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# Fitting of local densities in periodic systems

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We present a formalism for density fitting, a widely used method in molecular context, to approximate the electron repulsion integrals between local densities in periodic systems. An efficient treatment is achieved through a separation of the fitting into a reciprocal space part, done with an extended, but momentless fitting basis set, and a direct space part with a small, local set of usual Gaussian-type orbitals. This approach can be applied to periodic Hartree-Fock, Kohn-Sham, post-Hartree-Fock correlation, etc. methods. We demonstrate the efficiency of the method in the periodic local Møller-Plesset perturbation theory of the second order, which in the conventional formulation is for crystals very expensive.

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## I. INTRODUCTION

Four-center electron repulsion integrals (ERIs),

$$K_{\mu\sigma,\nu\tau}=(\rho_{\mu\sigma}|\rho_{\nu\tau})\equiv\int d\mathbf{r}_1\int d\mathbf{r}_2\rho_{\mu\sigma}(\mathbf{r}_1)\frac{1}{r_{12}}\rho_{\nu\tau}(\mathbf{r}_2), \quad (1)$$

play a central role in the formalism of Kohn-Sham or quantum chemical methods for molecular or crystalline systems. Here by $\rho$ we denote density distributions, each being a product of two local orbitals ($\rho_{\mu\sigma}=\chi_\mu\chi_\sigma$), which can be either basis functions (e.g., Gaussian-type orbitals, etc.) or their linear combinations (e.g., Wannier functions, etc.). Such densities are essentials in the localized-function reformulation of the methods like Hartree-Fock,[1] Kohn-Sham,[2] post-Hartree-Fock treatment,[3–6] etc. Moreover, local densities are also constituents of the Bloch-function-based methods if the atomic-orbital basis set is employed.[7]

As a rule, evaluation of ERIs represents a computational bottleneck to many of the existing methods. An approximate but much more efficient treatment for such integrals is achieved by the density fitting (DF)[8–13] technique (sometimes referred to as resolution of identity[14]). The product densities $\rho$ are expanded into an auxiliary basis $\{\phi_Q(\mathbf{r})\}$:

$$\rho_{\mu\sigma}(\mathbf{r})\approx\tilde{\rho}_{\mu\sigma}(\mathbf{r})=\sum_Q d_{\mu\sigma,Q}\phi_Q(\mathbf{r}). \quad (2)$$

The fitting coefficients $d_{\mu\sigma,Q}$ are determined variationally by minimizing, e.g., the Coulomb self-repulsion of the difference density $|\rho_{\mu\sigma}-\tilde{\rho}_{\mu\sigma}|$. This condition leads to projection of the density $\rho_{\mu\sigma}$ onto the auxiliary vector space according to the Coulomb metric:

$$d_{\mu\sigma,Q}=\sum_{Q'}(\mu\sigma|Q')[\mathbf{J}^{-1}]_{Q'Q}, \quad (3)$$

$$\mathbf{J}_{Q'Q}=(Q'|Q). \quad (4)$$

Dunlap[11,15] has proposed a "robust" expression for the fitted ERIs that guarantees the error in the integral to be quadratic with respect to the fitting error in the densities:

$$K_{\mu\sigma,\nu\tau}\approx\tilde{K}_{\mu\sigma,\nu\tau}=(\tilde{\rho}_{\mu\sigma}|\rho_{\nu\tau})+(\rho_{\mu\sigma}|\tilde{\rho}_{\nu\tau})-(\tilde{\rho}_{\mu\sigma}|\tilde{\rho}_{\nu\tau}). \quad (5)$$

Due to the choice of the Coulomb metric this three-term formula simplifies to

$$K_{\mu\sigma,\nu\tau}\approx\tilde{K}_{\mu\sigma,\nu\tau}=(\tilde{\rho}_{\mu\sigma}|\rho_{\nu\tau})=\sum_Q d_{\mu\sigma,Q}(Q|\nu\tau). \quad (6)$$

Though introduced as a formal mathematical trick, DF can essentially enter in the reformulation of many well-known quantum chemical approaches, and the effect of the approximation on the results is variationally minimized. In the last decade it has become a routine and efficient tool in quantum chemistry of molecules. At the same time, an adaptation of DF to periodic systems is still rather scarce.[16–19] Several problems arise due to the infinite nature of crystals when using Coulomb metric: (i) the ranges for the auxiliary indices become infinite due to the slow decay of the integrals; (ii) the application of formula (3) is not possible in direct space, which implies inversion of an infinite matrix; and (iii) the reciprocal space formulation is problematic due to the convergence problems in the Fourier transforms and the large number of **k**-points needed.

The long-range character of the support for the fitted densities in periodic systems has been investigated in Refs. 20–23. Although the singularity which appears in the Fourier transform of the metric matrix can be analytically eliminated,[23] the poorly (conditionally) converging series still remain, which demand quite an effort to be dealt with. On the other hand, the requirement for an infinite support for fitting local densities seems to be an artifact of the formalism rather than a physical necessity.

The problem can be partly circumvented by using the overlap metric, which would imply the fast decaying overlap integrals in Eqs. (3) and (4) and nonproblematic Fourier transform. However, the Fourier transform of the Coulomb integrals cannot be avoided.[18] Moreover, the simplification of Eq. (6) would not hold in this case, leading to a more complicated formalism.

Recently, in order to get rid of the conditionally converging terms in the DF, we proposed a dipole-correction technique based on the overlap metric.[18] This method was however lacking the "robustness" introduced in Eq. (5), which manifested itself in rather extensive fitting basis sets needed and large fitting errors for the virtual functions having small norm in a so-called pseudo-canonical basis.[24] As a result, such a scheme, though providing the principal possibility to perform local second-order Møller-Plesset perturbation theory (LMP2) calculations for crystals with relatively large unit cells, was not able to recover a part of the correlation energy and demanded an accurate preparation of the fitting basis sets.

In this Brief Report we present an approach which efficiently overcomes the above difficulties, allowing to make fitting of local densities in infinite periodic systems essentially a local procedure. We apply the method to calculating the correlation energy at the LMP2 level.

## II. THEORY

We start with introducing the Poisson-type fitting basis set.[25,26] For a given Gaussian-type orbital (GTO, to be labeled as $G$), the corresponding Poisson-type orbital (PTO, labeled as $P$) is defined as

$$P(\mathbf{r}) = -\nabla^2/4\pi \cdot G(\mathbf{r}). \tag{7}$$

An appealing property of PTO fitting functions is that they simplify the Coulomb two-electron integrals [Eq. (3)] to one-electron integrals, which decay exponentially or faster.[26] This property eliminates the convergence problems in the Fourier transformation of the integrals with PTOs. In other words, the lattice summations involving such integrals converge exponentially, which implies that though the PTO basis is formally extended to infinity, only a local set of such functions, located in a finite region around the fitted density, essentially participates in the Fourier transform (the so-called "Fourier-directed local fit"[18]).

However, since PTOs hold neither charge nor multipole moments of any other order[27] (which actually causes such a fast decay of the integrals), an auxiliary basis set consisting solely of these functions cannot describe the density sufficiently well. Thus, PTOs should still be complemented by GTOs for the purpose of reproducing the multipole moments of the fitted densities. Despite the fact that only a small number of the auxiliary GTOs is needed, the inclusion of these functions restores all the problems of periodic DF mentioned above.

We now introduce a mixed extended/local auxiliary basis set, possessing a "rich" PTO part with functions scattered over the whole infinite volume of the crystal, and a "small" local GTO part with GTOs of different angular momenta centered on a few atomic sites covered by the fitted density. In other words, small local GTO-fit-domains are defined for each density. Such a basis now implies that the fit with both parts is local: a formally extended but essentially local fit with the PTOs, and a pure local fit with the GTO subset, analogous to molecular local fit of Refs. 12 and 13, but with much smaller fit-domains.

The standard DF formalism [Eq. (5)] is not consistent with such a choice for the auxiliary basis, as it can be performed neither in reciprocal nor in the direct space. Indeed, the PTO-fit in direct space implies an infinite matrix inversion, while the GTO set cannot be transformed to the reciprocal space, since it is not translationally invariant. In order to separate these two parts we construct a new set of functions (labeled as $\Gamma$), by Coulomb-projecting the GTOs out from the space spanned by the PTOs:

$$|\Gamma) = |G) - \sum_{PP'} |P)[\mathbf{J}^{[P]}]^{-1}_{P,P'}(P'|G), \tag{8}$$

where $[\mathbf{J}^{[P]}]$ is the block of the $\mathbf{J}$ matrix containing only integrals between PTOs. The effect that the $G \Rightarrow \Gamma$ transformation has on the block of three-index integrals can be schematically pictured as

$$(\mu\sigma|\mathbf{Q}) = [(\mu\sigma|\mathbf{G}) \quad (\mu\sigma|\mathbf{P})] \Rightarrow [(\mu\sigma|\mathbf{\Gamma}) \quad (\mu\sigma|\mathbf{P})],$$

while the two-index integrals' matrix (which in a crystal is in principle infinite) becomes block diagonal:

$$\mathbf{J} = \begin{bmatrix} (\mathbf{G}|\mathbf{G}) & (\mathbf{G}|\mathbf{P}) \\ (\mathbf{P}|\mathbf{G}) & (\mathbf{P}|\mathbf{P}) \end{bmatrix} \Rightarrow \begin{bmatrix} (\mathbf{\Gamma}|\mathbf{\Gamma}) & \mathbf{0} \\ \mathbf{0} & (\mathbf{P}|\mathbf{P}) \end{bmatrix} \equiv \begin{bmatrix} \mathbf{J}^{[\Gamma]} & \mathbf{0} \\ \mathbf{0} & \mathbf{J}^{[\mathbf{P}]} \end{bmatrix}.$$

It is easy to see from Eq. (8) that off-diagonal terms $(\mathbf{P}|\mathbf{\Gamma})$ are zero, which finally decouples the $\mathbf{\Gamma}$ part from the PTO part in the inversion of the metric matrix $\mathbf{J}$. Summarizing, the set $\mathbf{\Gamma}$ possesses the following important properties: (i) it is a local set, since it is formed from the local $\mathbf{G}$ set and the same set but fitted by PTOs (see below); (ii) it can carry multipole moments, since it differs from $\mathbf{G}$ only by some linear combinations of momentless PTOs; and (iii) the robust fit with the set $\mathbf{\Gamma}$ can be performed independently from the PTO-fit, since the inversion of the $\mathbf{J}$ matrix is now conveniently factorized. The latter allows us to subdivide the fitting of the integrals in two separate contributions:

$$\tilde{K} = \tilde{K}^P + \tilde{K}^\Gamma. \tag{9}$$

The first term is the fit of the integrals through PTOs only, which constitute the major fraction of the auxiliary basis set and can be efficiently handled in reciprocal space without any convergence problems. The second term is the local fit with a small number of $\Gamma$ functions and is processed in direct space. Essential is that both terms are now treated locally and the problems of DF in three-dimensional (3D) crystals as listed above are thus eliminated.

In periodic systems the matrix elements of totally symmetric operators like $1/r_{12}$ are invariant upon the translation by a lattice vector $\mathbf{R}_X$,

$$(X_{\mathbf{R}_X}|Y_{\mathbf{R}_Y}) = (X_0|Y_{(\mathbf{R}_Y-\mathbf{R}_X)}) \equiv J_{X,Y;\mathbf{R}}, \tag{10}$$

with $X_{\mathbf{R}_X}(\mathbf{r}) = X(\mathbf{r}-\mathbf{R}_X)$ and $\mathbf{R} = \mathbf{R}_Y - \mathbf{R}_X$. The discrete Fourier transform operator $\hat{\mathcal{F}}_{\mathbf{k}}$ can be used to generate the reciprocal space image of the $J_{X,Y;\mathbf{R}}$ set on a suitable sampling mesh of $N_{\mathbf{k}}$ $\mathbf{k}$-points:

$$J_{X,Y}(\mathbf{k}) = \hat{\mathcal{F}}_{\mathbf{k}}[J_{X,Y;\mathbf{R}}] = \sum_{\mathbf{R}} J_{X,Y;\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}}. \tag{11}$$

The back-Fourier-transform operator is denoted by $\hat{\mathcal{F}}^{-1}_{\mathbf{R}}$. Evaluation of the three- and two-center integrals $(\mu\nu|\mathbf{P})$ and $(\mathbf{P}|\mathbf{P})$ is straightforward and cheap, since, as explained above, these are always reduced to one-electron integrals.

Then the Fourier transform is easy owing to the exponential (or faster) decay of these integrals with the interorbital separation. We then assemble the Fourier image of the $\widetilde{K}^P$ term in reciprocal space and back-transform it,

$$\widetilde{K}^P_{\mu\sigma,\nu\tau;\mathbf{R}} = \hat{\mathcal{F}}^{-1}_{\mathbf{R}}[\widetilde{K}^P_{\mu\sigma,\nu\tau}(\mathbf{k})] = \hat{\mathcal{F}}^{-1}_{\mathbf{R}}\left[\sum_P d_{\mu\sigma,P}(\mathbf{k})J^*_{\nu\tau,P}(\mathbf{k})\right], \tag{12}$$

where

$$d_{\mu\sigma,P}(\mathbf{k}) = \sum_{P'} J_{\mu\sigma,P'}(\mathbf{k})[\mathbf{J}^{[P]}(\mathbf{k})]^{-1}_{P',P} \tag{13}$$

is defined in the analogy to formula (3). Due to the exponential decay of the integrals $\widetilde{K}^P$, built on momentless densities, not a large number of **k**-points is required (for discussion see Refs. 18 and 24).

Now we switch to $\widetilde{K}^\Gamma$, the second term in Eq. (9). Apparently, owing to expressions (2) and (3) a function $\Gamma$ [Eq. (8)] can be interpreted as a difference between a GTO $G$ and this very GTO fitted by the PTO part of the auxiliary basis. Indeed, the quantity $\Sigma_{P'}[\mathbf{J}^{[P]}]^{-1}_{P,P'}(P'|G)$ is nothing else than the coefficient $d_{G,P}$ corresponding to such a fit. Thus, the two- and three-index direct space integrals with $\mathbf{\Gamma}$, $J_{\Gamma,\Gamma'}$ and $J_{\mu\sigma,\Gamma}$, respectively, are obtained employing the same PTO-fit as described above for $\widetilde{K}^P$ along the lines of Eqs. (12) and (13) by formally considering the GTOs $G$ as densities to be fitted,

$$J_{\Gamma,\Gamma';\mathbf{R}} = J_{G,G';\mathbf{R}} - \hat{\mathcal{F}}^{-1}_{\mathbf{R}}\left[\sum_P d_{G,P}(\mathbf{k})J^*_{G',P}(\mathbf{k})\right]. \tag{14}$$

An analogous equation holds for the integrals $J_{\mu\sigma,\Gamma;\mathbf{R}}$. Again, since only PTOs are employed as fitting functions, convergence is no longer an issue for this procedure. Besides, the PTO-fit cannot completely reproduce the **G** set and thus obliterate the $\Gamma$-basis.

Once the integrals $J_{\Gamma,\Gamma'}$ and $J_{\mu\sigma,\Gamma}$ are calculated, the fitting coefficients $d_{\mu\sigma,\Gamma}$ can be obtained in the direct space using the molecular DF expression (5). Due to the local restriction, the $\mathbf{\Gamma}$-sets for the "bra" and "ket" densities might not coincide and thus one has to invert the metric matrix for each of the fitted densities separately. On the other hand, these matrices are small and the inversion is cheap. However, in such a local fit the reduction of the three-term formula (5) to one term [Eq. (6)] does not hold. Hence the final expression for the $\Gamma$-fitted integral takes the form

$$\widetilde{K}^\Gamma_{\mu\sigma,\nu\tau} = \sum_{\Gamma\in[\mu\sigma]} d_{\mu\sigma,\Gamma}(\nu\tau|\Gamma) + \sum_{\Gamma\in[\nu\tau]} (\mu\sigma|\Gamma)d_{\nu\tau,\Gamma} - \sum_{\Gamma\in[\mu\sigma]}\sum_{\Gamma'\in[\nu\tau]} d_{\mu\sigma,\Gamma}(\Gamma|\Gamma')d_{\nu\tau,\Gamma'}. \tag{15}$$

Here by $[\mu\sigma]$ we denote the $\Gamma$-fit domain of the density $\rho_{\mu\sigma}$, and the **R** index has been made implicit.

## III. DISCUSSION AND APPLICATION

The described scheme provides a simple and general way to fit local densities in a periodic system. Its main advantage is that it allows to treat local densities through a local DF, rather than an extended one as in the previous approaches.[16,17,19] As will be shown below, using this method the post-Hartree-Fock electronic correlation calculations in 3D systems with moderate number of atoms in a unit cell become routine, while without it[3,5,28] they are difficult or even impossible. This technique can also be generalized to the molecular case, although with less advantages since no periodicity and thus reciprocal space fitting is then available.

The different nature of PTOs and GTOs clearly suggests that they should be treated separately. Then the PTOs serve for a detailed description of the densities, while the GTOs add to the fit the required multipole moments. Such a separation allows a substantial flexibility in treating the multipole moments with a high accuracy. In periodic systems it is important to reproduce precisely the lower moments (especially the charges) of the fitted densities, since even small discrepancies can cause catastrophic behavior in the lattice summations of the slowly decaying ERIs. Varga[22,23] has shown that the charge is exactly reproduced in the extended Coulomb fit with GTO-fitting basis. In the local approach this might not be fulfilled, but this task can be accomplished by adding moment constraints in the fitting functional.[4,10,23] The additional cost is negligible, since the constraints enter only the "small" $\widetilde{K}^\Gamma$ fit, while the momentless $\widetilde{K}^P$ fit remains unaffected. For chargeless densities (which occur, e.g., in LMP2; see below) cancellation of the charge can be achieved even more simply by just not including $s$-type GTOs in the auxiliary basis.

Optimized PTO fitting basis sets already exist for molecular DF for a number of elements[29,30] and can be employed for periodic calculations. Very diffuse PTOs should be excluded from the basis sets, since in a 3D packed system they would not improve the accuracy of the fit but instead can generate artificial tails in the fitted densities.

Note that the proposed method cannot be straightforwardly reformulated for employing the overlap metric. A robust expression in this case requires a three-term formula, similar to Eq. (5), involving two-index Coulomb integrals.[18] Since it is not possible to simultaneously block-diagonalize both Coulomb and overlap matrices, the separation [Eq. (9)] cannot be achieved, which leads to a substantial complication of the formalism and loss of efficiency. However, since the described technique solves the convergence problems of the Coulomb metric, the need for the overlap metric becomes marginal.

We have implemented the described method in the context of the periodic LMP2 method for approximating the ERIs $(ia|jb)$ where the $i$, $j$ and $a$, $b$ are localized orbitals for occupied (symmetry-adapted Wannier functions[31]) and virtual (projected atomic orbitals) spaces, respectively. The LMP2 method allows to perturbatively evaluate the correlation energy of the electronic structure[4] using the periodic Hartree-Fock solution[32] as a reference.

Table I compiles the results of LMP2 calculations for a selection of crystals with different types of bonding, symmetry, unit-cell sizes and basis sets. The performance is analyzed by comparing the results with and without DF for the calculations with a truncated number of orbital excitation

TABLE I. LMP2 energies (in millihartree) per unit cell. Test calculations with the cut-off distance of 2 Å for the orbital excitation pairs are reported using exact ($E^{\text{test}}$) and fitted ($E_{\text{DF}}^{\text{test}}$) ERIs, along with the basis sets, respective CPU times ($t$) on a single AMD64 Opteron 2.6 GHz processor, and relative fitting errors ($|\Delta E|/E^{\text{test}}$). $E_{\text{DF}}^{\text{full}}$ and $t_{\text{DF}}^{\text{full}}$ refer to the same calculations but with all pairs included: the pairs up to 5 Å are treated by DF, beyond 5 Å through the multipole expansion and extrapolation technique (Ref. 4). For each crystal the space group (Symm.) and lattice constant (Latt. par., in Å) are provided.

| System | Symm. | Latt. par. | Basis set | $E^{\text{test}}$ | $t^{\text{test}}$ | $E_{\text{DF}}^{\text{test}}$ | $t_{\text{DF}}^{\text{test}}$ | $\|\Delta E\|/E^{\text{test}}$ | $E_{\text{DF}}^{\text{full}}$ | $t_{\text{DF}}^{\text{full}}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Diamond | $Fd\bar{3}m$ | $a$=3.57 | 6–21G* | −230.225 | 16 days | −230.286 | 4 min | 0.03 % | −260.153 | 30 min |
| Ice XI | $Cmc2_1$ | see Ref. 4 | 6–311G** | −874.234 | 4 days | −874.174 | 15 min | 0.01 % | −886.149 | 35 min |
| $CO_2$ | $Pa\bar{3}$ | $a$=5.55 | 6–311G(3$d$) | −2 205.274 | 2 days | −2 205.532 | 30 min | 0.01 % | −2 261.651 | 2 h |
| MgO | $Fm\bar{3}m$ | $a$=4.21 | 8–511G*/8–411G* | −232.080 | 19 h | −232.060 | 8 min | 0.01 % | −243.205 | 20 min |
| $\beta$-$SiO_2$ | $Fd\bar{3}m$ | $a$=7.47 | 66–21G*/6–31G* | −802.391 | 9 h | −802.469 | 3 min | 0.01 % | −825.427 | 6 min |
| Ar | $Fm\bar{3}m$ | $a$=5.23 | ECP/[4$s$4$p$3$d$2$f$] | −222.072 | 13 days | −222.037 | 5 min | 0.02 % | −228.774 | 10 min |

pairs (up to a cut-off distance of 2 Å). The true LMP2 energy with the whole list of orbital pairs included has been only calculated using the DF method, since the conventional calculations are in most cases out of reach (in the case of diamond, for instance, the estimated time for such a calculation would be a few months). Fitting basis sets optimized for double-zeta-(diamond, MgO, $\beta$-quartz) and triple-zeta-quality (argon, ice, $CO_2$) orbital basis sets were employed. It is seen from the table that the DF approximation allows to remarkably improve performance without introducing any significant error in the energy. This makes it possible to evaluate the correlation energy for crystals at the LMP2 level without a great computational effort.

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