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Long-range correlation energies from frequency-dependent weighted exchange-hole dipole polarisabilities

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Long-range correlation energies are calculated using an approximation of the single-particle density-density response function of the system that leads to an expression requiring only occupied orbitals and eigenvalues. Dipole-dipole polarisabilities and isotropic leading-order dispersion coefficients obtained from this approximation are shown to be in a reasonable agreement with corresponding values from the experiment or dipole oscillator strength distributions. The localised polarisabilities were used to calculate a long-range correlation correction to a hybrid-generalised gradient approximation functional using a proper damping function at short ranges. It was found that the hybrid density-functional theory+dispersion method obtained in this way has a comparable accuracy than high-level *ab initio* wave function methods at a much lower computational cost. This has been analysed for a number of systems from the GMTKN30 database including subsets for noncovalently bound complexes, relative energies for sugar conformers and reaction energies and barrier heights of pericyclic reactions of some medium sized organic molecules. © 2012 American Institute of Physics. [doi:10.1063/1.3672236]

I. INTRODUCTION

It is well known that density-functional theory methods (DFT) (Ref. 1) that are based on the local density approximation or the generalised gradient approximation (GGA) are unable to describe the important long-range correlation interactions between molecular systems that are not bound by covalent bonds.^{2–9} The reason for this stems from the fact that these functionals contain exchange-correlation energy densities which are only locally dependent on the electron density and its derivatives and therefore lack the capability to describe interactions of molecular regions that are spatially separated. More recent (semi-local) hybrid meta GGA's (Refs. 10–13) are able to mimic long-range interactions more accurately, but they behave qualitatively incorrect in the asymptotic regions of molecule-molecule interaction potentials and therefore do not represent a satisfying solution to the long-range correlation problem of DFT.

Because of this, a number of methods were developed in recent years to improve DFT methods for describing dispersion interactions. Without the claim for completeness these may be categorised into hybrid methods combining elements of DFT with wave function methods,^{14–22} methods which directly model the exchange-correlation functionals in terms of the density and its derivatives using nonlocal integral kernels,^{23–28} or methods which employ the well-known asymptotic form of the dispersion interaction combined with proper damping functions.^{29–41} Certainly, the first type of methods can be regarded as the most accurate methods, but their computational expense commonly exceeds the

favourable low cost of standard DFT methods even though they often are less expensive than correlated wave function methods. Methods that fall into the second type of category are probably most within the realm of DFT and recent developments have shown that they are not only accurate for describing intermolecular interaction energies,^{25,27,42} but there is also some progress with respect to their efficiency that is a prerequisite for their applicability for large systems.^{27,42}

The currently most popular and computationally most efficient DFT methods that include long-range correlations are methods that contain damped atom-atom dispersion interaction energy terms, termed as DFT+D (DFT+Dispersion) methods hereafter. Conventionally, the atomic dispersion coefficients were obtained by fitting procedures to reproduce molecular C_6 values, binding energies and bond distances for a number of (usually small) systems.^{30,37,38} The coefficients obtained in this way are thus fixed values that do not depend on the chemical environment. A more recent DFT+D method by Grimme *et al.*, termed as DFT-D3, uses data from time-dependent density functional theory to obtain atom-atom dispersion coefficients using frequency-dependent polarisabilities calculated for corresponding hydride molecules of the two interacting atoms.³⁹ It is thus less empirical than older DFT+D methods and allows also to describe hybridisation states within the molecule. The DFT-D3 method should therefore be more generally applicable than DFT+D methods including fixed atomic dispersion coefficients.

Another approach that may be categorised as DFT+D method is the exchange-hole dipole moment model (XDM) by Becke and Johnson.^{31–36} In this method, the long-range interaction between two atomic or molecular systems is related to the interaction of the exchange-hole dipole moments of the two systems. This (at first sight) heuristic ansatz was used to

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calculate dispersion coefficients for a number of atomic and molecular systems. Using a partitioning of the polarisabilities into atomic terms it was then possible to decompose the dispersion coefficients into interatomic terms. These were used to calculate long-range correlation corrections to a standard xc functional using an empirical damping function.³² The results for dispersion coefficients and intermolecular interactions obtained by this method were remarkably good.^{32,33,43} In Ref. 34, this approach was also extended by including C_8 and C_{10} coefficients as well.

In recent independent works, Angyan,⁴⁴ Ayers,⁴⁵ and I (Ref. 46) have analysed the origin of the XDM model by Becke and Johnson starting from the exact nondamped long-range correlation energy expression to the intermolecular interaction energy (see Ref. 47 for an analysis of the link between the dispersion interaction energy with the full exchange-correlation hole). It was found that indeed the dispersion interaction energy can be related to the exchange-hole dipole moments of the interacting monomers if a number of simple approximations for the response functions of the two monomers are employed. However, the functional form for the asymptotic dispersion interaction energy obtained in this way differs from the one reported by Becke and Johnson.^{44–46} It has been shown that this more rigorously derived expression yields quite accurate static polarisabilities and isotropic dispersion coefficients for a number of small molecules if the underlying mean excitation energy is approximated by the scaled HOMO-LUMO gap of the systems calculated from Hartree-Fock theory.⁴⁶

In this work, the approach from Ref. 46 will be refined by using a more realistic approximation to the response function than the Unsöld approximation⁴⁸ used in Ref. 46, see Sec. II A. It will be shown in Sec. II B that with this new approximation a reasonable agreement of static polarisabilities and dispersion coefficients to accurate reference values is obtained. The main aim of this work is then to develop a long-range correlation functional, on the basis of the exchange-hole approximation, which can be combined with standard DFT functionals contributing to the short-range correlations. For this the polarisabilities obtained from the approximate response function are distributed among the atomic centres and then localised using the scheme presented in Sec. II C. Using these localised polarisabilities it is then possible to calculate long-range atom-atom correlation contributions via the Casimir-Polder expression. This expression is combined with a hybrid functional using a proper damping function as shown in Sec. II D. It should be noted that this approach is closely related to the local response dispersion (LRD) method by Sato and Nakai.⁴⁰ The LRD method uses a local approximation of the response function developed by Dobson and Dinte⁴⁹ which is based on a simple model of the density-density response function of the homogeneous electron gas (see also a related work by Andersson *et al.*⁵⁰). From this response function Sato *et al.* derive localised polarisabilities that are used in very much the same way as in the current work to calculate atom-atom dispersion energy contributions to the total correlation energy in a DFT+D scheme using a damping function for short ranges. The main difference of the current work to the LRD approach by Sato *et al.* is that here

the form of the approximate response function is not derived from a model system as the homogeneous electron gas, but it is obtained from some direct approximations imposed on the known form of the uncoupled response function. The response function obtained in this way, in contrast to the LRD method, shares some common properties with the exact response function: it is nonlocal in space and possesses poles at discrete resonance frequencies, the latter, however, being only crude approximations to the exact excitation energies of the many-body response function. Due to the nonlocality of the response function, in this work it is therefore necessary to apply a localisation method to the distributed polarisabilities in order to derive atomic polarisabilities, while in the LRD method the local form of the response function directly allows to transform the distributed polarisabilities into local ones, see Ref. 40.

In Sec. IV, the new approach will be tested both, for predicting intermolecular interaction energies and for a couple of benchmark sets from the GMTKN30 database to study the performance for relative conformational energies, reaction energies and reaction barriers. Section V summarises the results and concludes.

II. DISPERSION INTERACTIONS FROM APPROXIMATE SINGLE-PARTICLE RESPONSE FUNCTIONS

A. The weighted exchange-hole approximation to the response function

Consider two separated subsystems A and B with nonoverlapping electron densities ρ_A and ρ_B . The exact correlation contribution in second order of the intermolecular fluctuation potential to the interaction energy of this system is then given by

$$E_c^{(2)}(A-B) = -\frac{1}{2\pi} \int_0^\infty d\omega \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \times \chi^A(\mathbf{r}_1, \mathbf{r}_3, i\omega) \chi^B(\mathbf{r}_2, \mathbf{r}_4, i\omega) \frac{1}{r_{12}} \frac{1}{r_{34}}, \quad (1)$$

where $1/r_{ij}$ is the Coulomb-interaction operator and $\chi^A(\mathbf{r}_1, \mathbf{r}_2, i\omega)$ and $\chi^B(\mathbf{r}_1, \mathbf{r}_2, i\omega)$ are the density-density response functions of the two systems evaluated at imaginary frequencies $i\omega$. Equation (1) is the well known Casimir-Polder expression of the dispersion interaction between two molecules A and B ^{51,52} and apparently appeared first in a seminal work by Longuet-Higgins.⁵³ It is an exact equation for the second-order intermolecular correlation energy provided that the exact response functions χ_A and χ_B of the subsystems A and B are known. In praxis, however, the response functions of the monomers have to be approximated. Basically there exist two options for this: the uncoupled approach in which the response function is written in terms of orbitals and orbital energies that are the eigenfunctions and eigenvalues of a single-particle operator; and the coupled approach where (at least partially) the electron-electron interactions neglected in the uncoupled approach are accounted for. The most often used coupled methods are time-dependent Hartree-Fock⁵¹ (also

known as random-phase approximation) and time-dependent density functional theory.⁵⁴ Both methods start from the same expression for the uncoupled response function,

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) = -4 \sum_{ia} \frac{\varepsilon_{ia}}{\varepsilon_{ia}^2 + \omega^2} \phi_{ia}(\mathbf{r}_1) \phi_{ia}(\mathbf{r}_2), \quad (2)$$

and then take higher order electron-electron interactions into account through the solution of a Dyson-type equation that can be solved in several ways.⁵⁵ In Eq. (2), indices $i, (j, k, \dots)$ label occupied orbitals and indices $a, (b, c, \dots)$ label unoccupied orbitals and the convention is used that $\varepsilon_{ia} = \varepsilon_a - \varepsilon_i$ and $\phi_{ia}(\mathbf{r}) = \phi_i(\mathbf{r})\phi_a(\mathbf{r})$ with $\varepsilon_{i,a}$ and $\phi_{i,a}$ denoting occupied/unoccupied orbital energies and orbitals, respectively. Closed-shell formalism is used throughout in this work. Moreover it is assumed that the orbitals are real-valued without loss of generality.

If the response functions of the monomers A and B are approximated by Eq. (2) and inserted in Eq. (1) then the so-called uncoupled dispersion interaction energy is obtained that is of zeroth order in the *intramonomer* fluctuation potential. This is the intermolecular correlation contribution that is contained in supermolecular second-order perturbation theory methods, e.g., second-order Møller-Plesset perturbation theory.^{56,57} In Ref. 46, the uncoupled response function of Eq. (2) has been approximated by replacing the orbital energy differences ε_{ia} all by a constant mean excitation energy $\Delta\varepsilon$ which corresponds to the so-called Unsöld approximation^{48,52,58} or CEDA (common energy denominator approximation)^{59,60} to the response function:

$$\tilde{\chi}_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) = -4 \frac{\Delta\varepsilon}{\Delta\varepsilon^2 + \omega^2} \sum_{ia} \phi_{ia}(\mathbf{r}_1) \phi_{ia}(\mathbf{r}_2). \quad (3)$$

This is a rather crude approximation since it assumes that the response function, if evaluated at real frequencies, has only one single pole while the true response function has infinitely many (at the excitation energies of the many-body system). Nevertheless, using Eq. (3) with a proper choice for $\Delta\varepsilon$ it has been shown in Ref. 46 that reasonable dipole-dipole polarisabilities and C_6 dispersion coefficients can be obtained for a range of small molecules. Sylvain *et al.* have, after applying the orbital basis set completeness relation (see below), investigated modifications to Eq. (3) using some scaled sums over inverse occupied orbital energies instead of the term $\Delta\varepsilon/(\Delta\varepsilon^2 + \omega^2)$ and obtained reasonable results for static dipole polarisabilities by this approach using, however, very small basis sets (this work was done in 1987).⁵⁸ In this work, a more reasonable approximation is used by retaining the occupied orbital energy shifts and replacing only the unoccupied orbital energies in Eq. (2) by a constant value $\bar{\nu}$: $\varepsilon_{ia} \approx \bar{\nu} - \varepsilon_i = \Delta\varepsilon_i$. With this the uncoupled response function can be written as

$$\bar{\chi}_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) = -4 \sum_{ia} \frac{\Delta\varepsilon_i}{\Delta\varepsilon_i^2 + \omega^2} \phi_{ia}(\mathbf{r}_1) \phi_{ia}(\mathbf{r}_2) \quad (4)$$

and using the completeness relation of the orbital basis $\sum_i \phi_i(\mathbf{r}_1)\phi_i(\mathbf{r}_2) + \sum_a \phi_a(\mathbf{r}_1)\phi_a(\mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2)$:

$$\begin{aligned} \bar{\chi}_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) &= -4 \sum_i \frac{\Delta\varepsilon_i}{\Delta\varepsilon_i^2 + \omega^2} \\ &\times \left[\phi_i^2(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) - \sum_j \phi_{ij}(\mathbf{r}_1) \phi_{ij}(\mathbf{r}_2) \right] \end{aligned} \quad (5)$$

$$\begin{aligned} &= - \sum_i \bar{\lambda}_i(\omega) \left[\phi_i^2(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \right. \\ &\quad \left. - \sum_j \phi_{ij}(\mathbf{r}_1) \phi_{ij}(\mathbf{r}_2) \right] \end{aligned} \quad (6)$$

$$\begin{aligned} &= -\rho(\mathbf{r}_1) \left[2 \frac{\sum_i \frac{1}{2} \bar{\lambda}_i(\omega) \phi_i^2(\mathbf{r}_1)}{\rho(\mathbf{r}_1)} \delta(\mathbf{r}_1 - \mathbf{r}_2) \right. \\ &\quad \left. - 2 \frac{\sum_{ij} \frac{1}{2} \bar{\lambda}_i(\omega) \phi_{ij}(\mathbf{r}_1) \phi_{ij}(\mathbf{r}_2)}{\rho(\mathbf{r}_1)} \right], \end{aligned} \quad (7)$$

with the electronic density $\rho(\mathbf{r}) = 2 \sum_i \phi_i^2(\mathbf{r})$. The second term in parenthesis in Eq. (7) has the same form as the exchange hole density^{31,46} but with weight factors $\bar{\lambda}_i(\omega)$ within the summation that emphasize orbital contributions with higher lying orbital energies. Because of this, this quantity is termed as a “weighted” exchange-hole (WXhole) in this work, though it does not integrate to -1 but to the function $-\sum_i \frac{1}{2} \bar{\lambda}_i \phi_i^2(\mathbf{r})/\rho(\mathbf{r})$ (omitting the spin-factor) and therefore is not related to a probability function in a simple way. Analogously, the first term in parenthesis in Eq. (7), which is a local contribution to the response function, weights energetically higher lying orbital contributions favoured in comparison to lower lying orbital contributions. The expression in Eq. (7) may be compared with the Unsöld approximation to the response function in Ref. 46, Eq. (9) in which the first term from Eq. (7) reduces to a scaled delta operator and the second term to the exchange-hole density.

The response function of Eq. (6) fulfills the desired symmetry, reciprocity and charge condition:^{49,61}

$$\bar{\chi}_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \bar{\chi}_0(\mathbf{r}_2, \mathbf{r}_1, \omega), \quad (8)$$

$$\bar{\chi}_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \bar{\chi}_0(\mathbf{r}_1, \mathbf{r}_2, -\omega), \quad (9)$$

and

$$\begin{aligned} &\int d\mathbf{r}_1 \bar{\chi}_0(\mathbf{r}_1, \mathbf{r}_2, \omega) \\ &= - \int d\mathbf{r}_1 \sum_i \bar{\lambda}_i(\omega) \left[\phi_i^2(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) - \sum_j \phi_{ij}(\mathbf{r}_1) \phi_{ij}(\mathbf{r}_2) \right] \\ &= - \sum_i \bar{\lambda}_i(\omega) \phi_i^2(\mathbf{r}_2) + \sum_{ij} \bar{\lambda}_i(\omega) \phi_{ij}(\mathbf{r}_2) \delta_{ij} \\ &= 0. \end{aligned} \quad (10)$$

B. Dipole polarisabilities and dispersion coefficients from weighted exchange-hole response functions

Generally, frequency dependent dipole(-dipole) polarisabilities can be computed from the response function $\chi(\mathbf{r}_1, \mathbf{r}_2, \omega)$ using

$$\alpha_{\alpha\beta}(\omega) = \int d\mathbf{r}_1 d\mathbf{r}_2 r_1^\alpha r_2^\beta \chi(\mathbf{r}_1, \mathbf{r}_2, \omega) \quad \alpha, \beta \in \{x, y, z\}, \quad (11)$$

and thus, using Eq. (6), dipole polarisabilities from the weighted exchange-hole approximation are given by

$$\alpha_{\alpha\beta}(\omega) = - \sum_i \bar{\lambda}_i(\omega) \langle \phi_i | r^\alpha r^\beta | \phi_i \rangle + \sum_{ij} \bar{\lambda}_{ij}(\omega) \langle \phi_i | r^\alpha | \phi_j \rangle \langle \phi_i | r^\beta | \phi_j \rangle, \quad (12)$$

with $\langle \phi_i | r^\alpha r^\beta | \phi_i \rangle = \int d\mathbf{r} r^\alpha r^\beta \phi_i^2(\mathbf{r})$ which is a simple second moment integral and $\langle \phi_i | r^\alpha | \phi_j \rangle = \int d\mathbf{r} r^\alpha \phi_{ij}(\mathbf{r})$ which is a simple dipole moment integral over two occupied orbitals i and j . The isotropic (average) dipole polarisabilities are given by $\bar{\alpha} = \frac{1}{3} \sum_\alpha \alpha_{\alpha\alpha}$.

The asymptotic form of the long-range correlation energy of Eq. (1) between two closed-shell molecules A and B is given by⁵²

$$E_{\text{disp}}(A-B) = -\frac{C_6^{AB}}{r_{AB}^6} - \frac{C_8^{AB}}{r_{AB}^8} - \frac{C_{10}^{AB}}{r_{AB}^{10}} - \dots, \quad (13)$$

where r_{AB} denotes the distance between the two monomers and $C_6, C_8, \dots$ are the isotropic dispersion coefficients. The leading-order C_6 coefficient can be obtained from the frequency-dependent dipole polarisabilities $\bar{\alpha}^A(i\omega)$ and $\bar{\alpha}^B(i\omega)$ of the monomers using the following Casimir-Polder expression:⁵²

$$C_6^{AB} = \frac{3}{\pi} \int_0^\infty d\omega \bar{\alpha}^A(i\omega) \bar{\alpha}^B(i\omega). \quad (14)$$

Higher-order polarisabilities are obtained using similar equations as Eq. (14) by replacing the dipole polarisabilities with quadrupole, octupole, etc., polarisabilities. The isotropic C_6 dispersion coefficients in the weighted exchange-hole approximation are readily obtained by insertion of Eq. (12) evaluated for the two monomers A and B into Eq. (14).

Isotropic polarisabilities were calculated using Eq. (12) with Hartree-Fock (HF) and density-functional theory (DFT) orbitals and orbital eigenvalues, respectively. In case of DFT, a hybrid functional termed revPBE0(1.0) containing a 25% exact exchange admixture was used, see Sec. II D for details. Since the occupied orbital energies are quite different in both cases, the mean unoccupied orbital energies $\bar{\nu}$ used in the response function in Eq. (7) were chosen differently in both cases. For this the value of $\bar{\nu}$ has been optimised such that the resulting polarisabilities have the least deviation to the experimental reference values shown in the last column of Table I. The result of this optimisation yielded $\bar{\nu} = 0.3$ in case of HF and $\bar{\nu} = 0.4$ in case of revPBE0(1.0), indicating that the occupied revPBE0(1.0) eigenvalues generally lie higher than corresponding orbital energies from HF. Note that it was

TABLE I. Isotropic dipole polarisabilities $\bar{\alpha}(\omega = 0)$ (in a.u.) calculated by Eq. (12) using orbitals and orbital energies from Hartree-Fock (HF) theory and density-functional theory with the revPBE0(1.0) functional (see Sec. II D). The molecular geometries were taken from Refs. 46 and 109 and the aug-cc-pVTZ basis set has been used. The experimental values from the last column are compiled from Refs. 109–111. The last line contains the average absolute deviations to the reference values in %.

System	HF	revPBE0(1.0)	Exp.
He	1.30	1.53	1.379
Ne	3.42	4.16	2.669
Ar	11.67	12.44	11.08
H ₂	3.84	4.10	5.428
HF	5.94	6.98	5.606
H ₂ O	9.13	10.33	9.642
NH ₃	12.52	13.69	14.56
CH ₄	14.65	15.71	17.27
N ₂	12.64	13.45	11.54
HCN	16.71	17.54	17.5
CO	12.34	13.45	13.18
CO ₂	17.95	20.37	16.92
C ₂ H ₂	21.48	21.89	23.53
C ₂ H ₄	24.43	25.43	28.26
C ₂ H ₆	25.97	27.98	28.52
C ₃ H ₈	37.56	40.59	39.96
C ₆ H ₆	66.08	67.46	69.5
$ \Delta $ [%]	14.2	12.49	

found that the optimal value of $\bar{\nu}$ showed not a large dependency on the orbitals, i.e., for hybrid functionals with the same amount of exact exchange the optimal value of $\bar{\nu}$ was very similar. The results for the static polarisabilities are shown in Table I. It can be observed that both, for HF and revPBE0(1.0) there is a fairly good agreement with the reference polarisabilities. The revPBE0(1.0) polarisabilities tend to be larger on average than the HF polarisabilities and are slightly more accurate with a deviation of 12.5% to the reference values compared to an average deviation of 14.2% in case of HF.

Using the optimised mean values of $\bar{\nu}$, isotropic C_6 dispersion coefficients were calculated using Eq. (14) for the molecules of the first column of Table II. A comparison of the frequency dependence of the respective polarisabilities with those from time-dependent Hartree-Fock (TDHF) showed that the decrease of the polarisabilities from Eq. (12) for larger imaginary frequencies is too slow compared to TDHF, yielding significantly larger dispersion coefficients. The diagrams in Figure 1 show this for the WXhole method using the revPBE0(1.0) functional (green lines) in case of the water and the acetylene molecule. It can be observed that both, in case of H₂O and C₂H₂ the WXhole polarisabilities differ strongly from the TDHF polarisabilities for larger values of ω . Therefore, similar to the method by Tang,⁶² a scaling factor is introduced in the $\bar{\lambda}_i(i\omega)$ factors in the response function of Eq. (6) which is then given by

$$\bar{\lambda}_i(i\omega) = \frac{4(\bar{\nu} - \varepsilon_i)}{(\bar{\nu} - \varepsilon_i)^2 + \mu\omega^2}, \quad (15)$$

TABLE II. Isotropic $C_6(A - A)$ dispersion coefficients (in a.u.) calculated with Eq. (14) using orbitals and orbital energies from Hartree-Fock (HF) theory and density-functional theory with the revPBE0(1.0) functional (see Sec. II D). The molecular geometries were taken from Refs. 46 and 109 and the aug-cc-pVTZ basis set has been used. The DOSD (dipole oscillator strength distribution) values from the last column are compiled from Refs. 32, 112–115. The last line contains the average absolute deviations to the reference values in %.

System	HF	revPBE0(1.0)	DOSD
He	1.26	1.32	1.458
Ne	8.42	9.20	6.383
Ar	75.3	69.7	64.30
H ₂	8.10	7.51	12.11
HF	21.7	22.9	19.04
H ₂ O	46.2	46.7	45.37
NH ₃	81.5	79.1	89.08
CH ₄	112.3	106.2	129.6
N ₂	93.3	86.3	73.43
HCN	147.0	134.6	135.0
CO	87.9	84.7	81.31
CO ₂	185.9	191.9	157.8
C ₂ H ₂	223.0	197.3	204.1
C ₂ H ₄	293.2	268.3	300.5
C ₂ H ₆	344.7	329.8	381.8
C ₃ H ₈	714.1	688.2	768.1
C ₆ H ₆	2045.5	1837.9	1723.0
$ \Delta $	10.5	14.2	

with μ having generally a value of larger than one to correct the frequency dependence of the weighted exchange-hole polarisabilities. As for the static dipole polarisabilities the value of μ was optimised both, for HF and revPBE0(1.0) to reproduce isotropic C_6 dispersion coefficients from dipole oscillator strength distributions (DOSD), see Table II. The result of this optimisation was $\mu = 1.5$ in case of HF and $\mu = 2.0$ in case of revPBE0(1.0). The effect this modification has on the frequency dependence is shown by the blue lines in the diagrams in Figure 1 for H₂O and C₂H₂. In case of H₂O, the WXhole polarisability actually now underestimated the TDHF polarisability for larger values of ω , however, compensating the overestimation of $\alpha(i\omega)$ at small values of ω so that a fairly good estimation of the $C_6(\text{H}_2\text{O}-\text{H}_2\text{O})$ dispersion coefficient is obtained through some error cancellation, see Table II. In case of C₂H₂, the WXhole polarisability nicely agrees with the TDFH one for all values of ω if μ is set to 2.0.

The C_6 dispersion coefficients for HF and revPBE0(1.0) using the optimised values of μ are shown in Table II. It can be seen that the revPBE0(1.0) values are a bit lower on average than the HF values and the mean percentual deviation of the revPBE0(1.0) dispersion coefficients to the DOSD reference values of the last column of Table II is a bit larger (14.2%) than with HF (10.5%). Notable cases where both, the HF and revPBE0(1.0) dispersion coefficients have a larger deviation to the corresponding DOSD dispersion coefficient are H₂ where the C_6 value is strongly underestimated and CO₂ for which a significant overestimation of the C_6 value is found, see Table II. Note that in both cases the same is true also for the static dipole polarisabilities, see Table I.

FIG. 1. Frequency-dependent polarisabilities from time-dependent Hartree-Fock (TDHF) and the weighted exchange-hole approximation (WXhole) of Eq. (12) using the revPBE0(1.0) xc functional (in a.u.). The aug-cc-pVTZ basis set was used. (a) H₂O; (b) C₂H₂.

C. Localised polarisabilities from the weighted exchange-hole approximation

In order to obtain localised polarisabilities from Eq. (11), the polarisabilities are first distributed among the atomic centres A, B according to

$$\alpha_{lm,l'm'}^{AB}(\omega) = \int_{V_A} \int_{V_B} d\mathbf{r} d\mathbf{r}' R_{lm}^A(\mathbf{r}) \bar{\chi}_0(\mathbf{r}, \mathbf{r}', \omega) R_{l'm'}^B(\mathbf{r}'), \quad (16)$$

where the integrations are performed over the atomic basins $V_{A,B}$ and $R_{lm}^{A,B} = R_{lm}(\mathbf{r} - \mathbf{R}^{A,B})$ are regular spherical harmonics located at the atomic centres. In this work, the molecular volume is partitioned using a superposition of atomic densities (Hirshfeld partitioning) similar to the scheme used in Refs. 32, 63, and 64:

$$\int d\mathbf{r} \rightarrow \int d\mathbf{r} \sum_A w_A(\mathbf{r}) = \int d\mathbf{r} \sum_A \frac{\rho_A(\mathbf{r})}{\rho_{\text{total}}(\mathbf{r})}, \quad (17)$$

where $\rho_A(\mathbf{r})$ corresponds to the free spherical density of atom A and $\rho^{\text{total}}(\mathbf{r}) = \sum_A \rho_A(\mathbf{r})$ so that the sum of the individual weight functions $w_A(\mathbf{r})$ yields $\sum_A w_A(\mathbf{r}) = 1$. In this work, the atomic densities are approximated by spherical Slater densities determined using Slater's rules, see Ref. 65. With this Eq. (16) is written as

$$\alpha_{lm,l'm'}^{AB}(\omega) = \int d\mathbf{r} w_A(\mathbf{r}) \times \int d\mathbf{r}' w_B(\mathbf{r}') R_{lm}^A(\mathbf{r}) \bar{\chi}_0(\mathbf{r}, \mathbf{r}', \omega) R_{l'm'}^B(\mathbf{r}'). \quad (18)$$

The total molecular dipole-dipole polarisability components can be calculated from the distributed ones using

$$\alpha_{\alpha\beta} = \sum_A \sum_B \mathbf{r}_\alpha^A \alpha_{\alpha q}^{AB} \mathbf{r}_\beta^B + \mathbf{r}_\alpha^A \alpha_{q\beta}^{AB} + \alpha_{\alpha q}^{AB} \mathbf{r}_\beta^B + \alpha_{\alpha\beta}^{AB},$$

where α_{qq}^{AB} is a distributed charge-flow component, $\alpha_{q\beta}^{AB}$ and $\alpha_{\alpha q}^{AB}$ are distributed charge-dipole and dipole-charge components and $\alpha_{\alpha\beta}^{AB}$ is a distributed dipole-dipole component. In order to turn the distributed polarisabilities of Eq. (18) into local ones, the components shared by two sites, that commonly are nonzero, have to be removed, i.e., $\alpha_{lm,l'm'}^{AB}(\omega) = 0$ if $A \neq B$. This has to be done such that the following sum-rule is fulfilled,

$$\sum_A \alpha_{q\zeta}^{AB} = 0 \quad \zeta = q, x, y, \dots,$$

which ensures that the total molecular charge is conserved. There is no unique way to obtain localised polarisabilities from distributed ones and a number of methods have been developed for this purpose.^{66–68} In this work, the localisation method of LeSueur and Stone⁶⁶ will be used as implemented in the Orient program.⁶⁹ Note that the total molecular polarisability is conserved using this method, i.e., once the localised polarisabilities are obtained the total polarisability components can be calculated by using

$$\alpha_{\alpha\beta}(\omega) = \sum_A \alpha_{\alpha\beta}^{AA}(\omega).$$

Table III shows localised isotropic polarisabilities obtained from the LeSueur-Stone method for the WXhole polarisabilities for some small molecules in comparison to localised coupled Hartree-Fock (CHF) polarisabilities from Lillestolen *et al.*⁶⁷ (at $\omega = 0$). It can be seen that for those molecules where the total polarisabilities from WXhole and CHF are close to each other, namely CO, C₂H₂, and C₂H₄, the percentual contributions of the atomic polarisabilities to the total polarisability are quite similar. In contrast to this, for H₂O and CO₂ the absolute values for the localised polarisabilities from WXhole and CHF deviate more from each other. In case of CO₂, one even finds that the WXhole polarisability for carbon is about 60% larger than the corresponding CHF value and in case of H₂O the polarisability for hydrogen is more than twice as large as the CHF value, see Table III. These differences can be attributed to the differences between the WXhole and the CHF response functions. Both, for WXhole and CHF the atomic polarisability for carbon increases in

TABLE III. Localised isotropic polarisabilities (in a.u.) calculated from the WXhole response function using the LeSueur-Stone method with the revPBE0(1.0) xc-functional (see Sec. II D). The molecular geometries were taken from Refs. 46 and 109 and the aug-cc-pVTZ basis set has been used. The reference values from the fifth column are coupled Hartree-Fock (aug-cc-pVDZ basis set) polarisabilities taken from Ref. 67. Columns 4 and 5 display the percentual contributions to the respective total polarisabilities.

Molecule	Site	$\bar{\alpha}^A$	%	Ref.	%
CO	C	7.89	59	7.37	61
	O	5.56	41	4.79	39
	total	13.45		12.15	
CO ₂	C	6.31	31	3.97	26
	O	7.03	34.5	5.53	37
	total	20.37		15.02	
H ₂ O	O	5.61	54	5.69	71
	H	2.36	23	1.14	14.5
	total	10.33		7.97	
C ₂ H ₂	C	8.46	39	9.46	42
	H	2.48	11	1.80	8
	total	21.89		22.53	
C ₂ H ₄	C	7.27	29	7.54	27
	H	2.72	10.5	3.10	11.5
	total	25.43		27.48	

the order of the molecules CO₂ < C₂H₄ < C₂H₂ reflecting the chemical environment in both cases: in the CO₂ molecule the more electronegative bonding partner reduces the polarisability of carbon compared to the hydrocarbon molecules in which the bonding partner is more electropositive.

D. Correlation energies from the localised weighted exchange-hole polarisabilities

Using the localised isotropic polarisabilities from the LeSueur-Stone method (see Sec. II C) the long-range correlation energy between two molecules A and B can be calculated as

$$E_c^{(2)}(A-B) = -\frac{3}{\pi} \sum_{n \in A} \sum_{m \in B} \frac{1}{R_{nm}^6} \int_0^\infty d\omega \bar{\alpha}^n(i\omega) \bar{\alpha}^m(i\omega). \quad (19)$$

Note that Eq. (19) accounts only for the leading order contribution to the asymptotic expansion of the dispersion energy, i.e., higher-order contributions that have a distance dependence of $1/R^n$ with $n = 8, 10, \dots$ are neglected. Moreover Eq. (19) is, in contrast to the nonexpanded dispersion energy expression from Eq. (1), valid only if the two monomers have a large distance from each other, that is, if the distances R_{nm} between two atoms n and m are larger than typical intramolecular bond distances within the molecule. At shorter distances the correlation contribution from Eq. (19) has to be properly damped. This is true also, because the aim is here to combine Eq. (19) with density-functional theory to account for the short-range interaction contributions as is done in common DFT+D methods. Standard (hybrid-)DFT methods are able to describe intermolecular correlation energies if the monomers are closer to each other. Thus Eq. (19) has to be damped for

short distances R_{nm} . One possibility to do this is to use the functional form

$$E_c^{(2)}(A-B) = -\frac{3}{\pi} \sum_{n \in A} \sum_{m \in B} \frac{f_{\text{damp}}(R_{nm})}{R_{nm}^6} \times \int_0^\infty d\omega \bar{\alpha}^n(i\omega) \bar{\alpha}^m(i\omega), \quad (20)$$

with

$$f_{\text{damp}}(R_{nm}) = \begin{cases} 0 & \text{if } R_{nm} \rightarrow 0, \\ 1 & \text{if } R_{nm} \rightarrow \infty. \end{cases}$$

Note now that the decomposition of the polarisabilities into atomic contributions allows to extend the expression of Eq. (20) to describe the long-range correlation energy of the total supersystem (AB) and not just the interaction part of it by summing over all distinct atom pairs:

$$E_{c,lr}^{(2)} = -\frac{3}{\pi} \sum_{n < m} \frac{f_{\text{damp}}(R_{nm})}{R_{nm}^6} \int_0^\infty d\omega \bar{\alpha}^n(i\omega) \bar{\alpha}^m(i\omega), \quad (21)$$

where the subscript lr is used to denote that the energy expression is a long-range correlation functional. The functional of Eq. (21) now evidently also describes the long-range part of intramolecular correlation effects. If used in a supermolecular calculation, however, this intramolecular correlation contribution does not contribute to the interaction energy between two molecules if the local polarisabilities of the dimer system and the monomers (or the corresponding atom-atom dispersion coefficients) are identical. While this usually is the case in conventional DFT+D methods, which often use fixed atomic dispersion coefficients, in the current approach the local polarisabilities within the dimer might differ from their values within the monomers due to the perturbing field of the other monomer in the dimer calculation. While this in principle describes a physical response effect, the actual contribution might depend on the localisation method used to transform the distributed polarisabilities to local ones. It has been found that using the LeSueur-Stone localisation method the relaxation effect that causes differing local polarisabilities on the atomic centres in the dimer and the monomers is very small.

In this work, the damping function developed by Grimme *et al.* (see Ref. 39, Eq. (4)) is used which uses atomic cut-off radii R_{AB}^0 determined from first-order DFT atom-atom interaction energies. This damping function contains two additional global parameters, a “steepness” parameter (α_6) and a scaling factor for the cutoff radii ($s_{r,6}$). As in the work by Grimme *et al.* the value of the steepness parameter is fixed to $\alpha_6 = 14$ while the scaling factor $s_{r,6}$ is adapted to the density functional, see below. Note that the value of the steepness parameter has not been fitted but has been manually adjusted such that the dispersion correction is $< 1\%$ of the total absolute undamped dispersion correction for typical covalent bond distances, see Ref. 39.

Since the form of the damping function will depend on the type of density functional used to calculate the short-range contributions to the correlation energy, the problem of combining Eq. (21) with DFT energies will now briefly be discussed. Studying the interaction potentials of rare gas

dimers from some common density functionals it has been found by a number of groups that some functionals yield attractive interactions in these dimers while others do not.^{70,71} Functionals that fall into the first type of category are, e.g., PBE (Perdew-Burke-Ernzerhof),⁷² PW91 (Perdew-Wang),⁷³ and TPSS (Tao-Perdew-Staroverov-Scuseria),¹¹ and functionals that fall in the second group of functionals are, e.g., BLYP (Becke-Lee-Yang-Parr),^{74,75} and B3LYP (Becke’s 3-parameter hybrid density functional).^{76,77} Thus one finds that apparently those functionals that obey the Lieb-Oxford bound,⁷⁸ namely PBE, PW91, and TPSS, provide also more accurate interaction energies for van-der-Waals systems. In this context, it is important to note that attractive interaction energies can already be described by the exchange part of the functional, see Refs. 79, 80 for a more detailed analysis of the role of the exchange functional in the description of intermolecular interactions. For example in case of the Neon dimer the PBE exchange functional yields a binding energy of -0.11 kcal/mol at a bond distance of $5.84 a_0$. Therefore, if Eq. (20), which is negative definite, is to be combined with supermolecular DFT interaction energies, it would be desirable that the corresponding functional would not mimic dispersion interactions, otherwise there would be some double-counting of electron correlation effects in the mid-range region of the interaction potentials. One possibility to solve this problem would be to use so-called short-range density functionals^{14,25,81–83} which are used in range-separated hybrid DFT-WFT (wave function theory) methods.^{17,18,84} Another remedy to this problem is to design density functionals in such way that their long-range correlation contributions to intermolecular interaction energies is reduced.^{38,85,86}

Here, the second approach is followed using a modified hybrid PBE0 functional.⁸⁷ For this the empirical coefficient κ of the original PBE exchange functional,⁷² that is fixed to a value of $\kappa = 0.804$ in Ref. 72 to satisfy the local Lieb-Oxford bound, is modified, thus weakening the Lieb-Oxford bound. In Ref. 88, it has been shown that using a value of $\kappa = 1.245$ in the PBE functional, then termed as revised PBE (revPBE) functional, considerably improves atomic total energies and atomisation energies compared to the original PBE. Here the value of κ is set to a value of 1.0 that is an approximate average of the original value (0.804) and the revised value (1.245). It is found that by this choice the resulting hybrid functional, termed as revPBE0(1.0) in this work, and which is identical to the PBE0 functional with exception of the modified exchange PBE part, gives the most balanced description of strongly interacting hydrogen-bridged and dispersion dominated complexes if combined with the long-range correlation term of Eq. (21). The total energy for a molecular system is then calculated as

$$E^{\text{WXhole}} = E^{\text{revPBE0}(1.0)} + E_{c,lr}^{(2)}, \quad (22)$$

where the long-range correlation contribution $E_{c,lr}^{(2)}$ is calculated using the orbitals and eigenvalues from a precedent Kohn-Sham calculation using the revPBE0(1.0) functional. The scaling factor $s_{r,6}$ for the cutoff radii in the damping function used in conjunction with this functional has been set to a value of $s_{r,6} = 1.0$.

The acronym WXhole from now on will be used for referring to the hybrid method of Eq. (22) using the revPBE0(1.0) functional.

III. TECHNICAL DETAILS

The hybrid DFT-WXhole method (from now on termed as WXhole method for convenience) described in Sec. II D has been tested for several benchmark sets, namely the S22 and a subset of the $S66 \times 8$ databases developed by Hobza *et al.*^{89,90} and five subsets of the GMTKN30 database developed by Grimme^{91–93} (note that the GMTKN30 database itself contains the S22 database set).

The S22 and $S66 \times 8$ databases contain intermolecular complexes for small to medium sized (~ 20 atoms per monomer) organic molecules. The S22 set contains 22 complexes which are in their equilibrium structure and comprises hydrogen-bridged systems, dispersion dominated systems and mixed type systems, i.e., systems in which the electrostatic and dispersion interactions have an equal weight. The $S66 \times 8$ database is a recently developed extension to the S22 database containing 66 dimer systems at equilibrium and nonequilibrium structures. The nonequilibrium structures in this database were obtained by scaling the intermolecular distances in the optimised structure by values of 0.9, 0.95, 1.05, 1.10, 1.25, 1.50 and 2.0 resulting in 8 structures for a given dimer system altogether in each case. In this work, the following subset of the $S66 \times 8$ database for studying the performance of WXhole has been used: $C_2H_2-H_2O$ (E), $CH_3NH_2-H_2O$ (E), $C_2H_4-C_5H_{12}$ (D), $Bz-C_2H_2$ (M), Bz_2 (D) (which is identical to the corresponding parallel displaced structure from the S22 database, but with a slightly different geometry, see Ref. 90) and $(pyridine)_2$ (M). The acronyms in parenthesis stand for E: electrostatics-dominated, D: dispersion-dominated and M: mixed, measured by the ratios of the dispersion over the electrostatic interaction energies obtained from DFT-SAPT (Refs. 19 and 20) calculations. The basis set extrapolated second-order Møller-Plesset perturbation theory (MP2) and coupled-cluster singles doubles with perturbative triples (CCSD(T)) reference values for the S22 complexes were taken from Ref. 94 and those for the $S66 \times 8$ complexes from Ref. 90.

From the GMTKN30 database the following subsets were chosen: IDISP containing 6 systems for studying intramolecular dispersion interactions, HEAVY28 designed to study the interaction energies of 28 heavy element hydrides, BHPERI for studying the barrier heights of 26 pericyclic reactions, DARC for studying the reaction energies of 14 Diels-Alder reactions and SCONF is a database of 17 sugar conformers for studying their relative energies. The geometries and reference values for these databases were all taken from Ref. 91.

The DFT calculations and the calculation of the distributed polarisabilities from the WXhole response function were all done using the Molpro quantum chemistry program.⁹⁵ The def2-QZVP basis set^{96,97} has been used throughout as it was found that it yields results close to the basis set limit and avoids linear dependencies of basis set functions for the larger molecules due to only moderately

diffuse functions. For the heavier elements ($Z > 36$) in the HEAVY28 benchmark set small core effective pseudopotentials of the Stuttgart/Cologne group were used.^{98,99} In the calculations with more than 400 basis functions, density fitting was used to approximate the the Coulomb- and (exact-) exchange matrices employing the cc-pVQZ-JKFit auxiliary basis sets by Weigend¹⁰⁰ augmented with one additional diffuse function by building the progression ratio $\varepsilon_1^2/\varepsilon_2$ where ε_1 was the most-diffuse exponent already present and ε_2 the next most diffuse one if both existed, or $\varepsilon_1/2.5$ if only one exponent existed beforehand (implemented by Gerald Knizia in the Molpro basis set library⁹⁵). All calculations for the databases containing intermolecular complexes (S22, $S66 \times 8$, and HEAVY28) were done using the Boys and Bernardi¹⁰¹ counterpoise correction scheme to reduce the basis set superposition error. The threshold for molecular integration grids in the DFT calculations and the calculation of the localised polarisabilities was set to a value of 10^{-8} that adapts the integration grid such that the numerical integration over the Slater-Dirac exchange energy kernel does not differ by more than this value from the corresponding analytical integral for each respective molecule. This value turned out to be sufficiently accurate. The frequency integration in Eq. (20) was done numerically using a 10-point Gauss-Legendre quadrature.¹⁰²

For the calculation of the localised polarisabilities the Orient4.7 program by Stone *et al.*⁶⁹ has been used using the distributed polarisabilities from the WXhole method as input. The final calculation of the damped dispersion energies was then done using an own written Python script.

It should be noted here that the WXhole method described in this work is more computationally demanding than conventional DFT+D methods that use fixed atom-atom dispersion coefficients. The most time-consuming step is the calculation of the distributed polarisabilities which requires operations that scale as $N_{\text{atom}}N_{\text{occ}}^2N_{\text{grid}}$ and $N_{\text{atom}}^2N_{\text{occ}}N_{\text{grid}}$ with N_{atom} the number of atomic centres, N_{occ} the number of occupied orbitals and N_{grid} is the number of quadrature points of the numerical integration grid. The overall scaling behaviour of the approach therefore is N^4 with the system size and thus by one order of magnitude larger than the (asymptotic) scaling behaviour of the DFT calculation itself. Practically, however, the calculation of the distributed polarisabilities required less CPU time than the DFT calculation itself for all systems studied in this work. For example, the DFT calculation for the adenine-thymine base pair required about 2 h to converge (in 13 SCF cycles) while the corresponding calculation of the distributed polarisabilities for this systems took only 25 min (10 frequency integration points) using the same DFT quadrature grid. The calculations were done on a 2.96 Ghz Intel i7-870 processor in serial mode.

IV. RESULTS

A. S22 dimer systems

Table IV shows the interaction energies for the S22 complexes calculated with the WXhole method compared to extrapolated MP2 and CCSD(T) results. Note that the table

TABLE IV. Intermolecular interaction energies for the S22 complexes (in kcal/mol). The mean absolute errors (mae) and relative deviations ($|\Delta|$) to the CCSD(T) reference values are shown for each group of complexes (hydrogen bonded: top, dispersion dominated: middle and mixed-type: bottom). The last two lines show the total mean absolute errors and total relative deviations, respectively.

Dimer	MP2/cbs	CCSD(T)/cbs	WXhole
(NH ₃) ₂ (C _{2h})	− 3.16	− 3.17	− 2.95
(H ₂ O) ₂ (C _s)	− 4.98	− 5.02	− 4.97
(HCOOH) ₂ (C _{2h})	− 18.57	− 18.80	− 19.54
(CHONH ₂) ₂	− 15.84	− 16.12	− 16.28
Uracil-Uracil (C _{2h})	− 20.41	− 20.69	− 21.01
2-Pyridoxine-2-Aminopyridine	− 17.37	− 17.00	− 17.91
AT (WC)	− 16.54	− 16.74	− 17.63
mae	0.20		0.47
$ \Delta $ [%]	1.26		3.57
(CH ₄) ₂ (D _{3d})	− 0.49	− 0.53	− 0.47
(C ₂ H ₄) ₂ (D _{2d})	− 1.58	− 1.50	− 1.47
Bz-CH ₄ (C ₃)	− 1.81	− 1.45	− 1.30
Bz-Bz (C _{2h})	− 4.96	− 2.62	− 2.24
Pyrazine-Pyrazine (C _s)	− 6.91	− 4.20	− 3.89
Uracil-Uracil (C ₂)	− 11.10	− 9.74	− 10.16
Indole-Bz (stacked)	− 8.09	− 4.59	− 4.27
AT (stacked)	− 14.83	− 11.66	− 12.21
mae	1.70		0.28
$ \Delta $ [%]	38.62		7.68
C ₂ H ₄ -C ₂ H ₂ (C _{2v})	− 1.67	− 1.51	− 1.67
Bz-H ₂ O (C _s)	− 3.54	− 3.29	− 3.45
Bz-NH ₃ (C _s)	− 2.66	− 2.32	− 2.31
Bz-HCN (C _s)	− 5.16	− 4.55	− 4.49
Bz-Bz (C _{2v})	− 3.63	− 2.71	− 2.71
Indole-Bz (T-shaped)	− 6.98	− 5.62	− 5.76
Phenole-Phenole	− 7.76	− 7.09	− 7.10
mae	0.61		0.08
$ \Delta $ [%]	16.24		2.77
mae (total)	0.88		0.27
$ \Delta $ [%] (total)	19.61		4.81

is partitioned into three groups: hydrogen-bridged systems (top), dispersion dominated complexes (middle) and mixed type complexes (bottom).

For the hydrogen-bridged systems it can be observed that with only one exception, namely the CHONH₂ dimer, the MP2 values are closer to the CCSD(T) results than the interaction energies from WXhole. In total, the mean absolute error of the WXhole method for the hydrogen-bridged systems is more than twice as large as with MP2 and amounts to 0.47 kcal/mol, see Table IV. Note, however, that this error still lies within the range of the desired chemical accuracy of 0.5 kcal/mol. In case of the dispersion dominated complexes, see group in the middle in Table IV, it is known that the MP2 interaction energies in most cases crucially overestimate the CCSD(T) interaction energies due to an improper description of the dispersion interaction energy on an uncoupled Hartree-Fock level, see Refs. 56, 57, and 103. In contrast to this, the average percentual deviation of WXhole to CCSD(T) for the dispersion dominated group is much smaller than with MP2, see Table IV. However, it can be observed that in case of the

stacked Bz₂ (benzene dimer) the WXhole interaction energy strongly underestimates the CCSD(T) reference interaction energy, see Table IV. This will be investigated more in detail in Sec. IV B. For the mixed-type complexes the WXhole method shows the best performance with a deviation of only 0.08 kcal/mol to the CCSD(T) reference results.

As a consequence the total performance of the WXhole method for the S22 complexes is much better than with MP2 if the CCSD(T) method is taken as reference, see statistical errors in the bottom lines of Table IV. Note that a similar good performance is also found for the related XDM method by Becke and Johnson^{31–36} and the LRD method by Sato *et al.*⁴⁰ In case of the LRD method, the total mean absolute error for the S22 systems was found to be 0.27 kcal/mol if C₆, C₈ and C₁₀ terms are accounted for⁴⁰ and thus the LRD method has an accuracy that is comparable to the present approach. In case of the XDM method, a very recent benchmark of Burns *et al.* yields even a mean absolute deviation of only 0.19 kcal/mol for the combination of the XDM correction with the B3LYP functional.¹⁰⁴

The S22 database comprises only dimers in their equilibrium structure and is therefore not sufficient to analyse the quality of a method to reproduce potential energy surfaces. Thus, in Sec. IV B, the performance of the WXhole method will also be tested for nonequilibrium geometries for some dimer systems. A comparison of the WXhole method to the DFT+D3 method by Grimme for the S22 systems (that itself is a subset of the GMTKN30 database) will be made in Sec. IV C.

B. Six subsets of the S66 × 8 dimer systems

Figures 2(a)–2(f) display the interaction energy curves for the six dimers chosen from the S66 × 8 database. On the abscissa axis in the diagrams the scaling factor for the equilibrium distance (yield by the MP2 method) of the respective systems is plotted, and therefore represents a relative but not absolute measure for the distance of the monomers, see Ref. 90 for details.

It can be seen that for some dimers, namely C₂H₄-C₅H₁₂, Bz-C₂H₂ (Bz: benzene) and Py₂ (Py: pyridine) the WXhole method yields too large equilibrium distances compared to the CCSD(T) reference curves. As a result, the true binding energy from the WXhole method is lower than if it would be calculated at the equilibrium structures of the S66 database. In case of Bz₂, the actual minimum for WXhole lies about −0.2 kcal/mol lower than at the minimum structure of the S66 database. As a consequence, the binding energy of WXhole for the π - π stacked Bz₂ dimer is closer to the extrapolated CCSD(T) reference result than the first estimate for the S22 database, see Table V. As can be seen in Figure 2(e), also the minimum of the CCSD(T) curve is somewhat displaced to the right compared to the minimum at the scaling factor of 1.0 that refers to the minimum distance yield by the MP2 method, see Ref. 90.

For the two electrostatic bound complexes C₂H₂-H₂O (Figure 2(a)), and CH₃NH₂-H₂O (Figure 2(b)), one can observe that the MP2 curves are very close to the CCSD(T) interaction curves, as expected, while the WXhole curve

FIG. 2. Interaction energy curves for six dimers from the S66 $\times$ 8 database. (a) $C_2H_2-H_2O$; (b) $CH_3NH_2-H_2O$; (c) $C_2H_4-C_5H_{12}$; (d) $Bz-C_2H_2$; (e) $Bz-Bz (\pi-\pi)$; (f) pyridine-pyridine.

TABLE V. Binding energies for a subset of 6 dimers from the S66 database (in kcal/mol). The first column contains the reference number for the respective dimer used in the S66 database. The last two lines show the mean absolute errors (in kcal/mol) and the average absolute percentual errors to the CCSD(T)/cbs reference values.

Ref. no.	dimer	MP2/cbs	SCS-MP2/cbs	CCSD/cbs	CCSD(T)/cbs	WXhole
3	CH ₃ NH ₂ -H ₂ O	-7.084	-6.391	-6.595	-6.908	-7.21
24	Bz ₂ (π - π)	-4.703	-2.905	-1.762	-2.822	-2.43
44	C ₂ H ₄ -C ₅ H ₁₂	-2.151	-1.280	-1.524	-2.005	-1.90
50	Bz-C ₂ H ₂ (CH- π)	-3.463	-2.648	-2.493	-2.867	-2.94
58	Pyridine ₂ (CH-N)	-4.367	-3.576	-3.688	-4.146	-4.04
59	C ₂ H ₂ -H ₂ O	-2.873	-2.553	-2.731	-2.850	-2.99
mae		0.50	0.40	0.47		0.19
\Delta		17.2	13.1	15.7		5.6

in case of C₂H₂-H₂O underestimates the CCSD(T) curve slightly and in case of CH₃NH₂-H₂O the WXhole curve is very close to the MP2 curve. For all other systems (Figures 2(c)–2(f)) the WXhole interaction energy curves are clearly closer to the CCSD(T) reference curves than the MP2 curves which partially show a strong overbinding compared to CCSD(T). Note that the Bz-C₂H₂ dimer has a T-shaped structure and is therefore comparable to the CH- π bound Bz₂ structure from the S22 database, see Table IV. In Ref. 105, it was argued that the CH- π bound Bz₂ structure from the S22 data base actually should be categorised as dispersion bound complex, since the ratio of the dispersion interaction energy over the total sum of all polarisation terms up to second order of the intermolecular perturbation theory expansion exceeds a value of 0.7.¹⁰⁵ In all six dimers the interaction energies at larger intermonomer distances are close to each other with exception of the ethyne-water dimer in which the WXhole method slightly overestimates the binding energies yield by the MP2 and CCSD(T) method, see Figure 2(a). As the dispersion correction at larger distances has a stronger contribution to the total interaction energy than at smaller distances it can be concluded from this observation that the long-range correlation contribution is well reproduced by the WXhole method in the considered systems. In contrast to this, it can be seen in Figure 2 that in the repulsive regions of the interaction potential the WXhole interaction energies tend to underestimate, while the MP2 interaction energies tend to overestimate the CCSD(T) interaction energies. Since the interaction energies of the WXhole method in the repulsive regions of the interaction potentials more strongly depend on the damping function a further refinement of the damping function parameters might be necessary in order to improve the performance of the method for smaller monomer distances.

In Table V, the binding energies for the six dimers calculated with MP2, SCS-MP2 (spin-component scaled MP2 (Ref. 106)), CCSD, CCSD(T), and WXhole are shown. Note that in case of WXhole the corresponding values were obtained from a cubic splines interpolation of the close minimum regions of the interaction curves using solely the energy data from the geometries of the S66 $\times$ 8 database and are therefore only given with three significant digits in Table V. As can be seen, both SCS-MP2 and CCSD improve

the MP2 interaction energies on average for the six dimers, but the improvement is not large, see statistical errors displayed in the last two lines of Table V. In contrast to this, the WXhole method yields the most balanced description for the binding energies as the deviations from the CCSD(T) reference values are similar for the electrostatics-dominated and the dispersion-dominated complexes. In total, the mean absolute error and the average percentual errors to CCSD(T) for the binding energy of WXhole is clearly smaller than with the other methods from Table V.

C. Performance for five subsets from the GMTKN30 database

In order to assess the applicability of the WXhole method for predicting other properties than the intermolecular interaction energies of organic molecules, five additional (the S22 database is included in the GMTKN30 database) benchmark sets from the GMTKN30 database of Grimme *et al.* were considered, see Sec. III for a short description. For these benchmark sets, a broad number of DFT values are available to compare with, including values obtained by the recently developed DFT-D3 method from Grimme *et al.*³⁹ In order to test the performance of WXhole against the DFT-D3 method, the Figures 3(a)–3(f) therefore show the mean absolute deviations for the six databases for the WXhole method (red bars) and 22 different hybrid DFT-D3 methods (green bars) (please refer to Ref. 92 for a reference to the different functionals shown). Note that the DFT-D3 method differs from the current approach not only with respect to the differently calculated atomic C_6 coefficients, but it also takes higher-order multipole interactions into account using approximate atomic C_8 coefficients calculated from the atomic C_6 values.³⁹ In addition, the diagrams in Figure 3 also show the mean absolute deviations of the MP2 and SCS-MP2 method for comparison (blue bars).

As can be observed in Figure 3(a), the WXhole method is among the best DFT-D3 functionals for the S22 benchmark set and only the M06-D3 method performs slightly better. Most of the functionals displayed in the diagram have errors that are more than 0.1 kcal/mol larger than yield with WXhole. The SCS-MP2 method improves the performance of the MP2 method on average, but still its mean absolute error is

FIG. 3. Performance of WXhole (red bars), hybrid DFT-D3 methods (green bars) and MP2/SCS-MP2 (blue bars) for six subsets of the GMTKN30 database. (a) S22; (b) HEAVY28; (c) IDISP; (d) SCONF; (e) DARC; (f) BHPER1.

more than twice as large as with the WXhole method. For the HEAVY28 benchmark set, testing interactions between heavy element hydrides, and the IDISP benchmark set, testing intramolecular interactions, however, the performance of the WXhole approach deteriorates compared to the S22 set. While for the HEAVY28 database the error for WXhole is about 0.1 kcal/mol worse than for the best DFT-D3 functionals for this test set, in case of the IDISP database the deviation to the errors for the best functionals is even more than 3 kcal/mol. Note that the systems of the IDISP database are very large and that the reference interaction energies were estimated on the MP2.5 level¹⁰⁷ of theory only and not using the CCSD(T) method. The comparison of different methods for this benchmark set therefore relies somewhat on the assumption that the MP2.5 reference values are good estimates for the interaction energies obtained by coupled-cluster and higher level correlation methods. It can be seen in Figure 3(c) that the WXhole method is slightly better than MP2 for the description of intramolecular correlation effects which shows that, if not highly accurate for this case, it at least does not give a completely unreasonable description of intramolecular correlation.

The three test sets SCONF, DARC, and BHPERI are considered here in order to investigate the performance of the WXhole method also for other chemical properties, namely conformational energies, reaction energies and reaction barriers. Note that in all three benchmark sets the system sizes are that large that long-range correlation contributions will considerably contribute to the respective property. For example comparing the revPBE0 against the revPBE0-D3 functional (revised PBE0 functional including the D3 dispersion correction by Grimme) shows improvements of the mean absolute deviations to the reference data of 1 kcal/mol for SCONF, 4.2 kcal/mol for DARC and 3.3 kcal/mol for BHPERI using the dispersion correction. As can be seen in the diagrams in the Figures 3(d)–3(f) the WXhole method performs fairly well for these benchmark sets. In case of the SCONF benchmark set, WXhole ranks in the middle between the best and more worse DFT-D3 methods while for the DARC and BHPERI benchmark sets the WXhole method belongs to the best performing methods. A more detailed comparison of the WXhole method to one of the best DFT-D3 methods, namely revPBE0-D3, for the six benchmark sets can be found in the supporting information.¹⁰⁸

V. SUMMARY

A new method has been developed that enables the calculation of response properties and long-range correlation energies by using a model of the response function which depends only on occupied orbitals and orbital energies. This model for the response function has been obtained by refining the recently developed exchange-hole model of the response function from Ref. 46 by replacing the constant mean excitation energy with occupied orbital energy shifts that more accurately model the structure of the response function at resonance frequencies. The response function obtained in this way contains a nonlocal contribution that is similar to the exchange-hole density, but contains weight

factors stemming from the occupied orbital energy shifts. Because of this the new approach is termed as “weighted exchange-hole” (WXhole) method in this work. Two parameters in the response function were introduced, one standing for the average energy of an unoccupied state and another one improving the frequency dependence of the response function, see Eq. (15). Both were individually optimised for Hartree-Fock and a hybrid density functional termed as revPBE0(1.0), to reproduce static dipole-dipole polarisabilities and isotropic C_6 dispersion coefficients. Considering the crude approximations underlying the WXhole model, the agreement of calculated polarisabilities and dispersion coefficients with accurate reference results was fairly good. Both, for Hartree-Fock and revPBE0(1.0) the average absolute deviations to corresponding reference results for a number of small molecules was found to be about 10–14% only.

The main motivation of this work was to use the WXhole method for describing long-range correlation energies in order to improve the deficiencies of common density functionals that are unable to describe the weak interactions between noncovalently bound systems. This could be achieved by deriving localised frequency-dependent polarisabilities from the distributed WXhole polarisabilities using the method from LeSueur and Stone.⁶⁶ Long-range correlation energies could then be calculated from the polarisabilities using the well known leading order asymptotic form of the dispersion interaction energy summing over distinct atom pairs. In order to combine this long-range correlation term with a hybrid density functional method, termed as revPBE0(1.0), the damping function of Grimme *et al.* was used.

The hybrid DFT-WXhole method, termed as WXhole in this work for convenience, has been tested for a number of benchmark sets for studying inter- and intramolecular interaction energies, reaction energies and reaction barriers and relative energies for molecular conformations. It has been found that the WXhole method yields fairly accurate interaction energies for organic molecules while in case of the interaction energies of heavy element hydrides and some test systems for studying intramolecular correlation effects the performance of the method was found to be worse, but still reasonable if compared to results yielded by the MP2 method. For the test sets including sugar conformers, Diels-Alder reactions and pericyclic reaction barriers the performance of the WXhole method again was very good and similar to the performance of the best hybrid DFT-D3 methods.

It has to be noted that the present approach certainly has deficiencies compared to standard DFT+D methods with respect to the computational efficiency. This mainly stems from the comparably expensive calculation of distributed polarisabilities required in the DFT-WXhole method. It has been observed, however, that this step conventionally required only fractions of the CPU time of the preceding Kohn-Sham calculation itself. The method therefore can easily be applied to fairly large molecules for which also DFT calculations are still feasible. The main advantage of the DFT-WXhole hybrid method over the standard DFT+D methods, i.e., DFT+D methods that use empirical dispersion coefficients and also the recently developed DFT-D3 method by Grimme,³⁹ is that the long-range correlation energies are calculated from a model

of the response function that explicitly depends on the occupied Kohn-Sham orbitals and eigenvalues, no external data, e.g., atomic dispersion coefficients or, as in the case of the DFT-D3 method, polarisability data from TDDFT calculations, is required. The WXhole correlation energy expression therefore will naturally depend on the chemical environment in contrast to the correlation corrections used in the DFT-D1/2 methods^{37,38} (note that in the DFT-D3 method a model is introduced to make the atomic dispersion coefficients dependent on the chemical environment using the coordination number for a given atom). Thus the DFT-WXhole method offers a less empirical approach compared to standard DFT+D methods for the study of large molecular systems in which the long-range correlation contributions become important.

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