Exchange-hole dipole moment and the dispersion interaction: High-order dispersion coefficients

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Exchange-hole dipole moment and the dispersion interaction: High-order dispersion coefficients

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In recent publications [A. D. Becke and E. R. Johnson, J. Chem. Phys. **122**, 154104 (2005); E. R. Johnson and A. D. Becke **123**, 024101 (2005)] we have demonstrated that the position-dependent dipole moment of the exchange hole can be used to generate dispersion interactions between closed-shell systems. Remarkably accurate C_6 coefficients and intermolecular potential-energy surfaces can be obtained from Hartree-Fock occupied orbitals and polarizability data alone. In the present work, our model is extended to predict C_8 and C_{10} coefficients as well. These higher-order coefficients are obtained as easily as C_6 and with comparable accuracy. © 2006 American Institute of Physics. [DOI: 10.1063/1.2139668]

I. INTRODUCTION

The "exchange" or "Fermi" hole is a representation of pair probability in a Slater determinant wave function that has tremendous interpretive power. The exchange energy of a Slater determinant may be written in the form

$$E_X = \sum_\sigma \frac{1}{2} \iint \rho_\sigma(r_1) \frac{h_{X\sigma}(r_1, r_2)}{r_{12}} d^3 r_2 d^3 r_1, \tag{1}$$

where σ denotes up or down electron spin, ρ_σ is the σ-spin density, and

$$h_{X\sigma}(r_1, r_2) = -\frac{1}{\rho_\sigma(r_1)} \sum_{ij} \psi_{i\sigma}(r_1) \psi_{j\sigma}(r_1) \psi_{i\sigma}(r_2) \psi_{j\sigma}(r_2) \tag{2}$$

is the σ-spin exchange hole. The summation is over orbitals of σ spin, assumed to be real in the present work. Note that the coordinates r_1 and r_2 are not equivalent in Eq. (2), and r_1 will be called the "reference" point.

The exchange-hole definition allows us to *visualize* the effects of self-interaction correction and exchange.[1] It is a conditional probability.[2] When a reference electron is at r_1 the hole measures the depletion of probability, with respect to the total electron density ρ, of finding another same-spin electron at r_2. The probability of finding another same-spin electron "on top" of the reference electron (i.e., at $r_2 = r_1$) is completely extinguished,

$$h_{X\sigma}(r_1, r_1) = -\rho_\sigma(r_1), \tag{3}$$

in accordance with the Pauli exclusion principle. The hole is always negative, as can be seen by rewriting Eq. (2) as

$$h_{X\sigma}(r_1, r_2) = -\frac{1}{\rho_\sigma(r_1)} \left[\sum_i \psi_{i\sigma}(r_1) \psi_{i\sigma}(r_2) \right]^2, \tag{4}$$

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

$$\int h_{X\sigma}(r_1, r_2) d^3 r_2 = -1, \tag{5}$$

easily proved from Eq. (2) and the orthonormality of the orbitals $\psi_{i\sigma}$.

As an electron moves through a system, it is accompanied by this hole. Its shape, in terms of the variable r_2, depends on the electron's instantaneous position r_1. The electron plus its hole has *zero charge* overall [guaranteed by Eq. (5)] but a *nonzero dipole moment* in general.[3] Indeed, the dipole moment of the hole and its reference electron is easily obtained by integration over r_2 in Eq. (2),

$$d_{X\sigma}(r_1) = \left[\frac{1}{\rho_\sigma(r_1)} \sum_{ij} r_{ij\sigma} \psi_{i\sigma}(r_1) \psi_{j\sigma}(r_1) \right] - r_1, \tag{6}$$

$$r_{ij\sigma} = \int r_2 \psi_{i\sigma}(r_2) \psi_{j\sigma}(r_2) d^3 r_2. \tag{7}$$

Only in the uniform electron gas, or at centers of inversion symmetry in atoms and molecules, does the dipole moment vanish. We hypothesized in Ref. 3 that this *instantaneous in space* dipole moment could be used to generate a dispersion interaction by polarizing a far system according to its polarizability α. After angular integration of the resulting dipole-induced-dipole interaction, integration over reference points r_1, and further heuristic arguments, we obtained a simple formula for the isotropic C_6 dispersion coefficient between systems A and B,

$$C_6 = \frac{\langle d_X^2 \rangle_A \langle d_X^2 \rangle_B \alpha_A \alpha_B}{\langle d_X^2 \rangle_A \alpha_B + \langle d_X^2 \rangle_B \alpha_A}, \tag{8}$$

with $\langle d_X^2 \rangle$ defined by

$$\langle d_X^2 \rangle = \sum_\sigma \int \rho_\sigma(r_1) d_{X\sigma}^2(r_1) d^3 r_1, \tag{9}$$

and the dipole moment $d_{X\sigma}(r_1)$ given by Eq. (6). These equations apply to atomic or molecular monomers A or B.

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Post-Hartree-Fock C_6 coefficients from Eq. (8) agree remarkably well with accurate reference data.[3,4] The somewhat heuristic derivation in Ref. 3, however, is not entirely satisfying. The present work introduces a more rigorous approach. We derive not only a formula for C_6, but formulas for the higher coefficients C_8 and C_{10} as well. We eliminate molecular polarizabilities from the model also. Free atomic polarizabilities of the constituent atoms are used instead. This greatly enhances its convenience and will allow application of the model to *intra*molecular interactions as well.

We begin with a review of the second-order perturbation theory of the dispersion interaction in Sec. II. We then make approximations to the theory for the case of interatomic interactions in Sec. III. In Sec. IV the model is generalized to intermolecular interactions. Section V offers concluding remarks. The end result is a model of both interatomic and intermolecular C_6, C_8, and C_{10} dispersion coefficients requiring only Hartree-Fock occupied orbitals of the monomers and free atomic polarizabilities. Throughout this work, $d_{X\sigma}(r_1)$ is the central object. The model is computationally and conceptually elegant and it works quite well, as will be demonstrated on interatomic and intermolecular test sets in Sec. III and IV.

II. PERTURBATION THEORY OF THE DISPERSION INTERACTION

The formulas in this section are from the review of Dalgarno and Davison[5] to which we refer the reader for background information. We restrict ourselves to atomic systems in this and the next section.

For two nonoverlapping atoms A and B, second-order perturbation theory gives the following dispersion energy of interaction:

$$E_{\text{disp}} = - \sum_{\ell_A=1}^{\infty} \sum_{\ell_B=1}^{\infty} \frac{\varepsilon_2(\ell_A, \ell_B)}{R^{2(\ell_A+\ell_B+1)}}. \quad (10)$$

If the ground states of both atoms have zero angular momentum, and if both z axes point along the internuclear vector, then

$$\varepsilon_2(\ell_A, \ell_B) = \lambda(\ell_A, \ell_B) \sum_a \sum_b \frac{|\langle \psi_A^a | M_{\ell_A} | \psi_A^0 \rangle|^2 |\langle \psi_B^b | M_{\ell_B} | \psi_B^0 \rangle|^2}{E_A^a + E_B^b - E_A^0 - E_B^0}, \quad (11)$$

where a and b denote excited states of A and B, respectively, M_ℓ denotes the $m=0$ component of the total ℓ-pole moment operator,

$$M_\ell = \sqrt{4\pi} \sum_i r_i^\ell Y_\ell^0(\Omega_i) \quad (12)$$

(with summation over all electrons in A or B as appropriate and with prefactor $\sqrt{4\pi}$ included in the definition for later convenience), and

$$\lambda(\ell_A, \ell_B) = \frac{(2\ell_A + 2\ell_B)!}{(2\ell_A + 1)(2\ell_B + 1)(2\ell_A)!\,(2\ell_B)!}. \quad (13)$$

We now make a "closure" approximation, common in second-order perturbation theory,[6] in order to eliminate the

summations over excited states. If the denominator in Eq. (11) is replaced by an "average" excitation energy,

$$E_A^a + E_B^b - E_A^0 - E_B^0 \approx \Delta E_A + \Delta E_B, \quad (14)$$

then

$$\varepsilon_2(\ell_A, \ell_B) \cong \frac{\lambda(\ell_A, \ell_B)}{\Delta E_A + \Delta E_B} \sum_a \sum_b |\langle \psi_A^a | M_{\ell_A} | \psi_A^0 \rangle|^2 |\langle \psi_B^b | M_{\ell_B} | \psi_B^0 \rangle|^2. \quad (15)$$

Noting that

$$\langle \psi_A^0 | M_{\ell_A} | \psi_A^0 \rangle = \langle \psi_B^0 | M_{\ell_B} | \psi_B^0 \rangle = 0, \quad (16)$$

by assumption (since atoms A and B have zero angular momentum and $\ell_A, \ell_B \geq 1$), the excited-state summations over a and b may be extended to include the ground states and, using completeness of the states ψ_A^a and ψ_B^b ($a=0$ and $b=0$ included), we get the approximate formula,

$$\varepsilon_2(\ell_A, \ell_B) \cong \lambda(\ell_A, \ell_B) \frac{\langle \psi_A^0 | M_{\ell_A}^2 | \psi_A^0 \rangle \langle \psi_B^0 | M_{\ell_B}^2 | \psi_B^0 \rangle}{\Delta E_A + \Delta E_B}, \quad (17)$$

involving ground-state expectation values of the *squared* total ℓ_A-pole and ℓ_B-pole operators in A and B.

The squared multipole operator,

$$M_\ell^2 = 4\pi \sum_i r_i^\ell Y_\ell^0(\Omega_i) \sum_j r_j^\ell Y_\ell^0(\Omega_j), \quad (18)$$

contains a one-body part from the diagonal terms and a *two-body* part from the cross terms. Though not problematic in atoms, the two-body part is not amenable to atomic decomposition as will later be required for *molecules* in Sec. IV. We therefore propose, in the next section, a simple and elegant *one-electron* approximation for the expectation value of M_ℓ^2 which will easily adapt itself to molecular systems in Sec. IV.

III. THE MODEL

When an electron is at distance r from the center of a zero angular momentum (and hence spherically symmetric) atom, the exchange-hole dipole moment $d_{X\sigma}$ is directed toward the nucleus. Viewed from afar, the dipole field is the same as the field of two unit point charges of opposite sign at distances r and $(r-d_{X\sigma})$ from the nucleus. This is illustrated in Fig. 1. The position of the inner positive charge is the mean position of the exchange hole. Notice that, with respect to the nucleus as origin, the point-charge dipole of Fig. 1 also has nonzero *quadrupole, octopole*, etc., multipole moments due to its displacement from the nucleus. The ℓ-pole moment of Eq. (12) is given by

$$M_\ell = -\sqrt{4\pi}[r^\ell - (r-d_{X\sigma})^\ell]Y_\ell^0(\Omega), \quad (19)$$

when the reference electron is at polar coordinates r and Ω.

Let us eliminate the Ω dependence by *angular averaging* the squared M_ℓ moment as follows:

$$M_\ell^2(angular\ average) = [r^\ell - (r-d_{X\sigma})^\ell]^2. \quad (20)$$
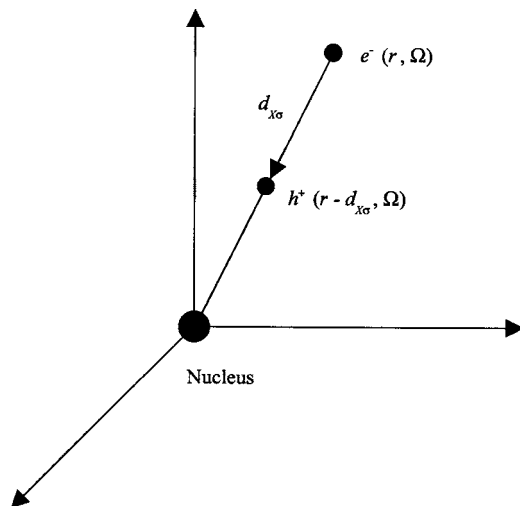
If we now assume that the *density-weighted integral*

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).

$$\langle M_\ell^2 \rangle = \sum_\sigma \int \rho_\sigma(\mathbf{r})[r^\ell - (r - d_{X\sigma})^\ell]^2 d^3\mathbf{r} \tag{21}$$

is a reasonable substitute for the expectation values of M_ℓ^2 in Eq. (17), then a very simple perturbation-theory approximation is obtained,

$$\varepsilon_2(\ell_A, \ell_B) \cong \lambda(\ell_A, \ell_B)\frac{\langle M_{\ell_A}^2\rangle_A \langle M_{\ell_B}^2\rangle_B}{(\Delta E_A + \Delta E_B)}, \tag{22}$$

involving only one-electron integrals in the numerator.

Using $\lambda(1, 1) = 2/3$, $\lambda(1, 2) = \lambda(2, 1) = 1$, $\lambda(1, 3) = \lambda(3, 1) = 4/5$, and $\lambda(2, 2) = 14/5$, and comparing Eq. (10) with

$$E_{\text{disp}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots, \tag{23}$$

we derive formulas for C_6, C_8, and C_{10},

$$C_6 \cong \frac{2}{3}\frac{\langle M_1^2\rangle_A \langle M_1^2\rangle_B}{(\Delta E_A + \Delta E_B)}, \tag{24}$$

$$C_8 \cong \frac{\langle M_1^2\rangle_A \langle M_2^2\rangle_B + \langle M_2^2\rangle_A \langle M_1^2\rangle_B}{(\Delta E_A + \Delta E_B)}, \tag{25}$$

$$C_{10} \cong \frac{4}{5}\frac{\langle M_1^2\rangle_A \langle M_3^2\rangle_B + \langle M_3^2\rangle_A \langle M_1^2\rangle_B}{(\Delta E_A + \Delta E_B)} + \frac{14}{5}\frac{\langle M_2^2\rangle_A \langle M_2^2\rangle_B}{(\Delta E_A + \Delta E_B)}. \tag{26}$$

Note that, even though Eqs. (24)–(26) contain dipole, quadrupole, and octopole moment integrals, only the magnitude of the exchange-hole *dipole* moment $d_{X\sigma}$ is actually needed. In practice, $d_{X\sigma}$ is precomputed at all points of a numerical integration grid using Eq. (6), and subsequent numerical evaluation of the multipole moment integrals is very economical.

It remains to determine the effective atomic excitation energies ΔE_A and ΔE_B. These are hard to deduce from direct physical arguments. We think the best strategy is to extract effective excitation energies from second-order perturbation

theory in some independent manner. The perturbation theory of polarizability will be used for this purpose.

For an atom (having zero permanent dipole moment) the second-order perturbation theory of dipole polarizability α gives, after making the same "average excitation energy" approximation as in Sec. II,

$$\alpha = \frac{2\langle \mu^2\rangle}{3\Delta E}, \tag{27}$$

where μ^2 is the square of the total dipole moment operator. See Ref. 6 for a thorough and comprehensible derivation. If the atom is spherically symmetric, then

$$\langle \mu^2\rangle = \langle M_1^2\rangle, \tag{28}$$

where the moment operator is as defined in Eq. (12). Solving for ΔE, we obtain

$$\Delta E = \frac{2\langle M_1^2\rangle}{3\alpha}. \tag{29}$$

This is what we use for ΔE_A and ΔE_B in Eqs. (24)–(26), with the approximate one-electron integral of Eq. (21) for $\langle M_1^2\rangle$. Atomic polarizabilities are taken from readily available tabulations such as Ref. 7.

C_6, C_8, and C_{10} dispersion coefficients for all combinations of the atoms H, He, Ne, Ar, Kr, and Xe have been computed from Hartree-Fock orbitals and compared with accurate reference data in Table I. Orbitals were computed with the fully numerical NUMOL program[8] and all integrations required by the model were performed "post-Hartree-Fock" on NUMOL numerical grids.[9]

There is an abundance of highly accurate C_6 data available in the literature, but few sources of accurate C_8's and C_{10}'s. Very accurate coefficients are known for the H–H and H–He systems.[10] The remainder of the reference data is from many-body perturbation theory calculations (MBPT) with dispersion coefficients obtained from frequency-dependent polarizabilities.[11,12]

Our model performs quite well on the 21 interatomic C_6's in Table I, with a mean absolute percent error (MAPE) of 3.4%. For C_8 the model shows good performance, but with a larger MAPE of 21.5%. The MAPE for C_{10} is 8.4%. We cannot rationalize the somewhat larger MAPE for the C_8's compared with the C_6's and the C_{10}'s at this time. Our model is based on several approximations and does not incorporate dynamical correlation effects in the hole. The agreement between our calculated dispersion coefficients and the MBPT results is therefore very encouraging considering the simplicity and the minimal computational cost of our method, a negligible fraction of the cost of the Hartree-Fock orbital calculations.

In the next section, the model is extended from atomic to molecular systems.

IV. FROM ATOMS TO MOLECULES

We have so far assumed that A and B are zero angular momentum, spherically symmetric atoms. Since the multipole integrals of Eq. (21) depend on origin for $\ell \geq 2$, it is not immediately clear how to generalize the model to multi-

TABLE I. C_6, C_8, and C_{10} coefficients for atomic pairs (a. u.).

	C_6 calc.	C_6 lit.	C_8 calc.	C_8 lit.	C_{10} calc.	C_{10} lit.
H–H[a]	6.75	6.49	152.0	124.4	3 299	3286
H–He[a]	2.98	2.82	48.25	41.75	760.9	858.7
H–Ne[b]	5.69	5.69	111.6	97.8	1 969	2221
H–Ar[b]	20.12	19.86	560.4	442.1	12 703	12 617
H–Kr[b]	29.43	29.15	920.2	732.2	22 743	23 441
H–Xe[b]	45.12	44.14	1687	1 357	47 273	51 088
He–He[c]	1.64	1.46	16.10	14.11	157.7	183.2
He–Ne[b]	3.09	3.07	40.96	36.18	453.2	545.1
He–Ar[b]	9.79	9.57	210.8	167.5	3 277	3 701
He–Kr[b]	14.05	13.65	350.3	280.0	6 122	7 257
He–Xe[b]	20.86	19.92	647.8	525.0	13 316	16 674
Ne–Ne[b]	5.83	6.55	97.32	90.34	1 277	1 536
Ne–Ar[b]	18.60	19.75	464.0	390.1	8 551	9 335
Ne–Kr[b]	26.70	28.01	757.4	638.1	15 563	17 658
Ne–Xe[b]	39.71	40.52	1 370	1162	32 748	38 978
Ar–Ar[b]	62.74	64.54	2 082	1623	51 891	49 063
Ar–Kr[b]	90.95	93.16	3 329	2 617	91 195	88 260
Ar–Xe[b]	137.4	138.0	5 871	4 669	183 934	184 250
Kr–Kr[b]	132.1	135.1	5 286	4 187	158 503	155 450
Kr–Xe[b]	200.1	201.3	9 234	7 389	315 196	316 030
Xe–Xe[b]	304.7	302.3	15 924	12 807	615 431	619 840
MAPE[d]	3.4	⋯	21.5	⋯	8.4	⋯

[a]Reference 10.
[b]Reference 11.
[c]Reference 12.
[d]MAPE: mean absolute percent error.

nuclear systems. We propose a logical method in this section for constructing C_6, C_8, and C_{10} coefficients in intermolecular cases from approximate *interatomic* coefficients.

We assume that, for each of $m=6$, 8, and 10, an intermolecular C_m can be written as a sum over *interatomic* coefficients $C_{m,ij}$,

$$C_m = \sum_i^A \sum_j^B C_{m,ij}. \tag{30}$$

Now and hereafter, A and B denote *molecules*, with i referring to an atom in molecule A and j referring to an atom in molecule B. Molecule A (and similarly molecule B) will be partitioned into "atoms" by Hirshfeld atomic weight functions[13]

$$w_i(\boldsymbol{r}) = \frac{\rho_i^{\text{at}}(\boldsymbol{r})}{\sum_n \rho_n^{\text{at}}(\boldsymbol{r})}, \tag{31}$$

where ρ^{at} is a sphericalized free atomic density placed at the appropriate nucleus, and the n summation is over all atoms in the molecule. Weight function $w_i(\boldsymbol{r})$ has value close to 1 at points in the vicinity of nucleus i and close to 0 everywhere else. Moreover, the $w_i(\boldsymbol{r})$ sum to 1 everywhere,

$$\sum_i w_i(\boldsymbol{r}) = 1. \tag{32}$$

Other partitioning schemes are possible. The Hirshfeld scheme has been used in our previous work[4] and we continue to use it here.

We generalize Eqs. (24)–(26) to *atoms in molecules* by replacing subscripts A and B with i and j,

$$C_{6,ij} = \frac{2}{3} \frac{\langle M_1^2 \rangle_i \langle M_1^2 \rangle_j}{(\Delta E_i + \Delta E_j)}, \tag{33}$$

$$C_{8,ij} \cong - \frac{\langle M_1^2 \rangle_i \langle M_2^2 \rangle_j + \langle M_2^2 \rangle_i \langle M_1^2 \rangle_j}{(\Delta E_i + \Delta E_j)}, \tag{34}$$

$$C_{10,ij} \cong \frac{4}{5} \frac{\langle M_1^2 \rangle_i \langle M_3^2 \rangle_j + \langle M_3^2 \rangle_i \langle M_1^2 \rangle_j}{(\Delta E_i + \Delta E_j)} + \frac{14}{5} \frac{\langle M_2^2 \rangle_i \langle M_2^2 \rangle_j}{(\Delta E_i + \Delta E_j)}, \tag{35}$$

where $\langle M_\ell^2 \rangle_i$ is defined by

$$\langle M_\ell^2 \rangle_i = \sum_\sigma \int w_i(\boldsymbol{r}) \rho_\sigma(\boldsymbol{r}) [r^\ell - (r - d_{X\sigma})^\ell]^2 d^3\boldsymbol{r} \tag{36}$$

[i.e., Eq. (21) with the atomic partitioning function $w_i(\boldsymbol{r})$ inserted in the integrand] with a similar formula for atoms j in B. The energy ΔE_i, and similarly ΔE_j, is given by the following generalization of Eq. (29):

$$\Delta E_i = \frac{2\langle M_1^2 \rangle_i}{3\alpha_i}, \tag{37}$$

where α_i is the *effective* polarizability of atom i in molecule A.

For α_i we propose the approximation

TABLE II. C_6, C_8, and C_{10} coefficients for molecule-atom and molecule-molecule pairs (a. u.).

	C_6 calc.	C_6 lit.	C_8 calc.	C_8 lit.	C_{10} calc.	C_{10} lit.
H_2–He[a]	4.78	4.05	59.03	55.43	780	1 005
H_2–Ne[b]	9.08	8.19	143.3	130.0	2 086	2 611
H_2–Ar[b]	31.24	27.76	750.9	588.8	14 254	15 539
H_2–Kr[b]	45.48	40.41	910.2	975.5	26 081	29 289
H_2–Xe[b]	69.15	60.54	2321	1 808	55 646	64 764
N_2–He[c]	10.84	9.76	202.5	219.2	3 046	5 184
N_2–Ne[c]	20.61	20.23	455.8	497.6	8 000	12 842
N_2–Ar[c]	71.77	65.52	2 179	1 982	51 103	64 192
N_2–Kr[c]	104.71	94.40	3 537	3 139	91 053	112 990
N_2–Xe[c]	159.8	139.5	6 375	5 452	187 446	229 260
Cl_2–He[c]	21.64	23.48	508.1	810.3	⋯	⋯
Cl_2–Ne[c]	41.14	47.98	1 107	1 770	⋯	⋯
Cl_2–Ar[c]	142.9	161.5	5 022	6 765	⋯	⋯
Cl_2–Kr[c]	208.3	234.8	8 034	10 505	⋯	⋯
Cl_2–Xe[c]	317.5	351.2	14 190	17 688	⋯	⋯
H_2–H_2[a]	15.70	12.15	233.5	212.6	3 799	4 741
H_2–N_2[a]	36.24	30.54	768.5	771.7	⋯	⋯
N_2–N_2[a]	83.89	75.63	2310	2 489	⋯	⋯
MAPE[d]	12.7	⋯	16.5	⋯	21.2	⋯

[a]Reference 12.
[b]Reference 11.
[c]Reference 14.
[d]MAPE: mean absolute percent error.

$$\alpha_i = \frac{\langle r^3 \rangle_i}{\langle r^3 \rangle_{i,\text{free}}} \alpha_{i,\text{free}}, \qquad (38)$$

where $\langle r^3 \rangle_i$ is the integral,

$$\langle r^3 \rangle_i = \int r^3 w_i(\boldsymbol{r}) \rho(\boldsymbol{r}) d^3\boldsymbol{r}, \qquad (39)$$

and $\langle r^3 \rangle_{i,\text{free}}$ is the analogous integral,

$$\langle r^3 \rangle_{i,\text{free}} = \int r^3 \rho_{i,\text{free}}(\boldsymbol{r}) d^3\boldsymbol{r}, \qquad (40)$$

for the *free* atom i. This approximation is motivated by the qualitative, if not quantitative, general relationship between polarizability and volume. We expound on this relationship in the Appendix rather than digressing here. We note, however, that this is not the same definition of α_i as in Ref. 4. Our previous definition[4] involved *molecular* polarizabilities. The new definition, Eq. (38), involves only free atomic polarizabilities. We return to this point at the end of the section.

The origin with respect to which r and $(r - d_{X\sigma})$ are defined in Eqs. (36) and (39) is the position of nucleus i. In Eq. (36) we furthermore assume, as in Fig. 1, that $\boldsymbol{d}_{X\sigma}$ is *directed toward nucleus i* when evaluating $\langle M_\ell^2 \rangle_i$. Since the direction of the exchange-hole dipole moment at any given point in a molecule is surely toward the nearest nucleus, this is physically reasonable. Hirshfeld atoms in molecules are not perfectly spherically symmetric, however, and $\boldsymbol{d}_{X\sigma}$ is not directed *exactly* toward nucleus i. Figure 1 is thus an approximation for an atom in a molecule. Its validity will be assessed by looking at computed data.

In Table II, we report C_6, C_8, and C_{10} coefficients for a test set of 18 molecule-atom and molecule-molecule pairs. As in Sec. III, fully numerical Hartree-Fock computations

were carried out on the monomers with the NUMOL program[8] and all moment integrations were performed on NUMOL numerical grids.[9] Free atomic polarizabilities for the effective excitation energies ΔE_i and ΔE_j are from Ref. 7. The MBPT literature data are from Refs. 11, 12, and 14. Literature data were unavailable for the C_{10} coefficients of the Cl_2-atom complexes and for H_2–N_2 and N_2–N_2.

MAPEs are 12.7% for C_6, 16.5% for C_8, and 21.2% for C_{10}. These errors are of the same order as the atom-atom pair errors in Sec. III, thus validating the assumptions and approximations of this section. Again the agreement with accurate data is very encouraging for such a simple and computationally inexpensive method.

On the much more extensive test set of 178 intermolecular C_6's compiled in Ref. 4, we obtain a MAPE of 9.1% compared with the MAPE of 11.1% we previously obtained[4] using molecular polarizabilities in Eq. (8). This is a significant advance, since we now require free atomic polarizabilities only [i.e., see Eq. (38)] and no molecular polarizabilities at all.

V. SUMMARY AND OUTLOOK

The idea, introduced in Ref. 3, that the position-dependent dipole moment of an electron plus its exchange hole can be used to generate C_6 dispersion coefficients, has been extended in this work to C_8 and C_{10} coefficients. A point-charge dipole *at a nonzero distance* from a nucleus (see Fig. 1) has quadrupole, octopole, and higher moments as well with respect to that nucleus. This model can be used to estimate, by simple one-electron integrations, total multipole moment expectation values that occur in the perturbation theory of the dispersion interaction. Approximate formulas for C_6, C_8, and C_{10} are thereby derived.

In Ref. 15, we showed how the C_6 model of Refs. 3 and 4 can be transformed into a *density-functional* model depending on local density, the local gradient and Laplacian of the density, and the local kinetic-energy density. This is possible because $d_{X\sigma}$ can be estimated, at any given point in an atom or molecule, using these local densities.[15] The present $C_6/C_8/C_{10}$ model is similarly transcribable into density-functional form. The overall MAPEs for all test systems in Tables I and II are, for the orbital dependent $d_{X\sigma}$ of Eq. (6), 7.7% for C_6, 19.2% for C_8, and 12.8% for C_{10}. The analogous MAPEs for the density-functional approximation to $d_{X\sigma}$ are 10.9% for C_6, 16.3% for C_8, and 13.3% for C_{10}. We see that the density-functional model works about as well as the explictly orbital-dependent model.

Given the tremendous simplicity and economy of the model, it is very gratifying that its results compare well with accurate reference data. In future work, C_8 and C_{10} will be incorporated into modeling of intermolecular potential-energy surfaces. We have already developed a post-Hartree-Fock approach to intermolecular interactions[4,15] that works remarkably well using C_6. The π-stacked conformations of the benzene dimer stand out, however, as the poorest cases.[15] Addition of C_8 and C_{10} terms may offer improvement. Future applications of the model to intramolecular dispersion energies are also planned.

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APPENDIX: ATOMIC POLARIZABILITY AND VOLUME

In Sec. IV, the effective polarizability α_i of an atom in a molecule is related to its *free* polarizability $\alpha_{i,\text{free}}$ by Eq. (38),

$$\alpha_i = \frac{\langle r^3 \rangle_i}{\langle r^3 \rangle_{i,\text{free}}} \alpha_{i,\text{free}},$$

where $\langle r^3 \rangle_i$ and $\langle r^3 \rangle_{i,\text{free}}$ are the density-weighted integrals of r^3 over the Hirshfeld atom-in-the-molecule density and the free-atom density, respectively. The density-weighted r^3 in-

tegration is a simple, parameter-free, numerical measure of atomic "volume," which is in turn related to polarizability.

Polarizability has the same dimensionality as volume. Classical models of polarizability, such as the conducting sphere model[16] or the uniform-density sphere model,[17] yield a polarizability equal to R^3 where R is the radius of the sphere. For "real" chemical systems, strong linear correlations between polarizability and volume have been empirically demonstrated.[18] It is therefore reasonable to propose, as in Eq. (38), that the ratio of the polarizability of a Hirshfeld atom in a molecule to its free polarizability is equal to the ratio of its Hirshfeld *volume* to its free volume. Considering that Hirshfeld atomic densities are only slightly perturbed from free densities, this would seem to be a sound proposition.

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