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Exchange-hole dipole moment and the dispersion interaction revisited

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We have recently introduced a model of the dispersion interaction based on the position-dependent dipole moment of the exchange hole [J. Chem. Phys. **122**, 154104 (2005)]. The original derivation, involving simple dipole-induced-dipole electrostatics, was somewhat heuristic, however, and lacking in rigor. Here we present a much more satisfying derivation founded on second-order perturbation theory in the closure approximation and a semiclassical evaluation of the relevant interaction integrals. Expressions for C_6 , C_8 , and C_{10} dispersion coefficients are obtained in a remarkably straightforward manner. Their values agree very well with *ab initio* reference data on dispersion coefficients between the atoms H, He, Ne, Ar, Kr, and Xe. We also highlight the importance of the exchange-hole contribution to the dispersion coefficients, especially to C_6 .
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I. INTRODUCTION

In a previous paper,¹ we introduced a conceptually appealing model of C_6 dispersion coefficients generated by the position-dependent dipole moment of an electron and its exchange hole. The model was extended to C_8 and C_{10} coefficients in Ref. 2, incorporated into density-functional theory in Ref. 3, and has been applied to intermolecular and intramolecular van der Waals (vdW) potential energy surfaces in Refs. 4–6.

We use occupied orbitals only, either Hartree-Fock or Kohn-Sham, and our C_6 , C_8 , and C_{10} 's involve no fitting of parameters whatsoever. Appealing and successful as the model is, however, the original derivation was highly intuitive and heuristic. The dipole-induced-dipole approach of Ref. 1 was simplistic, even missing a factor of 4. The perturbation-theory approach of Ref. 2 replaced multielectron expectation values with effective one-electron integrals, only partially supported by the subsequent analysis of Angyan.⁷

Here we introduce a much more satisfying approach. We begin with second-order perturbation theory in the closure approximation and then model the dispersion interaction in a semiclassical way. The model is “semiclassical” in that the dispersion interaction is treated as a classical multipole-multipole interaction, yet quantum effects are included through the exchange hole. The resulting derivation of expressions for C_6 , C_8 , and C_{10} dispersion coefficients is straightforward and, we think, delightfully simple. This work provided an independent verification of our previous expressions^{2,4,5} based on angular momentum coupling formulas from Ref. 8, and, indeed, uncovered an error in Ref. 8.

To set the stage, we review in Sec. II the nature of correlation in electronic systems and how correlation affects the

instantaneous dipole moments generated by electrons in atoms. In Sec. III our new dispersion interaction model is developed. Dispersion coefficients are presented in Sec. IV for all atom pairs between H, He, Ne, Ar, Kr, and Xe to demonstrate the quality of the model and to highlight the importance of the exchange-hole contribution, especially to C_6 .

II. THE EXCHANGE-HOLE DIPOLE MOMENT

As an electron moves through a multielectron system, it repels other electrons from its vicinity through a combination of “Pauli” and “Coulomb” correlations. Pauli correlation arises from multielectron wave-function antisymmetry and acts between electrons of parallel spin. It has the consequence that the probability of finding *another* electron of parallel spin at the position of a given electron is *zero*. Coulomb correlation arises from the $1/r$ repulsive interaction between electron pairs and acts between electrons of both opposite and parallel spins. Coulomb correlation is much less important than Pauli correlation. In, e.g., a single Slater determinant (Hartree-Fock theory), Pauli correlation contributes a significant exchange-energy component to the total energy. Coulomb correlation, on the other hand, contributes nothing in Hartree-Fock theory. We therefore consider only Pauli correlations in this work and assume that each monomer in an intermolecular interaction is described by a single Slater determinant.

If an electron of σ spin is at point \mathbf{r}_1 in a system, the extent to which Pauli correlation depletes the probability (with respect to the total statistical electron density) of finding another electron at point \mathbf{r}_2 is given by⁹

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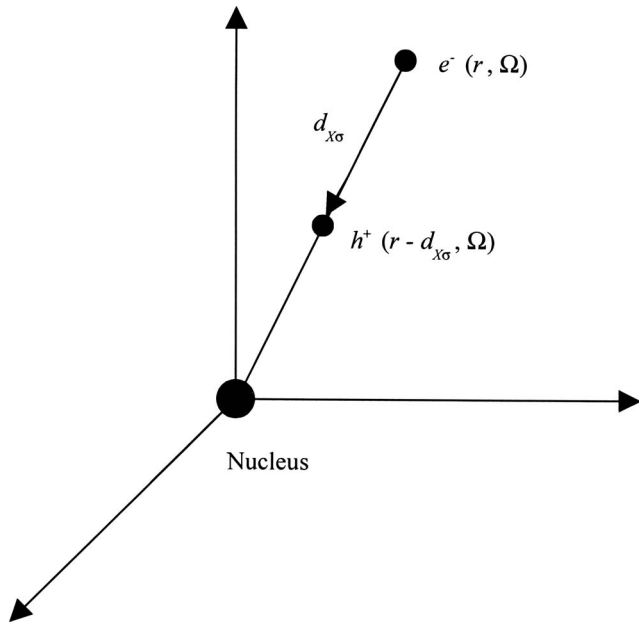


FIG. 1. Exchange-hole dipole geometry (e^- is the reference position of a σ -spin electron and h^+ is the mean position of its exchange hole).

$$h_{X\sigma}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{\rho_\sigma(\mathbf{r}_1)} \sum_{ij} \psi_{i\sigma}(\mathbf{r}_1) \psi_{j\sigma}(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) \psi_{j\sigma}(\mathbf{r}_2) \quad (1)$$

called the *exchange* or *Fermi* “hole.” The summation is over all occupied orbitals of σ spin, assumed in this paper to be real, and ρ_σ is the total σ -spin electron density. The Fermi hole is a powerful conceptual device. As an electron moves through a system, its Fermi hole accompanies it. The shape of the hole depends on the electron’s instantaneous position \mathbf{r}_1 and its normalization is always -1 (easy to prove by integrating over \mathbf{r}_2 and using orthonormality of the orbitals).

The electron plus its hole is neutral overall. The hole is generally not, however, spherically symmetric around \mathbf{r}_1 . Even in systems with spherically symmetric total densities, the hole is nonspherical unless \mathbf{r}_1 is at the center of the system. Thus the electron plus its hole has an \mathbf{r}_1 -dependent *non-zero dipole moment* given by¹

$$d_{X\sigma}(\mathbf{r}_1) = \left[\frac{1}{\rho_\sigma(\mathbf{r}_1)} \sum_{ij} \psi_{i\sigma}(\mathbf{r}_1) \psi_{j\sigma}(\mathbf{r}_1) \times \int \mathbf{r}_2 \psi_{i\sigma}(\mathbf{r}_2) \psi_{j\sigma}(\mathbf{r}_2) d^3\mathbf{r}_2 \right] - \mathbf{r}_1. \quad (2)$$

The situation is depicted for an electron in a spherical atom in Fig. 1. When the electron e^- is at distance r from the nucleus and at solid angle Ω , the mean position h^+ of the hole is at distance $(r - d_{X\sigma})$. Notice, furthermore, that higher multipole moments $M_{\ell\sigma}$ with respect to the nucleus as origin can be defined by e^- and h^+ as well:²

$$M_{\ell\sigma} = -[r^\ell - (r - d_{X\sigma})^\ell], \quad (3)$$

all directed along Ω and all depending on the magnitude of the exchange-hole dipole moment only.

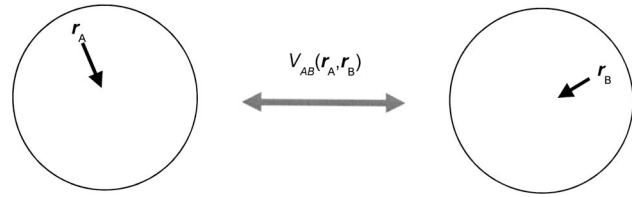


FIG. 2. Interaction between multipole moments of an electron and its exchange hole at \mathbf{r}_A in atom A and an electron and its exchange hole at \mathbf{r}_B in atom B. The vectors represent the instantaneous dipole moments.

The two-point picture of Fig. 1 is an approximate model of the electron and its hole. Therefore, the higher moments, $\ell > 1$, of Eq. (3) are approximate. Exact $\ell > 1$ moments *could* be computed by appropriate generalizations of Eq. (2) to higher orders. The great strength of the two-point model, however, is its dependence *only* on $d_{X\sigma}$. This is the key to transforming our theory into density-functional form as in Refs. 3 and 6.

In the absence of correlation (i.e., if electron motions were truly independent of each other) an electron at \mathbf{r} and Ω in a spherical atom would generate the following moments;

$$M_{\ell\sigma}(\text{uncorrelated}) = -r^\ell \quad (4)$$

along Ω . In atoms containing only s electrons, the exchange hole is centered at the nucleus ($d_{X\sigma} = r$) and Eqs. (3) and (4) are identical. In atoms with p, d, f, \dots electrons, however, the exchange hole is removed from the nucleus ($d_{X\sigma} < r$) and the uncorrelated moments, Eq. (4), are significantly larger than the correlated moments, Eq. (3). It has long been known¹⁰ that uncorrelated moments yield highly erroneous, far too large, dispersion coefficients. The effect of Pauli correlation and the exchange hole in p, d, f, \dots atoms is therefore critical. This will be aptly demonstrated in Sec. IV.

III. THE DISPERSION INTERACTION

If the first-order, ground-state energy correction due to a perturbation V_{pert} is zero:

$$E^{(1)} = \langle V_{\text{pert}} \rangle = 0 \quad (5)$$

then the second-order correction is approximately given by

$$E^{(2)} = -\frac{\langle V_{\text{pert}}^2 \rangle}{\Delta E_{\text{av}}} \quad (6)$$

where the expectation values are in the ground state and ΔE_{av} is an *average* excitation energy. This well-known result, derived in many standard textbooks,¹¹ is called the “closure” or Unsöld approximation.

Consider two spherically symmetric atoms separated by a large internuclear distance R , and suppose that an electron is at position \mathbf{r}_A in atom A and an electron is at position \mathbf{r}_B in atom B (see Fig. 2). As established in the previous section, the electron at \mathbf{r}_A generates multipole moments with respect to nucleus A given by Eq. (3) and directed along \mathbf{r}_A . The electron at \mathbf{r}_B similarly generates multipole moments with respect to nucleus B. For the perturbation V_{pert} in Eq. (6), we

take the multipole-multipole interaction energy as follows:

$$V_{AB}(\mathbf{r}_A, \mathbf{r}_B) = V_{1,1} + V_{1,2} + V_{2,1} + V_{1,3} + V_{3,1} + V_{2,2}, \quad (7)$$

where subscripts 1, 2, and 3 denote dipole, quadrupole, and octopole moments, respectively, and we include all terms contributing to orders r^{-3} , r^{-4} , and r^{-5} .

The individual terms are given by¹²

$$V_{1,1}(\mathbf{r}_A, \mathbf{r}_B) = \frac{M_1(r_A)M_1(r_B)}{R^3}(-3c_{AC}c_B + c_{AB}), \quad (8a)$$

$$V_{1,2}(\mathbf{r}_A, \mathbf{r}_B) = \frac{3}{2} \frac{M_1(r_A)M_2(r_B)}{R^4}(5c_{AC}^2c_B - 2c_{BC}c_{AB} - c_A), \quad (8b)$$

$$V_{2,1}(\mathbf{r}_A, \mathbf{r}_B) = \frac{3}{2} \frac{M_2(r_A)M_1(r_B)}{R^4}(-5c_{AC}^2c_B + 2c_{AC}c_{AB} + c_B), \quad (8c)$$

$$V_{1,3}(\mathbf{r}_A, \mathbf{r}_B) = \frac{1}{2} \frac{M_1(r_A)M_3(r_B)}{R^5}(-35c_{AC}^3c_B + 15c_{BC}^2c_{AB} + 15c_{AC}c_B - 3c_{AB}), \quad (8d)$$

$$V_{3,1}(\mathbf{r}_A, \mathbf{r}_B) = \frac{1}{2} \frac{M_3(r_A)M_1(r_B)}{R^5}(-35c_{AC}^3c_B + 15c_{AC}^2c_{AB} + 15c_{AC}c_B - 3c_{AB}), \quad (8e)$$

$$V_{2,2}(\mathbf{r}_A, \mathbf{r}_B) = \frac{3}{4} \frac{M_2(r_A)M_2(r_B)}{R^5}(35c_{AC}^2c_B^2 - 20c_{AC}c_{BC}c_{AB} - 5c_A^2 - 5c_B^2 + 2c_{AB}^2 + 1), \quad (8f)$$

where c_A , c_B , and c_{AB} are the following direction cosines:

$$c_A = \hat{\mathbf{r}}_A \cdot \hat{\mathbf{R}} = \cos \theta_A, \quad (9a)$$

$$c_B = \hat{\mathbf{r}}_B \cdot \hat{\mathbf{R}} = \cos \theta_B, \quad (9b)$$

$$c_{AB} = \hat{\mathbf{r}}_A \cdot \hat{\mathbf{r}}_B = \cos \theta_A \cos \theta_B + \sin \theta_A \sin \theta_B \cos(\phi_B - \phi_A), \quad (9c)$$

$\hat{\mathbf{R}}$ is the unit vector from A to B , and (θ_A, ϕ_A) and (θ_B, ϕ_B) are the polar angles of $\hat{\mathbf{r}}_A$ and $\hat{\mathbf{r}}_B$ with respect to $\hat{\mathbf{R}}$.

Now evaluate the expectation value $\langle V_{\text{pert}}^2 \rangle$ in Eq. (6) by squaring $V_{AB}(\mathbf{r}_A, \mathbf{r}_B)$ and integrating over all points \mathbf{r}_A in atom A (weighted by the atomic density of A) and all points \mathbf{r}_B in atom B (weighted by the atomic density of B). The result is

$$E_{\text{disp}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots, \quad (10)$$

with dispersion coefficients given by

$$C_6 = \frac{2 \langle M_{1/A}^2 \rangle \langle M_{1/B}^2 \rangle}{\Delta E_{\text{av}}}, \quad (11a)$$

$$C_8 = \frac{\langle M_{1/A}^2 \rangle \langle M_{2/B}^2 \rangle + \langle M_{2/A}^2 \rangle \langle M_{1/B}^2 \rangle}{\Delta E_{\text{av}}}, \quad (11b)$$

$$C_{10} = \frac{4}{3} \frac{\langle M_{1/A}^2 \rangle \langle M_{3/B}^2 \rangle + \langle M_{3/A}^2 \rangle \langle M_{1/B}^2 \rangle}{\Delta E_{\text{av}}} + \frac{14}{5} \frac{\langle M_{2/A}^2 \rangle \langle M_{2/B}^2 \rangle}{\Delta E_{\text{av}}}, \quad (11c)$$

and with atomic moment integrals given by

$$\langle M_{\ell}^2 \rangle = \sum_{\sigma} \int \rho_{\sigma}(\mathbf{r}) M_{\ell\sigma}^2 d^3\mathbf{r}. \quad (12)$$

The derivation is very straightforward for C_6 and C_8 , though laborious for C_{10} . These expressions are the same as our previous expressions in Ref. 2 except for the coefficient of the first term in Eq. (11c). The expression in Ref. 2 is incorrect due to an arithmetic error inherited from Ref. 8.

A more elegant derivation based on angular momentum coupling theory is presented in Appendix A.

We assume (see Appendix B) that the average excitation energy ΔE_{av} is the sum of the average excitation energies of the constituent atoms:

$$\Delta E_{\text{av}} = \Delta E_A + \Delta E_B \quad (13)$$

and that, for each atom, ΔE is related to its *polarizability* by the same perturbation theory used to obtain the dispersion energy.^{1,2,10} The atomic polarizability α is defined by

TABLE I. C_6 coefficients for atomic pairs (a.u.). MAPE: mean absolute percent error. MPE: mean percent error. MaxAPE: maximum absolute percent error. Literature values from Ref. 15.

Atom pair	Eq. (3)	Eq. (4)	Ref. 15
H-H	6.76	6.76	6.49
H-He	2.99	2.99	2.82
H-Ne	5.69	6.74	5.69
H-Ar	20.13	25.91	19.86
H-Kr	29.44	39.25	29.15
H-Xe	45.14	63.52	44.14
He-He	1.64	1.64	1.46
He-Ne	3.09	4.26	3.07
He-Ar	9.81	15.20	9.57
He-Kr	14.08	23.03	13.65
He-Xe	20.91	37.07	19.92
Ne-Ne	5.83	12.52	6.55
Ne-Ar	18.60	41.67	19.75
Ne-Kr	26.71	63.19	28.01
Ne-Xe	39.72	101.23	40.52
Ar-Ar	62.71	144.30	64.54
Ar-Kr	90.93	218.78	93.16
Ar-Xe	137.4	351.4	138.0
Kr-Kr	132.1	331.7	135.1
Kr-Xe	200.1	532.7	201.3
Xe-Xe	304.7	855.8	302.3
MAPE	3.4	85.0	...
MPE	0.3	85.0	...
MaxAPE	12.1	183.1	...

TABLE II. C_8 coefficients for atomic pairs (a.u.). MAPE: mean absolute percent error. MPE: mean percent error. MaxAPE: maximum absolute percent error. Literature values from Ref. 15.

Atom pair	Eq. (3)	Eq. (4)	Ref. 15
H–H	152.1	152.1	124.4
H–He	48.37	48.37	41.75
H–Ne	111.7	105.2	97.8
H–Ar	560.5	507.8	442.1
H–Kr	920.6	807.9	732.2
H–Xe	1688	1431	1357
He–He	16.15	16.15	14.11
He–Ne	41.05	39.47	36.18
He–Ar	211.2	201.6	167.5
He–Kr	351.0	328.2	280.0
He–Xe	649.2	600.6	525.0
Ne–Ne	97.40	108.98	90.34
Ne–Ar	464.2	528.9	390.1
Ne–Kr	757.8	864.4	638.1
Ne–Xe	1 370	1 582	1 162
Ar–Ar	2 082	2 408	1 623
Ar–Kr	3 329	3 866	2 617
Ar–Xe	5 869	6 895	4 669
Kr–Kr	5 287	6 188	4 187
Kr–Xe	9 234	10 978	7 389
Xe–Xe	15 922	19 305	12 807
MAPE	21.5	27.2	...
MPE	21.5	27.2	...
MaxAPE	28.2	50.7	...

TABLE III. C_{10} coefficients for atomic pairs (a.u.). MAPE: mean absolute percent error. MPE: mean percent error. MaxAPE: maximum absolute percent error. Literature values from Ref. 15.

Atom pair	Eq. (3)	Eq. (4)	Ref. 15
H–H	4 438	4 438	3 286
H–He	1 065.3	1 065.3	858.7
H–Ne	2 619	2 267	2 221
H–Ar	16 496	12 977	12 617
H–Kr	29 671	21 956	23 441
H–Xe	62 297	42 843	51 088
He–He	214.2	214.2	183.2
He–Ne	598.8	500.3	545.1
He–Ar	4 475	3 567	3 701
He–Kr	8 499	6 486	7 257
He–Xe	18 896	13 853	16 674
Ne–Ne	1 625	1 317	1 536
Ne–Ar	11 050	9 087	9 335
Ne–Kr	20 399	16 678	17 658
Ne–Xe	43 819	35 826	38 978
Ar–Ar	64 960	52 050	49 063
Ar–Kr	114 390	90 550	88 260
Ar–Xe	232 344	182 168	184 250
Kr–Kr	198 379	155 528	155 450
Kr–Xe	395 106	307 395	316 030
Xe–Xe	766 727	592 409	619 840
MAPE	21.5	9.1	...
MPE	21.5	−0.5	...
MaxAPE	35.1	35.1	...

$$E^{(2)} = -\frac{1}{2}\alpha\mathbf{F}^2 = -\frac{\langle V_{\text{pert}}^2 \rangle}{\Delta E}, \quad (14)$$

where \mathbf{F} is the electric field vector and, in the present semi-classical approach,

$$V_{\text{pert}} = -\mathbf{d}_{X\sigma}(\mathbf{r}) \cdot \mathbf{F}, \quad (15)$$

when an electron is at position \mathbf{r} in the atom. Squaring V_{pert} , integrating over all points \mathbf{r} in the atom (weighted by the atomic density), and using that $\mathbf{d}_{X\sigma}(\mathbf{r})$ is collinear with \mathbf{r} , we get

$$\langle V_{\text{pert}}^2 \rangle = \frac{1}{3}\langle M_1^2 \rangle F^2, \quad (16)$$

where $\langle M_1^2 \rangle$ is the atomic dipole moment integral, Eq. (12), with $\ell=1$. Solving for ΔE gives

$$\Delta E = \frac{2}{3} \frac{\langle M_1^2 \rangle}{\alpha}. \quad (17)$$

Atomic polarizabilities α are conveniently tabulated in, e.g., Ref. 13.

Substituting Eq. (17) into Eqs. (11a)–(11c), we finally obtain

$$C_6 = \frac{\alpha_A \alpha_B \langle M_1^2 \rangle_A \langle M_1^2 \rangle_B}{\langle M_1^2 \rangle_A \alpha_B + \langle M_1^2 \rangle_B \alpha_A}, \quad (18a)$$

$$C_8 = \frac{3}{2} \frac{\alpha_A \alpha_B (\langle M_1^2 \rangle_A \langle M_2^2 \rangle_B + \langle M_2^2 \rangle_A \langle M_1^2 \rangle_B)}{\langle M_1^2 \rangle_A \alpha_B + \langle M_1^2 \rangle_B \alpha_A}, \quad (18b)$$

$$C_{10} = 2 \frac{\alpha_A \alpha_B (\langle M_1^2 \rangle_A \langle M_3^2 \rangle_B + \langle M_3^2 \rangle_A \langle M_1^2 \rangle_B)}{\langle M_1^2 \rangle_A \alpha_B + \langle M_1^2 \rangle_B \alpha_A} + \frac{21}{5} \frac{\alpha_A \alpha_B \langle M_2^2 \rangle_A \langle M_2^2 \rangle_B}{\langle M_1^2 \rangle_A \alpha_B + \langle M_1^2 \rangle_B \alpha_A}, \quad (18c)$$

These are identical to expressions in previous papers^{4,5} except for the coefficient of the first term in C_{10} . The above C_{10} formula is correct.

The incorrect constant [6/5 instead of 2 in the first term of Eq. (18c)] in our previous papers^{2,4,5} has negligible impact on the previous results or conclusions. Recalculation of the binding energies of our 45 intermolecular benchmark complexes of Ref. 4, for example, insignificantly changes the mean absolute percent error (MAPE) from 14.1% to 13.7%.

IV. CALCULATIONS AND CONCLUSIONS

Tables I–III give dispersion coefficients from Eqs. (18a)–(18c) for all pairs of the atoms H, He, Ne, Ar, Kr, and Xe. The dipole moments, Eq. (2), and moment integrals, Eq. (12), are numerically integrated over Hartree-Fock orbitals from the NUMOL program of Becke and Dickson.¹⁴ Atomic polarizabilities are from Ref. 13. Results for both exchange-hole corrected and uncorrelated moments, Eqs. (3) and (4) respectively, are presented in order to demonstrate the importance of exchange effects. For C_6 , the latter is equivalent to the early Kirkwood-Muller model (see Ref. 10 and references therein). *Ab initio* reference data are from Ref. 15.

Our C_6 values are in excellent agreement with the reference data. The mean absolute percent error (MAPE) is only

3.4%. Our C_8 's and C_{10} 's are reasonably good, with MAPEs of 21.5% and 21.5%, though not as good as our C_6 's.

The uncorrelated C_6 's, on the other hand, have an enormous MAPE of 85.0%. The uncorrelated C_8 's and C_{10} 's are fortuitously better than the uncorrelated C_6 's due to the fact that the moment integrals $\langle M_\ell^2 \rangle$ are less affected by exchange as ℓ increases.¹⁶ At the same time, the far-too-large uncorrelated $\langle M_1^2 \rangle$ integrals in the denominators of Eqs. (18b) and (18c) drive the C_8 and C_{10} values down.

The importance of Pauli correlation (exchange) in dispersion coefficients, especially C_6 , is well demonstrated by these data. We expect that the effects of Coulomb correlation, ignored here, would be small, reducing our dispersion coefficients only slightly.

In conclusion, the present dispersion model is much more satisfying than our previous models.^{1,2} We obtain the same expressions for C_6 , C_8 , and C_{10} dispersion coefficients as before (with the exception of a corrected constant in the C_{10} expression) in a very straightforward and elegant manner. The generalization from atoms to molecules, and to intermolecular and intramolecular vdW potential energy sur-

faces, proceeds without change as in Refs. 4–6. The present work nicely reinforces the theoretical underpinnings of our vdW methodology.

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APPENDIX A: ANGULAR MOMENTUM COUPLING THEORY

Equations (11a)–(11c) can be derived using the formulas of angular momentum coupling theory as found, e.g., in Ref. 8. The potential energy of interaction, as in Fig. 2, between two spherical atoms A and B is given by

$$V_{AB}(\mathbf{r}_A, \mathbf{r}_B) = \sum_{\ell_A=0}^{\infty} \sum_{\ell_B=0}^{\infty} \frac{V_{\ell_A \ell_B}}{R^{\ell_A + \ell_B + 1}}. \quad (\text{A1})$$

If the coordinate axes in A and B are parallel and their z axes point along \mathbf{R} (the vector from A to B), then

$$V_{\ell_A \ell_B}(\mathbf{r}_A, \mathbf{r}_B) = \sum_{m=-\ell_{\min}}^{+\ell_{\min}} \frac{(-)^{\ell_B} 4\pi(\ell_A + \ell_B)!}{[(2\ell_A + 1)(2\ell_B + 1)(\ell_A - m)!(\ell_A + m)!(\ell_B - m)!(\ell_B + m)!]^{1/2}} M_{\ell_A}(r_A) Y_{\ell_A}^m(\theta_A, \phi_A) M_{\ell_B}(r_B) Y_{\ell_B}^{-m}(\theta_B, \phi_B), \quad (\text{A2})$$

where ℓ_{\min} is the smaller of ℓ_A and ℓ_B . If V_{AB} is squared and integrated over all \mathbf{r}_A in A (weighted by the atomic density of A) and all \mathbf{r}_B in B (weighted by the atomic density of B), all cross terms vanish thanks to orthogonality of the spherical harmonic functions. We get the dispersion series, Eq. (10), again with

$$C_6 = \lambda_{1,1} \frac{\langle M_1^2 \rangle_A \langle M_1^2 \rangle_B}{\Delta E_{\text{av}}}, \quad (\text{A3a})$$

$$C_8 = \lambda_{1,2} \frac{\langle M_1^2 \rangle_A \langle M_2^2 \rangle_B + \langle M_2^2 \rangle_A \langle M_1^2 \rangle_B}{\Delta E_{\text{av}}}, \quad (\text{A3b})$$

$$C_{10} = \lambda_{1,3} \frac{\langle M_1^2 \rangle_A \langle M_3^2 \rangle_B + \langle M_3^2 \rangle_A \langle M_1^2 \rangle_B}{\Delta E_{\text{av}}} + \lambda_{2,2} \frac{\langle M_2^2 \rangle_A \langle M_2^2 \rangle_B}{\Delta E_{\text{av}}}, \quad (\text{A3c})$$

and (see Ref. 8),

$$\begin{aligned} \lambda_{\ell_A \ell_B} &= \frac{[(\ell_A + \ell_B)!]^2}{(2\ell_A + 1)(2\ell_B + 1)} \\ &\times \sum_{m=-\ell_{\min}}^{+\ell_{\min}} \frac{1}{(\ell_A - m)!(\ell_A + m)!(\ell_B - m)!(\ell_B + m)!} \\ &= \frac{(2\ell_A + 2\ell_B)!}{(2\ell_A + 1)(2\ell_B + 1)(2\ell_A)!(2\ell_B)!} \end{aligned} \quad (\text{A4})$$

The atomic moment integrals $\langle M_\ell^2 \rangle$ are as defined in Eq. (12). Evaluating the $\lambda_{\ell_A \ell_B}$: $\lambda_{1,1}=2/3$, $\lambda_{1,2}=1$, $\lambda_{1,3}=4/3$, $\lambda_{2,2}=14/5$, we obtain the same coefficients as in Eqs. (11a)–(11c).

APPENDIX B: AVERAGE EXCITATION ENERGIES

The assumption, Eq. (13), that the average excitation energy of the AB system is the sum of the average excitation energy of A and the average excitation energy of B may not be obvious. We therefore give a simple proof here.

Denote the excitation energies of A by E_i and the excitation energies of B by E_j and the number of excited states by N_A and N_B , respectively. Then the average excitation energy of A is

$$\Delta E_A = \frac{1}{N_A} \sum_i E_i \quad (\text{B1})$$

and similarly for B . If A and B interact weakly, the excitation energies of the AB system are $E_i + E_j$ and the number of excited states is $N_A N_B$. The average excitation energy of AB is therefore

$$\begin{aligned} \Delta E_{AB} &= \frac{1}{N_A N_B} \sum_i \sum_j (E_i + E_j) \\ &= \frac{1}{N_A N_B} \sum_i \sum_j E_i + \frac{1}{N_A N_B} \sum_i \sum_j E_j \\ &= \frac{1}{N_A N_B} N_B \sum_i E_i + \frac{1}{N_A N_B} N_A \sum_j E_j = \Delta E_A + \Delta E_B, \end{aligned} \quad (\text{B2})$$

as assumed in Eq. (13).

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