Generating van der Waals coefficients to arbitrary orders of the atom–atom interaction

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Abstract

A recursion procedure is presented for deriving the dispersion coefficients \( C_k^{(s)} \) of the van der Waals interaction between two atoms in spherically symmetric ground states to arbitrary high orders \( k \) of perturbation theory. The complete asymptotic expansion for the dispersion interaction between two ground-state hydrogen atoms up to \( C_{30} \) (including terms arising from tenth order perturbation theory) are then generated using a pseudo-state expansion for the two atom Green’s function.

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The van der Waals attraction determines the interaction between two atoms(molecules) at large distances, \( R \) from each other. The van der Waals interaction impacts the precise determination of inter-atomic potential curves [1], and has a major impact on the binding and properties of many molecules [2–7]. Most recently, the development of cold-atom physics [8] has led to increased interest in determining the van der Waals coefficients of the alkali atoms [9–12].

The van der Waals interaction between any two atoms is usually developed as a power series of the inverse inter-atomic distance \( R^{-1} \)

\[
E_{\text{disp}} = - \sum_{s=6} C_s \frac{R_s}{R},
\]

where the \( C_s \) are the dispersion coefficients. The most widely used theoretical techniques to determine the \( C_6 \) use sum rules based on the optical properties of the two atoms [13]. These sum rules are derived by applying second order perturbation theory to the multipole moments of the interaction \( \hat{V}(R) \) between the two atoms. In the literally, thousands of calculations of the dispersion coefficients one can only identify very few calculations that go beyond second order perturbation theory (see [12,14–17] and references therein). Indeed, a general approach to determine the dispersion coefficients for the simplest possible case of two ground-state hydrogen atoms does not exist. In the present Letter, higher order perturbation theory is used to develop a recursive procedure that can be used to generate dispersion coefficients of arbitrary \( s \) while incorporating terms that arise from all orders of perturbation theory.

The interaction between the atomic multipole moments in the asymptotic region with \( R \gg a_0 \) can be written in the form of an power series of \( R^{-1} \) [14], e.g.,

\[
\hat{V}(R) = \sum_{l=1}^{\infty} \sum_{l'=1}^{\infty} \hat{v}_{l'l'}(\mathbf{n}) R^{l+l'-1},
\]

\[
\hat{v}_{l'l'}(\mathbf{n}) = (-1)^l \sqrt{\frac{(2L)!}{(2l')!(2l)!}} C_l(n) \cdot \left[ \hat{Q}_l \otimes \hat{Q}_{l'} \right]_{l'},
\]

where \( L = l + l' \), \( \hat{Q}_l = r^l C_l(\theta, \phi) \) is the operator of atomic \( 2^l \)-pole electric moment, the unit vector \( \mathbf{n} = R/R \) points from the first atom (unprimed) to the second atom (primed). The \( C_l(\theta, \phi) \) and \( C_L(n) \) are the modified spherical functions [18] of atomic electron’s position vector

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\( \mathbf{r} = \{r, \theta, \phi\} \) and the inter-atomic unit vector \( \mathbf{n} \), respectively.

The dispersion interaction energy \( E^{\text{disp}} = E(R) - E_0 \) (here \( E(R) \) is the joint energy of two atoms, and \( E_0 = E_E + E_g \) is the energy of the independent atoms in their ground \( s \)-states \( |0\rangle = |g\rangle |g\rangle \)) and the wave function of the two-atomic system \( \psi \) may be expanded in power series of the operator (2) (see, e.g. [19], [14]):

\[
E^{\text{disp}} = \langle 0 | \hat{V} | \psi \rangle = \sum_{k=2}^{\infty} E^{(k)},
\]

(4)

\[
\psi = |0\rangle - G(\hat{V} - E^{\text{disp}})|\psi\rangle = \sum_{k=0}^{\infty} \psi^{(k)},
\]

(5)

where \( \psi^{(0)} = |0\rangle \). \( G \) is the reduced Green’s function which may be derived by subtraction of the ground-state term from the spectral expansion of the complete Green’s function \( G_E \) in the limit of \( E \rightarrow E_0 \):

\[
G(r_1, r_2; r_1', r_2') = \lim_{E \rightarrow E_0} \left\{ G_E(r_1, r_2; r_1', r_2') - \frac{\langle r_1 | g \rangle \langle r_1' | g \rangle \langle g | r_2 \rangle \langle g | r_2' \rangle}{E_0 - E} \right\}.
\]

(6)

The normalization condition \( \langle \psi | 0 \rangle = \langle 0 | \psi \rangle = 1 \) yields \( \langle \psi^{(k)} | 0 \rangle = \delta_{k0} \).

The recursion relation for the \( (k - 1) \)-th order correction to the wave function follows from (4) and (5):

\[
\psi^{(k-1)} = -G \psi^{(k-2)} + \sum_{k=2}^{k=2} E^{(k)} G |\psi^{(k-1-k)}\rangle
\]

(7)

where \([k/2]\) stands for the integral part of the fraction \( k/2 \) and

\[
\psi^{(k)} = \sum_{k_1=2}^{k_2} \sum_{k_2=2}^{k_2} \cdots \sum_{k_p=2}^{k_p} (-1)^{k-1+k_2}
\]

\[
\times E^{(k_1)} E^{(k_2)} \cdots E^{(k_p)} B^{(k-k_2-1)}_p |0\rangle,
\]

(8)

where \( k_2 = k_1 + k_2 + \ldots + k_p \), and \( k_2 \) is the maximal value of \( k_1 \) defined by \( k_2 = k - 2p - 1 \) and \( k_2 = k - 2p - 1 - \sum_{j=1}^{p-1} (k_j - 2) \) and obeying the inequalities \( 2p \leq k_2 \leq k - 2 \). The operators \( B^{(q)}_p \) transforming the ground-state wave function \( |0\rangle \) into \( |\psi^{(k-1)}\rangle \) may be determined from the recursion relations

\[
B^{(q)}_p = GB^{(q)}_{p-1} + UB^{(q-1)}_p, \quad U = G \hat{V},
\]

(9)

\[
p = 1, \ldots, [k/2] - 1, \quad q = 1, \ldots, k - 2p - 1,
\]

and the starting equations

\[
B^{(0)}_p = 0; \quad B^{(1)}_p = G^2 U; \quad B^{(q)}_0 = U^q.
\]

(10)

With the use of (7) and (8) the terms of the series in (4) may be presented as

\[
E^{(k)} = \langle 0 | \hat{V} | \psi^{(k-1)}\rangle = \sum_{p=0}^{[k/2]-1} \langle 0 | \hat{V} | \psi^{(k-1)}\rangle = \sum_{p=0}^{[k/2]-1} E^{(k)}_p,
\]

(11)

where

\[
E^{(k)}_p = \sum_{k_1=2}^{k_2} \sum_{k_2=2}^{k_2} \cdots \sum_{k_p=2}^{k_p} (-1)^{k-1+k_2} E^{(k_1)}_1 E^{(k_2)}_2 \cdots E^{(k_p)}_p A^{(k-k_2-k_3-\ldots-k_p)}_p
\]

(12)

and

\[
A^{(q+1)}_p = \langle 0 | \hat{V} B^{(q)}_p | 0 \rangle.
\]

(13)

The summation over \( k \) in Eq. (4) and \( k_1 \) in Eq. (7) starts from \( k = 2 \), since \( E^{(1)} = \langle 0 | \hat{V} | 0 \rangle = 0 \). In Eq. (11) for \( E^{(2)} \) and \( E^{(3)} \) only one term with \( p = 0 \) appears:

\[
E^{(2)} = E^{(2)}_0 = A^{(2)}_0 = \langle 0 | \hat{V} U | 0 \rangle,
\]

(14)

\[
E^{(3)} = E^{(3)}_0 = A^{(3)}_0 = \langle 0 | \hat{V} U^2 | 0 \rangle.
\]

(15)

For arbitrary order, the \( E^{(k)}_0 \) term of Eq. (11), which is usually referred to as the ‘diagram’ term, consists of one compound matrix element,

\[
E^{(k)}_0 = (-1)^{k-1} A^{(k)}_0 = (-1)^{k-1} \langle 0 | \hat{V} U^{k-1} | 0 \rangle.
\]

(16)

For the ground-state atoms, this term is negative for even \( k \) and positive for odd \( k \) and is the largest contribution to the sum of Eq. (11). Therefore, the even-order terms of the energy (4) are attractive, whereas odd-order terms are repulsive.

Starting from \( k = 4 \), the ‘off-diagram’ terms, \( E^{(k)}_p \) with \( p \geq 1 \) appear in Eq. (11). Every ‘off-diagram’ term may consist of several terms, involving lower-order energy corrections:

\[
E^{(4)}_1 = -E^{(2)} A^{(2)}_1,
\]

(17)

\[
E^{(5)}_1 = E^{(2)} A^{(3)}_1 - E^{(3)} A^{(2)}_1,
\]

(18)

\[
E^{(6)}_1 = -E^{(2)} A^{(4)}_1 + E^{(3)} A^{(3)}_1 - E^{(4)} A^{(2)}_1,
\]

(19)

\[
E^{(6)}_2 = -E^{(2)} A^{(2)}_2.
\]

(20)

One can continue generating expressions indefinitely. Explicit expressions for all terms up to tenth order can be found in [20].

Expressions for the factors \( A^{(q)}_p \) may be written on the basis of Eqs. (13), (9) and (10). It is important to note, that \( A^{(q)}_p > 0 \), so the sign of the term \( E^{(k)}_p \) of Eq. (12), is \((-1)^{k+p-1}\) and the sign \((-1)^{k-1}\) of the leading term \( E^{(k)}_0 \) in the sum (11) determines the sign of the \( k \)-th order correction.

Using the power series for the asymptotic interaction (2), every factor (13) and hence, every energy correction (11) may be expanded in power series of \( R^{-1} \). The sum of all multi-polarities for each of two atoms in every matrix element is even due to parity conservation. Hence, the even-order terms of Eq. (11) will include only even
powers of $R^{-1}$, starting from $R^{-6}$ and the odd-order terms include only odd powers of $R^{-1}$, starting from $R^{-11}$.

After separating the even-order part from the odd-order part of the series (11)

$$E_{\text{disp}} = E_{\text{even}} + E_{\text{odd}},$$

the equations for energy may be converted into equations for van der Waals coefficients. The even-order part of the energy equations (4), consisting of the $E^{(2n)}$ terms contributes to Eq. (1) with even powers of $R^{-1}$,

$$E_{\text{even}} = - \sum_{n=1}^{\infty} \sum_{j=0}^{\infty} \frac{C_{6n+2j}^{(2n)}}{R^{6n+2j}} = - \sum_{m=1}^{\infty} \frac{C_{2m}}{R^{2m}},$$

where the sum in $n$ runs over the orders $k = 2n$ of the perturbation theory for the atom–atom interaction (2), the sum in $\lambda$ runs over the overall orders $(4n + 2\lambda)$ of the multipole expansions for the asymptotic interaction operators in the terms (12) for the energy correction (11). Thus, the two-fold series may include several terms with one and the same power of $R^{-1}$ from different orders $n$ and $\lambda$ which hold the relation $s = 2m + n + 2\lambda$.

These terms are combined in a single series over $2m$ with positive constants.

The odd-power parts of Eq. (4) with $s = 2m + 5$ come from the terms with $k = 2n + 1$ and give a positive (repulsive) contribution to the dispersion energy. It is written as

$$E_{\text{odd}} = - \sum_{n=1}^{\infty} \sum_{j=0}^{\infty} \frac{C_{6n+5+2j}^{(2n+1)}}{R^{6n+5+2j}} = - \sum_{m=3}^{\infty} \frac{C_{2m+5}}{R^{2m+5}},$$

with the $C_{2m+5}$ being negative.

Expressions for the constants $C_{(k)}$ of (1) are derived from expansion of the corresponding energy correction $E^{(k)}$ given by Eqs. (11)–(13) as a power series in $R^{-1}$. The van der Waals coefficients $C_{(k)}$ replace the energies $E^{(k)}$, and the factors $A_{p}^{(k)}$ are replaced by coefficients $a_{p}^{(k)}$.

By analogy with (11), it is convenient to present a separate term of the $k$th-order constant $C_{(k)}$ as

$$C_{s}^{(k)} = \sum_{p=0}^{[k/2]-1} C_{p,s}^{(k)},$$

where $[k/2]$ is the integer part of $k/2$ and

$$C_{p,s}^{(k)} = (-1)^{k+p} \sum_{k_1=2}^{k} \sum_{k_2=2}^{k} \cdots \sum_{k_{p-1}=2}^{k} \sum_{s_1=0}^{s} \cdots \sum_{s_{p-1}=0}^{s} \frac{(-1)^{s_2} C_{n_1}^{(k_1)} C_{s_1}^{(k_2)} \cdots C_{s_{p-2}}^{(k_{p-2})}}{E_{p,a} - E_{0}} a_{p}^{(k)},$$

with $s_{p} = s_{1} + s_{2} + \ldots + s_{p}$. The summation over each $s_{i}$ ($i = 1, 2, \ldots, p$) starts at a lower limit, $(t_{i} = 3k_{i} + 2$ for odd $k_{i}$) that depends on that value of $k_{i}$. The smallest value of $s = s_{p}$ for the $k_{G} = k_{S} - k_{G}$ term is denoted $t_{G}$. The upper limits are given by $t_{p}^{k_{i}} = s_{1} + 1$ and $t_{p}^{k_{i}} = s_{1} + 1 - k_{G} = s_{1} + 1 - \sum_{i=1}^{3} (s_{i} - t_{i})$ with $t_{2} = t_{1} + 1$, $t_{2} + \ldots + t_{p}$. The inequality, $s_{p} \leq s_{1} - t_{G}$ constrains the sums. The first few terms are,

$$C_{0,0}^{(k)} = (-1)^{k} a_{0,0}^{(k)}$$

$$C_{1,0}^{(k)} = (-1)^{k+1} \sum_{k_{1}=2}^{k} \sum_{s_{1}=0}^{s_{1}} C_{(k_{1})}^{(k_{1})} C_{s_{1}}^{(k_{2})} a_{2, s_{1} - s_{1}}^{(k_{2})}$$

$$C_{2,0}^{(k)} = (-1)^{k+4} \sum_{k_{1}=2}^{k} \sum_{k_{2}=2}^{k} \sum_{s_{1}=0}^{s_{1}} \sum_{s_{2}=0}^{s_{2}} \sum_{s_{3}=0}^{s_{3}} (-1)^{s_{1}+s_{2}+s_{3}} C_{(k_{1})}^{(k_{1})} C_{(k_{2})}^{(k_{2})} a_{2, s_{1} - s_{1}, s_{2} - s_{2}}^{(k_{2})} a_{2, s_{3} - s_{3}}^{(k_{3})},$$

The identities for the fifth and sixth order terms are

$$C_{5}^{(s)} = -a_{0,0}^{(5)} + \sum_{s_{1}=0}^{s_{1}} C_{(s_{1})}^{(s_{1})} C_{(s_{1})}^{(s_{1})} a_{1, s_{1} - s_{1}}^{(s_{1})}$$

$$C_{6}^{(s)} = a_{0,0}^{(6)} + \sum_{s_{1}=0}^{s_{1}} C_{(s_{1})}^{(s_{1})} C_{(s_{1})}^{(s_{1})} a_{1, s_{1} - s_{1}}^{(s_{1})} + \sum_{s_{1}=0}^{s_{1}} C_{(s_{1})}^{(s_{1})} C_{(s_{1})}^{(s_{1})} a_{1, s_{1} - s_{1}}^{(s_{1})}$$

$$+ \sum_{s_{1}=0}^{s_{1}} C_{(s_{1})}^{(s_{1})} C_{(s_{1})}^{(s_{1})} a_{1, s_{1} - s_{1}}^{(s_{1})} + \sum_{s_{1}=0}^{s_{1}} C_{(s_{1})}^{(s_{1})} C_{(s_{1})}^{(s_{1})} a_{1, s_{1} - s_{1}}^{(s_{1})}$$

The complete tabulation of expressions up to tenth order are given elsewhere [20].

The quantities $a_{p}^{(k)}$ may be presented in terms of two-atomic matrix elements, for which the radial matrix elements are

$$\rho_{p_{1}p_{2}p_{3} \ldots p_{t}}^{(j_{1}j_{2} \ldots j_{t})} = \langle 0 \mid r^{p_{1}} r^{p_{2}} \cdots r^{p_{t}} (g_{j_{1}j_{2} \ldots j_{t}}) r^{p_{t+1}} \cdots (g_{j_{i+1}j_{i+1}}) r^{p_{i+1}} \cdots (g_{j_{t}j_{t}}) r^{p_{t}} \cdots (g_{j_{1}j_{1}}) r^{p_{1}} \mid 0 \rangle,$$

where $p_{i}$ are non-negative integers with $\sum_{i=1}^{t} p_{i} = p$, and $g_{j_{i}j_{i}}$ is a two-atomic radial Green’s function which can be written in pseudo-state notation [21–23, 12] as

$$\left( g_{j_{1}j_{2}} (r_{j_{1}} r_{j_{2}}) r_{j_{1}+1} r_{j_{2}+1} \right) = \sum_{n_{1}, n_{r}} \left( r_{j_{1}} \mid n_{1} j_{1} \rangle \langle n_{1} j_{1} \mid r_{j_{1}+1} \rangle \langle n_{1} j_{1} \mid n_{r} j_{r} \rangle \langle n_{r} j_{r} \mid r_{j_{r}+1} \rangle \right) (E_{n_{r}j_{r}} - E_{0})^{1/p_{r}}$$

where $n_{i}$ denotes a radial pseudo-state with angular momentum $J_{r}$. The $l_{i}$ in Eq. (31) denote the polarity of the transitions between those states. For $s$-state atoms $J_{1} = l_{1}$, $J_{k-1} = l_{k}$, and using the notation, $s = 3k + 2\lambda$, the second order term is

$$a_{p=6+2l}^{(2)} = \sum_{k_{1}=1}^{s_{1}} \frac{(2\lambda + 4)!}{(2l_{1} + 1)! (2l_{1} + 1)! (2l_{1} + 1)!} \frac{l_{1}^{l_{1}} l_{1}^{l_{1}}}{l_{1}^{l_{1}} l_{1}^{l_{1}}}.$$
and the radial matrix element is

\[
\langle r_1', r_2', \ldots | r_1 | \rangle = \sum_{\ell_1, \ldots, \ell_n} \frac{\langle g, 0 | r_1 | i_1, J_1 \rangle \langle i_1, J_1 | r_2 | i_2, J_2 \rangle \langle i_2, J_2 | r_3 | \ldots | g, 0 \rangle}{(E_{i_1'} - E_0)^{1/2}} \times \langle J_1', J_2', \ldots | r_1 | r_2 | r_3 | \ldots \rangle,
\]

where \( E_{i_1} = E_{i_1} + E_{i_2} \). The third-order term with \( s = 3k + 2a + 2 \)

\[
a_{[1]}^{(3)} = (4 + \lambda) \sum_{\ell_1, \ell_2, \ell_3} A_{\ell_1, \ell_2, \ell_3} A_{\ell_1', \ell_2', \ell_3'} \times B_{\ell_1, \ell_2, \ell_3} B_{\ell_1', \ell_2', \ell_3'},
\]

where \( A_{\ell_1, \ell_2, \ell_3} \) and \( B_{\ell_1, \ell_2, \ell_3} \) have been given previously [14,16].

The factors \( A_{\ell_1, \ell_2, \ell_3} \) consist of all the distinguishable expressions that can be obtained by distributing the \( p \) additional Green's functions among the existing Green's functions in Eq. (31). For example, one has:

\[
A_{\ell_1, \ell_2, \ell_3} = \sum_{i_1, i_2} \sum_{J_1, J_2} \sum_{l_1, l_2} \sum_{J_{l_1}, J_{l_2}} A_{i_1, i_2} A_{J_1, J_2} A_{l_1, l_2} A_{J_{l_1}, J_{l_2}}
\]

with

\[
A_{i_1, i_2} = (\ell_1, \ell_2) \langle g, 0 | r_1 | i_1, J_1 \rangle \langle i_1, J_1 | r_2 | i_2, J_2 \rangle \langle i_2, J_2 | \ldots | g, 0 \rangle/[(E_{i_1'} - E_0)^{1/2}].
\]

For an arbitrary even-order term \( a_{[2n]}^{(2a)} = \sum_{i_1, \ldots, i_{2n}} \sum_{J_1, \ldots, J_{2n}} \sum_{l_1, \ldots, l_{2n}} \sum_{J_{l_1}, \ldots, J_{l_{2n}}} \sum_{k_1, \ldots, k_{2n}} A_{i_1, \ldots, i_{2n}} A_{J_1, \ldots, J_{2n}} A_{l_1, \ldots, l_{2n}} A_{J_{l_1}, \ldots, J_{l_{2n}}} \times C_{k_1, \ldots, k_{2n}} C_{J_{k_1}, \ldots, J_{k_{2n}}} \times P_{i_1, \ldots, i_{2n}, J_1, \ldots, J_{2n}, l_1, \ldots, l_{2n}, J_{l_1}, \ldots, J_{l_{2n}}}
\]

where \( \lambda = 0, 1, \ldots \) and \( P \) is the generalization of Eqs. (36)-(38) to additional intermediate states.

The angular factor \( Q \) is written

\[
Q_{i_1, \ldots, i_n, J_1, \ldots, J_n, l_1, \ldots, l_n} = \left( \prod_{n=1}^{n} \left( \frac{[L_l + 1]}{[J_1]} \right) \right)^{1/2} \times C_{J_{l_1}, J_{l_2}, \ldots, J_{l_n}} C_{J_{l_1}'}, \ldots, C_{J_{l_n}'} \times P_{i_1, \ldots, i_n, J_1, \ldots, J_n, l_1, \ldots, l_n, J_{l_1}, \ldots, J_{l_n}}
\]

with

\[
L_l = l_1 + l_1', \quad i = 1, 2, \ldots, n
\]

and

\[
\sum_{i=1}^{2n} L_i = 2\lambda + 4n.
\]

For \( n = 2 \) the product over \( j \) of this equation turns into unity. Eq. (41) includes the product of \((4n - 4)\) angular coefficients, of which \((3n - 3)\) are Clebsch-Gordan coefficients and the other \((n - 1)\) are \(9j\) symbols [18]. Eq. (41) is completely general and is valid for all orders of perturbation theory. The sums in Eq. (40) run over all possible values that are compatible with parity and angular momentum selection rules with the restriction that \( l > 0 \). The number of terms in Eq. (40) increases rapidly as \( n \) and \( \lambda \) increase. To put this in perspective, there were 33,450,435 different terms for \( C_{20}^{(6)} \). The angular coefficients are always positive.
The factors $P^{i_1f_1,i_2f_2,...,i_{2n+1}f_{2n+1}}_{j_1J_1,j_2J_2,...,j_{2n+1}J_{2n+1}}$ are combinations of the $(2n+1)$th-order radial matrix elements, similar to those of Eqs. (36)–(38).

The radial matrix elements were computed by diagonalizing the non-relativistic Hamiltonian for hydrogen in an orthonormalized basis of Laguerre type orbitals [16] with $N$ functions per $J$. Once the radial matrix elements of the pseudo-states are determined, the calculation of the $C_s$ reduce to the multiple summations over combinations of radial matrix elements.

Care must be taken in the evaluation of the radial sums since the number of terms in the pseudo-state sum. The first term of 10th-order, namely $C_{15}$ for almost all of the basis sets of reasonable size, typically $N = 6$ for a 10th-order calculation results in $10^{14}$ terms in the pseudo-state. The time taken can grow explosively as $N$ increase. For example, setting $N = 6$ for a 10th-order calculation results in $10^{14}$ terms in the pseudo-state sum. The first term of 10th-order, namely $C_{30}^{(10)}$ has 1764 different angular combinations, so one has to sum with $1.8 \times 10^{17}$ terms! This would give a total calculation time of 57 years on a single CPU machine with an evaluation rate of $10^{10}$ terms/s.

The problem is reduced to manageable proportions by constructing super-matrices formed from products of radial matrix elements summed over the intermediate state. This permitted calculations with pseudo-state basis. The factorial-type increase of the $C_s$ is evident in Table 1. These coefficients are complete for $k = 6$.

The $C_s = \sum C_s^{(k)}$ dispersion coefficients up to $s = 30$ are presented in Table 1. These coefficients are complete in that all the contributing orders $k$ of perturbation theory are included. The relative contributions of the three lowest orders of perturbation theory to each $C_s$ are listed. The relative size of the higher order terms increases monotonically for the even and odd terms with the net contribution from the higher order terms being larger than the second order for $C_{30}$. For the odd $C_s$, the fifth order and high order terms comprise 13% of $C_s$ by $s = 29$.

The factorial-type increase of the $C_s$ with $s$ evident in Table 1 is expected since it was shown long ago that the van der Waals expansion was an asymptotic expansion [24,25]. This behavior occurs because of the use of Eq. (2) in regions of space where it is no longer valid [6,21,22,24,25]. It is known that the perturbation theory of the Stark series in hydrogen is also asymptotic in perturbation order due to the unbounded nature of the dipole operator [26]. The multipole operator, Eq. (3) is also an unbounded operator and this results in an asymptotic dispersion series in multipole order [20]. The increasing size of the fourth and higher order terms at increasing $s$ does raise the possibility that the higher order terms ($k$) in the van der Waals expansion become increasingly important as $s$ increases.

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The digits that believed to have some uncertainty are underlined. The relative importance of the three lowest order terms is shown as the parameters $C_s^{(k=2)}/C_s^{(k=4)}$ and $C_s^{(k=4)}/C_s^{(k=6)}$ where $k_0 = 2(3)$ for even(odd) $s$. The notation $a/b$ is used to represent $a \times 10^b$.

The present Letter describes the evaluation of the dispersion interaction to all orders of perturbation theory. The only limitations on the ability to extend the calculation indefinitely are those imposed by computing power. It certainly would be interesting to apply the Fourier transform technique of Koide et al. [21,22] to the present approach since this would probably permit the construction of a mathematically well-behaved dispersion interaction that was valid for all polarities and to all orders of perturbation theory. This would then permit calculation of the dispersion interaction to arbitrary precision (at least for atomic hydrogen) without any of the concerns that arise from the use of an interaction that is only valid in the asymptotic region.

References