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# Fast evaluation of density functional exchange-correlation terms using the expansion of the electron density in auxiliary basis sets

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## Abstract

The most time-consuming step in molecular calculations using approximate density functional theory is the evaluation of Coulomb and exchange-correlation terms. We investigate the possibility of fast and sufficiently accurate evaluation of both terms using the expansion of molecular electronic density in atom-centered auxiliary basis sets. Such an approach is shown to be about an order of magnitude faster than usual approaches in which only Coulomb terms are treated using the approximated density. Test calculations suggest that auxiliary basis sets of moderate size are sufficient to achieve good accuracy of molecular properties such as geometries and reaction energies. © 1997 Published by Elsevier Science B.V.

## 1. Introduction

Density functional theory (DFT) methods of quantum chemistry have the advantage of relatively low computational cost combined with reasonable accuracy of predicted molecular properties for a wide variety of molecular systems [1]. The speed of the DFT calculations for not very large molecules is limited mainly by the CPU time required for the evaluation of matrix elements arising from a Coulomb energy term

$$E_{\text{Coul}} = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}d^3\mathbf{r}', \quad (1)$$

and an exchange-correlation energy term, usually approximated by a functional of the type

$$E_{\text{xc}} = \int e_{\text{xc}}(\rho_{\alpha}(\mathbf{r}), \rho_{\beta}(\mathbf{r}), \nabla\rho_{\alpha}(\mathbf{r}), \nabla\rho_{\beta}(\mathbf{r})) d^3\mathbf{r}. \quad (2)$$

Within the Kohn–Sham formalism the electron den-

sity for each spin  $\sigma = \alpha, \beta$  is expressed in terms of one-electron wavefunctions

$$\rho_{\sigma}(\mathbf{r}) = \sum_{n=1}^{N_{\sigma}} |\psi_{n,\sigma}(\mathbf{r})|^2, \quad (3)$$

which in most common practical implementations are sought in the form of a basis set expansion

$$\psi_{n,\sigma}(\mathbf{r}) = \sum_{i=1}^N C_{in,\sigma} \chi_i(\mathbf{r}). \quad (4)$$

In this case, the electron density (Eq. (3)) becomes a sum of  $N^2$  contributions

$$\rho_{\sigma}(\mathbf{r}) = \sum_{i,j=1}^N D_{ij,\sigma} \chi_i(\mathbf{r}) \chi_j(\mathbf{r}), \quad (5)$$

and this leads to an  $N^4$  term expression for the Coulomb energy

$$E_{\text{Coul}} = \frac{1}{2} \sum_{i,j=1}^N \sum_{k,l=1}^N D_{ij} D_{kl} \times \int \int \frac{\chi_i(\mathbf{r}) \chi_j(\mathbf{r}) \chi_k(\mathbf{r}') \chi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \quad (6)$$

as well as to  $KN^2$  operations in computing the exchange-correlation energy (Eq. (2)),

$$E_{\text{xc}} = \sum_{m=1}^K w_m e_{\text{xc}}(\mathbf{r}_m), \quad (7)$$

$K$  being the number of quadrature points used for numerical integration of the exchange-correlation energy density  $e_{\text{xc}}(\mathbf{r})$ .

Thus the cost of evaluating the terms in Eqs. (6) and (7) scales formally like the forth and third powers of the molecular size. It is obvious that for large molecules only a small fraction of the basis function products in Eq. (5) give a significant contribution to the energy, so that with appropriate program implementation, the time for the calculation of Eqs. (6) and (7) can approach quadratic and linear growth, respectively. Yet many interesting problems in chemistry are connected with molecular systems of moderate size ( $\approx 20$ – $50$  atoms) so efficient methods of avoiding the  $N^4$  and  $KN^2$  steps are clearly desirable.

As far as Coulomb term is concerned, a widely used technique in DFT implementations [2–4] is based on the approximate re-expansion of the density (Eq. (5)) in auxiliary atom-centered basis sets

$$\rho(\mathbf{r}) \approx \tilde{\rho}(\mathbf{r}) = \sum_{k=1}^M d_k \eta_k(\mathbf{r}), \quad (8)$$

and substituting for the true density in Eq. (1) its approximate counterpart, obtaining instead of Eq. (6) an expression

$$\tilde{E}_{\text{Coul}} = \frac{1}{2} \sum_{k,l=1}^M d_k d_l v_{kl}, \quad (9)$$

$$v_{kl} = \int \int \frac{\eta_k(\mathbf{r}) \eta_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}'. \quad (10)$$

The best approximation of the Coulomb energy [5] is

obtained if the expansion coefficients in Eq. (8) are determined as to minimize the self-repulsion of residual density

$$\int \int \frac{[\rho(\mathbf{r}) - \tilde{\rho}(\mathbf{r})][\rho(\mathbf{r}') - \tilde{\rho}(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' = \min, \quad (11)$$

which leads to a system of linear equations

$$\sum_{l=1}^M d_l v_{kl} = g_k, \quad (12)$$

with

$$g_k = \sum_{i,j=1}^N D_{ij} u_{ijk}, \quad (13)$$

$$u_{ijk} = \int \int \frac{\chi_i(\mathbf{r}) \chi_j(\mathbf{r}) \eta_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}'. \quad (14)$$

Thus the expansion coefficients depend linearly on the elements of the density matrix and the approximate Coulomb energy (Eq. (9)) is a quadratic function of the density matrix elements like its accurate representation in Eq. (6). By variation of Eq. (9) with respect to density matrix an approximate counterpart of Coulomb matrix is obtained

$$\tilde{V}_{ij} = \frac{\partial \tilde{E}_{\text{Coul}}}{\partial D_{ij}} = \sum_{k=1}^M d_k u_{ijk}, \quad (15)$$

which can be used in variational determination of one-electron wavefunctions (Eq. (4)) in the self-consistent Kohn–Sham calculation.

As is well documented by Eichkorn et al. [4] such a replacement of the accurate Coulomb energy expression (Eq. (6)) by the approximation in Eq. (9) leads to much faster evaluation of Coulomb terms with insignificant loss of accuracy, provided well optimized auxiliary basis sets are used. When the three-index integrals (Eq. (14)) are computed once and kept in memory during SCF iterations (an in-core algorithm) this reduces the CPU time for the Coulomb terms by a factor of 100, and even re-computing these integrals twice at each SCF iteration (a direct algorithm) when forming Eqs. (13) and (15) gives a speed-up of more than 10 [4]. In the case of the in-core algorithm the bottleneck of the calculation becomes the numerical integration required to evalu-

ate the exchange-correlation terms. Thus, it is highly desirable to accelerate this part of calculation, which is the main purpose of our present work.

Usually in DFT implementations [2,3], in order to compute exchange-correlation terms faster, the exchange-correlation energy density per electron

$$U_{xc}(\mathbf{r}) = \frac{e_{xc}(\mathbf{r})}{\rho(\mathbf{r})} \quad (16)$$

and exchange-correlation potential (omitting spin labels for simplicity)

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \quad (17)$$

are approximated by auxiliary basis set expansions

$$U_{xc}(\mathbf{r}) \approx \tilde{U}_{xc}(\mathbf{r}) = \sum_k x_k \xi_k(\mathbf{r}), \quad (18)$$

$$V_{xc}(\mathbf{r}) \approx \tilde{V}_{xc}(\mathbf{r}) = \sum_k y_k \xi_k(\mathbf{r}). \quad (19)$$

The coefficients  $x_k$  and  $y_k$  are determined by the least-squares fitting of corresponding accurate quantities on the grid of points. The exchange-correlation energy is then computed as

$$E_{xc} \approx \tilde{E}_{xc} = \sum_{i,j,k} D_{ij} x_k s_{ijk}, \quad (20)$$

as well as the exchange-correlation contribution to the Kohn–Sham matrix is evaluated as the matrix elements of the approximated potential  $V_{xc}$ ,

$$F_{ij}^{xc} \approx \tilde{F}_{ij}^{xc} = \sum_k y_k s_{ijk}, \quad (21)$$

where the three-index overlap integrals are

$$s_{ijk} = \int \chi_i(\mathbf{r}) \chi_j(\mathbf{r}) \xi_k(\mathbf{r}) d^3\mathbf{r}. \quad (22)$$

Unfortunately, there are three significant drawbacks in such approach:

(a) To obtain the fitting coefficients  $x_k$  and  $y_k$  the quantities in Eqs. (16) and (17) have to be evaluated on the grid which implies the evaluation of the density in the form in Eq. (5) or using both Eqs. (3) and (4) — the process with formal cubic growth in the computational effort with increasing molecular size.

(b) The matrix elements in the form in Eq. (21) are not variational with respect to the energy expres-

sion (Eq. (20)) unless the expansion basis set  $\{\xi_k\}$  is complete — this precludes accurate analytical evaluation of the total energy gradients [6].

(c) Whereas in the local-density approximation the function  $U_{xc}(\mathbf{r})$  decays fast at larger distances from a finite system (molecule), recent ‘gradient-corrected’ density functionals are able to reproduce its correct asymptotic behavior

$$\lim_{r \rightarrow \infty} U_{xc}(r) = -\frac{1}{r}, \quad (23)$$

in this case it would be extremely difficult to approximate it with Gaussian-type basis sets.

An improved approach which eliminates the most unpleasant drawback (b) was proposed by Dunlap et al. [6]. This approach is also based on the approximation in Eq. (18), but takes into account all the terms necessary to obtain the true variational expression for the exchange-correlation matrix elements. Yet the problems (a) and (c) still remain unsolved, the latter especially difficult for a non-local-density-functional case.

Our new proposal is to use the approximation of the density (Eq. (8)) for each spin with Coulomb-optimized coefficients determined through Eqs. (12) and (13) for the representation of the exchange-correlation term in the total energy expression. In this way the exchange-correlation contribution to the Kohn–Sham matrix can be easily obtained variationally by differentiating with respect to the density matrix

$$\tilde{F}_{ij,\sigma}^{xc} = \frac{\partial \tilde{E}_{xc}}{\partial D_{ij,\sigma}}. \quad (24)$$

After simple manipulations we obtain

$$\tilde{F}_{ij,\sigma}^{xc} = \sum_{k=1}^M q_{k,\sigma} u_{ijk}, \quad (25)$$

$$\sum_{l=1}^M q_{l,\sigma} v_{kl} = f_{k,\sigma}, \quad (26)$$

$$f_{k,\sigma} = \sum_{m=1}^K w_m \left[ \frac{\partial e_{xc}(\mathbf{r}_m)}{\partial \rho_\sigma} \eta_k(\mathbf{r}_m) + \frac{\partial e_{xc}(\mathbf{r}_m)}{\partial (\nabla \rho_\sigma)} \cdot \nabla \eta_k(\mathbf{r}_m) \right]. \quad (27)$$

In our implementation at each SCF iteration the following operations are performed to compute the two-electron contribution to the Kohn–Sham matrix:

- form the vectors  $g_{k,\sigma}$  (Eq. (13)) for each spin;
- obtain density expansion coefficients  $d_{k,\sigma}$  by solving the linear system (Eq. (12)); this is done using the precomputed inverse of  $v_{kl}$ ;
- evaluate the vectors  $f_{k,\sigma}$  (Eq. (27)) by numerical integration;
- obtain the vectors  $q_{k,\sigma}$  (Eq. (26)) using inverse of  $v_{kl}$ ;
- sum up  $d_k$  and  $q_{k,\sigma}$  and form both Coulomb and exchange-correlation contributions together using Eqs. (15) and (25).

The analytical derivatives of the total energy with respect to some external parameter (such as the nuclear coordinate) can be easily computed within our approach. It is easy to show that

$$E'_{\text{Coul}} = \sum_{k=1}^M \sum_{i,j=1}^N d_k D_{ij} u'_{ijk} - \frac{1}{2} \sum_{k,l=1}^M d_k d_l v'_{kl}, \quad (28)$$

$$E'_{\text{xc}} = \sum_{m=1}^K [w'_m e_{\text{xc}}(\mathbf{r}_m) + w_m e'_{\text{xc}}(\mathbf{r}_m)]_{d_k = \text{const}} + \sum_{\sigma=\alpha,\beta} \left[ \sum_{k=1}^M \sum_{i,j=1}^N q_{k,\sigma} D_{ij,\sigma} u'_{ijk} - \sum_{k,l=1}^M q_{k,\sigma} d_{l,\sigma} v'_{kl} \right], \quad (29)$$

where a prime denotes differentiation with respect to the external parameter of interest.

The outlined approach requires significantly less CPU time for numerical integration in comparison with usual approaches because at each grid point  $\mathbf{r}_m$  the density (Eq. (8)) is evaluated as a sum of  $M$  terms against the  $N(N+1)/2$  term expression in Eq. (5) or the  $NN_\sigma$  process using both Eqs. (3) and (4). The same applies to the evaluation of quantities in Eq. (27) instead of  $N(N+1)/2$  contributions to the matrix elements of the exchange-correlation potential at each grid point. As shown in Ref. [4] the auxiliary basis sets of dimension  $M < 3N$  are sufficient for practically accurate representation of the Coulomb terms, but this does not necessarily mean that in our implementation the exchange-correlation terms have the same sensitivity to basis set incom-

pleteness. Before passing to the next section where the results of our test calculations are presented, some comments are relevant concerning the algorithms used in our program.

We use contracted Gaussian-type basis sets to expand Kohn–Sham wavefunctions (Eq. (4)) and auxiliary uncontracted Gaussian-type basis sets to approximate electron density; in both cases the basis functions have true real spherical harmonic factors. The rate determining step in the calculations using the outlined approach, is the processing of the three-index Coulomb-type integrals (Eq. (14)). At present only the direct algorithm is available which makes use of the fact that the product of two Gaussian-type functions can be expressed in terms of partial derivatives of a simple Gaussian function. Using various useful relations presented in Ref. [7] we are able to organize the computation of Eqs. (13) and (15) in an efficient way, which will be demonstrated by the timings presented in the next section.

For numerical integration of the exchange-correlation energy density we prefer to use a modification of the integration scheme derived by Becke [8] in which the molecular integrand is decomposed into a sum of atomic contributions in the following way:

$$\int e_{\text{xc}}(\mathbf{r}) d^3\mathbf{r} = \sum_i \int e_{\text{xc}}^{(i)}(\mathbf{r}) d^3\mathbf{r}, \quad (30)$$

$$e_{\text{xc}}^{(i)}(\mathbf{r}) = \frac{e_{\text{xc}}(\mathbf{r})}{\sum_j e_{\text{xc},j}(\mathbf{r})} e_{\text{xc},i}(\mathbf{r}), \quad (31)$$

where  $e_{\text{xc},i}(\mathbf{r})$  is a spherically averaged exchange-correlation energy density of the isolated  $i$ -th atom. In our experience for this particular integrand the decomposition (Eq. (31)) is a better choice than using the general-purpose nuclear weight functions of Becke [8], especially for molecules containing heavy atoms — this is mainly due to the fact that the ratio in Eq. (31) is close to unity because the molecular property  $e_{\text{xc}}(\mathbf{r})$  is reasonably well modeled by the superposition of atomic properties  $e_{\text{xc},i}(\mathbf{r})$ . Each integral in the sum in Eq. (30) is computed in a spherical coordinate system centered at the corresponding nucleus, using for angular integration the quadratures of Lebedev [9,10] with 50, 110, 194, 302, 434, 590, 770, 974 or 1202 points. The particu-

lar number of angular points for each radial shell is determined at the first SCF iteration by trying quadratures of increasing order until the difference in this shell's contribution to  $E_{xc}$  is less than the predefined value of 0.000001 au. For the radial integration the number of points is fixed to 30, 40, 55, 80 for H–He, Li–Ne, Na–Ar and K–Kr, respectively.

We should note that our program also has the option of accurate representations of both the Coulomb and exchange-correlation terms based on expressions in Eqs. (6) and (7). This option allows the automatic checking of energies and optimized geometries obtained in the calculation involving the approximated density.

## 2. Tests of accuracy and speed

In order to estimate the errors introduced into computed molecular properties by the use of the approximated density we have carried out test calculations for a number of molecules listed in Table 1.

Table 1

Deviations of molecular properties computed with the approximate approach of the present work from the values obtained using the accurate representation of both the Coulomb and exchange-correlation terms

Molecule	$\Delta E^a$	$\Delta E/N_{\text{atom}}^b$	$\Delta r^c$	$\Delta \alpha^d$
CH <sub>4</sub>	0.00014	0.00003	< 0.01 <sup>e</sup>	–
NH <sub>3</sub>	–0.00112	–0.00028	0.09	0.19
H <sub>2</sub> O	–0.00048	–0.00016	0.04	0.08
HF	0.00025	0.00013	0.06	–
C <sub>2</sub> H <sub>2</sub>	–0.00032	–0.00008	0.04	–
C <sub>2</sub> H <sub>4</sub>	–0.00104	–0.00017	< 0.01 <sup>e</sup>	< 0.01 <sup>e</sup>
C <sub>2</sub> H <sub>6</sub>	0.00036	0.00005	0.01	0.02
cyclo-C <sub>3</sub> H <sub>6</sub>	–0.00009	–0.00001	< 0.01 <sup>e</sup>	< 0.01 <sup>e</sup>
C <sub>6</sub> H <sub>6</sub>	–0.00309	–0.00026	–0.03	–
HCONH <sub>2</sub>	–0.00183	–0.00031	0.13	0.17
P <sub>2</sub>	–0.00029	–0.00015	0.14	–
P <sub>4</sub>	–0.00222	–0.00056	–0.09	–
Cl <sub>2</sub>	0.00410	0.00205	–0.27	–
VOCl <sub>3</sub>	0.00131	0.00026	0.12	0.15
HCo(CO) <sub>4</sub>	0.00302	0.00030	–	–
Co <sub>2</sub> (CO) <sub>8</sub>	0.00478	0.00027	–	–
Mn <sub>2</sub> (CO) <sub>10</sub>	0.00631	0.00029	–	–

<sup>a</sup> Accuracy of the total energy (au).

<sup>b</sup> The latter divided by the number of atoms.

<sup>c</sup> Maximum deviation in bond distances (pm).

<sup>d</sup> Maximum deviation in bond angles (degrees).

<sup>e</sup> Deviations are below standard optimization tolerance.

Table 2

CPU times (in seconds on a 366 MHz DEC Alpha workstation) for the most time-consuming steps of one DFT SCF iteration

Molecule	$N^a$	$M^b$	$K^c$	$t_{\text{coul}}^d$	$t_{\text{xc}}^e$	$t_{\text{SCF}}^f$
C <sub>6</sub> H <sub>6</sub>	150	300	35000	5.2	4.5	0.8
VOCl <sub>3</sub>	136	358	16300	3.9	1.4	0.5
HCo(CO) <sub>4</sub>	194	435	32000	9.0	3.7	1.2
Co <sub>2</sub> (CO) <sub>8</sub>	376	850	60000	49.6	8.6	9.9
Mn <sub>2</sub> (CO) <sub>10</sub>	452	1010	83000	102.5	18.0	17.5

No use of symmetry is made.

<sup>a</sup> Number of orbital basis functions.

<sup>b</sup> Number of auxiliary basis functions.

<sup>c</sup> Number of quadrature points.

<sup>d</sup> Time for three-index Coulomb integral contributions.

<sup>e</sup> Time for numerical integration.

<sup>f</sup> Time to solve the SCF equations.

All the calculations have been performed using the BLYP exchange-correlation functional [11,12]. For the expansion of Kohn–Sham wavefunctions (Eq. (4)) the TZVP basis sets of Schäfer et al. [13] are chosen. Obviously the accuracy of the present method depends upon the particular auxiliary basis sets used to represent the electron density. Here we use decontracted auxiliary basis sets from the work of Eichkorn et al. [4] which are optimized for the representation of the Coulomb energy (Eq. (9)) with an accuracy of 0.0001 au per atom [4]. The geometry optimizations were performed with the help of analytical gradients based on Eqs. (28) and (29), with a standard criterion of the maximum gradient component being less than 0.0001 au. For larger cases such as Co<sub>2</sub>(CO)<sub>8</sub> we are not able to report the accuracy of the computed geometric parameters because, without use of symmetry, accurate calculations turned out to be too time consuming.

The figures in Table 1 indicate that the method of the present work, in conjunction with above-mentioned basis sets, has a numerical accuracy sufficient for most purposes. Especially good are the geometries of organic molecules — the errors are often below the standard tolerance of the geometry optimization. The use of smaller than TZVP basis sets to represent the Kohn–Sham wavefunctions leads to significantly larger errors in computed molecular properties — for example, the bond lengths are typically overestimated by more than 1.0 pm.

The small errors introduced by our approximation are well justified when the speed of calculation is

important. Table 2 gives some typical examples of CPU times required for calculations on moderate size molecules. Note that we do not make use of molecular symmetry. From this data it can be concluded that the time for the numerical integration (Eq. (27)) is close to that needed for the matrix operations in solving the SCF equations and much smaller than the time for evaluation of the quantities in Eqs. (13) and (15). Even assuming that the in-core algorithm can allow 10 times faster evaluation of Eqs. (13) and (15), the time for numerical integration will not add significantly to the total CPU time. This means that the main objective of the present work — to eliminate the numerical integration bottleneck — is achieved at the expense of somewhat reduced but still reasonable accuracy of the results of the calculation.

### 3. Conclusions

The method described in this work allows us to come close to the limit where the dominant step in the DFT calculation is the solution of the SCF equations for not very large molecules. Such a reduction of time needed to form Kohn–Sham matrix is achieved at the expense of small errors that can be further reduced by increasing the size of auxiliary basis sets, without adding much to the total CPU time. Even if the accuracy of such an approximation does not seem sufficient, due to its speed this method

can be useful in geometry searches — the geometry obtained being an excellent initial guess for a more accurate treatment.

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