Implementation of gradient-corrected exchange-correlation potentials in Car-Parrinello total-energy calculations

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The application of gradient-corrected exchange-correlation functionals in total-energy calculations using a plane-wave basis set is discussed. The usual form of the exchange-correlation potential includes gradients whose calculation requires the use of a high-quality representation of the density which is computationally expensive in both memory and time. These problems may be overcome by defining an exchange-correlation potential for the discrete set of grid points consistent with the discretized form of the exchange-correlation energy that is used in Car-Parrinello-type total-energy calculations. This potential can be calculated exactly on the minimum fast-Fourier-transform grid and gives improved convergence and stability as well as computational efficiency.

First-principles total-energy calculations based on density-functional theory¹ have become the major theoretical tool in solid-state physics, surface science, and molecular physics. Pseudopotential calculations using a planewave basis set and a Car-Parrinello approach to energy minimization^{2,3} have become increasingly important since this allows use to be made of the fast Fourier transform (FFT). Although the local-density approximation (LDA) to exchange and correlation gives a good description of many solid-state properties, for many applications it appears to be essential to go beyond the LDA by including gradient corrections. This is particularly important where accurate molecular bonding energies are required⁴ as in, for example, dissociative chemisorption.⁵ For bulk properties the need for gradient corrections is less clear although some improvements over LDA have been reported in calculations for semiconductors⁶ and transition metals.⁷ Unfortunately, the currently popular generalized gradient approximations (GGA) to the exchange-correlation energy functional (such as that of Perdew and Wang⁸ or Becke and Perdew⁹) give rise to potentials which are rapidly varying functions near to ion cores as has been noted previously in the context of pseudopotential generation.¹⁰ Because of this, and in order to calculate the required gradients accurately, a large number of plane waves are needed to represent these exchangecorrelation potentials accurately. In this paper it is pointed out that the exchange-correlation energy is, in practice, invariably approximated. It is shown that it is possible to construct an exchange-correlation potential which is consistent with this approximate form of the exchange-correlation energy and which can be calculated exactly much more efficiently than the conventional exchange-correlation potential.

First recall the use of FFT's in Car-Parrinello-type totalenergy calculations.^{2,3} This makes use of the fact that the kinetic energy and Hartree energy/potential are easily calculated in reciprocal space (the Hartree potential, for example, becomes a simple product in reciprocal space) while the electron-ion potential energy is easily calculated in real space since the required integrals can be performed exactly as sums over the points of the minimum FFT grid. Here we define the minimum FFT grid as the smallest on which the charge density can be unambiguously represented. If the plane-wave expansion of the wave functions is restricted to reciprocallattice vectors with magnitude $G \leq G_{max}$ then the Fourier components of the charge density are restricted to $G \leq 2G_{\text{max}}$. Similarly, only those Fourier components of the potential with $G \leq 2G_{\text{max}}$ are relevant and therefore a FFT grid spanning these reciprocal-lattice vectors is required. Only the exchange-correlation energy/potential cannot be calculated exactly on this real space grid since it involves nonlinear functions of the density which must have Fourier components with $G > 2G_{\text{max}}$. This is not a problem in the LDA since in this case the exchange-correlation potential is very slowly varying and the high Fourier components are entirely negligible. In the GGA, however, significant errors may occur. In the following, we restrict ourselves to the nonspin-polarized case, although the arguments apply equally well if spin polarization is included.

In general the gradient-corrected exchange-correlation energy is written

$$E_{\rm xc}[n] = \int f_{\rm xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) d\mathbf{r}.$$
(1)

For simplicity we exclude any possible $\nabla^2 n$ dependence which causes no particular difficulties. For a small change δn in the density the corresponding change in the exchangecorrelation energy is

$$\delta E_{\rm xc} = \int \frac{\delta E_{\rm xc}}{\delta n(\mathbf{r})} \, \delta n(\mathbf{r}) d\mathbf{r} = \int v_{\rm xc}(\mathbf{r}) \, \delta n(\mathbf{r}) d\mathbf{r} \qquad (2)$$

which defines the exchange-correlation potential as the functional derivative of E_{xc} with respect to the density *n*, i.e.,

$$v_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})} = \frac{\partial f_{\rm xc}}{\partial n(\mathbf{r})} - \nabla \cdot \frac{\partial f_{\rm xc}}{\partial \nabla n(\mathbf{r})} .$$
(3)

Since the GGA potential is a rapidly varying function it requires a large number of plane waves (i.e., a large FFT grid) to be accurately represented. Moreover, since the energy depends on $|\nabla n|$, one finds from Eq. (3) that in order to obtain $v_{\rm xc}$ one requires not only $|\nabla n|$ but also $\nabla^2 n$ and

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 $\nabla n \cdot \nabla |\nabla n|$. It is this final term which causes the problems since the Fourier expansion of $|\nabla n|$ is not restricted to terms with $G \leq 2G_{\text{max}}$. Thus, calculation of the exchangecorrelation potential using FFT's on the minimum FFT grid is inevitably inaccurate. This can result in instabilities with the total-energy oscillating above the correct minimum (see later). The usual procedure for overcoming these problems is to evaluate the gradients (in particular, the problem term $\nabla n \cdot \nabla |\nabla n|$) using an improved representation of the density.¹¹ In fact, one can see that the Fourier representation of $|\nabla n|^2$ is restricted to terms with $G \leq 4G_{\text{max}}$ so that it is possible to calculate $\nabla |\nabla n|^2$ exactly by FFT on a grid which is linearly twice the size of the minimum grid (i.e., eight times the number of grid points). One can then obtain the exact values of $\nabla |\nabla n|$ at the grid points using

$$\nabla |\nabla n| = \frac{\nabla |\nabla n|^2}{2|\nabla n|}.$$
 (4)

This enables us to calculate the exact value of the exchangecorrelation potential of Eq. (3) at any grid point, albeit at significant expense in computer time and memory because of the larger FFT grid. It should be remembered, however, that its value on every grid point is still insufficient for an exact representation of the rapidly varying exchange-correlation potential.

We now show that a more efficient method of calculating the exchange-correlation potential can be found if we examine more closely the way in which the exchange-correlation *energy* is actually calculated in practice. In practice, the integral in Eq. (1) is replaced by a sum over the N real space points **R** of the minimum FFT grid, i.e., we approximate the exchange-correlation energy $E_{\rm xc}$ of Eq. (1) by a discretized form

$$\tilde{E}_{\rm xc}[n] = \frac{\Omega_{\rm cell}}{N} \sum_{\mathbf{R}} f_{\rm xc}(n(\mathbf{R}), |\nabla n(\mathbf{R})|), \qquad (5)$$

where Ω_{cell} is the unit cell volume. We therefore choose to *define* the exchange-correlation energy by this discrete sum and ask for the potential consistent with this definition. The appropriate (discretized) exchange-correlation potential \tilde{v}_{xc} is defined, equivalently to Eq. (2), in terms of the change in \tilde{E}_{xc} due to a small change in the density

$$\delta \tilde{E}_{\rm xc} = \sum_{\mathbf{R}} \frac{d\tilde{E}_{\rm xc}}{dn(\mathbf{R})} \,\delta n(\mathbf{R}) = \frac{\Omega_{\rm cell}}{N} \sum_{\mathbf{R}} \tilde{v}_{\rm xc}(\mathbf{R}) \,\delta n(\mathbf{R}). \quad (6)$$

Note that E_{xc} can be considered as a *function* of the N values of the charge density at the grid points (both explicitly and implicitly through the ∇n dependence of f_{xc}) and it is an ordinary derivative rather than a functional derivative which appears in Eq. (6). This definition of the exchangecorrelation potential tends to the functional derivative of Eq. (3) in the limit of an infinite number of grid points N. By direct differentiation of Eq. (5) we obtain

$$\tilde{v}_{\rm xc}(\mathbf{R}) = \frac{N}{\Omega_{\rm cell}} \frac{d\tilde{E}_{\rm xc}}{dn(\mathbf{R})}$$
$$= \frac{\partial f_{\rm xc}}{\partial n(\mathbf{R})} + \sum_{\mathbf{R}'} \frac{\partial f_{\rm xc}}{\partial \nabla n(\mathbf{R}')} \cdot \frac{d\nabla n(\mathbf{R}')}{dn(\mathbf{R})} .$$
(7)

To interpret the final derivative here it must be remembered that a change in the charge density at any grid point will affect the charge-density gradient at all points since

$$\nabla n(\mathbf{r}) = \sum_{\mathbf{G}} i\mathbf{G}n(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}} = \frac{1}{N}\sum_{\mathbf{G},\mathbf{R}} i\mathbf{G}n(\mathbf{R})e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{R})}, \quad (8)$$

where the G are the N reciprocal-lattice vectors of the minimum (reciprocal space) FFT grid. Substituting this into Eq. (7) and replacing G by -G we obtain

$$\tilde{v}_{\rm xc}(\mathbf{R}) = \frac{\partial f_{\rm xc}}{\partial n(\mathbf{R})} - \frac{1}{N} \sum_{\mathbf{G},\mathbf{R}'} i\mathbf{G} \cdot \frac{\partial f_{\rm xc}}{\partial \nabla n(\mathbf{R}')} e^{i\mathbf{G} \cdot (\mathbf{R} - \mathbf{R}')} \quad (9)$$

which, since f_{xc} depends on ∇n only through its magnitude, becomes

$$\tilde{v}_{xc}(\mathbf{R}) = \frac{\partial f_{xc}}{\partial n(\mathbf{R})} - \frac{1}{N} \sum_{\mathbf{G},\mathbf{R}'} i\mathbf{G} \cdot \frac{\nabla n(\mathbf{R}')}{|\nabla n(\mathbf{R}')|} \frac{\partial f_{xc}}{\partial |\nabla n(\mathbf{R}')|} \times e^{i\mathbf{G} \cdot (\mathbf{R} - \mathbf{R}')}.$$
(10)

Only discrete Fourier transforms appear in Eq. (10) so that this \tilde{v}_{xc} can be calculated exactly using FFT's on the minimum FFT grid, i.e., no higher-quality representation of the charge density is required. This is of obvious benefit with regard to computational speed and memory requirements but also, by discretizing the potential in a manner consistent with the energy functional, it eliminates any problems of convergence and stability. Replacing $\partial f_{xc} / \partial \nabla n$ by its Fourier transform in Eq. (3) it is not difficult to show that Eq. (10) is equivalent to Eq. (3) in the large-N limit. On the minimum FFT grid, however, the potentials of Eqs. (3) and (10) will be different. Given the charge density on the real space grid, only eight FFT's are necessary to obtain \tilde{v}_{xc} from Eq. (10) on the real space grid. The only functions needed, in addition to $f_{\rm xc}$, are the first derivatives $\partial f_{\rm xc} / \partial n$ and $\partial f_{\rm xc} / \partial |\nabla n|$ which are somewhat easier to derive than the second derivatives required to evaluate the conventional potential. Subroutines for calculating the necessary functions for the GGA functional of Perdew and Wang⁸ are available from the authors.

As an illustration of these points, Fig. 1 shows the convergence of energies for a single hydrogen atom in a large cell (a cube of side 8.1 Å) with a $48 \times 48 \times 48$ FFT grid. Here the GGA functional of Perdew and Wang⁸ is used. For the hydrogen ion the bare Coulomb potential is used. The calculations are performed using the code CASTEP.³ We use only a single k point (the gamma point) and an energy cutoff of 350 eV. Although this is not sufficient to converge the total energy fully, it is adequate to illustrate the points considered here. Each iteration involves two conjugate gradient steps.¹² Using the new potential of Eq. (10) the energy converges rapidly to its minimum value. Using the conventional exchange-correlation potential of Eq. (3), however (calculated on the same FFT grid), the energy fluctuates above the

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FIG. 1. Total energy vs number of iterations for a single hydrogen atom in a large (8.1-Å cube) unit cell. Each iteration consists of two conjugate gradient steps. Using the new potential of Eq. (10) (solid line) and using the conventional potential of Eq. (3) calculated on the same FFT grid (dashed line).

correct minimum. In this case the energy may increase because the exchange-correlation potential is not accurately represented, i.e., the incorrect value of the energy gradient with respect to changes in the wave function (and hence charge density) is obtained. If the conventional potential is calculated on the larger grid of 8N points [as described above Eq. (4)] most of the errors are eliminated, the energy converging to a value 5×10^{-5} eV above the correct minimum. Of course, such calculations are far more time consuming than calculations which use the minimum FFT grid.

Finally, we consider the error arising from the discretization of the exchange-correlation energy functional. This results in a converged total energy which is dependent on the atomic positions relative to the grid points. In effect the grid points break the crystal symmetry so that slightly asymmetric charge densities and small spurious Hellmann-Feynman forces occur. We have calculated, for hydrogen and for magnesium, the variation of energy and force on a single atom positioned along a line joining nearest-neighbor grid points. For hydrogen, the cell size, energy cutoff, etc. are as above for Fig. 1. For magnesium a cubic cell of side 8 Å is used with an energy cutoff of 150 eV and a $32 \times 32 \times 32$ FFT grid. The Mg ion is represented by a pseudopotential in the Kleinman-Bylander form¹³ and in this case the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ special k point is used. Figure 2 shows the total energy relative to the value when the ion is centered on a grid point (the total energy is -12.284 eV and -22.907 eV for H and Mg, respectively). Typical energy variations for these single atoms



FIG. 2. Variation of energy with atomic position along a line joining one real space grid point (x=0) to a neighboring grid point (x=1). For hydrogen (solid line) grid point separation is 0.169 Å and for magnesium (dashed line) grid point separation is 0.25 Å.

are 10^{-4} eV. The spurious Hellman-Feynman forces obtained are exactly consistent with this energy variation and are typically of order 10^{-3} eV/Å. These forces are too small to give any significant error in molecular dynamics so the discretization [Eq. (5)] is justified. It is interesting that these forces tend to push a hydrogen atom onto a grid point whereas a magnesium atom is pushed away from a grid point. We expect this to be related to the fact that for magnesium we are working with a pseudopotential which gives a minimum (pseudo)charge density at the ion core, i.e., $\nabla^2 n$ at the ion core is positive for magnesium whereas it is negative for hydrogen.

To summarize, it has been shown that a discretized form of GGA exchange-correlation potential can be defined, consistent with the discretized exchange-correlation energy used in Car-Parrinello-type total-energy calculations, and can be calculated exactly by FFT on the minimum Car-Parrinello FFT grid. This enables one to perform efficient, fully selfconsistent and completely stable gradient-corrected calculations. The error due to discretizing the exchange-correlation energy functional appears as spurious but insignificant Hellmann-Feynman forces.

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