

Dispersion Forces: Neither Fluctuating Nor Dispersing

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Supporting Information

ABSTRACT: Dispersion forces are ubiquitous in chemistry, yet they are often misunderstood. This article provides background into why they are called dispersion forces and explains how to describe them in terms of time-independent quantum mechanics. The article also describes the breakdown of the multipole series that is often used to describe dispersion forces, and it comments on the representation of dispersion forces in molecular mechanics. In general, the article tries to provide a proper framework for understanding and describing dispersion forces.

KEYWORDS: Upper-Division Undergraduate, Graduate Education/Research, Physical Chemistry, Interdisciplinary/Multidisciplinary, Noncovalent Interactions, Quantum Chemistry, Molecular Modeling

“Intermolecular forces, or more broadly, noncovalent interactions either within or between molecules, are central to an understanding of a wide range of chemical and biological phenomena.”¹ Noncovalent interactions are important in almost all branches of chemistry, and dispersion forces are the most pervasive, since they are always present, even for systems with no net charges and no permanent multipole moments. The leading term in the dispersion interaction potential between ground-state atoms or molecules varies as $-C_6/R^6$ at large separation between two subsystems, where the minus sign indicates that the potential is attractive, C_6 is a coefficient, and R is the distance between the subsystems. However, there are several aspects of dispersion forces that lead to confusion, so let us see if we can straighten these out.

We can start with the name. Why are dispersion forces called dispersion forces? It dates back to a 1930 paper by Eisenschitz and London.² They derived what is now known as the London approximation to the C_6 coefficient. In the middle of the derivation, we have a section included here as Figure 1. My

$$\mu_k = e \int r_1 \psi_1(1) \bar{\psi}_k(1) = e \int r_2 \varphi_1(2) \bar{\varphi}_k(2),$$

so können wir (57) folgendermaßen schreiben:

$$\Delta E_2 = -\frac{1}{R^6} \sum_{k', k''} \frac{\mu_k^2 \mu_{k''}^2}{\epsilon_1 E_1 - \epsilon_0 E_k} [\cos(\mu_{k'} \mu_{k''}) - 3 \cos(\mu_{k'} R) \cos(\mu_{k''} R)]^2. \quad (57a)$$

Die Momente μ_k stehen in unmittelbarem Zusammenhang mit den f -Werten der Dispersionstheorie. Diese f -Werte sind bekannt, sie sind von

Figure 1. Excerpt from ref 2. Copyright 1930. Reprinted with permission from Nature/Springer.

translation of the key sentence is “The moments μ_k are directly related to the f -values of dispersion theory.” The relevant definition of dispersion in this quotation is the technical definition pertaining to optical dispersion, which is “the separation of light into colors by refraction or diffraction with formation of a spectrum.”³ Therefore, dispersion theory describes the dependence of the index of refraction on the frequency of the radiation,⁴ and these forces are named

dispersion forces because the theoretical equations that London used to describe them involved some of the same quantities that occur in dispersion theory. Therefore, nothing is being dispersed by dispersion forces. Unfortunately, I see them called dispersive forces much too often, and it always makes me cringe.

It is informative to go a little deeper into the background that led to the naming of dispersion forces. Dispersion theory in physics originated as the theory of how the refractive index n depends on the frequency ω of the radiation field. Kronig and Kramers^{5,6} generalized this by showing the existence of a complex function of ω , the dielectric response function, whose real part is associated with the refraction of light and whose imaginary part is associated with the absorption of light. In general the real part of a complex function of a real variable may be written as an integral over the imaginary part and vice versa; these are called Hilbert transforms by mathematicians, but most physicists call them dispersion relations because the most well-known example is the Kronig–Kramers relation between the real and imaginary parts of the dielectric response function. In quantum mechanics, the integral becomes a sum, as shown in another paper of London’s;⁷ in modern notation, this equation becomes⁸

$$n(\omega) - 1 = (\text{constant}) \sum_k \frac{f_k}{\omega_k^2 - \omega^2} \quad (1)$$

where ω is frequency of the radiation, ω_k is the frequency of a transition, and f_k is the oscillator strength of the transition (the oscillator strength is equal to London’s “ f -value” and it tells us, using the dipole selection rule, the strength of light absorption due to the transition). One can also write this as

$$n(\omega) - 1 = (\text{constant}) \sum_k \frac{\omega_k \mu_k^2}{\omega_k^2 - \omega^2} \quad (2)$$

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where μ_k is the transition dipole of the transition. Equation 2 may be compared to the quantum mechanical formula for the static dipole polarizability α of an atom or a molecule:

$$\alpha = (\text{constant}) \sum_k \frac{\mu_k^2}{\omega_k} \quad (3)$$

Note that the static dipole polarizability is usually just called the polarizability, and I will follow that convention here. In the limit where ω tends to zero (slowly varying electric field), eq 2 reduces to eq 3. So we see that there is a striking resemblance of the theoretical frameworks for refraction and molecular polarization. Dispersion theory predates quantum mechanics, and it was London who pointed out that the same polarization phenomena responsible for refraction are the forces involved in what we now call dispersion forces.

The analogy London worked with is as follows. The polarizability determines the electric polarization of an atom or molecule by an electrostatic field such as the electrostatic field due to another atom or molecule. The polarizability also controls the electric polarization of a material in the presence of the electric field of a light wave. The dependence of the polarization on frequency is described by dispersion theory because the polarizability is related to the refractive index by the Clausius–Mossotti–Lorentz–Lorenz equation.⁹ Therefore, the theory of induced polarization in molecules resembles dispersion theory. In particular, in the limit where the subsystems are far apart, the size of the dipole moment induced by an external field is proportional to the polarizability, as is the refractive index. Therefore, the formula for C_6 resembles that for the dispersion of n , i.e., $n(\omega)$. Consequently, following London, we call these dispersion forces. The leading term in the polarization of a molecule by an electric field is the induced dipole moment.

Another potentially confusing aspect of dispersion forces is that they are often described in time-dependent language. This is found in almost all textbooks and pedagogical articles; I will give only two examples: “the dynamic, random behavior of the electron cloud may result in a momentary distortion of the symmetric electron distribution, establishing a transient dipole moment”¹⁰ and (in considering the interaction between two well separated hydrogen atoms) “although the hydrogen atom is spherically symmetrical on the average, at any instant the electron is in a position such that the atom has a dipole moment. This instantaneous dipole has a field, and this field tends to polarize the other atom, while the dipole changes, even reverses with high frequency, if the polarization of the other atom keeps phase, the net effect is attractive...”.¹¹ A general summary of the typical argument goes something like the following for the interaction of atom A with atom B: An instantaneous fluctuation in A gives rise to a dipole moment. This dipole moment induces a favorable dipole moment in B, and the interaction between these two instantaneous dipoles is attractive. Instantaneous fluctuations in B also induce favorable dipoles in A, and these also contribute to an attractive interaction potential. Dispersion is thereby described as the interaction of mutually induced dipole moments. There is nothing wrong with this argument, when stated properly and when properly understood, but it is not a correct description of dispersion forces in the electronic ground state. When almost all of the rest of our quantitative discussion of molecular properties and interactions is carried out in the language of the time-independent Schrödinger equation and stationary-state wave functions, it seems odd that most

elementary textbooks and much of the research literature reverts to time-dependent language to describe dispersion forces. Also, it can also lead to misinterpretations for the following reason. It turns out that these forces do not change or fluctuate over time in the ground electronic state; the dispersion forces can be completely understood in terms of time-independent quantum mechanics with stationary states that do not fluctuate in time, whereas the above way of describing them might make one think that dispersion forces really do involve time dependence.

Let us start over and describe the phenomenon of dispersion forces by time-independent quantum mechanics (as was done by London). We know that, except for one-electron systems, electronic wave functions cannot be written in terms of a single configuration, but rather require a superposition of configurations:

$$\Psi = \sum_k c_k \psi_k \quad (4)$$

where ψ_k is a configuration state function, and c_k is a coefficient. (A “configuration” is a particular way of assigning electrons to orbitals, e.g., $1s^2 2s^2$ or $1s^2 2p^2$ for Be, and a “configuration state function” is an approximate wave function corresponding to a particular configuration.) All quantities in eq 4 are independent of time; Ψ solves the time-independent Schrödinger equation, and eq 4 is sometimes called a configuration interaction (CI) wave function.

Let us consider a concrete example, namely, the interaction of two He atoms, which we label A and B. The dominant configuration (the ψ_k corresponding to the largest c_k) is $1s_A^2 1s_B^2$, but to obtain the correct wave function we must include other configurations. Some linear combinations of configuration state functions have nonzero dipole moments (a positive linear combination of $1s_A^2$ and $1s_A 2p_{xA}$ on the atom A function corresponds to a charge distribution of A that has a positive dipole moment in the x direction, and a negative linear combination of $1s_A^2$ and $1s_A 2p_{xA}$ on the atom A function corresponds to a charge distribution of A that has a positive dipole moment in the negative x direction). For an isolated He atom, combinations with nonzero dipole moments would always occur with coefficients such that the resulting Ψ after all configurations are added together in eq 4 has no net dipole moment.

The net dipole moment of He_2 is also zero, but to understand dispersion we have to consider more than the net dipole moment of the dimer; we must consider the individual dipole moments of the monomers. Let us consider that atom A is on the left side of the x -axis, and atom B is on the right side of the x -axis. For either atom let us call the local dipole moment positive if the positive end is on the left and negative if the negative end is on the left. Then, a $++$ or $--$ arrangement of dipole moments is attractive (lowers the energy of He_2 because the negative end of one dipole is pointing toward the positive end of the other), and a $+-$ or $-+$ arrangement is repulsive (raises the energy of He_2). This is illustrated in Figure 2. Now a $+-$ or $-+$ configuration has no net dipole, but a $++$ or $--$ arrangement has a nonzero dipole moment. Since He_2 , by symmetry, cannot have a net dipole moment, the $++$ or $--$ configurations must have equal coefficients so the contributions to the dipole moment cancel. However, they can have bigger coefficients than the $+-$ and $-+$ configurations, and by the variational principle, which says that the set of coefficients that most lowers the energy is the correct one, the net contribution to the molecular energy of the sum of the $++$ or $--$ configurations will outweigh the net contribution

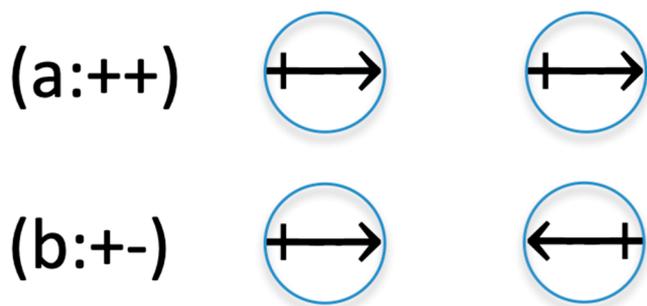


Figure 2. In part a, both dipoles point to the right (i.e., they both have a + sign). Thus, the left atom has a negatively polarized charge on its right side, and the right atom has a positively polarized charge on its left. The electrostatic interaction between the atoms is dominated by the closest charges. Since the closest charges have opposite signs, the electrostatic interaction is attractive. In part b, the dipoles point in opposite directions, and the electrostatic interaction is repulsive.

to the molecular energy of the sum of the $+ -$ and $- +$ configurations. Thus, the coefficients of the configurations are correlated, which is an example of electron correlation. The presence of the $++$ and $--$ configurations in the time-independent CI wave function provides the time-independent description of the dispersion force. We may say that the $+$ combination of configurations on the left helium induces a greater wave function amplitude for dimeric configurations in which the right helium is also plus, and vice versa. In this way, we have explained dispersion in terms of time-independent electron correlation. This can be summarized by calling the dispersion interaction an interaction between two mutually induced dipoles. Notice that this is like a molecular example of Schrödinger's cat, which is often used to illustrate the nonclassical nature of the superposition of probability amplitudes in quantum mechanics. In particular, the wave function of the helium dimer simultaneously has $++$, $--$, $+ -$, and $- +$ characters (which are classically incompatible characters, just as dead cats and live cats are incompatible), but it has these characters in a time-independent fashion; it is not fluctuating in time between having these characters.

At a more advanced level, we may consider the ψ_k to be vectors in a Hilbert space,¹² and then we can say that dispersion corresponds to a time-independent correlation of atomic components of Hilbert space vectors rather than to a time-dependent correlation of atomic dipole moment vectors in physical space.

So far we have concentrated on induced dipole moments, and those are the leading terms in a series (a multipole series^{13–15}) describing the interaction of neutral systems when the interacting systems are far apart. The induced dipole-induced dipole interactions are responsible for the $-C_6/R^6$ long-range form, and the R^{-6} dependence of dispersion energies may be explained by the induced nature of the dipole moments as follows. Dipole–dipole interaction potentials vary as R^{-3} . The magnitude of the dipole induced on B by the dipole of A is therefore proportional to R^{-3} , and the interaction of the two dipoles is also proportional to R^{-3} ; multiplying these factors gives R^{-6} .

The multipole expansion provides a completely correct analytical model at long-range, but there is no completely correct analytical model at short-range. As the interacting systems approach one another, the description of dispersion

forces as proportional to R^{-6} breaks down at van der Waals distances for two reasons:

- (i) As the distance R between the two interacting fragments decreases, the multipole series gains appreciable contributions from induced quadrupoles, octupoles, hexadecapoles, and higher-order terms, leading to the series

$$V_{\text{dispersion}} \sim -\frac{C_6}{R^6} - \frac{C_7}{R^7} - \frac{C_8}{R^8} - \dots \quad (5)$$

An interesting quirk of the multipole series is the R^{-7} term; this term is missing for atoms¹⁶ and molecules with an inversion center, or when one does rotational averaging, but in general, although it is widely neglected, it is present;¹⁷ the almost universal neglect of this term is yet one more example of a widespread misconception about dispersion.

- (ii) The assumption underlying a multipole expansion is that the interacting charge distributions do not overlap. Overlap is significant at van der Waals distances, so the multipole treatment is invalid (because the derivation of the multipole series assumes nonoverlapping charge distributions), and the multipole series tends to overestimate the true effect; consequently one thinks of the dispersion as being damped. In fact, the series (eq 5) is what is known in mathematics as an asymptotic expansion.¹⁸ In such a series, at values of R where the series is useful, as one proceeds through the terms, the first few terms get successively smaller and provide a useful approximation, but eventually the terms in the series start to increase and the series diverges. As R decreases and overlap becomes greater, the series diverges at a lower order (i.e., at an earlier term), and as R decreases further, the series eventually becomes useless. The optimum approximation that can be obtained from an asymptotic expansion is to stop at the smallest term and retain all the previous terms plus half of the smallest term.

The optimum geometry of a molecule (for example, the equilibrium geometry of a van der Waals complex) is a position of minimum potential energy (where here we are speaking of the Born–Oppenheimer potential energy^{19,20} as in a potential energy surface that is a function of the internal coordinates, and we are discussing the geometry where this function has a minimum). In fact, at a van der Waals minimum, by the very fact that it is a minimum of the potential, the net force on the atoms must vanish (force being the negative gradient of the potential energy); therefore, the magnitude of the repulsive force equals (and cancels) the attractive force. In uncharged nonpolar molecules, the repulsive forces come from charge overlap that is unfavorable due to the Pauli principle (“exchange repulsion”²¹), and the general importance of repulsive forces at van der Waals minima implies significant charge cloud overlap. As R decreases toward the van der Waals minimum and overlap becomes nonnegligible, one must also consider exchange repulsion, the onset of covalency, partial charge transfer, changes in intrafragment average charge distributions, and changes in intrafragment correlation energy. These effects are not in the multipole series that describes dispersion forces.

One sometimes takes account of these issues by explicitly including overlap in one's model of intermolecular forces,^{22,23} but once the charge clouds overlap, there is no unique way to separate dispersion or damped dispersion from other contributions to the interaction energy. Another way to say this is

that there is no unique way to separate the configuration interaction terms corresponding to correlated multipole moments on individual (no longer separated) subsystems from other configuration interaction effects such as the change in intrasubsystem correlation energy due to the perturbation of the charge cloud. The best attempt to separate the effects is probably symmetry-adapted perturbation theory²⁴ (SAPT), which is a form of perturbation theory modified to take better account of antisymmetry, but it is not unique.

In light of the severe failure of the nonoverlapping dispersion theory at van der Waals distances, the attractive noncovalent interaction at van der Waals distances should not be called dispersion. Some recommended other names are “medium-range correlation energy”, “dispersion-like”, or “damped dispersion”. It is recommended to use the simple term “dispersion” only for the large- R regime where overlap of fragments may be neglected and where the treatment of London is valid.

Intermolecular forces are often calculated by density functional theory or molecular mechanics, and understanding modern simulations requires one to understand how dispersion and damped dispersion are represented in these kinds of theory. I have added a discussion of the treatment of dispersion in density functional theory as a [Supporting Information](#) document, and next I comment on the treatment of dispersion in molecular mechanics.

A force is a partial derivative of a potential energy function, and a “force field” is a term used in computational chemistry to denote the full set of interatomic forces as a function of the positions of the atoms; the forces are the gradients of a potential energy function, and the force field is usually specified by giving the potential energy function. Molecular mechanics^{25–27} is the method of approximating the potential energy function of interacting atoms or molecules by a combination of three kinds of terms: valence terms (typically harmonic springs for bond stretches and bends and trigonometric functions for torsions), electrostatic interactions (typically Coulomb interactions between partial charges on the atoms), and so-called van der Waals potentials to represent everything else. (Some old force fields omit the electrostatic terms.²⁸) For example, it is very common to describe van der Waals potentials in a molecular mechanics force field as a sum of interatomic Lennard-Jones 12-6 potentials:

$$V_{\text{vdW}} = \frac{C_{12}}{R^{12}} - \frac{C_6}{R^6} \quad (6)$$

where C_{12} and C_6 are positive parameters, and R is the distance between two atoms. The R^{-6} term in such a potential energy function is an empirical way to include not only dispersion and damped dispersion but also induction forces (induction forces are due to the interaction of a permanent moment with an induced moment), which are represented in an average way. The van der Waals term must include not only the long-range induced-dipole–induced-dipole R^{-6} dispersion effect, but also the higher multipoles, the damping of the dispersion, the induction, and the steric repulsion when two atoms get close (sometimes called exchange repulsion), and it must also make up for errors in the highly approximate treatment of electrostatics; therefore, one should not interpret the C_6 term as accurately representing the induced-dipole–induced-dipole long-range term, but rather recognize C_{12} and C_6 as catch-all parameters. A further complication is that many molecular mechanics force fields are parametrized to try to predict liquid-

phase data, where the interaction is further affected by solvation. (Some recent work²⁹ attempts to make the individual terms in the force field represent individual physical interactions, but such work should not be confused with the way that widely used molecular mechanics force fields are parametrized.)

A final comment concerns excited electronic states. It is easy to convince oneself (for example, by variational arguments) that the long-range dispersion interaction between two ground-state species is always attractive. But for excited states, this is not true; it can be attractive or repulsive.³⁰ There is very little work in the literature on dispersion interactions between species when one or both is in an excited electronic state. This is an important subject for further investigation.

I hope this essay has cleared up some of the confusion about the semantics and the physics of dispersion interactions and their calculation by the methods of computational chemistry.

■ SUMMARY OF PEDAGOGICAL CONSIDERATIONS

It might be useful to summarize the key issues where instructors might change their approach when teaching dispersion interactions:

- (1) Dispersion forces do not disperse anything but are named after the similarity of their quantum mechanical treatment to the mathematical treatment of optical dispersion.
- (2) Dispersion forces, like other features of potential energy surfaces, may be described by time-independent quantum mechanics, where they are a manifestation of electron correlation and quantum mechanical superposition. One should not imply that they require time-dependent electron density distributions.
- (3) The series in powers of $(1/R)$ that describes dispersion (as well as interactions involving permanent multipole moments) is an asymptotic series, not a convergent series. The series breaks down when the charge clouds of the interacting systems overlap, as they do at van der Waals distances.
- (4) One should distinguish true dispersion interactions at large R from damped dispersion at van der Waals distances.
- (5) In the general case, the second term in the asymptotic series describing dispersion is an R^{-7} term, not an R^{-8} term as usually assumed.
- (6) Terms with the form of $-C_6/R^6$ appear in most molecular mechanics potentials, but they do not represent just dispersion and damped dispersion; they also make up for the low-level treatment of electrostatic interactions in most molecular mechanics potential functions.
- (7) Dispersion interactions in excited electronic states need not be attractive.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: [10.1021/acs.jchemed.8b01044](https://doi.org/10.1021/acs.jchemed.8b01044).

Treatment of dispersion in density functional theory (PDF)

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Notes

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■ REFERENCES

- (1) Williams, L. C.; Underwood, S. M.; Klymkowsky, M. W.; Cooper, M. M. Are Noncovalent Interactions an Achilles Heel in Chemistry Education? A Comparison of Instructional Approaches. *J. Chem. Educ.* **2015**, *92*, 1979–1987.
- (2) Eisenschitz, R.; London, F. Über das Verhältnis der van der Waalschen Kräfte zu den homöopolaren Bindungskräften. *Eur. Phys. J. A* **1930**, *60*, 491.
- (3) Merriam-Webster Dictionary; <https://www.merriam-webster.com/dictionary/dispersion>.
- (4) Condon, E. U. Molecular Optics. In *Handbook of Physics*; Condon, E. U., Odishaw, H., Eds.; McGraw-Hill: New York, 1958; pp 6–111.
- (5) de L. Kronig, R. On the Theory of Dispersion of X-rays. *J. Opt. Soc. Am.* **1926**, *12*, 547–557.
- (6) Kramers, H. A. Die Dispersion und Adsorption von Röntgenstrahlen. *Z. Phys.* **1930**, *30*, 522–523.
- (7) London, F. Die Zahl der Dispersionselektronen in der Undulationsmechanik. *Eur. Phys. J. A* **1926**, *39*, 322–326.
- (8) Dalgarno, A.; Lynn, N. Properties of the Helium Atom. *Proc. Phys. Soc., London, Sect. A* **1957**, *70*, 802–808.
- (9) Von Hippel, A. Dielectrics. In *Handbook of Physics*; Condon, E. U., Odishaw, H., Eds.; McGraw-Hill: New York, 1958; p 4–113.
- (10) Gottschalk, E.; Venkataraman, B. Visualizing Dispersion Interactions. *J. Chem. Educ.* **2014**, *91*, 666–672.
- (11) Pitzer, K. S. *Quantum Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1953; p 200.
- (12) Prugovecki, E. *Quantum Mechanics in Hilbert Space*, 2nd ed.; Dover: Mineola, NY, 1981.
- (13) Berry, R. S.; Rice, S. A.; Ross, J. *Physical Chemistry*, 2nd ed.; Oxford University Press: New York, 2000; p 301.
- (14) Bentley, J. Atomic Multipole Expansions of Molecular Charge Densities. Electrostatic Potentials. In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1981; pp 63–84.
- (15) Gelessus, A.; Thiel, W.; Weber, W. Multipoles and Symmetry. *J. Chem. Educ.* **1995**, *72*, 505–508.
- (16) Halpern, A. Dispersion Interactions Between Rare Gas Atoms: Testing the London Equation Using ab initio Methods. *J. Chem. Educ.* **2011**, *88*, 174–177.
- (17) Piecuch, P. Spherical Tensor Theory of Long-Range Interactions in a System of *N* Arbitrary Molecules Including Quantum-Mechanical Many-Body Effects. II. Anisotropic Dispersion Interactions in the First Three Orders of Perturbation Theory. *Mol. Phys.* **1986**, *59*, 1085–1095.
- (18) Kaplan, I. G. *Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials*; Wiley: Chichester, UK, 2006; pp 38ff, 98ff.
- (19) Tully, J. C. Perspective on “Zur Quantumtheorie der Molekeln. *Theor. Chem. Acc.* **2000**, *103*, 173–176.
- (20) Atkins, P.; Friedman, R. *Molecular Quantum Mechanics*, 4th ed.; Oxford University Press: Oxford, 2005; pp 249–251.
- (21) Viquez Rojas, C. I.; Fine, J.; Slipchenko, L. V. Exchange-repulsion energy in QM/EFP. *J. Chem. Phys.* **2018**, *149*, 094103.
- (22) Koide, A.; Meath, W. J.; Allnatt, J. R. Second Order Charge Overlap Effects and Damping Functions for Isotropic Atomic and Molecular Interactions. *Chem. Phys.* **1981**, *58*, 105–119.
- (23) Tang, K. T.; Toennies, J. P. An improved simple model for the van der Waals potential based on universal damping functions for the dispersion coefficients. *J. Chem. Phys.* **1984**, *80*, 3726–3741.
- (24) Jeziorski, B.; Moszynski, R.; Szalewicz, K. Perturbation Theory Approach to Intermolecular Potential Energy Surfaces of van der Waals Complexes. *Chem. Rev.* **1994**, *94*, 1887–1930.
- (25) Hagler, A. T.; Ewig, C. S. On the Use of Quantum Energy Surfaces in the Derivation of Molecular Force Fields. *Comput. Phys. Commun.* **1994**, *84*, 131–155.
- (26) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. Second Generation Force Field for the Simulation of Proteins, Nucleic Acids, and Organic Molecules. *J. Am. Chem. Soc.* **1995**, *117*, 5179–5197.
- (27) Mackerell, A. D.; Wiorkiewicz-Kuczera, J.; Karplus, M. An All-Atom Empirical Energy Function for the Simulation of Nucleic Acids. *J. Am. Chem. Soc.* **1995**, *117*, 11946–11975.
- (28) Boyd, D. B.; Lipkowitz, K. B. Molecular Mechanics: The Method and its Underlying Philosophy. *J. Chem. Educ.* **1982**, *59*, 269–274.
- (29) Verma, P.; Wang, B.; Fernandez, L. E.; Truhlar, D. G. Physical Molecular Mechanics Method for Damped Dispersion. *J. Phys. Chem. A* **2017**, *121*, 2855–2862.
- (30) Li, J.; Cramer, C. J.; Truhlar, D. G. Two-response-Time Model Based on CM2/INDO/S2 Electrostatic Potentials for the Dielectric Polarization Component of Solvatochromic Shifts on Vertical Excitation Energies. *Int. J. Quantum Chem.* **2000**, *77*, 264–280.

SUPPORTING INFORMATION
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It is straightforward to understand the presence of dispersion (at least at long range when the interacting subsystems do not overlap) in wave function theory because it arises by a straightforward application of perturbation theory.¹ However, the representation of dispersion in density functional theory has been the source of a certain amount of confusion. It is sometimes stated (unfortunately this occurs frequently) that density functional theory does not include dispersion. That is wrong. Density functional theory is an exact theory,^{2,3,4} but in practice its accuracy is limited by the fact that we do not know the exact density functional, and so we use approximations to it. Some (but not all) of the available approximations do not include terms that are nonzero when the charge clouds of the interacting systems do not overlap. Density functionals with this property cannot represent dispersion at long range. But some approximate functionals do correctly include dispersion,⁵ and so they can in principle obtain accurate energies even in the long-range nonoverlapping regions. Technically this involves using a nonlocal correlation functional whereas the most commonly used functionals use local approximations for correlation. A local approximation is one where the energy density at a point is a function of quantities (most prominently electron density and its gradient) evaluated at the point, whereas a nonlocal approximation requires an integral over space to approximate the energy density at a single point in space.

The repulsion due to overlapping charge clouds is sometimes called exchange repulsion or Pauli repulsion, and it is the dominant factor behind short-range repulsion between atoms and molecules. Exchange repulsion is already appreciable at van der Waals distances and this involves overlap, so even functionals with local correlation functionals can give accurate results at van der Waals geometries, and some (but not all) of them predict medium-range correlation energy quite well.^{6,7}

In recent years, a new industry has appeared, adding "dispersion" to density functional theory, leading to formulations often called DFT+D.^{8,9} In these theories, an expression having the form of long-range dispersion times a damping factor is added to density functional theory, with parameters adjusted to reproduce noncovalent binding energies. The added term is often interpreted as dispersion; this is not right. In fact, it is also not right to call the added term damped dispersion because these correction terms include not only damped dispersion but also other systematic corrections to density functional theory. My comments here are not directed at the usefulness of the theory;

DFT+D is very useful for many applications as an empirical way to correct some of the failings of those density functionals that do not do a good enough job of including noncovalent interactions. However, it should not be claimed that density functional theory does not include dispersion, and one should not interpret the added molecular mechanics terms as solely consisting of damped dispersion interactions.

Summary. Molecular mechanics terms that vary $-C_6/R^6$ at large R are widely used as add-ons to density functional calculations when the latter do not predict accurate intermolecular forces. These terms should not be interpreted as solely due to dispersion and damped dispersion; they also make up for the deficiencies of the approximate density functionals. Some, but not all, density functionals predict accurate dispersion and/or damped dispersion without such empirical correction terms.

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- 1 Atkins, P.; Friedman, R. *Molecular Quantum Mechanics*; 4th edition; Oxford University Press: New York, 2005; pp. 414-417.
 - 2 Kohn, W.; Becke, A. D.; Parr, R. G. Density Functional Theory of Electronic Structure. *J. Phys. Chem.* **100**, 12974-12980 (1996).
 - 3 Bell, S.; Dines, T. J.; Chowdhry, B. Z.; Withnall, R. Computational Chemistry Using Modern Electronic Structure Methods. *J. Chem. Educ.* **2007**, *84*, 1364-1370.
 - 4 Levy, M. Universal Variational Functionals of Electron Densities, First-Order Density Matrices, and Natural Spin-Orbitals and Solution of the ν -Representability Problem. *Proc. Natl. Acad. Sci. USA* **76**, 6062-6065 (1979).
 - 5 Puzder, A., Dion, M., & Langreth, D. C. Binding Energies in Benzene Dimers: Nonlocal Density Functional Calculations. *J. Chem. Phys.* **124**, 164105 (2006).
 - 6 Zhao, Y. & Truhlar, D. G. Applications and Validations of the Minnesota Density Functionals. *Chem. Phys. Lett.* **502**, 1-13 (2011).
 - 7 Wang, Y.; Jin, X.; Yu, H. S.; Truhlar, D. G.; He, X. Revised M06-L Functional for Improved Accuracy on Chemical Reaction Barrier Heights, Noncovalent Interactions, and Solid-State Physics. *Proc. Natl. Acad. Sci. USA* **114**, 8487-8492 (2016).
 - 8 Grimme, S. (2011). Density Functional Theory with London Dispersion Corrections. *WIREs Comput. Mol. Sci.* **1**, 211-228 (2011).
 - 9 Caldeweyher, E.; Ehlert, S.; Hansen, A.; Neugebauer, H.; Spicher, S.; Bannwarth, C.; Grimme, S. A Generally Applicable Atomic-Charge Dependent London Dispersion Correction. *J. Chem. Phys.* **150**, 154122 (2019).