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Non-self-consistent Density-Functional Theory Exchange-Correlation Forces for GGA Functionals

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Abstract: When using density functional theory (DFT), generalized gradient approximation (GGA) functionals are often necessary for accurate modeling of important properties of biomolecules, including hydrogen-bond strengths and relative energies of conformers. We consider the calculations of forces using non-self-consistent (NSC) methods based on the Harris–Foulkes expression for energy. We derive an expression for the GGA NSC force on atoms, valid for a hierarchy of methods based on local orbitals, and discuss its implementation in the linear scaling DFT code Conquest, using a standard (White–Bird) approach. We investigate the use of NSC structural relaxations before full self-consistent relaxations as a method for improving convergence. Example calculations for glycine and small alanine peptides suggest that NSC pre-relaxations of the structure are indeed useful to save computer effort and time.

1. Introduction

Density functional theory (DFT) has become a standard technique in materials simulations over the last twenty years and is making an increasing impact in theoretical studies of biochemical systems, especially those involving radicals¹ and catalysis by metals.² While plane waves are often used as a basis in condensed phases, local orbital basis functions make it natural to work with a hierarchy of methods from non-self-consistent (NSC) DFT calculations based on the Harris–Foulkes (HF) expression for total energy^{3,4} to full DFT, as well as providing an ideal framework for linear scaling implementations. This hierarchy gives us the power to perform many exploratory calculations rather quickly at low precision, and then increase the precision in a well-controlled way. The purpose of this paper is to extend our

previous treatment of forces⁵ for local orbital methods to non-self-consistent GGA calculations, to discuss its implementation in the Conquest linear scaling DFT code^{6,7} and to explore one aspect of the hierarchical approach: the efficacy of an initial NSC relaxation in speeding up SC relaxations.

For biological systems requiring ab initio accuracy, typically QM/MM methods are used,⁸ though with recent developments in linear scaling DFT,⁹ whole molecules or large portions of molecules can be addressed.^{10–12} For small QM regions, hybrid functionals can be used, but this is still not practical for large regions despite progress with local Hartree–Fock methods¹³ and screened hybrid functionals,¹⁴ so GGA is still important for large biochemical applications¹⁵ and is necessary for properties such as hydrogen-bond strengths and relative energies of conformers.¹⁶ The localization of linear scaling methods also makes them natural candidates for embedding techniques, such as QM/MM, and for embedding full DFT calculations into less precise calculations such as NSC techniques.¹⁷

We recall the hierarchy of electronic structure methods⁵ of different accuracy for clarity. A first possibility is to perform fully self-consistent DFT calculations with a fixed

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basis of pseudoatomic local orbitals (PAOs).^{6,18–21} Even more accurate is to allow the local orbitals to vary by expanding them in a sufficiently complete basis, such as B-splines²² or periodic sinc functions.²³ We call this full DFT. For lower precision calculations, on the other hand, we can use the non-self-consistent (NSC) Harris–Foulkes functional with a fixed and often limited basis of PAOs and fix the electronic density (often to a superposition of atomic densities).²⁴ Methods using a limited, fixed PAO basis bear similarities with standard tight binding and, for this reason, are sometimes called *ab initio* tight binding (AITB). When NSC methods are used, the forces can be written⁵ so that there is a clear contribution to the total force from the difference between input and output charge densities; here, we derive a form for this force in which the exchange–correlation functional depends on the gradient of the charge density, as well as the charge itself (as is the case for GGA functionals). We note that the calculation of a correction to the forces on ions caused by incomplete convergence of self-consistency cycle is important for consistency between energy and forces, and has been considered before,^{25,26} though not in the context of local orbital or linear scaling methods (which present particular challenges, requiring locality and expressions in terms of density matrices rather than KS orbitals). A scheme to accelerate LDA molecular dynamics using NSC LDA forces and local orbitals has also been proposed.²⁷

The paper is laid out as follows: in the next section, we summarize the local orbital approach to DFT, recalling in particular the linear scaling implementation and NSC forces; we then derive the expression for NSC forces with reference to a uniform grid (though the result can be easily extended to other implementations); we then present tests comparing full SC structural relaxation and NSC, followed by SC structural relaxation, and conclude.

2. Local Orbitals and Non-Self-Consistent Forces

As explained in detail elsewhere,⁵ we perform DFT calculations using a basis set of local orbitals (known as support functions in Conquest), $\phi_{i\alpha}(\mathbf{r})$, where i denotes an atom and α is a local orbital on the atom. We assume throughout the use of pseudopotentials, though this is not restrictive. The total energy is then written

$$E_{\text{Tot}} = E_{\text{kin}} + E_{\text{ps}} + E_{\text{Har}} + E_{\text{XC}} + E_{\text{c}} \quad (1)$$

where the kinetic (E_{kin}) and pseudopotential (E_{ps}) energies are found as usual, E_{c} is the core–core Coulomb interaction, and the Hartree (E_{Har}) and exchange–correlation (E_{XC}) energies depend on the charge density

$$n(\mathbf{r}) = 2 \sum_n f_n |\psi_n(\mathbf{r})|^2 \quad (2)$$

where $\psi_n(\mathbf{r})$ is a Kohn–Sham eigenstate and f_n are orbital occupancies.

The Kohn–Sham eigenstates are written in terms of the local orbitals

$$\psi_n(\mathbf{r}) = \sum_{i\alpha} u_{i\alpha}^n \phi_{i\alpha}(\mathbf{r}) \quad (3)$$

We note that the local orbitals are strictly localized within some cutoff radius, and are in general nonorthogonal ($\langle \phi_{i\alpha} | \phi_{j\beta} \rangle = S_{ij\alpha\beta}$). For local orbitals $\phi_{i\alpha}(\mathbf{r})$, whose form is fixed, the total energy of the system is only a function of the expansion coefficients $u_{i\alpha}^n$ and the ground state is found by minimizing the energy with respect to the coefficients, while imposing orthonormality on the KS eigenstates and self-consistency. This gives self-consistent DFT; full DFT can be achieved by writing the local orbitals in terms of a sufficiently complete basis. If, instead, the charge density is fixed and composed of a superposition of pseudoatomic densities

$$n^{\text{in}}(\mathbf{r}) = \sum_i \eta_i(|\mathbf{r} - \mathbf{R}_i|) \quad (4)$$

with $\eta_i(|\mathbf{r} - \mathbf{R}_i|)$ the spherically symmetric density for atom i which has position \mathbf{R}_i , then we have non-self-consistent DFT. We use the Harris–Foulkes energy^{3,4} and write

$$E_{\text{Tot}} = E_{\text{BS}} + \Delta E_{\text{Har}} + \Delta E_{\text{XC}} + E_{\text{c}} \quad (5)$$

Here the Hartree and exchange–correlation double counting terms (ΔE_{Har} and ΔE_{XC}) are calculated with $n^{\text{in}}(\mathbf{r})$. In standard DFT, the band-structure energy is given by a sum over KS eigenenergies, $E_{\text{BS}} = \sum_i f_i \epsilon_i$, where f_i is the occupation. The band-structure energy can also be written in terms of a density matrix, ρ , as $E_{\text{BS}} = 2\text{Tr}[\rho H]$. In linear scaling DFT codes,^{6,7,19,20,23} the energy is variationally minimized with respect to the density matrix, with an explicit localization constraint imposed (a good approximation for systems with a gap, where there the density matrix decays exponentially with distance).²⁸ The Harris–Foulkes energy agrees exactly with the standard KS expression (eq 1) at self-consistency, and away from self-consistency deviates from that energy by an amount second order in the deviation of $n^{\text{in}}(\mathbf{r})$ from the self-consistent ground state $n(\mathbf{r})$.

The forces can be conveniently written in terms of the density matrix, whether this is found by exact diagonalization or linear scaling techniques, and the form of the equations is identical, as explained in detail elsewhere.⁵ The final form is

$$\mathbf{F}_i = \mathbf{F}_i^{\text{ps}} + \mathbf{F}_i^{\text{P}} + \mathbf{F}_i^{\text{NSC}} + \mathbf{F}_i^{\text{c}} \quad (6)$$

where there are Hellmann–Feynman contributions from the motion of the pseudopotentials (denoted ps), Pulay contributions from the motion of basis functions with the atoms (denoted P; we note that some linear scaling codes use basis functions which do not move with atoms, and do not have these forces), contributions from non-self-consistency (denoted NSC) and finally from ionic core interaction (denoted c).

The only difference between the SC and NSC forms is the NSC force term itself, which is written

$$\mathbf{F}_i^{\text{NSC}} = - \int d\mathbf{r} [\delta V_{\text{Har}}(\mathbf{r}) \nabla_i n^{\text{in}}(\mathbf{r}) + \delta n(\mathbf{r}) \nabla_i V_{\text{XC}}(\mathbf{r})] \quad (7)$$

where $\delta n(\mathbf{r}) = n^{\text{out}}(\mathbf{r}) - n^{\text{in}}(\mathbf{r})$ is the difference between the input density and the density built from the KS orbitals (eq 2), $\delta V_{\text{Har}}(\mathbf{r})$ is the Hartree potential because $\delta n(\mathbf{r})$ and $\nabla_i V_{\text{XC}}(\mathbf{r})$ is the gradient of the exchange–correlation potential

for the input density with respect to the position of atom i . The derivation of $\mathbf{F}_i^{\text{NSC}}$ previously given⁵ assumed an LDA functional and needs to be reworked for GGA.

GGA functionals take the form

$$E_{\text{xc}}[n(\mathbf{r})] = \int d\mathbf{r} f_{\text{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r})) \quad (8)$$

Note that this is commonly written in a different but equivalent form, using enhancement factors F_{xc} , so that $f_{\text{xc}} = n \varepsilon_{\text{x}}^{\text{unif}}(n) F_{\text{xc}}(n, \nabla n)$, where $\varepsilon_{\text{x}}^{\text{unif}}$ is the uniform electron gas exchange energy density. The GGA kernel f_{xc} depends explicitly on both the electronic density, $n(\mathbf{r})$, and its gradient, $\nabla n(\mathbf{r})$ (which will be denoted $\mathbf{g}(\mathbf{r})$ for brevity). In almost all GGA functionals the dependence is only on the magnitude of the gradient, $|\nabla n(\mathbf{r})|$; we preserve the full gradient both for completeness and because the algebra is clearer; we use the magnitude of the gradient at the end of the derivation. The gradient of the potential with respect to the position of the atom i needed to compute (eq 7) becomes

$$\nabla_i V_{\text{xc}}(\mathbf{r}) = \mu'_{\text{xc}}[n(\mathbf{r}), \mathbf{g}(\mathbf{r})] \nabla_i n(\mathbf{r}) \quad (9)$$

with $\mu'_{\text{xc}}(n) = dV_{\text{xc}}/dn(\mathbf{r})$. The exchange-correlation potential is written²⁹

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})} = \frac{\partial f_{\text{xc}}}{\partial n(\mathbf{r})} - \nabla \cdot \frac{\partial f_{\text{xc}}}{\partial \mathbf{g}(\mathbf{r})} \quad (10)$$

3. GGA NSC Forces

To derive the GGA NSC force on atoms, we must account for the grid normally used to calculate the energy and potential. We first consider some conditions that must be met in order to avoid inaccuracies in numerical calculations.

3.1. Conditions on a Grid. It would be possible, in principle, to work from the exact expression for the energy and take a suitable discretization on the grid. However, there is no a priori guarantee that the resulting forces would be consistent with the energy on the *same* grid. Problems with structural relaxation and energy conservation in molecular dynamics can arise if the force is not consistent with the discretized energy. We formulate two principles that must be followed in the derivation:

- (1) The exchange-correlation potential must be the exact derivative of the approximate exchange-correlation energy. The Kohn–Sham equations are Euler equations that result from the condition of total energy stationarity with respect to the charge density. On a grid, the total energy will not be exact, but the approximate equations must nevertheless remain stationary.
- (2) Forces must be exact derivatives of the approximate energy. Of course, because the energy is calculated on a grid, the expression for the force will also be an approximation. However, to use forces in structural relaxations, there must be well-defined zero-force atomic positions.

To enforce these principles, one must first approximate E_{xc} on a grid and then obtain the potential and forces from the resulting expression, rather than representing V_{xc} and \mathbf{F}_i on the grid directly. If possible, the same grid should be used

to represent the charge density, the energy, the potential, and the forces on atoms.

3.2. White–Bird Approach. In the next three sections, we will assume that we work on a regular grid, with three-dimensional periodic boundary conditions, which allows us to calculate gradients efficiently using FFTs; the resulting formulas can be easily generalized to other schemes such as atom-centered quadrature.³⁰ We start by approximating the GGA exchange-correlation energy (eq 8) as a sum over grid points l

$$E_{\text{xc}}[\{n_l\}] = \omega \sum_l f_{\text{xc}}(n_l, \mathbf{g}_l) \quad (11)$$

with ω the volume per grid point, the value of the charge density at a grid point l written as $n(\mathbf{r}_l) = n_l$ and its gradient $\nabla n(\mathbf{r}_l) = \mathbf{g}(\mathbf{r}_l) = \mathbf{g}_l$.

The first quantity to be obtained from the energy is the exchange-correlation potential. This was done by White and Bird,²⁹ who noted that although direct discretization of the exact potential (eq 10) is possible in this case, it is still inconvenient, because a grid twice as fine as the minimal grid (the density grid) is necessary to avoid inaccuracies.

The White–Bird approach notes that derivatives on the minimal grid are nothing but linear transformations on the *same* grid. For example, the gradient of the density can be expressed as

$$\mathbf{g}_l = \frac{1}{N} \sum_{m,l'} i\mathbf{G}_m n_l e^{i\mathbf{G}_m(\mathbf{r}_l - \mathbf{r}_{l'})} \quad (12)$$

where we write the reciprocal lattice vectors associated with the uniform grid as \mathbf{G}_m . This transformation uses two Fourier transforms to form the gradient.

The transformation can be written as

$$\mathbf{g}_l = \sum_{l'} \mathbf{e}_{l,l'} n_{l'} \quad (13)$$

with $\mathbf{e}_{l,l'} = -\mathbf{e}_{l',l}$ given by

$$\mathbf{e}_{l,l'} = \frac{1}{N} \sum_m i\mathbf{G}_m e^{i\mathbf{G}_m(\mathbf{r}_l - \mathbf{r}_{l'})} \quad (14)$$

Principle 1 from section 3.1 requires that

$$\delta E_{\text{xc}} = \sum_l \frac{dE_{\text{xc}}}{dn_l} \delta n_l = \omega \sum_l V_{\text{xc},l} \delta n_l \quad (15)$$

Equivalently, using local orbitals as basis functions, the energy (eq 11) is minimized by varying the coefficients of the local orbitals (eq 3), $u_{i\alpha}^n$, so that

$$\frac{\partial E_{\text{xc}}}{\partial u_{i\alpha}^n} = \omega \sum_l \frac{df_{\text{xc},l}}{dn_l} \frac{\partial n_l}{\partial u_{i\alpha}^n} \quad (16)$$

Both eqs 15 and 16 imply that the exchange-correlation potential for GGA functionals of the form (eq 8) is the total derivative $V_{\text{xc},l} = \omega^{-1} dE_{\text{xc}}/dn_l = df_{\text{xc}}/dn_l$. Because the KS matrix elements are also sums on a grid

$$\langle \phi_{i\alpha} | V_{\text{xc}} | \phi_{j\beta} \rangle = \omega \sum_l \phi_{i\alpha,l} V_{\text{xc},l} \phi_{j\beta,l} \quad (17)$$

with $\phi_{i\alpha,l} = \phi_{i\alpha}(r_l)$, the exchange-correlation potential can be expressed as

$$V_{xc,l} = \frac{\partial f_{xc}}{\partial n_l} + \sum_{l'} \frac{\partial f_{xc}}{\partial \mathbf{g}_{l'}} \cdot \frac{\partial \mathbf{g}_{l'}}{\partial n_l} = \frac{\partial f_{xc}}{\partial n_l} + \sum_{l'} \frac{\partial f_{xc}}{\partial \mathbf{g}_{l'}} \cdot \mathbf{e}_{l',l} \quad (18)$$

Note that this is the discrete counterpart of the exact potential (eq 10), but it was obtained directly from the discretized energy and yields an expression on the same grid as the density.

Once the discretized potential has been found, the Harris–Foulkes double-counting XC correction term results from following the original derivation^{3,4} but applied to the energies on the density grid. The result is simply

$$\Delta E_{xc}[\{n_l\}] = \omega \sum_l (f_{xc}(n_l^{\text{in}}, \mathbf{g}_l) - n_l^{\text{in}} V_{xc,l}^{\text{in}}) \quad (19)$$

3.3. Expression of the GGA NSC Force. To correctly derive the force on a grid, we proceed from the approximate energies (eqs 11 and 19) and the expression for the NSC force (eq 7). Considering only the NSC XC GGA force, we find that on a grid the correct expression is

$$\mathbf{F}_i^{\text{NSC,xc}} = -\omega \sum_l \delta n_l \nabla_i V_{xc,l} \quad (20)$$

This is the natural discretization of the last term in eq 7.

From eq 18, the gradient of the potential, $\nabla_i V_{xc,l}$, necessary to evaluate the force, is

$$\begin{aligned} \nabla_{ip} V_{xc,l} &= \frac{\partial^2 f_{xc,l}}{\partial n_l^2} \nabla_{ip} n_l + \sum_q \frac{\partial^2 f_{xc,l}}{\partial n_l \partial g_{lq}} \nabla_{ip} g_{lq} + \\ &\sum_{l'q} \frac{\partial^2 f_{xc,l'}}{\partial g_{l'q} \partial n_{l'}} e_{l',l}^q \nabla_{ip} n_{l'} + \sum_{l'qr} \frac{\partial^2 f_{xc,l'}}{\partial g_{l'q} \partial g_{l'r}} e_{l',l}^q e_{l',l'}^r \nabla_{ip} g_{l'r} \end{aligned} \quad (21)$$

where p , q , and r are Cartesian components. Alternatively, using the linear relationship (eq 13) between the density and its gradient

$$\begin{aligned} \nabla_{ip} V_{xc,l} &= \frac{\partial^2 f_{xc,l}}{\partial n_l^2} \nabla_{ip} n_l + \sum_{l'q} \frac{\partial^2 f_{xc,l}}{\partial n_l \partial g_{l'q}} e_{l',l}^q \nabla_{ip} n_{l'} + \\ &\sum_{l'q} \frac{\partial^2 f_{xc,l'}}{\partial g_{l'q} \partial n_{l'}} e_{l',l}^q \nabla_{ip} n_{l'} + \sum_{l'qr} \frac{\partial^2 f_{xc,l'}}{\partial g_{l'q} \partial g_{l'r}} e_{l',l}^q e_{l',l'}^r \nabla_{ip} n_{l'} \end{aligned} \quad (22)$$

We now insert eq 22 into eq 20, rearrange and define, for clarity, the following quantities:

$$L_l^{(1)} = \omega \delta n_l \frac{\partial^2 f_{xc,l}}{\partial n_l^2} \quad (23)$$

$$L_l^{(2)} = \omega \sum_{l'q} \delta n_{l'} \frac{\partial^2 f_{xc,l}}{\partial g_{l'q} \partial n_l} e_{l',l}^q \quad (24)$$

$$L_l^{(3)} = -\omega \sum_{l'q} \delta n_{l'} \frac{\partial^2 f_{xc,l'}}{\partial n_{l'} \partial g_{l'q}} e_{l',l}^q \quad (25)$$

$$L_l^{(4)} = -\omega \sum_{l'r} M_{l'r} e_{l',l}^r \quad (26)$$

with

$$M_{l'r} = \sum_{l'q} \delta n_{l'} \frac{\partial^2 f_{xc,l}}{\partial g_{l'q} \partial g_{l'r}} e_{l',l}^q \quad (27)$$

where we have used the symmetry of the transformation $\mathbf{e}_{l',l} = -\mathbf{e}_{r,l}$. $L_l^{(1)}$ is just a scalar quantity and $L_l^{(2)}$ is the dot product of a vector (a derivative of f_{xc}) and $\nabla \delta n_l$. Both $L_l^{(3)}$ and $L_l^{(4)}$ are divergences. Finally, $M_{l'r}$ is the dot product of $\nabla \delta n_l$ and a dyadic, that is, a vector.

The final expression for the non-self-consistent exchange-correlation force is simply

$$\mathbf{F}_i^{\text{NSC,xc}} = -\sum_l L_l^{\text{tot}} \nabla_i n_l = -\sum_l L_l^{\text{tot}} \nabla_i \eta_i (l\mathbf{r}_l - \mathbf{R}_l) \quad (28)$$

with $L_l^{\text{tot}} = L_l^{(1)} + L_l^{(2)} + L_l^{(3)} + L_l^{(4)}$, that is, the sum of eqs 23–26, and \mathbf{R}_l an atomic position, as usual. The second equality is true for superpositions of atomic densities η_i of the form of eq 4.

The continuum equivalent of the force is

$$\mathbf{F}_i^{\text{NSC,xc}}(\mathbf{r}) = -\int d\mathbf{r}' L^{\text{tot}}(\mathbf{r}') \nabla_i \eta_i (l\mathbf{r} - \mathbf{R}_l) \quad (29)$$

which happens to have the same basic dependence on the atomic densities as the LDA force,⁵ but with a more complicated expression for the factor $L^{\text{tot}}(\mathbf{r})$

$$\begin{aligned} L^{\text{tot}}(\mathbf{r}) &= \frac{\partial^2 f_{xc}}{\partial n(\mathbf{r})^2} \delta n(\mathbf{r}) + \frac{\partial^2 f_{xc}}{\partial n(\mathbf{r}) \partial \mathbf{g}(\mathbf{r})} \cdot \nabla \delta n(\mathbf{r}) - \\ &\nabla \cdot \left(\frac{\partial^2 f_{xc}}{\partial n(\mathbf{r}) \partial \mathbf{g}(\mathbf{r})} \delta n(\mathbf{r}) + \frac{\partial^2 f_{xc}}{\partial \mathbf{g}(\mathbf{r}) \partial \mathbf{g}(\mathbf{r})} \cdot \nabla \delta n(\mathbf{r}) \right) \end{aligned} \quad (30)$$

This form can be used to derive discretizations for other integration grid schemes where necessary.

3.4. Implementation details. A subtlety about the implementation of eq 28 is that, in many widespread GGA functionals, the kernel frequently depends on the gradient only through its modulus and, therefore, all derivatives with respect to the gradient have to be expressed accordingly. The two relevant derivatives are the vector

$$\frac{\partial^2 f_{xc}}{\partial n_l \partial \mathbf{g}_l} = \frac{\partial^2 f_{xc}}{\partial n_l \partial |\mathbf{g}_l|} \frac{\mathbf{g}_l}{|\mathbf{g}_l|} \quad (31)$$

and a dyadic made of the following components:

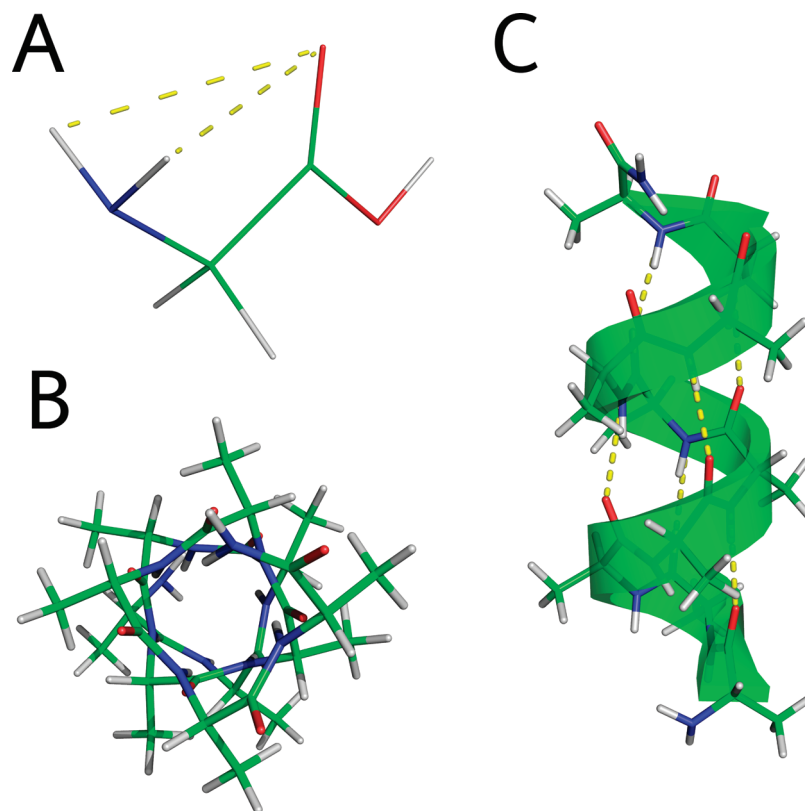
$$\frac{\partial^2 f_{xc}}{\partial g_{lp} \partial g_{lq}} = \frac{\partial^2 f_{xc}}{\partial |\mathbf{g}_l|^2} \frac{g_{lp} g_{lq}}{|\mathbf{g}_l|^2} + \delta_{pq} \frac{\partial f_{xc}}{\partial |\mathbf{g}_l|} \frac{1}{|\mathbf{g}_l|} - \frac{\partial f_{xc}}{\partial |\mathbf{g}_l|} \frac{g_{lp} g_{lq}}{|\mathbf{g}_l|^3} \quad (32)$$

The latter appears in $M_{l'r}$, in a dot product with $\nabla \delta n_l$, which can be simplified for implementation as

$$\frac{\mathbf{g}_l \cdot \nabla \delta n_l}{|\mathbf{g}_l|^2} \left(\frac{\partial^2 f_{xc}}{\partial |\mathbf{g}_l|^2} - \frac{1}{|\mathbf{g}_l|} \frac{\partial f_{xc}}{\partial |\mathbf{g}_l|} \right) \mathbf{g}_l + \frac{1}{|\mathbf{g}_l|} \frac{\partial f_{xc}}{\partial |\mathbf{g}_l|} \nabla \delta n_l \quad (33)$$

When working on a regular grid, as we assume, it is possible to use only eight Fourier transforms to evaluate the force: four to determine the vector quantity $\nabla_i \delta n(\mathbf{r})$, which appears in eqs 24 and 27 (one direct transform of the scalar $\delta n(\mathbf{r})$, a product with the reciprocal lattice vectors and one inverse per component), and four to obtain the divergence of terms eqs 25 and 26, which can be computed together. This number of FFTs is identical to the computational effort needed to evaluate the functional itself, since eq 10, in the

Scheme 1. Self-Consistently Relaxed Structures of Glycine (A) and Amide-Terminated Deca-alanine in α -Helical Conformation, Viewed along Its Axis (B) and Laterally (C)^a



^a Hydrogen bonds are represented by dashed lines. Color scheme: C, green; N, blue; O, red; H, white.

White–Bird formulation, also involves the calculation of only one gradient and one divergence.

4. Applications

In this section, we will perform a NSC pre-relaxation before refining the structure fully self-consistently. GGA functionals are a useful test as they are more expensive to evaluate than LDA, and hence the potential savings are also more important.

We report on structure relaxations of glycine and two homopolymers of alanine, penta-alanine (5 amino acid residues) and deca-alanine (10 residues), using the PBE GGA functional.³¹ We chose these systems because their relaxed structures strongly depend on hydrogen-bond interactions (Scheme 1). The structure of glycine was built de novo, but with a geometry close to the minimum energy conformer, that is, with the hydrogens of the amino group facing the carbonyl oxygen of the carboxylic acid. In this conformation, two hydrogen bonds are formed which contribute to stabilize the molecule. Both oligopeptides of alanine were built in an α -helix conformation, using an experimental structure (PDB 2DPQ) as a template.³² This structure was obtained using X-ray diffraction crystallography, and hence, the hydrogens were missing. Furthermore, most residues were not alanines, and we built our model system by replacing all amino acid side chains by methyl groups, in arbitrary conformations.

Structural relaxations were carried out using a standard conjugate gradient (CG) algorithm in the implementation

available in Conquest. The code uses periodic boundary conditions, but we made sure that the (orthorhombic) cell was big enough to prevent interactions between different images of the molecules. To avoid unwanted rotations, one bond of glycine was kept constrained to a fixed axis. In the polypeptides, only the side chains and hydrogens were relaxed: since the positions of the backbone atoms are experimental, in many practical situations we will want to keep them fixed even if they do not fully agree with our level of theory. The systems were small enough to make exact diagonalization of the Hamiltonian feasible. Consequently, the results should be of general validity and comparable to those obtained by other codes that use standard cubic scaling DFT. We note that the force formulas are identical for linear scaling, and have been used to test larger systems, such as DNA.¹²

All structures were relaxed by two methods. In the first one, a two-step protocol was applied. The initial structure was first relaxed non-self-consistently. The resultant intermediate structure was then relaxed fully self-consistently. We refer to this as method A. In the second method, the initial structure was completely relaxed self-consistently until convergence. This is method B.

Each CG step involves several evaluations of the functional, for two reasons. A line search is necessary to locate the minimum energy along the direction of the gradient. This search is common to both NSC and SCF methods. In addition, in SCF calculations, repeated evaluations are

Table 1. Comparison of SCF Relaxations of One Amino Acid and Two Peptides, with (Method A) and without (Method B) NSC Pre-relaxation^a

		method A		method B	
		step 1 (NSC)	step 2 (SCF)	total 1 + 2	only SCF
glycine ^b	CG steps	32	16	48	21
	functional evaluations	116	733	849	805
	total energy (Ha)	-56.625449	-56.475861		-56.475870
penta-alanine ^c	CG steps	105	23	128	53
	functional evaluations	373	1180	1553	2961
	total energy (Ha)	-242.121314	-241.541173		-241.541182
deca-alanine ^d	CG steps	73	28	101	75
	functional evaluations	299	1081	1380	3036
	total energy (Ha)	-474.779129	-473.372474		-473.372670

^a All relaxations were conducted using a conjugate gradient algorithm until the maximum force component was below 5.0×10^{-4} Ha Bohr⁻¹. NSC calculations were continued self-consistently in the second step of method A. ^b Ten atoms, two of them constrained to a fixed axis to avoid rotations. ^c Fifty-four atoms, of which 38 were allowed to move and the rest (the heavy atoms of the backbone) were kept static. ^d One hundred four atoms, of which only 73 moved.

Table 2. Root Mean Square Deviations (Å) between the Structures of the Molecules in Table 1 at Several Levels of Relaxation^a

			method A		method B
			step 1 (NSC)	step 2 (SCF)	only SCF
glycine	unrelaxed method A	step 1 (NSC)	0.097	0.069	0.069
		step 2 (SCF)		0.063	0.062
					0.008
penta-alanine	unrelaxed method A	step 1 (NSC)	0.279	0.269	0.258
		step 2 (SCF)		0.082	0.094
					0.023
deca-alanine	unrelaxed method A	step 1 (NSC)	0.320	0.301	0.298
		step 2 (SCF)		0.068	0.076
					0.017

^a For each molecule, the compared structures are initial guess (unrelaxed), relaxed non-self-consistently (method A, step 1) and then self-consistently (method A, step 2), and relaxed fully self-consistently from the unrelaxed structure until convergence (Method B). The completely relaxed structures are labelled method A, step 2 (SCF) and method B, only SCF, and the RMSDs show that both methods lead essentially to the same minimum, in agreement with the energies in Table 1.

performed to reach self-consistency (typically, of the order of 10), while only one is necessary in the NSC case. Counting the total number of functional evaluations summed over all relaxation steps is, therefore, a better estimate of computational expense and calculation time than using the number of relaxation steps as a measure.

Table 1 compiles our results for the systems described above. While the total number of CG steps tends to increase if method A is applied, compared to a full SCF relaxation (method B), the NSC pre-relaxation consistently reduces the number of CG steps in the SCF part of the calculation (compare Step 2 of Method A with Method B in the table). This result suggests that the NSC equilibrium point is not far from the SCF one. Root mean square deviations (rmsd; Table 2) support this idea, with distances to the initial unrelaxed structure of similar magnitude for all (totally or partially) relaxed structures and RMSDs about 1 order of magnitude lower between the final relaxed structures by both methods. Thus, the rmsd values show that, at least in these examples, both methods lead to essentially the same energy minimum; this is an indication that problems with local minima are unlikely to be more common with NSC pre-relaxation. The total energies of the completely relaxed structures, also shown in Table 1, confirm this conclusion: the maximum difference found between the SCF values by

both methods, which happened for deca-alanine, was 0.0002 Ha (or 0.1255 kcal/mol) and would satisfy chemical accuracy criteria.

Table 1 also shows that, except for glycine (a very small system), where the number of evaluations of the energy functional is very similar with and without NSC pre-relaxation, the NSC pre-relaxation can save a significant portion of energy evaluations. Indeed, this portion is as high as about 50% for both example peptides.

5. Discussion and Conclusions

This work presents the expression for the non-self-consistent exchange-correlation contribution to the DFT force on atoms when GGA functionals of the standard form are used. This expression is necessary to perform non-self-consistent ab initio tight binding electronic structure calculations with this important class of functionals. It also makes it possible to carry out NSC pre-relaxations of condensed-matter systems and molecular structures. Moreover, the expression of the force can also be used to correct the forces of poorly converged self-consistent calculations.

We have shown that the expression can be computed on a regular grid using only 8 Fourier transforms. This is the same as for the evaluation of the functional itself, which makes the force calculation efficient. Furthermore, as was the case for LDA functionals, the expression remains

unchanged in linear scaling algorithms and can thus be applied to large systems.

We have presented geometry optimization results on small and medium size biomolecular systems using the Conquest code. Although we have not used the linear-scaling capabilities of the code in this work, large biomolecules, in particular hydrated DNA,¹² have already been studied with Conquest. The calculations in this work show that NSC pre-relaxations can assist in finding equilibrium geometries faster than by using only self-consistent methods. This will be important in larger problems, for which $O(N)$ will be essential.

For the two small alanine peptides considered, there were important savings (of almost 50%) in the total number of functional evaluations, the most expensive part of the calculation. (For glycine, the smallest amino acid, the pre-relaxation made only a small difference: 849 and 805 Harris–Foulkes energy evaluations respectively). This is a promising result and indicates that the method could be of general validity. However, to gain confidence in this conclusion, more calculations are needed. In particular, globular proteins could be more difficult problems than the simple α -helical structures presented here. Finally, we should note that we used a conjugate gradient algorithm. The interrelationships of the pre-relaxation method with other, more efficient geometry optimization approaches should be evaluated in the future.

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Supporting Information Available: Coordinates of glycine, penta-alanine, and deca-alanine, before and after relaxation by the two methods described, have been deposited. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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