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A simple model is presented in which the instantaneous dipole moment of the exchange hole is used to generate a dispersion interaction between nonoverlapping systems. The model is easy to implement, requiring no electron correlation (in the usual sense) or time dependence, and has been tested on various atomic and molecular pairs. The resulting C_6 dispersion coefficients are remarkably accurate. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1884601]

I. INTRODUCTION

The classical explanation of the dispersion or van der Waals interaction between chemically inert systems is familiar even to introductory chemistry students. Given two inert or widely separated systems, an *instantaneous* dipole moment on one system *induces* a dipole moment on the other. The attraction between these moments results in an interaction which, in the limit of large separation R, has the behavior

$$E_{\text{disp}} = -\frac{C_6}{R^6}, \tag{1}$$

where C_6 is a constant whose value depends on the systems involved. This picture begs the obvious question. How do "instantaneous" dipole moments arise in systems which may otherwise have a zero permanent dipole moment? How, for example, do instantaneous dipole moments originate in a noble gas atom?

The usual quantum mechanical approach is complicated (we recommend Ref. 1 for a nice treatment). Electron correlation invokes the mixing of *excited* states with the ground state, creating virtual or "transition" dipole moments that interact with each other. Second-order perturbation theory and additional approximations[1] give the famous London formula (in atomic units) for the dispersion energy between two systems A and B,

$$E_{\text{disp}} = -\frac{3}{2}\left(\frac{I_A I_B}{I_A + I_B}\right)\frac{\alpha_A \alpha_B}{R^6}, \tag{2}$$

which conveniently depends on properties, the ionization energy I and polarizability α, that are experimentally accessible. The London formula is instructive for understanding trends but is prone to large errors. Correlated *ab initio* calculations of high quality can produce accurate dispersion energy curves[2] but are very demanding and provide little physical insight. Also, a rigorous expression for C_6 involving frequency dependent polarizability $\alpha(i\omega)$ is known,[3]

$$C_6 = \frac{3}{\pi}\int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega)d\omega, \tag{3}$$

which can be used to compute accurate C_6 values from time-dependent electronic structure calculations.[4,5] These are also

very demanding, however, and must be performed with care.

Methods able to produce C_6 coefficients of *reasonable* quality, without the demands of the highly accurate approaches, are widely useful. Here we present such a method. It is based on a novel answer to the question posed at the outset. How do instantaneous dipole moments arise in a quantum system? We propose that *spherical asymmetries* in the *exchange hole* are the source.

II. THE PRESENT MODEL

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 r_1. The hole is given by the expression

$$h_{X\sigma}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{\rho_\sigma(\mathbf{r}_1)}\sum_{ij}\psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2), \tag{4}$$

where $\mathbf{r}_2$ defines the shape of the hole and $\mathbf{r}_1$ 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. The σ-spin exchange energy $E_{X\sigma}$ is related to the exchange hole by

$$E_{X\sigma} = \frac{1}{2}\int\int\rho_\sigma(\mathbf{r}_1)\frac{h_{X\sigma}(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}d^3\mathbf{r}_2 d^3\mathbf{r}_1. \tag{5}$$

This simple deconstruction of the exchange energy of a Slater determinant has great conceptual power[6] which will be exploited presently.

The exchange-hole definition enables us to *visualize* the effects of self-interaction correction and exchange. When an electron is at $\mathbf{r}_1$, the hole measures the depletion of probability (with respect to the total electron density ρ) of finding another same-spin electron at $\mathbf{r}_2$. The probability of finding another same-spin electron at $\mathbf{r}_2 = \mathbf{r}_1$ is completely extinguished,

$$h_{X\sigma}(\mathbf{r}_1,\mathbf{r}_1) = -\rho_\sigma(\mathbf{r}_1), \tag{6}$$

as required by the Pauli exclusion principle. The hole is always negative, as can be seen by rewriting Eq. (4) as

$$h_{X\sigma}(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\frac{1}{\rho_\sigma(\boldsymbol{r}_1)}\Big[\sum_i \psi_{i\sigma}(\boldsymbol{r}_1)\psi_{i\sigma}(\boldsymbol{r}_2)\Big]^2 \tag{7}$$

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

$$\int h_{X\sigma}(\boldsymbol{r}_1,\boldsymbol{r}_2)d^3\boldsymbol{r}_2 = -1. \tag{8}$$

This is easy to prove from Eq. (4) and the orthonormality of the orbitals $\psi_{i\sigma}$. Equation (8) guarantees that the electron *plus its hole* always has *zero charge* overall.

The hole is not, in general, spherically symmetric around $\boldsymbol{r}_1$. Only in a uniform electron gas does it have spherical symmetry. Even in systems with spherically symmetric densities, the hole is aspherical unless $\boldsymbol{r}_1$ is at the center of the system. Thus the electron plus its Fermi hole, though of zero charge overall, generally has a *nonzero dipole moment*. Since the exchange energy, Eq. (5), senses only the spherical average of the hole around each $\boldsymbol{r}_1$, a nonzero dipole moment has no effect on the energy of the system containing the electron. Might the asphericity of the hole be the source, however, of the instantaneous dipole moment responsible for the dispersion interaction with *other* systems?

Consider a second system (B) at position $\boldsymbol{R}$ relative to the first (A) and assume that the distance R is large compared to the sizes of A and B. The instantaneous dipole moment $\boldsymbol{d}_{X\sigma}(\boldsymbol{r}_1)$ of the exchange hole plus its electron at point $\boldsymbol{r}_1$ in system A generates an electric field

$$\boldsymbol{E} = \frac{3(\boldsymbol{d}_{X\sigma}\cdot\boldsymbol{R})\boldsymbol{R}}{R^5} - \frac{\boldsymbol{d}_{X\sigma}}{R^3} \tag{9}$$

at position $\boldsymbol{R}$. If system B has polarizability α_B, then a dipole moment of value

$$\boldsymbol{d}_{\text{ind}} = \alpha_B\boldsymbol{E} \tag{10}$$

is induced in B. The electrostatic interaction between these dipoles has energy,

$$V_{\text{dip-dip}} = \frac{\boldsymbol{d}_{X\sigma}\cdot\boldsymbol{d}_{\text{ind}}}{R^3} - \frac{3(\boldsymbol{d}_{X\sigma}\cdot\boldsymbol{R})(\boldsymbol{d}_{\text{ind}}\cdot\boldsymbol{R})}{R^5}, \tag{11}$$

which, after substituting Eqs. (10) and (9), becomes

$$V_{\text{dip-dip}} = -\alpha_B\left[\frac{d_{X\sigma}^2}{R^6} + \frac{3(\boldsymbol{d}_{X\sigma}\cdot\boldsymbol{R})^2}{R^8}\right]. \tag{12}$$

The *orientation averaged* isotropic interaction (i.e., averaged over all orientations of $\boldsymbol{d}_{X\sigma}$) is obtained by integrating over angles as follows:

$$V_{\text{dip-dip}}^{\text{avg}} = -\frac{\alpha_B}{4\pi}\int_0^{2\pi}\int_0^\pi \left(\frac{d_{X\sigma}^2}{R^6} + \frac{3d_{X\sigma}^2}{R^6}\cos^2\vartheta\right)\sin\vartheta\, d\vartheta\, d\varphi$$

$$= -\frac{2d_{X\sigma}^2\alpha_B}{R^6}, \tag{13}$$

where ϑ and φ are polar angles with respect to the direction $\boldsymbol{R}$. The resulting $V_{\text{dip-dip}}^{\text{avg}}$ thus depends on the magnitude squared, $d_{X\sigma}^2(\boldsymbol{r}_1)$, of the exchange-hole dipole moment at each *body centered* reference point $\boldsymbol{r}_1$ in system A.

Now integrate over $\boldsymbol{r}_1$ in system A and over α and β spins as well. Denoting this integral by $\langle d_X^2\rangle$, we have

$$\langle d_X^2\rangle_A = \int \rho_\alpha(\boldsymbol{r}_1)d_{X\alpha}^2(\boldsymbol{r}_1)d^3\boldsymbol{r}_1 + \int \rho_\beta(\boldsymbol{r}_1)d_{X\beta}^2(\boldsymbol{r}_1)d^3\boldsymbol{r}_1, \tag{14}$$

and we obtain the following formula for the total dipole-dipole interaction energy:

$$U_{\text{dip-dip}}^{AB} = -2\langle d_X^2\rangle_A\alpha_B/R^6. \tag{15}$$

The same derivation with systems A and B interchanged gives

$$U_{\text{dip-dip}}^{BA} = -2\langle d_X^2\rangle_B\alpha_A/R^6, \tag{16}$$

which is not, unfortunately, the same as Eq. (15). For unlike systems our model lacks A-B symmetry. An appropriate averaging of Eqs. (15) and (16) will be suggested below. For like systems, however, there is no ambiguity and the dipole-dipole interaction energy is

$$U_{\text{dip-dip}} = -2\langle d_X^2\rangle\alpha/R^6. \tag{17}$$

Initial tests of Eq. (17) on various atomic dimers (computation of $\langle d_X^2\rangle$ is described in the following section) gave interesting results. Despite the simplicity of the underlying model, Eq. (17) reproduces known C_6 values with remarkable accuracy if divided by a factor of 4. An incorrect prefactor is not surprising. Our model takes dipole-dipole potential energy into account, but not kinetic energy[7] or charge rearrangement[8] effects. These, especially the latter, are very difficult to model. That Eq. (17) *does* work well with a modified prefactor is, in our opinion, fascinating. We therefore take a heuristic approach (for now) and propose the formula

$$C_6 = \tfrac{1}{2}\langle d_X^2\rangle\alpha \tag{18}$$

for like-system interactions.

For unlike systems a suitable average of Eqs. (15) and (16) needs to be taken with, in light of the above, prefactors divided by 4. Straightforward algebraic averaging is unsuccessful. Geometric averaging also fails. Recognizing that successful combination formulas in the literature (e.g., London formula or Slater–Kirkwood formula[9]) feature a sum of some property of A and B in a *divisor*, we propose averaging *inverses* as follows:

$$\frac{2}{C_6} = \frac{1}{C_6^{AB}} + \frac{1}{C_6^{BA}}, \tag{19}$$

which, after inserting C_6 coefficients divided by 4 from Eqs. (15) and (16), gives

$$C_6 = \frac{\langle d_X^2\rangle_A\langle d_X^2\rangle_B\alpha_A\alpha_B}{\langle d_X^2\rangle_A\alpha_B + \langle d_X^2\rangle_B\alpha_A}. \tag{20}$$

If this heuristic approach is unsatisfying, Eq. (20) can be derived by strong theoretical arguments as well. There are connections between the formulas of this section and the second-order perturbation theory of the dispersion interaction. We draw these connections in the Appendix rather than digressing now. In the following section, Eq. (20) is applied without further ado to a wide variety of atomic and molecular, like and unlike, interactions.

TABLE I. Calculated C_6 coefficients for atomic pairs, in atomic units.

Atoms	Calculated C_6	Literature C_6[a]
He–He	1.64	1.47
He–Ne	3.09	3.13
He–Ar	9.81	9.82
He–Kr	14.08	13.6
He–Xe	20.91	18.3
Ne–Ne	5.83	6.87
Ne–Ar	18.61	20.7
Ne–Kr	26.72	28.7
Ne–Xe	39.73	37.8
Ar–Ar	62.71	67.2
Ar–Kr	90.93	94.3
Ar–Xe	137.4	129
Kr–Kr	132.1	133
Kr–Xe	200.1	184
Xe–Xe	304.7	261
H–H	6.76	6.49
H–Li	71.64	66.4
H–Na	85.76	71.8
H–K	143.2	109
Li–Li	1528	1390
Li–Na	1683	1450
Li–K	2910	2320
Na–Na	1879	1510
Na–K	3230	2410
K–K	5567	3890
He–H	2.99	2.82
He–Li	24.17	22.6
He–Na	29.53	24.4
He–K	48.88	38.0
Ne–H	5.69	5.71
Ne–Li	46.51	44.0
Ne–Na	56.79	47.7
Ne–K	94.02	74.9
Ar–H	20.13	20.0
Ar–Li	185.7	175
Ar–Na	224.8	189
Ar–K	373.6	292
Kr–H	29.44	28.5
Kr–Li	278.7	259
Kr–Na	336.7	281
Kr–K	560.0	433
Xe–H	45.14	40.9
Xe–Li	446.5	404
Xe–Na	537.5	438
Xe–K	895.3	669
MAPE[b]	14.0 (9.8[c])	⋯

[a]Literature values from Ref. 14.
[b]Mean absolute percent error relative to the literature values.
[c]Excluding atomic pairs involving potassium.

III. COMPUTATIONS AND APPLICATIONS

The calculation of C_6 dispersion coefficients in the present model requires only $\langle d_X^2 \rangle$ and α for individual systems. We take polarizability data from tables instead of computing α ourselves. Accurate values are readily available.[10] This leaves as our only task the computation of $\langle d_X^2 \rangle$. $\langle d_X^2 \rangle$ is a sum of two terms, one for each spin, as in Eq. (14):

TABLE II. Isotropic C_6 coefficients for molecular pairs, in atomic units.

Molecules	Calculated C_6	Literature C_6[a]
H_2–H_2	14.01	12.11
N_2–N_2	66.62	73.39
CH_4–CH_4	115.3	129.6
CH_4–CO_2	128.7	142.6
CO_2–CO_2	143.7	158.7
Methane–acetylene	147.5	162.5
Acetylene–CO_2	164.7	178.2
Acetylene–acetylene	188.7	204.1
Acetylene–ethylene	225.3	247.7
Acetylene–ethane	241.9	278.9
Ethylene–ethylene	270.1	300.5
Acetylene–propylene	320.2	367.6
Ethane–ethane	310.6	381.8
Acetylene–propane	332.8	395.6
Propylene–propylene	548.6	662.8
Propane–propane	589.4	768.1
MAPE[b]	12.5	⋯

[a]Literature values from Refs. 5 and 18.
[b]Mean absolute percent error relative to the literature values.

$$\langle d_X^2 \rangle = \langle d_{X\alpha}^2 \rangle + \langle d_{X\beta}^2 \rangle, \tag{21}$$

where

$$\langle d_{X\sigma}^2 \rangle = \int \rho_\sigma(\boldsymbol{r}_1) d_{X\sigma}^2(\boldsymbol{r}_1) d^3\boldsymbol{r}_1. \tag{22}$$

Recall that $d_{X\sigma}^2(\boldsymbol{r}_1)$ is the magnitude squared of the dipole moment of the electron plus its exchange hole at reference point $\boldsymbol{r}_1$. Given a set of occupied orbitals $\psi_{i\sigma}$, the dipole moment is easily computed by integrating over $\boldsymbol{r}_2$ in Eq. (4):

$$\boldsymbol{d}_{X\sigma}(\boldsymbol{r}_1) = \left[\frac{1}{\rho_\sigma(\boldsymbol{r}_1)} \sum_{ij} \boldsymbol{r}_{ij\sigma} \psi_{i\sigma}(\boldsymbol{r}_1) \psi_{j\sigma}(\boldsymbol{r}_1) \right] - \boldsymbol{r}_1, \tag{23}$$

$$\boldsymbol{r}_{ij\sigma} = \int \boldsymbol{r} \psi_{i\sigma}(\boldsymbol{r}) \psi_{j\sigma}(\boldsymbol{r}) d^3\boldsymbol{r}. \tag{24}$$

Note that the dipole moment of a neutral object is origin independent and we therefore conveniently use the molecular origin in Eq. (23). All integrations, the moment integrations of Eq. (24) and the integration of Eq. (22), are performed numerically.[11] The cost of computing $\langle d_X^2 \rangle$ is negligible compared to the cost of computing the orbitals themselves.

Orbitals are obtained in this work from the grid-based NUMOL program of Becke and Dickson.[12] We use (spin unrestricted) Hartree–Fock orbitals in these first tests.[13] Hartree–Fock orbitals are preferable to, e.g., local-density approximation (LDA) or generalized gradient approximation (GGA) Kohn–Sham orbitals because the Fermi-hole dipole moment is sensitive to orbital behavior at long range. We therefore avoid the well-known long-range deficiencies of the LDA and GGA Kohn–Sham potentials. The dependence of $\langle d_X^2 \rangle$ on orbitals and electron correlation will be explored in greater detail in future work.

In Tables I and II, we present C_6 dispersion coefficients obtained from Eq. (18) for like systems and Eq. (20) for unlike systems for a variety of atomic and molecular pairs.

TABLE III. Calculated C_6 coefficients for atomic pairs, in atomic units.

Atoms	Eq. (20) C_6	Eq. (A4) C_6	Literature C_6[a]
He–He	1.64	1.64	1.47
He–Ne	3.09	3.61	3.13
He–Ar	9.81	12.19	9.82
He–Kr	14.08	17.95	13.6
He–Xe	20.91	27.87	18.3
Ne–Ne	5.83	8.12	6.87
Ne–Ar	18.61	26.58	20.7
Ne–Kr	26.72	39.02	28.7
Ne–Xe	39.73	60.21	37.8
Ar–Ar	62.71	91.02	67.2
Ar–Kr	90.93	134.3	94.3
Ar–Xe	137.4	209.1	129
Kr–Kr	132.1	198.4	133
Kr–Xe	200.1	309.2	184
Xe–Xe	304.7	482.7	261
H–H	6.76	6.76	6.49
H–Li	71.64	71.64	66.4
H–Na	85.76	89.97	71.8
H–K	143.2	157.2	109
Li–Li	1528	1528	1390
Li–Na	1683	1727	1450
Li–K	2910	3062	2320
Na–Na	1879	1992	1510
Na–K	3230	3522	2410
K–K	5567	6230	3890
He–H	2.99	2.99	2.82
He–Li	24.17	24.17	22.6
He–Na	29.53	31.16	24.4
He–K	48.88	54.25	38.0
Ne–H	5.69	6.20	5.71
Ne–Li	46.51	47.38	44.0
Ne–Na	56.79	61.38	47.7
Ne–K	94.02	106.8	74.9
Ar–H	20.13	22.94	20.0
Ar–Li	185.7	191.7	175
Ar–Na	224.8	246.4	189
Ar–K	373.6	429.1	292
Kr–H	29.44	34.19	28.5
Kr–Li	278.7	289.1	259
Kr–Na	336.7	371.3	281
Kr–K	560.0	646.7	433
Xe–H	45.14	54.11	40.9
Xe–Li	446.5	467.5	404
Xe–Na	537.5	599.3	438
Xe–K	895.3	1044	669
MAPE[b]	14.0	31.7	⋯

[a]Literature values from Ref. 14.
[b]Mean absolute percent error relative to the literature values.

The mean absolute percent error (MAPE) of our atom-atom C_6's in Table I relative to highly accurate literature values[14] is 14.0%. The potassium atom is a significant outlier. Omitting all cases involving potassium leads to a reduced MAPE of 9.8%. Our C_6's are in slightly better agreement with literature values than the approximate density-functional method of Andersson, Langreth, and Lundqvist,[15] which yields a MAPE of 15.5% for the same set of 45 noble gas and alkali atom pairs.

TABLE IV. Atomic values of $\langle d_X^2 \rangle$, $\langle \mu^2 \rangle$, and α, in atomic units.

Atom	$\langle d_X^2 \rangle$	$\langle \mu^2 \rangle$	α
He	2.37	2.37	1.38
Ne	4.36	6.08	2.67
Ar	11.31	16.42	11.09
Kr	15.74	23.64	16.78
Xe	22.30	35.34	27.32
H	3.00	3.00	4.50
Li	18.61	18.61	164
Na	23.10	24.49	163
K	37.98	42.50	293

Isotropic C_6 coefficients for molecule-molecule pairs are reported in Table II. We use B3LYP[16]/6-31G $(2df,p)$ geometries obtained from the Gaussian98 program package.[17] Our calculated values tend to be smaller than accurate literature values,[5,18] but a reasonably good MAPE of 12.5% is achieved. C_6's from Eq. (3) combined with time-dependent Hartree–Fock calculations of frequency dependent polarizabilities have been reported by Spackman[5] for eight of the sixteen systems in this set. His results also underestimate accurate values, and their MAPE of 12.6% is similar to the 12.5% obtained from our much simpler time-independent model.

The present method performs remarkably well given its simplicity. Neither time dependence, nor excited states, are necessary. The instantaneous dipole moment of the exchange hole, and the polarizability of the partner system, is all we require.

IV. CONCLUSIONS

This work proposes an elegant connection between exchange-hole asphericity and the dispersion interaction. If the position dependent dipole moment of the exchange hole (plus its electron) in a system A is considered to induce dipole moments in another system B, then a C_6 dispersion coefficient of very good accuracy can be obtained through Eq. (20). The model works for molecular as well as atomic systems.

This approach may have practical benefits in addition to its fundamental theoretical appeal. We hope to incorporate it into molecular structure and molecular mechanics codes in future work in order to efficaciously handle long range interactions.

APPENDIX: CONNECTIONS WITH SECOND-ORDER PERTURBATION THEORY

We refer the reader to Ref. 1 for an excellent and comprehensible account of the second-order perturbation theory of the dispersion interaction. We will here adopt notation and formulas from Chap. 12 of this book. Equation (12.32) of

Ref. 1 is obtained when all excitation energies in system A are approximated by a constant "average" value ΔE_A and similarly for system B:

$$E_{\text{disp}} = -\frac{2}{3}\left(\frac{1}{\Delta E_A + \Delta E_B}\right)\frac{\langle\mu_A^2\rangle\langle\mu_B^2\rangle}{R^6}. \tag{A1}$$

The quantity $\langle\mu^2\rangle$ is the expectation value of the squared dipole moment operator

$$\mu^2 = \left(\sum_i q_i \boldsymbol{r}_i\right)^2 = \sum_k q_k^2 r_k^2 + \sum_{i\neq j} q_i q_j \boldsymbol{r}_i \cdot \boldsymbol{r}_j, \tag{A2}$$

where the sums are over all particles including nuclei. It is assumed that A and B have zero total charge and zero permanent dipole moment. From the analogous second-order perturbation theory of polarizability α, and again making an average excitation-energy approximation, one obtains[1]

$$\alpha = \frac{2\langle\mu^2\rangle}{3\Delta E}. \tag{A3}$$

This equation can be used to eliminate $\langle\mu^2\rangle$ from Eq. (A1) thus deriving the London formula, Eq. (2), after further approximating ΔE by the ionization energy. Alternatively, we can eliminate ΔE from Eq. (A1) and derive another formula,

$$E_{\text{disp}} = -\left[\frac{\langle\mu_A^2\rangle\langle\mu_B^2\rangle}{\langle\mu_A^2\rangle\alpha_B + \langle\mu_B^2\rangle\alpha_A}\right]\frac{\alpha_A\alpha_B}{R^6}, \tag{A4}$$

the focus of which is $\langle\mu^2\rangle$. The μ^2 operator, Eq. (A2), consists of nuclear and electron one-body operators and two-body operators arising from the cross terms. In an *atom* the nuclear parts can be ignored and $\langle\mu^2\rangle$ in the Hartree–Fock approximation is given by

$$\langle\mu^2\rangle = \int r^2\rho(\boldsymbol{r})d^3\boldsymbol{r} - \sum_{ij}\left(r_{ij\alpha}^2 + r_{ij\beta}^2\right), \tag{A5}$$

where r is distance from the nucleus, $\rho(\boldsymbol{r})$ is the total electron density, and $\boldsymbol{r}_{ij\sigma}$ is the moment integral of Eq. (24).

$\langle\mu^2\rangle$ is not the same quantity as $\langle d_X^2\rangle$. For atoms containing only s electrons, however, $\langle\mu^2\rangle$ and $\langle d_X^2\rangle$ *are* identical and are both given by

$$\langle d_X^2\rangle = \langle\mu^2\rangle = \int r^2\rho(\boldsymbol{r})d^3\boldsymbol{r}. \tag{A6}$$

The fact that $\langle d_X^2\rangle$ equals $\langle\mu^2\rangle$ in atoms such as H, He, Li, and Be suggests an obvious way to incorporate $\langle d_X^2\rangle$ into a dispersion model. Simply replace $\langle\mu^2\rangle$ everywhere in Eq. (A4) by $\langle d_X^2\rangle$. This gives Eq. (20) of the text and confirms our heuristically obtained result.

How well does Eq. (A4) itself perform? C_6 values from Eq. (A4) are presented in Table III for the same atom-atom pairs as in Table I. We see that C_6 values from Eq. (20) are superior to those from Eq. (A4). The MAPE arising from Eq. (A4) is 31.7%, more than twice the MAPE of 14.0% arising from Eq. (20). Our exchange-hole-based model therefore offers, in addition to conceptual beauty, a significant advance over the putative model of Eq. (A4).

Individual values of $\langle d_X^2\rangle$, $\langle\mu^2\rangle$, and α for the atoms comprising our atomic C_6 test set are presented in Table IV. These may be of interest to some readers.

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