

# Fast computation of DFT nuclear gradient with multiresolution\*

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**Abstract:** We present an efficient algorithm for evaluating the exchange-correlation contribution to the nuclear gradients of density-functional theory calculation within the local spin-density approximation. The algorithm is an extension of the multi-resolution exchange-correlation (mrXC) method, which treats smooth and compact parts of the electron density separately. The nuclear gradient of the smooth density is calculated on the even-spaced grid while the compact part of the density is handled on the normal atom-centered grid (ACG). The overall formalism is still formally based on the ACG, and thus does not change the results of the existing ACG-based algorithms for all-electron density-functional theory (DFT) calculations. The variation of the positions and weights of ACG owing to the nuclear perturbation is also handled rigorously. Benchmark calculations with different basis sets and sizes of ACG show that mrXC reduces the computational cost by several times without loss of accuracy. It also lessens the impact on the CPU time when the size of the ACG is increased.

**Key words:** density-functional theory, exchange-correlation, planewaves, quantum chemistry.

**Résumé :** On a développé un algorithme efficace pour évaluer la contribution échange-corrélation aux gradients nucléaires pour des calculs selon la théorie de la fonctionnelle de la densité, dans les limites de l'approximation de la densité de spin locale. L'algorithme est une extension de la méthode de l'échange-corrélation à multirésolution (ECmr) qui traite séparément des parties lisses et compactes de la densité électronique. Le gradient nucléaire de la densité lisse est calculé sur une grille à espaces réguliers alors que la partie compacte de la densité est traitée sur la grille normale centrée sur l'atome (GCA). Le formalisme global est malgré tout basé sur une grille normale centrée sur l'atome et ne change donc par les résultats des algorithmes existants basés sur les GCA pour les calculs selon la TFD pour tous les électrons. La variation des positions et des poids de la GCA due à une perturbation nucléaire est traitée d'une façon rigoureuse. Des calculs repères avec divers ensembles de base et diverses tailles de GCA montrent que la méthode ECmr réduit de beaucoup les coûts de calcul sans perte de précision. Elle réduit aussi l'impact que pourrait avoir une augmentation de la taille de la GCA sur le temps requis de l'unité centrale.

**Mots-clés :** théorie de la fonctionnelle de la densité (TFD), échange-corrélation, ondes planes, chimie quantique.

## Introduction

Numerical integration of the exchange-correlation (XC) terms is one of the major bottlenecks in a density-functional theory (DFT) calculation. We have recently devised a novel scheme called multiresolution XC (mrXC) and showed its ability to speed up the calculation of the energy with local spin density approximation (LSDA) by three to five times.<sup>1,2</sup> The essence of mrXC is to divide the XC terms into *smooth* (low resolution) and *compact* (high resolution) categories, and treat the former more efficiently. In this paper, we will present the mrXC algorithm for the calculation of analytical gradients of the LSDA energy with respect to the nuclear coordinates, which is fundamental to nearly all types of applications.

Tremendous progress has been made to enhance the performance of DFT since the 1990s, with most of the effort on the reduction of the computational cost for Coulomb and Hartree-Fock (HF) exchange interactions. One of the most recent examples is the development of the Fourier transform

Coulomb (FTC) method,<sup>3</sup> of which we have made a new implementation in combination with other latest efficient Coulomb algorithms.<sup>4</sup> FTC replaces the most expensive part of the Coulomb interaction, namely the computation of four-index electronic repulsive integrals of diffuse basis functions with small exponents, with an accurate numerical evaluation using planewaves as the auxiliary basis. The computational cost of FTC scales as  $O(N^2)$  with respect to the size of the basis set and as  $O(V \log V)$  with respect to the size of the molecule ( $V$ ), versus  $O(N^4)$  and  $O(V^2)$ , respectively, for the conventional approach. Prior to FTC, the most efficient way of calculating the Coulomb energy was the combination of the continuous fast multipole method (CFMM) and the J-engine method. CFMM<sup>5</sup> is the first linear-scaling method for the calculation of Coulomb interaction, which reduces the computational cost of the calculation of Coulomb interaction among the well-separated Gaussians from quadratic scaling to linear. The J-engine technology<sup>6</sup> that reduced the calculation time of the Coulomb interaction in short range by 5–10 fold was developed some time later. We showed that FTC ac-

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celerates the Coulomb calculation further, by up to six times, by replacing the most time-consuming part of the J-engine calculation of the integrals containing three and four diffuse basis functions with an efficient numerical integration. The combination of FTC, CFMM, and J-engine represents the state-of-the-art in accurate Coulomb calculation with Gaussian basis functions while maintaining rigorous control of the error. Other efficient but approximating methods exist, such as the resolution-of-the-identity scheme that has been shown to have significant errors in total energy, but small errors in relative energy.<sup>7</sup> Much progress has also been made for the linear-scaling calculation of HF exchange,<sup>8,9</sup> required for hybrid DFT methods.

The other computational bottleneck besides the Coulomb and HF exchange energies, is the XC energy, and its share of the computational cost of a DFT calculation has increased significantly with the improvement of the performance of the others. A typical numerical quadrature for XC is the superposition of atom-centered grids (ACGs).<sup>10</sup> In such a grid, the density of the grid points is very high near nuclei because the electron density changes rapidly in this region, and becomes increasingly lower away from the nucleus as the electron density changes more slowly. While this is necessary for functions with high resolutions such as compact basis functions, it is not necessary for smooth functions with low resolutions. FTC has shown that accurate and efficient numerical integration can be done on a quite sparse even-spaced cubic grid (ESCG) for quantities related to smooth functions. It is, however, impossible to mix the ACG and the ESCG directly without loss of accuracy because the XC functional has a complicated nonlinear dependency on the total electron density that cannot be separated into smooth and compact terms without significant approximation. MrXC overcomes this difficulty by the introduction of two fast transformations between the ESCG and the ACG, which ensures accuracy while maintaining maximum efficiency.

## Algorithm

An LSDA functional,  $f$ , is a nonlinear function of electron spin densities  $\rho_\alpha$  and  $\rho_\beta$ . The integration of  $f$  yields the XC energy, and is done numerically on an ACG grid in a standard DFT calculation:

$$[1] \quad E_{\text{XC}} = \sum_i w_i f[\rho_\alpha(\bar{r}_i), \rho_\beta(\bar{r}_i)] \equiv \sum_i \varepsilon_{\text{XC}}(i)$$

where  $i$  is the index for each point on the ACG, and  $w_i$  is the weight for that point. The computation of the density is as follows:

$$[2] \quad \rho_{\sigma i} \equiv \rho_\sigma(\bar{r}_i) = \sum_{\mu\nu} P_{\mu\nu}^\sigma \phi_\mu(\bar{r}_i) \phi_\nu(\bar{r}_i) \\ \equiv \sum_{\mu\nu} P_{\mu\nu}^\sigma \phi_{\mu\nu}(\bar{r}_i), \quad \sigma = (\alpha, \beta)$$

in which  $\mathbf{P}^\sigma$  is the spin density matrix and  $\phi_\mu$  and  $\phi_\nu$  are atomic basis functions. We use the two-indexed symbol  $\phi_{\mu\nu}$  to denote the product of two basis functions or the basis function pair (BFP). The contribution of the XC energy to the nuclear gradient of the total DFT energy is to take the derivative of the XC energy with respect to the nuclear coordinates while the density matrix remains constant.<sup>11</sup> Denoting

it as  $E_{\text{XC}}^{\bar{A}}$  with  $\bar{A}$  being the coordinates of atom  $A$ , one obtains from eq. [1] through chain rule:

$$[3] \quad E_{\text{XC}}^{\bar{A}} \equiv \frac{\partial E_{\text{XC}}}{\partial \bar{A}} \Big|_{\mathbf{P}} \\ = \sum_i \left[ w_i (f_i^{\rho_\alpha} \rho_{\alpha i}^{\bar{A}} + f_i^{\rho_\beta} \rho_{\beta i}^{\bar{A}}) + w_i^{\bar{A}} f_i \right] \equiv \sum_i \varepsilon_{\text{XC}}^{\bar{A}}(i)$$

with the following definitions:

$$[4] \quad f_i \equiv f[\rho_\alpha(\bar{r}_i), \rho_\beta(\bar{r}_i)], \quad f_i^{\rho_\sigma} \equiv \frac{\partial f_i}{\partial \rho_\sigma} \\ \rho_{\sigma i}^{\bar{A}} \equiv \sum_{\mu\nu} P_{\mu\nu}^\sigma \frac{d}{d\bar{A}} [\phi_{\mu\nu}(\bar{r}_i)], \quad \sigma = (\alpha, \beta)$$

The nuclear gradient of a BFP on the ACG has two components. One is the derivative of each basis function with respect to its atomic position, or the *explicit* nuclear derivative. The other is the derivative of each ACG point with respect to the position of the atom that originates the point, or the *implicit* nuclear derivative. Those two derivatives, denoted as  $\rho_{\sigma i}^{\bar{A}}$  and  $\rho_{\sigma i}^{\bar{A}}$ , respectively, are defined below:

$$[5] \quad \rho_{\sigma i}^{\bar{A}} = \sum_{\mu\nu} \left( P_{\mu\nu}^\sigma \frac{\partial \phi_{\mu\nu}(\bar{r}_i)}{\partial \bar{A}} + P_{\mu\nu}^\sigma \frac{\partial \bar{r}_i}{\partial \bar{A}} \cdot \frac{\partial \phi_{\mu\nu}(\bar{r}_i)}{\partial \bar{r}_i} \right) \\ \equiv \rho_{\sigma i}^{\bar{A}} + \rho_{\sigma i}^{\bar{A}}$$

The evaluation of eq. [3] is dominated by calculating the nuclear gradient of the electron density,  $\rho_{\sigma i}^{\bar{A}}$ , as it involves loops over BFPs and atomic coordinates at each ACG point. The calculation of the nuclear gradient of the weight involves only the loop over the atomic coordinates. The electron density value at each ACG point required for the calculation of the derivative of the functional,  $f_i^{\rho_\sigma}$ , is identical to the last iteration of SCF, which precedes the nuclear gradient calculation.

In the context of mrXC, the electron spin density is separated into smooth and compact parts, with the calculation of the smooth part done on an ESCG, while the compact part is calculated directly on the ACG. The motivation for an ESCG comes from two observations. First, the calculation associated with the smooth part of the density is the computational bottleneck with the ACG as it has large spatial extent and covers many more grid points than the compact part of the density. Second, the ESCG has been used for DFT calculations with pseudopotentials with high efficiency. In a calculation with pseudopotentials, only the smooth part of the density is optimized, and the Coulomb and XC terms are calculated on the ESCG. This procedure has been applied successfully for the studies of solids, especially when combined with Car–Perrilleno-type of molecular dynamics.<sup>12</sup> Efforts have been made to combine the ACG and the ESCG for the full electron calculation by separated integrations.<sup>13</sup> This scheme however involves significant approximation and numerical imprecision, as the XC functional is not a linear function of density. By contrast, mrXC keeps the integration formally on the ACG and thus maintains the full accuracy. The actual calculation associated with smooth density is done on the ESCG for the time-consuming components,

namely the density and the XC matrix elements. The values calculated on the ESCG are projected onto the ACG grid through accurate interpolations.

The mrXC algorithm classifies each BFP as either smooth or compact. A smooth pair meets the condition that its value at any point in space can be interpolated accurately from those on an ESCG within a tight tolerance:

$$[6] \quad \tilde{\phi}_{\mu\nu i} = \sum_{\bar{m}} C_{\bar{m}} \tilde{\phi}_{\mu\nu}, \quad \bar{m} \equiv (m_x, m_y, m_z)$$

In the above equation,  $\bar{m}$  is a 3-dimensional index for the points on the ESCG, and  $C_{\bar{m}}$  the interpolation coefficient.  $C_{\bar{m}}$  is a function of the position of the point  $i$  and the positions of a small number of ESCG points surrounding that point. The sparsity of  $C_{\bar{m}}$  allows for very fast transformation of numerical values between the two grids. We use a tilde ( $\sim$ ) to denote a smooth function and a caret ( $\wedge$ ) to denote a compact function. It then follows that the smooth density  $\tilde{\rho}$  on the ACG can be calculated as

$$[7] \quad \tilde{\rho}_{\sigma i} = \sum_{\bar{m}} C_{\bar{m}} \tilde{\rho}_{\sigma \bar{m}}$$

and its explicit nuclear gradient as

$$[8] \quad \tilde{\rho}_{\sigma i}^{\wedge(\bar{A})} = \sum_{\bar{m}} C_{\bar{m}} \tilde{\rho}_{\sigma \bar{m}}^{\wedge(\bar{A})}, \quad \tilde{\rho}_{\sigma i}^{\wedge(\bar{A})} = \sum_{\bar{m}} C_{\bar{m}}^{\wedge(\bar{A})} \tilde{\rho}_{\sigma \bar{m}}$$

Two ESCGs with different grid densities are used in the calculation of the smooth density for the XC energy with mrXC. First, the smooth density is calculated on the less dense grid that is sufficiently accurate for a Fourier expansion of the density. Then, it undergoes a Fourier transform to the more dense ESCG. The latter allows an accurate local interpolation onto an ACG using eqs. [6] and [7]. One could follow the same procedure to produce the nuclear gradient of the smooth density on the ACG, which would be accurate. However, it will not be efficient as it will require many Fourier transformations, owing to the number of nuclear perturbations involved. Instead, one would wish to calculate directly on the coarse ESCG grid the nuclear gradient of  $E_{XC}$  contributed from the nuclear gradient of the smooth density. This can be achieved through a reverse interpolation by combining eqs. [7] and [3] for the contribution of the explicit nuclear derivative of the smooth density to  $E_{XC}$ :

$$[9] \quad \begin{aligned} \tilde{E}_{XC}^{\wedge(\bar{A})} &\equiv \sum_i w_i (f_i^{\rho\alpha} \tilde{\rho}_{\alpha i}^{\wedge(\bar{A})} + f_i^{\rho\beta} \tilde{\rho}_{\beta i}^{\wedge(\bar{A})}) \\ &= \sum_i \sum_{\bar{m}} w_i (f_i^{\rho\alpha} C_{\bar{m}} \tilde{\rho}_{\alpha \bar{m}}^{\wedge(\bar{A})} + f_i^{\rho\beta} C_{\bar{m}} \tilde{\rho}_{\beta \bar{m}}^{\wedge(\bar{A})}) \\ &\equiv \sum_{\bar{m}} [(\sum_i w_i f_i^{\rho\alpha} C_{\bar{m}}) \tilde{\rho}_{\alpha \bar{m}}^{\wedge(\bar{A})} + (\sum_i w_i f_i^{\rho\beta} C_{\bar{m}}) \tilde{\rho}_{\beta \bar{m}}^{\wedge(\bar{A})}] \\ &\equiv \sum_{\bar{m}} (\tilde{f}_{\bar{m}}^{\rho\alpha} \tilde{\rho}_{\alpha \bar{m}}^{\wedge(\bar{A})} + \tilde{f}_{\bar{m}}^{\rho\beta} \tilde{\rho}_{\beta \bar{m}}^{\wedge(\bar{A})}) \end{aligned}$$

In the above equation, evaluation of  $\tilde{f}_{\bar{m}}^{\rho\sigma}$  takes little time, as only a few neighboring points of the ESCG are involved in the interpolation of each ACG point. We should also note that  $\tilde{f}_{\bar{m}}^{\rho\sigma}$  is not equal to  $f_{\bar{m}}^{\rho\sigma}$  on the ESCG. The latter is a function of total electron spin densities, which include the smooth and compact parts.

In a DFT energy calculation with mrXC,<sup>1</sup> the smooth density is first calculated on an ESCG that is less dense than the one needed for the local interpolation, i.e., eq. [9]. Such a transformation between two ESCGs can be expressed as

$$[10] \quad \tilde{\rho}_{\sigma m} = \sum_{|k_j| \leq \frac{1}{2} D_m} \tilde{\rho}_{\sigma}(k_j) e^{2\pi i k_j \cdot \bar{r}_m} = \sum_{|k_j| \leq \frac{1}{2} D_n} \tilde{\rho}_{\sigma}(k_j) e^{2\pi i k_j \cdot \bar{r}_n},$$

$$k_{j+1} - k_j = (L_x^{-1}, L_y^{-1}, L_z^{-1})$$

In the above equation,  $D_m$  and  $D_n$  are the grid densities of the dense and coarse ESCGs, respectively,  $L_x$ ,  $L_y$ , and  $L_z$  the dimensions of the ESCG.  $\tilde{\rho}_{\sigma}(\bar{k})$  is the Fourier transformation of the smooth density calculated on the coarse ESCG according to eq. [2]:

$$[11] \quad \tilde{\rho}_{\sigma}(k_j) = \sum_{\bar{n}} \tilde{\rho}_{\sigma \bar{n}} e^{-2\pi i k_j \cdot \bar{r}_n}$$

The computation of the density on an ESCG (eq. [2]) involves a loop over BFPs and is computationally more expensive than the fast Fourier transformations (FFTs) required in eqs. [10] and [11]. The transformation from the coarse grid to the dense grid, shown in eq. [10], provides a significant gain in efficiency as the number of the ESCG points, and thus the computational cost of the smooth density on the grid, scale cubically with respect to the grid density. A BFP is judged as smooth when it is represented on the coarse grid within a tight threshold of error, a scheme developed and implemented by Fusti-Molnar in Q-Chem Program:<sup>14</sup>

$$[12] \quad 1 - \frac{\int_{-\frac{1}{2} D_n}^{\frac{1}{2} D_n} |\tilde{\phi}_{\mu\nu}(\bar{k})| d^3 k}{\int_{-\infty}^{\infty} |\tilde{\phi}_{\mu\nu}(\bar{k})| d^3 k} < \text{threshold}$$

This screening process takes little CPU time as it is done analytically for each BFP.

To apply mrXC for the calculation nuclear gradient, it is evident from the first few equations that one needs to obtain  $\tilde{\rho}_{\sigma \bar{m} \bar{A}}$  on the dense ESCG. While one can do so with the same procedure as above starting from  $\tilde{\rho}_{\sigma \bar{m} \bar{A}}$  on the coarse ESCG, it would require one FFT for each atomic coordinate within the molecular framework. We will instead calculate  $\tilde{E}_{XC}^{\wedge(\bar{A})}$  directly on the coarse ESCG by the following reformulation with the help of eqs. [9] and [10]:

$$[13] \quad \begin{aligned} \sum_{\bar{m}} \tilde{f}_{\bar{m}}^{\rho\alpha} \tilde{\rho}_{\alpha \bar{m}}^{\wedge(\bar{A})} &= \sum_{|k_j| \leq \frac{1}{2} D_m} \tilde{\rho}_{\sigma}^{\wedge(\bar{A})}(k_j) \sum_{\bar{m}} \tilde{f}_{\bar{m}}^{\rho\sigma} e^{2\pi i k_j \cdot \bar{r}_m} \\ &\equiv \sum_{|k_j| \leq \frac{1}{2} D_m} \tilde{\rho}_{\sigma}^{\wedge(\bar{A})}(k_j) \tilde{f}^{\rho\sigma}(k_j) \\ &= \sum_{\bar{n}} \tilde{\rho}_{\sigma \bar{n}}^{\wedge(\bar{A})} \sum_{|k_j| \leq \frac{1}{2} D_n} \tilde{f}^{\rho\sigma}(k_j) e^{-2\pi i k_j \cdot \bar{r}_n} \\ &\equiv \sum_{\bar{n}} \tilde{\rho}_{\sigma \bar{n}}^{\wedge(\bar{A})} \tilde{f}_{\bar{n}}^{\rho\sigma} \end{aligned}$$

with the following:

$$[14] \quad \tilde{\rho}_{\sigma \bar{n}}^{\wedge(\bar{A})} = \sum_{\mu\nu} P_{\mu\nu}^{\sigma} \phi_{\mu\nu}^{\wedge(\bar{A})}, \quad \tilde{\rho}_{\sigma}^{\wedge(\bar{A})}(k_j) = \sum_{\bar{n}} \tilde{\rho}_{\sigma \bar{n}}^{\wedge(\bar{A})} e^{-2\pi i \bar{k}_j \cdot \bar{r}_n}$$

Equation [13] leads to the calculation of the contribution

of the explicit nuclear derivative of the smooth density to the XC energy gradient as follows:

$$[15] \quad \tilde{E}_{\text{XC}}^{(\bar{A})} = \sum_n (\tilde{f}_n^{\rho_\alpha} \tilde{\rho}_{\alpha n}^{\bar{A}} + \tilde{f}_n^{\rho_\beta} \tilde{\rho}_{\beta n}^{\bar{A}}) \\ = \sum_n \sum_{\mu\nu} (\tilde{f}_n^{\rho_\alpha} P_{\mu\nu}^\alpha + \tilde{f}_n^{\rho_\beta} P_{\mu\nu}^\beta) \phi_{\mu\nu}^{\bar{A}}$$

We should note that the formulism in eq. [15] resembles the calculation of nuclear gradients of Coulomb energy with FTC if one replaces  $(\tilde{f}_n^{\rho_\alpha} P_{\mu\nu}^\alpha + \tilde{f}_n^{\rho_\beta} P_{\mu\nu}^\beta)$  with the Coulomb potential. Thus, further reduction of CPU time can be realized when these two methods are applied in concert.

We have shown hitherto how to apply mrXC to the calculation of the nuclear gradient of the DFT energy without the consideration of perturbations of ACG points with the atoms. This perturbation arises when the ACG point is centered on the perturbing atom and accounts for a small but numerically significant correction. In the current Q-Chem Program, such a correction is done through a simple procedure utilizing translational invariance of the nuclear gradients of a molecule. When an ACG point is centered on atom A, its contribution to the nuclear gradient of XC energy is calculated as

$$[16] \quad E_{\text{XC}}^{\bar{A}}(i) = -\sum_{B \neq A} E_{\text{XC}}^{\bar{B}}(i), \quad i \in A$$

This formulism is, however, not applicable to mrXC as it requires the nuclear gradient of the smooth density at every ACG point, which we have intentionally avoided. Instead, we start from eq. [5] and recognize that  $\frac{\partial \rho_i}{\partial \bar{r}_i}$  is the identity matrix when  $i$  is originated from A and zero otherwise, which leads the following expression for this correction from each spin:

$$[17] \quad w_i f_i^{\rho_\sigma} \rho_{\sigma i}^{\bar{A}} = w_i f_i^{\rho_\sigma} \sum_{\mu\nu} P_{\mu\nu}^\sigma \frac{\partial \phi_{\mu\nu}(\bar{r}_i)}{\partial \bar{r}_i} \equiv w_i f_i^{\rho_\sigma} \nabla \rho_{\sigma i}, \quad i \in A$$

We use  $\nabla$  to denote the partial derivative with respect to the electronic coordinate  $\bar{r}_i$ .

Finally, we arrive at the expression of the mrXC contribution to the nuclear gradients as

$$[18] \quad E_{\text{XC}}^{\bar{A}} = \tilde{E}_{\text{XC}}^{(\bar{A})} + \sum_{i \in A} \left( w_i f_i^{\rho_\alpha} (\nabla \tilde{\rho}_{\alpha i} + \nabla \hat{\rho}_{\alpha i}) \right. \\ \left. + w_i f_i^{\rho_\beta} (\nabla \tilde{\rho}_{\beta i} + \nabla \hat{\rho}_{\beta i}) \right) \\ + \sum_i \left( w_i f_i^{\rho_\alpha} \tilde{\rho}_{\alpha i}^{(\bar{A})} + w_i f_i^{\rho_\beta} \tilde{\rho}_{\beta i}^{(\bar{A})} + w_i^{\bar{A}} f_i \right)$$

with the nonsmooth density,  $\hat{\rho}$ , and its nuclear derivatives calculated directly on the ACG.

## Performance of mrXC

We have implemented the above algorithm to calculate mrXC energy gradients within the quantum chemistry package Q-Chem.<sup>14</sup> Its performance is tested with the DFT energy and gradient calculations using two different basis sets and two choices of ACG. Taxol (C<sub>47</sub>H<sub>51</sub>N<sub>14</sub>O), a natural cancer drug with a globular structure, was chosen as the test mole-

cule. The two sizes of ACG are SG-1<sup>15</sup> and unpruned (100, 302) grid. SG-1 is a pruned (50, 94) grid with about 3000 points per atom. The (100, 302) grid has 100 radial points,<sup>16</sup> and 302 angular points,<sup>17</sup> resulting in 30 200 points per atom. The accuracy of the former is considered moderate, and accuracy of the latter is high. The threshold of the smoothness is set at 10<sup>-6</sup>, and the grid densities of the coarse and fine ESCGs are 3.8 and 5.7, respectively. The benchmarks are run on a 2.5 GHz quad-core Pentium processor.

Table 1 lists the results of the calculations. The third column shows the percentage of BFPs that are classified by mrXC as smooth. The fourth column shows the accuracy of mrXC in total DFT energy with the error per atom listed in the parentheses. The mean-absolute-errors (MAEs) and the maximum errors of the nuclear gradient with mrXC are listed in columns five and six. The errors are calculated using the full ACG calculations as the reference. One can see that mrXC classifies more than 90% of BFPs as smooth but yields errors less than one micro-Hartree (10<sup>-6</sup> au) per atom in total energy, and about 10<sup>-5</sup> au in gradient. These errors are well within the tolerance of numerical precision for a typical DFT calculation.

The calculation associated with smooth BFPs can be done more efficiently on the ESCG than on the ACG. Column seven in Table 1 shows the CPU time directly on the ACG, with and without mrXC, for the computation of the electron density and its nuclear gradients. Column eight in Table 1 shows the CPU time for the same computation on the ESCG. The calculation of these two quantities takes the vast majority of the CPU (>95%) for the calculation of the nuclear gradient of the XC energy. One can see that it only took 12 s to do the calculation with smooth BFPs with SG-1 grid and 6–311G(df,pd) basis, in comparison with 357 s (405–48) that it takes on the ACG for the same calculation. The transformation steps — FFT and divided-difference — between the ACG and ESCG take a relatively small amount of CPU time and are listed in column nine. From those numbers, we can calculate the speedups mrXC provides, and they are listed in Table 1, column 10. As one can see, mrXC provides speed-up of 6–10 times for the gradient part of the calculation. Further gain of efficiency can be achieved when the calculation on the ESCG is combined with the Coulomb calculation with FTC, and thus becomes “free.” The speedups for this scenario are listed in Table 1, column 11.

Table 1 also lists the results with different basis sets and sizes of ACG. One can see from the numbers that there is more efficient gain with cc-pVTZ basis than with 6–311G(df,pd). This is due to the fact that the former has more functions in the valence region than the latter. Smooth BFPs are more likely formed with those valence basis functions than core functions as the former have smaller exponents. MrXC also provides better performance gain as the grid size increases, because the computational cost on ACG increases with the ACG grid size, but the cost on the ESCG remains unchanged. By reducing the workload on the ACG, mrXC minimizes the impact of enlarging the ACG on CPU time. A large ACG is often desirable due to increased accuracy, and has even been shown necessary for a numerically reliable description of intermolecular interactions.<sup>18</sup>

**Table 1.** The performance of mrXC for the calculation of the nuclear gradients of taxol with LSDA functional.

Basis (no. of BFs)	Method	Compact BFPs (%)	Error in energy (micro-Hartree)	Error in gradient (au)		CPU time (s)			Speed-up	
				MAE	Max.	ACG	ESG	Interpolation	with FTC	
<b>ACG SG-1</b>										
6-311G(df,pd)	ACG only					405				
2111	MrXC	10.00	37.79 (0.33)	6.36E-06	6.21E-05	48	12	6	6.19	7.58
cc-pVTZ	ACG only					698				
2574	MrXC	8.60	8.27 (0.07)	3.09E-06	2.77E-05	72	28	6	6.59	8.96
<b>ACG (100, 302)</b>										
6-311G(df,pd)	ACG only					2715				
	MrXC	10.00	49.34 (0.44)	1.19E-06	1.38E-05	265	12	34	8.73	9.08
cc-pVTZ	ACG only					5204				
	MrXC	8.60	13.20 (0.12)	7.68E-07	7.36E-06	424	28	29	10.83	11.50

Note: The numbers in parentheses in the 4th column (Error in energy) are errors per atom. MrXC, multiresolution exchange-correlation method; LSDA, local spin density approximation; ACG, atom-centered grid; BF, basis function; BFP, basis function pair; MAE, mean absolute error; ESG, even-spaced grid; FTC, Fourier transform Coulomb method; SG-1, pruned grid (50, 94) with ca. 3000 points per atom.

## Conclusions

We have shown how to seamlessly combine the ESCG and the ACG for the numerical integration of the nuclear gradient of the XC part of the DFT energy with LSDA functionals. The algorithm is the extension of the mrXC method, which treats the smooth and the compact parts of the electron density separately. The nuclear gradient of the smooth density is calculated on the ESCG, while the compact part of the density is handled on the ACG. The overall technique is still formally based on the ACG, and thus does not change the results of the existing ACG-based algorithms for all-electron DFT calculations. The variation of the positions and weights of ACG owing to the nuclear perturbation is also handled rigorously. The benchmark calculations on the drug molecule taxol with different basis sets and sizes of ACG show that mrXC reduces the computational cost without loss of accuracy. MrXC also lessens the impact of increase in the size of the ACG on the CPU time. We are working on extending the method to all common types of DFT functionals.

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