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Fast local-MP2 method with density-fitting for crystals. I. Theory and algorithms

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When solving the Møller-Plesset second order perturbation theory (MP2) equations for periodic systems using a local-correlation approach [J. Chem. Phys. **122** (2005) 094113], the computational bottleneck is represented by the evaluation of the two-electron Coulomb interaction integrals between product distributions, each involving a Wannier function and a projected atomic orbital. While for distant product distributions a multipolar approximation performs very efficiently, the four index transformation for close-by distributions, which by far constitutes the bottleneck of correlated electronic structure calculations of crystals, can be avoided through the use of density fitting techniques. An adaptation of that scheme to translationally periodic systems is described, based on Fourier transformation techniques. The formulas and algorithms adopted allow the point symmetry of the crystal to be exploited. Problems related to the possible divergency of lattice sums of integrals involving fitting functions are identified and eliminated through the use of Poisson transformed fitting functions and of dipole-corrected product distributions. The iterative scheme for solving the linear local MP2 (LMP2) equations is revisited. Prescreening in the evaluation of the residual matrix is introduced, which significantly lowers the scaling of the LMP2 equations.

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I. INTRODUCTION

We have recently described a local-correlation program CRYSCOR for the solution of the Møller-Plesset second order perturbation theory (MP2) equations for periodic systems.[1] Essentially, it combines the availability of an accurate Hartree-Fock (HF) solution of the problem in an atomic-orbital (AO) Gaussian-type-function (GTF) representation, as provided by the CRYSTAL code,[2,3] with the extension to the periodic problem of local correlation techniques[4] as implemented, in particular, in the MOLPRO program for molecular systems.[5–12] The correlated methods are, in most cases, more accurate than DFT, and mandatory for systems, where dispersive forces play an important role in binding (e.g., molecular crystals). These methods allow for a systematical treatment of the phenomenon of electron Coulomb correlation. The aim of the CRYSCOR project is to provide a powerful and general-purpose computational tool, to be used for a variety of applications of condensed matter physics and chemistry, since at present correlated methods available for extended systems like crystals, polymers, or other solid state materials, are rather scarce.[13–18] However, the first implementation of the local MP2 scheme for crystals[1] could only be used for very small systems (vide infra). To overcome this problem such that realistic systems can be studied is the aim of the present paper.

Special attention has been devoted to the efficient exploitation not only of translational, but also of point-group symmetry of the crystal. The computational cost of the local MP2 method scales as $O(n)$, n being the "size" of the irreducible part of the unit cell (IUC) of the crystal, at least asymptotically, i.e., for large n. The reason is that the local ansatz[4,19–21] permits us to consider only pair excitations from occupied to virtual local functions which are all "close" to each other. Because of symmetry, one of them can be imposed to belong to the IUC. The prefactor depends on the tolerances that must be adopted in order to achieve acceptable accuracy (for instance, within 1% of the canonical MP2 energy). These concern, primarily, (i) the threshold adopted for truncating the tails of the local functions, which span the occupied HF manifold [Wannier functions (WFs)] and the virtual manifold [projected atomic orbitals (PAO)]; (ii) the size of the WF domains, which determines the maximum distance between the two WFs and the two PAOs involved in a pair excitation beyond which the corresponding amplitudes can be taken as negligible; and (iii) the cutoff radius for the distance between the WFs in an excitation pair, beyond which the contributions of the corresponding pair energies can also be regarded as negligible.

Due to the much denser packing of crystalline rather than molecular structures, it turns out that with reasonable values of such tolerances, the prefactor is so high that the computations are very demanding, even for the simplest crystals. An analysis of the costs shows that the bottleneck is the evaluation of the four-index electron repulsion integrals. We shall indicate briefly as PD the product distribution of a WF times a PAO. An essential reduction of the costs is obtained from the use of a multipolar approximation for the Coulomb interaction between distant PDs, which permits us to evaluate the largest part of the integrals with high accuracy and at a relatively small cost.[1] Evaluating the remaining "close-by" integrals which involve overlapping PDs still takes most of the time, if the standard procedure is followed. These integrals are obtained by computing analytically four-index integrals in AO basis, followed by a four-index transformation of those from AO to WF-PAO basis. For each integral in the WF-PAO basis the number of basic integrals to be evaluated scales as the fourth power both of the basis set size, and of the support of WFs and PAOs, which depend in turn on the truncation parameters indicated in items (i) and (ii) in the list above. Suitable algorithms can be used in order to reduce the burden of the other most time-consuming step, namely, the four-index transformation, and to optimally attribute the contribution of each given AO integral to the various WF-PAO integrals which may need it.[1] Nevertheless, the extremely steep scaling of the cost of this *integral step* with the strictness of the truncation parameters prevents CRYSCOR from performing very high quality computations with simple systems, or even fair quality ones with complex crystalline structures.

A way out of this difficulty is provided by density fitting (DF) techniques, which have proved to be very powerful in the context of local-correlation calculations for molecules..[22–25] Essentially, after expressing each PD as a linear combination of a suitable set of AO-like fitting functions (FF) $\Xi_P(\mathbf{r})$, the four-index integrals are advantageously expressed in terms of two- and three-index integrals involving PDs and FFs. In order to fully exploit the benefits of this technique some problems must be solved, however. Most importantly, the $O(N^3)$ scaling associated with the inversion of the interaction matrix between FFs can be avoided by introducing specific "fitting domains" for the different PDs, and performing the inversion within each of them.[22,23] This in turn requires using a robust formulation of the DF equations,[26] as proposed by some of us.[23]

On the contrary to molecular methods, where DF has become a routine approach,[26–39] implementations of DF for crystals are rather rare and cover only cases of density functional theory[40,41] and the Hartree-Fock method.[42,43] For infinite periodic systems the DF scheme is essentially more complicated than for molecules, especially when local approximations are involved. Introduction of fitting domains[22] in the case of a crystal would not be efficient because such domains are inconsistent with the translational symmetry. On the other hand, a DF scheme with the fitting basis set covering the whole direct space[42,43] is not attractive either, due to (i) convergence problems of lattice summations and (ii) inefficiency of an infinite support for representing localized functions. Therefore, an approach for applying the DF scheme for periodic local correlation calculations has been devised.

Such adaptation of DF to a periodic context for use in local-MP2 calculations is the subject of this paper. The periodic character of the system entails that we have to deal here with functions (FFs and PDs) which transform into one another through lattice translations. This fact permits important simplifications in the computational procedure through the use of Fourier transform (FT) techniques. This is true in particular for the inversion step, where specific fitting domains are no longer needed. On the other hand, we are faced with lattice sums (infinite, in principle) which have been recognized as a possible source of convergence problems in DF techniques.[43] It is shown below that it is feasible to get rid of such problems through the use of Poisson-type functions,[44] which has proved being beneficial in the molecular context.[45–47]

In this work we present the theory, while the calibration of the technique and the analysis of its performance in a number of applications is discussed in a companion paper (paper II).[48] The outline of this article is as follows.

After briefly reviewing molecular DF, its reformulation for use in MP2 periodic calculations is presented in Sec. II. For enforcing convergence of lattice sums, the scheme is applied to dipole-corrected PDs, that is, distributions whose lowest nonzero electric moments are quadrupoles. The problem of the density of the sampling **k**-net in reciprocal space is next addressed, and relationships are derived which allow point-group symmetry to be exploited. The appendixes present general aspects of the implementation, which are important for the efficiency of the method. A detailed discussion of the algorithms for the method will be published elsewhere.

II. THEORY

A. Density fitting for molecular systems

Let us briefly summarize, for ease of reference, the DF technique[26–39] as used in the framework of local-correlation treatments of molecular systems, for evaluating the electron repulsion integrals

$$K_{ab}^{ij} = (ia|jb) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_{ia}(\mathbf{r}_1) r_{12}^{-1} \rho_{jb}(\mathbf{r}_2). \qquad (1)$$

Here and in the following, the indices $(i,j,\ldots)$, $(a,b,\ldots)$ denote WFs and PAOs, respectively, and ρ_{ia} denotes the corresponding PDs. It consists in substituting the exact PDs ρ_{ia} by approximated ones $\tilde{\rho}_{ia}$ which are expanded in an auxiliary fitting basis $\{\Xi_P(\mathbf{r})\}$ as

$$\rho_{ia}(\mathbf{r}) \equiv \phi_i(\mathbf{r})\phi_a(\mathbf{r}) \approx \tilde{\rho}_{ia}(\mathbf{r}) = \sum_P d_P^{ia} \Xi_P(\mathbf{r}). \qquad (2)$$

Upper case Latin letters will be used to identify FFs, for consistency with the notation adopted in the molecular DF.[22] The optimal fitting coefficients d_P^{ia} are determined by minimizing the error functional

$$\Delta_w = (\rho_{ia} - \tilde{\rho}_{ia}|\hat{w}_{12}|\rho_{ia} - \tilde{\rho}_{ia}), \qquad (3)$$

where $\hat{w}_{12}$ is a suitable two-electron weight operator, which must be positive definite. The fitting coefficients can then be obtained as

$$d_P^{ia} = \sum_Q W_Q^{ia} [W^{-1}]_{QP}. \qquad (4)$$

The matrix elements in this equation are the two- and three-index integrals

$$W_{PQ} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \Xi_P(\mathbf{r}_1) \hat{w}_{12} \Xi_Q(\mathbf{r}_2),$$

$$W_P^{ia} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \Xi_P(\mathbf{r}_1) \hat{w}_{12} \rho_{ia}(\mathbf{r}_2). \qquad (5)$$

The robust formula proposed by Dunlap[26] can be employed for expressing the approximated electron repulsion integrals, which guarantees that the error is second order with respect to the fitting error in densities, regardless of the choice of the operator $\hat{w}_{12}$:

$$\begin{aligned}\tilde{K}^{ij}_{ab} &= (\tilde{\rho}_{ia}|\rho_{jb}) + (\rho_{ia}|\tilde{\rho}_{jb}) - (\tilde{\rho}_{ia}|\tilde{\rho}_{jb}) \\ &= \sum_{Q} d^{ia}_{Q} J^{jb}_{Q} + \sum_{P} J^{ia}_{P} d^{jb}_{P} - \sum_{RT} d^{ia}_{R} J_{RT} d^{jb}_{T}. \qquad (6)\end{aligned}$$

We are therefore allowed to adopt the most convenient choice; two main possibilities are usually considered. If $\hat{w}_{12}=r_{12}^{-1}$, W become Coulomb repulsion integrals, to be indicated as J and; if $\hat{w}_{12}=\delta_{12}$, they reduce to overlap integrals, S. A further possibility would be the attenuated Coulomb operator discussed in Ref. 49.

In case of the Coulomb metric ($\hat{w}_{12}=r_{12}^{-1}$) and if the fitting domain is identical for all PDs (Ref. 23) the robust formula simplifies to

$$\tilde{K}^{ij}_{ab} = \sum_{PQ} J^{ia}_{P}[J^{-1}]_{PQ} J^{jb}_{Q}. \qquad (7)$$

If instead the overlap metric ($\hat{w}_{12}=\delta_{12}$) is used there is no simplification and we always have

$$\begin{aligned}\tilde{K}^{ij}_{ab} &= \sum_{PQ} \{S^{ia}_{P}[S^{-1}]_{PQ} J^{jb}_{Q} + J^{ia}_{P}[S^{-1}]_{PQ} S^{jb}_{Q}\} \\ &\quad - \sum_{PQRT} S^{ia}_{P}[S^{-1}]_{PR} J_{RT}[S^{-1}]_{TQ} S^{jb}_{Q}. \qquad (8)\end{aligned}$$

In the following any integrals involving FFs will be denoted as FF integrals. Two- and three-index FF integrals of Coulomb type appear in both Eqs. (7) and (8). Due to the long-range character of the r_{12}^{-1} operator, they have normally non-negligible values over the whole molecule.

This problem can be considerably alleviated using Poisson-type functions (PTFs) for the large majority of FFs.[46] For a given GTF (Ξ_{Q}), the corresponding PTF (Ξ'_{Q}, to be labeled as Q') is defined as follows:

$$\Xi'_{Q}(\mathbf{r}) = \hat{P}\Xi_{Q}(\mathbf{r}) \equiv \frac{-\nabla^2}{4\pi}\Xi_{Q}(\mathbf{r}). \qquad (9)$$

By exploiting the identity [which holds for any $f(\mathbf{r})$ which vanishes more quickly than r^{-1} as $r\to\infty$]

$$\int d\mathbf{r}_2 \frac{\hat{P}f(\mathbf{r}_2)}{r_{12}} = f(\mathbf{r}_1) \qquad (10)$$

it can be seen that the Coulomb FF-integrals involving PTFs are reduced to overlap integrals involving the associated GTFs:

$$J^{jb}_{Q'} = S^{jb}_{Q}, \quad J_{P'Q'} = S_{P'Q} = S_{PQ'}. \qquad (11)$$

These integrals are not only easier to calculate (the second is simply proportional to a kinetic integral between GTFs), but have also a much quicker decay. However, due to the fact that multipoles of PTFs are zero, it is necessary to include in the fitting set a small number of GTFs: their purpose is to describe the total charge and higher multipoles of the PD, while the PTFs move the charge around and produce an accurate description of the PD. In an MP2 application, where all PDs have zero charge because local occupied and virtual orbitals are mutually orthogonal, there is no need for the use of s-type GTFs.

B. Density fitting in periodic systems

Let us reformulate the expressions of Sec. II A for the case of a periodic system. We shall derive the equations in the simpler case where the $\hat{w}_{12}=r_{12}^{-1}$ metric is adopted, and generalize them finally to the other case.

Each WF or PAO or FF is identified by a double index: $\mathbf{j}\equiv j\mathcal{J};\mathbf{a}\equiv a\mathcal{A};\mathbf{P}\equiv P\mathcal{P};\ldots$, the former identifying the *type* of the function in a finite set, the latter (calligraphic font) the lattice vector of the crystalline cell where the function is located: $\phi_{\mathbf{j}}(\mathbf{r})\equiv\phi_{j\mathcal{J}}(\mathbf{r})\equiv\phi_{j0}(\mathbf{r}-\mathbf{R}_{\mathcal{J}})$, and so on. This notation has been chosen in order to be consistent with that used in Ref. 1. In the following, the WF index i is always associated to the zero reference cell, and we shall write i instead of $i0$. Equation (7) becomes (M_F is the number of FFs per cell):

$$\tilde{K}^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}} = \sum_{P=1}^{M_F}\sum_{\mathcal{P}} d^{ia\mathcal{A}}_{P\mathcal{P}} J^{j\mathcal{J}b\mathcal{B}}_{P\mathcal{P}}, \qquad (12)$$

$$d^{ia\mathcal{A}}_{P\mathcal{P}} = \sum_{Q=1}^{M_F}\sum_{\mathcal{Q}} J^{ia\mathcal{A}}_{Q\mathcal{Q}}[J^{-1}]_{Q\mathcal{Q}P\mathcal{P}}. \qquad (13)$$

In fact, these formulas cannot be used without careful analysis, because they imply, in principle, infinite sums over the lattice vectors. The inversion of the infinite J matrix is especially delicate.[43]

The above scheme can be conveniently reformulated in reciprocal space. Consider a set of $N_k=N_1\times N_2\times N_3$ regularly spaced reciprocal-space sampling points $\mathbf{k}$ (forming a Monkhorst net[50]):

$$\mathbf{k} = \sum_{t=1}^{3}\frac{K_t}{N_t}\mathbf{b}_t. \qquad (14)$$

The three integers N_t are known as shrinking factors, K_t are integers from 0 to N_t-1, and $\mathbf{b}_t$ are basis vectors of the reciprocal lattice. In fact, it is convenient to bring each sampling point as close as possible to the origin through a reciprocal-lattice translation so as to make it to belong to the first Brillouin Zone (BZ), whereby all point group operations transform a sampling point into another.[51] The resulting set of $\mathbf{k}$ points will be indicated as $\mathbb{M}$. For each sampling point the FT of the J quantities can be obtained with respect to the lattice vectors labeling the FFs:

$$J_{PQ}(\mathbf{k}) = \sum_{\mathcal{Q}} J_{P0Q\mathcal{Q}}\exp[\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{Q}}],$$

$$J^{ia\mathcal{A}}_{P}(\mathbf{k}) = \sum_{\mathcal{P}} J^{ia\mathcal{A}}_{P\mathcal{P}}\exp[\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{P}}]. \qquad (15)$$

The fitting coefficients at each $\mathbf{k}$ can be defined in the reciprocal space

$$\begin{aligned}d^{ia\mathcal{A}}_{P}(\mathbf{k}) &\equiv \sum_{Q} J^{ia\mathcal{A}}_{Q}(\mathbf{k})\{[J(\mathbf{k})]^{-1}\}_{QP} \\ &= \sum_{Q}\sum_{\mathcal{Q}} J^{ia\mathcal{A}}_{Q\mathcal{Q}}\sum_{\mathcal{P}}[J^{-1}]_{Q\mathcal{Q}P\mathcal{P}}\exp[\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{P}}] \\ &= \sum_{\mathcal{P}} d^{ia\mathcal{A}}_{P\mathcal{P}}\exp[\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{P}}], \qquad (16)\end{aligned}$$

and these are the FT of the direct-space counterparts given in Eq. (13). In Eq. (16) it is assumed that the lattice sums of the matrices $J_{Q\mathcal{Q}}^{ia\mathcal{A}}$, $J_{P0Q\mathcal{Q}}$, and $[J^{-1}]_{P0Q\mathcal{Q}}$ converge (see Sec. II C and the discussion in paper II concerning the possible singularity of the inverse FF overlap matrices), so that the order of the summation in the double sums over the lattice indices can be interchanged, and that the inverse of the $J(\mathbf{k})_{QP}$ matrix in the reciprocal space is the FT of the inverse of the $J_{P\mathcal{P}Q\mathcal{Q}}$ matrix:

$$\begin{aligned}\sum_{Q}\left(\sum_{\mathcal{Q}}[J^{-1}]_{P0Q\mathcal{Q}}\exp[\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{Q}}]\right)J_{QP'}(\mathbf{k}) &= \sum_{Q}\sum_{\mathcal{Q}}[J^{-1}]_{P0Q\mathcal{Q}}\sum_{\mathcal{P}'}J_{Q\mathcal{Q}P'\mathcal{P}'}\exp[\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{P}'}]\\ &= \sum_{\mathcal{P}'}\exp[\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{P}'}]\sum_{Q\mathcal{Q}}[J^{-1}]_{P0Q\mathcal{Q}}J_{Q\mathcal{Q}P'\mathcal{P}'} = \delta_{PP'}.\end{aligned} \tag{17}$$

It is worth noting here that the fitting coefficients in the reciprocal space are obtained by just multiplying a vector of length M_F by the inverse of an $M_F \times M_F$ matrix.

We now define $\mathcal{B}=\mathcal{L}\oplus\mathcal{J}$, where $\mathcal{L}$ labels the relative position of the PAO $\phi_{b\mathcal{B}}(\mathbf{r})$ with respect to the WF $\phi_{j\mathcal{J}}(\mathbf{r})$ in the second PD. All the PDs $\rho_{j\mathcal{J},b(\mathcal{L}\oplus\mathcal{J})}(\mathbf{r})$ are identical apart from a rigid translation by $\mathbf{R}_{\mathcal{J}}$. The FT of the $\widetilde{K}$ integrals at each $\mathbf{k}$ with respect to $\mathbf{R}_{\mathcal{J}}$ becomes

$$\widetilde{K}^{i,j}_{a\mathcal{A},b\mathcal{L}}(\mathbf{k}) = \sum_{\mathcal{J}}\widetilde{K}^{i,j\mathcal{J}}_{a\mathcal{A},b(\mathcal{L}\oplus\mathcal{J})}\exp[\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{J}}] = \sum_{P}d_P^{ia\mathcal{A}}(\mathbf{k})J_P^{jb\mathcal{L}}(\mathbf{k}). \tag{18}$$

Following a similar pattern, the robust expression for $\widetilde{K}(\mathbf{k})$ corresponding to the choice $\hat{w}_{12}=\delta_{12}$ is obtained as

$$\begin{aligned}\widetilde{K}^{i,j}_{a\mathcal{A},b\mathcal{L}}(\mathbf{k}) &= \sum_{Q}d_Q^{ia\mathcal{A}}(\mathbf{k})J_Q^{jb\mathcal{L}}(\mathbf{k}) + \sum_{P}J_P^{ia\mathcal{A}}(\mathbf{k})d_P^{jb\mathcal{L}}(\mathbf{k})\\ &\quad - \sum_{RT}d_R^{ia\mathcal{A}}(\mathbf{k})J_{RT}(\mathbf{k})d_T^{jb\mathcal{L}}(\mathbf{k}), \quad \text{with}\end{aligned}$$

$$d_Q^{ia\mathcal{A}}(\mathbf{k}) = \sum_{P}S_P^{ia\mathcal{A}}(\mathbf{k})\{[S(\mathbf{k})]^{-1}\}_{PQ}. \tag{19}$$

Note the similarity of Eq. (19) with the robust expressions for the molecular case, Eqs. (7) and (8). Here, however, the sums are restricted to the short list of the M_F FFs belonging to a given cell. If the Monkhorst net is suitably dense (see Sec. II D) the approximated electron repulsion integrals can finally be obtained by back-Fourier transform (BFT)

$$\widetilde{K}^{i0,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}} = \frac{1}{N_k}\sum_{\mathbf{k}}\widetilde{K}^{i,j}_{a\mathcal{A},b(\mathcal{B}\ominus\mathcal{J})}(\mathbf{k})\exp[-\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{J}}]. \tag{20}$$

Four essential simplifications have been achieved: (i) only FF integrals of quantities with their first index in the zero cell need to be calculated; (ii) the only lattice sums needed are those implied by the FT of the FF integrals [Eq. (15)]; (iii) the time required for the inversion of the J or S matrix is of order $N_k \times (M_F)^3$ and is usually negligible; (iv) each $\mathbf{k}$ point is treated independently, which is amenable for an easy and efficient parallelization of this step (this will be addressed in future work).

To make this approach accurate and efficient, some aspects must be carefully considered, however. First, one must make sure that the lattice sums in the FT of FF integrals are convergent; secondly, an appropriate density of the Monkhorst net must be selected; thirdly, all simplifications related to the presence of a local symmetry must be exploited; finally, a convenient prescreening technique must be employed, related to the LMP2 equations to be solved. Let us discuss the four problems separately.

C. Convergence of lattice sums

Serious problems can arise in the implementation of the reciprocal space approach due to the fact that the lattice series implicit in the FT of the Coulomb matrices J may diverge or converge slowly. The strategy outlined below is based on the use of PTFs as a fitting basis set, augmented by a relatively small set of GTFs, and on the restriction of the FT technique to dipole-corrected PDs. As in the molecular case (see Sec. II A), PTFs enormously simplify the evaluation of FF integrals, because they vanish exponentially and all of their multipoles are zero. The few GTFs which must be included in the fitting set at each crystal cell, are needed to describe the multipoles of the PDs.

In the present case, no GTFs of s type need to be included, because all PDs have zero charge. Moreover, the use of only PTFs as s-type fitting functions preserves the zero charge of PDs in the fitting. Otherwise, a fictitious charge could appear due to imperfectness of the fit and thus an additional constraint on the fitting coefficients in the functional (3) would have to be imposed.[28] This nice property of the PTF fitting basis is especially important in case of periodic systems, since an error in the Coulomb integrals, induced by this nonzero charge, will not vanish with the distance between the fitted densities and might affect the convergence of the lattice summations.

Still, p-type GTFs are required which must account for the dipoles of PDs, but they give rise to Coulomb series which are only conditionally convergent. This inconvenience may be circumvented by virtue of dipole-corrected PDs.

To each PD $\rho^i_{a\mathcal{A}}(\mathbf{r})$ a p-type function is associated $\Pi^i_{a\mathcal{A}}(\mathbf{r})$, which has the same dipole. The dipole-corrected PD

$$\rho'^{i}_{a\mathcal{A}}(\mathbf{r}) = [\rho^i_{a\mathcal{A}}(\mathbf{r}) - \Pi^i_{a\mathcal{A}}(\mathbf{r})] \tag{21}$$

has zero charge and dipole, and can therefore be described without use of s- and p-type GTFs, so avoiding abovementioned convergence problems. Dunlap's robust formula, with implicitly defined symbolism, then takes the form

$$\begin{aligned}\widetilde{K}^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}} &= (\rho'^{i}_{a\mathcal{A}} + \Pi^i_{a\mathcal{A}}|\widetilde{\rho}'^{j\mathcal{J}}_{b\mathcal{B}} + \Pi^{j\mathcal{J}}_{b\mathcal{B}}) + (\widetilde{\rho}'^{i}_{a\mathcal{A}} + \Pi^i_{a\mathcal{A}}|\rho'^{j\mathcal{J}}_{b\mathcal{B}} + \Pi^{j\mathcal{J}}_{b\mathcal{B}})\\ &\quad - (\widetilde{\rho}'^{i}_{a\mathcal{A}} + \Pi^i_{a\mathcal{A}}|\widetilde{\rho}'^{j\mathcal{J}}_{b\mathcal{B}} + \Pi^{j\mathcal{J}}_{b\mathcal{B}})\\ &= \widetilde{K}'^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}} + (\rho^i_{a\mathcal{A}}|\Pi^{j\mathcal{J}}_{b\mathcal{B}}) + (\Pi^i_{a\mathcal{A}}|\rho^{j\mathcal{J}}_{b\mathcal{B}}) - (\Pi^i_{a\mathcal{A}}|\Pi^{j\mathcal{J}}_{b\mathcal{B}}).\end{aligned} \tag{22}$$

To make this expression more explicit let us associate to each atom $A\mathcal{A}$ a shell (set of AOs with same exponent and angular momentum) of p-type GTFs, the same on all atoms, with dipole moments m along the three axes

$$\pi_{A\mathcal{A}} \equiv (\pi_x, \pi_y, \pi_z)_{A\mathcal{A}},$$

$$m = \int d\mathbf{r}\, x \pi_x(\mathbf{r}) = \int d\mathbf{r}\, y \pi_y(\mathbf{r}) \int d\mathbf{r}\, z \pi_z(\mathbf{r}). \tag{23}$$

If $\mu^i_{a\mathcal{A}}$ is the dipole moment of the PD $\rho^i_{a\mathcal{A}}(\mathbf{r})$, we can define

$$\Pi^i_{a\mathcal{A}}(\mathbf{r}) = \frac{\mu^i_{a\mathcal{A}}}{m}\pi_{A\mathcal{A}}(\mathbf{r}) = \sum_{t=1}^{3} \frac{(\mu_t)^i_{a\mathcal{A}}}{m}\pi_{t,A\mathcal{A}}(\mathbf{r}), \tag{24}$$

where A is the atom to which the PAO a belongs. With this convention the symmetry properties of $\rho^i_{a\mathcal{A}}(\mathbf{r})$ and $\rho'^i_{a\mathcal{A}}(\mathbf{r})$ and the spatial region they occupy are the same. Equation (22) simplifies to

$$\begin{aligned}\widetilde{K}^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}} = \widetilde{K}'^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}} + \frac{\mu^j_{b\mathcal{B}\ominus\mathcal{J}}}{m}(\rho^i_{a\mathcal{A}}|\pi_{B\mathcal{B}}) + \frac{\mu^i_{a\mathcal{A}}}{m}(\rho^j_{b(\mathcal{B}\ominus\mathcal{J})}|\pi_{A(\mathcal{A}\ominus\mathcal{J})}) \\ - \sum_{t,t'=1}^{3} \frac{(\mu_t)^i_{a\mathcal{A}}(\mu_{t'})^j_{b\mathcal{B}\ominus\mathcal{J}}}{m^2}(\pi_{t,A0}|\pi_{t',B(\mathcal{B}\ominus\mathcal{A})}).\end{aligned} \tag{25}$$

All integrals in this expression, being just of two- and three-index type, are easily calculated. The "primed" dipole corrected exchange integrals in Eq. (25), $\widetilde{K}'^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}$, are calculated exactly as in Eqs. (18) and (19), after subtracting from each PD $\rho^i_{a\mathcal{A}}(\mathbf{r})$ the three GTFs $\pi_{t,A\mathcal{A}}$ (24) with the appropriate coefficients.

Apart from the p-type-GTF integrals, which are eliminated by the dipole correction, the three-index Coulomb integrals involving higher angular momentum GTFs still need to be Fourier transformed. However, their number is relatively small and, furthermore, the corresponding lattice sums do converge, though slowly. It is important to mention here that all fitting functions have finite ranges in the direct space, which are at the same time consistent with the translational symmetry and subsequent FT. To underline the locality of fitting in the above sense we introduce for further reference the term "Fourier-directed local fitting."

D. k sampling

The density of the Monkhorst net is a critical issue. The computational cost of the FT and BFT steps expressed in Eqs. (15)–(20) is proportional to the number of sampling points N_k. Too dense nets would unnecessarily increase the cost of the calculation, while inaccurate or wrong K values can result from the use of too small shrinking factors.

To analyze this problem, let us define a superlattice in direct space whose super-translation vectors $\mathbf{A}_t$ are proportional to the original translation vectors $\mathbf{a}_t$ through the shrinking factors of the Monkhorst net:

$$\mathbf{A}_1 = N_1\mathbf{a}_1, \quad \mathbf{A}_2 = N_2\mathbf{a}_2, \quad \mathbf{A}_3 = N_3\mathbf{a}_3.$$

A general vector of the super-lattice, labeled by $\bar{\mathcal{A}}$, is

$$\mathbf{R}_{\bar{\mathcal{A}}} = \eta_1\mathbf{A}_1 + \eta_2\mathbf{A}_2 + \eta_3\mathbf{A}_3,$$

where η_i is an arbitrary integer.

The vectors $\mathbf{A}_i$ define the super-Wigner-Seitz cell (SWSC) of the superlattice, which contains the N_k translation vectors of the original lattice $\mathbf{R}_{\mathcal{P}}$, which are either inside the SWSC or at its surface. This set of translations within the SWSC form a finite translation group with the multiplication law modulo $\bar{\mathcal{A}}$. The irreducible representations of this group will be marked by vectors $\mathbf{k}$ forming a set $\mathbb{M}$. The second orthogonality relation for this group reads

$$\frac{1}{N_k}\sum_{\mathbf{k}\in\mathbb{M}} \exp[\imath\mathbf{k}\cdot(\mathbf{R}_{\mathcal{Q}} - \mathbf{R}_{\mathcal{P}})] = \sum_{\mathbf{R}_{\bar{\mathcal{A}}}} \delta_{\mathcal{Q},(\mathcal{P}\oplus\bar{\mathcal{A}})}. \tag{26}$$

Consider a matrix A whose row and column indices correspond to direct lattice vectors and possess translational invariance ($A_{\mathcal{P}\mathcal{Q}}{=}A_{(\mathcal{P}\oplus\mathcal{R})(\mathcal{Q}\oplus\mathcal{R})}$). Additionally, we assume that the elements of the matrix A decay with the distance between the vectors $\mathcal{P}$ and $\mathcal{Q}$ sufficiently fast. Taking into account the FT of the matrix A

$$A(\mathbf{k}) = \sum_{\mathbf{R}_{\mathcal{P}}} A_{0\mathcal{P}} \exp(\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{P}}) \tag{27}$$

and Eq. (26), for the BFT of $A(\mathbf{k})$, $\mathcal{A}_{0\mathcal{P}}$, on the set $\mathbb{M}$ of the $\mathbf{k}$ vectors one obtains

$$\begin{aligned}\mathcal{A}_{0\mathcal{P}} &= \frac{1}{N_k}\sum_{\mathbf{k}\in\mathbb{M}} A(\mathbf{k})\exp[-\imath\mathbf{k}\cdot\mathbf{R}_{\mathcal{P}}] \\ &= \frac{1}{N_k}\sum_{\mathbf{R}_{\mathcal{Q}}} A_{0\mathcal{Q}} \sum_{\mathbf{k}\in\mathbb{M}} \exp[\imath\mathbf{k}\cdot(\mathbf{R}_{\mathcal{Q}} - \mathbf{R}_{\mathcal{P}})] \\ &= \sum_{\mathbf{R}_{\bar{\mathcal{A}}}} A_{0(\mathcal{P}\oplus\bar{\mathcal{A}})}.\end{aligned} \tag{28}$$

Thus, the resulting matrix $\mathcal{A}_{0\mathcal{P}}$, obtained in the FT-BFT procedure, has the periodicity of the superlattice with respect to index $\mathcal{P}$. The essential point is that the matrix $\mathcal{A}_{0\mathcal{P}}$ replicates the initial matrix $A_{0\mathcal{P}}$ within the SWSC if the values $A_{0\mathcal{P}}$ outside the SWSC are negligibly small. In other words, if the SWSC defined by the three integers N_1, N_2, N_3 is such that it contains all non-negligible elements of the direct space $A_{0\mathcal{Q}}$ matrix, the FT-BFT procedure on the corresponding set $\mathbb{M}$ of the $\mathbf{k}$ vectors reconstructs the elements $A_{\mathcal{P}\mathcal{Q}}$, which have the vector $\mathbf{R}_{\mathcal{Q}\ominus\mathcal{P}}$ inside this SWSC, or on its border.

Hence, the number of $\mathbf{k}$ points in the FT-BFT scheme described in Sec. II B should be chosen such that the BFT [Eq. (20)] of the four-index integrals $\widetilde{K}'^{i,j}_{a\mathcal{A},b(\mathcal{B}\ominus\mathcal{J})}(\mathbf{k})$ correctly reproduces the integrals $\widetilde{K}'^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}$. An adequate $\mathbf{k}$-net would define a SWSC with a set of translational $\mathcal{J}$ vectors, containing all the non-negligible direct-space four-index integrals.

The PD $\rho'^i_{a\mathcal{A}}(\mathbf{r})$ is a localized function which is concentrated around the WF ϕ_i, since, according to the LMP2 approach, the PAO ϕ_a is "close" to ϕ_i. The integrals $\widetilde{K}^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}$ decay with respect to the distance R_{ij} between the WFs ϕ_i and $\phi_{j\mathcal{J}}$ as $1/R^3_{ij\mathcal{J}}$, which corresponds to the dipole-dipole interaction between the PDs $\rho'^i_{a\mathcal{A}}(\mathbf{r})$ and $\rho'^{j\mathcal{J}}_{b\mathcal{B}}(\mathbf{r})$ (the PDs hold no charge due to WF-PAO orthogonality). But the back-

Fourier transform is applied not to the integrals $\tilde{K}^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}$ but rather to the dipole corrected ones $\tilde{K}'^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}$ (see Sec. II C), and these decay as $1/R^5_{ij\mathcal{J}}$ according to the quadrupole-quadrupole interaction. Taking into account the fact that the WF ϕ_i is always anchored in the reference cell, one can conclude that the integrals $\tilde{K}'^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}$ with an absolute value larger than a chosen threshold span a finite and not exceedingly large number of unit cells $\mathcal{J}$, surrounding the reference cell. This set of unit cells forms the SWSC, which in turn dictates the density of the adequate Monkhorst net.

Moreover, since the integrals related to "distant" ij pairs are calculated by multipole expansion,[1] the Fourier back-transformed integrals have the index $\mathcal{J}$ corresponding to the reference unit cell or to one near it. This means that the number of $\mathbf{k}$ points which are really needed is even smaller, as follows from formula (28): when all indices $\mathcal{P}$ are close to $\mathbf{0}$, shorter vectors $\mathbf{A}_i$ can be chosen.

The non-negligible integrals $\tilde{K}'^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}$ and the corresponding set of $\mathcal{J}$ vectors can be prescreened by using the multipole-based integral estimates method of Lambrecht *et al.*[52,53] But if the DF technique is used to only obtain a relatively small fraction of the non-negligible integrals, such a prescreening would significantly overestimate the density of the $\mathbf{k}$ meshes needed for the calculations. Presently, the Monkhorst shrinking factors are an input parameter in the code. The actual $\mathbf{k}$ meshes giving accurate results for different structures are discussed in paper II. Here we just mention that for crystals with small unit cells (diamond, BeS, etc.) an $8\times8\times8$ Monkhorst net is sufficient. For systems with larger unit cells, sparser $\mathbf{k}$ meshes can be used.

E. Exploitation of local symmetry

In this section we generalize the considerations introduced in our previous papers and concerning the exploitation of the point symmetry of the crystal[1] by considering the effect of each point group operator on the basic "objects" in our expressions: AOs, PAOs, symmetry adapted WFs,[54] PDs and, in the present instance, FFs. Here we use a Greek letter: $\alpha,\beta,\ldots$, as a general label of these objects and, as usual: $\mathcal{A},\mathcal{B},\ldots$, to denote the crystal cell to which they belong.

The general space group operator of the crystal can be expressed as the product of a "local" operator $\hat{V}_0$ and a pure translational operator $\hat{T}$,

$$\widehat{(V_0,T)} = \hat{V}_0\hat{T};\quad \hat{V}_0 = \{S_V|\mathbf{f}_V\}. \tag{29}$$

Each operator $\hat{V}_0$ comprises a 3×3 matrix, S_V, and a fractional translation $\mathbf{f}_V$, which rotate and translate the $\mathbf{r}=(x,y,z)$ coordinate, correspondingly.

The local symmetry embodied in the h local operators can be exploited as follows. All primary quantities implied in periodic DF have the form [see Eq. (5)]

$$\mathbf{C}_{\alpha\mathcal{A},\beta(\mathcal{B}\oplus\mathcal{A})} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \mathbf{g}_{\alpha\mathcal{A}}(\mathbf{r}_1)\hat{w}_{12}\mathbf{h}_{\beta(\mathcal{B}\oplus\mathcal{A})}(\mathbf{r}_2) = \mathbf{C}_{\alpha0,\beta\mathcal{B}}. \tag{30}$$

Here, $\mathbf{g}_{\alpha\mathcal{A}}(\mathbf{r})$ (and analogously, $\mathbf{h}_{\beta(\mathcal{B}\oplus\mathcal{A})}$) is a "shell" of l functions $\{g_{\alpha_m}(\mathbf{r}-\mathbf{R}_{\mathcal{A}})\}$ "belonging" to cell $\mathcal{A}$, which are equivalent to the parent ones in the reference cell zero $[\mathbf{g}_\alpha(\mathbf{r})]$ except for the lattice translation $\mathbf{R}_{\mathcal{A}}$.

Under $\hat{V}_0$, these functions transform into a linear combination of the functions of a symmetry related shell $\mathbf{g}_{\alpha_V\mathcal{A}^\alpha_V}$, generally belonging to another crystalline cell $\mathcal{A}^\alpha_V$. For instance, under inversion, the three $2p$ functions on a carbon atom (C_A) in diamond transform into a combination of the three $2p$ functions on the other carbon atom in the primitive cell (C_B), generally centered in a different crystal cell. This can be written in formulas,

$$\hat{V}_0 g_{\alpha_m}(\mathbf{r}-\mathbf{R}_{\mathcal{A}}) = \sum_{m'=1}^{l} X^\alpha_{V,mm'} g_{\alpha_{V,m'}}(\mathbf{r}-\mathbf{R}_{\mathcal{A}^\alpha_V}) \tag{31}$$

or, more compactly,

$$\hat{V}_0\mathbf{g}_{\alpha\mathcal{A}} = \mathbf{X}^\alpha_V \cdot \mathbf{g}_{\alpha_V\mathcal{A}^\alpha_V}. \tag{32}$$

Here, $\mathbf{R}_{\mathcal{A}^\alpha_V}=S_V\mathbf{R}_{\mathcal{A}}+\mathbf{R}^\alpha_{0V}$ is the sum of two lattice vectors. The former simply results from the rotation of $\mathbf{R}_{\mathcal{A}}$, while the latter, being independent of $\mathcal{A}$, specifies the crystal cell where $\mathbf{g}_{\alpha_V}$ is located when $\hat{V}_0$ acts on the parent $\mathbf{g}_\alpha$ shell. The $l\times l$ transformation matrix $\mathbf{X}^\alpha_V$ and the $\mathbf{R}^\alpha_{0V}$ vectors are automatically constructed by the program for each "type" of object and each operator. Since $\hat{w}_{12}$ is a totally symmetric operator, acting with $\hat{V}_0$ on Eq. (30) (exploiting its invariance with respect to any rotation) yields

$$\begin{aligned}\mathbf{C}_{\alpha0,\beta\mathcal{B}} &= \int d\mathbf{r}_1 \int d\mathbf{r}_2 \hat{V}_0[\mathbf{g}_\alpha(\mathbf{r}_1)\hat{w}_{12}\mathbf{h}_\beta(\mathbf{r}_2-\mathbf{R}_{\mathcal{B}})]\\ &= (\mathbf{X}^\alpha_V \times \mathbf{X}^\beta_V)\cdot \mathbf{C}_{\alpha_V0,\beta_V\mathcal{B}^{\alpha,\beta}_V},\quad \text{where}\end{aligned}$$

$$\mathbf{R}_{\mathcal{B}^{\alpha,\beta}_V} = \mathbf{R}_{\mathcal{B}^\beta_V} - \mathbf{R}^\alpha_{0V}. \tag{33}$$

This expression concisely describes how all integrals can be obtained from an irreducible set in direct space. It also allows us to connect $\mathbf{C}_{\alpha,\beta}(\mathbf{k})$ to the symmetry related set of integrals at another sampling point $\mathbf{k}_V=S_V\mathbf{k}$, by exploiting the fact that $(S_V\mathbf{k})\cdot(S_V\mathbf{R})=\mathbf{k}\cdot\mathbf{R}$. With simple manipulations one obtains

$$\begin{aligned}\mathbf{C}_{\alpha_V,\beta_V}(\mathbf{k}_V) = {}&[(\mathbf{X}^\alpha_V)^{-1}\times(\mathbf{X}^\beta_V)^{-1}]\cdot\mathbf{C}_{\alpha,\beta}(\mathbf{k})\\ &\times\exp[\imath\mathbf{k}_V\cdot(\mathbf{R}^\beta_{0V}-\mathbf{R}^\alpha_{0V})].\end{aligned} \tag{34}$$

Two schemes can be followed for exploiting local symmetry by using this expression. Either from the knowledge of all $\mathbf{C}(\mathbf{k})$'s in the irreducible wedge of the BZ (IBZ) their value is obtained in the whole BZ, or from the knowledge of the irreducible set of integrals $\{\mathbf{C}(\mathbf{k})\}_{\mathrm{irred}}$ in the whole BZ all $\mathbf{C}(\mathbf{k})$'s are obtained. According to convenience, either scheme can be adopted, as illustrated in Appendix C. Note, finally, that the so-called time-reversal symmetry can be used to restrict in all cases the calculation to one half of the BZ, i.e.,

$$\mathbf{C}_{\alpha,\beta}(\mathbf{k}) = \mathbf{C}^\star_{\alpha,\beta}(-\mathbf{k}). \tag{35}$$

F. LMP2 equations

The contribution from a WF pair to the total correlation energy decays asymptotically with the inverse sixth power of the distance between the two WFs. Since in 3D crystals the average number of pairs at distance R increases as R^2, the actual decay rate of the correlation energy in crystals is $1/R^4$. So the saturation of the energy with the increase of the cutoff distance occurs at much larger distances than in molecules (see paper II for a detailed analysis of this problem). The number of $(i,j\mathcal{J})$ pairs to include in the calculation may then be fairly large which makes solving the LMP2 equations an expensive task.

In the present work, the approach employed for solving the LMP2 equations and presented in the previous paper[1] was significantly revised. The modifications mainly concern the techniques adopted for the evaluation of the residuals ($R^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}=K^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}+A^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}+B^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}$). The presently adopted prescriptions are as follows:

$$A^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}} = \sum_{c\mathcal{C},d\mathcal{D}\in D_{i,j\mathcal{J}}} [f^{\mathcal{C}\ominus\mathcal{A}}_{ac} T^{i,j\mathcal{J}}_{c\mathcal{C},d\mathcal{D}} S^{\mathcal{B}\ominus\mathcal{D}}_{db} + S^{\mathcal{C}\ominus\mathcal{A}}_{ac} T^{i,j\mathcal{J}}_{c\mathcal{C},d\mathcal{D}} f^{\mathcal{B}\ominus\mathcal{D}}_{db}], \tag{36}$$

$$\begin{aligned} B^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}} = &- \sum_{c\mathcal{C},d\mathcal{D}\in D_i} S^{\mathcal{C}\ominus\mathcal{A}}_{ac} \beta'^{\,i,j\mathcal{J}}_{c\mathcal{C},d\mathcal{D}} S^{\mathcal{B}\ominus\mathcal{D}}_{db} \\ &- \sum_{c\mathcal{C},d\mathcal{D}\in D_{j\mathcal{J}}} S^{\mathcal{C}\ominus\mathcal{A}}_{ac} \beta''^{\,i,j\mathcal{J}}_{c\mathcal{C},d\mathcal{D}} S^{\mathcal{B}\ominus\mathcal{D}}_{db}, \end{aligned} \tag{37}$$

$$\beta'^{\,i,j\mathcal{J}}_{c\mathcal{C},d\mathcal{D}} = \sum_{k\mathcal{K}\in P_i} T^{i,k\mathcal{K}}_{c\mathcal{C},d\mathcal{D}} f^{\mathcal{J}\ominus\mathcal{K}}_{kj}, \tag{38}$$

$$\beta''^{\,i,j\mathcal{J}}_{c\mathcal{C},d\mathcal{D}} = \sum_{k\mathcal{K}\in P_{j\mathcal{J}}} f^{\mathcal{K}}_{ik} T^{k\mathcal{K},j\mathcal{J}}_{c\mathcal{C},d\mathcal{D}}. \tag{39}$$

Here S and f denote the overlap and Fock matrices, respectively, and T are the excitation amplitudes. The sum in Eq. (36) runs over all PAOs in the WF pair domain $D_{i,j\mathcal{J}}$. In Eq. (37) the sums are running over the "united domains" of i or $j\mathcal{J}$, that is,

$$D_{j\mathcal{J}} = \bigcup_{k\mathcal{K}} D_{j\mathcal{J},k\mathcal{K}}, \tag{40}$$

with the union comprising not only symmetry-unique pairs of the pair list, but rather all close-by pairs of WF $j\mathcal{J}$. Finally, the sums in Eqs. (38) and (39) run consequently over the $k\mathcal{K}$ WFs which can form close-by pairs with WF i (P_i) or $j\mathcal{J}$ ($P_{j\mathcal{J}}$), respectively. The solution of the LMP2 equations is found when all the residuals $R^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}$ become zero.[1]

In periodic systems, the computational cost for computing the residual scales nominally as $O(N^2)$, where N is the number of pairs or, in 3D crystals, as R^6_{cut} (R_{cut} is the cutoff distance for the pairs included in the calculation), since the number of pairs increases cubically with the cutoff distance. Moreover, although the number of different $i,j\mathcal{J}$ pairs can be reduced by considering only symmetry irreducible ones,[1] in the sums of Eqs. (38) and (39) one has to take into account *all* possible WFs $k\mathcal{K}$ forming pairs with i or $j\mathcal{J}$.

Advantage can be taken, however, of the sparsity of the f,S,T matrices. Due to the exponential decay of WFs and PAOs, the elements of the Fock and overlap matrices also decay exponentially with respect to the distance between the corresponding functions. The amplitudes $T^{i,j\mathcal{J}}_{a\mathcal{A},b\mathcal{B}}$ decay as $R^{-6}_{i,j\mathcal{J}}$ with the distance between the WFs i and $j\mathcal{J}$. Exploiting this sparsity is very important and leads to a reduction of the overall scaling for the equation solver. The scaling of the most expensive B term [Eqs. (37)–(39)] then reduces from $O(N_{\text{irr}}N)$ to just $O(N_{\text{irr}})$, where N_{irr} is the number of symmetry unique pairs. In 3D crystals this corresponds to the R^3_{cut} scaling rather than R^6_{cut}.

III. FINAL REMARKS

The approach described in this paper has been implemented in the CRYSCOR code. The performance of the method is demonstrated in companion paper II, where test calculations were carried out for diamond, a three-layer MgO slab, and two molecular crystals, proton ordered ice, and carbon dioxide. The intention here is to demonstrate that our *ab initio* post-HF method makes it feasible to routinely account for electron correlation also in cases of relatively complex periodic systems.

Work is going on to make the code more efficient and powerful. One of the parameters which influence the computational resources in periodic-density-fitting-LMP2 (though not as severe as in LMP2) calculations is the spread of the WFs. In molecular crystals, where the inclusion of electron correlation is vital for providing reliable results, WFs are usually quite well localized within the molecules forming the crystal. This makes CRYSCOR especially efficient in the very important case of molecular crystals. However, even if WFs are not that well localized, there are ways to increase their compactness, by, first, dropping the mutual orthogonality condition and, second, by chopping the Wannier function tails (in this case one has to reformulate the MP2 method for a non-HF reference by including also singles in the MP2 equations).[55] Implementation of this technique into the CRYSCOR code is planned for the near future.

Another important advancement for the CRYSCOR code is the introduction of a dual basis set in order to augment the virtual manifold for the LMP2 calculation by additional functions without interfering with the periodic HF calculation, which does not allow for the use of diffuse GTFs. Furthermore, we plan to develop explicitely correlated methods for crystals: the F12 technique,[56] which for molecules proved to be a very efficient way to rectify the slow basis set convergence of orbital product based methods, once available for periodic systems, will allow to perform DF-LMP2 calculations close to the basis set limit. The effect of the correlation correction on the density matrix, and thus on such ground state observables as x-ray structure factors and directional Compton profiles is presently being explored.[57]

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APPENDIX A: CALCULATION OF THE INTEGRALS

For the DF procedure with the overlap metric (equation (19)) the following integrals are computed.

(1) Two-index overlap $S_{PQ\mathcal{Q}}$ and Coulomb $J_{PQ\mathcal{Q}} = (P|Q\mathcal{Q})$ integrals between all pairs of FF shells (either GTFs or PTFs).

(2). Three-index overlap $S'^{ia\mathcal{A}}_{P\mathcal{P}}$ and Coulomb $J'^{ia\mathcal{A}}_{P\mathcal{P}} = [(ia\mathcal{A})'|P\mathcal{P}]$ integrals between the reducible set of dipole-corrected PDs, and symmetry irreducible FF shells.

In the case of the Coulomb metric the overlap integrals are not needed and thus not calculated. The ranges for the $\mathcal{P}$ (or $\mathcal{Q}$) indices of the FF, needed to be taken into account for DF in an infinite periodic system are discussed in Appendix B.

In order to obtain the three-index integrals with the dipole corrected PDs $J'^{ia\mathcal{A}}_{P\mathcal{P}}$ and $S'^{ia\mathcal{A}}_{P\mathcal{P}}$ [see Eq. (24)], additional two-index integrals $J_{P\mathcal{P},\Pi^i_{a\mathcal{A}}}$ and $S_{P\mathcal{P},\Pi^i_{a\mathcal{A}}}$ (the latter only for the overlap metric) are calculated, so that

$$J'^{ia\mathcal{A}}_{P\mathcal{P}} = J^{ia\mathcal{A}}_{P\mathcal{P}} - J_{P\mathcal{P},\Pi^i_{a\mathcal{A}}}. \tag{A1}$$

The range for the index $\mathcal{P}$ in the integrals $J_{P\mathcal{P},\Pi^i_{a\mathcal{A}}}$ coincides with the one of their three-index counterparts.

For obtaining the true four-index integrals from the "dipole corrected" ones [Eq. (22)] one additionally needs the following sets of integrals to be calculated.

(1) Two-index integrals $J_{\pi_A B\mathcal{B}} = (\pi_A|\pi_{B\mathcal{B}})$ between the *p*-type shell of functions centered on atoms A and $B\mathcal{B}$.

(2) Three-index integrals $J^{ia\mathcal{A}}_{\pi_{B\mathcal{B}}} = (ia\mathcal{A}|\pi_{B\mathcal{B}})$ between PDs and the *p*-type shell of functions for the reconstruction of the four-index integrals.

The function $\pi_{B\mathcal{B}}$ is centered on the same site as the corresponding PAO $B\mathcal{B}$, thus the amount of such integrals to be computed is known *a priori* and usually not large.

Owing to translational symmetry all the integrals are calculated having the first index in the reference cell. The AO two-electron integrals are evaluated according to the Obara-Saika scheme.[58]

APPENDIX B: FITTING RANGE AND SYMMETRY

At first the "fitting radius" R_F is estimated, which is the maximum among the lengths of the direct lattice vectors $\mathbf{R}_{\mathcal{P}}$. To obtain this estimate a trial evaluation of the three-index overlap integrals involving AOs and FFs with the most diffuse exponents is performed. The radius R_F is such that none of these integrals with $R_{\mathcal{P}} \leq R_F$ is above a certain threshold. All the three-index integrals with $R_{\mathcal{P}} \leq R_F$ are evaluated explicitly (see Appendix A). However, the slowly decaying three-index Coulomb integrals with the GTFs have significant values even if $R_F < R_{\mathcal{P}} < R_{\max}$. But since for these integrals the overlap between the WF-PAO PDs and FFs is negligible, it is possible to evaluate accurately the corresponding long-range contribution by multipole expansion (see Appendix C).

Next, for each WF in the pair list, say $j\mathcal{J}$, a codomain $\aleph(j\mathcal{J})$ is defined which includes PAOs either in the domain $j\mathcal{J}$ or of any other WF from the symmetry-unique pair list, forming a pair with $j\mathcal{J}$. Then each WF from a nonzero cell is translated to the reference cell together with its codomain. In the set of all PDs, $iA\mathcal{A}[A\mathcal{A} \in \aleph(i)]$, a symmetry irreducible subset $\{PD\}_{\text{irr}} = (iA\mathcal{A})_{\text{irr}}$ is identified, according to Eq. (33).

To further improve the efficiency of the method it is convenient to convert this list into an equivalent one, containing *all* needed $iA\mathcal{A}$ objects, but only irreducible FFs, to be provided to the routines for the calculation of FF integrals. In order to do that the correspondence

$$[iA\mathcal{A}(P\mathcal{P})_{\text{irr}}] \leftrightarrow [(iA\mathcal{A})_{\text{irr}}P\mathcal{P}] \tag{B1}$$

is established. This procedure allows one to adapt the point symmetry also for the AO-based three-index untransformed integrals and to treat them on the same symmetry footing as the transformed ones (see Appendix A). Inclusion of the point symmetry at the level of AO-based integrals considerably reduces the number of such integrals to be calculated and transformed, improving so the performance of the DF routines and reducing the memory resources needed.

APPENDIX C: FOURIER TRANSFORM

The FT of two-index matrices (S,J) is performed in a straightforward way once and for all. The transformed matrices are obtained only for **k** points belonging to IBZ. Then the metric matrix (the matrix of two-index overlap or Coulomb integrals) is inverted for each of these **k** points. Finally the two-index matrices, corresponding to the rest of the BZ, are obtained using symmetry relations [Eq. (34)]. The FT of three-index objects, on the other hand, must be performed for all **k** points in the BZ [but still taking advantage of the time-reversal symmetry, Eq. (35)], since only the symmetry-irreducible $ia\mathcal{A}$ objects are considered (see Sec. II E).

At this stage the long-range contribution to the FT of Coulomb integrals involving a GTF $P\mathcal{P}$ with $R_F < R_{\mathcal{P}} < R_{\max}$ (where $R_{\max}$ is prescreened according to a given tolerance) is evaluated via multipolar expansion. Each PD $\rho'^{i}_{a\mathcal{A}}(\mathbf{r})$ is represented by a set $\{X^m_l(ia\mathcal{A})\}$ of electric multipoles with angular momentum $l \leq l_{\max}$ and centered in the centroid $\mathbf{C}_i$ of WF i. Similarly, the general GTF $P\mathcal{P}$ (characterized by angular quantum numbers $\bar{l},\bar{m}$) has just one nonzero electric multipole moment $X^{\bar{m}}_{\bar{l}}(P)$ centered in $\mathbf{C}_P + \mathbf{R}_{\mathcal{P}}$, which is the position in the reference cell of the atom to which P belongs, plus the lattice vector $\mathcal{P}$.

The long-range (LR) contribution to the FT of these integrals is then approximated by

$$[J^{ia\mathcal{A}}_P(\mathbf{k})]^{\text{LR}} \approx X^{\bar{m}}_{\bar{l}}(P) \times \sum_{l,m} \left\{ X^m_l(ia\mathcal{A}) \sum_{\mathcal{P}}{}' [\exp(\imath \mathbf{k} \cdot \mathbf{R}_{\mathcal{P}}) V^{\bar{m}m}_{\bar{l}l}(\mathbf{r})] \right\}. \tag{C1}$$

Here, $V^{\bar{m}m}_{\bar{l}l}(\mathbf{r})$ is the Coulomb interaction operator between the two multipoles at the relative position $\mathbf{r}=\mathbf{C}_P+\mathbf{R}_{\mathcal{P}}-\mathbf{C}_i$, and $\Sigma'_{\mathcal{P}}$ is restricted to the long-range lattice vectors. After performing this sum, we can finally express the required long-range contribution in terms of the long-range FT of the interaction operator for each different pair of centers $\mathbf{C}_i$, $\mathbf{C}_P$ in the reference cell,

$$[J_P^{ia\mathcal{A}}(\mathbf{k})]^{\mathrm{LR}} \approx X_{\bar{l}}^{\bar{m}}(P)\sum_{l,m} X_l^m(ia\mathcal{A})V_{\bar{l}l}^{\bar{m}m}(\mathbf{k};\mathbf{C}_i,\mathbf{C}_P). \quad \text{(C2)}$$

The interaction between multipole sets is then evaluated separately for each $\mathbf{k}$ point and summed to the previously transformed matrices.

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