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A density-functional model of the dispersion interaction

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We have recently introduced [J. Chem. Phys. **122**, 154104 (2005)] a simple parameter-free model of the dispersion interaction based on the instantaneous in space, dipole moment of the exchange hole. The model generates remarkably accurate interatomic and intermolecular C_6 dispersion coefficients, and geometries and binding energies of intermolecular complexes. The model involves, in its original form, occupied Hartree-Fock or Kohn-Sham orbitals. Here we present a density-functional reformulation depending only on total density, the gradient and Laplacian of the density, and the kinetic-energy density. This density-functional model performs as well as the explicitly orbital-dependent model, yet offers obvious computational advantages. © 2005 American Institute of Physics. [DOI: 10.1063/1.2065267]

I. INTRODUCTION

In Ref. 1, a simple model of the dispersion interaction was introduced which proposed that its source is the position-dependent dipole moment of the exchange hole. The idea underpinning this model is that a dipole moment instantaneous in *real space*, rather than instantaneous in virtual configuration space or in time, might be responsible for dispersion.

The exchange-hole dipole moment at any given point in a system A is assumed to induce an instantaneous dipole moment in another system B at separation R from A . The resulting potential energy of interaction, at large R , after angular averaging and density-weighted integration over all points in A , is given by

$$U_{\text{dip-dip}}^{AB} = -2\langle d_X^2 \rangle_A \alpha_B / R^6 \quad (1)$$

and the reverse interaction is similarly given by

$$U_{\text{dip-dip}}^{BA} = -2\langle d_X^2 \rangle_B \alpha_A / R^6. \quad (2)$$

In these expressions, α_A and α_B are the isotropic polarizabilities of A and B , and $\langle d_X^2 \rangle$ is the following integral:

$$\langle d_X^2 \rangle = \int \rho_\alpha(\mathbf{r}) d_{X\alpha}^2(\mathbf{r}) d^3\mathbf{r} + \int \rho_\beta(\mathbf{r}) d_{X\beta}^2(\mathbf{r}) d^3\mathbf{r}, \quad (3)$$

where ρ_α and ρ_β are up- and down-spin densities, and $d_{X\sigma}^2(\mathbf{r})$ is the squared exchange-hole dipole moment of the σ -spin electrons at point \mathbf{r} .

It was argued in Ref. 1, using second-order perturbation theory, that the appropriate combination of Eqs. (1) and (2) for the total A - B dispersion energy at long range, including kinetic and charge rearrangement effects, is

$$E_{\text{disp}} = -\frac{C_6}{R^6}, \quad (4)$$

$$C_6 = \frac{\langle d_X^2 \rangle_A \langle d_X^2 \rangle_B \alpha_A \alpha_B}{\langle d_X^2 \rangle_A \alpha_B + \langle d_X^2 \rangle_B \alpha_A}. \quad (5)$$

Thus the computation of isotropic intermolecular C_6 dispersion coefficients involves a simple integration, Eq. (3), over the position-dependent $d_{X\sigma}^2(\mathbf{r})$ of the systems involved, and knowledge of their isotropic polarizabilities.

The exchange-hole dipole moment $d_{X\sigma}(\mathbf{r})$, for which expressions are given in Sec. II, depends only on time-independent, occupied, Hartree-Fock or Kohn-Sham orbitals. No time dependence, virtual orbitals, or correlation (in the usual sense of the word) are involved. If polarizabilities are taken from tables, or otherwise calculated, then intermolecular C_6 's can be easily and elegantly computed in a post-Hartree-Fock or post-Kohn-Sham manner from Eq. (5). Though not exact, C_6 's from Eq. (5) are remarkably good considering the simplicity of the model. On a test set of 178 accurate interatomic and intermolecular data,² this model has a mean absolute error of only 11.1%.

Furthermore, we derived in Ref. 2 an algebraic decomposition of Eq. (5) for an intermolecular C_6 into interatomic pair terms:

$$C_6 = \sum_{ij} C_{6,ij}, \quad (6)$$

where i refers to an atom in system A and j to an atom in system B , positing the dispersion energy expression

$$E_{\text{disp}} = -\sum_{ij} \frac{C_{6,ij}}{R_{ij}^6}. \quad (7)$$

With suitable damping of each term at small R_{ij} , a post-Hartree-Fock model of intermolecular interactions was tested on geometries and binding energies of 20 intermolecular complexes with very encouraging results.²

In the present work we derive an approximate formula for the exchange-hole dipole moment $d_{X\sigma}(\mathbf{r})$ depending only on the local spin density, its gradient and Laplacian, and the local kinetic-energy density. Thus we obtain a *density-functional* model of intermolecular dispersion interactions. In

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contemporary density-functional theory (DFT) language, this is called a “meta-generalized-gradient-approximation” (meta-GGA) for the dispersion interaction.

In Sec. II, the underlying model of Ref. 1 is briefly reviewed. In Sec. III, its density-functional reformulation is introduced and tested on interatomic and intermolecular C_6 's. The exchange-hole model of Becke and Roussel³ (to be denoted BR) is the key. The BR model was the first exchange meta-GGA in the literature and has been fruitful in many contexts. It has been generalized to include current-density dependence,⁴ thereby solving a long-standing problem in the density-functional theory of open-shell atomic states.⁵ It is the basis of a promising new approach to the molecular non-dynamical correlation problem.^{6,7} Here we exploit a further property of the Becke-Roussel exchange hole, namely, that the BR hole has *nonzero dipole moment*.

In Sec. IV, our decomposition of intermolecular dispersion energy into interatomic pair terms² is reviewed and recast into the present BR framework. In Sec. V, the test set of 20 intermolecular geometries and binding energies employed in Ref. 2 is expanded to 41 complexes, and our original and the present dispersion models are assessed on these complexes in a post-Hartree-Fock manner. Finally, concluding remarks and a preview of future work are offered in Sec. VI.

II. THE BASIC MODEL

We refer the reader to Ref. 1 for a complete account of the present model. A summary of the underlying theory is provided here to set the stage for its density-functional reformulation in Sec. III.

Consider an electron of σ spin in an atomic or molecular system. As it moves through the system it is accompanied by an exchange (or Fermi) hole whose shape depends on the electron's instantaneous position \mathbf{r} . The hole is given by the expression

$$h_{X\sigma}(\mathbf{r}, \mathbf{r}') = -\frac{1}{\rho_{\sigma}(\mathbf{r})} \sum_{ij} \psi_{i\sigma}(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}') \psi_{j\sigma}(\mathbf{r}'), \quad (8)$$

where \mathbf{r}' defines the shape of the hole and \mathbf{r} is called the “reference” point. Summation is over all orbitals of σ spin (Hartree-Fock or Kohn-Sham, and assumed in this paper to be real) and ρ_{σ} is the total σ -spin electron density.

When an electron is at \mathbf{r} , the hole measures the depletion of probability, with respect to the total electron density ρ , of finding another same-spin electron at \mathbf{r}' . Several important and well-known properties of the hole are easily deduced from Eq. (8). The probability of finding another same-spin electron at $\mathbf{r}' = \mathbf{r}$ is completely extinguished,

$$h_{X\sigma}(\mathbf{r}, \mathbf{r}) = -\rho_{\sigma}(\mathbf{r}), \quad (9)$$

as required by the Pauli exclusion principle. The hole is always negative, as can be seen by rewriting Eq. (8) as

$$h_{X\sigma}(\mathbf{r}, \mathbf{r}') = -\frac{1}{\rho_{\sigma}(\mathbf{r})} \left[\sum_i \psi_{i\sigma}(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}') \right]^2 \quad (10)$$

and the hole always contains exactly (minus) one electron:

$$\int h_{X\sigma}(\mathbf{r}, \mathbf{r}') d^3\mathbf{r}' = -1. \quad (11)$$

The electron plus its hole, therefore, always has zero overall charge.

Useful information on the behavior of the hole *near* the reference point can be obtained from a Taylor expansion of the spherical average of $h_{X\sigma}(\mathbf{r}, \mathbf{r}')$ around \mathbf{r} . To second order in the interelectronic distance s , we have

$$h_{X\sigma}(\mathbf{r}, \mathbf{r} + s) = -\rho_{\sigma} - Q_{\sigma}s^2 + \cdots, \quad (12)$$

where

$$Q_{\sigma} = \frac{1}{6} \left[\nabla^2 \rho_{\sigma} - 2\tau_{\sigma} + \frac{1}{2} \frac{(\nabla \rho_{\sigma})^2}{\rho_{\sigma}} \right] \quad (13)$$

and where

$$\tau_{\sigma} = \sum_i (\nabla \psi_{i\sigma})^2 \quad (14)$$

is the “kinetic-energy” density (without a factor of $\frac{1}{2}$). This short-range information is an important ingredient in the BR model.³ It is through Eqs. (12)–(14) that local density gradients enter.

The hole is generally not spherically symmetric around \mathbf{r} . Only in a uniform electron gas does it have spherical symmetry. Even in systems with spherically symmetric densities, the hole is nonspherical unless \mathbf{r} is at the center of the system. Thus the electron plus its exchange hole generally has a *nonzero dipole moment*, given by a simple integration over \mathbf{r}' in Eq. (8):

$$\mathbf{d}_{X\sigma}(\mathbf{r}) = \left[\frac{1}{\rho_{\sigma}(\mathbf{r})} \sum_{ij} \mathbf{r}_{ij\sigma} \psi_{i\sigma}(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) \right] - \mathbf{r}, \quad (15)$$

where

$$\mathbf{r}_{ij\sigma} = \int \mathbf{r}' \psi_{i\sigma}(\mathbf{r}') \psi_{j\sigma}(\mathbf{r}') d^3\mathbf{r}' \quad (16)$$

and only the occupied orbitals are involved.

If this *instantaneous in space* nonzero dipole moment $\mathbf{d}_{X\sigma}(\mathbf{r})$ in a system A is allowed to *induce* a dipole moment in another system B , far from A , then simple electrostatics, angular averaging, and a density-weighted \mathbf{r} integration lead to the formulas in Sec. I for the isotropic C_6 of an A - B dispersion interaction.¹ The integrations required in Eqs. (3) and (16) may be carried out numerically,⁸ or analytically in the case of Eq. (16).

Equations (15) and (16) for $\mathbf{d}_{X\sigma}(\mathbf{r})$ are exact, and the computation of the $\langle d_X^2 \rangle$ expectation value of Eq. (3) is an order of N^3 task. Though of relatively minor cost compared to the computation of the orbitals themselves, a linear scaling $\langle d_X^2 \rangle$ procedure would be highly desirable in the wake of rapid ongoing advances in linear scaling Hartree-Fock, density-functional, and density-matrix technologies. The Becke-Roussel meta-GGA model of the exchange hole³ allows such a linearization.

III. DENSITY-FUNCTIONAL REFORMULATION

The BR model³ places a normalized, off-center, exponential function,

$$-\frac{a^3}{8\pi}e^{-ar}, \quad (17)$$

at a distance b from the reference position \mathbf{r} of a σ -spin electron. Enforcing Eq. (9), that the value of the hole at the reference point is $-\rho_\sigma$, gives the equation

$$\rho_\sigma = \frac{a^3}{8\pi}e^{-ab}. \quad (18)$$

Requiring, also, that the model hole have the same quadratic short-range behavior near \mathbf{r} as the exact hole gives a second equation,

$$Q_\sigma = \frac{\rho_\sigma}{6b}(a^2b - 2a), \quad (19)$$

where Q_σ is given by Eqs. (13) and (14). Then, setting $x = ab$, simultaneous solution of Eqs. (18) and (19) is achieved by solving the nonlinear problem,

$$\frac{xe^{-2x/3}}{(x-2)} = \frac{2}{3}\pi^{2/3}\frac{\rho_\sigma^{5/3}}{Q_\sigma}, \quad (20)$$

following which b is obtained from

$$b^3 = \frac{x^3e^{-x}}{8\pi\rho_\sigma} \quad (21)$$

and finally $a=x/b$. Equation (20) is easily solved, for all possible ρ_σ and Q_σ , by the Newton-Raphson method.⁹

The BR model was motivated³ by the hydrogenic atom as a prototype system. It reproduces, by construction, the *exact* exchange hole of a *hydrogenic atom* at any reference point. In any other system, it is an approximation to the exact hole that has correct normalization, Eq. (11), and correct short-range behavior, Eq. (12), at all reference points. Comparative plots of the spherically averaged BR hole may be found in Ref. 3. The model is sufficiently flexible to accommodate positive or negative curvatures Q_σ and even *infinitely negative* Q_σ as occurs at every nuclear cusp (see Ref. 3).

For the present purposes, notice that the BR model hole, like the exact hole, is *not spherically symmetric* around \mathbf{r} and has a nonzero dipole moment. Indeed, the (squared) dipole moment of the electron plus its BR hole is given by

$$d_{\text{BR}\sigma}^2(\mathbf{r}) = b^2, \quad (22)$$

where b is determined by the local density and curvature, $\rho_\sigma(\mathbf{r})$ and $Q_\sigma(\mathbf{r})$, through Eqs. (20) and (21). All the C_6 formulas of Sec. I, therefore, may be cast into density-functional form simply by replacing $\langle d_X^2 \rangle$ of Eq. (3) by the following Becke-Roussel analog:

$$\langle d_{\text{BR}X}^2 \rangle = \int \rho_\alpha(\mathbf{r})d_{\text{BR}X\alpha}^2(\mathbf{r})d^3\mathbf{r} + \int \rho_\beta(\mathbf{r})d_{\text{BR}X\beta}^2(\mathbf{r})d^3\mathbf{r}, \quad (23)$$

whose computational cost scales linearly with the system size.

This BR analog of our original theory has been tested on accurate C_6 data, compiled in Ref. 2, for 178 atom and molecule pairs. The mean absolute percent error (MAPE) is 15.0, only slightly worse than the MAPE of 11.1 for the exact-exchange-based theory.

In Sec. IV, we review our dispersion energy decomposition scheme of Ref. 2, and Eq. (7), in preparation for an assessment of this BR model on geometries and binding energies of intermolecular complexes in Sec. V.

IV. INTERATOMIC DECOMPOSITION

The fundamental quantity on which our model is based is the integrand of Eq. (3), the squared exchange-hole dipole moment density at \mathbf{r} :

$$d_X^2(\mathbf{r}) = \rho_\alpha(\mathbf{r})d_{X\alpha}^2(\mathbf{r}) + \rho_\beta(\mathbf{r})d_{X\beta}^2(\mathbf{r}), \quad (24)$$

or its BR analog from Eq. (23):

$$d_{\text{BR}X}^2(\mathbf{r}) = \rho_\alpha(\mathbf{r})d_{\text{BR}X\alpha}^2(\mathbf{r}) + \rho_\beta(\mathbf{r})d_{\text{BR}X\beta}^2(\mathbf{r}). \quad (25)$$

We will refer to this quantity as the “dipole density” from now on. Being a local function of \mathbf{r} , the dipole density in a molecule may be easily partitioned into atomic components using any suitable real-space atomic partitioning scheme such as Bader partitioning,¹⁰ smoothed Voronoi partitioning,⁸ or Hirshfeld partitioning.¹¹ We used the Hirshfeld scheme in our earlier work, Ref. 2, and we use it in the present work as well.

An atomic weight function $w_i(\mathbf{r})$ is constructed for each atom i in a molecule as follows:

$$w_i(\mathbf{r}) = \frac{\rho_i^{\text{at}}(\mathbf{r})}{\sum_n \rho_n^{\text{at}}(\mathbf{r})}, \quad (26)$$

where ρ^{at} is a free sphericalized atomic density placed at the appropriate nucleus, and the n summation is over all atoms in the molecule. Clearly, the weight functions sum to 1 everywhere,

$$\sum_n w_n(\mathbf{r}) = 1, \quad (27)$$

and $w_i(\mathbf{r})$ has value close to 1 at points in the vicinity of atom i and close to 0 everywhere else. The dipole density on atom i is thus given by

$$\langle d_X^2 \rangle_i = \int w_i(\mathbf{r})d_X^2(\mathbf{r})d^3\mathbf{r} \quad (28)$$

or by its BR analog.

Polarizability is not related to a local function of \mathbf{r} , is not additive (i.e., molecular polarizabilities are not sums of free atomic polarizabilities), and is therefore not so easy to partition into atomic components. We suggested in Ref. 2 the following reasonable *ansatz*:

$$\alpha_i = \frac{\langle d_X^2 \rangle_i}{\langle d_X^2 \rangle} \alpha, \quad (29)$$

where α is the total polarizability of the molecule. In other words, the polarizability of atom i in the molecule is proportional to the fraction of the dipole density owned by the

atom. In addition to being a reasonable ansatz, we discovered² that, *given* this definition, our model C_6 of Eq. (5) algebraically decomposes into a sum over atomic pair C_6 's as in Eq. (6):

$$C_6 = \sum_i^A \sum_j^B C_{6,ij}, \quad (30)$$

where

$$C_{6,ij} = \frac{\langle d_X^2 \rangle_i \langle d_X^2 \rangle_j \alpha_i \alpha_j}{\langle d_X^2 \rangle_i \alpha_j + \langle d_X^2 \rangle_j \alpha_i} \quad (31)$$

and where we adopt the convention, here and in the rest of this section, that index i refers to an atom in system A and index j refers to an atom in B .

Equations (30) and (31) motivate the dispersion energy formula of Eq. (7), which requires damping of each term at small R_{ij} . In Ref. 2, a novel energy-based damping,

$$E_{\text{disp}} = - \sum_{ij} \frac{C_{6,ij}}{(\kappa C_{6,ij}/E_{C,ij}) + R_{ij}^6}, \quad (32)$$

was proposed in which $E_{C,ij}$ is the sum of the absolute values of the correlation energies of the free atoms i and j (with 21 mH, half the He value, taken for H) and κ is a universal parameter limiting the dispersion energy of each ij pair to $-E_{C,ij}/\kappa$ at small R_{ij} . This formula contains only one, universal, empirical parameter κ (with value of the order of 1000) and, unlike other formulas in the literature, requires no Van der Waals radii.

Since free atomic correlation energies are well defined¹² the dispersion energy, Eq. (32), contains *no empirical parameters* except for κ . The interatomic $C_{6,ij}$ coefficients are computed from the occupied molecular orbitals through the dipole density of Eq. (24) or (25), and the atomic partitionings of Eqs. (28) and (29), without any empiricism or fitting whatsoever. We test this dispersion energy formula on a variety of intermolecular complexes in Sec. V.

V. COMPUTATIONS AND ASSESSMENT

In Ref. 2, tests were performed on 20 intermolecular complexes using Hartree-Fock orbitals from the basis-set-free NUMOL program.¹³ Since NUMOL Hartree-Fock calculations are practical on small systems only, we have developed a post-GAUSSIAN98 methodology for larger systems in the present work. We employ the GAUSSIAN98 program¹⁴ to compute Hartree-Fock/aug-cc-pVTZ orbitals using the keyword "output=wfn" to create a WFN file. Orbital information is read from the WFN file and all the quantities needed in the present work, including density gradients, Laplacians, and kinetic-energy densities, are analytically evaluated at all points of a numerical integration grid.⁸ All the integrations are then carried out on the numerical grid.

Intermolecular energies are strongly affected by dynamical correlation. It is not sufficient to add a dispersion correction such as Eq. (32) to the Hartree-Fock energy alone. A dynamical correlation term must be included as well. We choose the dynamical correlation functional of Becke,¹⁵ as

modified in Ref. 16 to incorporate BR exchange. Denoting this functional as E_C^{BR} , our target total energy is

$$E_{\text{tot}} = E_{\text{HF}} + E_C^{\text{BR}} + E_{\text{disp}}. \quad (33)$$

The two variations of our theory, involving the dipole density of the exact exchange hole, Eq. (24), or the dipole density of the BR model hole, Eq. (25), will be denoted as "XX" and "BR," respectively, in this section. In either case, E_{tot} is evaluated using Hartree-Fock orbitals and therefore the present work, as was the work of Ref. 2, is best described as "post-Hartree-Fock."

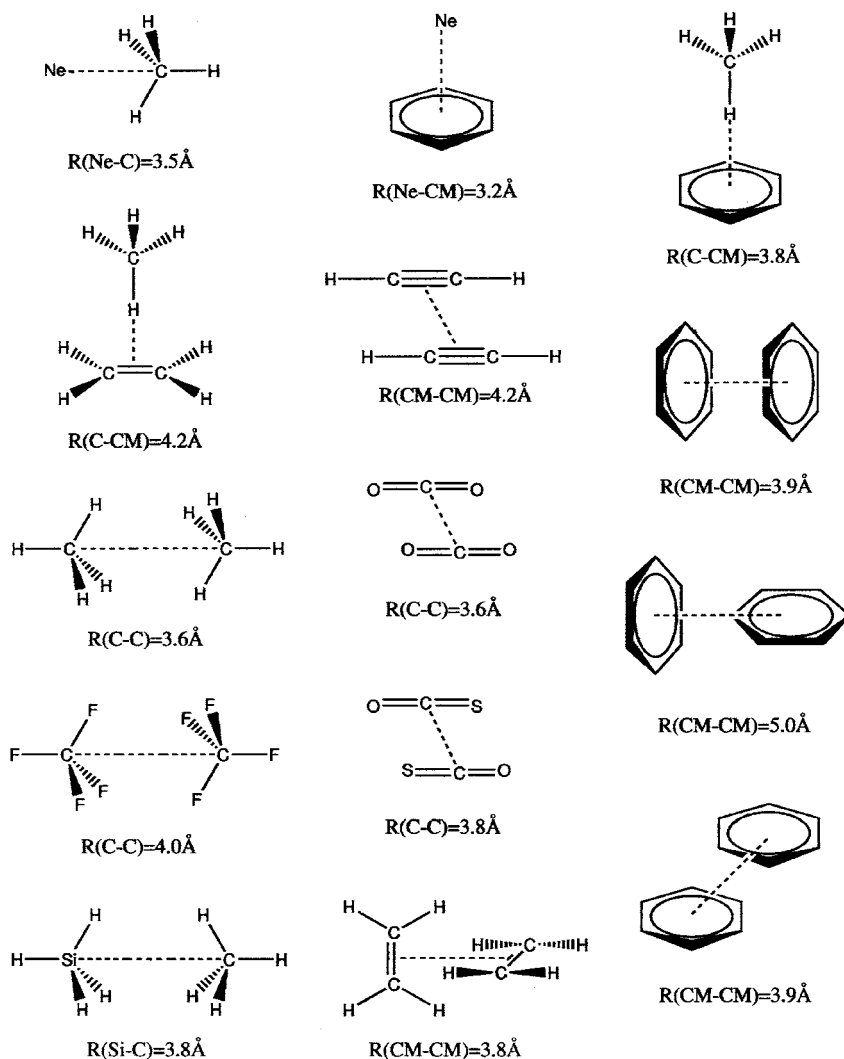
We have applied the XX and BR post-Hartree-Fock methods to the calculation of minimum-energy separations and binding energies for a test set of 41 Van der Waals complexes involving dispersion, dipole-induced dipole, dipole-dipole, and hydrogen-bonding interactions. The conformations of these complexes are shown in Fig. 1. The geometries of all monomers were optimized using CCSD/aug-cc-pVTZ,¹⁴ except for the benzene geometry which was taken from Ref. 17. Counterpoise-corrected¹⁸ HF/aug-cc-pVTZ potential-energy surfaces (PESs) were then generated for each of the complexes by keeping the monomer geometries fixed and varying up to three intermonomer coordinates in increments of 0.1 Å or 5°. Post-HF evaluations of the dynamical BR correlation energy and both XX and BR dipole densities were performed on the complex at each point on the PES and on the separated monomers (not counterpoise corrected). Polarizabilities of all the species were taken from Ref. 19, except for FCl for which no value was available. The polarizability of FCl was calculated using HF/aug-cc-pVTZ. The lowest-energy point on the resulting $E_{\text{HF}} + E_C^{\text{BR}} + E_{\text{disp}}$ PES was deemed the optimized geometry of the complex. Binding energies (BEs) were computed as the total-energy difference between the optimized complex and the separated monomers.

Our calculated intermonomer separations and binding energies are listed in Table I and compared to high-level reference data.^{20–30} The reference geometries are also shown in Fig. 1. We divide the complexes into classes according to the type of Van der Waals interaction involved, though in many cases the binding may involve several interaction types. An optimum value of $\kappa=800$ was selected by minimizing the MAPE in the calculated BEs. The optimum κ is the same for both the XX and the BR models.

There is little difference between the results obtained from the XX or the BR dipole densities for this set of Van der Waals complexes. The mean absolute error (MAE) for the intermonomer separations is identical for both XX and BR, and the MAPE in the binding energies differs by only 0.1% between the two approaches. It is gratifying that the more efficient BR approach is no less accurate than the exact-exchange approach of our earlier work.²

The agreement between our calculated separations and the high-level reference data is excellent, with a MAE of

a) Dispersion



b) Dipole-Induced Dipole

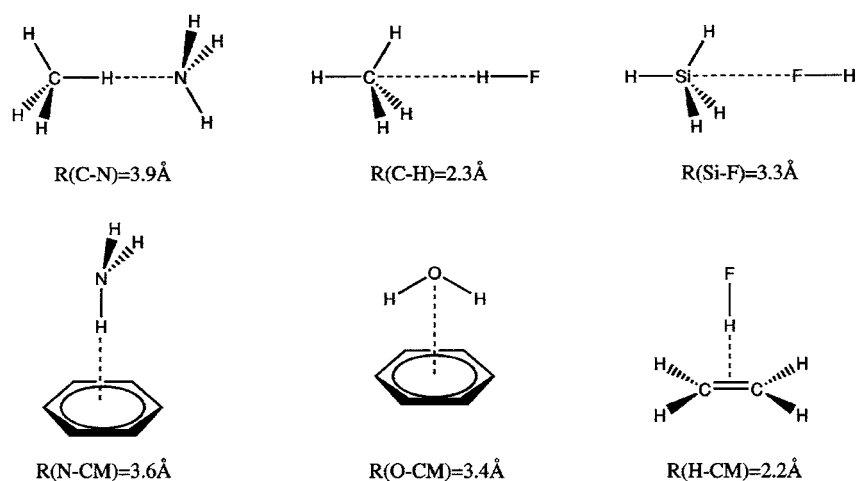
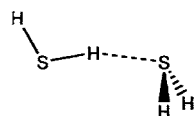


FIG. 1. Structures of Van der Waals complexes and reference intermonomer separations obtained from high-level theory. See Table I for references. Complexes are arranged by interaction types: (a) dispersion, (b) dipole-induced dipole, (c) dipole-dipole, and (d) H-bond.

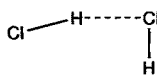
0.08 Å. For the set of 41 complexes, our methods have maximum errors of 0.4 Å (XX) and 0.3 Å (BR), the worst cases being overestimation of the monomer separations in the parallel and slipped-parallel conformations of the benzene

dimer. There is also a good agreement with high-level reference data for our calculated BEs, with MAPEs of 15.4% (XX) and 15.3% (BR). Our methods show similar mean errors for each class of Van der Waals interactions. The parallel

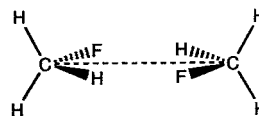
c) Dipole-Dipole



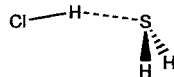
$$R(\text{H-S})=2.8\text{\AA}$$



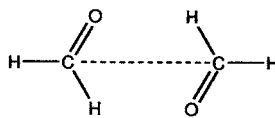
$$R(\text{H-Cl})=2.5\text{\AA}$$



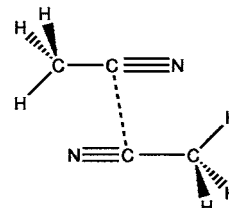
$$R(\text{C-C})=3.9\text{\AA}$$



$$R(\text{H-S})=2.5\text{\AA}$$

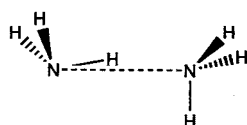


$$R(\text{C-C})=3.6\text{\AA}$$

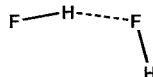


$$R(\text{C-C})=3.4\text{\AA}$$

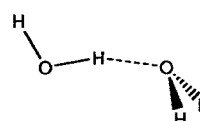
d) H-Bond



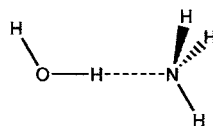
$$R(\text{N-N})=3.3\text{\AA}$$



$$R(\text{H-F})=1.9\text{\AA}$$



$$R(\text{H-O})=2.0\text{\AA}$$



$$R(\text{O-N})=3.0\text{\AA}$$



$$R(\text{N-H})=1.9\text{\AA}$$

FIG. 1. (Continued).

and slipped-parallel benzene dimers are again the worst cases, with MAPEs improving to 12.8% (XX) and 13.1% (BR) if these π -stacked complexes are omitted from the statistics.

The π -stacked benzene dimer conformations are also a difficult case for MP2, which, with the aug-cc-pVQZ basis set, overestimates the binding energies by 98.2% and 82.8% for the parallel and slipped-parallel conformations, respectively.¹⁷ Also, most “standard” DFTs predict a separation for the slipped-parallel benzene dimer that is far too long by ca. 2 Å and fail to predict any binding for the parallel conformation.³¹ Therefore the present methods, while having relatively large errors for the π -stacked benzene dimers as well, nevertheless represent major improvements over both MP2 and standard DFTs for which these are pathological cases.

To assess our results in the context of recent literature we compare with the work of Grimme,³² who added an empirical dispersion correction to the BLYP (Ref. 33) exchange-correlation functional and applied his method to a set of 28 Van der Waals complexes. Grimme obtained C_6 coefficients from fits to the experimental C_6 data and reported parameters for C, N, O, H, and halogen atoms. An additional global scaling parameter was used to improve the

binding energies. This yielded a MAE of 0.09 Å for separations and a MAPE of 20.4% for binding energies. Our method has significantly lower binding-energy errors, the more remarkable considering that our C_6 coefficients are completely free of empirical parametrization or fitting.

In a recent study of 28 Van der Waals complexes,²⁹ B971 (Ref. 34)/6-311++G(3df,3pd) was found to be the best standard DFT for structure prediction and, with counterpoise correction, was also the best for calculating binding energies. In Table II, we present a direct comparison between our methods and B971/6-311++G(3df,3pd) for the 26 complexes common between this data set and the current work. The two complexes omitted are the parallel benzene dimer, which is predicted to be unbound by B971, and the formic acid dimer, in which there is significant monomer distortion in the dimer and thus our rigid monomer approach is not appropriate. Our methods perform far better than B971 for the calculation of both optimized separations and binding energies for dispersion-bound complexes and perform similarly for the other classes of Van der Waals complexes. The high accuracy of our calculated geometries and binding energies, particularly in comparison with standard DFTs, is

TABLE I. Calculated intermonomer separations and binding energies ($\kappa=800$). Mean absolute errors (MAE), relative to high-level reference data, are shown for the separations and mean absolute percent errors (MAPE) are shown for the binding energies.

Complex	Separation (Å)			Binding energy (kcal/mol)		
	XX	BR	High level	XX	BR	High Level
Dispersion						
He ₂	3.0	2.9	3.0 ^a	0.021	0.022	0.022 ^a
He-Ne	2.9	2.9	3.0 ^a	0.053	0.057	0.041 ^a
He-Ar	3.4	3.4	3.5 ^a	0.065	0.063	0.057 ^a
Ne ₂	2.9	2.9	3.1 ^a	0.105	0.113	0.084 ^a
Ne-Ar	3.4	3.4	3.5 ^a	0.125	0.121	0.134 ^a
Ar ₂	3.8	3.8	3.8 ^a	0.216	0.199	0.285 ^a
He-N ₂ linear	3.9	3.9	3.9 ^b	0.044	0.045	0.053 ^b
He-N ₂ T shape	3.4	3.4	3.4 ^b	0.062	0.063	0.066 ^b
He-FCI	3.9	3.9	3.9 ^c	0.082	0.087	0.097 ^c
FCI-He	3.5	3.5	3.5 ^c	0.185	0.182	0.182 ^c
Ne-CH ₄	3.3	3.3	3.5 ^d	0.20	0.20	0.22 ^d
Ne-C ₆ H ₆	3.3	3.3	3.2 ^d	0.35	0.39	0.47 ^d
CH ₄ -C ₂ H ₄	4.3	4.3	4.2 ^e	0.44	0.45	0.50 ^e
(CH ₄) ₂	3.7	3.7	3.6 ^d	0.40	0.41	0.51 ^d
(CF ₄) ₂	3.8	3.8	4.0 ^f	0.76	0.92	0.78 ^f
CH ₄ -SiH ₄	3.8	3.8	3.8 ^g	0.72	0.74	0.81 ^g
CH ₄ -C ₆ H ₆	4.0	4.0	3.8 ^h	0.90	0.94	1.23 ^h
(C ₂ H ₂) ₂	4.2	4.2	4.2 ^d	1.52	1.51	1.34 ^d
(CO ₂) ₂	3.6	3.6	3.6 ⁱ	1.60	1.61	1.37 ⁱ
(OCS) ₂	3.8	3.8	3.8 ^j	1.44	1.40	1.40 ^j
(C ₂ H ₄) ₂	3.7	3.7	3.8 ^d	1.37	1.39	1.42 ^d
P-(C ₆ H ₆) ₂ ^k	4.2	4.2	3.9 ^l	0.34	0.48	1.70 ^l
T-(C ₆ H ₆) ₂ ^m	5.0	5.0	5.0 ^l	2.26	2.43	2.61 ^l
SP-(C ₆ H ₆) ₂ ⁿ	4.3	4.2	3.9 ^l	1.28	1.47	2.62 ^l
MA(P)E	0.09	0.09	...	18.1	17.4	...
Dipole-induced dipole						
CH ₄ -NH ₃	3.9	3.9	3.9 ^e	0.72	0.73	0.73 ^e
SiH ₄ -HF	3.2	3.2	3.3 ^o	0.86	0.88	0.73 ^o
CH ₄ -HF	2.3	2.3	2.3 ^e	1.74	1.74	1.65 ^e
NH ₃ -C ₆ H ₆	3.8	3.8	3.6 ^p	2.56	2.63	2.22 ^p
H ₂ O-C ₆ H ₆	3.3	3.3	3.4 ^p	3.80	3.89	3.17 ^p
C ₂ H ₄ -HF	2.1	2.1	2.2 ^o	5.51	5.51	4.47 ^o
MA(P)E	0.08	0.08	...	13.8	15.2	...
Dipole-dipole						
(H ₂ S) ₂	2.9	2.9	2.8 ^d	1.67	1.63	1.66 ^d
(HCl) ₂	2.5	2.5	2.5 ^d	2.04	1.99	2.01 ^d
(H ₃ CF) ₂	3.8	3.8	3.9 ^o	2.76	2.82	2.33 ^o
H ₂ S-HCl	2.5	2.5	2.5 ^d	3.46	3.42	3.35 ^d
(H ₂ CO) ₂	3.6	3.6	3.6 ^e	4.44	4.47	3.37 ^e
(H ₃ CCN) ₂	3.3	3.3	3.4 ^o	6.46	6.49	6.16 ^o
MA(P)E	0.06	0.06	...	10.1	10.6	...

TABLE I. (Continued.)

Complex	Separation (Å)			Binding energy (kcal/mol)		
	XX	BR	High level	XX	BR	High Level
Hydrogen bonded						
(NH ₃) ₂	3.3	3.3	3.3 ^d	3.21	3.21	3.15 ^d
(HF) ₂	1.8	1.8	1.9 ^d	5.45	5.46	4.57 ^d
(H ₂ O) ₂	1.9	1.9	2.0 ^d	5.61	5.61	4.97 ^d
H ₂ O–NH ₃	2.9	2.9	3.0 ^d	6.67	6.67	6.09 ^d
HCN–HF	1.8	1.8	1.9 ^e	8.05	8.06	7.30 ^e
MA(P)E	0.07	0.07	...	10.8	10.9	...
Overall	0.08	0.08	...	15.4 (12.8) ^q	15.3 (13.1) ^q	...
MA(P)E						

^aReference 20.^bReference 21.^cReference 22.^dReference 23.^eReference 2.^fReference 24.^gReference 25.^hReference 26.ⁱReference 27.^jReference 28.^kParallel conformation.^lReference 17.^mT-shaped conformation.ⁿSlipped-parallel conformation.^oReference 29.^pReference 30.^qValues in parentheses are errors determined by omitting parallel and slipped-parallel benzene dimer values.

very promising for applications such as protein structure prediction in which Van der Waals interactions are the primary determinants of structure and energetics.

VI. CONCLUSIONS AND OUTLOOK

The present work introduces a density-functional model of the dispersion interaction with the *physics* of dispersion explicitly incorporated. The underlying idea,¹ that the non-zero, instantaneous *in space*, dipole moment of the exchange hole is the source of induced dipole moments in far systems,

is elegant and easy to implement. The exchange-hole dipole moment depends on local density, gradient and Laplacian of the density, and the local kinetic-energy density. The model predicts, without any empirical parameters whatsoever, intermolecular C_6 dispersion coefficients of very good accuracy.

With a previously derived² algebraic decomposition of our intermolecular C_6 formula into interatomic pair terms, and a novel energy-based damping² of each term at small R_{ij} , a density-functional theory of intermolecular interactions is obtained. Geometries and binding energies for a test set of 41 intermolecular complexes are predicted with remarkable ac-

TABLE II. Mean absolute errors (MAE) in separations and mean absolute percent errors (MAPE) in binding energies for 26 Van der Waals complexes. The B971 values in parentheses were not corrected for basis-set superposition error. The B971 results were obtained from the data in Ref. 29.

Interaction type	MAE in separation (Å)			MAPE in binding energy (%)		
	B971/ 6-311++G(3df,3pd)	XX	BR	B971/ 6-311++G(3df,3pd)	XX	BR
Dispersion	0.34 (0.30)	0.11	0.10	44.7(50.1)	16.7	17.3
Dipole-induced dipole	0.09 (0.05)	0.08	0.08	16.9(13.6)	13.8	15.2
Dipole-dipole	0.04 (0.03)	0.06	0.06	13.1(9.4)	18.4	19.7
Hydrogen bonded	0.07 (0.06)	0.07	0.07	3.4(5.7)	8.7	8.7
Overall	0.20 (0.17)	0.09	0.09	28.2(30.2)	15.0	15.8

curacy invoking only one, universal, empirical parameter. The worst results occurred for the π -stacked conformations of the benzene dimer. We believe that this will be rectified in future work by adding a C_8/R^8 term in the dispersion energy.

The model in its present form requires the polarizability of each monomer. Although polarizability data are readily available for numerous systems, these are inconvenient in general and are fundamentally problematic for *intramolecular* dispersion interactions. In future work, therefore, we will also investigate how to remove molecular polarizability from the theory.

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