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# Upper and Lower Bounds to Long-Range Forces between Two Hydrogen Atoms*

Millard H. Alexander
*Department of Chemistry, Harvard University, Cambridge, Massachusetts* 02138

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Bell's technique for the calculation of long-range dispersion-force coefficients is transformed to yield rigorous upper and lower bounds to these coefficients. The bounds involve in a systematic way the negative oscillator strength sums $S(-k)$ of the two interacting atoms. By a slight modification, we are also able to bound the leading relativistic correction to the long-range potential. Application of the method to the interaction between two hydrogen atoms yields extremely tight bounds to all the relevant coefficients.

## I. INTRODUCTION

It is well known that at large interatomic separations the interaction potential between two nonoverlapping spherically symmetric atoms may be expanded in inverse powers of the interatomic separation.[1, 2] In recent years, many authors have attempted to establish error bounds to the coefficients in this expansion in terms of other theoretically or experimentally determined quantities.[3–14] We might mention in particular the work of Weinhold,[7] whereby known van der Waals coefficients are used to predict unknown ones, or the elegant techniques of Langhoff and Karplus[9, 10] and Gordon,[11, 12] whereby bounds to the van der Waals coefficients are obtained from knowledge of the oscillator-strength sums of the individual atoms.

In this paper, we show how the technique developed by Bell[15, 16] to obtain approximate values of the van der Waals coefficients may be easily transformed to yield rigorous bounds. These bounds involve the oscillator-strength sums of the individual atoms. By a slight modification, we are also able to bound the leading relativistic correction to the long-range interaction potential. We then use these results to compute high-accuracy upper and lower bounds to the dominant expansion coefficients in the case of the long-range interaction between two hydrogen atoms.

## II. METHOD

The usual expression for the long-range unretarded interaction between two nonoverlapping spherically symmetric atoms $a$ and $b$ in their ground state is[1, 2]

$$V_{ab}(R) = -\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} C_M^{ab} R^{-M} \quad , \tag{1}$$

where $M = 2(n+m+1)$, $R$ is the interatomic separation, and $C_M^{ab}$ is the coefficient for the ($2n$-pole)–($2m$-pole) dispersion interaction between atoms $a$ and $b$. Explicitly we have, in atomic units,[1, 2]

$$C_M^{ab} = K_{nm}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}\frac{f_j^n(a) f_k^m(b)}{\omega_j^n(a)\omega_k^m(b)[\omega_j^n(a)+\omega_k^m(b)]} \quad , \tag{2}$$

where $K_{nm} = \frac{1}{4}(2n+2m)!/(2n)!(2m)!$ . (3)

In the above expression, the $2n$-pole oscillator strengths[1, 16, 17]

$$f_j^n(a) = 2\omega_j^n(a)\,|\langle O_a|r^n P_n(\cos\vartheta)|j_a\rangle|^2 \tag{4}$$

refer to excitation from the ground state of system $a$ to a($2n$-pole)-allowed excited state $j$ with excitation frequency $\omega_j^n = E_j^n - E_0$. The double summation in (2) includes an integration over the continuum of each atom.

Alternatively, the coefficient $C_M^{ab}$ may be expressed as

$$C_M^{ab} = \frac{2K_{nm}}{\pi}\int_0^{\infty}\alpha_a^n(iu)\alpha_b^m(iu)\,du \quad , \tag{5}$$

involving the integral over imaginary frequency of the $2n$- and $2m$-pole dynamic polarizabilities of atoms $a$ and $b$, namely,[1, 17, 18]

$$\alpha_a^n(\omega) = \sum_{n=1}^{\infty}\frac{f_j^n(a)}{[\omega_j^n(a)]^2-\omega^2} \quad . \tag{6}$$

Most recent attempts at obtaining bounds to the $C_M^{ab}$ have started from Eq. (5) rather than from Eq. (2), being based on the idea that by first setting bounds to the polarizability at imaginary frequency it would then be possible to bound the $C_M^{ab}$ via Eq. (5).[6–13]

We shall present an alternate approach. Following Bell,[15, 16] we define a quantity $E_{nm}$ to be the smaller of the lowest allowed excitation frequencies of atoms $a$ and $b$; in other words,

$$E_{nm} = \min[\omega_1^n(a), \omega_1^m(b)] \quad . \tag{7}$$

Then, if we further define the variables

$$x_j = E_{nm}/\omega_j^n(a) \tag{8}$$

and
$$y_k = E_{nm}/\omega_k^m(b) \quad , \tag{9}$$

we may rewrite Eq. (2) as

$$C_M^{ab} = K_{nm} E_{nm}^{-3} \sum_j \sum_k f_j^n(a) f_k^m(b) \varphi(x_j, y_k) \quad , \tag{10}$$

where the function $\varphi(x, y)$ is given by

$$\varphi(x, y) = x^2 y^2/(x+y) \quad . \tag{11}$$

From their definition, the two variables $x_j$ and $y_k$ are limited to the range $0 \leqslant x_j, y_k \leqslant 1$.

At this point, Bell[15, 16] chose to approximate the function $\varphi(x, y)$ by a finite sum of selected powers of $x$ and $y$, namely,

$$\varphi(x, y) \simeq \sum_p \sum_q A_{pq} x^p y^q \quad , \tag{12}$$

with the coefficients $A_{pq}$ chosen in order that the approximate function be accurate in the range $0 \leqslant x, y \leqslant 1$. Using this approximation, Bell can write[15, 16]

$$C_M^{ab} \simeq K_{nm} E_{nm}^{-3} \times \sum_p \sum_q \sum_j \sum_k A_{pq} f_j^n(a) f_k^m(b) x_j^p y_k^q \tag{13a}$$

or

$$C_M^{ab} \simeq K_{nm} \sum_p \sum_q A_{pq} E_{nm}^{(p+q-3)} S_n^a(-p) S_m^b(-q) \quad . \tag{13b}$$

In going from Eq. (13a) to Eq. (13b), Bell[15, 16] has used the definitions of $x_j$ and $y_k$ [Eqs. (8) and (9)] as well as that of the $2n$- and $2m$-pole oscillator-strength sums, namely,

$$S_n^a(r) = \sum_{j=1}^{\infty} f_j^n(a) [\omega_j^n(a)]^r \quad , \tag{14}$$

and likewise for atom $b$.

Now, since the oscillator strengths $f_j^n(a)$ and $f_k^m(b)$ are by definition positive, we recognize that it would be possible to obtain upper and lower bounds to the $C_M^{ab}$ simply by choosing the coefficents $A_{nm}$ in Eq. (12) in such a way that the resulting power series is always an upper or lower bound to the function $\varphi(x, y)$ in the range $0 \leqslant x, y \leqslant 1$. To do so, we shall proceed as outlined below.

## III. UPPER AND LOWER BOUNDS TO $C_M^{ab}$

We first use simple algebra to write

$$xy(x+y)^{-1} = \tfrac{1}{4}[(x+y) - (x-y)^2/(x+y)] \quad . \tag{15}$$

Recalling the well-known expansion of $(1-z)^{-1}$ for $z < 1$,

$$(1-z)^{-1} = \sum_{r=0}^{\infty} z^r \quad , \tag{16}$$

we may make the identification $z = 1 - \frac{1}{2}(x+y)$ to obtain

$$(x+y)^{-1} = \tfrac{1}{2} \sum_{r=0}^{\infty} [1 - \tfrac{1}{2}(x+y)]^r \quad , \tag{17}$$

which, together with Eqs. (11) and (15), yields[19]

$$\varphi(x, y) = \tfrac{1}{4} xy(x+y) - \tfrac{1}{8} xy(x-y)^2 \sum_{r=0}^{\infty} [1 - \tfrac{1}{2}(x+y)]^r \quad . \tag{18}$$

Since each term in the summation is positive and since the whole sum enters in with a minus sign, it is obvious that truncating the sum at any finite number of terms $N$ will yield an upper bound to the function $\varphi(x, y)$. In other words,

$$\varphi(x, y) \leqslant \varphi_N(x, y) = \tfrac{1}{4} xy(x+y) - \tfrac{1}{8} xy(x-y)^2 \sum_{r=0}^{N} [1 - \tfrac{1}{2}(x+y)]^r \quad . \tag{19}$$

Expanding, we obtain

$$\varphi_N(x, y) = \tfrac{1}{4}(x^2 y + y^2 x) - \tfrac{1}{8} \sum_{r=0}^{N} \sum_{i=0}^{r} \sum_{j=0}^{i} \sum_{k=0}^{2} (-1)^{i+k} \times 2^{-i} \binom{r}{i} \binom{i}{j} \binom{2}{k} x^{i-j-k+3} y^{j+k+1} \quad . \tag{20}$$

Recalling the definitions of $x$ and $y$ [Eqs. (8) and (9)] and of the oscillator-strength sums [Eq. (14)], we may introduce the above result into Eq. (10) to establish the upper bound

$$C_M^{ab} \leqslant \tfrac{1}{4} K_{nm} [S_n^a(-2) S_m^b(-1) + S_n^a(-1) S_m^b(-2)] - \tfrac{1}{8} E_{nm} K_{nm} \sum_{r=0}^{N} \sum_{i=0}^{r} \sum_{j=0}^{i} \sum_{k=0}^{2} \left[ (-1)^{i+k} (\tfrac{1}{2} E_{nm})^i \times \binom{r}{i} \binom{i}{j} \binom{2}{k} S_n^a(-i+j+k-3) S_m^b(-j-k-1) \right] \quad , \tag{21}$$

requiring all the sum rules $S_n(k)$ for

$$-1 \geqslant k \geqslant -N-3 \quad . \tag{22}$$

The first term in Eq. (21), obtained by ignoring the quadruple sum, is itself an upper bound. In the case of the dipole-dipole interaction between identical atoms, this term is

$$\tfrac{3}{4} S_2^a(-2) S_2^a(-1) \quad , \tag{23}$$

which may be written as

$$\tfrac{1}{2} \alpha(a) \langle \psi_0 | (\sum_i r_i)^2 | \psi_0 \rangle \quad . \tag{24}$$

In going from (23) to (24) we have made use of the well-known results that $S(-2)$ is equal to the static dipole polarizability $\alpha$ and that $S(-1)$ is equal to two-thirds the ground-state average $\langle 0|(\sum_i r_i)^2 \times|0\rangle$.[17] It is interesting to note that (24), which we recall to be an upper bound, is none other than Salem's modification of the classic Kirkwood-Müller formula.[20, 21]

In deriving a lower bound to $C_M^{ab}$, we first use Eq. (17) to write

$$\varphi(x, y)=\tfrac{1}{2}x^2y^2\sum_{r=0}^{\infty}[1-\tfrac{1}{2}(x+y)]^r \quad . \tag{25}$$

Since each term in the summation is positive, truncation at any finite number of terms will yield the lower bound

$$\varphi(x, y)\geqslant\varphi_N(x, y)=\tfrac{1}{2}x^2y^2\sum_{r=0}^{N}[1-\tfrac{1}{2}(x+y)]^r \quad . \tag{26}$$

As before, we can substitute this result into Eq. (10), expand, and use the definitions of $x$ and $y$ to write, after some straightforward algebra

$$C_M^{ab}\geqslant\tfrac{1}{2}E_{nm}K_{nm}\sum_{r=0}^{N}\sum_{i=0}^{r}\sum_{j=0}^{i}(-\tfrac{1}{2}E_{nm})^i\binom{r}{i}\binom{i}{j} \times S_n^a(-i+j-2)S_m^b(-j-2) \quad , \tag{27}$$

requiring in this case all the oscillator-strength sums for $-2\geqslant k\geqslant -N-2$. In the dipole-dipole case, the first term in the above expression

$$\tfrac{3}{4}E\alpha(a)\alpha(b) \tag{28}$$

is the well-known London expression,[22] modified by setting the so-called "average excitation energy" for both systems equal to the lowest dipole-allowed transition energy. Both Tang[8] and Kramer[14] have recognized (28) to be a lower bound.

Both Langhoff and Karplus[9, 10] and Gordon[11, 12] have recently developed powerful techniques for obtaining upper and lower bounds to the $C_M^{ab}$ from a knowledge of only the even oscillator-strength sums $S(-2k)$. The bounds derived above require additional information in the form of the odd sums $S(-2k-1)$.

## IV. UPPER AND LOWER BOUNDS TO RELATIVISTIC INTERACTIONS

Recently, Meath and Hirschfelder[23] have shown that for large interatomic separations the relativistic corrections to the usual Hamiltonian yield corrections to the interatomic potential which may be expanded in inverse powers of the interatomic separation $R$. For spherical systems, the leading dipole-dipole term is [23, 24]

$$V_{\text{rel}}(R)=\alpha^2D_4^{ab}(R)R^{-4} \quad , \tag{29}$$

where $\alpha$ is the fine-structure constant. The interaction coefficient $D_4$ is given by

$$D_4^{ab}=\tfrac{1}{2}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}\frac{f_j(a)f_k(b)}{\omega_j(a)+\omega_k(b)} \quad , \tag{30}$$

$f_j$ and $f_k$ being the usual dipole oscillator strengths. We now use the ideas developed above to derive upper and lower bounds to $D_4^{ab}$.

As in Sec. III we define the quantities

$$E=\min[\omega_1(a), \omega_1(b)] \quad , \tag{31}$$

$$x_j=E/\omega_j(a) \quad , \tag{32}$$

and

$$y_k=E/\omega_k(b) \tag{33}$$

to write

$$D_4^{ab}=\tfrac{1}{2}E^{-1}\sum_j\sum_k f_j(a)f_k(b)\chi(x_j, y_k) \quad , \tag{34}$$

where the function $\chi(x, y)$ is defined by

$$\chi(x, y)=xy/(x+y) \quad . \tag{35}$$

From the results of Sec. III, we conclude that $\chi(x, y)$ can be bounded by

$$\chi(x, y)\leqslant\tfrac{1}{4}(x+y)-\tfrac{1}{8}(x-y)^2\sum_{r=0}^{N}[1-\tfrac{1}{2}(x+y)]^r \tag{36}$$

and by

$$\chi(x, y)\geqslant\tfrac{1}{2}xy\sum_{r=0}^{N}[1-\tfrac{1}{2}(x+y)]^r \quad . \tag{37}$$

As before, we can expand Eq. (36) and introduce the result into Eq. (34) to obtain the upper bound

$$D_4^{ab}\leqslant\tfrac{1}{8}[S^a(0)S^b(-1)+S^a(-1)S^b(0)] - \frac{E}{16}\sum_{r=0}^{N}\sum_{i=0}^{r}\sum_{j=0}^{i}\sum_{k=0}^{2}(-1)^{i+k}(\tfrac{1}{2}E)^i \times\binom{r}{i}\binom{i}{j}\binom{2}{k}S^a(-i+j+k-2)S^b(-j-k) \quad , \tag{38}$$

involving the dipole oscillator strength sums $S(k)$ for $0\geqslant k\geqslant -N-2$. Analogously, expansion of Eq. (37) and introduction of the result into Eq. (34) will yield the lower bound

$$D_4^{ab}\geqslant\tfrac{1}{4}E\sum_{r=0}^{N}\sum_{i=0}^{r}\sum_{j=0}^{i}(-\tfrac{1}{2}E)^i\binom{r}{i}\binom{i}{j} \times S^a(-i+j-1)S^b(-j-1) \quad , \tag{39}$$

involving the dipole oscillator-strength sums for $-1\geqslant k\geqslant -N-1$.

## V. NUMERICAL RESULTS FOR THE INTERACTION BETWEEN TWO HYDROGEN ATOMS

The use of the above bounds to long-range interaction coefficients depends on the availability of some or all of the oscillator-strength sums for atoms $a$ and $b$. For the hydrogen atom, Bell,[16, 25] extending some earlier work of Dalgarno and collaborators,[26, 27] showed that the negative $2n$-pole oscillator-strength sums $S_n(-k)$ could be related to the first column of a matrix $A^n_{r,s}$:

$$S_n(-k) = 2^{k+1-2n} n(2n)!\,A^n_{k,0} \ , \tag{40}$$

where the individual matrix elements $A^n_{r,s}$ are generated by the recursion relation

$$A^n_{r,s} = [A^n_{r-1,s-1} + (2s+2n+2)A^n_{r-1,s} + (s+1)(s+2n+2)A^n_{r-1,s+1}]/4(s+n) \ , \tag{41}$$

subject to the restrictions $A^n_{0,0}=1$ and $A^n_{r,s}=0$ for $r, s<0$ and for $s>r$.

From Eqs. (40) and (41) it is a simple matter to generate all the sums required in Eqs. (21), (27), (38), and (39). In Table I, we show the behavior as a function of the truncation limit $N$ of the upper and lower bounds to the dipole-dipole dispersion coefficient for the interaction between two hydrogen atoms. We see that convergence is both uniform and swift. We note that the upper bound of Eq. (21) converges somewhat faster than the lower bound of Eq. (27). Indeed, if we use only the sum rules $S(k)$ for $-1 \geqslant k \geqslant -4$, the upper bound of 6.525 is in error by 0.4% whereas the lower bound of 6.430 is in error by 1.1%.

In Table II appear values of the important multipole-dispersion coefficients as well as the dipole-dipole relativistic coefficient in the case of the interaction between two ground-state hydrogen atoms. The results shown were obtained with a truncation limit of $N=33$. We see that the bounds are extremely tight and are in good agreement with previously calculated values of the interaction constants.

TABLE I. Convergence of upper and lower bounds to long-range dipole-dipole interaction between two hydrogen atoms.[a]

| $N$ | $C_{\text{upper}}$[b] | $C_{\text{lower}}$[c] |
|---|---|---|
| 0 | 6.574 219 | 5.695 313 |
| 1 | 6.524 780 | 6.288 574 |
| 2 | 6.508 816 | 6.430 710 |
| 3 | 6.503 087 | 6.473 003 |
| 4 | 6.500 845 | 6.487 834 |
| 5 | 6.499 899 | 6.493 732 |
| 10 | 6.499 077 | 6.498 716 |
| 15 | 6.499 033 | 6.498 984 |
| 20 | 6.499 028 | 6.499 017 |
| 25 | 6.499 027 | 6.499 024 |
| 30 | 6.499 027 | 6.499 026 |

[a] Exact value is $C=6.499\,027$; see Table II.

[b] Equation (21) of text.

[c] Equation (27) of text.

TABLE II. Coefficients of long-range interaction between two hydrogen atoms.

| $C_M$[a] | Upper bound | Lower bound | Previous result[b] |
|---|---|---|---|
| $C_6$ | 6.499 026 71 | 6.499 026 60 | 6.499 026 7[c, d, e] |
| $C_8$ | 124.399 086 | 124.399 069 | 124.399 1[c] |
| $C_{10}$[f] | 1135.214 04 | 1135.213 91 | 1135.214[c] |
| $C_{10}$[g] | 2150.614 42 | 2150.614 04 | 2150.614[c] |
| $D_4$[h] | 0.462 806 8 | 0.462 805 2 | 0.462 806 5[i] |

[a] The subscript denotes the associated inverse power of the interatomic separation in $V(R) = \sum_M C_M R^{-M}$.

[b] This column contains only the most accurate of the values available in the literature.

[c] W. Kołos, Int. J. Quantum Chem. 1, 169 (1967); variation-perturbation results.

[d] Reference 4 of text, error bounds from perturbation theory using operator techniques.

[e] M. O'Carrol and J. Sucher, Phys. Rev. Letters 21, 1143 (1968); exact calculation.

[f] Quadrupole-quadrupole interaction.

[g] Dipole-octupole interaction.

[h] Relativistic interaction, $V_{\text{rel}}(R) = D_4 \alpha^2 R^{-4}$.

[i] Reference 24 of text; variation-perturbation results.

TABLE III. Upper and lower bounds to the long-range dipole-dipole interaction coefficient between two helium atoms.[a, b]

| $C_{\text{upper}}$ | $C_{\text{lower}}$ | Oscillator-strength sums |
|---|---|---|
| 1.461 | 1.446 | $S(-1) - S(-6)$[c] |
| 1.479 | 1.467 | $S(-1)$[d] |
| | | $S(-2)$[e] |
| | | $S(-3) - S(-6)$[c] |
| 1.459 | 1.444 | $S(-1)$[d] |
| | | $S(-2) - S(-6)$[f] |
| 1.473 | 1.460 | $S(-1)$[d] |
| | | $S(-2)$[e] |
| | | $S(-3) - S(-6)$[f] |
| 1.484 | 1.474 | $S(-1)$[d] |
| | | $S(-2)$[e] |
| | | $S(-3)$, $S(-5)$[f] |
| | | $S(-4)$, $S(-6)$[g] |

[a] Results from Eqs. (21) and (27) of text with truncation limit $N$ chosen so as to incorporate all dipole sums $S(k)$ with $-1 \geq k \geq -6$.

[b] Exact value is $C_6 = 1.4605 \pm 0.0025$; Ref. 5 of text.

[c] Reference 24 of text.

[d] C. L. Pekeris, Phys. Rev. 115, 1216 (1959).

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[f] Reference 29 of text.

[g] Reference 10 of text.

## VI. DISCUSSION

In view of the accurate results obtained above, one would be tempted to move on to larger systems. Values for some or all of the dipole oscillator-strength sums $S(k)$ for $-1 \geqslant k \geqslant -6$ are available in the literature, in particular for the rare gases.[10,27-29] These sums are usually obtained from a semiempirical fit of the available experimental absorption and dispersion spectra of the atom in question. Unfortunately, as Langhoff and Karplus[10] and Gordon[12] have pointed out, the error in these semiempirical oscillator-strength sums is unknown, with the result that the numerical bounds to the dipole-dipole dispersion coefficients depend closely on which set of sums is used. Hence, the bounds are no longer rigorous.

To illustrate this problem, we have computed bounds to the dipole-dipole coefficient for the interaction between two helium atoms using Eqs. (21) and (27) and various published values of the oscillator-strength sums $S(k)$ for $-1 \geqslant k \geqslant -6$. The results are shown in Table III. We see that the "bounds" vary by several percent, depending on which values of the sums are used. Indeed, in several cases, the lower bound lies above the true value. It would be possible to circumvent this difficulty by explicitly incorporating the uncertainty in the oscillator-strength sums into Eqs. (21) and (27). This would probably lead to bounds on the $C_M^{ab}$ too loose to be of great interest.

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