBE (LDA) error of  $9 \text{ cm}^{-1}$  ( $5 \text{ cm}^{-1}$ ) for Si and of  $14 \text{ cm}^{-1}$  ( $15 \text{ cm}^{-1}$ ) for C. The two pictures of Fig. 1 show that while PBE is definitely worse than LDA for Si, it is as accurate as LDA for C. However, it must be noticed that in the case of Si the average PBE error is comparable with typical LDA errors found in other solids.

In Fig. 2, we compare the computed PBE phonon dispersions of Al and Cu to experimental data. For reference we plot also the LDA phonon dispersions. As in the semiconductor case, both PBE and LDA calculations have been performed at the theoretical lattice constants reported in Table I. While the LDA phonon dispersions of Al reproduce accurately the experiment,<sup>20,21</sup> those of Cu are quite stiffer. For instance, the calculated frequency of the longitudinal acoustic mode at X differs from experiment by 6.2%, in agreement with other pseudopotential<sup>22</sup> and all-electron<sup>21</sup> calculations. PBE lattice constants of Al and Cu are larger than the LDA

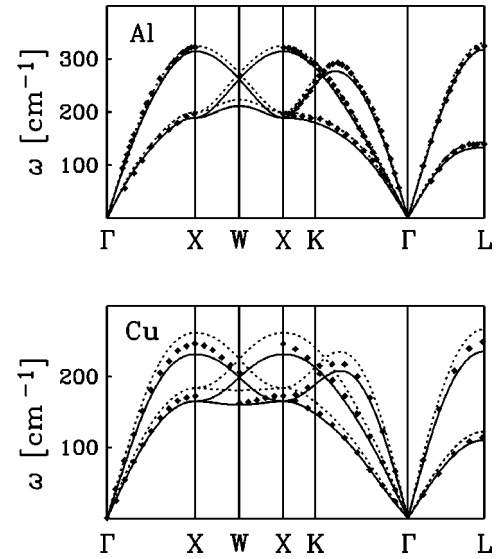


FIG. 2. Calculated PBE phonon dispersions (solid lines) for fcc Al and Cu, compared to inelastic neutron scattering data (solid diamond) and to calculated LDA dispersions (dotted lines).

ones and all the phonon frequencies are softer. On average<sup>31</sup> the difference between LDA and PBE is about  $10 \text{ cm}^{-1}$  for Al and  $20 \text{ cm}^{-1}$  for Cu. PBE overcorrects the LDA error with respect to experimental data, lowering the phonon frequencies below the experiment. The average PBE (LDA) error with respect to experiment has been estimated as for Si and C. We find an error of  $6 \text{ cm}^{-1}$  ( $4 \text{ cm}^{-1}$ ) for Al and  $6 \text{ cm}^{-1}$  ( $11 \text{ cm}^{-1}$ ) for Cu. In these metals, large variations of phonon frequencies with the temperature are observed. Experimental phonon spectra have been measured for both Al (Ref. 34) and Cu (Ref. 35) at  $T=80 \text{ K}$ , a temperature low enough to allow a safe comparison with our  $T=0 \text{ K}$  calculations. From Fig. 2 we conclude that PBE is better than LDA for Cu and it is slightly worse for Al. In both cases, however, PBE can replace LDA in phonon calculations. This might be important in applications where GGA's are required, as for instance, studies of molecules adsorbed on metallic surfaces.<sup>7</sup>

Since PBE and LDA lattice constants differ by 1.6% (Si), 1.0% (C), 2.5% (Al), and 3.5% (Cu), it is interesting to compare PBE and LDA phonon dispersions computed at the same lattice constant in order to quantify the effect of the GGA lattice expansion on the final results. In Figs. 3 and 4 we show LDA and PBE phonon dispersions of Si, C, Al, and Cu computed at the experimental lattice constants of Table I. The most striking feature is the stiffening of the PBE frequencies which become higher than the LDA ones. The average differences are  $9 \text{ cm}^{-1}$  (Si),  $11 \text{ cm}^{-1}$  (C),  $17 \text{ cm}^{-1}$  (Al), and  $16 \text{ cm}^{-1}$  (Cu). This fact is compatible with a previous GGA calculation of the Si dielectric constant,<sup>8</sup> where it is found that GGA leads to a reduction of the electronic screening with respect to LDA at the same lattice constant. The decreased capability of the valence electrons to screen the ion-ion interaction leads to higher interatomic force constants.

In conclusion, we have shown that, with the exception of Si, PBE phonon dispersions compared to experimental data are of the same quality as the LDA ones. For Cu GGA re-

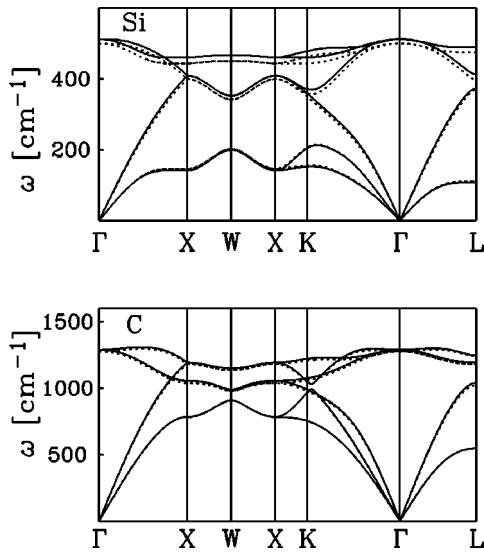


FIG. 3. Calculated PBE (solid lines) and LDA (dotted lines) phonon dispersions for fcc Si and C, both computed at the experimental lattice constant.

sults are even better than GGA. This fact could encourage GGA phonon calculations for those systems, which, for a better description of other properties, require the inclusion of GGA's. Furthermore, we have shown that accurate structural parameters do not guarantee accurate phonon dispersions and focusing only on the cohesive energies and structural properties is not sufficient to evaluate a GGA functional. In the future the accuracy of computed phonon dispersions, as well

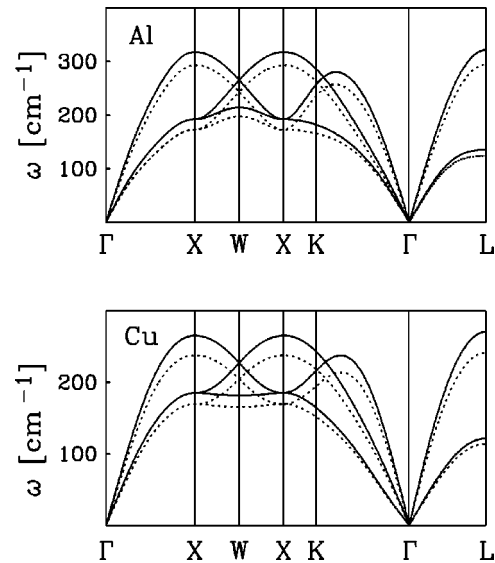


FIG. 4. Calculated PBE (solid lines) and LDA (dotted lines) phonon dispersions for fcc Al and Cu, both computed at the experimental lattice constant.

as other response properties, could be an additional benchmark for testing new and more powerful total energy functionals.

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