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Interatomic Methods for the Dispersion Energy Derived from the Adiabatic Connection Fluctuation-Dissipation Theorem

Alexandre Tkatchenko[1], Alberto Ambrosetti[1], and Robert A. DiStasio Jr.[2]
[1] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195, Berlin, Germany*
[2] *Department of Chemistry, Princeton University, Princeton, NJ 08544, USA*

Interatomic pairwise methods are currently among the most popular and accurate ways to include dispersion energy in density functional theory (DFT) calculations. However, when applied to more than two atoms, these methods are still frequently perceived to be based on *ad hoc* assumptions, rather than a rigorous derivation from quantum mechanics. Starting from the adiabatic connection fluctuation-dissipation (ACFD) theorem, an exact expression for the electronic exchange-correlation energy, we demonstrate that the pairwise interatomic dispersion energy for an arbitrary collection of isotropic polarizable dipoles emerges from the second-order expansion of the ACFD formula. Moreover, for a system of quantum harmonic oscillators coupled through a dipole–dipole potential, we prove the equivalence between the full interaction energy obtained from the Hamiltonian diagonalization and the ACFD correlation energy in the random-phase approximation. This property makes the Hamiltonian diagonalization an efficient method for the calculation of the many-body dispersion energy. In addition, we show that the switching function used to damp the dispersion interaction at short distances arises from a short-range screened Coulomb potential, whose role is to account for the spatial spread of the individual atomic dipole moments. By using the ACFD formula we gain a deeper understanding of the approximations made in the interatomic pairwise approaches, providing a powerful formalism for further development of accurate and efficient methods for the calculation of the dispersion energy.

I. INTRODUCTION

Van der Waals (vdW) forces are ubiquitous in nature, and they play a major role in determining the structure, stability, and function for a wide variety of systems, including proteins, nanostructured materials, as well as molecular solids and liquids. A significant attractive part of the vdW energy corresponds to the dispersion energy, which arises from correlated fluctuations between electrons. Therefore, accurate treatment of the dispersion energy is essential for improving our understanding of biological and chemical systems, as well as (hard and soft) condensed matter systems in general. Many encouraging ideas and methods have been proposed in recent years for approximately including the missing long-range dispersion interactions in density functional theory (DFT) [1–6]. Despite significant progress in the field of modeling vdW interactions during the last decade, many questions still remain unanswered and further development is required before a truly universally applicable (accurate and efficient) method emerges. For example, interatomic vdW potentials are frequently employed for the modeling of hybrid inorganic/organic interfaces [7–10], neglecting the relatively strong long-range Coulomb screening present within inorganic bulk materials. On the other hand, the popular non-local vdW-DF functionals [11–13] use a homogeneous dielectric approximation for the polarizability, which is not expected to be accurate for molecules. Nevertheless, the interaction energies between small organic molecules turn out to be reasonably accurate. Understanding the physical reasons of why these different approaches "work well" outside of their expected domain of applicability is important for the development of more robust approximations.

Interatomic pairwise dispersion approaches, typically dubbed DFT-D [3] or DFT+vdW [14], are among the most widely used methods for including dispersion energy in DFT. Such approaches approximate the dispersion energy in a pairwise fashion, *i.e.* as a sum over unique atom pairs. Despite their simplicity, these effective pairwise models provide remarkable accuracy when applied to small molecular systems, in particular when accurate dispersion coefficients (C_n) are employed for atoms in molecules [15]. Only recently have efforts been focused on going beyond the effective pairwise treatment of vdW contributions, for example, the role of the non-additive three-body interatomic Axilrod-Teller-Muto term was assessed [16, 17]. Furthermore, an efficient and accurate interatomic many-body dispersion (MBD) approach to dispersion interactions has recently been proposed [18]. The MBD description of vdW interactions is essential for the description of extended molecules and molecular solids; however, the influence of MBD interactions can already become significant when considering the interactions between relatively small organic molecules [18, 19].

Despite the popularity and the relative accuracy of the DFT-D and DFT+vdW methods, they are still widely perceived to be based on *ad hoc* assumptions. For the dispersion interaction between two spherical atoms i and j, the pairwise $C_6^{ij} R_{ij}^{-6}$ formula has been known since the seminal work of London [20, 21]. However, to the best of our knowledge, the generalization of London's formula for an arbitrary collection of N spherical atoms has not been explicitly derived from first principles. Furthermore, at short interatomic distances, the dispersion interaction is significantly weaker than the corresponding asymptotic expansion, and *ad hoc* approximations become necessary for the functional form of the damping. It is shown in this

work that the switching function used to damp the dispersion interaction at short distances arises from a short-range screened Coulomb potential, whose physical role is to account for the spatial spread of the individual atomic polarizabilities.

Since the dispersion energy arises from correlated fluctuations between electrons, it is intrinsically a many-body phenomenon, an accurate description of which requires a quantum mechanical treatment. For this purpose, the adiabatic connection fluctuation-dissipation (ACFD) theorem, which provides a general and exact expression for the exchange-correlation energy [22, 23], allows us to calculate the dispersion energy in a seamless and accurate fashion, naturally including many-body effects. In this work, we show that the ACFD theorem provides a firm theoretical basis for the development and understanding of interatomic pairwise and many-body dispersion methods. In particular, we derive the well-known C_6/R^6 interatomic pairwise summation formula as the second-order expansion of the ACFD correlation energy, and demonstrate that this formula is valid for an arbitrary collection of N fluctuating dipoles, each of which is characterized by an individual frequency-dependent polarizability. By applying the ACFD formalism we also prove, for a system of quantum harmonic oscillators (QHOs) coupled within the dipole approximation, the mathematical equivalence between the exact dispersion energy and the correlation energy in the random-phase approximation (RPA). This analytical result makes the coupled-oscillator model (with a relatively minimal computational cost) an ideal candidate for the inclusion of MBD effects in DFT. Finally, we show the relevance of MBD energy on the binding energies of dimers in the S22 database. The full many-body description consistently reduces mean relative errors with respect to the interatomic pairwise approximation, showing the largest improvements for the most extended systems. The ACFD formula leads to a deeper understanding of the approximations made in the development of the DFT-D and DFT+vdW approaches, and provides a natural formalism for further improvement of methods for computing the dispersion energy.

II. THE PAIRWISE INTERATOMIC DISPERSION ENERGY FROM THE ACFD FORMULA

The ACFD theorem is an exact expression for the exchange-correlation energy of a system of nuclei and electrons, described by a response function $\chi(\mathbf{r}, \mathbf{r}', \omega)$ [22, 23]. The response function χ measures the response at point $\mathbf{r}$ due to a change of the potential at point $\mathbf{r}'$ as a function of time or (Fourier-transformed) frequency ω. Here our interest lies in the dispersion energy, which is contained in the electron correlation energy. Therefore we start by writing the ACFD formula exclusively for the correlation energy (Hartree atomic units are used throughout)

$$E_c = -\frac{1}{2\pi}\int_0^\infty d\omega \int_0^1 d\lambda \mathrm{Tr}[(\chi_\lambda - \chi_0)v], \qquad (1)$$

in which χ_0 is the bare or non-interacting response function, which can be computed given a set of single-particle orbitals [24, 25] ϕ_i (with corresponding eigenvalues ϵ_i and occupation numbers f_i) as

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = 2\sum_{i,j}(f_i - f_j)\frac{\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})}{\epsilon_i - \epsilon_j + i\omega}, \quad (2)$$

χ_λ is the interacting response function at Coulomb coupling strength λ, defined *via* the self-consistent Dyson screening equation $\chi_\lambda = \chi_0 + \chi_0(\lambda v + f_{xc}^\lambda)\chi_\lambda$, $v = |\mathbf{r} - \mathbf{r}'|^{-1}$ is the Coulomb potential, and Tr denotes the trace operator over spatial variables $\mathbf{r}$ and $\mathbf{r}'$. Using the ACFD formula, the adiabatic connection between the non-interacting system (with $\lambda = 0$) and the fully interacting system (with $\lambda = 1$), yields the full correlation energy of the system of interest. Obviously, the correlation energy obtained from the ACFD formula contains the full many-body dispersion energy as well as other electron correlation effects.

In practice, the exact form of the exchange-correlation kernel f_{xc}^λ in the Dyson equation is not known. Neglecting the explicit dependence of f_{xc} on λ, analytic integration can be carried out over λ. This is the case, for example, for the widely employed random-phase approximation (RPA) [26, 27], or the full potential approximation (FPA) [28]. In the RPA, $f_{xc} = 0$, while in the FPA $\chi_\lambda = \chi_1$, *i.e.* the λ integration is carried out using the fully interacting response function. In what follows, we will employ the RPA method, which has been shown to yield reliable results for a wide variety of molecules and extended systems [29–43]. Using the Dyson equation, the ACFD correlation energy expression in Eq. (1) takes on the following form in the RPA

$$E_{c,\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^\infty d\omega \int_0^1 \frac{d\lambda}{\lambda}\mathrm{Tr}\left[\frac{(\lambda v\chi_0)^2}{1 - \lambda v\chi_0}\right]. \qquad (3)$$

Integration over λ in Eq. (3) leads to the following expansion for the correlation energy in terms of $\chi_0 v$ [44, 45]

$$E_{c,\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^\infty d\omega \sum_{n=2}^\infty \frac{1}{n}\mathrm{Tr}[(\chi_0 v)^n]. \qquad (4)$$

Let us now apply the ACFD-RPA approach to a collection of fluctuating dipoles representing the atomic system of interest. Each atom i is characterized by its position $r_i = \{x_i, y_i, z_i\}$ and a frequency-dependent dipole polarizability $\alpha_i(\mathrm{i}\omega)$. For the moment, we assume that the atoms are separated by a sufficiently large distance, allowing us to use the bare Coulomb potential to describe the interaction between dipoles. The general case will be addressed in the next section. The response function for each atom i takes the form [46]

$$\chi_i(\mathbf{r}, \mathbf{r}', \mathrm{i}\omega) = -\alpha_i(\mathrm{i}\omega)\nabla_{\mathbf{r}}\delta^3(\mathbf{r} - \mathbf{r_i}) \otimes \nabla_{\mathbf{r}'}\delta^3(\mathbf{r}' - \mathbf{r_i}), \quad (5)$$

where δ is the three-dimensional Dirac delta function, and $\otimes$ is the tensor (outer) product.

Now it will be shown that the second-order ($n = 2$) term in Eq. (4) yields the pairwise interatomic dispersion energy. In the remainder of this section we drop the λ index of the response function, because the atomic polarizabilities can be derived from a mean-field or an explicit many-body calculation. Furthermore, the second-order $n = 2$ term in Eq. (4) turns out to be the same if the expansion is carried out in terms of χ_0 or χ_1 [44]. For a collection of N atoms in the dipole approximation, the χv matrix can be written as AT. Here, A is a diagonal $3N \times 3N$ matrix, with $-\alpha_i(\mathrm{i}\omega)$ values on the diagonal blocks. The T matrix is the dipole-dipole interaction matrix, with 3×3 ij tensors given by $T_{ij} = \nabla_{\mathbf{r_i}} \otimes \nabla_{\mathbf{r_j}} v_{ij}$ ($T_{ii} = 0$). For two atoms ($\alpha_1(\mathrm{i}\omega)$ and $\alpha_2(\mathrm{i}\omega)$) separated by a distance $R = |\mathbf{r_1} - \mathbf{r_2}|$ on the x axis, the AT matrix becomes

$$\begin{pmatrix} 0 & 0 & 0 & \frac{2\alpha_1(\mathrm{i}\omega)}{R^3} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{\alpha_1(\mathrm{i}\omega)}{R^3} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{\alpha_1(\mathrm{i}\omega)}{R^3} \\ \frac{2\alpha_2(\mathrm{i}\omega)}{R^3} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{\alpha_2(\mathrm{i}\omega)}{R^3} & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{\alpha_2(\mathrm{i}\omega)}{R^3} & 0 & 0 & 0 \end{pmatrix}. \tag{6}$$

The second-order ($n = 2$) term of the ACFD-RPA expression in Eq. (4) with the above matrix as input leads to

$$E^{(2)}_{c,\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^\infty d\omega \alpha_1(\mathrm{i}\omega)\alpha_2(\mathrm{i}\omega)\mathrm{Tr}[{T_{12}}^2] = -\frac{C_6^{12}}{R^6}, \tag{7}$$

where the Casimir-Polder identity has been used to determine C_6^{12} from the corresponding dipole polarizabilities. The above equation is the familiar expression for the long-range dispersion interaction between two atoms.

Equation 7 can be easily generalized to the case of N atoms. The use of the trace operator in Eq. (4) requires multiplication of column i of the AT matrix by the corresponding row i. Since for any given T_{ij}, $\mathrm{Tr}[{T_{ij}}^2] = 6/R_{ij}^6$, where R_{ij} is the distance between atoms i and j, the second-order expansion of Eq. (4) for N atoms leads to this simplified form

$$E^{(2)}_{c,\mathrm{RPA}} = -\frac{1}{2}\sum_i \sum_j \frac{C_6^{ij}}{R_{ij}^6}. \tag{8}$$

This of course is the familiar expression for the dispersion energy for an assembly of N atoms used in the DFT-D and DFT+vdW methods. We note that the above derivation of the pairwise dispersion energy from the ACFD formula does not make any assumptions regarding the geometry of the atomic assembly or the functional form of the frequency-dependent polarizabilities. Furthermore, we note that employing the FPA instead of the RPA would not change the conclusions presented above.

While the second-order expansion of Eq. (4) for isotropic polarizabilities yields the familiar pairwise interatomic dispersion energy given by Eq. (8), the former equation is more general. It allows for the use of full polarizability tensors, enabling an anisotropic treatment of the dispersion energy. In this regard, the polarizability anisotropy has been found to play a non-negligible role for intermolecular dispersion interactions [47, 48].

We note that the higher-order terms in the RPA expansion of the correlation energy include two contributions: higher-than-pairwise many-body interactions (up to N-th order) and the response screening (up to *infinite* order). As an example of the beyond-pairwise many-body interactions captured in the RPA expansion of the correlation energy, the third-order term includes the well-known Axilrod-Teller-Muto three-body energy [49]. The higher-order response screening can be easily illustrated for two interacting atoms i and j by expanding Eq. (4) (explicit dependence of the polarizabilities on $\mathrm{i}\omega$ assumed):

$$E_{c,\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^\infty d\omega \left(\frac{6\alpha_i\alpha_j}{R_{ij}^6} + \frac{36\alpha_i^2\alpha_j^2}{R_{ij}^{12}} + \ldots\right), \tag{9}$$

in which the second-order term corresponds to the "standard" C_6/R^6 dispersion interaction between i and j, and the higher-order terms (which only survive with even powers of n) correspond to the response screening of the polarizability of atom i by the presence of atom j and vice versa. Further analysis of these many-body contributions is presented in Sections IV and V.

III. THE DAMPING OF THE DISPERSION ENERGY AT SHORT DISTANCES

Correlation energy calculations carried out using the ACFD formula usually employ the response function χ_0 computed using a set of occupied and virtual one-particle orbitals [see Eq. (2)], determined from semilocal DFT, Hartree-Fock, or hybrid self-consistent-field calculations. In this scenario, χ_0 is typically a fairly delocalized object, which includes orbital overlap effects between occupied and virtual states. However, even in this case, the use of certain approximations for the exchange-correlation kernel f_{xc} can lead to divergencies for close inter-particle separations [30]. When the response function is localized, leading to a diagonal form, the details of the overlap between orbitals are lost. For example, this is clearly the case for an assembly of fluctuating point dipoles. When two point dipoles come into close contact, the Coulomb interaction between them diverges. In fact, depending on the absolute values of the polarizability, the head-to-tail alignment between two dipoles can lead to an infinite polarizability even for a *finite* (non-zero) separation between the dipoles [50]. This is clearly an unphysical situation, which is mitigated in practice by the finite extent of electronic orbitals. From a slightly different perspective, the dipole moment should be spread out in space,

and this effect naturally introduces damping when the polarizabilities overlap.

The most straightforward way to incorporate overlap effects for a set of fluctuating point dipoles is through a modification of the interaction potential. Thus, instead of using the bare Coulomb potential $v = |\mathbf{r} - \mathbf{r}'|^{-1}$, a modified potential should be employed that accounts for orbital overlap at short distances. We take the polarizability of each atom i to correspond to a quantum harmonic oscillator (QHO)

$$\alpha(\mathrm{i}\omega) = \frac{\alpha_0}{1 + (\omega/\omega_0)^2}, \tag{10}$$

where α_0 is the static dipole polarizability, and ω_0 is an effective excitation frequency. Since the ground state QHO wavefunction has a gaussian form, the interaction between two QHOs (or atoms) i and j leads to a modified Coulomb potential

$$v_{ij}^{gg} = \frac{\mathrm{erf}(r_{ij}/\sigma_{ij})}{r_{ij}}, \tag{11}$$

where r_{ij} is the interatomic distance, σ_{ij} is an effective width, $\sigma_{ij} = \sqrt{\sigma_i^2 + \sigma_j^2}$, obtained from σ_i and σ_j, the gaussian widths of atoms i and j, respectively. Since the polarizability relates the response of a dipole moment to an applied electric field, the σ_i and σ_j parameters correspond to the distribution of the dipole moment, and not of the charge. The width of the gaussian distribution is directly related to the polarizability in classical electrostatics [51].

Using Eq. (11), the dipole interaction tensor for atoms i and j becomes

$$\begin{aligned} T_{ij}^{ab} &= \nabla_{\mathbf{r_i}} \otimes \nabla_{\mathbf{r_j}} v_{ij}^{gg} \\ &= -\frac{3 r_a r_b - r_{ij}^2 \delta_{ab}}{r_{ij}^5} \left(\mathrm{erf}(\frac{r_{ij}}{\sigma_{ij}}) - \frac{2}{\sqrt{\pi}} \frac{r_{ij}}{\sigma_{ij}} e^{-(\frac{r_{ij}}{\sigma_{ij}})^2} \right) \\ &+ \frac{4}{\sqrt{\pi}} \frac{1}{\sigma_{ij}^3} \frac{r_a r_b}{r_{ij}^2} e^{-(\frac{r_{ij}}{\sigma_{ij}})^2}, \end{aligned} \tag{12}$$

where a and b specify general Cartesian coordinates (x,y,z), r_a and r_b are the respective components of the interatomic distance r_{ij}, and δ_{ij} is the Kronecker delta function. It can be clearly seen that the above expression reduces the interaction between dipoles at short distance, in comparison to the bare dipole interaction potential. Even in the zero-distance limit, it converges to a finite value. Therefore, the description of the polarizabilities by a dipole distribution instead of a point naturally introduces short-range damping effects, which have been so far included using *ad hoc* models in the DFT-D and DFT+vdW approaches.

Both DFT-D and DFT+vdW methods use a distance-dependent damping function $f_{\mathrm{damp}}(r_{ij})$, which multiplies the $C_6^{ij} R_{ij}^{-6}$ dispersion energy. The function $f_{\mathrm{damp}}(r_{ij})$ converges to zero or a small finite value at zero distance between two atoms [52]. At large distances, $f_{\mathrm{damp}}(r_{ij})$ saturates to unity, typically for distances 20% larger than the sum of the van der Waals radii of the two atoms. Besides these two constraints the functional form of the damping is essentially arbitrary. Some evidence suggests [53] that the binding energies are not significantly affected by the functional form of the damping, as long as two adjustable parameters are used. One of these parameters controls the steepness, while the other determines the onset of the damping in terms of the distance. Typically, only one of these parameters is adjusted for a given DFT functional by minimizing the error with respect to high-level quantum-chemical binding energies. Another disadvantage of the damping function, as used in DFT-D and DFT+vdW methods, is the need to define van der Waals radii, which are not quantum mechanical observables.

Inspection of Eq. (12) shows that, when using a QHO approximation for the spatial spread of the polarizability, the damping function is more complicated than a purely multiplicative function. This complication arises due to the last exponentially decaying term in T_{ij}^{ab}. Although this conclusion is based on a QHO model, the same conclusion holds for other models, such as hydrogenic atoms. We conclude that our findings are likely to be valid in general, meaning that the damping function must be derived from a model Coulomb potential that naturally accounts for short-range dipole distribution overlap effects [18]. The coupling of the dispersion energy to a given DFT functional might still require empirical parameter(s), as we illustrate below. However, a seamless coupling may be achieved by using the range-separation of the Coulomb potential in the calculation of the DFT correlation energy. The approach presented in this section can be employed in the development of such a range-separation procedure.

IV. EFFICIENT EVALUATION OF THE ACFD-RPA ENERGY FOR A SYSTEM OF QUANTUM HARMONIC OSCILLATORS

The ACFD-RPA approach to the correlation energy has proven to be promising for a wide variety of molecules and extended systems [29–43]. The largest drawback of ACFD-RPA calculations is their relatively high computational cost, resulting in a steep increase in the required computational time with system size. The conventional scaling of the ACFD-RPA calculations is N^5, where N is the number of basis functions. This can be reduced to N^4, when resolution-of-the-identity, or density-fitting, techniques are employed to compute the four-centered two-electron Coulomb integrals [45].

If we only aim at computing the long-range vdW energy, it is possible to associate a single quantum harmonic oscillator (QHO) to every atom. For such a system, in which the QHOs interact within the dipole approximation, one can circumvent evaluation of the four-centered two-electron Coulomb integrals (and costly summations

over the virtual/unoccupied functions) via application of the QHO selection rules [54–56]. In this section, we will demonstrate that the ACFD-RPA correlation energy for a system of QHOs interacting through a dipole potential is equivalent to the interaction energy obtained from diagonalizing the corresponding Hamiltonian matrix. Within this formalism, the computational scaling will be reduced to N^3 (via the diagonalization step), where N is simply the number of atoms in the molecular system of interest. Further computational savings can be obtained if one computes the interaction energy with efficient path integral techniques [57, 58], instead of diagonalizing the coupled QHO Hamiltonian matrix, allowing for the efficient computation of the many-body dispersion energy during Monte Carlo (MC) and molecular dynamics (MD) simulations.

Throughout the remainder of this Section, we will restrict the derivation to a system of one-dimensional QHOs in order to simplify the notation. The extension to three-dimensional QHOs is straightforward and does not alter the conclusions.

A. The Hamiltonian for a System of Coupled QHOs

For a system of N QHOs interacting within the dipole approximation, the Hamiltonian can be written as [18]:

$$\hat{H} = -\sum_{p}^{N} \frac{\nabla_{\xi_p}^2}{2} + \sum_{p}^{N} \frac{\omega_p^2 \xi_p^2}{2} + \sum_{p>q}^{N} \omega_p \omega_q \sqrt{\alpha_p \alpha_q} \xi_p T_{pq} \xi_q \,, \tag{13}$$

where ξ_p represents the displacement of the p-th oscillator from its equilibrium distance weighted by the square root of its mass. The first two terms in this Hamiltonian represent the kinetic energy and the confining potential corresponding to a set of independent QHOs with unit charge and characteristic frequency ω_p (*i.e.*, the eigenvalues of the non-interacting, single-particle QHO Hamiltonian matrix). The third term describes the interoscillator coupling via the dipole-dipole interaction, which also depends on ω_p, as well as α_p, the QHO static dipole polarizability, and T_{pq}, the $N \times N$ dipole-dipole interaction tensor (as defined in Section II). Due to the quadratic (bilinear) dependence of the Hamiltonian on the ξ_p coordinates, it is possible to obtain an exact solution for the QHO interaction energy via diagonalization of the following C^{QHO} matrix:

$$C_{pq}^{\mathrm{QHO}} = \delta_{pq}\omega_p^2 + (1-\delta_{pq})\omega_p\omega_q\sqrt{\alpha_p\alpha_q}\, T_{pq} \,. \tag{14}$$

The resulting interaction energy, $E_{c,\mathrm{QHO}}$, is then computed as the difference between the eigenvalues of the *coupled* system of QHOs (obtained via diagonalization of the C^{QHO} matrix) and the eigenvalues of the *uncoupled* system of QHOs (the characteristic frequencies), *i.e.*,

$$E_{c,\mathrm{QHO}} = \frac{1}{2}\sum_{i}^{N} (\sqrt{\bar{\omega}_i^2} - \omega_i) \,. \tag{15}$$

From Eq. (15), the interaction energy for a system of coupled QHOs is characterized by a set of normal modes, whose corresponding frequencies are shifted with respect to the non-interacting characteristic frequencies due to the presence of dipole–dipole coupling:

$$\bar{\omega}_i^2 = \omega_i^2 + \Delta_i \,. \tag{16}$$

B. The ACFD-RPA Correlation Energy for a System of Coupled QHOs

After performing the integration over the coupling constant λ in Eq. (3), the ACFD-RPA correlation energy can be written in the following form (an alternative yet equivalent expression to Eq. (4)) [59]:

$$E_{c,\mathrm{RPA}} = \frac{1}{2\pi}\int_0^\infty d\omega\, \mathrm{Tr}[\ln(1-\chi_0 v) + \chi_0 v]. \tag{17}$$

As discussed in Section II, $\chi_0 v$ corresponding to a set of coupled QHOs can be written in matrix form as AT (See Eq. (6)) by utilizing the QHO selection rules and the inherent locality of the QHO polarizabilities. Since $\mathrm{Tr}[AT] = 0$, the ACFD-RPA correlation energy for a system of coupled QHOs can be written as

$$E_{c,\mathrm{RPA}} = \frac{1}{2\pi}\int_0^\infty d\omega\, \ln det[C^{\mathrm{RPA}}(\mathrm{i}\omega)] \,, \tag{18}$$

in which the C^{RPA} matrix is defined as follows:

$$C_{pq}^{\mathrm{RPA}}(\mathrm{i}\omega) = \delta_{pq} + (1-\delta_{pq})\alpha_p(\mathrm{i}\omega)T_{pq} \,. \tag{19}$$

C. Deconvolution of the ω_p and $\bar{\omega}_p$ Dependencies in the C^{RPA} Matrix

In order to disentangle the ω_i and $\bar{\omega}_i$ dependencies in the C^{RPA} matrix, we seek to rewrite C^{RPA} as the product of two diagonal ω-dependent matrices which separately contain ω_p and $\bar{\omega}_p$, respectively. This is accomplished by first extracting the free QHO polarizabilities in the C^{RPA} matrix via

$$C^{\mathrm{RPA}}(\mathrm{i}\omega) = -A(\mathrm{i}\omega)B(\mathrm{i}\omega) \,, \tag{20}$$

where $A_{pq}(\mathrm{i}\omega) = -\delta_{pq}\alpha_q(\mathrm{i}\omega)$ (*c.f.* Section II) is a diagonal $N \times N$ matrix which only depends on the uncoupled characteristic frequencies, ω_p, and

$$B_{pq}(\mathrm{i}\omega) = \delta_{pq}\alpha_p(\mathrm{i}\omega)^{-1} + (1-\delta_{pq})T_{pq} \tag{21}$$

is a non-diagonal $N \times N$ matrix which depends on both ω_p and $\bar{\omega}_p$. Since the dipole–dipole interaction tensor is frequency independent, one can follow the procedure suggested in Ref. [60] and recast the $B(\mathrm{i}\omega)$ matrix as

$$B(\mathrm{i}\omega) = B(0) + D\omega^2 \equiv B(0) + \delta_{pq}(\alpha_p(0)\omega_p^2)^{-1}\omega^2 \tag{22}$$

in which the D matrix has been defined explicitly. In this form, $B(\mathrm{i}\omega)$ can now be written in terms of a diagonal matrix by solving the following generalized eigenvalue problem:

$$B(0)\mathbf{t}_n = \tilde{\omega}_n^2 D\mathbf{t}_n\,, \tag{23}$$

where $\mathbf{t}_n$ $(n = 1,\ldots,N)$ is a complete set of N-dimensional vectors which diagonalize the D matrix, *i.e.*, $\mathbf{t}_m^T D\mathbf{t}_n = \delta_{mn}$. This is easily seen if one defines $\tilde{T} = [\mathbf{t}_1, \mathbf{t}_2, \ldots, \mathbf{t}_N]$, from which

$$\tilde{T}^T B(\mathrm{i}\omega)\tilde{T} = \Omega(\mathrm{i}\omega) \equiv \delta_{pq}(\omega^2 + \tilde{\omega}_p^2)\,. \tag{24}$$

The C^{RPA} matrix can now be written in terms of the two diagonal matrices $A(\mathrm{i}\omega)$ and $\Omega(\mathrm{i}\omega)$:

$$C_{\mathrm{RPA}}(\mathrm{i}\omega) = -A(\mathrm{i}\omega)(\tilde{T}^T)^{-1}\Omega(\mathrm{i}\omega)\tilde{T}^{-1}\,. \tag{25}$$

The matrix $A(\mathrm{i}\omega)$, containing the free polarizabilities, will only depend on the uncoupled QHO frequencies ω_p. The coupled QHO frequencies, $\bar{\omega}_p$, on the other hand, will be present inside the $\Omega(\mathrm{i}\omega)$ matrix through its dependence on the $\tilde{\omega}_p$. The relationship between the $\tilde{\omega}_p$ and $\bar{\omega}_p$ can be determined by defining a diagonal matrix F such that $F^T F = D$,

$$F_{pq} = \delta_{pq}(\alpha_p(0)\omega_p^2)^{-1/2} \tag{26}$$

and observing the fact that $B(0) = F^T C^{\mathrm{QHO}} F$, which allows for diagonalization of the coupled C^{QHO} matrix, *i.e.*,

$$\tilde{T}^T B(0)\tilde{T} = \tilde{T}^T F^T C^{\mathrm{QHO}} F\tilde{T} = \Omega(0)\,. \tag{27}$$

Hence, $\Omega(0)$ is the matrix of the coupled eigenvalues of C^{QHO} and $\tilde{\omega}_i^2 = \bar{\omega}_i^2$.

D. Frequency Integration and the Contributions from the ω_p and $\bar{\omega}_p$ Poles

Before proceeding to the integration over frequency in Eq. (18), we first consider the logarithm operating on C^{RPA}:

$$\ln det[C^{\mathrm{RPA}}] = \ln det[-A\Omega] + \ln det[(\tilde{T}^T)^{-1}\tilde{T}^{-1}]\,, \tag{28}$$

in which Eq. (25) was used. Since $(\tilde{T}\tilde{T}^T)^{-1} = D$ and

$$(-A(\mathrm{i}\omega)\Omega(\mathrm{i}\omega))_{pq} = \delta_{pq}\frac{\alpha_p(0)}{1+\omega^2/\omega_p^2}(\bar{\omega}_p^2 + \omega^2)\,, \tag{29}$$

all that remains in the expression for $E_{c,\mathrm{RPA}}$ is N integrals of the form

$$E_{c,\mathrm{RPA}} = \frac{1}{2\pi}\sum_{p=1}^{N}\int_0^\infty d\omega\,\ln\left(\frac{\bar{\omega}_p^2+\omega^2}{\omega_p^2+\omega^2}\right)\,, \tag{30}$$

which, after integration by parts and the use of Eq. (16), becomes

$$E_{c,\mathrm{RPA}} = \frac{1}{2\pi}\sum_{p=1}^{N}\int_0^\infty d\omega\frac{2\Delta_p\omega^2}{(\omega_p^2+\omega^2)(\bar{\omega}_p^2+\omega^2)}\,. \tag{31}$$

This integrand shows both a pair of *coupled* ($\omega = \pm i\bar{\omega}_p$) and *uncoupled* ($\omega = \pm i\omega_p$) QHO poles. Extending the integral to $-\infty$ by symmetry and closing the integration path in the upper imaginary half plane results in the fact that only the QHO poles possessing a positive imaginary component provide a non-zero contribution to $E_{c,\mathrm{RPA}}$. By explicitly performing the frequency integration, the coupled and uncoupled poles will contribute with a $|\bar{\omega}_i|/2$ and $-\omega_i/2$ term, respectively. From Eq. (15), the sum of these contributions for each of the N QHOs yields $E_{c,\mathrm{QHO}}$.

Hence, the ACFD-RPA correlation energy for a set of QHOs coupled through a dipole–dipole potential is equivalent to the interaction energy that one obtains upon exact diagonalization of the Hamiltonian for a system of coupled QHOs. The coupled QHO normal modes naturally include many-body effects in complete analogy to the ACFDT-RPA energy. Although Eq. (15) gives no further insight concerning the nature of these many-body effects, we have demonstrated how the coupled QHO model naturally provides beyond-pairwise many-body energy contributions (up to N-th order) and the RPA response screening (up to infinite order). As a result, diagonalization of the coupled QHO Hamiltonian allows for an effective RPA treatment of long-range vdW interactions at a significantly reduced computational cost. As such, the coupled QHO model represents a highly efficient and tractable method for the calculation of the many-body vdW energy in large scale systems. Furthermore, we stress that the present results do not depend on the choice of the T matrix. Any shape of the dipole–dipole interaction (as long as it remains frequency-independent) would not alter the validity of these conclusions.

V. THE IMPORTANCE OF MANY-BODY EFFECTS FOR THE INTERATOMIC DISPERSION ENERGY

The pairwise dispersion energy is an approximate form that we derived starting from the exact ACFD formula for the correlation energy in Eq. (1). This derivation was based on two approximations: (i) Analytic integration over the adiabatic connection parameter λ using $f_{xc} = 0$ (RPA) (ii) Second-order truncation of the logarithmic series expansion resulting from (i). While the first approximation was proven to hold exactly for a system of coupled QHOs, the logarithmic series truncation limits the validity of the pairwise approximation to second-order perturbation theory. In this section, we assess the effect of going beyond the pairwise approximation. This analysis is complementary to our recent work showing the

importance of many-body dispersion energy for a variety of molecules and solids [18, 19]. The difference here is that our analysis is now based on the rigorous ACFD-RPA expression.

We model each atom i as a QHO as explained in the previous section. The input parameters α_0 and ω_0 in Eq. (10) are obtained from first-principles by using the Tkatchenko-Scheffler (TS) method [14]. In practice, for a given molecule, we carry out a DFT calculation using the PBE exchange-correlation functional [61]. The resulting self-consistent electron density is then partitioned into atomic contributions using the Hirshfeld approach [62]. Both α_0 and ω_0 are then defined as functionals of the atomic electron density. We note in passing that using densities from different functionals leads to essentially the same final results (for further details see Ref. [14]). The width σ_i of every QHO in Eq. (10) is determined by using Eq. (12) in the limit of zero-distance between two dipoles, $\sigma_i = \left(\sqrt{2/\pi}\alpha_i/3\right)^{\frac{1}{3}}$ [51].

For small and medium size molecules, the TS method yields intermolecular C_6 coefficients in excellent agreement with experimental values obtained from dipole-oscillator strength distributions [14]. In this case, the input TS polarizabilities $\alpha^{\rm TS}$ correspond more closely to the fully interacting response function χ_1 than to the non-interacting response function χ_0 used in Eq. (4). Expanding ACFD-RPA formula in terms of the interacting response function χ_1, instead of χ_0, leads to the following expression for the correlation energy [44]

$$E_c = -\frac{1}{2\pi}\int_0^\infty d\omega \sum_{n=2}^{\infty}(-1)^n \left(1-\frac{1}{n}\right) {\rm Tr}[(\chi_1 v)^n]. \quad (32)$$

Comparing Eq. (32) to Eq. (4), it is clear that the second-order term remains the same, albeit operating now on χ_1 instead of χ_0. This fact demonstrates that the origin of the polarizabilities does not modify the pairwise additive expression for the dispersion energy, further strengthening our derivation of the pairwise interatomic methods from the ACFD formula in Section II. In contrast, the coefficients of the higher-order terms differ significantly between Eq. (32) and Eq. (4). In fact, the terms with even powers of n carry a negative sign in Eq. (32), while all the terms in Eq. (4) are positive. We note that the modified Coulomb potential W' proposed in Ref. [18] leads to a similar switch in the sign of the many-body energy contributions.

Widely used (semi)-local and hybrid functionals in DFT, such as PBE [61], PBE0 [65, 66], and B3LYP [67, 68], are relatively successful for the short-range correlation energy. In contrast, our approach based on the QHO model, is constructed to accurately describe the long-range correlation energy. A seamless connection between a given DFT functional and the QHO model requires an explicit modification of the DFT functional correlation hole. This offers an interesting direction for future work. Here, instead we introduce an empirical parameter β that multiplies the QHO–QHO interaction parameter σ in Eq. (11). A value of β larger than unity corresponds to an interaction that is shifted to larger distances, effectively capturing only the long-range part of the correlation energy.

TABLE I. Performance of different functionals with dispersion energy on the S22 database of intermolecular interactions. The errors are measured with respect to basis-set extrapolated CCSD(T) calculations of Takatani *et al.* [63]. Mean absolute relative errors (MARE in %), standard deviation (SD in kcal/mol), and mean absolute errors (MAE in kcal/mol) are reported. The postfix "-2D" means that the dispersion energy is added using the second-order expansion of Eq. (32), while "-∞D" means that the dispersion energy is computed to infinite order. The DFT calculations have been carried out with the FHI-aims code [64] using a large numeric tier 3 basis set. For DFT, this basis set is converged to better than 0.05 kcal/mol compared to the basis set limit [15].

	β	MARE	SD	MAE
PBE-2D	2.06	11.6%	0.84	0.64
PBE-∞D	2.50	7.1%	0.57	0.43
PBE0-2D	2.12	11.4%	0.96	0.72
PBE0-∞D	2.52	7.2%	0.66	0.52

TABLE II. Performance of PBE0 functional including effective pairwise dispersion (PBE0-2D) and the full many-body dispersion (PBE0-∞D) on the dispersion-bound complexes contained in the S22 database, with respect to the basis-set extrapolated CCSD(T) calculations of Takatani *et al.* [63]. All values are reported in kcal/mol. The DFT calculations have been carried out with the FHI-aims code [64] using a large numeric tier 3 basis set. For DFT, this basis set is converged to better than 0.05 kcal/mol compared to the basis set limit [15].

	PBE0-2D	PBE0-∞D	CCSD(T)
Methane dimer	-0.63	-0.58	-0.53
Ethene dimer	-1.64	-1.37	-1.48
Benzene–Methane	-1.45	-1.48	-1.45
Benzene dimer (C_{2h})	-1.80	-2.50	-2.62
Pyrazine dimer	-3.00	-3.23	-4.20
Uracil dimer	-8.80	-9.57	-9.74
Indole–Benzene Stack	-3.15	-4.54	-4.59
Adenine–Thymine Stack	-9.86	-11.80	-11.66

In order to assess the accuracy of different approximations to the ACFD formula, we have chosen to use the S22 database of intermolecular interactions [69], a widely used benchmark database with binding energies calculated by a number of different groups using high-level quantum chemical methods [63, 69]. In particular, we use the recent basis-set extrapolated CCSD(T) binding energies calculated by Takatani *et al.* [63]. These binding energies are presumed to have an accuracy of ≈ 0.1 kcal/mol (1% relative error). This level of accuracy al-

lows an unbiased assessment of approximate approaches for treating dispersion interactions. Table I summarizes the results of our calculations on the S22 database. We used two different non-empirical DFT functionals: PBE [61] and PBE0 [65, 66]. For every functional, we have carried out two tests: (i) using the second-order expansion of Eq. (32), and (ii) using the full (infinite) series in Eq. (32). The β parameter has been adjusted for every combination of functional and method. We note that the approach presented here does not require the definition of van der Waals radii—all the necessary information is contained in the input frequency-dependent polarizabilities and the adjusted β parameter.

An analysis of the performance of different methods on the S22 database in Table I reveals that the addition of the pairwise dispersion energy in the QHO approximation yields a mean absolute error (MAE) with respect to CCSD(T), which is typically a factor of 2 larger than for DFT-D and DFT+vdW methods [15, 16]. We note that the MAE can be reduced significantly by using a steeper functional form for the damping of the short-range interaction [18]. The QHO approximation describes every atom as a single gaussian function, which leads to a smooth damping of the dispersion energy at short distances. Thus, even hydrogen-bonded systems are significantly stabilized. Interestingly, the inclusion of the infinite order dispersion energy beyond the pairwise approximation noticeably reduces the errors and increases the β value for every tested functional. Both of these results are desirable, since a larger value of β means that the dispersion energy is shifted to larger distances. In particular, the error is reduced for *all* dispersion-bound systems when going from PBE0-2D to PBE0-∞D as shown in Table II (the exception is the benzene-methane dimer, where both PBE0-2D to PBE0-∞D yield essentially the same results). The most pronounced deviation between PBE0-2D and PBE0-∞D is observed for the largest dispersion-bound adenine–thymine complex. The CCSD(T) method yields a binding energy of –11.7 kcal/mol, while PBE0-2D yields –9.9 kcal/mol, and PBE-∞D improves the estimate to –11.8 kcal/mol. This agrees with our previous findings using an interatomic many-body dispersion method [18], and demonstrates that the many-body dispersion energy becomes significant as the molecule size increases.

VI. CONCLUSIONS

The widely used DFT-D and DFT+vdW methods that compute the dispersion energy as a pairwise sum over atoms have been derived from the quantum mechanical adiabatic connection formula. This derivation puts interatomic dispersion methods on a firm theoretical basis. We have shown that the damping of the dispersion energy at short interatomic distances is connected to the spatial spread of the dipole moment. We have also demonstrated that the non-additive many-body effects beyond the pairwise approximation play an important role for the binding energies of dispersion-bound complexes. Moreover, given the equivalence between the exact and RPA treatment of the coupled QHO model, the full many-body dispersion energy can be efficiently computed with a single matrix diagonalization.

There are many avenues remaining for future work, including, for example, (i) different approximations to the ACFD formula, (ii) the role of input polarizabilities into the ACFD formula, (iii) the role of anisotropy and localization in the input polarizabilities, (iv) the role of higher multipole moments in the response function, and (v) improving the coupling between DFT and the long-range dispersion energy. The adiabatic connection formula provides a powerful framework for the development of accurate and efficient approaches for computing the correlation energy in general and the dispersion energy in particular.

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