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Denis Usvyat

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Linear-scaling explicitly correlated treatment of solids: Periodic local MP2-F12 method

Denis Usvyat^{a)}

Institute of Physical and Theoretical Chemistry, University of Regensburg, Universitätsstraße 31, D-93040 Regensburg, Germany

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Theory and implementation of the periodic local MP2-F12 method in the 3^*A fixed-amplitude ansatz is presented. The method is formulated in the direct space, employing local representation for the occupied, virtual, and auxiliary orbitals in the form of Wannier functions (WFs), projected atomic orbitals (PAOs), and atom-centered Gaussian-type orbitals, respectively. Local approximations are introduced, restricting the list of the explicitly correlated pairs, as well as occupied, virtual, and auxiliary spaces in the strong orthogonality projector to the pair-specific domains on the basis of spatial proximity of respective orbitals. The 4-index two-electron integrals appearing in the formalism are approximated via the direct-space density fitting technique. In this procedure, the fitting orbital spaces are also restricted to local fit-domains surrounding the fitted densities. The formulation of the method and its implementation exploits the translational symmetry and the site-group symmetries of the WF's. Test calculations are performed on LiH crystal. The results show that the periodic LMP2-F12 method substantially accelerates basis set convergence of the total correlation energy, and even more so the correlation energy differences. The resulting energies are quite insensitive to the resolution-of-the-identity domain sizes and the quality of the auxiliary basis sets. The convergence with the orbital domain size is somewhat slower, but still acceptable. Moreover, inclusion of slightly more diffuse functions, than those usually used in the periodic calculations, improves the convergence of the LMP2-F12 correlation energy with respect to both the size of the PAO-domains and the quality of the orbital basis set. At the same time, the essentially diffuse atomic orbitals from standard molecular basis sets, commonly utilized in molecular MP2-F12 calculations, but problematic in the periodic context, are not necessary for LMP2-F12 treatment of crystals. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4829898>]

I. INTRODUCTION

The determinantal expansion of the wave function is the starting point of the standard quantum chemical models, such as configuration interaction (CI), many body perturbation theory (MBPT), or coupled cluster (CC). Despite great success of these methods in countless applications to molecular or even crystalline systems, high accuracy calculations remain computationally very expensive. One of the problems, contributing to the high cost of the correlated calculations, is the need for rich basis sets due to slow convergence of the correlation energy with the basis set size.

The electron correlation manifests in the many-electron wavefunction as a cusp at the point of coalescence of two electrons and a Coulomb hole around it. The proper description of this feature requires terms linear in inter-electron distance r_{12} , which are absent in the determinantal expansion of the wavefunction. This deficiency, which is actually responsible for the slow basis set convergence of the correlation energy, can be repaired by explicitly adding such terms in the wavefunction. Such an approach is usually referred to as explicitly correlated treatment, and the corresponding methods are marked by a suffix "R12." First attempt to use r_{12} -dependent terms in

the wavefunction by Hylleraas, dating back to 1929, turned out to be very efficient for accurate calculation of the ionization potential of helium atom.¹ Application of this method to larger systems, however, appeared to be computationally difficult because of expensive and numerous three- and four-electron integrals appearing in the formalism.

Through years several variants of the method have been proposed.^{2,3} A computationally convenient scheme, which factorizes three- and four-electron integrals into products of two-electron integrals by means of resolution of the identity (RI), was developed by Kutzelnigg³ and Kutzelnigg and Klopper,⁴⁻⁶ making the explicit correlation technique affordable beyond a-few-electron systems.⁷⁻¹¹ It has been realized at some point that the correlation factor r_{12} is, in fact, problematic for larger systems, since although correctly describing the cusp itself, it can be harmful in the far away regions due to its non-physical growth. Substitution of the explicit r_{12} factor by some local function of r_{12} (which is usually denoted by the suffix "F12" in the method notation) fixes this problem and has now become standard in the explicitly correlated approaches. Particularly accurate description at a moderate orbital basis set level is achieved with the Slater-type geminal $\frac{1}{\gamma} \exp(-\gamma r_{12})$ as the correlation function.¹²

In the last decade hierarchies of approximations for the F12 method have been developed and implemented for

^{a)}denis.usvyat@chemie.uni-regensburg.de

different levels of the correlated treatment within MBPT,^{13–22} CC,^{23–32} or multireference^{33–37} theories, as well as a universal second order F12 correction,³⁸ applicable to any correlated method. As has recently been shown, the F12 treatment can be efficiently combined with the local correlation scheme^{18,19,21,32,39} or other techniques, based on the virtual space truncation.^{40–42} This allows for low or even linear scaling of the computational cost with the molecular size, opening a way to approach the basis set limit for quite extended molecules. Such methods also benefit from the ability of the F12 treatment to reduce or even eliminate the domain or the virtual space truncation error, which is intrinsically related to basis set incompleteness.

Periodic systems are effectively infinite and thus computationally more difficult than molecules. For polymers, however, developed methods reach a relatively high level, such as CCSD⁴³ for the ground state and EOM-CCSD⁴⁴ for the excited state. An implementation of a 1D periodic MP2-F12 method has also been reported.⁴⁵ For 3D-periodic systems, there exist several variants of periodic MP2^{46–50} and random phase approximation^{51,52} methods. Very recently plane-wave implementations of several techniques beyond MP2 have been reported, including CCSD,⁵³ CCSD(T),⁵⁴ and MP2-F12.⁵⁵ The latter work demonstrated that the F12 treatment can indeed be an efficient complement to the conventional description of electronic correlation in the delocalized plane wave basis.

High-level treatment of solids can also be achieved within the finite-cluster approximation, using various flavors of fragment approaches.^{56–62} These techniques can, in principle, employ any of the available molecular methods, including explicitly correlated ones. At the same time, obtaining highly accurate results with such methods can become rather expensive. Moreover, representation of a periodic system with finite clusters might be rather sensitive to the choice of embedding, which, in order not to ruin the accuracy of the calculations, has to be properly set up.

The 3D packing and formal endlessness of crystals impose essential limitations on the use of atomic orbital (AO) basis sets in periodic calculations. Due to the mutual non-orthogonality of the standard Gaussian-type orbitals (GTOs), rich AO basis sets, or those, containing diffuse orbitals, become quasi-redundant in the periodic case, leading to numerical problems in the calculations. The latter can in some cases be overcome by substantial tightening of the computational tolerances. However, it enormously raises the computational cost, while the gain due to the formal richness of the basis set might remain marginal. Indeed, a quasi-redundant basis set spans an essentially smaller space than formally assigned to it, depriving the possibility to control its actual quality. With that, a systematic improvement of the basis set and energy extrapolation to the basis set limit become problematic. Generally the highest level of the AO basis set routinely applicable for periodic calculations is triple-zeta, which is usually sufficient for Hartree-Fock (HF) or density functional theory calculations, but not so for an accurate correlated description.

One way to circumvent this problem is to employ orthogonal plane wave basis^{47,63} or a combination of AOs and plane waves. Although, adaptation of this technique to the lo-

cal correlation approach is rather difficult, such developments are under way in our group and will be presented in forthcoming publications. The F12 technique is a second major practical possibility to solve the basis set problem in the periodic correlated calculations. In this paper, we report a 3D periodic local MP2-F12 method in its **3*A** fixed-amplitude approximation.¹³ The performance of this method is analyzed in an application to the LiH crystal, for which MP2 basis set limit benchmarks exist in the literature.

II. THEORY

The method described below is closely related to the molecular local MP2-F12 theory by Werner and co-workers.²¹ The notations in this paper follow the general nomenclature for periodic local methods, developed in Refs. 64–67. At the same time, it is also to a large extent compatible with the molecular MP2-F12 formalism of Refs. 13 and 21. The indices i, j, k, \dots and a, b, \dots denote, respectively, the localized occupied orbitals [Wannier functions (WFs)], and local virtual orbitals, for which projected atomic orbitals (PAOs)^{68–71} are employed. Auxiliary (fitting) functions used for the density fitting of 4-index integrals are denoted by the indices P, Q, \dots . Greek symbols stand for the RI-auxiliary basis functions (α, β, \dots), as well as for the orbital basis functions (μ, ν, \dots). The symbols r, s, \dots are used as universal indices for orbitals (occupied, virtual, or auxiliary), when their actual character is not relevant. The conventional font indices refer to the orbitals within one cell, while the calligraphic font indices specify the cells, the corresponding orbitals are centered in.

A. LMP2-F12 energy

In order to introduce the F12 correction to periodic LMP2, we recapitulate the relevant aspects of the latter.⁶⁵ The first-order wavefunction in the periodic closed-shell local MP2 theory is defined as

$$\begin{aligned} \Psi_{LMP2}^{[1]} &= \frac{1}{2} \sum_{i\mathcal{I}j\mathcal{J}} \sum_{aAbB \in [i\mathcal{I}j\mathcal{J}]_{\text{virt}}} T_{aAbB}^{i\mathcal{I}j\mathcal{J}} \Psi_{i\mathcal{I}j\mathcal{J}}^{aAbB} \quad (1) \\ &= \frac{1}{2} \sum_{ij\mathcal{J}} \sum_{aAbB \in [ij\mathcal{J}]_{\text{virt}}} T_{aAbB}^{ij\mathcal{J}} \\ &\quad \times \sum_{\mathcal{I}} \Psi_{i\mathcal{I}j(\mathcal{I})}^{a(A\oplus\mathcal{I})b(B\oplus\mathcal{I})}. \quad (2) \end{aligned}$$

The local approximation restricts the virtual space of each pair $ij\mathcal{J}$ to the so-called pair domain $[ij\mathcal{J}]_{\text{virt}}$, *i.e.*, to the PAOs that are centered on the atoms, spatially close to either i or $j\mathcal{J}$.^{65,68,70} The $\Psi_{i\mathcal{I}j\mathcal{J}}^{aAbB}$ are the spin-free configurations, obtained the usual way:^{72,73}

$$\Psi_{i\mathcal{I}j\mathcal{J}}^{aAbB} = \sum_{\sigma} \hat{a}_{aA,\sigma}^{\dagger} \hat{a}_{i\mathcal{I},\sigma} \sum_{\sigma'} \hat{a}_{bB,\sigma'}^{\dagger} a_{j\mathcal{J},\sigma'} \Psi_0, \quad (3)$$

where Ψ_0 is the HF determinant, \hat{a}^{\dagger} and \hat{a} are the creation and annihilation operators, respectively, and σ denotes the spin. Since the ground state is totally symmetric, the

excitation amplitudes T are invariant with respect to translations: $T_{a,AbB}^{i\mathcal{I}j\mathcal{J}} = T_{a(A\oplus\mathcal{I})b(B\oplus\mathcal{I})}^{ij(\mathcal{J}\oplus\mathcal{I})}$. The symbolical operations \oplus and \ominus applied to the cell indices indicate the actual operations over the corresponding translation vectors.

In the molecular MP2-F12 theory the first-order wavefunction is augmented with terms, explicitly dependent on the inter-electron distance r_{12} and orthogonal to the reference state. It is computationally convenient in general, and within the local correlation scheme even essential, to extend the orthogonality of the explicitly correlated part also to the space, spanned by the conventional configurations (the so-called ansatz **3**).¹³ Furthermore, in the resolution of the identity approach, the explicitly correlated part is projected onto a space of doubles configurations with the virtual space, spanned by a formally complete RI basis.^{6,13} In the periodic case these configurations can be denoted as $\Psi_{i\mathcal{I}j\mathcal{J}}^{\alpha A\beta B}$, with the Greek symbols standing for the RI basis set orbitals. In practice, the RI-basis is obviously finite, but the effect of this approximation is usually not dramatic. Furthermore, within the local correlation scheme the RI basis for a given pair $i\mathcal{I}j\mathcal{J}$ can also be confined to a specific domain $[i\mathcal{I}j\mathcal{J}]_{\text{RI}}$.²¹ Such a truncation significantly reduces the cost of the calculations without compromising their accuracy.

Most of the molecular F12 calculations employ the diagonal approximation, due to its efficiency. This approximation restricts the conventional configurations, the explicit part is projected on, to have the same occupied orbital pair indices as in the corresponding explicitly correlated electron pairs. Generally, diagonal ansätze are not orbital invariant. However, if the amplitudes corresponding to the explicit configurations are chosen to satisfy the cusp conditions^{74,75} (the so-called fixed-amplitude ansatz^{12,17}), the orbital invariance in the diagonal formalism is retained (*vide infra*).

Now generalizing the molecular formalism, in particular that of Refs. **13** and **21**, to the periodic case, we introduce the explicit configurations $\Psi_{i\mathcal{I}j\mathcal{J},p}$, with $p = \pm 1$, which within the diagonal approximation take the following form:

$$\Psi_{i\mathcal{I}j\mathcal{J},p} = \frac{1}{2} \sum_{\alpha A\beta B \in [i\mathcal{I}j\mathcal{J}]_{\text{RI}}} (\Psi_{i\mathcal{I}j\mathcal{J}}^{\alpha A\beta B} + p\Psi_{j\mathcal{J}i\mathcal{I}}^{\alpha A\beta B}) \times \langle \overline{\alpha A} \overline{\beta B} | \hat{Q}_{12}^{(i\mathcal{I}j\mathcal{J})} F_{12} | i\mathcal{I}j\mathcal{J}, p \rangle \quad (4)$$

with

$$|i\mathcal{I}j\mathcal{J}, p\rangle = \frac{1}{2}(|i\mathcal{I}j\mathcal{J}\rangle + p|j\mathcal{J}i\mathcal{I}\rangle). \quad (5)$$

The kernel of the integral in Eq. (4) consists of the correlation factor¹²

$$F_{12} = -\frac{1}{\gamma} \exp(-\gamma r_{12}), \quad (6)$$

confined by the scale parameter γ , and the pair specific strong-orthogonality projection operator²¹

$$\hat{Q}_{12}^{(i\mathcal{I}j\mathcal{J})} = 1 + \sum_{k\mathcal{K}l\mathcal{L} \in [i\mathcal{I}j\mathcal{J}]_{\text{occ}}} |k\mathcal{K}l\mathcal{L}\rangle \langle k\mathcal{K}l\mathcal{L}| - \sum_{aA,bB \in [i\mathcal{I}j\mathcal{J}]_{\text{virt}}} |aAbB\rangle \langle \overline{aA} \overline{bB}|$$

$$- \sum_{\substack{\alpha A \in [i\mathcal{I}j\mathcal{J}]_{\text{RI}} \\ k\mathcal{K} \in [i\mathcal{I}j\mathcal{J}]_{\text{occ}}}} (|\alpha A k\mathcal{K}\rangle \langle \overline{\alpha A} k\mathcal{K}| + |k\mathcal{K} \alpha A\rangle \langle k\mathcal{K} \overline{\alpha A}|). \quad (7)$$

The operator (7) projects out the configurations, involving occupied-to-occupied excitations, as well as, the pair-specific conventional periodic LMP2 doubles configurations (the summation over virtuals is restricted to those in the pair domain). The sum over occupied indices in the projector (7) runs in principle over all occupied orbitals. However, due to the local representation, the effect of the corresponding terms falls off exponentially as the distance between the orbital i or $j\mathcal{J}$ and the orbitals in the projector grows. Therefore, in addition to $[i\mathcal{I}j\mathcal{J}]_{\text{virt}}$ for the virtuals and $[i\mathcal{I}j\mathcal{J}]_{\text{RI}}$ for the auxiliary functions, we define pair domains $[i\mathcal{I}j\mathcal{J}]_{\text{occ}}$ to restrict the ranges for the occupied index summations as well. Truncation of the otherwise infinite summations ranges, possible within the local formalism, is essential to arrive at a practicable computational scheme for periodic systems.

Since the auxiliary functions (which are usually chosen as Gaussian-type orbitals) and the virtuals (PAOs in our approach), are nonorthogonal (PAOs are actually even redundant), the corresponding bra-parts of the projectors in (4) and (7) contain the pair specific contravariant vectors:

$$\langle \overline{\alpha A} | = \sum_{\alpha' A' \in [i\mathcal{I}j\mathcal{J}]_{\text{virt}}} [(S^{[ij\mathcal{J}]_{\text{virt}}})^{-1}]_{\alpha A, \alpha' A'} \langle \alpha' A' |, \quad (8)$$

$$\langle \overline{\alpha A} | = \sum_{\alpha' A' \in [i\mathcal{I}j\mathcal{J}]_{\text{RI}}} [(S^{[ij\mathcal{J}]_{\text{RI}}})^{-1}]_{\alpha A, \alpha' A'} \langle \alpha' A' |.$$

The matrices $(S^{[ij\mathcal{J}]_{\text{virt}}})^{-1}$ and $(S^{[ij\mathcal{J}]_{\text{RI}}})^{-1}$ are the inverses (or pseudo-inverses⁷⁶ in case of redundant sets, see also supplementary material⁷⁷) of the square blocks of the PAO and auxiliary basis overlap matrices, respectively, corresponding to the $[ij\mathcal{J}]_{\text{virt}}$ and $[ij\mathcal{J}]_{\text{RI}}$ domains.

The F12 part of the first order wavefunction is expressed through configurations $\Psi_{i\mathcal{I}j\mathcal{J},p}$:

$$\Psi_{F12}^{[1]} = \frac{1}{2} \sum_{p=\pm 1} \sum_{i\mathcal{I}j\mathcal{J}} T^{i\mathcal{I}j\mathcal{J},p} \Psi_{i\mathcal{I}j\mathcal{J},p} = \frac{1}{2} \sum_{p=\pm 1} \sum_{ij\mathcal{J}} T^{ij\mathcal{J},p} \sum_{\mathcal{I}} \Psi_{i\mathcal{I}j\mathcal{J} \oplus \mathcal{I},p}, \quad (9)$$

where again the translational symmetry has been utilized. The summation over both sets of indices $i\mathcal{I}$ and $j\mathcal{J}$ is formally full. This makes the set of the configurations, used in the expansion (9), redundant, since the explicit configurations (and thus the corresponding amplitudes) are symmetric with respect to permutation of the indices $i\mathcal{I}$ and $j\mathcal{J}$. Technically, however, such a form of the expansion is preferable, since utilization of translational symmetry makes i and $j\mathcal{J}$ indices no longer equivalent (the former is restricted to the reference cell). Besides, it leads to elimination of the unnecessary factors in the residual or energy expressions.²¹ Exploitation of the index-permutation symmetry as well as the point-group symmetry is introduced at a later stage (see Sec. II C).

The second-order F12 energy is defined via the Hylleraas functional, employing the standard Møller-Plesset partitioning of the Hamiltonian with the zeroth-order Fock operator $\hat{H}_0 = \hat{f}$ and energy E_0 .¹³

$$\begin{aligned}
 E^{[2]} &= \langle \Psi^{[1]} | \hat{f} - E_0 | \Psi^{[1]} \rangle + 2 \langle \Psi^{[1]} | \hat{H} | \Psi_0 \rangle \\
 &= \sum_{i\mathcal{I}j\mathcal{J}} \left[\sum_{aA,bB \in [i\mathcal{I}j\mathcal{J}]_{\text{virt}}} \tilde{T}_{aAbB}^{i\mathcal{I}j\mathcal{J}} (K_{i\mathcal{I}j\mathcal{J}}^{aAbB} + R_{i\mathcal{I}j\mathcal{J}}^{aAbB}) \right. \\
 &\quad \left. - \sum_{p=\pm 1} (2-p) T^{i\mathcal{I}j\mathcal{J},p} (V_{i\mathcal{I}j\mathcal{J},p} + R_{i\mathcal{I}j\mathcal{J},p}) \right] \\
 &= \left\{ \sum_{ij\mathcal{J}} \left[\sum_{aA,bB \in [ij\mathcal{J}]_{\text{virt}}} \tilde{T}_{aAbB}^{ij\mathcal{J}} (K_{ij\mathcal{J}}^{aAbB} + R_{ij\mathcal{J}}^{aAbB}) \right. \right. \\
 &\quad \left. \left. - \sum_{p=\pm 1} (2-p) T^{ij\mathcal{J},p} (V_{ij\mathcal{J},p} + R_{ij\mathcal{J},p}) \right] \right\} \\
 &\quad \times \sum_{\mathcal{I}} 1, \tag{10}
 \end{aligned}$$

where

$$\Psi^{[1]} = \Psi_{LMP2}^{[1]} + \Psi_{F12}^{[1]}, \tag{11}$$

$$\tilde{T}_{aAbB}^{i\mathcal{I}j\mathcal{J}} = 2T_{aAbB}^{i\mathcal{I}j\mathcal{J}} - T_{bBAa}^{i\mathcal{I}j\mathcal{J}}, \tag{12}$$

$$K_{i\mathcal{I}j\mathcal{J}}^{aAbB} = \langle i\mathcal{I}j\mathcal{J} | \frac{1}{r_{12}} | aAbB \rangle, \tag{13}$$

$$V_{i\mathcal{I}j\mathcal{J},p} = \langle i\mathcal{I}j\mathcal{J} | \frac{1}{r_{12}} \hat{Q}_{12}^{(i\mathcal{I}j\mathcal{J})} F_{12} | i\mathcal{I}j\mathcal{J}, p \rangle, \tag{14}$$

and $R_{i\mathcal{I}j\mathcal{J}}^{aAbB}$ and $R_{ij\mathcal{J},p}$ are, respectively, conventional and explicit residuals, which are discussed in detail in Sec. II B. In order to arrive at the last equality of Eq. (10) the invariance of the involved quantities with respect to translation symmetry operations is utilized. The definition (14) of the V -integral implies that

$$\sum_{\alpha A \beta B \in [i\mathcal{I}j\mathcal{J}]_{\text{RI}}} |\alpha A \beta B \rangle \langle \alpha A \beta B | \hat{Q}_{12}^{(i\mathcal{I}j\mathcal{J})} = \hat{Q}_{12}^{(i\mathcal{I}j\mathcal{J})}, \tag{15}$$

which is obviously valid for the complete RI-basis, but also when the RI-space of the domain $[ij\mathcal{J}]_{\text{RI}}$ includes all the occupied orbitals from $[ij\mathcal{J}]_{\text{occ}}$ and PAOs from $[ij\mathcal{J}]_{\text{virt}}$. In the untruncated F12 techniques, the equality (15) is usually achieved by uniting the AO and auxiliary basis sets to represent the RI-space (the so-called complementary auxiliary basis set [CABS] approach).⁷⁸

As is seen from Eq. (10), the energy in a periodic system is not well defined. For a cyclic model of a crystal it is proportional to the number of unit cell in the supercell, and for infinite crystal it becomes infinite. A meaningful and well-defined quantity, which is usually used in periodic studies, is the energy per unit cell. For the Hylleraas functional (10), it is given by the expression in the curly brackets, where one of the indices (e.g., i) is restricted to the reference cell. The

F12-energy per unit cell in the local representation is thus

$$E_{F12}^{[2]} = \sum_{p=\pm 1} (2-p) \sum_{ij\mathcal{J}} E_{F12}^{[2]}{}_{ij\mathcal{J},p} \tag{16}$$

with

$$E_{F12}^{[2]}{}_{ij\mathcal{J},p} = T^{ij\mathcal{J},p} (V_{ij\mathcal{J},p} + R_{ij\mathcal{J},p}). \tag{17}$$

The index $j\mathcal{J}$ in (16) is generally not restricted. However, since in the local representation and with the Slater-type-geminal (6) as the correlation function the pair F12-energies decay exponentially with $i-j\mathcal{J}$ interorbital distance, the pair list can be effectively truncated. Further reduction of the pair-list size is possible using index-permutation and point-group symmetry and is discussed in Sec. II C.

As is mentioned above, instead of minimizing the Hylleraas functional (10), the values for the explicit amplitudes can be taken from the coalescence conditions^{74,75} for symmetric and antisymmetric spatial wave-functions, which gives $T_{ij\mathcal{J},p}|_{p=1} = 1/2$ and $T_{ij\mathcal{J},p}|_{p=-1} = 1/4$.^{12,32,75} Importantly, such a scheme preserves the orbital invariance of the F12 energy within the diagonal approach,¹⁷ since the energy (16) reduces to the sum of traces of generalized R and V matrices times a factor.

The residuals $R_{ij\mathcal{J},p}$ in the fixed-amplitude approach are, obviously, not zero and need to be evaluated and plugged in the energy expression (17). The actual form of the residuals is discussed in Sec. II B.

B. The LMP2-F12 residual

The actual expressions for the residuals $R_{i\mathcal{I}j\mathcal{J}}^{aAbB}$ and $R_{ij\mathcal{J},p}$ depend on further approximations. Generally the conventional and explicitly correlated residuals are coupled via terms, proportional to Fock matrix elements from the virtual/complementary-auxiliary (i.e., part of the RI basis, orthogonal to the orbital basis) block.¹³ Decoupling of both residual equations can be achieved by introducing the so-called extended Brillouin condition (EBC) approximation,^{4,6,13} which assumes these elements to be zero. The F12 methods, using EBC approximation, are sometimes denoted by a star in the suffix (e.g., ansatz 3*). $R_{i\mathcal{I}j\mathcal{J}}^{aAbB}$ reduces then to the usual periodic LMP2 residual,⁶⁵ which becomes zero with the optimized LMP2 amplitudes. Within this approximation the F12 energy (16) is an additive correction to the standard LMP2 energy,⁶⁵ evaluated independently from the latter.

The expression for the explicit correlation residual, as follows from the Hylleraas functional (10), takes the form¹³

$$\begin{aligned}
 R_{ij\mathcal{J},p} &= V_{ij\mathcal{J},p} + B_{ij\mathcal{J},p} T^{ij\mathcal{J},p} \\
 &\quad - \sum_{k\mathcal{K}} (X_{ij\mathcal{J},p}^{k\mathcal{K}j\mathcal{J}} f_{ik\mathcal{K}} T^{k\mathcal{K}j\mathcal{J},p} \\
 &\quad + X_{ij\mathcal{J},p}^{ik\mathcal{K}} T^{ik\mathcal{K},p} f_{k\mathcal{K}j\mathcal{J}}), \tag{18}
 \end{aligned}$$

where f is the Fock matrix, and the expressions for the B - and X -integrals are given below.

Writing out explicitly the \hat{Q}_{12} -operator in Eq. (14) yields for the V -integral

$$\begin{aligned} V_{ij\mathcal{J},p} &= K_{ij\mathcal{J},p}^F + \sum_{k\mathcal{K},l\mathcal{L}\in[ij\mathcal{J}]_{\text{occ}}} K_{ij\mathcal{J}}^{k\mathcal{K}l\mathcal{L}} F_{ij\mathcal{J},p}^{k\mathcal{K}l\mathcal{L}} \\ &\quad - \sum_{aA,bB\in[ij\mathcal{J}]_{\text{virt}}} K_{ij\mathcal{J}}^{aAbB} \bar{F}_{ij\mathcal{J},p}^{aAbB} \\ &\quad - 2 \sum_{\substack{k\mathcal{K}\in[ij\mathcal{J}]_{\text{occ}} \\ \alpha A\in[ij\mathcal{J}]_{\text{RI}}}} K_{ij\mathcal{J},p}^{k\mathcal{K}\alpha A} \bar{F}_{ij\mathcal{J},p}^{k\mathcal{K}\alpha A}, \end{aligned} \quad (19)$$

with

$$K_{ij\mathcal{J},p}^F = \langle ij\mathcal{J} | \frac{1}{r_{12}} F_{12} | ij\mathcal{J}, p \rangle, \quad (20)$$

$$K_{ij\mathcal{J},p}^{r\mathcal{R}s\mathcal{S}} = \langle ij\mathcal{J} | \frac{1}{r_{12}} | r\mathcal{R}s\mathcal{S} \rangle, \quad (21)$$

$$F_{ij\mathcal{J},p}^{r\mathcal{R}s\mathcal{S}} = \langle ij\mathcal{J} | F_{12} | r\mathcal{R}s\mathcal{S} \rangle, \quad (22)$$

and

$$\begin{aligned} \bar{F}_{ij\mathcal{J},p}^{aAbB} &= \sum_{\substack{a'A'\in[ij\mathcal{J}]_{\text{virt}} \\ b'B'\in[ij\mathcal{J}]_{\text{virt}}}} [(S^{[ij\mathcal{J}]_{\text{virt}}})^{-1}]_{aA,a'A'} \\ &\quad \times F_{ij\mathcal{J},p}^{a'A'b'B'} [(S^{[ij\mathcal{J}]_{\text{virt}}})^{-1}]_{b'B',bB}, \\ \bar{F}_{ij\mathcal{J},p}^{\alpha Ak\mathcal{K}} &= \sum_{\alpha'A'\in[ij\mathcal{J}]_{\text{RI}}} [(S^{[ij\mathcal{J}]_{\text{RI}}})^{-1}]_{\alpha A,\alpha'A'} F_{ij\mathcal{J},p}^{\alpha'A'k\mathcal{K}}. \end{aligned} \quad (23)$$

Note that in the second and third terms of Eq. (19) (anti)symmetrization of the K -integrals with respect to the permutation of the orbital indices is not necessary, while in the last term this (anti)symmetrization allows for uniting both terms of (7) with mixed auxiliary-occupied summations in one term.

The terms in the residual (18) explicitly involving X -integral,

$$X_{i\mathcal{I}j\mathcal{J},p}^{k\mathcal{K}l\mathcal{L}} = \langle i\mathcal{I}j\mathcal{J} | F_{12} \hat{Q}_{12}^{(i\mathcal{I}j\mathcal{J})} F_{12} | k\mathcal{K}l\mathcal{L} \rangle, \quad (24)$$

actually need not be evaluated in the diagonal 3A-ansatz. As was mentioned in Refs. 6 and 13 and is discussed below, these terms are canceled with the identical terms of the opposite sign arising in the B -part of the residual. The latter quantity is quite involved and its efficient treatment requires further approximations. The general expression for the B -integral is

$$\begin{aligned} B_{i\mathcal{I}j\mathcal{J},p} &= \langle i\mathcal{I}j\mathcal{J} | F_{12} \hat{Q}_{12}^{(i\mathcal{I}j\mathcal{J})} \\ &\quad \times (\hat{f}_1 + \hat{f}_2) \hat{Q}_{12}^{(i\mathcal{I}j\mathcal{J})} F_{12} | i\mathcal{I}j\mathcal{J}, p \rangle, \end{aligned} \quad (25)$$

where the superscript of the Fock operator identifies the corresponding electronic coordinate. In order to avoid the double RI in (25), slowly converging with auxiliary basis set size, commonly the commutator $\hat{f}F_{12} = F_{12}\hat{f} + [\hat{f}, F_{12}]$ approach is used.⁴ From the Fock operator, only the kinetic energy \hat{t} and exchange operators do not commute with F_{12} . The ansatz A of the MP2-F12 theory,

which we employ in the following, disregards the exchange commutators.^{4,6,13} Combining this with the generalized Brillouin condition (i.e., neglect of the Fock matrix elements from the occupied/complementary-auxiliary block) and EBC, which altogether is commonly referred to as 3*A (Ref. 13) or A* (Ref. 14) approximation of the LMP2-F12 theory, yields for the B -integral:

$$\begin{aligned} B_{ij\mathcal{J},p} &= U_{ij\mathcal{J},p}^F + \sum_{k\mathcal{K},l\mathcal{L}\in[ij\mathcal{J}]_{\text{occ}}} U_{ij\mathcal{J}}^{k\mathcal{K}l\mathcal{L}} F_{ij\mathcal{J},p}^{k\mathcal{K}l\mathcal{L}} \\ &\quad - \sum_{aA,bB\in[ij\mathcal{J}]_{\text{virt}}} U_{ij\mathcal{J}}^{aAbB} \bar{F}_{ij\mathcal{J},p}^{aAbB} \\ &\quad - 2 \sum_{\substack{k\mathcal{K}\in[ij\mathcal{J}]_{\text{occ}} \\ \alpha A\in[ij\mathcal{J}]_{\text{RI}}}} U_{ij\mathcal{J},p}^{k\mathcal{K}\alpha A} \bar{F}_{ij\mathcal{J},p}^{k\mathcal{K}\alpha A} \\ &\quad + \sum_{k\mathcal{K}} (f_{ik\mathcal{K}} X_{ij\mathcal{J},p}^{k\mathcal{K}j\mathcal{J}} + X_{ij\mathcal{J},p}^{ik\mathcal{K}} f_{k\mathcal{K}j\mathcal{J}}) \end{aligned} \quad (26)$$

with the intermediate integrals

$$U_{ij\mathcal{J},p}^F = \frac{1}{2} \langle ij\mathcal{J} | [[F_{12}, t_1 + t_2], F_{12}] | ij\mathcal{J}, p \rangle, \quad (27)$$

$$U_{ij\mathcal{J},p}^{r\mathcal{R}s\mathcal{S}} = \langle ij\mathcal{J} | [F_{12}, t_1 + t_2] | r\mathcal{R}s\mathcal{S} \rangle. \quad (28)$$

Within the fixed-amplitude ansatz, the explicit X -dependent terms of residual (18) indeed cancel with those contained in the B -integral (26), making evaluation of the X -integral in the 3*A-ansatz superfluous.

To summarize, second order energy calculation in the LMP2-F12-3*A ansatz consists of independent evaluation of the conventional LMP2 energy and the explicit F12 component via Eq. (16). For the latter, initially the pair-list has to be set up, to restrict the otherwise infinite summation. This is discussed in Sec. II C. For each $ij\mathcal{J}$ pair from the pair-list, the domains $[ij\mathcal{J}]_{\text{occ}}$, $[ij\mathcal{J}]_{\text{virt}}$, and $[ij\mathcal{J}]_{\text{RI}}$ have to be defined, dictating the ranges for the intermediate integrals (20), (21), (22), (27), and (28), which are the key quantities of the F12 calculation. These integrals are evaluated through density fitting, as described in Secs. II D and III. Contraction of these quantities according to Eqs. (19) and (26) yields the integrals V and B and, with that, the residual and the F12 energy.

C. The F12 pair list

As is discussed above, the initial pair-list truncation is based on the exponential decay of the integrals $V_{ij\mathcal{J},p}$ and $B_{ij\mathcal{J},p}$, and thus of the pair energy contributions (17), with distance between i and $j\mathcal{J}$. Therefore, F12 pair list can be restricted to only strong and weak pairs, defined in the conventional LMP2 calculation. Indeed, in the standard LMP2 computational scheme,^{65,70} the integrals $(iaA|j\mathcal{J}bB)$ for distant $ij\mathcal{J}$ pairs are treated via the multipole approximation, implying that the product densities iaA and $j\mathcal{J}bB$ do not overlap. Therefore, the F12-energy contribution from such pairs is expected to be negligible.

Once the pair list is constructed, the number of pairs explicitly processed in the F12 calculation can be subject to

further reduction, based on symmetry arguments. It is straightforward to apply the index-permutation symmetry. Since the first index in the pair-list is always restricted to the reference cell, it has to be combined with the translational symmetry, yielding

$$E_{F12\,ij\mathcal{J}}^{[2]} = E_{F12\,ji(\ominus\mathcal{J})}^{[2]}. \quad (29)$$

This reduces the initial list by nearly a factor of 2.

The point group symmetry treatment is more involved, and can be applied only if the WFs are properly symmetrized. It is always possible to construct WFs such that they would form a basis of the irreducible representations (irreps) of the site groups, corresponding to the centroids of these WFs. The position of the WFs centroids and the irreps, according to which they transform, depend on the symmetry of the canonical Bloch states (of, in our case, the valence bands) the WFs are built from.⁷⁹ General localization procedures,^{80,81} however, do not guarantee that the resulting WFs automatically possess the needed symmetry, unless localization is performed directly in the spaces of the corresponding irreps.⁸² In our approach, the alternative route of Ref. 83 for the WF symmetrization is used, where the WFs are symmetrized *a posteriori*, i.e., after the localization procedure.

Point group symmetry treatment of the two-electron integrals and the doubles amplitudes of the periodic LMP2 theory has been briefly described in Refs. 65 and 84. In the Appendix we provide a detailed formalism of the symmetry treatment, based on the theory of induced representations of space groups,⁷⁹ in application to the periodic local F12 method in the diagonal approximation.

Restriction of the pair list to the symmetry irreducible pairs $\{ij\mathcal{J}\}_{\text{irr}}$ and evaluation of the corresponding weight factors $w_{ij\mathcal{J}}$ can be done by application of all the symmetry elements $(g|\mathbf{a} + \mathbf{R})$ with the condition (A8) (see the Appendix) to the centroids of the WFs in a pair and identifying the complete symmetry equivalent set (star) of centroid pairs. For a pair $i'j'\mathcal{J}$, a new centroid pair is generated, if the element $(g|\mathbf{a} + \mathbf{R})$ does not enter either the site group of the WF i' centroid \mathbf{q}_{i1} or of the WF $j'\mathcal{J}$ centroid $\mathbf{q}_{j1} + \mathbf{R}_{\mathcal{J}}$ (see the Appendix). Only one centroid pair from each star has to be added to the list, as the contribution from the rest can be taken into account by the weight factor. The F12 energy expression then takes the form

$$E_{F12}^{[2]} = \sum_{p=\pm 1} (2-p) \sum_{ij\mathcal{J} \in \{ij\mathcal{J}\}_{\text{irr}}} w_{ij\mathcal{J}} E_{F12\,ij\mathcal{J},p}^{[2]}. \quad (30)$$

If the symmetry of the bands, the Wannier functions correspond to, allows for a non-unique choice for their centroids,⁷⁹ the highest efficiency in the symmetry treatment would be achieved with those, having the lowest possible site group symmetry (i.e., the largest stars of the centroid pairs). This effect can also be considered from the angle of the symmetry equivalence concept of Refs. 85 and 86. The maximal savings are achieved with orbitals, exhibiting highest symmetry equivalence (and lowest symmetry invariance), which is actually a characteristic property of localized orbitals, constructed with the Boys localization functional.⁸⁷ A periodic direct-space generalization of the Boys method,⁸⁸ com-

bined with symmetrization of the WFs, is, however, not yet available.

Point group symmetry and index permutation symmetry (29) treatment of the pair list can be obviously combined. The result of the index permutation in some pairs might be equivalent to the action of certain point group operations, and, in such a case, does not bring any further reduction. However, generally the permutation of the indices is an independent symmetry operation, not reproduced by any other symmetry manipulation. In the latter case, the highest possible symmetry reduction factor is 96, which can occur for some pairs in a cubic crystal with 48 point group symmetry operations.

D. Local density fitting for 4-index integrals

Truncation of the pair-list and restriction of the contraction indices in Eqs. (19) and (26) to the corresponding domains lead to asymptotically linear scaling of the computational cost with the size of the unit cell. The contractions (19) and (26) themselves are inexpensive: their nominal complexity is $O(N^4)$, and the actual scaling is approximately $N_{\text{pair}} \langle N_{\text{occ}} \rangle^2$, $N_{\text{pair}} \langle N_{\text{virt}} \rangle^2$, and $N_{\text{pair}} \langle N_{\text{occ}} \rangle \langle N_{\text{RI}} \rangle$ for the second, third, and fourth terms, respectively. Here, N_{pair} denotes the number of pairs in the pair list, and $\langle N_{\text{occ}} \rangle$, $\langle N_{\text{virt}} \rangle$, and $\langle N_{\text{RI}} \rangle$ denote an average number of orbitals per corresponding pair domain. The N^5 -scaling contractions with the inverse overlap in (23) are more costly. However, since these transformations are performed within the pair domains, their actual cost, which is $N_{\text{pair}} \langle N_{\text{virt}} \rangle^3$ and $N_{\text{pair}} \langle N_{\text{occ}} \rangle \langle N_{\text{RI}} \rangle^2$ for the $\bar{F}_{ij\mathcal{J},p}^{aAbB}$ and $\bar{F}_{ij\mathcal{J},p}^{k\kappa\alpha A}$, respectively, is not too high either. The bottleneck of the whole F12 part of the calculation is evaluation of the individual integrals of Eqs. (19) and (26).

Conventionally such integrals are evaluated by transformation of the corresponding 4-index AO integrals,⁸⁹ which nominally scales as N^5 . Alternative technique for calculating these integrals, applied also in this work, is density fitting (DF) approximation,^{64,66,90-99} which decomposes the 4-index integrals into contractions of 3-index quantities. This method, although not reducing the nominal scaling of the integral evaluation, allows for much more efficient treatment even in the canonical case. Indeed, only the last contraction, i.e., the assembly of the target 4-index integrals from two 3-index objects, scales as N^5 , while all other transformations have N^4 scaling. Furthermore, by virtue of density fitting, the scaling of the computational cost of the MP2 or MP2-F12 methods with number of basis functions per center reduces from N^4 to N^3 . Local approximations further enhance the efficiency of calculations, since the assembly for each pair involves only pair-domain-restricted set of indices. The local restrictions can be imposed on the auxiliary index as well,^{21,66,95,96,98,99} bringing further savings.

In this work, we adapt the direct-space local density fitting technique, developed earlier for the periodic LMP2⁶⁶ and CIS⁹⁹ methods, to the two-electron integrals of the periodic local F12 theory. Consider a general two-electron integral $(ir\mathcal{R}|\hat{I}_{12}|j\mathcal{J}sS)$ (written in the chemical notation) with a multiplicative operator kernel I_{12} , which is the case for the integrals $K_{ij\mathcal{J},p}^F$, $K_{ij\mathcal{J},p}^{rR_sS}$, $F_{ij\mathcal{J},p}^{rR_sS}$, and $U_{ij\mathcal{J},p}^F$.¹⁴ Using the

robust DF scheme,^{93,100} this integral is approximated as

$$\begin{aligned}
 & (ir\mathcal{R}|\hat{I}_{12}|j\mathcal{J}s\mathcal{S}) \\
 &= \sum_{PP \in [ir\mathcal{R}]_{DF}} d_{PP}^{ir\mathcal{R}}(P\mathcal{P}|\hat{I}_{12}|j\mathcal{J}s\mathcal{S}) \\
 &+ \sum_{PP \in [j\mathcal{J}s\mathcal{S}]_{DF}} (ir\mathcal{R}|\hat{I}_{12}|P\mathcal{P})d_{PP}^{j\mathcal{J}s\mathcal{S}} \\
 &- \sum_{\substack{PP \in [ir\mathcal{R}]_{DF} \\ QQ \in [j\mathcal{J}s\mathcal{S}]_{DF}}} d_{PP}^{ir\mathcal{R}}(P\mathcal{P}|\hat{I}_{12}|Q\mathcal{Q})d_{QQ}^{j\mathcal{J}s\mathcal{S}} \\
 &= \sum_{PP \in [ir\mathcal{R}]_{DF}} d_{PP}^{ir\mathcal{R}}(js\mathcal{S}'|\hat{I}_{12}|P(\mathcal{P} \ominus \mathcal{J})) \\
 &+ \sum_{PP \in [js\mathcal{S}']_{DF}} (ir\mathcal{R}|\hat{I}_{12}|P(\mathcal{P} \oplus \mathcal{J}))d_{PP}^{js\mathcal{S}'} \\
 &- \sum_{\substack{PP \in [ir\mathcal{R}]_{DF} \\ QQ \in [js\mathcal{S}']_{DF}}} d_{PP}^{ir\mathcal{R}}(P|\hat{I}_{12}|Q(Q \oplus \mathcal{J} \ominus \mathcal{P}))d_{QQ}^{js\mathcal{S}'}.
 \end{aligned} \tag{31}$$

Here, the P , Q indices denote the fitting functions, $[ir\mathcal{R}]_{DF}$ are the local fit-domains, which comprise the fitting functions supporting a product density $|ir\mathcal{R})$, and $d_{PP}^{ir\mathcal{R}}$ are the fitting coefficients, corresponding to the expansion of the product density $|ir\mathcal{R})$ in the fitting basis. In the last equality the translational symmetry was used, with the unit cell index redefinition

$$S' = S \ominus \mathcal{J}. \tag{32}$$

The fitting coefficients depend on the choice of the metric \hat{I}_{12}^{met} for the space of the fitting functions:

$$d_{PP}^{ir\mathcal{R}} = \sum_{QQ \in [ir\mathcal{R}]_{DF}} (ir\mathcal{R}|\hat{I}_{12}^{met}|Q\mathcal{Q})[(I_{12}^{met})^{-1}]_{QQ,PP} \tag{33}$$

involving the inverse of the metric matrix

$$[I_{12}^{met}]_{QQ,PP} = (P\mathcal{P}|\hat{I}_{12}^{met}|Q\mathcal{Q}). \tag{34}$$

The $U_{ij\mathcal{J},p}^{r\mathcal{R}s\mathcal{S}}$ integral in the context of density fitting is more complicated, since the kinetic energy operator acts only on one of the two orbitals forming the product density (on the right of the operator in the physical notation). However, following the scheme of Ref. 97, if one opens the commutator and use the Hermiticity of the kinetic energy operator the $U_{ij\mathcal{J}}^{r\mathcal{R}s\mathcal{S}}$ integral can be written in the chemical notation as

$$\begin{aligned}
 U_{ij\mathcal{J}}^{r\mathcal{R}s\mathcal{S}} &= ([r\mathcal{R}, i]^{(\hat{i}_1)}|F_{12}|j\mathcal{J}s\mathcal{S}) \\
 &+ (ir\mathcal{R}|F_{12}|[s\mathcal{S}, j\mathcal{J}]^{(\hat{i}_2)}),
 \end{aligned} \tag{35}$$

where a special notation

$$|[s\mathcal{S}, j\mathcal{J}]^{(\hat{i}_2)}| = |j\mathcal{J}(\hat{i}s\mathcal{S}) - s\mathcal{S}(\hat{i}j\mathcal{J})| \tag{36}$$

was introduced. The integrals of Eq. (35), involving formal densities $|[r\mathcal{R}, i]^{(\hat{i}_1)}|$ and $|[s\mathcal{S}, j\mathcal{J}]^{(\hat{i}_2)}|$, can be then subject the standard DF procedure of Eq. (31).

The fitting metric does not have to coincide with the actual kernel of the fitted integral. In non-local density fitting, the choice $\hat{I}_{12}^{met} = \hat{I}_{12}$ reduces the robust fit to one term instead of three. However, in the local formalism (with different fit-domains for the bra- and ket-densities) this simplification does not hold. In most of the implementations of density fitting for two-electron integrals, the Coulomb metric $\hat{I}_{12}^{met} = r_{12}^{-1}$ is used, but there are examples of other choices (e.g., attenuated Coulomb metric,^{101,102} overlap metric,^{47,102} etc.). In this work we use two types of metric, depending on the kernel of the integral to be fitted. For the Coulomb integrals the Coulomb metric is employed, as in the conventional LMP2 part of the calculation. Furthermore, the integrals $K_{ij\mathcal{J}}^{aAbB}$ are calculated already at the LMP2 stage and need not be recalculated. For the 3-index two-internal integrals ($ik\mathcal{K}|P\mathcal{P}$), that appear only in the F12 part, the half-transformed intermediates ($i\mu\mathcal{M}|P\mathcal{P}$) of LMP2 can also be salvaged.

In periodic LMP2 calculations high efficiency in the density fitting is achieved by using Poisson-type orbital (PTO) fitting basis.^{103–105} PTOs, which are defined as Laplacians of GTOs, are momentless. Therefore, when a PTO is plugged in a 3- or 2-index Coulomb integral as a fitting function, it reduces the latter to a quickly decaying effective one-electron integral. This, on the one hand, curtails the range of the integrals to be calculated and processed, and, on the other hand, speeds up evaluation of the individual integrals. The fitting basis should also include some GTOs to fit the actual moments of the densities, but the amount of those is not large (commonly one GTO per each angular momentum and center).

All the integrals apart from the Coulomb ones are fitted with the metric $\hat{I}_{12}^{met} = F_{12}$. Since the use of PTOs in these integrals is problematic, the Coulomb metric would require recalculation of the 3- and 2-index Coulomb integrals with the pure GTO fitting basis set. Furthermore, F_{12} is the natural choice of the metric for the fit of $U_{ij\mathcal{J}}^{r\mathcal{R}s\mathcal{S}}$ (35), since with this metric the 3-index integrals needed for the assembly of U (31) and those used for DF coefficients (33),

$$([r\mathcal{R}, i]^{(\hat{i}_1)}|\hat{I}_{12}^{met}|P\mathcal{P}) = (ir\mathcal{R}|[\hat{I}_{12}^{met}, t_1]|P\mathcal{P}), \tag{37}$$

are of the same class. In case of the Coulomb metric for the U -integrals an additional set of integrals ($ir\mathcal{R}|[r_{12}^{-1}, t_1 + t_2]|P\mathcal{P}$) would be needed. In Ref. 97 it was noted that the metric $\hat{I}_{12}^{met} = r_{12}$ might lead to inaccurate fitting. Indeed, a good two-electron integral estimate of similarity between two densities has to emphasize the region, where r_1 is close to r_2 . The Coulomb metric, for example, strongly accentuates the contribution from this region. The extreme case in this respect is the overlap metric with its $\delta(r_1 - r_2)$ kernel. The r_{12} metric, on the contrary, depresses this contribution and is thus not a good metric for fitting purposes. However, substitution of r_{12} kernel with F_{12} fixes this deficiency.

A fit domain $[ir\mathcal{R}]_{DF}$ for a given density $|ir\mathcal{R})$ has to be chosen such that it provides a sufficient support for it. For automatic construction of these domains we follow the recipe of Ref. 66. For the products of a WF i and all the PAOs or

auxiliary functions centered on a given atom A , a common fit domain is used. It is determined by calculating pseudo-populations of densities $|iaA\rangle$ on atoms DD :

$$q_{DD}^{iAA} = \sum_{a \in A} \sum_{\mu \in D} [1 + P(i, aA)] \left(C_{\mu D, i} \sum_{\nu \in D} S_{\mu\nu}^{\text{AO}} C_{\nu(\mathcal{D} \ominus A), a} \right)^2, \quad (38)$$

which serve as a measure for their support. Here, C is the AO coefficients of the WFs and PAOs, S^{AO} is the AO overlap matrix, and P stands for the symmetric index-permutation operator. Then the fit domains $[iaA]_{\text{DF}}|_{a \in A}$ or $[i\alpha A]_{\text{DF}}|_{\alpha \in A}$ comprise the fitting functions, belonging to N_{DF} centers with the largest pseudo-populations q_{DD}^{iAA} . For the WF-WF densities, a separate fit-domain is built for each particular product $|ikK\rangle$ on the basis of similar pseudo-populations:

$$q_{DD}^{ikK} = \sum_{\mu \in D} [1 + P(i, kK)] \left(C_{\mu D, i} \sum_{\nu \in D} S_{\mu\nu}^{\text{AO}} C_{\nu(\mathcal{D} \ominus K), k} \right)^2. \quad (39)$$

It is seen from (31) that in all the quantities, involved in the DF procedure, the first index is restricted to the reference unit cell. The second index $r\mathcal{R}$ in the density $|ir\mathcal{R}\rangle$ is restricted to the so-called united domain of i . That is the union of all possible pair domains $[ij\mathcal{J}]_{\text{occ}}$, $[ij\mathcal{J}]_{\text{virt}}$, or $[ij\mathcal{J}]_{\text{RI}}$, depending on the type of r , for a given i . Since $j\mathcal{J}$ is also restricted according to the pair list $\{ij\mathcal{J}\}_{\text{irr}}$ (see Sec. II C), the corresponding united domains of i are confined to WFs, PAOs, or auxiliary functions which are in spatial vicinity of i .

The fitting function index of the DF coefficients in (31) and (33) runs only over the functions in the fit-domain of the corresponding density. Hence the set of DF coefficients is rather compact. For the 3-index integrals, contracted with the DF coefficients, the fitting function range is more extended, since it implies addition (or subtraction) of all possible \mathcal{J} vectors (see Eq. (31)). The main computational effort in the local F12 calculations goes actually in calculation of these integrals. Nevertheless, since \mathcal{J} does not go beyond the limits dictated by the pair list, the spatial localization of the fitting functions around the orbitals i is maintained. This preserves the linear-scaling of the local F12 method, based on density fitting, with the number of occupied orbitals i per cell.

Furthermore, 3-index integrals with short-range kernels (20), (22), (27), and (28), involving local orbitals, can obviously be subject to efficient prescreening, which can confine the fitting functions to even much smaller range. The Coulomb metric is not of short-range, but it effectively becomes such with the Poisson fitting functions, which form the main share of the fitting basis set. Thus only a very small fraction of the whole set of 3-index integrals, namely those with the Coulomb kernel and GTOs as the fitting functions, are immune to prescreening of the fitting function range. The range for the $|r\mathcal{R}\rangle$ orbitals in the $|ir\mathcal{R}\rangle$ densities can also be reduced with respect to that dictated by respective united domains by means of, e.g., Schwarz prescreening, which allows for a further decrease of the prefactor of the computational cost.

III. IMPLEMENTATION

Implementation of the periodic local F12 method is integrated in the CRYSCOR program package,⁴⁹ which is interfaced with the CRYSTAL code.¹⁰⁶ The latter provides the HF reference and the localized occupied orbitals.⁸¹ An *a posteriori* symmetrization of the Wannier functions is done also on the CRYSTAL side according to the algorithm of Ref. 83. The AO coefficients of the symmetrized Wannier functions are read from a file, generated by CRYSTAL, along with the corresponding symmetry information (the space group of the crystal, the site groups of the WFs' centering points, irreps of the site groups, WFs belong to, etc.). This information is then utilized to obtain the symmetry irreducible pair list $\{i\mathcal{J}\}$ and the weight factors $w_{ij\mathcal{J}}$ (see Sec. II C). Since a similar symmetry treatment is applied to the conventional LMP2 pair-list,⁸⁴ the same routines are used in the F12 part.

The pair domains $[ij\mathcal{J}]_{\text{occ}}$, $[ij\mathcal{J}]_{\text{virt}}$, and $[ij\mathcal{J}]_{\text{RI}}$ are constructed as unions of the corresponding individual WF domains of the orbitals i and $j\mathcal{J}$. An RI-domain of a WF i comprises the functions, belonging to its N_{RI} nearest-neighbour atoms. For the occupied-orbital domains a distance criterion is used as well: all WFs located within the cutoff distance of R_{occ} from the WF i (with respect to their centering points) are included in its domain. The PAO-domains can be obtained by means of the Boughton-Pulay procedure^{70,107} with an optional extension to adjacent atoms, or, similarly to the RI domains, by specifying the number N_{virt} of the nearest-neighbours with respect to the center of the WF i . The $[ij\mathcal{J}]$ pair domains define the summation ranges for calculating the V and B quantities in Eqs. (19) and (26), and the ranges of the $r\mathcal{R}$ and $s\mathcal{S}$ orbitals in the target integrals $(ir\mathcal{R}|\hat{L}_{12}|j\mathcal{J}s\mathcal{S})$, assembled in (31). Furthermore, on the basis of the pair-domains, united domains for each WF from the reference unit cell are built. The united domains define the ranges for the orbitals $r\mathcal{R}$ and $s\mathcal{S}'$ in the three-index integrals and DF-coefficients in Eqs. (31) and (33).

It is important to note that the frozen core approximation, commonly employed in correlated calculations, implies that WFs i and j from the electron pair list $\{ij\mathcal{J}\}$ are valence-only states and are thus constructed from the valence Bloch states. The WFs k and l from the projector \hat{Q}_{12} in Eq. (7), on the other hand, span the whole occupied space, including the core states. Mixing of the core and valence bands during the construction of a common set of Wannier functions would lead to loss of orbital invariance in frozen core MP2-F12 calculations. Indeed, the valence WFs in this case would be contaminated with some core contributions, while the canonical frozen core MP2-F12 would be free of such contamination. To avoid this problem, the localization of the core and valence WFs is carried out in two independent procedures, each employing only the bands of core and valence Bloch states, respectively.

The individual 3-index (as well as 2-index) AO integrals are computed using a module, written by Manby for the Molpro program,⁹⁷ and adopted in the CRYSCOR package under a License agreement. In the integrals involving the correlation factor (6), the latter is approximated by 6 Gaussian-type

geminals, fitted to the Slater type function according to the procedure of Ref. 13. The computational scheme and the algorithms for calculating and processing the 3- and 4-index integrals are similar to those, developed for the periodic density fitted LMP2 method,^{64,65,108} and are in detail explained in the supplementary material.⁷⁷

In our implementation, the occupied and virtual orbitals of the corresponding domains are not explicitly added to the auxiliary basis as suggested in Ref. 78 (the so-called CABS approach). Instead, the initial auxiliary basis set is *assumed* to be rich enough to already contain those (ABS approach, Ref. 6). In principle, this means that Eq. (15) is fulfilled only approximately. However, as calculations on LiH show (see Sec. IV C), this approximation appears not to be harmful, since the sensitivity of the results with respect to the quality of the RI basis turns out to be weak.

Finally, we note that the CRYSTAL code¹⁰⁹ presently cannot process basis functions with angular momentum higher than 3. This prevents from using the full correlation consistent orbital basis sets of quadruple-zeta quality and higher in the periodic LMP2 calculations, since the high angular momentum AOs (beyond f) have to be removed from the basis set (see, e.g., Ref. 110). In the context of the F12 method, this limitation also means that the Fock matrix (which is calculated on the CRYSTAL side) in the auxiliary basis is available only if the latter does not contain g-GTOs or higher. In the formalism of the 3*A ansatz, the Fock matrix in the auxiliary basis does not appear. In more sophisticated F12-Ansätze,¹³ however, such matrix (or the exchange part thereof) is needed. Therefore, with the present version of the CRYSTAL code the F12 treatment is effectively limited to the 3*A approximation. Other F12-approaches could be in principle possible, but with small RI-basis, e.g., like in the ansatz 1, which employs the orbital basis set for the RI.¹³ This ansatz, however, is known to provide relatively poor results and is thus impractical.⁶

Present unavailability of the Fock matrix in the RI basis also prevents us from using the RI basis to correct the HF basis set error (the so-called CABS singles approach),²⁷ commonly applied in molecular F12 studies. This technique is similar to the one used for correcting HF in the dual basis set scheme,^{71,111} and consists of adding the first-order singles contribution to the energy, which are calculated from the occupied-complementary auxiliary block of the Fock matrix.

IV. CALCULATIONS

To test the performance of the local LMP2-F12 method we apply it to the LiH crystal. This system has been recently studied at the correlated level by several groups, using both AO and plane wave basis sets in the framework periodic, as well as finite cluster approaches.^{47,50,55,58,112–114} It is virtually the only crystalline system, for which estimates for the basis set limit of the MP2 correlation energy have been benchmarked in the literature and thus can be used as a reference in this work. Besides, for this crystal a hierarchy of AO basis sets for periodic calculations has been constructed, providing progressively improved description.¹¹³

TABLE I. The RI-, virtual (PAO-), and occupied-orbital domains, corresponding to the reference WF in the LiH crystal. The domains are specified by the number of the coordination spheres (stars) of atoms (for the PAO- or RI-domains) or WFs (for the occupied-orbital domains) around the reference WF. The type and the number of the atoms in the given star as well as the distance to the reference WF are also provided. For the occupied-orbital domains the valence WFs are centered on H atoms and core WFs on Li.

Stars	Type of atoms	R_{cut} (Å)	$N_{\text{at}}/N_{\text{WF}}$
0	H	0	1
1	Li	2.0420	7
2	H	2.8878	19
3	Li	3.5368	27
4	H	4.0840	33
5	Li	4.5661	57
6	H	5.0019	81
7	H	5.7756	93

A. Specification of the computational parameters

Lithium hydride is a cubic crystal with two atoms and two correlated electrons (within the frozen core approximation) per cell. For the compatibility of the results of the current study with those reported earlier, we employ the experimental lattice parameter of 4.084 Å.

High symmetry of the crystal allows for substantial reduction of the pair-list size. At the same time, the symmetry adapted domains grow in big steps, as they have to include complete coordination spheres of atoms or WFs, surrounding a given WF. The information on the domains, corresponding to the first few coordination spheres used in the present work, is given in Table I.

Since the standard molecular AO basis sets are very difficult to process in the periodic HF calculations, the hierarchy of the orbital basis sets used in the calculations requires special attention. First, the basis sets A ([4s3p2d1f] for both Li and H atoms) from Ref. 113, as a representative of a decent quality periodic basis set was taken. This basis set does not yet cause convergence problems, while the HF energy is already close to the basis set limit value.¹¹³ For MP2, however, this basis set yields the energy above the cc-pVTZ result, obtained with finite clusters. Richer basis sets of Ref. 113: A(B) ([5s4p3d2f] for Li and [4s3p2d1f] for H) and A(BC) ([6s5p4d3f] for Li and [5s4p3d2f] for H) were also employed. These basis sets could be processed only in the dual basis set framework,⁷¹ where additional shells of AOs, denoted by a symbol in parenthesis, were used to span the virtual space only. The basis set A(B) differs from A only by additional s-, p-, d-, and f-shells on the Li atom with the exponents 0.14 a.u. for s-, p-, and d-shells and 0.18 a.u. for the f-shell. These exponents are noticeably lower than those of the most diffuse Li's AOs in the basis set A (0.21, 0.22, 0.6, and 0.7 a.u., respectively), but considerably higher than in molecular basis set, recommended for the F12 calculations (e.g., 0.0076, 0.0091, 0.041, and 0.081 in aug-cc-pVTZ¹¹⁵). Therefore, for the reference in the discussion below we introduce a term “*slightly diffuse orbitals*” to characterize the B-part of the basis A(B) with respect to both the basis set A and diffuse molecular basis sets.

In this work we also employed several smaller basis sets: (i) the $[3s2p1d]$ basis of Ref. 116 for Li and the $[2s1p]$ cc-pVDZ basis¹¹⁷ for H, denoted as A1; (ii) the same basis set for Li as in A1 and the $[3s2p1d]$ cc-pVTZ basis for H, denoted as A2; (iii) the $[4s3p2d1f]$ basis set A of Ref. 113 for Li and the $[3s2p1d]$ cc-pVTZ basis for H, denoted as A3.

In principle, standard molecular basis sets, including the augmented ones, could be formally used in periodic LMP2 or LMP2-F12 calculations in the dual basis set format. However, the computational cost of such calculations (i.e., the Fock matrix generation and subsequent correlated treatment) would become enormous due to inefficiency of direct space pre-screening in the presence of diffuse AOs. At the same time, due to the substantial redundancy appearing in such basis sets within a periodic grid of centers, the diffuse orbitals do not essentially improve the description, as was demonstrated in Ref. 113 [the basis set A(BCDE)].

As auxiliary basis sets we employed the standard MP2 fitting basis sets of Weigend,¹¹⁸ optimized for the orbital basis set of the cc-pVXZ family. Since the WFs in LiH are s -like orbitals, in the present study the same auxiliary basis sets were used for both the density fitting and RI. The fit domains were chosen to consist of 12 atoms (or more if dictated by the symmetry of the corresponding $|ir\mathcal{R}$ density). Since the Fock matrix, Wannier functions, and the symmetry information are provided by the CRYSTAL code, which, as noted above, has a limitation on the AO angular momentum,¹⁰⁹ in the present implementation of the LMP2-F12 program it cannot exceed $L_{max} = 3$ for orbital basis set and $L_{max} = 4$ for auxiliary basis set. The functions of standard basis sets, having the angular momentum beyond these limits, were disregarded in the calculations.

Technical parameters of the calculations were the following. In the HF calculation the reciprocal space was sampled by $12 \times 12 \times 12$ k-mesh, and the tolerances of 10^{-8} (ITOL1-3), 10^{-25} (ITOL4), and 10^{-100} (ITOL5) were chosen to control the accuracy of the integral evaluation.¹⁰⁹ Wannier functions and PAOs were generated with the $8 \times 8 \times 8$ mesh. In the LMP2 calculations, the electron repulsion integrals for the pairs with up to 8 Å of the interorbital distance were calculated by density fitting, from 8 till 12 Å by multipole approximation. The energy contribution from the pairs beyond 12 Å was estimated by extrapolation of the pair energies according to the C_6R^{-6} law,⁶⁵ where the pair specific C_6 parameters were fitted to the actual decay of the pair-energies in the range from 8 till 12 Å. If not stated otherwise, the value of 1 a.u. was taken for the parameter γ of the correlation factor (6). Other parameters of the calculations are specified below for each of the calculations explicitly.

B. Orbital basis set convergence

First we investigate the general performance of the LMP2-F12 method with respect to the orbital basis set it is combined with. In molecular studies the F12 correction is known to be a very efficient way to accelerate the basis set convergence. However, for high accuracy it is still recommended to employ an orbital basis set of not lower than of a triple zeta-quality, augmented with diffuse functions. Alternatively,

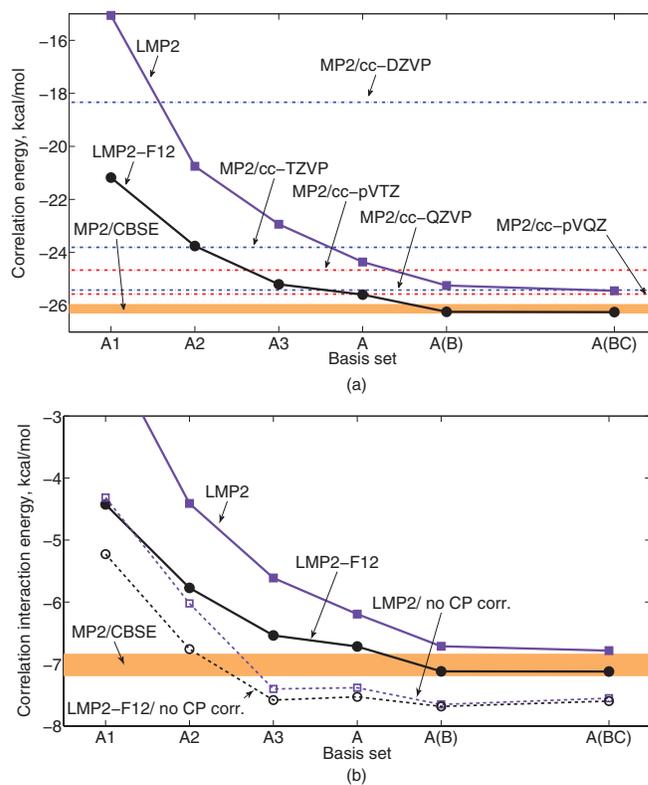


FIG. 1. Dependence of the LMP2 and LMP2-F12 correlation energy of the LiH crystal (a), and of the difference between correlation energies of LiH crystal and LiH molecule (with the same interatomic distance as in the crystal). For the basis set specifications see text and Ref. 113. The basis-set axis is scaled such that the unity length corresponds to the addition of one shell of AOs in each angular momentum for *one* of the atoms (either Li or H). In all the calculations, the MP2 auxiliary basis sets of cc-pV5Z quality, the 19-atom/WF domains, and 6 Å for the pair-list cutoff radius were used. For the correlation energy differences, both the counterpoise (CP) corrected (solid lines) and uncorrected (dashed lines) results are shown. In the former case, the LiH molecule was surrounded by 17 atoms, allowing for the same PAO and RI-domains as in the periodic calculation. For the reference, results of periodic MP2 calculations of Ref. 50, employing the cc-XZVP, X = D,T,Q basis sets, and finite-cluster calculations using hierarchical method of Ref. 58, employing cc-pVXZ, X = T,Q basis sets, are also given: blue and red horizontal lines, respectively. The window of the complete basis set estimates (CBSE) for the MP2 correlation energy spans the values, obtained in periodic AO,^{50,113} plane-wave,⁴⁷ and finite cluster approaches.^{58,114} For the CBSE of the correlation energy difference, the upper (MP2/cc-pVQ/5Z-extrapolated, -19.074 kcal/mol) and lower (MP2-F12/aug-cc-pV5Z, -19.156 kcal/mol) CBSEs for LiH molecule were subtracted from, respectively, the lower (-26.311 kcal/mol) and upper (-25.941 kcal/mol) edges of the periodic CBSE window.

tively, special basis sets developed for F12 calculations can be used,¹¹⁹ which also include rather diffuse functions. As discussed above, this is not an option for periodic AO-based calculations, where diffuse orbitals and thus the standard molecular basis sets require huge computational effort.

Fig. 1(a) presents the results of frozen core LMP2 and LMP2-F12 calculations employing a series of basis sets specified in Sec. IV A. As benchmarks we use the results of the periodic MP2 calculations with the cc-DZVP, cc-TZVP, and cc-QZVP basis sets,⁵⁰ and those obtained with the cc-pVTZ and cc-pVQZ basis sets¹²⁰ using the finite-cluster approach of Ref. 58. A window of frozen core complete basis set estimates (CBSE) from Refs. 47, 50, 58, 113, and 114 is also shown.

The convergence of the correlation energy with basis set in the periodic LMP2 calculations is indeed rather slow. The correlation energy with basis set A, which is formally richer than triple-zeta, is below the cc-TZVP result, but still noticeably above the cc-pVTZ one. Augmentation of the basis set A with further shells [i.e., employing the A(B) and A(BC) basis sets] lowers the energy to the quadruple-zeta benchmarks, yet remaining above the cc-pVQZ result. In Ref. 113 a further expansion of the basis set was considered, which, however, did not show a noticeable improvement until bond-centered orbitals were included.

Addition of the F12 correction substantially improves the description. The LMP2-F12 correlation energy with the A3 basis is already not far from the quadruple-zeta benchmark results, while the basis A drops below them, appearing within sub-kcal/mol proximity of CBSE. The A(B) and A(BC) energies are inside the CBSE window and, judging by the convergence pattern, at this level they are essentially converged. Analysis of the A and A(B) results clearly indicates the importance of *slightly diffuse* orbitals for F12 calculations. Indeed, it is these very orbitals that allow the LMP2-F12 energy to reach the limit value.

In molecular studies, the remaining error of the F12 treatment is known to be systematic, making this method even more effective for the physically relevant energy differences than for the formal total correlation energies. The LiH crystal is, however, not a good example in this respect, since the whole frozen core correlation energy contributes to the cohesive energy (the respective neutral atoms have no valence electron pairs). Nevertheless, in order to investigate the performance of the F12 method for the energy differences, we study the interaction energy in LiH with the reference to the LiH molecule (taken with the same Li-H distance as in the crystal). As is seen from Fig. 1(b) the deficiencies in the MP2-F12 energies of the LiH crystal and the molecule are indeed systematic and to a large extent cancel in the energy difference. The LMP2-F12 interaction energies with basis sets A3 and A are less than just half a kcal/mol off the CBSE, and the A(B) and A(BC) basis sets provide converged results. Interestingly, in molecular calculations the F12-A ansatz (in contrast to F12-B or F12-C ansätze) usually overestimates the basis set limit result.¹³ Yet, in LiH this is not the case, either for crystal or a molecule.

The LMP2-F12 interaction energies depicted in Fig. 1(b) with filled symbols (and solid lines) were calculated with counterpoise (CP) correction, i.e., the LiH molecule was surrounded with the 17 ghost atoms (5 Li and 12 H atoms) to form a 19 atom domain around the H atom (see Table I). However, since the F12 correction is expected to yield a nearly basis set limit result, the CP correction might be considered as unessential. Apparently this is not the case for LiH and the basis sets employed. With those, if only two centers of the LiH molecule are populated with atomic orbitals, the LMP2-F12 interaction energies still contain a sizable basis set superposition error (BSSE), even with the basis sets A(B) and A(BC). The reason why LMP2-F12 with periodic basis sets does not yield the limit for the LiH molecule, is the absence of really diffuse functions in these basis sets, which in molecular case become vital. Indeed, for these two basis sets, the

periodic correlation energy is virtually converged, while the molecular one is not (-18.65 kcal/mol with MP2-F12/A(BC) vs -19.07 kcal/mol from MP2/cc-pVQ/5Z-extrapolation or -19.16 kcal/mol with MP2-F12/aug-cc-pV5Z). At the same time, with aug-cc-pVTZ MP2-F12 gives for the LiH molecule virtually the basis set limit result (-19.07 kcal/mol). Fortunately, this deficiency can be to a large extent compensated by expansion of the orbital domains, possible only by inclusion of ghost atoms. In our case it is equivalent to performing a counterpoise corrected calculation of the interaction energy.

To summarize, for accurate LMP2-F12 results, the orbital basis sets should contain *slightly diffuse* orbitals in the periodic case (possibly processed via the dual basis set technique) and really diffuse ones in molecular calculations. Since in practical applications of the periodic LMP2 method the basis sets of the size/quality of A3 or A are usually utilized,^{71,110,121–124} for such basis sets, the lack of the diffuse functions has to be compensated by expansion of the PAO-domains (see also discussion in Sec. IV C). In the molecular reference calculations, such a domain expansion might require additional ghost centers to be added according to standard counterpoise procedure. The calculations on LiH suggest that even with such basis sets a sub-kcal/mol accuracy, commonly sufficient for applications, can be reached.

C. Influence of the local approximations

Finally, we investigate the influence of local approximations on the stability of the LMP2-F12 method. Table II compiles the LMP2-F12 correlation energies, computed with the basis set A and different domain or pair-list truncations, auxiliary basis sets and values for the correlation parameter γ , as well as the energy difference for the cases where the corresponding parameters could be varied also in the LiH molecule. As expected, the F12 treatment is effectively short-range, allowing for truncation of the pair list on the basis of the orbital spatial separation. Moreover, this truncation can be more aggressive than that for the weak/distant pairs in the LMP2 calculations (which also depends on the overlap between orbitals in the pair). As is seen from Table II, only the extreme diagonal-pair-only truncation leads to inaccurate results. If the first nearest WF neighbours are included ($R_{ij\mathcal{J}}^{\text{cut}} = 3$ Å, see Table I), the result is already sufficiently close to the converged one, and increase of the $R_{ij\mathcal{J}}^{\text{cut}}$ to 8 Å (i.e., the default cutoff distance for the weak pairs in LMP2) is not necessary.

To analyze the influence of the domain approximations, we start with the PAO-domains $[ij\mathcal{J}]_{\text{virt}}$. The convergence of the results with PAO-domain size is faster than that for the LMP2 correlation energy alone, but slower than expected from molecular local F12 studies.²¹ Convergence in the total energies is achieved only after extension of the domain to 19 atoms. Similar pattern is observed for the energy difference. We attribute such a behaviour to the lack of the *slightly diffuse* functions in the orbital basis (see the discussion in Sec. IV B). Extended domains compensate for the absence of such functions in the virtual space. For the A(B) basis, which does include *slightly diffuse* functions, a nearly converged result is achieved already with 7-atom domain:

TABLE II. The periodic LMP2-F12 correlation energy for LiH crystal ($E^{[2]} = E_{LMP2}^{[2]} + E_{F12}^{[2]}$), calculated using different PAO-, occupied-orbital and RI-domains, auxiliary basis sets, pair-list cutoff radius $R_{ij\mathcal{J}}^{\text{cut}}$, and explicit correlation factor parameter γ . Only one parameter is varied at a time. The reference calculation corresponds to the 19-atom/WF domains, the auxiliary basis set of VTZ quality,¹¹⁸ $R_{ij\mathcal{J}}^{\text{cut}} = 6 \text{ \AA}$, and $\gamma = 1.0 \text{ a.u.}$ The LMP2 energies were calculated with the V5Z-quality fitting basis.¹¹⁸ The correlation interaction energy ($\Delta E^{[2]} = E_{\text{cryst.}}^{[2]} - E_{\text{mol.}}^{[2]}$) of the LiH crystal with respect to the LiH molecule with the same Li-H distance as in the crystal is also given for the cases, where the parameter could be varied simultaneously in the crystal and the molecule. The LiH molecule was calculated with additional 17 nearest neighbour ghost atoms, cut out from the periodic structure and populated with the corresponding atomic orbitals. All energies are in kcal/mol.

Varied parameter	Parameter value	$E_{LMP2}^{[2]} + E_{F12}^{[2]}$	$\Delta E^{[2]}$
$R_{ij\mathcal{J}}^{\text{cut}}/\text{\AA}$	0	-25.285	
	3	-25.672	
	6	-25.692	
	8	-25.693	
$[ij\mathcal{J}]_{\text{virt}}/\text{atoms}$	1	-23.494	-5.541
	7	-25.498	-6.593
	19	-25.692	-6.711
	27	-25.717	
$[ij\mathcal{J}]_{\text{occ}}/\text{WFs}$	1	-26.105	
	7	-26.023	
	19	-25.692	
	27	-25.692	
	33	-25.683	
	81	-25.676	
$[ij\mathcal{J}]_{\text{RI}}/\text{atoms}$	1	-29.470	-9.612
	7	-25.693	-6.712
	19	-25.692	-6.711
	27	-25.691	
Auxiliary basis	VTZ	-25.692	-6.711
	VQZ	-25.600	-6.726
	V5Z	-25.597	-6.727
$\gamma/\text{a.u.}$	0.8	-25.688	-6.730
	1.0	-25.692	-6.711
	1.2	-25.647	-6.677

-26.201 kcal/mol vs -26.243 kcal/mol with 19-atom domain.

The occupied-orbital domains $[ij\mathcal{J}]_{\text{occ}}$, unlike the virtual ones, have to be complete from the onset, in a sense that they should guarantee strong orthogonality in the projector (7). They should contain all WFs, which have a non-negligible overlap with the WFs i and $j\mathcal{J}$ of the pair. As follows from Table II the occupied orbital domains should be extended at least up to the second nearest neighbours. However, since the number of occupied orbitals per cell is much smaller than that of PAOs or auxiliary functions, extension of these domains is not problematic.

Of the major importance for the efficiency of the LMP2-F12 is the effect of the quality of the RI basis sets and size of the RI-domains on the results. Indeed, the most expensive steps of the calculation are evaluation and processing of the integrals involving RI-auxiliary orbitals. A need for extended RI-domains would automatically lead to enlargement of both united RI- and united fit-domains, making calculation of the 3-index ($i\alpha\mathcal{A}|P\mathcal{P}$) integrals quite expensive. Besides, since

the quality of the fitting basis set has to be adapted to that of the RI basis set, the density fitting procedure for the integrals with the RI orbitals has the unfavorable quadratic scaling with RI basis set size, and computation of the DF coefficients $D_{PP}^{i\alpha\mathcal{A}}$ (Eq. (33)) even cubic scaling. At the same time, within the ABS approach,⁶ used in our method, inadequately small RI basis set can compromise the correctness of the strong orthogonality projector, since Eq. (15) then holds only approximately. Fortunately, the present results demonstrate a very weak sensitivity of the interaction and even total energies to the size of the RI basis. Only an extreme case of 1-atom RI-domain is inappropriate, while starting from 7-atom domains the energy virtually does not change. The influence of the auxiliary basis set quality is insignificant too, especially so for the energy differences. This suggests that auxiliary basis sets of triple-zeta quality and modest RI-domains (e.g., chosen the same as the PAO domains) could be sufficient to reach the sub-kcal/mol accuracy in periodic LMP2-F12 calculations.

Finally, we note that variation of the correlation factor parameter γ does not noticeably affect the results. This is in line with molecular studies,¹²⁵ reporting a very weak dependence of the MP2-F12 correlation energy on this parameter for a Slater-type geminal as the correlation factor. Although the dependence of the energy on this parameter is not exactly systematic, such that the discrepancy in the interaction energies is roughly as large as in the total energies, it does not exceed a few hundredths of a kcal/mol.

V. CONCLUSIONS

A periodic local MP2-F12 method in the fixed-amplitude 3^*A ansatz, using AO basis set, is described. The method is formulated in the direct space, employing WFs for the occupied space, PAOs for the virtual space, and atomic-centered orbitals for the RI space. Both translational and point-group symmetry are exploited. The point-group symmetry treatment is based on the site symmetry of the WF centroids.

Locality of the explicit correlation factor, chosen in a form of a Slater-type geminal, allows for truncation of the list of the explicitly correlated electron pairs on the basis of spatial proximity of the localized orbitals, representing these electrons. Furthermore, in the strong-orthogonality projector, the virtual, occupied, and RI spaces are restricted to pair-specific domains, comprising orbitals spatially close to at least one of the two WFs of the pair. The 4-index integrals are evaluated by means of direct space density fitting, with the fitting functions restricted to orbital-product-specific fit-domains. The local approximations reduce both the scaling of the computational cost to asymptotically linear and the prefactor.

Test calculations on the LiH crystal indicate that the F12 treatment indeed substantially accelerates the basis set convergence. With basis sets of triple-zeta quality, commonly used in periodic LMP2 applications, results of sub-kcal/mol proximity to the basis set limit can be obtained. Yet, for reaching the limit, the orbital basis sets should contain a little bit more diffuse orbitals, than usually employed in periodic studies (designated here as *slightly diffuse*). In case such functions become harmful for the underlying periodic HF method, they

can be treated within the dual basis set scheme. An alternative to diffuse functions could be inclusion of a small number of plane waves in the basis set, instead. Plane waves are mutually orthogonal and thus are not expected to cause redundancies in the basis. Development of combined AO/plane wave basis set for periodic methods is in progress in our group.

The results converge with the domain size reasonably fast, especially so for the RI-domains. The PAO domains should, however, be extended to the next nearest neighbours with respect to the standard ones. However, inclusion of the *slightly diffuse* orbitals in the AO basis alleviates this problem as well. Furthermore, orbital specific virtuals (OSVs) could be an efficient substitute for PAOs in this respect, since the former adapt themselves to span the virtual space in an optimal way (at least for diagonal pairs) without increasing the amount of virtual orbitals in the domain. A periodic LMP2 method based on OSVs has been already implemented in our group,¹²⁶ and adaptation of the F12 part to OSVs will be reported in one of the forthcoming publications.

After optimization and parallelization of the LMP2-F12 code, safe values for the computational parameter defaults will be assessed and the method will be included in the CRYSCOR package, to be used in practical applications. We also consider the LMP2-F12 method as an essential ingredient of accurate quantum chemical hierarchical scheme for crystalline systems, where a higher-order treatment is to be evaluated as a correction to the basis set limit periodic MP2 result. The third and higher order corrections (i.e., the difference between, e.g., CCSD(T) and MP2 energies) are usually of a shorter range and of a smaller magnitude than the second order energy and less sensitive to the basis set quality than the latter. Hence, such energy corrections can be calculated to a good accuracy, employing only moderate basis sets and cruder local approximations, and added to the periodic HF+LMP2-F12 result. Presently, calculation of the higher order corrections for periodic systems can be done using finite-cluster incremental scheme,¹²⁷ but development of fully automated periodic coupled cluster treatment is also in progress.

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APPENDIX: POINT GROUP SYMMETRY TREATMENT OF THE PAIR-LIST IN THE DIAGONAL PERIODIC LOCAL F12 FORMALISM

Consider a set of WFs $\{W_{i'}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{i1})\}$, centered on the point \mathbf{q}_{i1} and forming a basis of an irrep γ_i of the site group $S_{\mathbf{q}_{i1}}$. The index i' counts the basis vectors of the irrep γ_i . The site group $S_{\mathbf{q}_{i1}}$ comprises those symmetry operations $(g_w \hat{\mathbf{a}}_w + \mathbf{R}_w)^{(i1)}$ from the crystal's space group, which do not change the vector \mathbf{q}_{i1} :

$$(g_w \hat{\mathbf{a}}_w + \mathbf{R}_w)^{(i1)} \mathbf{q}_{i1} = \mathbf{q}_{i1}, \quad w = 1, 2, \dots, N_{\text{site}}^i, \quad (\text{A1})$$

where N_{site}^i is the number of symmetry elements in the site group $S_{\mathbf{q}_{i1}}$, and the index $i1$ means the first vector \mathbf{q}_{i1} from the star of N_{star}^i symmetry equivalent points \mathbf{q}_{it} , $t = 1, 2, \dots, N_{\text{star}}^i$ is considered. Although the elements of $S_{\mathbf{q}_{i1}}$ can contain non-zero proper \mathbf{R}_w and/or improper (fractional) \mathbf{a}_w translations, depending on the choice of the origin, this group is isomorphic to a certain point group $S^{(i)}$, containing orthogonal operations $g_w^{(i)}$ only. The groups $S^{(i)}$ and $S_{\mathbf{q}_{i1}}$ (as well as $S_{\mathbf{q}_{it}}$ for any t) have therefore a common set of irreps. By application of the symmetry operations from $S_{\mathbf{q}_{i1}}$ the WFs $\{W_{i'}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{i1})\}$ transform according to the irrep γ_i :

$$(g_w \hat{\mathbf{a}}_w + \mathbf{R}_w)^{(i1)} W_{i'}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{i1}) = \sum_{i''} D_{i''i'}^{(\gamma_i)}(g_w^{(i)}) W_{i''}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{i1}), \quad (\text{A2})$$

where $D^{(\gamma_i)}(g_w)$ is the matrix of the irrep γ_i , corresponding to the element $g_w^{(i)}$ of the point group $S^{(i)}$.

Now we choose a particular set of N_{star}^i operations $(g_t \hat{\mathbf{a}}_t + \mathbf{R}_t)_{\text{star}}^{(i1)}$ that generate the whole star of \mathbf{q}_{it} points from \mathbf{q}_{i1} :

$$(g_t \hat{\mathbf{a}}_t + \mathbf{R}_t)_{\text{star}}^{(i1)} \mathbf{q}_{i1} = \mathbf{q}_{it}, \quad (\text{A3})$$

and, thus, the WFs, centered on these points:

$$W_{i'}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{it}) = (g_t \hat{\mathbf{a}}_t + \mathbf{R}_t)_{\text{star}}^{(i1)} W_{i'}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{i1}). \quad (\text{A4})$$

Within this choice, a general symmetry element $(g \hat{\mathbf{a}} + \mathbf{R})$ of the space group, that transforms the point \mathbf{q}_{i1} into $\mathbf{q}_{it} + \mathbf{R}_{\mathcal{R}}$, can be always represented as a product of 3 operations:

$$(g \hat{\mathbf{a}} + \mathbf{R}) = (E \hat{\mathbf{R}}_{\mathcal{R}})(g_t \hat{\mathbf{a}}_t + \mathbf{R}_t)_{\text{star}}^{(i1)} (g_w \hat{\mathbf{a}}_w + \mathbf{R}_w)^{(i1)}, \quad (\text{A5})$$

where $(g_t \hat{\mathbf{a}}_t + \mathbf{R}_t)_{\text{star}}^{(i1)}$ has to match the point \mathbf{q}_{it} , the index w in $(g_w \hat{\mathbf{a}}_w + \mathbf{R}_w)^{(i1)}$ is obtained from the relation

$$g = g_t g_w, \quad (\text{A6})$$

and the translation $\mathbf{R}_{\mathcal{R}}$ has to satisfy the equation

$$\mathbf{R} = \mathbf{R}_{\mathcal{R}} + \mathbf{a}_t + \mathbf{R}_t + \hat{g}_t(\mathbf{a}_w + \mathbf{R}_w). \quad (\text{A7})$$

In the list of WFs pairs, which is the target object for the symmetry manipulations, the first WFs i are always centered in the zero cell. Hence, from the whole (infinite) set of possible symmetry operations $(g \hat{\mathbf{a}} + \mathbf{R})$ of the space group, only those are relevant, for which $\mathbf{R}_{\mathcal{R}}$ is zero, or

$$\mathbf{R} = \mathbf{a}_t + \mathbf{R}_t + g_t(\mathbf{a}_w + \mathbf{R}_w). \quad (\text{A8})$$

These operations form a group, isomorphic to the point group of the crystal. Application of a symmetry operation $(g \hat{\mathbf{a}} + \mathbf{R})$ (with the restriction (A8) for the \mathbf{R} translation) to $W_{i'}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{i1})$ then gives

$$(g \hat{\mathbf{a}} + \mathbf{R}) W_{i'}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{i1}) = \sum_{i''} D_{i''i'}^{(\gamma_i)}(g_w^{(i)}) W_{i''}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{i1}). \quad (\text{A9})$$

The second WF $W_{j'}^{(\gamma_j)}(\mathbf{r} - \mathbf{q}_{j1} - \mathbf{R}_{\mathcal{J}})$ in the pair behaves under application of symmetry operations in a similar way, but now with respect to the irrep γ_j of site group $S_{\mathbf{q}_{j1}}$, corresponding to the point $\mathbf{S}_{\mathbf{q}_{j1}}$. The difference is, however, that

it is not necessarily centered in the zeroth cell. This can be formally expressed as

$$W_{j'}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{j1} - \mathbf{R}_{\mathcal{J}}) = (E\hat{\mathbf{R}}_{\mathcal{J}})W_{j'}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{j1}). \quad (\text{A10})$$

With that, the result of the action of $(g\hat{\mathbf{a}} + \mathbf{R})$ on this function is

$$\begin{aligned} (g\hat{\mathbf{a}} + \mathbf{R})W_{j'}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{j1} - \mathbf{R}_{\mathcal{J}}) \\ = \sum_{j''} D_{j''j'}^{(\gamma_i)}(g_{w''}^{(j)})W_{j''}^{(\gamma_i)}(\mathbf{r} - \mathbf{q}_{j''} - \mathbf{R}_{\mathcal{J}}), \end{aligned} \quad (\text{A11})$$

with

$$\mathbf{R}_{\mathcal{J}'} = \mathbf{R}_{\mathcal{R}'} + \hat{g}\mathbf{R}_{\mathcal{J}}, \quad (\text{A12})$$

where the particular w' , t' , and \mathcal{R}' index values depend on the $(g\hat{\mathbf{a}} + \mathbf{R})$ operator and the choice of the set $(g_{t'}\hat{\mathbf{a}}_{\mathcal{R}'} + \mathbf{R}_{t'})^{(j1)}$ for generating the star of the points \mathbf{q}_{jt} , analogously to Eqs. (A5), (A6), and (A7).

Since the kernels of the integrals $V_{i'j'\mathcal{J},p}$ and $B_{i'j'\mathcal{J},p}$ are totally symmetric, application of the operation $(g\hat{\mathbf{a}} + \mathbf{R})$ to both orbitals i and $j\mathcal{J}$ simultaneously does not change the value of the integral. For a general diagonal integral

$$I_{ij\mathcal{J},p} = \langle ij\mathcal{J} | \hat{I}_{12} | ij\mathcal{J}, p \rangle \quad (\text{A13})$$

with a totally symmetric kernel \hat{I}_{12} , this leads to

$$\begin{aligned} I_{i'j'\mathcal{J},p} &= I_{(g\hat{\mathbf{a}}+\mathbf{R})(i'j'\mathcal{J}),p} \\ &= \sum_{i''i'''} (D_{i''i'}^{(\gamma_i)}(g_{w''}^{(i)})^* D_{i''i'''}^{(\gamma_i)}(g_{w'''}^{(i)})) \\ &\quad \times \sum_{j''j'''} (D_{j''j'}^{(\gamma_j)}(g_{w''}^{(j)})^* D_{j''j'''}^{(\gamma_j)}(g_{w'''}^{(j)})) \\ &\quad \times \langle i''j''j'''\mathcal{J}' | \hat{I}_{12} | i''i''j''j'''\mathcal{J}' \rangle, \end{aligned} \quad (\text{A14})$$

where the notation

$$|i''i''j''j'''\mathcal{J}'\rangle = W_{i''i''j''j'''\mathcal{J}'}(\mathbf{r} - \mathbf{q}_{i''i''}) \quad (\text{A15})$$

was introduced. Equation (A14) shows that a diagonal integral can be expressed as a linear combination of symmetry related integrals, which are, however, not necessarily diagonal, unless both irreps γ_i and γ_j are one-dimensional.

At the same time, the F12-energy (16) in the orbital-invariant diagonal formalism is linear with respect to the sum of the integrals of the type (A13). Summing up the right- and left-hand sides of Eq. (A14) over the basis vectors i' and j' of the irreps γ_i and γ_j , and using the unitarity of the irrep matrices one obtains

$$\sum_{i' \in \gamma_i} \sum_{j' \in \gamma_j} I_{i'j'\mathcal{J},p} = \sum_{i' \in \gamma_i} \sum_{j' \in \gamma_j} I_{(g\hat{\mathbf{a}}+\mathbf{R})(i'j'\mathcal{J}),p}. \quad (\text{A16})$$

This shows that although the individual integrals involving WF pairs $i'j'\mathcal{J}$ and $i''i''j''j'''\mathcal{J}'$, corresponding to symmetry equivalent centers, might not be identical, sums of such integrals over the vectors of the irreps γ_i and γ_j , and thus the related energy contributions, are, indeed, the same. Therefore it is sufficient to process only the pairs, where the WFs are centered on \mathbf{q}_{i1} and $\mathbf{q}_{j1} + \mathbf{R}_{\mathcal{J}}$, and multiply the corresponding pair energies by symmetry weight factors, equal to the number of elements in the stars of the center pairs. We note that

for the orbital-variant diagonal F12 ansatz,^{18,21,128} where the energy is not linear with respect to the sum of the integrals, such a symmetry equivalence of the pair energies holds only for one-dimensional irreps.

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