

Efficient and accurate numerical integration of exchange-correlation density functionals

Chun-Min Chang, Nicholas J. Russ, and Jing Kong*

Q-Chem, Inc., 5001 Baum Blvd., Suite 690, Pittsburgh, Pennsylvania 15213, USA

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We present a method for efficient calculation of exchange correlation in a density-functional theory calculation with Gaussian basis functions. It seamlessly combines the treatments of smooth (low-energy cutoff) and nonsmooth parts of the electron density such that computational performance can be maximized without approximation. Benchmark calculations show that the scheme can speed up the calculation of the exchange-correlation by as much as ten times or more without error.

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I. INTRODUCTION

Density-functional theory (DFT) is the major tool for quantum simulation of molecules and solids primarily due to its accuracy and computational efficiency. At the core of DFT is the so-called exchange-correlation (XC) functional, which contains the electron exchange and correlation effects. The XC functionals are complicated and require numerical integration. There are two common types of grid for the numerical integration. One is the even-spaced Cartesian grid (ESCG), mostly used in the study of solids with periodic boundary condition in conjunction with the use of Fourier functions as the basis. The use of Fourier functions allows efficient computation of the Hartree or Coulomb interaction by taking advantage of discrete fast Fourier transformation (FFT), but in practice is only applicable to the treatment of the smooth part of the electron density with low-energy cutoff. The typical solution for the nonsmooth part was to approximate it using a density-independent pseudopotential (PP). The integration of the XC matrix is typically calculated together with the Coulomb matrix, which offers the further advantage of computational efficiency.

The other type of grid is the atom-centered grid (ACG). The ACG quadrature for a molecule is the superposition of the quadrature of each atom. The latter is composed of radial and spherical parts, and is designed for the integration of exponential functions located on an atom. When the atomic quadrature is applied in a molecule, the weights are scaled in the regions where the points from different atoms overlap. An ACG can handle both nonsmooth and smooth parts of the electron density and is typically implemented in quantum chemistry programs and used extensively for the DFT calculation of molecules, where all of the electrons need to be explicitly included in the calculation for accuracy. In those programs, atom-centered Gaussians are used as the basis functions, and the Coulomb matrix of the Gaussians is evaluated separately from the XC matrix with the explicit computation of four-index Coulomb integrals. The localized Gaussian function allows the exploration of the sparsity of the XC matrix for computational efficiency. On the other hand, this approach is not as efficient as the one with ESCG for the calculation of the XC matrix associated with the smooth density because the Gaussian basis functions describing the

smooth density are expansive in space and offer the least computational advantage of locality.

In recent years, efforts have been made to extend the PP-based algorithms to include the treatment of nonsmooth functions using Gaussian basis functions. They are motivated by the demand of the calculation of systems with large unit cells in solids and liquids because the affordable energy cutoff with the PP method often does not provide sufficient accuracy in describing the variation of the electron density in the molecular environment. Furthermore, there is no density sparsity to take advantage of with Fourier functions as the basis. Various methods have been proposed to combine the local basis functions with the Fourier functions; the Gaussian augmented-plane-wave (GAPW) method [1,2] is a good representative of them. GAPW, developed from the projected augmented-wave method [3], uses Gaussians as basis functions, but approximates the density as the sum of three parts in space with different smoothness. Each part is represented by either Gaussians (for the hard and soft regions) or plane waves (for the smooth region). The XC matrix in the nonsmooth regions is evaluated on the ACG grid. There are two sources of inaccuracies in the approach of GAPW. First, the density is approximated through an expansion of a mixture of atom-centered Gaussians and plane waves. Secondly, the nonlinear XC functional is decomposed into a linear sum of the contributions from each of three parts of the density. Nonetheless this approach preserves the computational efficiency of the PP-based algorithms for the smooth part of the XC matrix and programs based on it, such as CP2K, are often used for molecular dynamics simulations. We note that other choices of local basis functions exist, such as localized numerical orbitals [4,5]. It is also possible to design Cartesian grids that are adaptive to the resolution of XC potential or density in real space [6,7].

In this paper, we present a method that seamlessly combines the advantages of ESCG and ACG without loss of accuracy, especially for the calculation of the XC matrix with Gaussian basis. It was shown, through the Fourier transform Coulomb (FTC) method, that the Coulomb matrix of the smooth part of the density with Gaussian basis functions can be calculated efficiently on ESCG with plane waves as the auxiliary basis with little error [8]. The conventional Coulomb method with Gaussian basis computes the four-center integrals and scales in $O(N^4)$ with respect to the size of the basis, with the majority of those integrals associated with the smooth Gaussians as they are extensive in space. FTC replaces the computation of

*Corresponding author: jkong@q-chem.com

those integrals with an accurate numerical integration scheme that scales in $O(N^2)$. Our implementation of FTC [9] shows that it overcomes the major deficiency of previous linear scaling methods of analytic integrals and fast multipoles. In the calculation of the Coulomb potential, different parts, smooth, far-field and near-field, can be evaluated separately and added together at the end. Such an approach cannot be applied to the evaluation of exchange-correlation potential, because the XC functional is a highly nonlinear function of density. Instead of separating the XC potential onto ESCG and ACG explicitly, we design a method to transform the grid values from one grid to another by local interpolation. The total density is derived by adding up on ACG the nonsmooth density and the smooth density transformed from ESCG. The XC potential then is calculated on ACG and integrated with the nonsmooth density to form the nonsmooth part of the XC matrix. The smooth part of the XC matrix is derived by integrating on ESCG the XC potential transformed from ACG with the smooth density. We call our scheme multiresolution XC (MRXC). It is worth noting that it is not based on multiresolution analysis. The results of MRXC with the local spin density approximation (LDA) functional have shown that MRXC yields three to five times improvement in efficiency without loss of accuracy [10]. Here, we extend MRXC to general-gradient-approximation (GGA) functionals [11,12], the most common type of XC functionals, and employ the cardinal B -spline method [13] for the local interpolation. The cardinal B spline has been applied to the particle-mesh Ewald method for the fast calculation of Coulomb interaction in molecular mechanic simulations [14] with a rigorous error limit. A screening scheme that enhances the performance further for large molecular systems is also presented.

II. ALGORITHM

A GGA functional f is the function of electron spin densities and their gradients, and can be integrated accurately on an ACG:

$$E_{XC} = \sum_i w_i f(\rho_i^\alpha, \rho_i^\beta, \nabla \rho_i^\alpha, \nabla \rho_i^\beta), \quad (1)$$

with

$$\rho_i^\sigma = \sum_{\mu\nu} P_{\mu\nu}^\sigma \phi_{\mu\nu,i}, \quad \nabla \rho_i^\sigma = \sum_{\mu\nu} P_{\mu\nu}^\sigma \nabla \phi_{\mu\nu,i}, \quad \sigma = (\alpha, \beta). \quad (2)$$

In the above equations, w_i is the weight of the ACG grid point i , μ, ν the indexes of the Gaussian basis functions. σ is the spin index where α, β represent spin up and spin down, respectively. $\phi_{\mu\nu}(\mathbf{r}) \equiv \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})$ is a basis function pair, and $P_{\mu\nu}^\sigma$ the spin-resolved density matrix. To obtain the XC matrix as part of the Hamiltonian matrix, one takes the derivative of E_{XC} with respect to $P_{\mu\nu}^\sigma$ and obtains

$$H_{\mu\nu}^\sigma = \sum_i w_i (f_i^{\rho^\sigma} \phi_{\mu\nu,i} + f_i^{\nabla \rho^\sigma} \cdot \nabla \phi_{\mu\nu,i}). \quad (3)$$

In the calculation of the XC matrix, the vast majority (>95%) of the computing effort is spent on the evaluation of the density on the grid and the formation of the XC matrix,

as they involve looping over the basis function pairs. We wish to enhance the performance of these two steps by calculating the smooth density and its gradient, and the smooth part of the matrix on the ESCG.

We first assume that some of the basis function pairs are smooth enough such that they can be accurately represented by their values on the ESCG grid through a local interpolation (the criteria for this representation will be established later):

$$\phi_{\mu\nu}(\mathbf{r}) = \sum_m C_m(\mathbf{r}) \phi_{\mu\nu}(\mathbf{r}_m), \quad (4)$$

where m is the index for the ESCG and $C_m(\mathbf{r})$ is the local interpolation function derived from the cardinal B spline:

$$C_m(\mathbf{r}) = \sum_l e^{2\pi i \mathbf{k}_l \cdot \mathbf{r}_m} \frac{\sum_{m'} M_j(\mathbf{r} - \mathbf{r}_{m'}) e^{-2\pi i \mathbf{k}_l \cdot \mathbf{r}_{m'}}}{\sum_{m''} M_j(\mathbf{r}_{m''}) e^{2\pi i \mathbf{k}_l \cdot \mathbf{r}_{m''}}}. \quad (5)$$

In the equation, M_j is a j th-order local recursion function defined as

$$M_j(x) = \frac{x + \frac{j}{2}}{j-1} M_{j-1}\left(x + \frac{1}{2}\right) + \frac{\frac{j}{2} - x}{j-1} M_{j-1}\left(x - \frac{1}{2}\right), \quad j > 2, \quad (6)$$

with

$$M_2(x) = \begin{cases} 1 - |x|, & |x| \leq 1 \\ 0, & |x| > 1 \end{cases}. \quad (7)$$

The gradient of the basis function pair can be calculated as

$$\nabla \phi_{\mu\nu}(\mathbf{r}) = \sum_{\mathbf{r}_m} \phi_{\mu\nu}(\mathbf{r}_m) \nabla C_m(\mathbf{r}), \quad (8)$$

where the expression for $\nabla C_m(\mathbf{r})$ can be readily derived from the following simple formula for the derivative of B -spline interpolation:

$$\frac{dM_j(x)}{dx} = M_{j-1}(x) - M_{j-1}(x-1). \quad (9)$$

Because the density is a linear combination of the basis function pairs, the smooth density $\tilde{\rho}^\sigma$ and its gradient can be simply calculated as

$$\tilde{\rho}^\sigma(\mathbf{r}) = \sum_m C_m(\mathbf{r}) \tilde{\rho}^\sigma(\mathbf{r}_m), \quad \mu\nu \in S, \quad (10)$$

$$\nabla \tilde{\rho}^\sigma(\mathbf{r}) = \sum_m \tilde{\rho}^\sigma(\mathbf{r}_m) \nabla C_m(\mathbf{r}), \quad \mu\nu \in S, \quad (11)$$

where S stands for the set of the basis function pairs that satisfy the smoothness condition [Eq. (4)]. These two equations show that one can calculate the smooth density and its gradient at any point in space through interpolation of the smooth density on the ESCG.

To form the XC matrix, one needs first to calculate the functional derivatives $f_i^{\rho^\sigma}$ and $f_i^{\nabla \rho^\sigma}$ at each ACG point. Since the functional is nonlinear with respect to the variables, the separation of the density into smooth and nonsmooth parts will not simply lead to the same separation for the functional and its derivatives. Instead, we will calculate the smooth densities and their gradients on the ACG according to Eqs. (10) and

(11), and calculate the nonsmooth density $\hat{\rho}^\sigma$ and its gradient $\nabla \hat{\rho}^\sigma$ directly on the ACG. The total density and its gradient on the ACG then become

$$\rho^\sigma = \bar{\rho}^\sigma + \hat{\rho}^\sigma, \quad \nabla \rho^\sigma = \nabla \bar{\rho}^\sigma + \nabla \hat{\rho}^\sigma. \quad (12)$$

Still, we wish to calculate the XC matrix elements that correspond to the smooth basis function pairs on the ESCG. To do this, one can reformulate Eq. (3) by using Eqs. (4) and (8) and obtain

$$H_{\mu\nu}^\sigma = \sum_m \tilde{f}_m^{\rho^\sigma} \phi_{\mu\nu}(\mathbf{r}_m), \quad \mu\nu \in S, \quad (13)$$

where

$$\tilde{f}_m^{\rho^\sigma} = \sum_i [w_i f_i^{\rho^\sigma} C_m(\mathbf{r}) + w_i f_i^{\nabla \rho^\sigma} \cdot \nabla C_m(\mathbf{r})]. \quad (14)$$

We note that Eqs. (11) to (14) also show that the smooth part of the calculation with a GGA functional can be done at essentially the same cost as that with a LDA functional because the evaluation with $\nabla C_m(\mathbf{r})$ takes little time. This is in contrast with the calculation using ACG only where the CPU time doubles for a GGA functional due to the need of explicit computation of terms involving the gradients of basis function at each grid point.

The above algorithm demonstrates an accurate route to evaluate the densities and their gradients and the formation of the XC matrices on the ESCG, as long as the basis function pairs are sufficiently smooth. The calculation with the smooth basis function pairs is the major component of the computational cost as their spatial ranges are greater than those of the nonsmooth basis function pairs. The evaluation of the functional derivatives on the ACG takes little time ($\sim 1\%$ of the total XC time) because it requires the loop over the grid points only. Major gains are achieved by shifting the computational cost of the two steps from the ACG to the ESCG for the smooth basis function pairs, as the ESCG has been shown better suited for the smooth basis function pairs in plane-wave programs and our own experience with FTC. The interpolation steps introduced in the algorithm consume little CPU time with a local interpolation scheme, where the value on an ACG point is determined by nearby ESCG points only.

Further efficiency gain can be achieved through a second interpolation step with Fourier functions. When interpolating a Gaussian function, using Fourier functions, which are global, will in general require a less dense ESCG than using local polynomials. The Fourier transform of a Gaussian function is a Gaussian in the momentum space and therefore has a limited effective range. Assuming the Fourier transforms of all the smooth basis function pairs are within a certain range K_s^{\max} , the maximum momentum corresponding to the ESP for the local interpolation, K_L^{\max} , will be larger as the maximum momentum is directly proportional to the grid density. That is, the following trivial relationship holds since all the $\bar{\phi}_{\mu\nu}(\mathbf{k})$'s are effective zero for $|\mathbf{k}| > K_s^{\max}$:

$$\begin{aligned} \phi_{\mu\nu}(\mathbf{r}) &= \sum_{|\mathbf{k}_n| < K_s^{\max}} \bar{\phi}_{\mu\nu}(\mathbf{k}_n) e^{-2\pi i \mathbf{k}_n \cdot \mathbf{r}} \\ &= \sum_{|\mathbf{k}_m| < K_L^{\max}} \bar{\phi}_{\mu\nu}(\mathbf{k}_m) e^{-2\pi i \mathbf{k}_m \cdot \mathbf{r}}. \end{aligned} \quad (15)$$

$[\bar{\phi}_{\mu\nu}(\mathbf{k})$ is the Fourier transform of $\phi_{\mu\nu}(\mathbf{r})$. n and m are grid point indexes for the sparse and the dense ESCGs, respectively].

To take advantage of this relationship, one can build the density on the sparse ESCG, transform the density into the momentum space by means of FFT, and then transform it back to the dense ESCG. This is more efficient than building the density on the latter directly because FFT is much faster than building the density. To apply the same trick to the formation of the XC matrix effectively on the sparse ESCG, one first needs to recognize that the Fourier transform of $\phi_{\mu\nu}$ in Eq. (13) is equivalent to the back transform of \tilde{f}^ρ as defined in Eq. (14):

$$H_{\mu\nu} = \sum_{|\mathbf{k}_l| < K_L^{\max}} \bar{\phi}_{\mu\nu}(\mathbf{k}_l) \tilde{f}_l^\rho, \quad \mu\nu \in S, \quad (16)$$

where \tilde{f}_l^ρ is the Fourier transform of $\tilde{f}_m^{\rho^\sigma}$:

$$\tilde{f}_l^\rho = \sum_m \tilde{f}_m^{\rho^\sigma} e^{2\pi i \mathbf{k}_l \cdot \mathbf{r}_m}. \quad (17)$$

Recognizing $\bar{\phi}_{\mu\nu}(\mathbf{k}) = \sum_{\mathbf{r}_n} \phi_{\mu\nu}(\mathbf{r}_n) e^{2\pi i \mathbf{k} \cdot \mathbf{r}_n}$ [the reverse of Eq. (15)], one finally arrives at

$$H_{\mu\nu} = \sum_n \tilde{f}_n^{\rho^\sigma} \phi_{\mu\nu}(\mathbf{r}_n), \quad \mu\nu \in S, \quad (18)$$

where $\tilde{f}_n^{\rho^\sigma}$ is the inverse Fourier transform of \tilde{f}_l^ρ to the sparse ESCG in position space.

Two factors determine the accuracy of MRXC. First, a smooth basis function pair needs to be fully expandable on the sparse ESCG. A basis function pair of two Gaussians is a Gaussian. Its smoothness is primarily determined by the exponent, but also depends on the angular momentum type. The Fourier transform of a Gaussian is a Gaussian and its completeness in the expansion of discrete Fourier functions depends on the upper limit of the momentum (or the grid density) in the plane-wave space. We use a single threshold to control the error ε of this expansion with the following criterion:

$$\varepsilon = \int_{-\infty}^{\infty} \left| \phi_{\mu\nu}(\mathbf{r}) - \int_{-K_s^{\max}}^{K_s^{\max}} \bar{\phi}_{\mu\nu}(\mathbf{k}) e^{-2\pi i \mathbf{k} \cdot \mathbf{r}} d\mathbf{k} \right|^2 d\mathbf{r}. \quad (19)$$

This integral can be evaluated analytically as follows using Parseval's theorem:

$$\begin{aligned} \varepsilon &= \int_{-\infty}^{\infty} |\phi_{\mu\nu}(\mathbf{r})|^2 d\mathbf{r} - 2 \int_{-K_s^{\max}}^{K_s^{\max}} \bar{\phi}_{\mu\nu}(\mathbf{k}) \bar{\phi}_{\mu\nu}^*(\mathbf{k}) d\mathbf{k} \\ &\quad + \int_{-K_s^{\max}}^{K_s^{\max}} \bar{\phi}_{\mu\nu}(\mathbf{k}) \bar{\phi}_{\mu\nu}^*(\mathbf{k}') \delta(\mathbf{k} - \mathbf{k}') d\mathbf{k} d\mathbf{k}' \\ &= \int_{-\infty}^{\infty} |\bar{\phi}_{\mu\nu}(\mathbf{k})|^2 d\mathbf{k} - \int_{-K_s^{\max}}^{K_s^{\max}} |\bar{\phi}_{\mu\nu}(\mathbf{k})|^2 d\mathbf{k} \\ &= \int_{K_s^{\max}}^{\infty} [|\bar{\phi}_{\mu\nu}(\mathbf{k})|^2 + |\bar{\phi}_{\mu\nu}(-\mathbf{k})|^2] d\mathbf{k}. \end{aligned} \quad (20)$$

Because $\bar{\phi}_{\mu\nu}(\mathbf{k})$ is the Fourier transform of a Gaussian basis function pair which is also a Gaussian function type, the integration can be derived analytically with a result containing Gauss error (erf) functions.

The second factor in the accuracy of MRXC is the local interpolation with B spline. It has a strict error bound, $(2k/K_L^{\max})^n$, which depends on the grid density and the interpolation order. In general we choose a finer ESCG for the local interpolation than that for the density evaluation and an interpolation order that will make the overall error of the local interpolation smaller than the error of the smoothness of the density [Eq. (19)]. The formulas to work with the two ESCGs are found in Eqs. (15)–(18).

III. RESULTS AND DISCUSSION

This algorithm has been implemented in the quantum chemistry program Q-CHEM [15]. The effectiveness of MRXC is illustrated with the DFT energy calculations with different molecule structures, basis sets, and ACG grids. The first molecule is a globular cluster of 132 carbon atoms with diamondlike structure. The second molecule is the drug molecule Taxel ($C_{47}NO_{14}H_{51}$). The two Gaussian basis sets are Pople’s 6-311G(df, pd) and Dunning’s correlation consistent cc-pvTZ, two types of commonly used basis sets. An ACG is specified with two numbers in parentheses, with the first being the number of radial points based on the Euler-Maclaurin scheme [16] and the second the number of angular points of the Lebedev method [17]. The weights are further scaled for molecules with Becke’s scheme [18]. Two sizes of ACG are compared. The first is a (50,94) grid pruned for efficiency with ~ 3000 points per atom [19]. It is considered of intermediate accuracy. The other ACG is a (100,302) grid, of high accuracy; it has 100 radial points and 302 angular points, resulting in 30 200 points per atom. Within MRXC, the density of the coarse ESCG is set as 3.8 per Bohr radius, corresponding to the cutoff of 143 Ry. The threshold for the error of smoothness [Eq. (19)] is set to 10^{-5} . The density of the fine ESCG for the B -spline interpolation is set as 5.7 per Bohr radius, and the B -spline interpolation order is set to 8.

The calculation results are listed in Table I. As one can see in the fourth column of the table, MRXC classifies more than 92 % of the effective basis function pairs as smooth with the sparse ESCG and the smoothness threshold specified above.

The bulk of the calculation of the density, density gradient, and XC matrix associated with those smooth basis function pairs are carried out on the sparse ESCG, with the results being interpolated back onto the ACG. Yet such a projection results in little error as compared with the results with ACG only, as shown in columns 5 and 6. The error per atom is on the order of a tenth of a microhartree or less, much lower than the error of SCF in a typical DFT calculation. Furthermore, this error is rigorously controlled by the Fourier expansion and the B spline interpolation.

The separation of the smooth and nonsmooth density with MRXC provides an excellent route to gain computational efficiency. Column 7 lists the CPU time with the conventional ACG approach, marked as “ACG only.” Columns 8–11 list the CPU times on various components of MRXC. With MRXC, the ACG handles the nonsmooth part of the density only and the corresponding CPU time is reduced more than ten times in comparison with the ACG-only calculation, roughly proportional to the percentage of the nonsmooth basis function pairs. The CPU time spent on the coarse ESCG for the calculation of the smooth part (column 9) is much less than that of the same calculation on the ACG. The other steps in the calculation of the smooth part, namely FFT and the local interpolation with B spline, do not take much CPU time as they do not involve looping over the smooth basis function pairs. The overall efficiency gain can be measured by the speed ups listed in column 12, which are obtained by dividing the “ACG only” CPU time by the sum of the CPU times on the coarse ESCG, FFT, and B spline. As discussed previously, the calculation of density and XC matrix on the coarse ESCG can be combined with the Coulomb calculation with the FTC method. Thus a higher speed up, as listed in the last column, can be achieved as the XC calculation on the coarse ESCG is considered “free” when FTC is used.

The performance gain with MRXC varies with molecules, basis sets, and sizes of ACG. The carbon cluster is favored as it is denser than Taxol and thus has a higher density of smooth basis function pairs. The larger ACG also benefits more from MRXC as adding more ACG points only increases the computational cost of the local B spline interpolation for the

TABLE I. The performance of MRXC. Each CPU time is measured for one build of the electron density and its gradient and the XC matrix on a 2.5 GHz Intel Xeon (BFP stands for ‘basis function pair’).

Molecule	Basis	ACG	Compact BFPs	Error in microhartrees	Error/atom in microhartrees	CPU time in seconds					Speed up	Speed up with FTC
						ACG only ^a	ACG ^a	ESCG ^b	FFT	B spline		
C_{132}	6-311G(df, pd)	SG-1	6.3 %	4.93	0.04	847	67	81	3	4	5.5	11.6
		(100,302)	6.3 %	1.95	0.01	4565	298	82	3	29	11.1	13.9
	cc-pVTZ	SG-1	6.1 %	49.63	0.38	1537	120	269	4	4	3.9	12.1
		(100,302)	6.1 %	12.12	0.09	9232	618	280	4	33	9.9	14.1
Taxol	6-311G(df, pd)	SG-1	7.1 %	2.07	0.02	200	21	40	5	3	2.9	7.0
		(100,302)	7.1 %	1.17	0.01	1034	104	40	5	25	6.0	7.8
	cc-pVTZ	SG-1	6.1 %	2.78	0.02	340	33	95	5	3	2.5	8.3
		(100,302)	6.1 %	1.62	0.01	1971	172	95	5	26	6.6	9.7

^aCPU time of calculating the density, density gradient, and the XC potential on the ACG.

^bCPU time of calculating the density and the XC potential on the coarse ESCG.

smooth part of the calculation. On the other hand, the smaller ACG gains more when the XC and Coulomb calculations are combined. Both basis sets show similar performance as their valence functions are of similar triple- ζ quality. We note that MRXC is not advantageous for molecules composed of a few atoms in a vacuum because there are too few basis function pairs relative to the size of ESCG. MRXC is, however, applicable to periodic systems of any size of cell as the electrons are dense everywhere and the smooth part of the electron density is already expanded in the periodic Fourier series.

Briefly, we have shown that one can combine the advantages of even-spaced and atom-centered grids for optimal efficiency

while retaining full accuracy for the calculation of exchange-correlation terms in DFT. The accuracy is maintained with a rigorous separation of smooth and nonsmooth densities based on basis function pairs. Benchmark calculations show that the scheme, MRXC, provides an efficiency gain of as much as a dozen times.

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