London dispersion forces by range separated hybrid density functional with second order perturbational corrections (RSH+MP2): the case of rare gas complexes

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Abstract

A satisfactory account of the van der Waals (London dispersion) forces is, in general, not possible by the Kohn-Sham method using standard local, semi-local GGA or meta-GGA density functionals. The recently proposed range-separated hybrid (RSH) approach, supplemented by second order perturbational corrections (MP2) to include long range dynamic correlation effects offers a physically consistent, seamless description of dispersion forces. It is based on a rigorous generalization of the Kohn-Sham method, where long-range exchange and correlation effects are treated by wave function methods, while short-range electron exchange and correlation are handled by local or semi-local functionals. The method is tested on a series of rare gas dimers in comparison with standard WFT and DFT approaches. In contrast to the most successful xc-functionals, which describe at best the vdW minimum, the RSH+MP2 approach is valid also in the asymptotic region and the potential curve displays the correct $1/R^6$ behaviour at large internuclear separations. In contrast to usual MP2 calculations, the basis set superposition error is considerably reduced, making RSH+MP2 an ideal tool for exploring the potential energy surface of weakly bound molecular complexes.
I. INTRODUCTION

Weak intermolecular forces, especially the London dispersion (or van der Waals, vdW) forces, continue to be a challenge for theoretical chemistry and solid state physics. In spite of their relatively small intensity, their universally attractive character and long range of action make that they contribute appreciably to the cohesion of various forms of the matter. In the absence of strong electrostatic or covalent interactions, London dispersion forces become predominant, and they are mainly responsible for the existence of the condensed phases of rare gases, the structure of layered solids, or the stacking of base pairs in the DNA, etc. They play a role in more complex chemical phenomena, like catalytic reaction mechanisms, organic reaction energies, conformational problems, and contribute to isomerization energies of branched alkanes, although in this latter case the contribution of mid-ranged correlation is thought to be the most important.

The density functional theory (DFT), despite of its spectacular successes to describe electronic structure and energetics of solids, atoms and molecules, is unable to provide a fully satisfactory description of these forces, at least not within the framework of the Kohn-Sham method using local (LDA) or semi-local functionals. Although the basic incapacity of the essentially local correlation functionals to account for long-range dynamic correlation effects has been recognized for a long time (see e.g. Ref. 2), the appearance of “reasonable” vdW minima on potential energy curves calculated by some of the generalized gradient approximations (GGA) or meta-GGA functionals has kept alive the hope that this kind of approach might become appropriate for the short-range part of the dispersion forces and can be used to describe at least nearest neighbor intermolecular interactions.

Recently, a series of works has been devoted to special parametrizations of new GGA, meta-GGA functionals, including a portion of Hartree-Fock exchange, in view of attaining a reasonable accuracy for bond lengths and energetics in vdW complexes, in particular in rare gas complexes. In this context, one is faced with several problems. First, it is desirable that such new functionals give not only a good account of the vdW minima, but maintain a reasonable accuracy in other respects as well. This problem is usually handled by careful fitting techniques, including a wide range of physical systems and properties. However, in spite of the efficacy of such a strategy, there is a risk to lose the control on the physical meaning of individual contributions to the total energy, leading to an uncomfortable
situation, when one has the right answer but not necessarily for the right reason.\textsuperscript{19} Even if from a purely pragmatic point of view it is acceptable, this situation becomes prejudicial as far as one needs to add corrections, like for the long-range component of the dispersion forces, admittedly missing from the semi-local density functional models.

Another kind of strategy consists in starting from Hartree-Fock exchange (HFX) and adding appropriate correlation corrections. The advantage of such an approach is that, by construction, the presence of a vdW minimum is directly related to the quality of the correlation functional. Again, local or semi-local correlation functionals can, at best, account for effects in the region of weak intermolecular overlap, while the reproduction of the $1/R^6$ asymptotic behavior would require strongly nonlocal functionals. This latter kind of approach is being explored by several groups. The so-called “exchange-hole model” of Becke and Johnson\textsuperscript{20–24} is based on an energy expression parametrized on the basis of the properties of the exchange hole and on experimental atomic polarizabilities. Seamless dispersion energy functionals\textsuperscript{25–28} that constitute a promising alternative, are based on the adiabatic connection fluctuation dissipation formulation of the correlation energy, and operate with approximate forms of the frequency-dependent dielectric function of the many-electron system. The Andersson-Langreth-Lundqvist model,\textsuperscript{29–35} belonging to this class of theory, developed first for solids, has been generalized for molecular systems as well. In the realm of conventional functionals, there is a renewal of interest for the semi-local Wilson-Levy (WL) correlation functional,\textsuperscript{36} which has been shown to provide very good results not only for rare gas complexes,\textsuperscript{37} but also for the stacking interactions of aromatic rings\textsuperscript{38} and in molecular crystals.\textsuperscript{39} However, further work should be done to check if the HFX-WL functional is amenable to further refinement and able to provide acceptable results for other properties, like covalent bonding geometries and energetics. A considerable shortcoming of the above methods is that, specifically designed for the dispersion interaction problem, they are not able to maintain the same accuracy as the most of the common density functionals for other properties.

The most accurate DFT-based approach is the density functional adaptation of the symmetry-adapted perturbation theory (DFT-SAPT), which is based on the Kohn-Sham densities and response properties of the interacting subunits.\textsuperscript{40–44} Since this approach is based on a partition to individual subsystems, that are stable chemical species, it is well-adapted for the study of weak intermolecular complexes, but cannot take care of dispersion
effects in other phenomena, like conformation problems or reactivity.

Finally, one should mention the family of the empirically corrected DFT calculations. Various proposals have been published in the literature to increment the DFT energy expression by a semi-empirically parametrized, damped $1/R^6$ term. Due to the non-systematic behavior of most of the standard density functionals regarding the vdw forces, specific correction schemes must be elaborated for almost each functional. Even if the correct asymptotics is ensured by the empirical term, one cannot exclude non-physical double counting of correlation effects at short and medium range. Recent developments in the field seem to solve some of these problems. The application of a simple scaling parameter makes possible to use a unique correction scheme for many functionals, and an appropriately chosen damping function may offer a practical solution to the double-counting problem.

The major problem, still unresolved, is related to the limited transferability of the $C_6$ dispersion parameters, which may lead to an underestimation of van der Waals energies involving unsaturated systems or anions.

A satisfactory density functional based, ab initio approach to London dispersion forces is supposed to describe both vdw minima and long-range asymptotic behavior by including correct physical ingredients. The energy expression should be seamless, i.e. valid for any separation of the atoms and independent of any hypothesis of predefined fragments. Moreover, it is desirable that the method, similarly to the Kohn-Sham calculation, converge rapidly with the basis set size, and be only moderately affected by basis set superposition errors.

Keeping in mind these objectives, a new approach based on the generalization of the Kohn-Sham theory, has been elaborated recently, to provide a seamless energy expression, which is valid at any interatomic and intermolecular separation, and is able to handle long-range dynamic correlation effects, responsible for the London dispersion forces. This model, which uses the explicit separation of short- and long-range electron repulsion in the Hamilton operator, is a combination of short-range local or semi-local exchange and correlation functionals with an explicit treatment of long-range exchange and correlation effects. As it has been shown by the group of Hirao, the range-separated hybrid (RSH) exchange functional, composed of short-range density functional and long-range Hartree-Fock exchange, leads to physically plausible repulsive potential curves for rare gas dimers and constitutes a convenient starting point for physically motivated approximations to the long-range correlation effects. One possibility is to combine the range-separated exchange
hybrid with the Andersson-Langreth-Lundqvist non-local dispersion functional.\textsuperscript{53–55} An alternative route, followed by us is to treat long-range correlation perturbationally, by second order MP2 theory. The first results obtained by this RSH+MP2 approach for rare gas\textsuperscript{50} and alkali-earth\textsuperscript{56} homo-dimers are encouraging. Recently, a higher order perturational treatment of the long-range correlation has been attempted at the CCSD(T) level,\textsuperscript{57,58} improving further the agreement between theory and experiments. It should be noted that the present combination of DFT and MP2, although bearing some similarities in its spirit with the recent B2-PLYP semi-empirical hybrid functional of Grimme\textsuperscript{48}, is quite different by the fact that it concentrates mainly on the long-range portion of the exchange and correlation effects.

The aim of this paper is to examine the performance of the RSH+MP2 approach for rare gas complexes. In the next section, Section II, a critical overview is given of the literature about DFT calculations on rare gas complexes. Comparison is done in reduced parameters (binding energies, bond lengths, etc.) of the potential curves, facilitating the analysis of all systems on the same scale. We overview briefly the possible physical reasons of the problems in describing vdW minima by local or semi-local density functionals and establish some guidelines for a more generally applicable density functional based approach for London dispersion forces.

The basic principles of our RSH+MP2 method is outlined in Section III, followed by technical details of the calculations (Section IV). The results are presented in the Section V by comparing them with a consistent set of reference data of “experimental” quality,\textsuperscript{59} with literature data obtained by LDA, PBE, TPSS\textsuperscript{60} and DFT+CCSD(T)\textsuperscript{57} methods, as well as with conventional MP2 and CCSD(T) approaches for a set of rare gas dimers (He\textsubscript{2}, Ne\textsubscript{2}, Ar\textsubscript{2}, Kr\textsubscript{2}, HeNe, HeAr, HeKr, NeAr, NeKr and ArKr). The problem of the basis set convergence and extrapolation of the RSH+MP2 energies to complete basis set (CBS) limit is discussed in Sec. V C, followed by an analysis of the basis set superposition error (BSSE) in the various approximations (Sec. V D). We conclude (Section VI) by a general discussion of advantages and possible shortcomings of the RSH+MP2 approach.
II. CRITICAL ANALYSIS OF DFT RESULTS

A. Choice of reference potential curves

Benchmarking theoretical predictions requires high-quality experimental data. This is particularly important when one deals with very small energy differences in the order of $\mu$H, like in the case of rare gas complexes.

Accurate analytical rare gas dimer potentials have been developed in a series of works by Aziz and his coworkers. These multiproperty fits of various analytical forms are based on a wide range of experimental data, including second virial coefficients, spectroscopic constants and transport properties. Ogilvie and Wang (OW) compiled experimental rare gas potentials available in the early nineties by using a unique potential function of polynomial form. The OW potential is well-adapted to determine spectroscopic constants for homo- and hetero-nuclear dimers, but less appropriate for the long-range, asymptotic part of the potential. A more recent compilation, taking into account new experimental data as well, is due to Tang and Toennies. Their potential energy expression, valid for a much wider range of internuclear distances, is defined as:

$$U(r) = Ae^{-br} - \sum_{n=3}^{N} f_{2n}(br) \frac{C_{2n}}{r^{2n}},$$  

(1)

where the damping function, $f_{2n}(br)$, is given by

$$f_{2n}(x) = 1 - e^{-x} \sum_{k=0}^{2n} \frac{x^k}{k!}.$$  

(2)

By a systematic use of the combination rules, these authors were able to derive a set of potentials of uniform quality, in very good agreement with the most reliable recent experimental potentials. Therefore, we recommend to use the 2003 Tang-Toennies (TT) potential for the validation of theoretical models.

According to Trouton’s rule of corresponding states, appropriately normalized rare gas dimer potentials are superimposable. The normalized (or reduced) potentials can be written as

$$\varepsilon(\xi) = U(\xi r_{\text{ref}})/U_{\text{ref}},$$  

(3)
where the reduced variables $\varepsilon = U/U_{\text{ref}}$ and $\xi = r/r_{\text{ref}}$, are defined with respect to the reference equilibrium distance $r_{\text{ref}}$ and the well-depth $U_{\text{ref}} = U(r_{\text{ref}})$.

Absolute values of these parameters are listed for the 10 dimers in Table I. This table reports two further characteristic parameters of the potential: the hard core radius factor, $\sigma$, defined by the relation $U(\sigma r_{\text{ref}}) = 0$ and the harmonic vibrational frequency, $\omega$, which has been obtained from the harmonic force constant $k$ and the dimer reduced mass $\mu$, as

$$\omega = \sqrt{\frac{k}{\mu}},$$  \hspace{1cm} (4)

where $k = (\partial^2 U/\partial r^2)_{r=r_{\text{ref}}}$. Atomic masses entering in the calculation of the reduced mass $\mu = M_1 M_2 / (M_1 + M_2)$, were taken from Refs. 66,67.

Although it is a common practice in the literature to describe potential energy curves, binding energies and equilibrium distances in absolute scales, the use of reduced potentials has some advantages in the discussion of theoretical results. The absolute scale might be useful to compare properties of different systems, and appreciate, e.g. that He-Ar and He-Kr have almost the same binding energy around 100 $\mu$H. However, in an absolute scale it is more difficult to compare the performance of a given method in a family of complexes, having equilibrium distances that may vary by about 2 Å and binding energies that can change by more than one order of magnitude. Therefore, all theoretical equilibrium results have been converted to reduced quantities, $\xi_m = r_m / r_{\text{ref}}$ and $\varepsilon_m = U(r_m) / U_{\text{ref}}$, where $r_m$ is the calculated equilibrium bond length. We call the attention to the fact that some of our reference values slightly differ from those cited in recent theoretical papers on rare gas complexes, taken from the compilation of OW. For instance, two recent studies$^{60,70}$ report the reference value of 15.6 meV (575 $\mu$H) for the binding energy of ArKr, taken from the compilation of OW, differing from the value of 14.4 meV (531 $\mu$H) recommended by TT, in a closer agreement with experimental data. The reference binding energies of 0.0025 eV (90.6 $\mu$H) attributed to HeAr and HeKr systems turn out to be slightly different from each other if one converts the OW data directly to $\mu$H units: 91.6 and 91.1 $\mu$H, respectively. Both of these values differ from 93.7 and 99.6 $\mu$H, recommended by TT.

The global performance of the different methods can be characterized by the mean error (ME), the mean absolute (or unsigned) error (MAE), and the standard deviation (SDEV) calculated on the basis of the reduced parameters. Taking into account that in reduced
parameters the reference value is 1, we have the following definitions:

\[
ME(a) = \frac{1}{N} \sum_{i=1}^{N} a_i - 1
\]

\[
MAE(a) = \frac{1}{N} \sum_{i=1}^{N} |a_i - 1|
\]

\[
SDEV(a) = \sqrt{\frac{\sum_{i=1}^{N} (a_i - 1 - ME(a))^2}{N - 1}}
\]

The mean percentage of errors (M%E), mean of absolute percentage of errors (MA%E) and the corresponding standard percentage deviation (S%DEV) is simply 100 times the previously defined quantities. The magnitude of standard deviation characterizes the systematic or random character of the results provided by a given methodology.

**B. Overview of DFT results on rare gas dimers**

Calculated potential curve parameters taken from the works of Patton and Pederson,\textsuperscript{70,71} Zhao and Truhlar,\textsuperscript{72} Perez-Jordá et al.\textsuperscript{37} and Walsh\textsuperscript{38} have been transformed to reduced quantities and summarized in Table II. The CCDS(T) results, taken from the work of Cybulski\textsuperscript{73,74} is cited for the sake of comparison. Various means and standard deviations for the binding energy and bond length are listed in the order of increasing M%E(\(\xi_m\)).

The smallest, albeit not negligible error is observed in the case of WFT CCSD(T) calculations.\textsuperscript{73,74} Small standard deviation is a sign of the systematic nature of the error, attributed to basis set incompleteness and indicating that the CCSD(T) model grasps correctly the physical basis of dispersion forces in all the systems of this family.

A remarkable case is that of the Wilson-Levy correlation functional,\textsuperscript{36} applied \emph{a posteriori} to Hartree-Fock densities.\textsuperscript{37,38} The mean unsigned percentage errors, obtained from binding energies calculated in Refs. 37 and 38 are amazingly good, almost as good as those obtained by CCSD(T), although with a ten times higher standard deviation, which remains nevertheless significantly smaller than that of any other DFT approach. As mentioned in the Introduction, there is admittedly no explanation for such a good performance of this functional.

It is a well-documented fact in the literature that the LDA approach seriously fails in
describing rare gas complexes: it overbinds strongly, i.e. the equilibrium distance is too small (by almost 15%) and the binding energy is much too high, by a factor of 4. In addition, the standard deviation of the reduced binding energies is about 2.6, supporting the view that there is no systematics in the behavior of LDA binding energies in the family of rare gas dimers.

An early attempt to explain the failure of LDA is due to Harris.\textsuperscript{75} His arguments are particularly pertinent, but the present-day literature on the subject seems to ignore them. (This can be partly due to the fact that these considerations have been published in the celebrated paper on the famous Harris-functional, therefore overlooked by most of the readers as an accessory development with respect to the main subject of the paper.) The first point to be remarked is that the binding character of the LDA potential curves should be entirely attributed to the local exchange functional; the variation of the LDA correlation energy, when increasing the distance of the two rare gas atoms is not strong enough to be taken as responsible for the binding. This holds for the overwhelming majority of GGA correlation functionals as well, with the remarkable exception of the WL functional, mentioned above. Harris’ analysis is based on the comparison of the Hartree-Fock and exchange-only Kohn-Sham expressions of the interaction energy in a minimal basis He\textsubscript{2} model. In the Hartree-Fock case, it is sufficient to consider two major contributions to the interaction energy: the positive (and repulsive) kinetic and the negative (and attractive) exchange components. Both of these interaction energy contributions vary as $S^2(R)$ with the interatomic separation, $R$, where $S(R)$ is the overlap of the atomic orbitals. The kinetic and exchange prefactors, $c_k$ and $c_x$, are practically constant in the critical region between $R = 4$ and $R = 6$ atomic units, so we can write:

\begin{equation}
\Delta E_{HF}(R) \approx (c_k - c_x)S^2(R). \tag{5}
\end{equation}

Since the module of the kinetic prefactor is larger that of the exchange, the Hartree-Fock interaction energy is positive and the potential curve is repulsive. In the exchange-only Kohn-Sham case, the energy expression is almost the same, excepted the Hartree-Fock exchange contribution, which is replaced by the LDA functional. While the kinetic energy continues to behave as $S^2(R)$, it can be shown that in the weak overlap region the exchange functional varies with the distance as $a_xS^2(R) + b_xS^{4/3}(R)$. Harris argued that the much faster $S^{4/3}$ decay of the LDA exchange destroys the equilibrium between kinetic and exchange
components, leading to an artificial minimum at relatively short internuclear separations. Obviously, the precise position of this minimum depends on subtle details of the orbitals and of the exchange functional, which explains the strongly random behavior found in different rare-gas systems. As noted by Harris, replacing the orbital expression of the kinetic energy by a density functional expression improves the equilibrium between kinetic and exchange components, explaining the relatively good performance of the original Gordon-Kim (GK) method. Similar arguments, invoking a cancelation of errors in semi-local kinetic and exchange functionals, have been invoked by Wesolowski in the context of the Kohn-Sham constrained electron density (KSCED) bifunctional approach.

Still, Harris’ arguments remain at a phenomenological level, without telling what is physically wrong with the LDA exchange functional, leading to the $S^{4/3}(R)$ decay of the LDA exchange contribution to the interaction energy. The possible role of the self-exchange error has been evoked by Rae, in the context of the GK formula. Application of Rae’s self-exchange correction removes the vdW minima of the original GK model, suggesting that the above problems might be related to self-interaction effects. Such a conclusion does not seem to be corroborated by numerical experience on the He$_2$ dimer using the Perdew-Zunger self-interaction energy correction: the LDA minimum is still there, only slightly modified. However, one should bear in mind that the Perdew-Zunger method does not remove completely the self-exchange error. In the light of these facts we are inclined to think that the LDA minima should be mainly ascribed to spurious, long-range self-interaction (self-exchange) effects and can be removed only by an exchange functional, which leads to asymptotically correct exchange potential.

Climbing to the next level on Jacob’s ladder of density functional approximations, i.e. to the GGA, quite systematic improvement is observed for most of the properties. The situation is much more complicated for vdW interactions and especially for rare gas dimers, where some functionals lead to strongly repulsive rare gas dimer potential curves (e.g. B86, B88), others are either almost as overbinding as LDA (e.g. PW91), or produce minima in relatively good agreement with experience.

In calculations using various exchange functionals, the presence or absence of vdW minima can be correlated with the shape of the GGA enhancement factor function, $F(s)$, where $s = |\nabla \rho|/\rho^{4/3}$ is the reduced gradient. As it has been pointed out first by Lacks and Gordon, the interaction energy is mostly determined by contributions coming from medium
and large values of the reduced gradient, or more precisely, from regions of small density and large density gradient.\(^{91}\) For instance, in the case of He\(_2\), for interatomic distances between 5 and 6 atomic units, about half of the LDA exchange interaction energy comes from regions where \(s > 1.5\). While the enhancement factor of various GGA functionals are similar for small \(s\), remarkable differences can be observed in the case of the most common functionals in the region of \(s > 2\). PW91 and PBE remain under the local Lieb-Oxford bound,\(^{96}\) i.e. \(F(s) < 1.68\), while the enhancement factor of Becke’s B88 and B86 functionals grow above this limit. Becke’s functionals do not lead to minima, since, by the coupled effect of a monotonically increasing enhancement factor and of the growing importance of high-\(s\) domains with increasing \(R\), the exchange decays with a higher than \(4/3\) power of \(S\). On the contrary, the PBE enhancement factor goes to saturation below the Lieb-Oxford bound, leading to a less pronounced decay of the exchange energy and maintaining the minimum on the potential curve. The PW91 enhancement factor goes over a maximum centered around \(s = 4\), and the integrated effect of the enhancement factor leaves the LDA exchange interaction energy component practically unchanged, leading to strongly overbinding PW91 results.

Tailoring exchange functionals in view of an improved description of weakly bound systems operate via the modification of the enhancement factor.\(^{16}\) This is the case, e.g. for the revPBE functional,\(^{97}\) which becomes repulsive for rare gas dimers, or the mPW91,\(^{98}\) and the modified PBE,\(^{99}\) GGA functionals, as well as the X3LYP\(^{17,18}\) hybrid GGA functional. It means that almost any kind of behavior of rare gas potentials can be produced by engineering the enhancement factor, making somewhat suspicious this strategy.

Concerning the next rungs of Jacob’s ladder, the performance of the hybrid functionals is mostly conditioned by the underlying GGA exchange. While the popular B3LYP hybrid functional\(^{100}\) is completely unadapted for vdW systems, the ab initio PBE0 or the recent B98 and B97-1 hybrid functionals give relatively small mean average errors, albeit with quite high standard deviations. Among the meta-GGA functionals and their hybrid variants, the ab initio TPSS and TPSSh produce quite reasonable mean errors. Up to date, it is the semi-empirical M05-2X functional\(^{15}\) that provides by far the best performances.

Summarizing density functional results, one can point out that at lower rungs of Jacob’s ladder it is difficult to have a proper account of the delicate problem of dispersion forces. Considering the high precision needed to reproduce tiny energy differences arising in weak intermolecular complexes, it is not surprising that the cancelation of errors between exchange
and correlation, usually cited to explain the success of DFT for the atomization energies of covalent molecules, is not a firm enough basis to obtain fully satisfactory results. It can be concluded that in addition to their well-known deficiency to account for the asymptotic decay of dispersion forces, even the most sophisticated functionals available for routine calculations nowadays are unable to provide a reliable description of vdW minima in rare gas dimers.

III. RANGE-SEPARATED HYBRID (RSH)+MP2 METHOD

Starting from existing density functionals, one is supposed to introduce corrections at two points. In a first step, the non-physical binding due to the wrong asymptotic behavior of approximate exchange functionals should be removed, and in a second step, the non-local long-range dynamic correlation should be added, without deteriorating the results for non-vdW systems. In both steps, conventional exchange and correlation functionals need to be corrected mainly for large interelectronic separations, \( r_{ij} \). Such a long-range corrected scheme for van der Waals systems has been suggested first by Kohn, Meier and Makarov. Our scheme uses also an explicit long-range/short-range decomposition of the electron interaction, taking a simple perturbational approach to handle long-range dynamic correlation effects.

The Kohn-Sham theory can be summarized by the following decomposition of the Hohenberg-Kohn universal Coulombic functional, \( F[n] \) of the density \( n(r) \) as

\[
F[n] = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle + E_{Hxc}[n],
\]

where the Hartree-exchange-correlation functional is the difference between the exact Coulombic functional, \( F[n] \), and \( T_s = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle \). The wave function that minimizes the total energy

\[
E = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle + E_{Hxc}[n] + \int d r v_{ne}(r)n(r),
\]

under the constraint of providing the exact density, \( n \), is the solution of the following independent particle effective Schrödinger equation:

\[
\{ \hat{T} + \hat{V}_{ne} + \hat{V}_{Hxc} \} \Phi = \mathcal{E} \Phi,
\]
with $\tilde{V}_{Hxc}$ operator corresponding to the one-particle local Hartree-exchange-correlation potential, $v_{Hxc}(r)$. Thus, provided that the exchange-correlation functional, $E_{xc}[n]$, is known and the Hartree component being trivial, the exact solution of the fully interacting many-body problem can be reduced to a much simpler independent-particle problem. The success of this approach depends on our ability to guess the unknown exchange-correlation functional, e.g. by transferring it from a known physical system.

As mentioned previously, such a transfer does not work equally well for all the cases. In particular, it has been shown that at very short-range (i.e. $r_{ij} \to 0$), the exchange contribution can be expressed as a local functional of the density and is therefore exact in the LDA. In the same limit, the correlation contribution can be expressed as a local functional of the on-top pair density which is generally accurate in the LDA. On the contrary, a LDA approximation applied to the whole range of Coulomb interaction transfers spurious long-range correlations of the uniform electron gas to a finite system, which has other kind, system-specific long-range correlations, necessitating an explicit treatment. A lot of effort has been invested in improving the functionals globally, making them satisfy exact conditions.\textsuperscript{113} Another possibility is to restrain the use of the LDA for the short-range part of the Coulomb interaction, where it works the best. This is the basic motivation of the range-separated approach.

A rigorous separation of the long- and short-range components of the Coulomb interaction function, $w_{ee}(r) = 1/r$, can be be written as

$$w_{ee}(r) = w_{le}^{lr,\mu}(r) + w_{le}^{sr,\mu}(r),$$

where $\mu$ is a parameter, governing the reach of the short-range interaction. Throughout this work the error-function parametrization of the screened interaction will be used, i.e.

$$w_{le}^{lr,\mu}(r) = \frac{\text{erf}(\mu r)}{r},$$

where $\mu$ is inversely proportional to the range of the short-range interaction.

Accordingly, the Hohenberg-Kohn functional can be partitioned differently, by treating
long-range Coulomb interactions together with the kinetic energy:

$$F[n] = \min_{\Psi^\mu \rightarrow n} \langle \Psi^\mu | \hat{T} + \hat{W}_{lr,\mu} | \Psi^\mu \rangle + E_{Hxc}^{sr,\mu}[n].$$ \hfill (11)

The minimizing wave function, $\Psi^\mu$, can be obtained from the corresponding Euler-Lagrange equation

$$\left\{ \hat{T} + \hat{W}_{lr,\mu} + \hat{V}_{ne} + \hat{V}_{Hxc}^{sr,\mu}[n] \right\} | \Psi^\mu \rangle = \mathcal{E}^\mu | \Psi^\mu \rangle,$$ \hfill (12)

with $\hat{V}_{ne} = \int \text{d}r v_{ne}(r) \hat{n}(r)$, $\hat{V}_{Hxc}^{sr,\mu}[n] = \int \text{d}r v_{\mu}^{sr,Hxc}(r) \hat{n}(r)$ with the short-range Hartree-exchange-correlation potential $v_{\mu}^{sr,Hxc}(r) = \delta E_{Hxc}^{sr,\mu}[n]/\delta n(r)$, and $\mathcal{E}^\mu$ is the Lagrange multiplier associated to the constraint of the normalization of the wave function. In contrast to the Kohn-Sham reference system, which is non-interacting, this equation defines the effective Hamiltonian $H^\mu$, corresponding to a long-range interacting reference system. Accordingly, the minimizing wave function is not a single Kohn-Sham determinant, but a multi-determinantal wave function, $| \Psi^\mu \rangle$, which provides the exact physical ground-state density for any $\mu$. The exact total energy can be written as

$$E = \langle \Psi^\mu | \hat{T} + \hat{W}_{lr,\mu} + \hat{V}_{ne} | \Psi^\mu \rangle + E_{Hxc}^{sr,\mu}[n].$$ \hfill (13)

The practical success of this scheme depends on the judicious choice of the range-separation parameter, $\mu$, which must confine the density functional approximation to the range of its optimal validity and performance. If this range is not too small, the wave function description takes benefit of a better convergence of the multi-determinantal expansion, mainly due to the absence of the Coulomb-cusp from the long-range problem. Combination of a long-range wave function treatment with a short-range density functional description has been successfully applied in DFT+CI (Configuration interaction) approach, or with a multi-configurational self-consistent field calculation (DFT+MCSCF), and in DFT+CCSD(T) (coupled cluster single double excitations with perturbative triple) scheme.

It can be expected that long-range dynamic correlation effects, which are at the origin of the London dispersion forces, are well described by a low-order many-body perturbational treatment, based on a single determinant reference state. Such a theory has been described recently, here we summarize only the main features.

Constraining the multideterminantal $| \Psi^\mu \rangle$ wave functions of Eq. (11) to a monodetermi-
nantal form, $|\Phi^\mu\rangle$, the Euler-Lagrange equation becomes:

$$\left\{ \hat{T} + \hat{V}_{ne} + \hat{V}_{lr,\mu}^{Hx,\text{HF}}[\Phi^\mu] + \hat{V}_{sr,\mu}^{\text{xc}}[\hat{n}_{\Phi^\mu}] \right\} |\Phi^\mu\rangle = \mathcal{E}_0^\mu |\Phi^\mu\rangle,$$

(14)

where $\hat{V}_{lr,\mu}^{Hx,\text{HF}}$ is the sum of the long-range Hartree and the long-range exchange operator defined in terms of the density operator $\hat{n}(r)$ and the first order density matrix operator $\hat{n}_1(r_1, r_2)$:

$$\hat{V}_{lr,\mu}^{Hx,\text{HF}}[\Phi] = \int \! \! \int dr_1 dr_2 w_{lr,\mu}^{\text{ee}}(r_{12}) \langle \Phi | \hat{n}(r_1) | \Phi \rangle \hat{n}(r_2)$$

(15)

$$\hat{V}_{lr,\mu}^{x,\text{HF}}[\Phi] = -\frac{1}{2} \int \! \! \int dr_1 dr_2 w_{lr,\mu}^{\text{ee}}(r_{12}) \langle \Phi | \hat{n}_1(r_2, r_1) | \Phi \rangle \hat{n}_1(r_1, r_2).$$

(16)

A new effective (non-interacting) Hamiltonian is defined, which combines long-range non-local exchange potential with short-range local (or semi-local) exchange-correlation potential. This model can be viewed as a new type of hybrid functional where the mixing of HF- and DFT-exchange is performed at the level of the interelectronic distance. The iterative resolution of Eq. (14) gives access to the one-determinant wave function $|\Phi^\mu\rangle$, which provides the range separated hybrid total energy as:

$$E^\mu,\text{RSH} = \langle \Phi^\mu | \hat{T} + \hat{V}_{ne} + \hat{V}_{lr,\mu}^{Hx,\text{HF}}[\Phi^\mu] + \lambda \hat{W}_{lr,\mu}^{\text{HF}} | \Phi^\mu \rangle + E_H[\Phi^\mu] + E_{x,\text{HF}}^{lr,\mu} + E_{\text{xc}}^{sr,\mu}[\hat{n}_{\Phi^\mu}].$$

(17)

Considering the range-separated hybrid solution as the zeroth order problem, a perturbational expansion of the total energy of the system can be written as

$$E^\mu,\lambda = \min_{\Psi_0} \left\{ \langle \Psi_0 | \hat{T} + \hat{V}_{ne} + \hat{V}_{lr,\mu}^{Hx,\text{HF}}[\Phi^\mu] + \lambda \hat{W}_{lr,\mu}^{\text{HF}} | \Psi_0 \rangle + E_{Hx,\text{HF}}^{sr,\mu}[\hat{n}_{\Psi_0}] \right\},$$

(18)

where $\hat{W}_{lr,\mu}^{\text{HF}} = \hat{W}_{lr,\mu}^{\text{ee}} - \hat{V}_{lr,\mu}^{Hx,\text{HF}}[\Phi^\mu]$ is the long-range fluctuation potential. Expanding $E^\mu,\lambda$ in power series of $\lambda$, application of the non-linear Rayleigh-Schrödinger perturbational theory,\textsuperscript{116–118} leads to the first order energy:

$$E^\mu,(0) + E^\mu,(1) = E^\mu,\text{RSH},$$

(19)

where $E^\mu,(0) = \mathcal{E}^\mu = \sum_{i \in \text{occ.}} \epsilon^\mu_i$ is the expectation value of the effective Hamiltonian, and
$E^{\mu,(1)}$ is equal to the double counting correction. By the virtue of a Brillouin-like theorem, valid for the self-consistent RSH solution, non-linearity effects cancel at the second order of perturbation and the corresponding energy correction turns out to be simply of the conventional MP2-form:

\[
E^{\mu,(2)} = \sum_{i<j, a<b} \left| \frac{\langle \Phi^{\mu}_{ij} \rightarrow ab | \hat{W}_{ee}^{lr,\mu} | \Phi^{\mu} \rangle}{\epsilon^{\mu}_{ij} - \epsilon^{\mu}_{ab}} \right|^2,
\]

(20)

with $|\phi_k^{\mu}\rangle$ spin-orbitals of $|\Phi^{\mu}\rangle$ and $\epsilon_k^{\mu}$, the corresponding eigenvalues. At the RSH+MP2 level the total energy is thus:

\[
E^{\mu,\text{RSH+MP2}} = E^{\mu,\text{RSH}} + E^{\mu,(2)}.
\]

(21)

So by comparing the previous equations with standard MP2 expressions, the only difference is the use of long-range interaction function $\hat{w}_{ee}^{lr,\mu}$ to determine two-electron integrals over the RSH eigenvectors and the appearance of RSH eigenvalues in the denominator.

### IV. COMPUTATIONAL DETAILS

All calculations presented in the next section have been carried out with the development version of MOLPRO package.\(^\text{119}\) The LDA variant of the RSH+MP2 method has been used, meaning that the short-range exchange-correlation terms have been treated on the local density approximation level.\(^\text{120}\) The range separation parameter has been set to 0.5 $a_0^{-1}$, as in our previous studies of the exchange-only range separated hybrid (RSHX) functional.\(^\text{121}\) The long-range portion of the correlation have been carried out with the standard MP2 module of the MOLPRO package, by simply changing the two-electron integrals and orbital energies according to Eq. (20).

In order to attain the $\mu$H precision required for the interaction energy calculations of lighter rare gas complexes, it is primordial to perform well-converged, numerically precise calculations, using fine supporting grids for the integrations, as well as the necessity of performing basis set superposition and grid superposition corrections. Therefore, strict
thresholds have been used. A value of $10^{-10}$ for the global convergence criterion as well as for the numerical quadrature exchange-correlation energy threshold ensured well-converged interaction energies. The well-established counterpoise\textsuperscript{122} procedure has been used to correct the BSSE arising in supermolecule calculations.

The choice of basis set is crucial for the study of weakly bound systems, like rare gas dimers, which require usually large, flexible basis sets, including diffuse functions as well. In order to facilitate a study of basis set effects, we took advantage of the family of correlation consistent basis sets, aug-cc-pVXZ [$X = D, T, Q, 5, 6$] of Dunning \textit{et al.},\textsuperscript{123} having a systematically improved quality controlled by the parameter $X$. This family of basis sets allows us to perform a proper basis set extrapolation\textsuperscript{124–126} for post-HF methods as well. Following the protocol used by several recent publications by DFT\textsuperscript{60} and DFT+CCSD(T) methods\textsuperscript{57} on these systems, we have employed the aug-cc-pVQZ (AVQZ) basis set. The LDA, PBE and TPSS results were directly taken from the work of Tao and Perdew\textsuperscript{60} for the heavier dimers, excepted the dimers containing He atom, where Ref. 60 used cc-pVQZ basis set instead of the aug-cc-pVQZ. Therefore, DFT calculations of dimers composed by He atom have been repeated with the augmented basis set for more consistency.

The minima of the potential curves were obtained by a second order fit based on fifteen points selected in an interval of -20 to +20 % around the experimental equilibrium geometries. This procedure has been checked against the results of the Ref. 60, and a very good agreement, within 1%, has been obtained for all the cases.

The basis set extrapolation procedure was based on the AVXZ family of basis sets, using $X=2$ to 5 or 6. Complete basis set (CBS) limit have been calculated from the 2-point extrapolation formula based on the $E(\infty) = E(X) + A/X^3$ assumption of Helgaker \textit{et al.}\textsuperscript{124}, and used by Lee and co-workers\textsuperscript{127–129} and others\textsuperscript{130} for vdW systems. Taking into consideration the fact that the RSH energy, just like the Hartree-Fock and Kohn-Sham energies have a much faster convergence than the correlation energy, this latter contribution have been treated separately. It means that the aug-cc-pV5Z RSH energies were considered as converged at the SCF level, and only the remaining correlation energies were extrapolated at the reference (experimental) equilibrium geometry for the four homodimers (He\textsubscript{2}, Ne\textsubscript{2}, Ar\textsubscript{2} and Kr\textsubscript{2}).
V. RESULTS AND DISCUSSIONS

A. Properties of the van der Waals minima

Counterpoise-corrected equilibrium distances, binding energies and vibrational harmonic frequencies of the 10 complexes are listed in terms of the previously defined reduced variables in Tables III, IV and V.

The computed equilibrium bond lengths confirm the well-known tendency of LDA to yield too short equilibrium distances, reflected by negative M%E of -13.6%. The improvement due to gradient corrections in PBE seems to be considerable, decreasing M%E to less than 1%. A quite large spread of the results, ranging from -7.8% for He$_2$ to 7.2% in the case of ArKr, indicates that this improvement is rather fortuitous and not really a systematic one. In effect, a further improvement of the functional, by including the kinetic energy density at the meta-GGA level (TPSS), worsens the agreement with experiment and an overestimation by more than 7% is found on the average, with the exception of the He-containing systems, that are underbound. The behavior of the MA%E and of the standard deviation, which increases slightly in the series of the LDA, PBE and TPSS functionals makes doubtful that the improvement of the exchange-correlation functional is able to improve fundamentally the quality of the description in weakly bound systems.

On the contrary, post-HF methods, i.e. MP2 and CSSD(T), provide reliable results within 2.8% and 1.7% of error respectively, independently of the system size. Combination of the short-range DFT and long-range WFT, like in the RSH+MP2 or DFT+CSSD(T), reduces significantly the mean unsigned error with respect to standard DFT calculations, reaching an accuracy close to that of the MP2 and CCSD(T) results, respectively. The RSH+MP2 approach provides slightly (less than 3%) overestimated equilibrium distances, in sharp contrast to the severe underestimation by LDA and the erratic behavior of PBE functionals.

Dissociation energies are listed in Table IV in terms of reduced variables. Again, the severe overbinding of the LDA approach is reflected by a systematic error of more than 400%. The possible reasons of this behavior have already been discussed previously. This particular trend tends to be reduced by increasing the number of electrons in the system. From He$_2$ ($N = 4$) the reduced well-depth of 10.12 decays monotonically towards the heaviest
member of the series, Kr\(_2\) \((N = 72)\), where it becomes only 2.03. The variation of the PBE and TPSS binding energies follows a similar trend, but within a narrower range. In some cases, like the Ne\(_2\) or NeAr, even an underbinding can be observed. On average PBE tends to overestimate the binding energies, while TPSS underbinds by about 20\%. Globally, even if the error for the second and third rung of the Jacob’s ladder is considerably reduced with respect to the LDA value, it is not justified to consider PBE and TPSS approaches as able to provide reliable results in the description of vdW complexes.

In the mean time, wave function methods produce errors of -25\% (MP2) and -17\% (CCSD(T)), but with a very small standard deviation. Obviously, an accurate reproduction of the binding energy with WFT methods would have required much larger basis sets. Using the same basis set, range separated approaches with explicit long-range correlation represent a net improvement: in the MP2 case the mean absolute error is reduced to 16 \%, for CCSD(T) is becomes 12 \%. The RSH+MP2 seems to be a reasonable compromise of cost and accuracy, since the error is about the same as with the full CCSD(T) calculations at lower computational requirements.

Harmonic frequencies characterize the curvature of the potential energy function at the vdW minima region. Even if experimental data always include anharmonicity, making a direct comparison of theory and experiment more difficult, a comparison with harmonic frequencies derived from “experimental-quality” potential curves remains of great interest. The main tendencies observed for the bond lengths and binding energies are confirmed by the data reported in Table V. The LDA approximation systematically overestimates the frequency by almost 144\% in average, GGA (PBE, 32\%) and meta-GGA (TPSS, 23\%) reduce mean errors systematically. For this property the standard deviation decreases regularly with the improvement of the functional. Nevertheless, even for TPSS it remains 4 times larger than for the MP2 wave function method, which has practically the same MA%E (21\%), as the TPSS functional, being almost as good as the CCSD(T). RSH+MP2 and DFT+CCSD(T) are slightly worse than their full wave function correlation counterparts and they have also the tendency of underestimating the harmonic frequency, in contrast to the pure DFT approximations, that mostly overestimate this quantity.

In conclusion, it turns out that the global accuracy of the RSH+MP2 approach outperforms standard DFT calculations for the description of the vdW complexes governed mainly by London dispersion forces. Taking into consideration the correct 1/\(R^6\) asymptotic be-
behavior of RSH+MP2 (see below), this combination of the short-range DFT and long-range WFT description, which ensures by construction that right results are obtained for physically right reasons, is undeniably superior to describe London dispersion forces as compared to conventional density functional approaches, even lying at relatively high rung of Jacob’s ladder. The extra costs, related to the perturbation sums can be kept low by appropriate implementations, which are not treated here.

In view of a complete assessment of the performance that one can expect from the RSH+MP2 approach, it would be desirable to check its convergence to the CBS limit and its sensitivity to BSSE effects. These issues will be treated after having discussed briefly the asymptotic behavior of the potential curves, in the last two subsections.

### B. Asymptotic behavior

The long-range asymptotic behavior of the London dispersion forces, neglecting retardation effects, takes a simple algebraic form:

\[ U(r) \approx -\sum_{n=3}^{N} \frac{C_{2n}}{r^{2n}} \quad (22) \]

where the coefficients \( C_{2n} \) are related to the dynamic multipole polarizabilities of the interacting subsystems via the Casimir-Polder formula.\(^{131}\) The inability of standard density functionals to describe this algebraic decay has been pointed out many times, and discussed recently by Ruzsinszky et al.\(^ {93}\) who showed that the observed decay of PBE and TPSS potential energy curves is exponential with an exponent that corresponds roughly to the asymptotic of the \( 4/3 \)th power of the monomer densities. The deviation from the expected exponent can be explained in the framework of a more detailed analytical model, which predicts that the interaction energy varies as \((c_k - a_x)S^2(R) - b_xS^{4/3}(R)\), where \( c_k \) is the kinetic energy prefactor, while \( a_x \) and \( b_x \) are the prefactors of the quadratic and the \( 4/3 \)-power contributions to the exchange. In fact the “empirical” exponent is smaller than the “exchange-only” prediction, because of the opposite-sign contribution of the \( S^2(R) \)-term.

The logarithmic plot of the reduced interaction energy in the intermediary (1.2 < \( \xi < 2.1 \)) region and the double logarithmic plot for 4.2 < \( \xi < 8.0 \), illustrated by Figure 1 (a) and (b) prove clearly that the RSH+MP2 approach follows perfectly the predicted algebraic
asymptotic behavior of the interaction energy. As discussed in 50, a slight overestimation of the effective $C_6$ dispersion coefficients is due to the second order approximation.

C. Complete basis set limit

The systematically convergent behavior of atomic and molecular electronic energies offers the possibility to estimate the CBS limit of total energies and energy differences by appropriately chosen extrapolation methods. The extrapolation procedure, outlined in the Computational Details section, have been applied to the 4 homo-dimers (He$_2$, Ne$_2$, Ar$_2$ and Kr$_2$) at their respective experimental equilibrium geometries, after removing BSSE by the counterpoise method. The CBS limit of reduced interaction energies, estimated at different levels of the correlation-consistent basis set, are summarized in Table VI. These values have been compiled with the help of the data reported in the two Tables provided as Supplementary Material.$^{132}$

It should be stressed that experimental geometries are usually not the optimal ones for a given complex and a given method. For instance, MP2 overestimates the bond length of He$_2$ and Ne$_2$ by 4–5%, which means that for these systems the experimental geometry is on the repulsive branch of the MP2 potential curve, explaining the relatively small value (around 0.5 to 0.6) of the reduced interaction energy. For Ar$_2$ and Kr$_2$ the bond length error is less than 1%, which lowers the reduced interaction energy. Similar considerations can be made for the CCSD(T) and RSH+MP2 methods. For instance, very small RSH+MP2 reduced interaction energies of the He$_2$ dimer have been obtained as a consequence of the 8% overestimation of the bond length by this approach.

Taking into account these remarks, absolute values of extrapolated interaction energies confirm the tendency of the MP2 approach to overestimate the London dispersion energies. This is the most apparent for heavier complexes, where the calculations were performed near to the proper MP2 minimum, and for which the CBS limit of the reduced interaction energy is larger than 1, i.e. the interaction energy overshoots. The same trend is observed in the case of the RSH+MP2 method, while the CCSD(T) results remain coherently below the limit of the experimental binding energy. This observation can be rationalized by the analysis of the asymptotic behavior of the MP2 interaction energy.$^{133}$ Although having the correct $1/R^6$ decay, the corresponding $C_6$ coefficient, proportional to the polarizabilities of
the monomers is overestimated, because the limiting form of the MP2 dimer energy leads to monomer polarizabilities in the uncoupled Hartree-Fock approximation. Even if this reasoning holds strictly only for the MP2 calculations, it seems to be valid for the RSH+MP2 interaction energies too. However, this latter approach seem to overshoot less, probably due to a beneficial participation of the short-range density functional to the response properties. The CCSD(T) CBS-limit remains consistently under the physical limit of 1, in agreement with the fact that the asymptotic value of the CCSD(T) interaction energy contains a much better approximation of the monomer polarizabilities.

The most remarkable feature in present context is related to the efficiency of the CBS extrapolation at different basis set levels. While for the fully WFT-based MP2 and CCSD(T) approaches there is a considerable difference of around 15% between the D-T and 5-6 (or Q-5) extrapolations, when using the RSH+MP2 method, the D-T extrapolation provides a reasonable estimation, around 5% or less, as compared to the 5-6 (or Q-5) extrapolations.

The explanation of this behavior resides in the fact that in the RSH+MP2 scheme only the long-range correlation contribution is treated explicitly, avoiding convergence problems related to the imperfect description of the electronic Coulomb cusp in standard correlated wave-function approaches.\textsuperscript{125,126} In this sense, the choice of a $X^{-3}$ extrapolation procedure is questionable, since this scheme relies directly to the cusp-description. However from a pure pragmatic point of view, few tests of the long-range correlation energy extrapolation based on simple exponential formulae,\textsuperscript{134,135} as used for RHF or KS energy, were not able to provide reliable results. This open question certainly requires a separate work.

Our observations lead to the important conclusion that the short-range DFT / long-range WFT combined approach has a much faster basis set convergence than the full-range WFT correlation methods and the CBS limit can be reasonably approached by a two-point extrapolation at the two lowest levels of basis set. This feature has the important practical consequence that the basis set convergence can be reached at a much lower level, reducing the computational cost considerably with respect to the usual MP2 and CCSD(T) methods.

\section*{D. Basis set superposition error}

It is a well-known fact that the BSSE arises from the long-range tails of one monomer that are used to improve the intramolecular description of the partner. Standard DFT
calculations are recognized to be less sensitive to this problem.\textsuperscript{136} Direct consequences of the BSSE on interaction potentials are usually twofold: a lowering of the equilibrium distance and an increase of the binding energy. These effects are explicitly confirmed by the data in Tables VII and VIII, where the mean differences between the non-corrected and corrected reduced equilibrium bond-lengths and reduced binding energies, respectively, are given in the aug-cc-pVQZ basis set.

The general trend in BSSE effects on the equilibrium distances is reflected by a negative mean in all cases, meaning that the BSSE tends to bring closer the monomers. Although the BSSE effect on the geometry is relatively small, the difference in the behavior of DFT and post-HF results is significant. The MP2 and CCSD(T) methods show, in average, a 1.2\% and 2.2\% of variation respectively, while LDA, PBE and TPSS show an almost 10 times smaller difference of 0.2\%. The RSH+MP2 takes benefit of its short-range DFT component, and suffers from a relatively small BSSE effect of 0.4\%. It can be concluded that, in contrast to standard MP2 and CCSD(T) calculations, the BSSE within the RSH+MP2 approach has only a tiny effect on the determination of the equilibrium bond-lengths.

The BSSE on the relative binding energies, Tab. VIII, is always positive. In the case of the LDA the BSSE effect is very strong, related to the too short equilibrium distance, exalting the overlap of subsystems. GGA and meta-GGA density functionals show a moderate BSSE in the order of 3.–4.4\%. Explicitly correlated CCSD(T) and MP2 are much more sensitive to the BSSE corrections, amounting to 17.9\% and 18.6\% of the reference well-depth for the ten studied rare gas dimers. Again, the moderate mean error of 6.7\% obtained by the RSH+MP2 calculations takes benefit of the short-range DFT description of the interelectronic interactions.\textsuperscript{50,56}

Fig. 2 represents the BSSE effect on the binding energies values for the ten rare gas dimers, as calculated by the PBE, TPSS, RSH+MP2, MP2 and CCSD(T) approaches. Visually, the behavior of the RSH+MP2 method is closer to that of the DFT methods than that of the standard post-HF calculations. The RSH+MP2 BSSE exceeds the critical 10\% limit only in two cases, that of HeNe and Ne\textsubscript{2}. When the number of electrons increases, BSSE corrections tend to be less significant and they are stabilized around 5\%. Altogether, we can conclude that moderate BSSE effects make RSH+MP2 a favorable approach to perform supermolecule studies of complicated potential energy surfaces influenced by weak London dispersion forces and justify the possible neglect of explicit counterpoise corrections.
VI. CONCLUSIONS

The modeling of missing London dispersion forces is one of the major challenges of modern density functional theory. The idea of using a range-separated treatment, as put forth first by Kohn, Meier and Makarov, is a most promising way to treat this problem in a satisfactory manner. The approach, we have described in this work, fits into this general framework by satisfying most of the criteria one may wish from a density functional based description of weak intermolecular complexes.

This combination of a range-separated hybrid, including long-range Hartree-Fock exchange, followed by second order perturbational treatment of long-range dynamical correlation, avoids by construction the double counting of correlation effects. The correct asymptotic behavior of the range-separated exchange functional excludes spurious self-interaction, which gives rise to artificial minima in the context of LDA and of many GGA exchange functionals. The RSH+MP2 energy expression is completely general and valid for any nuclear configuration, satisfying the conditions for a seamless theory. The use of many-body perturbation theory to describe correlation effects guarantees the size-consistency and the size-extensive character of the method. The asymptotic behavior of the total energy is qualitatively correct, even if the long-range dispersion coefficients are slightly overestimated in this second-order approximation.

It is very important to underline that the range-separated exchange-only hybrid (where long-range correlation is replaced by long-range density functional approximation) is a quite successful approach in itself, providing a thermochemical accuracy near to that of the popular PBE functional. By the virtue of correct exchange asymptotics, in several respects this theory is even superior to conventional functionals, including hybrid functionals, reflected by a considerably improved description of band gaps, reaction barriers, etc. In comparison to fully WFT correlated methods, the basis set convergence is much faster and intermolecular interaction energies are only slightly, sometimes negligibly, affected by the BSSE.

The performance and efficiency of the RSH+MP2 approach compares favorably to both DFT and WFT approaches. Not only it has the correct long-range behavior of the vdW interaction energies, impossible to reproduce by pure DFT calculations based on local or semi-local functionals, but the description of the minimum region is significantly improved, as reflected by smaller mean errors and their standard deviations. A considerable advantage
with respect to the pure WFT methods is the reduced cost of the RSH+MP2 calculations, related to their fast basis set convergence and small BSSE effects.

Nevertheless, further work should be done to check if these favorable properties are maintained for other classes of vdW complexes, like the stacking interaction of planar aromatic rings, e.g. the benzene dimer. The increasing system size makes necessary to improve computational algorithms, especially for the long-range correlation, where considerably gain is expected by a systematic application of multipole expansions,\textsuperscript{138} and/or the use of local correlation methods. It is also possible to go beyond the second order approach, as proved by the success of long-range CCSD(T) corrections. An alternative way could be the generalization of the adiabatic connection fluctuation-dissipation (ACFD) approach\textsuperscript{139–141} to the long-range correlation effects. Work along these lines is in progress.

Acknowledgments

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131 H. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948).

132 See EPAPS Document No. XXXX for total energies used in basis set extrapolation. This document can be reached through a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).


Figure 1. Gerber and Ángyán, Journal of Chemical Physics
Figure 2. Gerber and Ángyán, Journal of Chemical Physics
Figures

FIG. 1: Long-range behavior of the reduced potential curves for $\text{Ar}_2$. (a) Logarithmic plot of the reduced potential curves for the intermediary region as calculated by the PBE, MP2, CCSD(T) and RSH+MP2 methods. (b) Double logarithmic representation of the MP2, CCSD(T) and RSH+MP2 potential curves in the asymptotic region.

FIG. 2: Influence of the BSSE correction on ten rare gas dimers in percentage of the reference energy, in the aug-cc-pVQZ basis set.
## Tables

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**TABLE I**: Recommended homo- and heterodimer potential parameters after Tang and Toennies (TT), Ref. 59. Equilibrium distances ($r_{\text{ref}}$) are given in atomic units, binding energies ($U_{\text{ref}}$) are given in $\mu$H, harmonic vibrational frequency $\omega$ are in cm$^{-1}$ while hard-core radii ($\sigma$) are dimensionless. For the sake of comparison, bond lengths and binding energies are also given from the compilation of Ogilvie and Wang, Ref. 66,67.
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</tr>
<tr>
<td>B98</td>
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<td>5.17</td>
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<td>-24.61</td>
<td>59.96</td>
<td>8.50</td>
<td>8.35</td>
<td>6.59</td>
<td>72</td>
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<td>MPWB1K</td>
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<td>-22.79</td>
<td>64.08</td>
<td>5.50</td>
<td>4.50</td>
<td>5.48</td>
<td>72</td>
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<td>TPSSh</td>
<td>55.90</td>
<td>-37.44</td>
<td>50.24</td>
<td>9.02</td>
<td>8.93</td>
<td>6.28</td>
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<tr>
<td>mPW91PW91</td>
<td>57.15</td>
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<td>50.57</td>
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<td>4.50</td>
<td>5.41</td>
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<td>35.20</td>
<td>15.70</td>
<td>15.70</td>
<td>7.66</td>
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<td>B97-1</td>
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<td>35.35</td>
<td>85.53</td>
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<td>1.14</td>
<td>4.86</td>
<td>72</td>
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<tr>
<td>PBE</td>
<td>69.94</td>
<td>35.68</td>
<td>94.48</td>
<td>4.06</td>
<td>1.19</td>
<td>5.46</td>
<td>70</td>
</tr>
<tr>
<td>PBE</td>
<td>66.76</td>
<td>28.93</td>
<td>93.27</td>
<td>4.31</td>
<td>1.38</td>
<td>5.14</td>
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<tr>
<td>PBEPW91</td>
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<td>33.46</td>
<td>95.53</td>
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<td>0.84</td>
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<td>33.50</td>
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<td>94.44</td>
<td>6.06</td>
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<td>79.14</td>
<td>127.98</td>
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<td>147.70</td>
<td>189.06</td>
<td>4.87</td>
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<td>5.89</td>
<td>72</td>
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<td>PW91</td>
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<td>281.44</td>
<td>311.40</td>
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<td>264.85</td>
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<td>72</td>
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<td>387.03</td>
<td>387.03</td>
<td>261.48</td>
<td>13.27</td>
<td>-13.27</td>
<td>4.12</td>
<td>70</td>
</tr>
<tr>
<td>LDA</td>
<td>411.71</td>
<td>411.71</td>
<td>267.34</td>
<td>13.56</td>
<td>-13.56</td>
<td>4.04</td>
<td>72</td>
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TABLE II: Mean of absolute percentage errors (MA%E), mean of percentage of error (M%E), and standard deviation of the mean error for the 10 rare gas dimers calculated by the CCSDT WFT method, as well as a series of density functionals. The methods are in the order of increasing unsigned mean error.
<table>
<thead>
<tr>
<th>Syst.</th>
<th>LDA 60</th>
<th>PBE 60</th>
<th>TPSS 60</th>
<th>MP2</th>
<th>CCSD(T)</th>
<th>DFT+CCSD(T)</th>
<th>RSH+MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>He₂</td>
<td>0.806</td>
<td>0.923</td>
<td>0.954</td>
<td>1.044</td>
<td>1.014</td>
<td>1.066</td>
<td>1.079</td>
</tr>
<tr>
<td>HeNe</td>
<td>0.816</td>
<td>0.951</td>
<td>1.011</td>
<td>1.041</td>
<td>1.007</td>
<td>1.017</td>
<td>1.044</td>
</tr>
<tr>
<td>HeAr</td>
<td>0.841</td>
<td>0.974</td>
<td>1.029</td>
<td>1.026</td>
<td>1.013</td>
<td>1.012</td>
<td>1.026</td>
</tr>
<tr>
<td>HeKr</td>
<td>0.844</td>
<td>0.980</td>
<td>1.029</td>
<td>1.032</td>
<td>1.016</td>
<td>1.009</td>
<td>1.026</td>
</tr>
<tr>
<td>Ne₂</td>
<td>0.855</td>
<td>1.004</td>
<td>1.057</td>
<td>1.052</td>
<td>1.020</td>
<td>0.999</td>
<td>1.034</td>
</tr>
<tr>
<td>NeAr</td>
<td>0.871</td>
<td>1.022</td>
<td>1.104</td>
<td>1.034</td>
<td>1.020</td>
<td>0.989</td>
<td>1.020</td>
</tr>
<tr>
<td>NeKr</td>
<td>0.872</td>
<td>1.022</td>
<td>1.106</td>
<td>1.034</td>
<td>1.022</td>
<td>0.981</td>
<td>1.016</td>
</tr>
<tr>
<td>Ar₂</td>
<td>0.906</td>
<td>1.064</td>
<td>1.155</td>
<td>1.007</td>
<td>1.019</td>
<td>0.997</td>
<td>1.009</td>
</tr>
<tr>
<td>ArKr</td>
<td>0.913</td>
<td>1.072</td>
<td>1.153</td>
<td>1.005</td>
<td>1.020</td>
<td>0.994</td>
<td>1.007</td>
</tr>
<tr>
<td>Kr₂</td>
<td>0.921</td>
<td>1.083</td>
<td>1.157</td>
<td>1.008</td>
<td>1.023</td>
<td>0.991</td>
<td>1.008</td>
</tr>
</tbody>
</table>

MA%E 13.6 4.4 8.5 2.8 1.7 1.5 2.7
M%E -13.6 0.9 7.6 2.8 1.7 0.6 2.7
S%DEV 4.0 5.3 7.0 1.7 0.5 2.4 2.2

TABLE III: Reduced BSSE corrected equilibrium bond lengths $\xi_m$ of ten rare gas dimers in the aug-cc-pVQZ basis set. The mean percentage of errors (M%E), the mean absolute percentage of errors (MA%E) and the standard deviation (S%DEV) are also given.
<table>
<thead>
<tr>
<th>Syst.</th>
<th>LDA$^{60}$</th>
<th>PBE$^{60}$</th>
<th>TPSS$^{60}$</th>
<th>MP2</th>
<th>CCSD(T)</th>
<th>DFT+CCSD(T)$^{57}$</th>
<th>RSH+MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$_2$</td>
<td>10.120</td>
<td>3.532</td>
<td>2.333</td>
<td>0.564</td>
<td>0.850</td>
<td>0.622</td>
<td>0.581</td>
</tr>
<tr>
<td>HeNe</td>
<td>8.362</td>
<td>2.356</td>
<td>1.398</td>
<td>0.564</td>
<td>0.849</td>
<td>0.751</td>
<td>0.676</td>
</tr>
<tr>
<td>HeAr</td>
<td>5.758</td>
<td>1.609</td>
<td>0.676</td>
<td>0.731</td>
<td>0.864</td>
<td>0.836</td>
<td>0.848</td>
</tr>
<tr>
<td>HeKr</td>
<td>5.432</td>
<td>1.512</td>
<td>0.916</td>
<td>0.721</td>
<td>0.846</td>
<td>0.823</td>
<td>0.854</td>
</tr>
<tr>
<td>Ne$_2$</td>
<td>5.587</td>
<td>1.342</td>
<td>0.822</td>
<td>0.539</td>
<td>0.789</td>
<td>0.863</td>
<td>0.727</td>
</tr>
<tr>
<td>NeAr</td>
<td>4.152</td>
<td>0.938</td>
<td>0.573</td>
<td>0.706</td>
<td>0.810</td>
<td>0.968</td>
<td>0.874</td>
</tr>
<tr>
<td>NeKr</td>
<td>4.101</td>
<td>0.935</td>
<td>0.541</td>
<td>0.715</td>
<td>0.812</td>
<td>1.022</td>
<td>0.894</td>
</tr>
<tr>
<td>Ar$_2$</td>
<td>2.466</td>
<td>0.485</td>
<td>0.267</td>
<td>0.980</td>
<td>0.833</td>
<td>0.999</td>
<td>0.996</td>
</tr>
<tr>
<td>ArKr</td>
<td>2.263</td>
<td>0.437</td>
<td>0.229</td>
<td>0.999</td>
<td>0.836</td>
<td>1.024</td>
<td>1.003</td>
</tr>
<tr>
<td>Kr$_2$</td>
<td>2.035</td>
<td>0.374</td>
<td>0.190</td>
<td>1.012</td>
<td>0.833</td>
<td>1.044</td>
<td>0.998</td>
</tr>
</tbody>
</table>

MA%E  402.8  71.8  55.2  24.9  16.8  12.3  15.6
M%E   402.8  35.2 -20.6 -24.7 -16.8 -10.5 -15.5
S%DEV 264.3  98.6  65.3  18.3  2.3  14.0  14.4

TABLE IV: Reduced BSSE corrected binding energies $\varepsilon_m$ of ten rare gas dimers in the aug-cc-pVQZ basis set. The mean percentage of errors (M%E), the mean absolute percentage of errors (MA%E) and the standard deviation (S%DEV) are also given.
<table>
<thead>
<tr>
<th>Syst.</th>
<th>LDA&lt;sup&gt;60&lt;/sup&gt;</th>
<th>PBE&lt;sup&gt;60&lt;/sup&gt;</th>
<th>TPSS&lt;sup&gt;60&lt;/sup&gt;</th>
<th>MP2</th>
<th>CCSD(T)</th>
<th>DFT+CCSD(T)&lt;sup&gt;57&lt;/sup&gt;</th>
<th>RSH+MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>He&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.61</td>
<td>1.96</td>
<td>1.32</td>
<td>0.70</td>
<td>0.88</td>
<td>0.67</td>
<td>0.64</td>
</tr>
<tr>
<td>HeNe</td>
<td>3.17</td>
<td>1.49</td>
<td>1.16</td>
<td>0.72</td>
<td>0.90</td>
<td>0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>HeAr</td>
<td>2.74</td>
<td>1.25</td>
<td>1.08</td>
<td>0.80</td>
<td>0.90</td>
<td>1.03</td>
<td>0.78</td>
</tr>
<tr>
<td>HeKr</td>
<td>2.40</td>
<td>1.35</td>
<td>1.17</td>
<td>0.80</td>
<td>0.79</td>
<td>0.85</td>
<td>0.79</td>
</tr>
<tr>
<td>Ne&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>1.08</td>
<td>1.15</td>
<td>0.66</td>
<td>0.80</td>
<td>0.82</td>
<td>0.91</td>
</tr>
<tr>
<td>NeAr</td>
<td>2.35</td>
<td>1.04</td>
<td>0.67</td>
<td>0.79</td>
<td>0.81</td>
<td>0.86</td>
<td>0.96</td>
</tr>
<tr>
<td>NeKr</td>
<td>2.36</td>
<td>1.06</td>
<td>0.92</td>
<td>0.75</td>
<td>0.89</td>
<td>0.91</td>
<td>1.01</td>
</tr>
<tr>
<td>Ar&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>0.78</td>
<td>0.63</td>
<td>0.90</td>
<td>0.79</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>ArKr</td>
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<td>0.68</td>
<td>0.67</td>
<td>0.85</td>
<td>0.88</td>
<td>0.84</td>
<td>0.94</td>
</tr>
<tr>
<td>Kr&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.60</td>
<td>0.60</td>
<td>0.73</td>
<td>0.91</td>
<td>0.82</td>
<td>0.90</td>
<td>0.97</td>
</tr>
</tbody>
</table>

| MA%E | 144 | 32 | 23 | 21 | 15 | 15 | 14 |
| M%E  | 144 | 13 | -5 | -21 | -15 | -14 | -13 |
| S%DEV | 65 | 41 | 26 | 8 | 5 | 10 | 12 |

TABLE V: Reduced BSSE corrected harmonic vibrational frequencies $\omega$ of ten rare gas dimers in the aug-cc-pVQZ basis set. The mean percentage of errors (M%E), the mean absolute percentage of errors (MA%E) and the standard deviation (S%DEV) are also given.
<table>
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<tr>
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<th>CCSD(T)</th>
<th>RSH+MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>He₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-T</td>
<td>0.535</td>
<td>0.891</td>
<td>0.402</td>
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<tr>
<td>T-Q</td>
<td>0.560</td>
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<td>Q-5</td>
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<td>0.950</td>
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<td>5-6</td>
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<td>0.984</td>
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</tr>
<tr>
<td>Ne₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.672</td>
<td></td>
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<td>0.728</td>
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</tr>
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<td>0.987</td>
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</tr>
<tr>
<td>5-6</td>
<td>0.602</td>
<td>0.971</td>
<td>0.746</td>
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</tr>
<tr>
<td>Ar₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-T</td>
<td>0.987</td>
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<td>T-Q</td>
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<tr>
<td>Kr₂</td>
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<td></td>
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</tr>
<tr>
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<td>0.809</td>
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<tr>
<td>Q-5</td>
<td>1.151</td>
<td>0.965</td>
<td>1.048</td>
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</table>

TABLE VI: Estimated basis set reduced binding energies of He₂, Ne₂, Ar₂ and Kr₂ at the MP2, CCSD(T) and RSH+MP2 level, at the reference (experimental) geometry.
TABLE VII: Mean (M), absolute mean (AM) and standard deviation (SDEV) of the BSSE effect on reduced equilibrium distances of ten rare gas dimers in the aug-cc-pVQZ basis set.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE</th>
<th>TPSS</th>
<th>MP2</th>
<th>CCSD(T)</th>
<th>RSH+MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>-0.002</td>
<td>-0.000</td>
<td>-0.002</td>
<td>-0.012</td>
<td>-0.022</td>
<td>-0.001</td>
</tr>
<tr>
<td>AM</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.012</td>
<td>0.022</td>
<td>0.004</td>
</tr>
<tr>
<td>SDEV</td>
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<td>0.003</td>
<td>0.004</td>
<td>0.039</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>PBE</td>
<td>TPSS</td>
<td>MP2</td>
<td>CCSD(T)</td>
<td>RSH+MP2</td>
</tr>
<tr>
<td>-------</td>
<td>-----</td>
<td>-----</td>
<td>------</td>
<td>-----</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>M</td>
<td>0.143</td>
<td>0.044</td>
<td>0.034</td>
<td>0.186</td>
<td>0.179</td>
<td>0.067</td>
</tr>
<tr>
<td>AM</td>
<td>0.143</td>
<td>0.044</td>
<td>0.035</td>
<td>0.186</td>
<td>0.179</td>
<td>0.067</td>
</tr>
<tr>
<td>SDEV</td>
<td>0.143</td>
<td>0.032</td>
<td>0.031</td>
<td>0.082</td>
<td>0.097</td>
<td>0.036</td>
</tr>
</tbody>
</table>

TABLE VIII: Mean (M), absolute mean (AM) and standard deviation (SDEV) of the BSSE effect on reduced binding energies of ten rare gas dimers in the aug-cc-pVQZ basis set.