The London Approximation and the Calculation of Dispersion Interactions as a Sum of Atom–Atom Terms

Jonathan A. Yoffe and Gerald M. Maggiora

Departments of Biochemistry and Chemistry, University of Kansas, Lawrence, Kansas 66045, U.S.A.

A London approximation utilizing atomic valence state ionization potentials and static polarizabilities yields C_6 results in good agreement with accurate values for a number of systems. Generally there is considerable improvement over the results obtained using the London approximation in conjunction with molecular parameters and reasons for this are discussed.

Key words: London approximation – Atom–atom dispersion interactions.

1. Introduction

One method of calculating the dispersion part of the interaction between two large molecules is to consider the total result as a sum of interactions over the constituent parts of the molecules in question [1]. The division of a molecule into subunits can be performed in a variety of ways. For example, it is possible, and computationally convenient, to consider the total interaction as a sum of atom–atom interactions [1, 2], and two such methods have recently appeared in the literature. Huiszoon and Mulder [3] have determined C, N and H atom–atom potential parameters from *ab initio* dispersion energies for different azabenzene dimers using a fitting procedure. Miller [4, 5], on the other hand, fits experimental molecular static polarizabilities to an empirical function composed of a series of terms related to atom-like polarizabilities, and employs these parameters in the calculation of the induction and dispersion parts of the intermolecular interaction energy. Furthermore, Miller and Savchik [6] have shown that the molecular static polarizabilities of a wide variety of molecules calculated from the atom-like polarizability parameters using the functional form given in Sect. 3, are in excellent agreement with experiment. However, comparable comparisons with accurate data on induction and dispersion energies are considerably more difficult to obtain.

The long-range dispersion energy,

$$E_{\text{disp}} = -C_6 R^{-6} - C_8 R^{-8} - C_{10} R^{-10} \cdots. \tag{1}$$

is characterized by the intermolecular separation, R, and the dispersion coefficients, C_6, C_8, C_{10}, ..., which can in principle be determined from experimental data. The C_6 coefficient is the dominant term in the series and is accurately known for a number of molecular systems. Therefore, it can provide a reasonable test for assessing the adequacy of a theoretical procedure for describing intermolecular dispersion interactions.

In the present work we consider the use of Miller's atomic static polarizabilities in the calculation of the C_6 coefficients of several small molecules for which accurate values are known, and find that very reasonable values are obtained. However, the fact that the atomic parameters used by Miller yield excellent static molecular polarizabilities for an extensive set of molecules is no guarantee that the resulting C_6 values will be accurate as discussed in Sect. 2. Generally, use of the London approximation [7] with molecular values produces C_6 coefficients considerably below accurately known values, although Miller's sum of atomic terms using a London-type formula provides good results. The reasons behind this apparent anomaly will be considered, and the reliability and limitations of Miller's approach to the calculation of intermolecular dispersion interactions will be discussed.

2. Approximate Formulae for $C_6(A-B)$

The interpretation of approximate formulae for $C_6(A-B)$, has been given previously [8, 9] but we include a brief synopsis. Our notation will be that A, B, ... refer to the interacting molecules and $i, j, ...$ to the interacting subunits of the molecules, which in Miller's formalism are atoms. First, we consider values obtained using the molecular properties of the systems involved and express the frequency-dependent polarizability as

$$\alpha(\omega) = \bar{F}/(\bar{\omega}^2 - \omega^2) \tag{2}$$

where $\{\bar{F}, \bar{\omega}\}$ are molecular parameters and will be determined shortly. Then, since $C_6(A-B)$ is defined as [10]

$$C_6(A-B) = \frac{3}{\pi} \int_0^\infty \alpha^A(i\omega)\alpha^B(i\omega) \, d\omega \tag{3}$$

we obtain using Eqs. (2) and (3),

$$C_6(A-B) = \frac{3}{2} \frac{\bar{F}^A \bar{F}^B}{\bar{\omega}^A \bar{\omega}^B (\bar{\omega}^A + \bar{\omega}^B)}, \tag{4}$$

where all quantities are in atomic units [11].

Different choices of the pair $\{\bar{F}, \bar{\omega}\}$ yield different results. The molecular London approximation is obtained if the choices $\bar{\omega} = I$ and $\bar{F} = I^2\alpha(0)$, where I is the molecular ionization potential and $\alpha(0)$ the molecular static polarizability, are made, i.e.

$$C_6^L(A-B)_{mol} = \tfrac{3}{2}\alpha^A(0)\alpha^B(0)I^A I^B/(I^A + I^B). \tag{5}$$

As noted above [9], when this approximation is applied to various small molecular systems it leads to values for C_6 that are generally much lower than the accurate values. It has been pointed out previously [12] that values obtained using the molecular London approximation provide good but not rigorous lower bounds to the true values, a counterexample being provided by the C_6 value for the H_2–H_2 interaction. The Slater–Kirkwood approximation [13], which arises from the choices $\bar{F} = N$, the number of electrons in the molecule, and $\bar{\omega} = (N/\alpha(0))^{\frac{1}{2}}$, i.e.

$$C_6^{SK}(A-B)_{mol} = \tfrac{3}{2}\alpha^A(0)\alpha^B(0)[(\alpha^A(0)/N^A)^{\frac{1}{2}} + (\alpha^B(0)/N^B)^{\frac{1}{2}}]^{-1}, \tag{6}$$

yield C_6 values that are strict upper bounds to the accurate values [12] provided the experimental static polarizabilities are taken to be exact. It can easily be seen that the two methods lead to identical static polarizability results, recovering the experimental value. However, very different C_6 values are obtained, thus confirming the fact that good static polarizability values do not necessarily guarantee comparable C_6 results.

If C_6 is to be written as a sum of constituent contributions, instead of Eq. (2) we express $\alpha(\omega)$ as

$$\alpha(\omega) = \sum_i F_i/(\omega_i^2 - \omega^2) \tag{7}$$

where the $\{F_i, \omega_i\}$ are subunit parameters to be determined. Then from Eqs. (3) and (7) we have

$$C_6(A-B) = \tfrac{3}{2} \sum_{i \in A} \sum_{j \in B} \frac{F_i^A F_j^B}{(\omega_i^A + \omega_j^B)\omega_i^A \omega_j^B} \tag{8}$$

and once again different choices of $\{F_i, \omega_i\}$ yield different results. Recently it has been shown how the $\{F_i, \omega_i\}$ can be thought of in a point charge model context where F_i is a point charge, with $\sum_i F_i = N$, and ω_i its frequency of oscillation [14]. In the Miller formalism the pair $\{F_i, \omega_i\}$ are atomic parameters, and are described below.

3. Miller's Parameters and the London Formula

The functional form that Miller uses for the molecular static polarizability is [6]

$$\alpha(0) = \frac{4}{N}\left[\sum_i \tau_i\right]^2 \tag{9}$$

where τ_i is a parameter for the ith atom in its particular valence state and, as before, N is the number of electrons in the molecule. Then the atomic static polarizability of the ith atom is given by

$$\alpha_i(0) = \frac{4}{N_i}\tau_i^2 \tag{10}$$

with N_i the number of electrons for the ith atom.

Miller [4] considers the dispersion part of the intermolecular interaction energy as a sum over atom–atom interactions, i.e.

$$E_{\text{disp}} \simeq - \sum_{i \in A} \sum_{j \in B} C_6(i-j)/r_{ij}^6 \tag{11}$$

where r_{ij} is the interatomic distance, and i and j are summed over the atoms of molecules A and B, respectively. In addition he incorporates the van der Waals radii of the atoms into the expression and uses a reduced distance instead of r_{ij}. This ensures that the systems do not get too close together. Here, however, we deal with the unreduced distance, in which case the corresponding expression for the long-range interaction between two small molecular systems is usually written as

$$E_{\text{disp}} \simeq - \sum_{i \in A} \sum_{j \in B} C_6(i-j)/R^6 \tag{12}$$

where R is the intermolecular distance between the "centres" of the two molecules. Therefore, combining Eqs. (1) and (12) it follows that

$$C_6(A-B)_{\text{at}} = \sum_{i \in A} \sum_{j \in B} C_6(i-j), \tag{13}$$

which is the quantity we seek to investigate.

For many molecules there is an obvious centre, e.g. the carbon atom in methane, or a general point could be taken to be the centre of mass. For large systems this is not appropriate as there may be considerable differences in the various r_{ij}, such that R no longer provides a satisfactory measure· of the intermolecular separation.

Here we consider $C_6(A-B)_{\text{at}}$ as given by Eq. (13) with the London-type form used by Miller [4, 5]

$$C_6^{\text{L}}(i-j) = \tfrac{3}{2} \alpha_i^{A}(0) \alpha_j^{B}(0) I_i^A I_j^B / (I_i^A + I_j^B) \tag{14}$$

which corresponds to the choices for $\{F_i, \omega_i\}$ of

$$F_i = I_i^2 \alpha_i(0) = 4 I_i^2 \tau_i^2 / N_i, \tag{15a}$$

$$\omega_i = I_i \tag{15b}$$

where I_i and $\alpha_i(0)$ are the ionization potential and static polarizability (see Eq. (10)), respectively, of the ith atom in a given valence state.

4. Results for $C_6(A-A)$[1]

In order to clarify the relationship between the molecular and atomic London approximations in the calculation of dispersion interactions, we consider the interactions between various like species for which the accurate results of Meath et al. [16, 17] are available. The molecular London results can be

---

[1]   Calculations can also be carried out for dispersion coefficients between unlike systems, i.e., $C_6(A-B)$, using equations of Sect. 3.

Table 1. Molecular Parameters

Molecule	Ionization Potential[a]	$\alpha(0)$[b]	Static Polarizability	
			$\alpha(0)$, Eq. (9)	$\bar{\alpha}(0)$, Eq. (18)
H_2	0.5668	5.43	5.32	5.32
H_2O	0.4634	9.64	9.93	10.94
NH_3	0.3730	14.56	15.25	15.93
CH_4	0.4774	17.27	17.55	18.18

[a] Ref. [18].
[b] Refs. [16, 17].

obtained from Eq. (5), which simplifies to

$$C_6^L(A-A)_{mol} = \tfrac{3}{4}\alpha^A(0)^2 I^A. \tag{16}$$

Table 1 contains the molecular parameters required for the evaluation of Eq. (16). Molecular static polarizabilities obtained from Eqs. (9) and (18) are also included for comparison, *vide infra.* The appropriate atomic parameters are given in Table 2. In Table 3 we compare the atomic London values obtained from Eqs. (13) and (14) and the molecular London values obtained from Eq. (16) with the accurate results of Meath et al. [16, 17]. In addition, molecular Slater–Kirkwood values as given by Eq. (6) are reported. Sometimes N^A is replaced by N^{VA}, the number of valence electrons in molecule A, but here we use Eq. (6). For all the molecules except H_2, the Miller method is best, whereas for H_2 the molecular London value is closest to the accurate one. It is interesting to note that an average of the molecular London and Slater–Kirkwood values yields a very reasonable approximate result (see Ref. [9]).

Let us now consider why the values obtained from an atomic sum lie above the molecular London values. Replacing I_i^A of Eq. (14) with I_{min}^A, the smallest valence state ionization potential (VSIP) for a given molecule, and combining Eqs. (13) and (14) yields, for the atomic London case

$$C_6^L(A-A)_{min} = \tfrac{3}{4}\bar{\alpha}^A(0)^2 I_{min}^A \tag{17}$$

Table 2. Atomic Parameters

Atom	Valence State Ionization[a]	VSIP[b]	$\alpha_i(0)$[c]
H	s	0.5000	2.6615
C	tetetete → tetete	0.5355	7.5333
N	te²tetete → tetetete	0.5259	7.9410
O	te²te²tete → te²tetete	0.6762	5.6151

[a] te = tetrahedral ("sp³") hybrid orbitals.
[b] Ref. [15], except H [4].
[c] These values are obtained from τ_i values of Ref. [6] using Eq. (10).

Table 3. Comparison of Dipole–Dipole Dispersion Coefficients

Molecule	$C_6(A-A)^a_{expt}$	$C_6^L(A-A)^b_{at}$	$C_6^L(A-A)^c_{mol}$	$C_6^{SK}(A-A)^d_{mol}$
H_2	12.1	10.6	12.5	13.4
H_2O	45.4	52.4	32.3	71.0
NH_3	89.0	97.5	58.3	131.8
CH_4	129.6	127.5	106.8	170.2

[a] Accurate values taken from Refs. [16, 17].
[b] Atomic London values; Eqs. (13) and (14).
[c] Molecular London values, Eq. (16) using $\alpha(0)$'s from Refs. [16, 17].
[d] Slater–Kirkwood; Eq. (6) using $\alpha(0)$'s as footnote c.

where

$$\tilde{\alpha}^A(0) = \sum_i \alpha_i^A(0) \tag{18}$$

is just the sum of the atomic static polarizabilities given by Eq. (10). From Eqs. (9), (10) and (18), it can be shown that

$$\alpha^A(0) \leqslant \tilde{\alpha}^A(0), \tag{19}$$

which is a rigorous result that holds for the functional forms used in Eqs. (9) and (10)[2]. Combining this result with the observation that $I_{min}^A > I^A$, which holds for a very large number of molecules[3], yields

$$C_6^L(A-A)_{min} > C_6^L(A-A)_{mol}. \tag{20}$$

Since $C_6^L(A-A)_{min}$ represents a *lower bound* to $C_6^L(A-A)_{at}$ it clearly follows that

$$C_6^L(A-A)_{at} > C_6^L(A-A)_{mol}. \tag{21}$$

From the above arguments it also follows that

$$C_6^L(A-A)_{av} > C_6^L(A-A)_{mol}, \tag{22}$$

since $I_{av}^A \geqslant I_{min}^A > I^A$ [4]. Thus, it is also expected that a $C_6^L(A-A)_{mol}$ calculated by replacing I^A with I_{av}^A in the molecular London approximation, Eq. (16), will be in better agreement with the accurately determined value. However, it should be noted that I_{av}^A is not likely to be more than 0.1–0.2 a.u. above I^A for

---

[2]   Note that $\alpha^A(0)$ in Eq. (19) is an approximation to the molecular static polarizability calculated using Eq. (9). Since this number can sometimes be less than the experimental value [6], it does not always hold that $\tilde{\alpha}^A(0) \geqslant \alpha^A(0)_{expt}$, although deviation from experiment is generally quite small.
[3]   Compare the VSIP data in Table I of [4] and Table 4 of [15] with the experimental molecular ionization potentials given in [18].
[4]   A number of choices are possible for I_{av}^A. For example, I_{av}^A can be written as $I_{av}^A = (M^A)^{-1} \sum_{i=1}^{M^A} I_i^A$, where M^A is the number of atoms and I_i^A the VSIP, or as the *weighted* average $I_{av}^A = (N^A)^{-1} \sum_{i=1}^{M^A} N_i^A I_i^A$, where $N^A = \sum_{i=1}^{M^A} N_i^A$.

most molecules so that the resulting $C_6^L(A-A)$ value using I_{av}^A should not get too large.

It is also of interest to consider the sensitivity of the $C_6(A-A)$ coefficients to the parameters used in the calculations. $C_6(A-A)$ values, and hence dispersion interaction energies, will be more sensitive to errors in the static polarizabilities than to errors in the ionization potentials since the square of the static polarizability is used whilst the ionization potential appears only linearly in expressions such as Eqs. (16) and (17). The particular functional form used by Miller and Savchik [6] for the molecular static polarizability ensures that Eq. (19) holds, and this means that the $C_6^L(A-A)_{at}$ value is likely to be higher than the molecular London result due to *both* the polarizability and ionization potential terms. Furthermore, it should be noted that for any London approximation involving a sum over molecular subunits (e.g. bonds), improvements over the molecular London value must be obtained almost entirely from the subunit ionization potentials, since in general $\alpha(0) \sim \sum_i \alpha_i(0)$, where the summation is over all the molecular subunits. However, many "bond" approaches [19–21] do not employ a London-type approximation, and thus the above arguments may not strictly apply in these cases.

Thus, to sum up, the atomic London approximation for $C_6(A-A)$ yields better results than the molecular London approximation due to the functional form of the static polarizability [6] and whenever the minimum and/or average atomic VSIPs are greater than the molecular value. For the average VSIP this is likely to be the case for a large number of systems, regardless of what particular set of VSIP's are chosen (compare [4] and [15]). However, it is important to note that comparisons based on C_6 coefficients only apply to small or medium sized molecules where the intermolecular separation is accurately approximated by R; and, since the C_6 coefficients represent spherically averaged intermolecular interactions, accurate atomic London C_6 values for smaller systems do not necessarily imply that dispersion interactions between large, highly asymmetric molecules will be well described by a sum of London-type atom–atom terms.

The fact that the total molecular values of this paper obtained as a sum of atom–atom terms are good does not ensure the accuracy of the individual atom–atom contributions which become crucial when larger systems are considered. In such cases each atom–atom term must be calculated accurately and not just the total value due to the fact that the dispersion energy is given by an equation of the form shown in Eq. (11) and not Eq. (12). Thus additional tests are needed before the accuracy of the atomic London approximation can be considered entirely satisfactory. Nevertheless, we have shown that for small and medium size systems it may provide a satisfactory and computationally simple method for calculating dispersion energies.

References

1. Claverie, P.: Intermolecular interactions: From diatomics to biopolymers, Chapt. II, Pullman, B. Ed. New York: Wiley 1978
2. Abe, A., Jernigan, R. L., Flory, P. J.: J. Am. Chem. Soc. **88,** 631 (1966)
3. Huiszoon C., Mulder, F.: Mol. Phys. **38,** 1497 (1979)
4. Miller, K. J.: Biopolymers **18,** 959 (1979)
5. Miller K. J., Pycior, J. F.: Biopolymers **18,** 2683 (1979)
6. Miller K. J., Savchik, J. A.: J. Am. Chem. Soc. **101,** 7206 (1979)
7. London, F.: Trans. Faraday Soc. **33,** 8 (1937)
8. Mavroyannis C., Stephen, M. J.: Mol. Phys. **5,** 629 (1962)
9. Amos A. T., Yoffe, J. A.: Chem. Phys. Letters **39,** 53 (1976)
10. Landau L., Lifshitz, E. M.: Electrodynamics of continuous media, Chapt. IX. New York: Pergamon Press 1960
11. Shull H., Hall, G. G.: Nature **184,** 1559 (1959)
12. Langhoff P. W., Karplus, M.: J. Chem. Phys. **53,** 233 (1970)
13. Slater J. C., Kirkwood, J. G.: Phys. Rev. **37,** 682 (1931)
14. Yoffe, J. A.: Theoret. Chim. Acta (Berl.) **52,** 55 (1979)
15. Pilcher G., Skinner, H. A.: J. Inorg. Nucl. Chem. **24,** 937 (1962)
16. Zeiss G. D., Meath, W. J.: Mol. Phys. **33,** 1155 (1977)
17. Thomas G. F., Meath, W. J.: Mol. Phys. **34,** 113 (1977)
18. Herzberg, G.: Electronic spectra and electronic structure of polyatomic molecules, Appendix VI. New York: D. van Nostrand 1966
19. Amos A. T., Crispin, R. J.: Mol. Phys. **31,** 159 (1976)
20. Salem, L.: J. Chem. Phys. **37,** 2100 (1962)
21. Yoffe, J. A.: Theoret. Chim. Acta (Berl.) **51,** 121 (1979)