Many-body dispersion corrections for periodic systems: an efficient reciprocal space implementation

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I. Introduction

The development of van der Waals (vdW) corrections for density functional theory (DFT) methods is presently a very active research field. Despite the success of some of the relatively simple correction methods based on a pair-wise approximation to the vdW energy [1, 2], it is clear that many-body effects can contribute significantly to an accurate description of certain supramolecular and condensed-phase systems [3–7]. The simplest method to include some many-body (MB) effects in the London dispersion energy calculations consists in adding an Axilrod–Teller–Muto [8, 9] (ATM) 3-body correction term. However, depending on the nature of the system and its structure, the 3-body correction may turn out to be insufficient and one has to consider up to infinite order MB contributions. We note that these MB contributions are not described by the non-local van der Waals density functional [10], which is presently one of the most popular methods to take into account the vdW interactions within the DFT framework [11]. The MBD-vdw method of Tkatchenko et al
[6, 12, 13] represents an interesting and conceptually clean approach for including infinite-order many-body effects in the dispersion energy calculations. This method has been successfully tested on several supramolecular systems such as the dimers of the S12L [3] benchmark set [6], as well as crystalline systems such as graphite [6], crystals from the X23 benchmark set [4], aspirin crystals [5], and various molecular crystals [14].

Before discussing the essential features of the MBD approach, and in particular its specific contributions to non-additivity, it is useful to overview the main sources of non-additivity. Usually, this notion is defined in relation to the cluster expansion of the total energy. Suppose that we have a partition of the system in terms of some building blocks $B_k$. The total energy

$$E[\{B_k\}] = E_1 + E_2 + E_3 + E_{4+}$$

$$= \sum_k U_k[B_k] + \sum_{k<l} U_{kl}[B_k, B_l] + \sum_{k<l<m} U_{klm}[B_k, B_l, B_m] + E_{4+} + \ldots$$

can be written as a sum of one- ($E_1$), two- ($E_2$), three- ($E_3$) and higher order many-body ($E_{4+}$) contributions. The one-body term is the sum of the energies of the isolated building blocks ($U_k$). The two-body contribution is the sum of all pairwise interactions $U_{kl}$ and this part of the energy is considered as strictly additive, while the ensemble of higher-order contributions represents non-additive or many-body effects.

It is known from the theory of intermolecular forces that overlap-repulsion, induction, and dispersion forces may contain non-additive components, while electrostatic interactions are strictly additive. Non-additive overlap-repulsion and induction terms are included in conventional Kohn–Sham density functional theory calculations. We thus focus on the non-additivity of the dispersion interactions.

In a recent ‘Perspective’ paper, [15] Dobson distinguished three main types of non-additivity effects, which influence the London dispersion interactions. The non-additivity is understood here as the deviation from the sum of two-center interactions, where the centers in semi-classical models are usually atoms or bonds. Type A non-additivity is the most obvious one: it reflects the fact that the dispersion coefficients between pairs of atoms embedded in a many-electron system are different from the coefficients that one could derive from isolated atomic species. In some pair-wise dispersion correction schemes such as the Tkatchenko–Scheffler (TS) method [2] and its derivatives, this type A non-additivity is taken into account by considering the atoms-in-molecule polarizabilities that are scaled proportionally to the volume ratio between the free and embedded atoms. Type B non-additivity is due to the many-particle screening of the polarizabilities by electrodynamic effects. This is essentially the main physical content of the MBD model discussed here. Type C non-additivity effects are due to very large delocalization effects, arising mainly in small-gap or in gapless systems, showing metallic or metallic-like behavior, where the delocalization length is so large that the basic assumption that localizes the source of interactions to a relatively small-sized atomic or bond centers loses its meaning. This effect is out of the scope of the present study, since our model is limited to site-site dipolar fluctuations, whose length is comparable to the size of the interacting units (atoms or bonds).

Current implementations of the MBD-vdw method treat finite non-periodic and infinite, periodic systems on an equal footing. However, such an algorithm is not suitable for implementation within periodic boundary conditions (PBC), which is the usual computational framework in material physics. The main problem is that the dispersion energy converges rather slowly with the system size; hence the calculations with this approach require the use of relatively large supercells, with associated numerical cost. Ambrosetti et al [6], for instance, reported that in order to achieve convergence of the energy in real-space MBD calculations of graphite, a $11 \times 11 \times 7$ supercell containing as many as 3388 atoms was needed. In such cases the diagonalization of matrices of dimension over 10,000 has to be performed, which represents a significant additional computational load on top of the electronic calculation.

In this work we propose a reciprocal-space implementation of the most recent version of the MBD-vdw method proposed by Ambrosetti et al [6] (MBD@rsSCS) which is particularly well suited for the simulations of systems under periodic boundary conditions. Furthermore, we derive expressions for energy gradients of the vdW energy that are needed in structural relaxations and molecular dynamics simulations. Our formulation thus ensures that this useful approach can be employed in materials science calculations, even for large systems well beyond the scope of higher-level methods such as RPA (random phase approximation) or QMC (quantum Monte Carlo).

This paper is organized as follows. In section II we review the MBD@rsSCS method and provide the working equations needed for the efficient energy calculations under periodic boundary conditions. In section III the expressions for the energy gradients are given. Convergence tests for energies and gradients, and examples of practical applications of our implementation of the MBD@rsSCS method are discussed in section IV. Conclusions of the present work are given in section V. Detailed appendices are also included that further elaborate on the mathematical details.

II. Methodology

II.A. MBD@rsSCS method for a molecular case

The correlation energy in the random phase approximation (RPA) may be written as:

$$E_c = \int_0^\infty \frac{d\omega}{2\pi} \text{Tr} \{ \ln(1 - v\chi_0(i\omega)) + v\chi_0(i\omega) \},$$  \hspace{1cm} (1)

where $\chi_0$ is the bare response function of the system and $v$ is the interaction potential. Usually $\chi_0(r, r'; i\omega)$ is a two-point function computed using Kohn–Sham orbitals and orbital energies obtained from a density functional approximation.

However, it is also possible (e.g. [12]) to approximate $\chi_0$ by a sum of atomic contributions represented by quantum harmonic oscillators. This allows the spatial integrals to be
carried out analytically so that they can be replaced by finite matrices, greatly reducing the computational work. As shown by Ambrosetti et al [6], the dispersion energy in this approximation can be written as:

\[ E_{\text{disp}} = -\int_0^\infty \frac{\omega}{2\pi} \text{Tr}[\ln(1 - A_{LR}(\omega)T_{LR})], \]

(2)

with \( T_{LR} \) being the long-range interaction tensor, which describes the interaction of the screened polarizabilities embedded in the system in a given geometrical arrangement. For a system consisting of \( N_a \) atoms, the dimension of \( T_{LR} \) is \( 3N_a \times 3N_a \). The matrix elements of \( T_{LR} \) are defined as:

\[ T_{\alpha\beta}^{\rho\sigma}(j) = f(\tilde{S}_{vdw,ij}(\omega))T_{ij}^{\rho\sigma}, \]

(3)

where the usual full-range second-order interaction tensor is defined as:

\[ T_{ij}^{\rho\sigma} = \delta_{\rho\sigma} \frac{1}{r_{ij}} - \frac{3r_{ij}^2}{5r_{ij}^2} \delta_{\rho\sigma}. \]

(4)

The indices \( i \) and \( j \) label atoms, Greek symbols stand for the Cartesian components of the position vector \( r \). The damping function, \( f(\tilde{S}_{vdw,ij}(\omega)) \), is defined as follows:

\[ f(\tilde{S}_{vdw,ij}(\omega)) = \frac{1}{1 + \exp[-d(r_{ij}/\tilde{S}_{vdw} - 1)]} \]

with \( d \) being a parameter fixed to the value of six. The range-separation parameter \( \tilde{S}_{vdw} \) is proportional to the sum of the van der Waals radii \( (\tilde{R}_{vdw,i}) \) for the screened atoms \( i \) and \( j \), which are obtained by the self-consistent screening (SCS) procedure (see appendix B):

\[ \tilde{S}_{vdw,ij} = \beta(\tilde{R}_{vdw,i} + \tilde{R}_{vdw,j}). \]

(6)

The adjustable proportionality parameter \( \beta \) must be determined for the given DFT functional such as to minimize the mean absolute relative error (MARE) for interaction energies of the S66x8 benchmark set [16], see [6] for more details. In this work we use \( \beta = 0.83 \), as found for the PBE functional [6].

An element of the frequency-dependent polarizability matrix, \( A_{LR}(\omega) \), is defined as:

\[ A_{\alpha\beta}^{\rho\sigma}(\omega) = \tilde{\alpha}_{\alpha}^{\rho\sigma}(\omega) \delta_{ij} \delta_{\alpha\beta}. \]

(7)

where \( \tilde{\alpha}_{\alpha}^{\rho\sigma}(\omega) \) equals one third of trace of the frequency-dependent polarizability tensor for the short-range screened atom-in-molecule \( (\tilde{\alpha})(\omega) \) computed by solving the SCS equation:

\[ \tilde{\alpha}(\omega) = \alpha_{\Gamma}^{\text{TS}}(\omega)(1 - T_{SR}(\omega) \tilde{\alpha}(\omega)), \]

(8)

and \( \alpha_{\Gamma}^{\text{TS}}(\omega) \) is the frequency dependent polarizability of Hirshfeld’s atom-in-molecule [17], see appendix A (equation (A.4)). It is to be stressed that only near neighbors of each atom are assumed to contribute significantly to the self-consistent screening in equation (8). One can thus avoid double-counting the screening effects, which are present in the energy expression via the implicit solution of the interacting polarizability equation under the logarithm. Since the energy expression deals only with the long-range effects, the missing short-range screening had to be incorporated in a separate step.

In practice, the SCS equation is solved via partial contraction of the short-range many-body polarizability matrix, see appendix B. The short-range interaction tensor used in equation (8), in contrast to the long-range one, is defined as

\[ T_{\text{SR},ij}^{\rho\sigma}(\omega) = (1 - f(\tilde{S}_{vdw,ij}(\omega)))\partial_{\rho\sigma}^{ij} \left[ \frac{\text{erf}(r_{ij}/\sigma_{\rho\sigma}(\omega))}{r_{ij}} \right]. \]

(9)

In this expression, the damping function \( f(\tilde{S}_{vdw,ij}(\omega)) \) is defined using van der Waals radii \( (R_{vdw,i}) \) computed from the unscreened atoms-in-molecule polarizabilities, see appendix A (equation (A.6)):

\[ S_{vdw,ij} = \beta(R_{vdw,i} + R_{vdw,j}). \]

(10)

We note that the value of the adjustable parameter \( \beta \) is the same as in equation (6). After taking the second derivative indicated in equation (9) we obtain:

\[ T_{\text{SR},ij}^{\rho\sigma}(\omega) = (1 - f(\tilde{S}_{vdw,ij}(\omega))) \left\{ -T_{ij}^{\rho\sigma} \left[ \frac{\text{erf}(r_{ij}/\sigma_{\rho\sigma}(\omega))}{r_{ij}} \right] \right\} - \frac{2}{\sqrt{\pi}} \left( \frac{r_{ij}}{\sigma_{\rho\sigma}(\omega)} \right) e^{-\frac{r_{ij}^2}{\sigma_{\rho\sigma}^2(\omega)}} + \frac{4}{\sqrt{\pi}} \left( \frac{r_{ij}}{\sigma_{\rho\sigma}(\omega)} \right)^3 e^{-\frac{3r_{ij}^2}{\sigma_{\rho\sigma}^2(\omega)}} \]

(11)

where \( \sigma_{\rho\sigma}(\omega) \) is the frequency-dependent attenuation length for the atomic pair \( ij \) as defined in equation (B.2).

Finally, it should be mentioned that the many-body dispersion energy of equation (2) can alternatively be determined using the coupled fluctuating dipole model (CFDM) approach [12, 18] which has the advantage that the numerical integration over frequency is avoided. In the present work we focus on the original RPA framework since it allows us to derive the expressions for stress and forces in a simple and clear fashion.

II.B. A system under periodic boundary conditions

Let us consider a system under periodic boundary conditions (PBC) with \( N_a \) atoms per simulation cell of volume \( V \). The structure of this system is characterized by three lattice vectors \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) arranged in the matrix \( h = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3] \), and by the \( 3N_a \) Cartesian coordinates, \( r = [r_{ij}^3] \). The energy expression for such a system should include not only the interactions between atoms located in the same unit cell but also the interactions between atoms occupying different cells. This can be achieved by two different ways of implementing the MBD method: a real-space implementation, as employed by Tkatchenko et al [19, 20], or a reciprocal-space implementation, which we propose in this work.

In both cases, the screened frequency-dependent polarizabilities (equation (8)), which define the long-range polarizability matrix \( A_{LR}(\omega) \), are computed by the procedure described in appendix B using the short-range interaction tensor of dimension \( 3N_a \times 3N_a \), defined as follows:
where the summations are over \( N_{\text{at}} \) atoms contained in a single unit cell and all translations of the unit cell \( \mathbf{L} = \{ \pm h_1, \pm h_2, \pm h_3 \} \), \( r_{ij,L} \) is a distance between an atom \( i \) and atom \( j \) shifted from the original unit cell (\( \mathbf{L} = 0 \)) by a lattice translation \( h_1 \mathbf{a}_1 + h_2 \mathbf{a}_2 + h_3 \mathbf{a}_3 \), and the prime indicates that the term corresponding to \( \mathbf{L} = 0 \) is omitted from summation if \( i = j \). In practice, the (infinite) lattice sum in equation (12) is truncated when the interatomic distances \( r_{ij,L} \) are greater than a certain prescribed maximal interaction radius \( R_{\text{SR}}\text{cut} \). Although the tensor \( T_{\text{SR}} \) is used in the short-range SCS equation (equation (8)), a relatively large value of \( R_{\text{SR}}\text{cut} \) has to be used in order to obtain well converged screened polarizabilities. This is because the range separation is continuous and it is achieved by the use of a damping function (equation (5)) that grows relatively slowly with distance. In our calculations, \( R_{\text{SR}}\text{cut} \) was set to 120 Å, and a further increase of this value did not lead to significant change of the computed energies of systems considered in this work.

II.B.1. Real-space approach. In order take into account interactions between atoms located in different unit cells, a supercell consisting of \( N_{\text{cell}} = L_x \times L_y \times L_z \) multiples of the original cell is defined and used to compute dispersion energy:

\[
E_{\text{disp}} = \frac{1}{N_{\text{cell}}} \int_0^\infty \frac{d\omega}{2\pi} \text{Tr} \left\{ \mathbf{1} - A^{\text{cell}}_{\text{LR}}(\omega) \mathbf{T}_{\text{LR}}^{\text{cell}}(\omega) \right\},
\]

where the tensors \( \mathbf{T}_{\text{cell}} \) and \( A_{\text{cell}}^{\text{cell}} \) are defined as follows:

\[
A_{\text{cell},\alpha \beta}(\omega) = \delta_{\alpha \beta} \delta_{ij} \delta_{\tilde{j} \tilde{i}} \delta_{\tilde{\alpha} \tilde{\beta}},
\]

and

\[
T_{\text{LR},ij,\tilde{\alpha} \tilde{\beta}} = f(\tilde{\mathbf{x}}_{\text{SR}}, \mathbf{r}_{ij}, L_x, L_y, L_z) T_{\alpha \beta,\tilde{\alpha} \tilde{\beta}},
\]

with \( \tilde{i} \) being an index used to label atom \( i \) shifted from the original unit cell by a lattice translation \( L_x \mathbf{a}_1 + L_y \mathbf{a}_2 + L_z \mathbf{a}_3 \), and the minimum image convention is used in definition of vectors \( \mathbf{r}_{ij} = r_{ij,L} \). The dimensions of tensors \( \mathbf{T}_{\text{cell}} \) and \( A^{\text{cell}}_{\text{LR}} \) are \( (3N_{\text{at}}N_{\text{cell}}) \times (3N_{\text{at}}N_{\text{cell}}) \) which in most cases causes a drastic increase of computational cost compared to a molecule or a molecular complex.

II.B.2. Reciprocal-space approach. Expensive supercell calculations can be avoided through the use of reciprocal space. Let us consider the real-space MBD dispersion energy expression (equivalent to equation (13)) in the ACFDFT (adiabatic connection fluctuation-dissipation theorem) form, which includes both the integral over the frequency and over the interaction strength

\[
E^{\text{ACFDT}}_{\text{disp}} = \frac{1}{N_{\text{cell}}} \int_0^\infty \frac{d\omega}{2\pi} \text{Tr} \left\{ \mathbf{1} - A^{\text{cell}}_{\text{LR}}(\omega) \mathbf{T}_{\text{LR}}^{\text{cell}}(\omega) - A^{\text{cell}}(\omega) \mathbf{T}^{\text{cell}}(\omega) \right\},
\]

where

\[
A^{(0)}_{\text{LR}}(\omega) = \int_0^\infty d\omega T^{(0)}_{\text{LR}}(\omega),
\]

and

\[
T^{(0)}_{\text{LR}}(r, r') = T^{(0)}_{\text{LR}}(r - r')
\]

and \( T^{(0)}_{\text{LR}}(r, r) = 0 \) representing the dipole-dipole interactions between different atoms located respectively at \( r \) and \( r' \). The matrix \( A^{(0)}_{\text{LR}}(\omega) \) satisfies the following self-consistent, Dyson-like equation,

\[
A^{(0)}_{\text{LR}}(\omega) = A^{(0)}_{\text{cell}}(\omega) + \lambda A^{(0)}_{\text{LR}}(\omega) T^{(0)}_{\text{cell}} A^{(0)}_{\text{LR}}(\omega).
\]

In a periodic system, the atom at \( r \) can be described by a label \( a \), giving the position \( \mathbf{r}_a \) in the unit cell, and a lattice translation parameter \( \mathbf{L}_a \) labeling the cell. As a consequence of the translational invariance, the interaction tensor matrix elements depend only on the difference of the lattice translations \( \mathbf{L} = \mathbf{L}_i - \mathbf{L}_j \), thus \( T^{(0)}(\mathbf{r}_i - \mathbf{r}_j + \mathbf{L}) = T^{(0)}(\mathbf{L}) \), \( T^{(0)}(\mathbf{r}_i + \mathbf{L}) = T^{(0)}(\mathbf{L}) \). Let us write explicitly the matrix product under the trace (the subscript \( LR \) is omitted for the sake of notational clarity and sums over repeated Greek indices are implied):

\[
\sum_{m=1}^{N_{\text{cell}}} \sum_{c=1}^{N_{\text{cell}}} A^{(\lambda \alpha \gamma)}_{c\alpha c}(\omega) T^{(0)}_{\alpha \beta,\lambda \gamma}(\mathbf{L}) = \int_{\text{FBZ}} d\mathbf{k} \int_{\text{FBZ}} d\mathbf{k}' A^{(\lambda \alpha \gamma)}_{\mathbf{k}\mathbf{k}'}(\omega) T^{(0)}_{\alpha \beta,\lambda \gamma}(\mathbf{L}) e^{-\mathbf{i} \mathbf{L} \cdot \mathbf{k}'} \sum_{\mathbf{L}_m} e^{\mathbf{i} \mathbf{L} \cdot \mathbf{k}'},
\]

where \( \mathbf{L}_m \) runs over the \( N_{\text{cell}} \) sites of the Brillouin lattice. The Dirac delta function in equation (20) comes from the limit of infinite \( N_{\text{cell}} \), in which \( \mathbf{k} \) and \( \mathbf{k}' \) become vectors from the first Brillouin zone (FBZ) with volume \( \text{FBZ} = (2\pi)^3 \). The Fourier components of the interaction matrix elements are

\[
T^{(0)}_{\alpha \beta,\lambda \gamma}(\mathbf{L}) = \int_{\text{FBZ}} d\mathbf{k} \int_{\text{FBZ}} d\mathbf{k}' A^{(\lambda \alpha \gamma)}_{\mathbf{k}\mathbf{k}'}(\omega) T^{(0)}_{\alpha \beta,\lambda \gamma}(\mathbf{L}) e^{-\mathbf{i} \mathbf{k}' \cdot \mathbf{L}},
\]

where

\[
\sum_{\mathbf{L}} e^{\mathbf{i} \mathbf{L} \cdot \mathbf{k}'} \mathbf{L}_m = N_{\text{cell}} \mathbf{b}_{\mathbf{k}' \cdot \mathbf{k}},
\]

and

\[
A^{(0)}_{\alpha \beta,\lambda \gamma}(\mathbf{L}) = \int_{\text{FBZ}} d\mathbf{k} A^{(\lambda \alpha \gamma)}_{\mathbf{k}\mathbf{k}'}(\omega) T^{(0)}_{\alpha \beta,\lambda \gamma}(\mathbf{L}) e^{-\mathbf{i} \mathbf{k}' \cdot \mathbf{L}},
\]

In our calculations, the trace of matrix \( \mathbf{X} \) is defined as \( \text{Tr}[\mathbf{X}] = \sum_{\alpha \beta} X^{(0)}_{\alpha \beta} \) for a general system without symmetry. On a periodic lattice, the additional symmetries mean that the
trace becomes $N_{cc}^\gamma \text{Tr}[X] = \sum_{\alpha \delta} X_{\alpha \delta}^{\omega_{\omega}} \omega_{\omega} = \sum_{\alpha \delta} \frac{1}{V_{FBZ}} \int d\mathbf{k} X_{\alpha \delta}^{\omega_{\omega}}$
where we used the Fourier transform for $L = \mathbf{0}$ for the second identity. Thus, using (19) with $L = \mathbf{L}$, the ACFDT dispersion energy equation, equation (16) becomes
\[ E_{\text{disp}}^{\text{ACFDT}} = - \int_0^\infty \frac{d\lambda}{V_{FBZ}} \int d\mathbf{k} \sum_{m n} \frac{1}{2\pi} \text{Tr}\left\{ \sum_{\alpha} \left( A_{\alpha}^{\lambda}(\omega) T_{\alpha \gamma}^{\lambda}(\omega) - A_{\alpha}^{\lambda}(\omega) T_{\alpha \gamma}^{\lambda}(\omega) \right) \right\}, \]
where the trace operation involves the summation over the atomic sites of the Bravais lattice and on the Cartesian components of the polarizability and interaction matrices.

The Dyson equation, equation (17) can also be written in components:
\[ A_{ij}^{\lambda \alpha \beta}(\omega) = A_{ij}^{\lambda \alpha \beta}(\omega) + \lambda \sum_{m n} A_{m n}^{\lambda \alpha \beta}(\omega) T_{m n}^{\beta \beta}(\omega), \]
which can be transformed into a series of analogous steps as before to obtain a separate equation for each polarizability matrix $A_{\alpha \beta}^{\lambda \alpha \beta}(\omega)$ labeled by the vector $\mathbf{k}$ belonging to the FBZ:
\[ A_{\alpha \beta}^{\lambda \alpha \beta}(\omega) = A_{\alpha \beta}^{\lambda \alpha \beta}(\omega) + \lambda \sum_{cd} A_{cd}^{\lambda \alpha \beta}(\omega) T_{cd}^{\beta \beta}(\omega) A_{\alpha \beta}^{\lambda \alpha \beta}(\omega). \]
The iterative solution can equivalently be written in matrix notation as
\[ A_{\lambda}^{k}(\omega) = \sum_{\alpha = 0}^{\infty} \lambda^n (A^{(0)} T^{n})^{\alpha} A^{(0)}. \]
Here we used $A^{(0)} = A^{(0)} T^{0}$ (because the matrix is diagonal in $ij$ and thus is diagonal in $ab$ and non-zero only for $L = \mathbf{0}$) to give $A^{(0)} = \sum L^L L^{-L} A^{(0)}$ is independent of $k$.

Inserting the above series in the reciprocal space expression of the ACFDT dispersion energy makes it easy to perform the integration according to the adiabatic connection variable, $\lambda$. Provided that the sum is convergent, the resulting series can be re-summed as:
\[ E_{\text{disp}}^{\text{ACFDT}} = - \int_0^\infty \frac{d\lambda}{V_{FBZ}} \int d\omega \frac{1}{2\pi} \text{Tr}\left\{ \sum_{\alpha = 1}^{\infty} \frac{1}{n + 1} (A^{(0)}(\omega) T^{n})^{\alpha} \right\}, \]
where $\mathbf{T}_k$ is a $3N_a \times 3N_a$ matrix and $A(\omega)$ is a diagonal matrix of the same dimensions. The quantity $\text{Tr}\{ A^{\lambda}(\omega) T^{\lambda} \} = 0$ due to the fact that the diagonal blocks of $\mathbf{T}_k$ and the off-diagonal part of $A^{(0)}(\omega)$ are both zero.

Finally, the dispersion energy becomes:
\[ E_{\text{disp}} = - \int_0^\infty \frac{d\lambda}{V_{FBZ}} \frac{d\omega}{2\pi} \text{Tr}\{ \ln(1 + A^{(0)}(\omega) T_{LR}(\mathbf{k})) \}. \]

The elements of the reciprocal space long-range dipole-dipole interaction tensor $\mathbf{T}_{LR}(\mathbf{k})$ are, in general, complex numbers defined as:
\[ T_{\alpha \beta}^{\gamma \delta}(\mathbf{k}) = \sum_{L} f(S_{\alpha \beta}^{(0)}(\mathbf{r}_{\gamma \delta} L)) L_{\gamma \delta}^{\alpha \beta} e^{-i \mathbf{k} \cdot \mathbf{L}}. \]

The polarizability matrix $A_{LR}$, which is independent of $\mathbf{k}$, has already been defined by equation (7). It follows from the symmetry of the problem that the following relations hold: $T_{LR}(\mathbf{k})^* = T_{LR}(\mathbf{k})$, $T_{LR}(\mathbf{k}) = (T_{LR}(\mathbf{k}))^*$, and $T_{LR}(\mathbf{k}) = T_{LR}(\mathbf{k})$. In practice, the integration over the first Brillouin zone in equation (28) is performed using a numerical quadrature
\[ E_{\text{disp}} = - \sum_{k \in IBZ} w_k \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}\{ \ln(1 + A_{LR}(\omega) T_{LR}(\mathbf{k})) \}, \]
where the sum is taken over points of the irreducible part of the first Brillouin zone with weighting factors $w_k$ given by symmetry. For this purpose, a number of efficient schemes such as Monkhorst-Pack method [22] have been proposed. Note that dimensions of both $T_{LR}(\mathbf{k})$ and $A_{LR}$ matrices are $3N_a \times 3N_a$. Hence in the reciprocal-space implementation of the method one has to solve $N_{FBZ}$ (the number of quadrature points to integrate over the first Brillouin zone) problems of dimensionality of $3N_a$ instead of a single problem of dimensionality of $3N_a \times N_{cell}$, as in the real-space method. Such an algorithm is, in general, computationally much more effective.

III. Gradients and stresses

The expression for generalized forces (atomic forces and stresses) due to the MBD@rsSCS interaction in a system under PBC (equation (28)) takes the form:
\[ E_{\text{disp}} = - \sum_{k \in IBZ} w_k \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}\{ \frac{1}{1 + A_{LR}(\omega) T_{LR}(\mathbf{k})} G(\mathbf{k}, \omega) \}, \]
where
\[ G(\mathbf{k}, \omega) = \nabla [A_{LR}(\omega) T_{LR}(\mathbf{k})] = A_{LR}(\omega) [\nabla T_{LR}(\mathbf{k})] + [\nabla A_{LR}(\omega)] T_{LR}(\mathbf{k}) \]

involves variations in the long-range part of the Coulomb potential and the screened polarizabilities. Here $\nabla$ indicates derivatives with respect to ionic positions $r^a_\alpha$ or lattice parameters $h^\gamma$.

We note that in addition to the explicit derivatives with respect to the atomic positions and lattice parameters given in detail in the appendix C, there are also implicit derivatives involving the effective volumes of the sub-systems (equation (A1)), arising from possible changes in the partitioning. These contributions are in general assumed to be small and are neglected in our implementation.

IV. Numerical tests and applications

All calculations presented in this work have been performed using the periodic DFT code VASP [23–25], the keywords needed to perform a PBE + MBD@rsSCS calculation are described in appendix D. The DFT part of calculations have been performed using the Perdew–Burke–Ernzerhof (PBE) functional [26]. The electronic energies computed in self-consistent loops were converged to an accuracy of
As we can see from Table 1, $\epsilon_{\text{vdW}}$ increases linearly with $1/N_k$ and converges at $1/N_k \approx 0.1$.

In this section we examine the validity of the energy gradient expressions derived in Section III. As a simple model system we have chosen crystalline silicon with diamond structure. We note that the cell volume is the only free parameter to relax in the case of the unperturbed Si because the cell shape and the cell volume are determined independently of the cell shape.

### IV.A. Real space versus reciprocal space implementation

As an illustration of CPU-time saving due to the replacement of the real-space MBD at rsSCS method by its reciprocal-space implementation, let us consider dispersion energy calculation for a bilayer of graphene. In this example, the real-space calculations of dispersion energy were performed with a $16 \times 16 \times 1$ supercell (256 atoms) and the reciprocal-space calculations with a $\Gamma$-centered mesh of $16 \times 16 \times 1$ $k$-points (out of which only 73 points sampled the irreducible part of Brillouin zone and were actually used in the energy calculation (equation (30))). The planewave cutoff of 1000 eV was used in both cases. The calculations were performed on an ordinary desktop PC with four cores and 4 GB of RAM. As expected, both MBD implementations yielded identical dispersion energies ($\sim 90$ meV atom$^{-1}$) but the CPU times were drastically different: 1997 s (real-space) versus 6 s (reciprocal-space).

The remaining tests described in this section have been performed only with the reciprocal space implementation of the method.

### IV.B. Convergence of energy with respect to the number of $k$-points

In order to test the convergence of the energy with respect to the number of $k$-points we have chosen graphite, which is a typical vdW system. Ambrosetti et al [6] reported real-space MBD calculations for this system performed with a supercell consisting of $11 \times 11 \times 7$ multiples of the primitive cell and containing as many as 3388 atoms. This represents a significant computational load but, as discussed in Section IV.B and demonstrated in Section IV.A, identical results can be obtained more efficiently by using the reciprocal space approach with the primitive cell and a Brillouin-zone sampling by $11 \times 11 \times 7$ $k$-points. In our test calculations, the unit cell parameters $a_1 = a_2 = 2.459 \, \text{Å}$, and $c = 6.675 \, \text{Å}$.

In order to examine convergence of the vdW energy, the $k$-point grid used in DFT calculations was fixed at $16 \times 16 \times 8$, while that for the dispersion energy calculations (equation (30)) has been adjusted independently, using the formula $k_i = \text{int}(R_{\text{cut}}/|a_i|)$ where $R_{\text{cut}}$ is a parameter controlling the longest interatomic separation taken into account in dispersion energy calculations, int(x) expresses the integer part of x, and $k_i$ is the number of $k$-points in the direction of a vector that is reciprocal to a lattice vector $a_i$.

As obvious from Table 1, $R_{\text{cut}}$ of $\sim 40$ Å (corresponding to a $k$-point mesh of $16 \times 16 \times 6$) was needed to have $E_{\text{disp}}$ converged within $\sim 1$ meV cell$^{-1}$. The error in $E_{\text{disp}}$ decreases approximately linearly with the inverse of the number of $k$-points (or equivalently with the $1/R_{\text{cut}}^2$ term), see Figure 1. This relationship could be useful for extrapolating the converged values of $E_{\text{disp}}$ in the case of complicated systems with very long-range interactions. As the corresponding $k$-point mesh of $(16 \times 16 \times 6)$ is similar to the $k$-mesh used in the DFT energy ($E_{\text{DFT}}$) calculation $(16 \times 16 \times 8)$, it is of interest to compare the convergence of $E_{\text{disp}}$ with that of $E_{\text{DFT}}$. In our next test we use the same $k$-point mesh (again controlled using the parameter $R_{\text{cut}}$) for both $E_{\text{DFT}}$ and $E_{\text{disp}}$. The results are compiled in Table 2. Interestingly, the absolute error in the dispersion energy is comparable to that of the DFT energy in most cases and the convergence of the total energy within 1 meV cell$^{-1}$ is achieved with the same setting as needed for the convergence of the DFT part of the total energy. This result implies that the typical $k$-point setting used in uncorrected DFT is sufficient for routine DFT + MBD calculations.

### IV.C. Numerical tests of the gradients

In this section we examine the validity of the energy gradient expressions derived in Section III. As a simple model system we have chosen crystalline silicon with diamond structure. We note that the cell volume is the only free parameter to relax in the case of the unperturbed Si because the cell shape and the cell volume are determined independently of the cell shape.
atomic positions are fixed by symmetry. Although crystalline Si is not considered as a typical vdW system, it is a suitable test case for our purposes because it consists of highly polarizable atoms packed in relatively dense structure and therefore beyond-pairwise contributions play a significant role. The calculations have been performed using the primitive cell of Si, with a $8\times8\times8$ mesh of $k$-points, while the planewave cutoff was set to 1000 eV. The external pressure applied to a solid can be computed by averaging the diagonal components of the stress-tensor:

$$p_{\text{ext}} = -\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}).$$

(33)

Alternatively, $p_{\text{ext}}$ can be obtained from a fit of the energy variation versus the volume by a suitable equation of states (EOS), such as Murnaghan EOS [29], for which the volume dependence on the pressure is:

$$p_{\text{ext}} = \frac{B_0}{B_0'} \left( \frac{V}{V_0} \right)^{-B_0} - 1.$$  

(34)

Of course, if the corrections to the energy and to its gradients are mutually consistent, the two approaches must yield identical results. In figure 2 we compare the pressures computed using equation (33) with those determined from the EOS fitting (equation (34)) at different unit cell volumes. It is obvious that the vdW correction to the stress tensor is far from being negligible: if it is not applied, the agreement between the two approaches is very poor, while the pressure computed from the vdW corrected stress tensor agrees very well with the result of the EOS fit. Ambrosetti et al [6] suggested an approximation to the gradients in which the time-consuming derivative of polarizability matrix is neglected. As demonstrated in figure 2, this approximation leads to a systematic underestimation of the computed pressure.

In our second test we have compared the gradients computed analytically with those calculated numerically from the total energies using the five-point formula:

$$f'(x) = \frac{-f(x + 2\epsilon) + 8f(x + \epsilon) - 8f(x - \epsilon) + f(x - 2\epsilon)}{12\epsilon},$$

(35)

with $\epsilon = 0.005$ Å. As a model system, a distorted structure of the $2\times2\times2$ supercell of Si in the diamond phase has been used. The calculations have been performed on a mesh of $4\times4\times4$ $k$-points and with a planewave cutoff of 1000 eV. The maximal force acting on the atoms in the initial structure was $1.36$ eV Å$^{-1}$ (the contribution of MBD was $0.01$ eV Å$^{-1}$). For the pure PBE calculation, the root-mean-square deviation (RMSD) of analytical gradients ($g_a$) from the numerical ones ($g_n$) is $6.7 \cdot 10^{-5}$ eV Å$^{-1}$. When the MBD correction was taken into account, the RMSD increased to $9.7 \cdot 10^{-4}$ eV Å$^{-1}$. This small increase of the error compared to the uncorrected PBE is mainly due to the neglected electronic density-dependence of gradients (which enter via Hirshfeld volumes, see appendix A). In order to demonstrate this fact, a test simulation was performed in which all relative Hirshfeld volumes $v_{\text{rel}}^{\text{vdw}}$ were fixed at unity. The RMSD of gradients decreased to $6.9 \cdot 10^{-3}$ eV Å$^{-1}$ in this case, which is very similar to the result obtained using the uncorrected PBE method. We have also examined the quality of gradients computed with neglected $\nabla A_{1R}(\omega)$ term (see equation (31)), as suggested by Ambrosetti et al [6]. In this case, the RMSD is $2.9 \cdot 10^{-3}$ eV Å$^{-1}$, which is significantly larger than that obtained using the complete gradient formula. This result, combined with results of our test calculations of pressure, shows that the polarizability derivative contribution to the gradients is significant and should not be neglected in practical applications.

IV.D. Benchmark set X23

As a further test, we have performed atomic and lattice optimizations and cohesive energy calculations on the X23 benchmark set consisting of 23 molecular crystals. This benchmark set has been elaborated by Reilly and Tkatchenko [4] on the

**Table 2.** Variation of error for DFT ($\epsilon_{\text{DFT}}$), vdW ($\epsilon_{\text{vdW}}$), and total ($\epsilon_{\text{tot}}$) energies of graphite with the number of $k$-points.

<table>
<thead>
<tr>
<th>$R_{\text{cut}}$ (Å)</th>
<th>k-point mesh</th>
<th>$\epsilon_{\text{DFT}}$ (meV cell$^{-1}$)</th>
<th>$\epsilon_{\text{vdW}}$ (meV cell$^{-1}$)</th>
<th>$\epsilon_{\text{tot}}$ (meV cell$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$4 \times 4 \times 1$</td>
<td>38.3</td>
<td>97.9</td>
<td>136.2</td>
</tr>
<tr>
<td>15</td>
<td>$6 \times 6 \times 2$</td>
<td>88.3</td>
<td>23.9</td>
<td>112.2</td>
</tr>
<tr>
<td>20</td>
<td>$8 \times 8 \times 3$</td>
<td>$-2.8$</td>
<td>8.9</td>
<td>6.1</td>
</tr>
<tr>
<td>25</td>
<td>$10 \times 10 \times 4$</td>
<td>$-5.8$</td>
<td>4.5</td>
<td>$-1.3$</td>
</tr>
<tr>
<td>30</td>
<td>$12 \times 12 \times 4$</td>
<td>7.8</td>
<td>3.3</td>
<td>11.1</td>
</tr>
<tr>
<td>35</td>
<td>$14 \times 14 \times 5$</td>
<td>$-1.8$</td>
<td>1.6</td>
<td>$-0.2$</td>
</tr>
<tr>
<td>40</td>
<td>$16 \times 16 \times 6$</td>
<td>$-0.7$</td>
<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>50</td>
<td>$20 \times 20 \times 7$</td>
<td>$-0.8$</td>
<td>0.4</td>
<td>$-0.5$</td>
</tr>
<tr>
<td>60</td>
<td>$24 \times 24 \times 9$</td>
<td>0.4</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>80</td>
<td>$33 \times 33 \times 12$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Note:** The same $k$-point mesh was used for both the DFT and the vdW calculations. The error is defined with respect to the energy obtained from the calculation performed with the grid of $33 \times 33 \times 12$ $k$-points.
basis of earlier work of Otero-de-la-Rosa and Johnson [30]. The simulations have been performed with a plane-wave cutoff of 1000 eV and the k-point mesh for the Brillouin zone sampling was adjusted according to the size of each unit cell (see table S1 in the supplemental material7 (stacks.iop.org/JPhysCM/28/045201/mmedia)). The relaxed geometries compare well with the reference data (see table S2 in the supplemental material8 (stacks.iop.org/JPhysCM/28/045201/mmedia)): the mean absolute relative error (MARE) for the unit cell volumes and for the lengths of cell vectors are 1.9% and 1.2%, respectively. The reference cohesive energies were derived from the experimental sublimation enthalpies by Reilly and Tkatchenko [4], whereby the thermal effects and the zero-point energy have been taken into account. The accuracy of computed cohesive energies with respect to this reference is quite satisfactory (see table S3 in the supplemental material9 (stacks.iop.org/JPhysCM/28/045201/mmedia)), the mean absolute error (MAE) is 5.9 kJ mol\(^{-1}\) and the MARE is 7.6%. These values are similar to those reported for these systems by Ambrosetti et al [6] (MAE 5.0 kJ mol\(^{-1}\), MARE 6.6%), the relatively small differences in statistics are most likely due to the use of different computational setup, and the structure of systems for which the cohesive energies were computed (in this work we have used structures that were fully relaxed by the PBE + MBDr@rsSCS method while [6] does not report structural relaxations).

**IV.E. Benchmark set ICE10**

Brandenburg et al [7] have proposed a set of ten ice polymorphs as a benchmark set (ICE10) to test the performance of vdW-corrected DFT. The reference lattice geometries and lattice energies [31] were derived from experimental data, whereby the thermal effect and zero-point vibrations have been taken into account. In this work, we have performed calculations with the PBE + MBDr@rsSCS method. All systems under consideration were fully relaxed using the geometries and simulation setup of [7] (see supplemental material10 for details (stacks.iop.org/JPhysCM/28/045201/mmedia)). The results for the lattice energies and for the cell volumes are compiled in tables 3 and 4, respectively, and they are compared with the results of uncorrected PBE and of dispersion-corrected PBE + D\(^3\)\_ATM calculations [7, 32]. The PBE + D\(^3\)\_ATM method takes into account, beyond the pair interactions, three-body (of Axilrod–Teller–Muto (ATM) type [8, 9]) dispersion effects too. The ground-state geometries for all ICE10 systems are compiled in table S5 in the supplemental material11 (stacks.iop.org/JPhysCM/28/045201/mmedia). As shown in tables 3 and 4, the PBE + MBDr@rsSCS yields similar, albeit slightly worse results than the PBE + D\(^3\)\_ATM for both lattice energies and cell volumes. Compared to the

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Exp. [7]</th>
<th>PBE [7]</th>
<th>PBE + D(^3)_ATM</th>
<th>PBE + MBDr@rsSCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ih</td>
<td>30.9</td>
<td>30.2</td>
<td>29.2</td>
<td>29.0</td>
</tr>
<tr>
<td>II</td>
<td>24.0</td>
<td>24.5</td>
<td>23.3</td>
<td>23.1</td>
</tr>
<tr>
<td>III</td>
<td>25.3</td>
<td>26.4</td>
<td>24.6</td>
<td>24.2</td>
</tr>
<tr>
<td>VI</td>
<td>22.0</td>
<td>22.3</td>
<td>21.0</td>
<td>20.9</td>
</tr>
<tr>
<td>VII</td>
<td>19.3</td>
<td>20.4</td>
<td>19.0</td>
<td>19.0</td>
</tr>
<tr>
<td>VIII</td>
<td>19.1</td>
<td>20.4</td>
<td>19.2</td>
<td>19.1</td>
</tr>
<tr>
<td>IX</td>
<td>25.0</td>
<td>26.2</td>
<td>24.3</td>
<td>24.1</td>
</tr>
<tr>
<td>XIV</td>
<td>23.0</td>
<td>23.6</td>
<td>22.4</td>
<td>22.1</td>
</tr>
<tr>
<td>XV</td>
<td>22.3</td>
<td>22.9</td>
<td>21.6</td>
<td>21.4</td>
</tr>
<tr>
<td>MARE</td>
<td>—</td>
<td>3.6</td>
<td>2.8</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Note: The lattice energies including only the two-body part of dispersion correction are given in parentheses. Mean absolute errors (MAE), given in kcal mol\(^{-1}\), are computed only for the subset of structures, for which the reference data are available (polymorphs Ih to IX).

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Exp. [7]</th>
<th>PBE [7]</th>
<th>PBE + D(^3)_ATM</th>
<th>PBE + MBDr@rsSCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ih</td>
<td>3.6</td>
<td>3.2</td>
<td>2.7</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Note: Mean absolute errors (MARE) are given in Å\(^3\)/molecule.

experimental reference, the lattice energies are systematically overestimated with MARE = 2.4 kcal mol\(^{-1}\) (MARE for PBE + D\(^3\)\_ATM is 2.0 kcal mol\(^{-1}\)). The computed ground state volumes are underestimated, the computed MARE is 3.6% (MARE for PBE + D\(^3\)\_ATM is 2.8%). In close agreement with PBE + D\(^3\)\_ATM, PBE + MBDr@rsSCS predicts the magnitude of the beyond-pairwise dispersion interactions to be ~0.2 kcal mol\(^{-1}\) for all systems.

As shown by Brandenburg et al [7], the agreement of theory with experiment can be further improved if the semi-local DFT functional (PBE in this work) is replaced by a hybrid functional. This is, however, beyond the scope of the present study.

**IV.F. Layered systems**

Layered compounds represent an important class of materials in which van der Waals forces are essential for the cohesion. In this section, we examine the performance of the

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7 See supplemental material at [URL will be inserted by AIP] for the values of computed atoms-in-molecule polarizabilities, and numerical results for S22 and X40 benchmark sets.
8 See footnote 7.
9 See footnote 7.
10 See footnote 7.
11 See footnote 7.
MBD@rsSCS method to predict structural and binding properties of graphene bilayers, graphite, and hexagonal boron-nitride (h-BN). Our results are compared with the available experimental data and with computational results obtained by high-level methodologies, like diffusion Monte Carlo or Random Phase Approximation.

IV. F. 1. Graphene bilayers. Diffusion Monte Carlo (DMC) calculations of binding energies for the AB- and AA-stacked graphene bilayers have recently been obtained by Mostaani et al [33]. The reported interlayer binding energies ($E_{\text{bind}}$) and interlayer separations ($d$) are $E_{\text{bind}} = -17.7 \text{ meV}$ and $d_0 = 3.384 \text{ Å}$ for the AB-, and $E_{\text{bind}} = -11.5 \text{ meV}$ and $d = 3.495 \text{ Å}$ for the AA-stacked bilayer. In order to determine the interlayer binding energy and the interlayer separation predicted by the PBE + MBD@rsSCS method, we have performed a set of single point calculations with planewave cutoff of 600 eV and a mesh of $16 \times 16 \times 1$ k-points. The geometry of the unit cell used in these calculations has been derived from the experimental geometry of graphite [27, 28] with a lattice vector parallel with the graphene sheets being $a_1 = a_2 = 2.46 \text{ Å}$ and a lattice vector perpendicular to the sheets being $c = 40 \text{ Å}$. In figure 3, the PBE + MBD@rsSCS energy of the AB-stacked bilayer as a function of interlayer distance has been compared with the DMC results [33] and a fairly good agreement between these two profiles was found. The values of $E_{\text{bind}} (-20.7 \text{ meV})$ and $d_0 (3.436 \text{ Å})$ obtained by the PBE + MBD@rsSCS are reasonably close to the DMC values. The DMC energy profile for the AA-stacked bilayer is not available, hence we can compare only the values of $E_{\text{bind}}$ and $d_0$. In this case, the agreement is slightly worse than for the AB-stacking: $E_{\text{bind}} = -17.0 \text{ meV}$ (PBE + MBD@rsSCS) versus $-11.5 \text{ meV}$ (DMC); $d_0 = 3.495 \text{ Å}$ (PBE + MBD@rsSCS) versus 3.641 Å (DMC).

IV. F. 2. Graphite and hexagonal boron nitride. The optimized cell parameters and interlayer binding energies for graphite are presented in table 5. It is seen that the equilibrium crystal structure of graphite with an AB stacking is well reproduced, although the ‘c’ equilibrium distance is overestimated by about 0.1 Å in comparison with the experimental or RPA values. The binding energy calculated with the MBD correction is found to coincide exactly with the RPA value of 48 meV atom$^{-1}$ [34], while the bulk modulus at equilibrium is calculated to be 29 GPa with MBD@rsSCS in comparison with a value of 36 GPa with RPA.

Concerning graphite with an AA stacking, no experimental results are available, therefore we will compare our results to RPA calculations (see table 5). As for AB graphite, the equilibrium distance in the direction perpendicular to the layers is overestimated by about 0.1 Å, while the binding energy and the bulk modulus are slightly underestimated. Notice that the MBD@rsSCS binding energy of AB graphite was reported also in [6] with a result identical with the result of our calculation (the structural parameters were not reported in [6] since the geometry optimization was not performed).

In the case of hexagonal boron nitride (see again table 5), MBD@rsSCS provides a reasonable agreement with the experimental and RPA data for the equilibrium structure and the bulk modulus, but the binding energy is overestimated significantly (59 meV atom$^{-1}$ with MBD@rsSCS in comparison with 39 meV atom$^{-1}$ with RPA [35]). This discrepancy is probably related to the fact that the Hirshfeld partitioning scheme [17] used in the calculation of atomic polarizabilities (see appendix A) is suboptimal for treating of ionic systems [36, 37].

Furthermore, we have studied the elastic force as a function of the interlayer spacing in graphene and in h-BN. The maximum of this function is the force required to completely pull apart the layers of a material. This peak force is very difficult to calculate directly from high-level energy calculations due to its strong sensitivity to unavoidable numerical errors in the energy. Indeed the RPA data available for graphene and h-BN were actually of insufficient accuracy to find the force.

To obtain the illustrative force curves provided in figure 4

Table 5. Lattice parameters, interlayer binding energies, and bulk moduli for graphite and hexagonal boron-nitride.

<table>
<thead>
<tr>
<th>Method</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>$E_{\text{B}}$ (meV atom$^{-1}$)</th>
<th>$B_0$ (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite (AB stacking)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expt.</td>
<td>2.46</td>
<td>6.71</td>
<td>43</td>
<td>34–42</td>
<td>[27, 46–48]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>35 ± 10, 52 ± 5</td>
<td></td>
</tr>
<tr>
<td>RPA</td>
<td>n.a.</td>
<td>6.68</td>
<td>48</td>
<td>36</td>
<td>[34]</td>
</tr>
<tr>
<td>PBE + MBD@rsSCS</td>
<td>2.46</td>
<td>6.82</td>
<td>48</td>
<td>29</td>
<td>This work</td>
</tr>
<tr>
<td>Graphite (AA stacking)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPA</td>
<td>n.a.</td>
<td>3.5</td>
<td>36</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>PBE + MBD@rsSCS</td>
<td>2.46</td>
<td>3.61</td>
<td>40</td>
<td>26</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 3. Binding energy ($E_{\text{bind}}$) for the AB-stacked bilayer of graphene as a function of interlayer distance ($d$). The PBE + MBD@rsSCS results are compared with high-level diffusion Monte Carlo (DMC) data [33].

Table 5. Lattice parameters, interlayer binding energies, and bulk moduli for graphite and hexagonal boron-nitride.

- **Method**: Description of the method used for calculations
- **a** and **c**: Lattice parameters in Å
- **$E_{\text{B}}$** (meV atom$^{-1}$): Binding energy
- **$B_0$** (GPa): Bulk modulus
- **Reference**: Source of the data or comparison with other methods.
we instead used a parametrization in the spirit of Gould et al [38, 39] to fit available data to a curve with appropriate contact and asymptotic behaviours. The PBE + MBD@rsSCS results were obtained by numerical differentiation of the energy with respect to the interlayer distance, which was made possible by the high numerical accuracy of the calculations. As can be seen in figure 4, PBE + MBD@rsSCS does a decent job reproducing the peak force found using full RPA calculations, and is a suitable alternative to these substantially more demanding and numerically unreliable high-level calculations.

Finally, we have analyzed the asymptotic behavior of dispersion energy for the AB stacked graphite. For the case of large interlayer separations \(d\), the analytic work of Dobson et al [40, 41] suggests that the dispersion energy increases with the interlayer separation according to a \(\sim d^{-3}\) power law and such a behaviour has been confirmed also by accurate RPA calculations [34]. Following [34], the \(E_{\text{disp}}\) versus \(d\) function has been sampled by eight points from the interval 7.5 Å \(\leq d \leq 30\) Å and fitted by the function \(A - B/d^{3}\). In contrast to theory [40, 41] and the RPA calculations, the PBE + MBD@rsSCS method predicts \(n = 4.00\) which is basically identical to that obtained by simple pairwise correction schemes PBE-D2 [1] (4.01) and PBE + TS [2] (4.03).

IV.G. Toluene adsorption on graphene

The heat of adsorption \(\Delta H_{\text{ads}}\) of toluene on graphene has been measured experimentally using inverse gas chromatography by Lazar et al [42]. The value of \(\Delta H_{\text{ads}}\) reported for the range of temperatures between 343 K and 383 K is 13.5 kcal mol\(^{-1}\). Following [42], our simulations were performed with a graphene sheet modeled by a \(4 \times 4\) (32 atoms) supercell, the periodically repeated sheets were separated by a gap of 15 Å. The plane wave cutoff was set to 500 eV and the Brillouin zone was sampled by a mesh of \(4 \times 4 \times 1\) k-points. All atomic degrees of freedom were relaxed until forces acting on atoms were smaller than 0.005 eV Å\(^{-1}\). Assuming an ideal gas behavior of toluene in the gas phase and neglecting the vibrational contribution (which, according to data presented in [42], is comparable to the experimental error bar), the heat of adsorption can be expressed as:

\[
\Delta H_{\text{ads}} = E_{A+S} - (E_S + E_A) - 4k_B T,
\]

where \(E_S\), \(E_A\), and \(E_{A+S}\) are potential energies of substrate, adsorbate, and interacting system of substrate with adsorbate, respectively, \(k_B\) is the Boltzmann constant and \(T\) is the thermodynamic temperature. The simulation temperature was set to 363 K, which is the mean temperature considered in the experimental work of Lazar et al [42]. The value of \(\Delta H_{\text{ads}}\) computed using the PBE + MBD@rsSCS (14.2 kcal mol\(^{-1}\)) is found to be in reasonable agreement with experiment (13.5 kcal mol\(^{-1}\)).

V. Conclusions

The MBD@rsSCS dispersion-correction method of Ambrosetti et al [6] has been adapted for modeling systems under periodic boundary conditions, and a reciprocal \(k\)-space implementation of the approach has been presented. The convergence of dispersion energy with the number of \(k\)-points was tested and the \(k\)-point grid density used in typical DFT simulations was found to be sufficient to achieve a precision similar to that of the DFT energy. The analytical expressions for energy gradients needed for structural relaxations and molecular dynamics have been presented and tested numerically. It has been shown that the contribution of polarizability derivatives is significant and should not be neglected in accurate calculations. Examples of practical application of the MBD@rsSCS method have been presented, including geometry optimizations and lattice energy calculations for the X23 [4] and ICE10 [7] benchmark sets, selected layered materials, and adsorption of toluene on graphene. The reciprocal space implementation of the MBD@rsSCS method, which seems to be presently the most complete dispersion correction methodology from the point of view of its physical content, opens the way for performing routine calculations on solid state systems at a reasonable computational cost. Furthermore, the techniques presented in this work can be readily adapted to other approaches based on point-like dipole polarizability assumptions of similar general form.
Acknowledgments

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Appendix A. Calculation of atomic parameters

The free-atomic polarizabilities \( \alpha_p^{\text{atom}} \), dispersion interaction coefficients \( C_{\text{eff}}^{\text{pp}} \), and van der Waals radii \( R_{\text{vdW}}^{\text{atom}} \) are parameters of the MBD method and are tabulated for most of elements of the Periodic table, see [2] for more details. Polarizability of an atom-in-molecule is computed as follows:

\[
\alpha_p^{\text{TS}} = \alpha_p^{\text{atom}} \frac{V^{\text{eff}}}{V^{\text{free}}}. \tag{A.1}
\]

The ratio between interacting and free atom is defined using the Hirshfeld partitioning scheme [17] as

\[
\frac{V^{\text{eff}}}{V^{\text{free}}} = \frac{\int r^3 w_p(r)n(r) \, dr}{\int r^3 n_p^{\text{free}}(r) \, dr}. \tag{A.2}
\]

where \( n(r) \) is the charge density of system of interacting atoms, \( n_p^{\text{free}}(r) \) is the spherically averaged electron density of the neutral free atomic species \( p \), and \( w_p(r) \) is the Hirshfeld weight defined with respect to free atomic densities

\[
w_p(r) = \frac{n_p^{\text{free}}(r)}{\sum_q n_q^{\text{free}}(r)}. \tag{A.3}
\]

The summation in equation (A.3) is taken over all atoms present in the system. We remark that the effective volume formula, including an \( r^3 \) radial weighting, suggested originally by Johnson and Becke to rescale polarizabilities [43], was recently rationalized [44] within the framework of the statistical theory of atoms. The frequency dependent atom-in-molecule (AIM) polarizability is computed using:

\[
\tilde{\alpha}_p^{\text{iso}}(\omega) = \frac{3}{\pi} \frac{\alpha_p^{\text{TS}}}{(\omega/\omega_p)^2}. \tag{A.4}
\]

with characteristic frequency of an atom \( p \) defined as follows:

\[
\omega_p = \frac{4}{3} \frac{C_{\text{eff}}^{\text{pp}}}{\alpha_p^{\text{atom}}}. \tag{A.5}
\]

The van der Waals radius of AIM is obtained by rescaling the corresponding tabulated value as follows:

\[
R_{\text{vdW},p} = R_{\text{vdW},p}^{\text{atom}} \left( \frac{\alpha_p^{\text{TS}}}{\alpha_p^{\text{atom}}} \right)^{1/3}. \tag{A.6}
\]

Appendix B. Solution of the self-consistent equation for the polarizabilities

Following Tkatchenko and Scheffler [12], we define a matrix consisting of \( N^2 \) blocks \( R_{pq} \) of size \( 3 \times 3 \) where the elements of the individual blocks \((\alpha, \beta = \{x, y, z\})\) are defined as:

\[
R_{pq}^{\alpha\beta} = \frac{1}{\delta_p^{\text{atom}}} \delta_{pq} \delta_{\alpha\beta} + T_{\text{SR}}^{\alpha\beta}(\omega), \tag{B.1}
\]

which is an inverse of the many-body polarizability matrix \( \tilde{A}(\omega) = B^{-1}(\omega) \). The frequency dependent polarizability \( \delta_p^{\text{atom}} \) is given by equation (A.4) and the tensor \( T_{\text{SR}}^{\alpha\beta}(\omega) \) is defined by equation (9) for the molecular system and by equation (12) for the system under periodic boundary conditions.

The attenuation length \( \sigma_{pq}(\omega) \) for the pair of atoms \( p \) and \( q \) is defined as

\[
\sigma_{pq}(\omega) = \sqrt{\sigma_p^2(\omega) + \sigma_q^2(\omega)}, \tag{B.2}
\]

where the effective atomic radii are obtained from the relation

\[
\sigma_p(\omega) = \left( \frac{2}{\pi} \frac{\delta_p^{\text{atom}}}{3} \right)^{1/3}. \tag{B.3}
\]

The screened frequency-dependent isotropic polarizability \( \tilde{\alpha}_p^{\text{iso}}(\omega) \) is computed as one third of the trace of a \( 3 \times 3 \) polarizability tensor resulting from a partial contraction of the many-body polarizability matrix \( \tilde{A} \):

\[
\tilde{\alpha}_p^{\text{iso}}(\omega) = \frac{1}{3} \sum_{\alpha=1}^{N} \tilde{A}_{pq}^{\alpha\alpha}(\omega). \tag{B.4}
\]

The van der Waals radii for the screened atoms are computed as

\[
R_{\text{vdW},p} = R_{\text{vdW},p}^{\text{atom}} \left( \frac{\tilde{\alpha}_p^{\text{iso}}}{\alpha_p^{\text{atom}}} \right)^{1/3}, \tag{B.5}
\]

with \( R_{\text{vdW},p} \) and \( \alpha_p^{\text{TS}} \) being defined in equations (A.6) and (A.1), respectively.

Appendix C. Force and stress expressions

C.1. \( \nabla A_{\text{LR}}(\omega) \)

It follows from the definition of the matrix \( A_{\text{LR}} \) (equation (7)), that the position derivatives of its elements can be expressed
The derivative of the many-body polarizability matrix \( \mathbf{\alpha} \) (see equation (B.1)) with respect to \( \mathbf{r}_a \) can be written as (note that for the sake of brevity, the frequency dependence of \( \mathbf{A} \), and \( \mathbf{T}_{\text{SR}} \) is not indicated):

\[
\frac{\partial \mathbf{A}_{\beta\gamma}^{(j)}}{\partial \mathbf{r}_a} = \sum_{i'j'} T_{\text{SR},ij}^{(j)} \frac{\partial \mathbf{A}_{\beta\gamma}^{(i')}}{\partial \mathbf{r}_a} + \sum_{i'j'} T_{\text{SR},ij}^{(i')} \frac{\partial \mathbf{A}_{\beta\gamma}^{(j)}}{\partial \mathbf{r}_a}.
\]

(C.3)

The derivatives of the components of the many-body polarizability matrix \( \mathbf{\alpha} \) (equation (12)) become

\[
\frac{\partial \mathbf{T}_{\text{SR},ij}^{(j)}}{\partial \mathbf{r}_a} = (\delta_{ij} - \delta_{i'j'}) \sum_{k} T_{\text{SR},ik}^{(k)}
\]

\[
= -(\delta_{ij} - \delta_{i'j'}) \left\{ \frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} T_{\text{SR},ik}^{(k)} + (1 - f(S_{\text{vdW}},r_{i'k})) T_{\text{SR},ik}^{(k)} \right\}
\]

\[
\times \left[ \text{erf} \left( \frac{r_{i'k}}{\sigma_0} \right) - 2 \frac{r_{i'k}}{\sqrt{\pi}} e^{-\frac{r_{i'k}^2}{\sigma_0^2}} \right]
\]

\[
+ \frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} \left[ \frac{r_{i'k}}{\sigma_0} - \delta_{i'j'} \right]
\]

\[
\times \left[ T_{\text{SR},ik}^{(k)} \left( \frac{r_{i'k}}{\sigma_0} + \delta_{i'j'} \right) - T_{\text{SR},ik}^{(k)} \right]
\]

\[
+ 2 \frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} \left\{ \frac{1}{r_{i'k}} + 1 \right\} \right] - \left( \frac{r_{i'k}}{\sigma_0} - \delta_{i'j'} \right) e^{-\frac{r_{i'k}^2}{\sigma_0^2}}
\]

(C.4)

The derivative of the damping function (equation (5)) with respect to atomic positions takes the form:

\[
\frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} = (\delta_{ij} - \delta_{i'j'}) \frac{d}{S_{\text{vdW},ij}} r_{i'k} f^2(S_{\text{vdW},ij},r_{i'k})
\]

\[
\times e^{-d(r_{i'k}/S_{\text{vdW},ij} - 1)},
\]

(C.5)

The derivative of a component of the many-body polarizability matrix with respect to lattice vector components \( h_{\alpha\beta} \) is defined as follows

\[
\frac{\partial \mathbf{A}_{\beta\gamma}^{(j)}}{\partial \mathbf{h}_{\alpha\beta}} = \sum_{i'j'} A_{\beta\gamma}^{(j)} \frac{\partial \mathbf{A}_{\alpha\beta}^{(i')}}{\partial \mathbf{h}_{\alpha\beta}},
\]

(C.6)

where the strain derivative of the screened dipole-dipole interaction tensor writes:

\[
\frac{\partial T_{\text{SR},ij}^{(j)}}{\partial \mathbf{r}_a} = \sum_{\nu} T_{\text{SR},ij}^{(j)} \sum_{\nu} h_{\nu} T_{\text{SR},ij}^{(j)}
\]

(C.7)

We note that unlike the position derivative \( \frac{\partial T_{\text{SR},ij}^{(j)}}{\partial \mathbf{r}_a} \), the term \( \frac{\partial T_{\text{SR},ij}^{(j)}}{\partial \mathbf{h}_{\alpha\beta}} \) is non-vanishing in general. This is particularly important, as this latter term gives rise to the only forces that are active in monoatomic unit cells.

C.2. \( \nabla T_{\text{LR}}(\mathbf{k}) \)

The term \( \nabla T_{\text{LR}} \) can be computed by differentiating equation (29) with respect to atomic positions:

\[
\nabla T_{\text{LR},ij}^{(j)} = (\delta_{ij} - \delta_{i'j'}) \sum_{L} T_{\text{LR},ij}^{(j)}(\mathbf{r})
\]

\[
= (\delta_{ij} - \delta_{i'j'}) \left\{ \frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} T_{\text{SR},ik}^{(k)} + \sum_{L} T_{\text{LR},ij}^{(j)} \right\}
\]

\[
\times e^{-d(\mathbf{r}_a)}
\]

(C.8)

The damping function used in definition of \( T_{\text{LR}} \) (equation (29)) depends both explicitly and implicitly (via position dependence of \( S_{\text{vdW},ij} \)) on atomic positions, the term \( \frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} \) therefore writes:

\[
\frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} = \frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} + \frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} \frac{\partial S_{\text{vdW},ij}}{\partial \mathbf{r}_a}
\]

(C.9)

The first term on the right-hand side of equation (C.10) is analogous to equation (C.5):

\[
\frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} = f^2(S_{\text{vdW}},r_{i'k})e^{-d(r_{i'k}/S_{\text{vdW},ij} - 1)}
\]

\[
\times \frac{d}{S_{\text{vdW},ij}} r_{i'k} (\delta_{ij} - \delta_{i'j'}),
\]

(C.11)

The expression for the second term is as follows:

\[
\frac{\partial f(S_{\text{vdW}},r_{i'k})}{\partial \mathbf{r}_a} = \frac{f^2(S_{\text{vdW}},r_{i'k})e^{-d(r_{i'k}/S_{\text{vdW},ij} - 1)}}{S_{\text{vdW},ij}^2}
\]

\[
\times r_{i'k} (\delta_{ij} - \delta_{i'j'}),
\]

(C.12)
The atomic reference data can be optionally defined via 
flags \( \text{VDW\_alpha} \) (atomic polarizabilities in Bohr\(^2\)), \( \text{VDW\_C6} \) (atomic \( C_6 \) coefficients in J nm\(^{-6}\) mol\(^{-1}\)), and \( \text{VDW\_RO} \) (van der Waals radii of non-interacting atoms in Å).

### References