Third-order perturbation theory for van der Waals interaction coefficients

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The third-order expression for the dispersion interaction between two atoms is written as a sum over lists of transition matrix elements. Particular attention is given to the $C_3/R^6$ interaction which occurs in the homonuclear case when one atom is in an $S$ state and the other is in a $P$ state. Numerical values of the $C_3$ coefficient are given for the homonuclear alkali-metal dimers. The size of the $C_3$ dispersion coefficient ratio increases for the heavier alkali-metal atoms. The $C_{11}$ and $C_{13}$ coefficients between two helium atoms and lithium atoms in their ground states are also given.

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I. INTRODUCTION

One of the more interesting spin-offs in the field of cold-atom physics has been the development of photoassociation (PA) spectroscopy [1–3]. Besides being a pathway to the formation of various molecules, analysis of data from PA experiments has resulted in many of the most accurate atomic lifetime determinations [4]. In addition, one can identify many high-precision determinations of interatomic potential curves using PA spectroscopy [5–7]. Most recently, Le Roy et al. mapped out the $\text{Li}_2(1S\Sigma^+)\text{ and } \text{Li}_2(3P\Sigma^+)$ potential curves for the lithium dimer [8] to a new level of detail and precision. One result from the Le Roy et al. analysis was a value for the $2S\rightarrow 2P_{1/2}$ transition rate that was one order of magnitude more precise than any previously measured atomic oscillator strength [4].

Most of the PA experiments mapping out potential curves have been performed for homonuclear dimers [5–7]. The interatomic potential for the $nS-nP$ configurations of the photoexcited states have one atom in its ground state and the other atom in a dipole excited state. For such a system, the asymptotic part of the potential curve is sometimes written as the function of their distance $R$,

$$V_{\text{dip}}(R) = -\frac{C_3}{R^3} - \frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots \quad (1)$$

The inclusion of terms up to $O(R^{-10})$ can be regarded as something akin to the standard model for the dispersion interaction [9–13] aimed at getting a good representation of the entire potential surface. The $C_3$ term is sometimes called the resonant term and arises because the two atoms are identical with identical energy levels. However, Eq. (1) is incomplete to $O(R^{-10})$. Although it is not widely appreciated, third-order perturbation theory for two identical atoms is known to give rise to a term of order $O(R^{-9})$ [14].

The contribution of the third-order term to the analysis of PA experiments is currently unknown. This situation should be rectified since the most recent analysis of the potential curves asymptoting to the $^7\text{Li}(2S)^7\text{Li}(2P)$ states gave a value of $C_3 = 11.0024(2)\text{ a.u.} [8]$ that was $0.016\%$ larger than the value of $11.0007\text{ a.u.}$ coming from a finite mass Hylleraas calculation after corrections had been made to incorporate relativistic effects [15]. Given that this $C_3$ represents a level of precision close to one order of magnitude better than any previous determination, the possibility exists that the third-order dispersion coefficients could be influencing the $C_3$ derived from the analysis of the rovibrational spectrum.

There has been some research into the higher-order dispersion coefficients when both atoms are in spherically symmetric states [16–21]. The most comprehensive work was that by Ovianniuk and Mitroy [20,21] who determined the $C_n$ coefficients up to $n = 30$ and included terms up to tenth-order of perturbation theory. Apart from the work of Zhang et al. [14], which was specialized to $nS-nP$ configuration, there has been no work on the third-order dispersion coefficients for the general case. In the present work, we derive the general expressions for the third-order dispersion coefficients. The two most interesting cases are those when both atoms are in their ground states, and the case when one atom is in an $S$ state and the other is in a state with $L > 0$.

Numerical values of the $C_{11}$, $C_{13}$, and $C_{15}$ coefficients are first given for the hydrogen dimer since other high-accuracy calculations of these terms can be used as a validation check [18,20,21]. Values of $C_{11}$ and $C_{13}$ are computed using Hylleraas wave functions for the helium dimer ground state. The most precise descriptions of the helium dimer potential includes dispersion coefficients up to $C_{16}$ [22–25]. The two effects tend to supersed the only previous calculations of third-order $C_{11}$ and $C_{13}$ coefficients using configuration-interaction-type wave functions [23,24]. The $C_9$ coefficients were also computed for the He($1\,1S\,\rightarrow\,He(2\,1P\,\rightarrow\,He(2\,1S\,\rightarrow\,He(2\,3S\,\rightarrow\,He(2\,3P)$ dimers as a validation using the previously computed values of Zhang et al. [14] as a check. Numerical values of the $C_9$ and $C_{11}$ coefficients are given for the lowest $nS-nP$ configuration of the homonuclear alkali-metal dimers. Most of the values were computed using a fixed core Hartree-Fock plus semiempirical core-polarization Hamiltonian. There have been no previous calculations of the third-order dispersion coefficients for these alkali-metal–atom configurations.
II. The Third-Order Dispersion Interaction

The dispersion coefficients will initially be evaluated for two separate atoms in the atomic representation. Later, the modifications necessary to convert the atomic basis dispersion coefficients to a molecular basis will be discussed. The coefficients for the van der Waals interaction were computed by evaluating the sum over intermediate states with a pseudostate [16,26].

A. The multipole expansion

The dispersion interaction operator in the asymptotic region \( R \gg d_0 \) (\( d_0 \) is the Bohr radius) may be presented in the form of an expansion in power series of \( R^{-1} \) [27]:

\[
V(R) = \sum_{k=1}^{\infty} \sum_{k'=1}^{\infty} \frac{v_{kk'}(\hat{n})}{R^{k+k'+1}},
\]

where

\[
v_{kk'}(\hat{n}) = (-1)^k G_{kk'}^{\hat{n}, \hat{n}}(\sigma) \times Q^k(\rho) \] (K).

The coefficient \( G_{kk'}^{\hat{n}, \hat{n}} \) is

\[
G_{kk'}^{\hat{n}, \hat{n}} = \left[ \frac{(2K)!}{(2k')!(2k)!} \right]^{1/2},
\]

where \( K = k + k' \), \( Q^k(\sigma) = \sum_i \sigma_i^k C_i^k(\hat{\sigma}_i) \) and \( Q^k(\rho) = \sum_j \rho_j^k C_j^k(\hat{\rho}_j) \) are the operators of atomic \( k \)-pole electromagnetic moments for atoms (A) and (B), respectively, and the summation is from 1 to the number of electrons of each atom. The unit vector \( \hat{n} = \mathbf{R}/R \) points from the first atom (A) to the second atom (B). The \( C_i^k(\hat{\sigma}_i) \) and \( C_j^k(\hat{\rho}_j) \) are the spherical tensors [28] of angular variables of the \( i \)th or \( j \)th electron’s position vector \( \sigma_i = [\sigma_i, \theta_i, \phi_i] \) and \( \rho_j = [\rho_j, \theta_j, \phi_j] \) of atoms (A) and (B), correspondingly. \( C^k(\hat{n}) \) is the interatomic unit vector \( \hat{n} \). Defining the quantization axis in the \( \hat{n} \) direction simplifies Eq. (3) to

\[
v_{kk'}(\hat{n}) = (-1)^k G_{kk'}(\sigma) \times Q^k(\rho) \] (K).

B. The uncoupled general third-order matrix element

In atomic representation, the initial state for the A-B system is generally written as the product states of atoms A and B,

\[
\Psi^{(0)}(M) = \Psi_A(\sigma) \Psi_B(\rho) = n_{a_1} n_{a_2} n_{b_1} n_{b_2},
\]

with initial energy \( E^{(0)}_{n_{a_1} n_{a_2} n_{b_1} n_{b_2}} = E_{a_1} + E_{a_2} + M = m_a + m_b \). The electron-electron operator, Eq. (2), conserves \( M = m_a + m_b \) but not the individual \( m_a \) and \( m_b \).

According to perturbation theory, the third-order energy correction \( \Delta E^{(3)} \) is written as

\[
\Delta E^{(3)} = \sum_{n_{a_1}} \sum_{n_{a_2}} \sum_{n_{b_1}} \sum_{n_{b_2}} \frac{A_1}{(E_{n_{a_1}} - E_{n'_{a_1}})(E_{n_{a_2}} - E_{n'_{a_2}})}
\]

\[
\Delta E^{(1)} = \sum_{n_{a_1}} \sum_{n_{a_2}} \sum_{n_{b_1}} \sum_{n_{b_2}} \frac{A_2}{(E_{n_{a_1}} - E_{n'_{a_1}})^2},
\]

where \( \Delta E^{(1)} \) is the first-order energy correction. In the atomic representation, it can be expressed as

\[
\Delta E^{(1)} = \sum_{k,k',\mu} (-1)^{k+k'+\mu} G_{kk'}^{\mu \mu} \left[ \frac{l_a}{m_a - m_b} \right] \times \left[ \frac{l_b}{m_b} \right],
\]

where \( T_{2,2}^k \) and \( T_{2,2}^{k'} \) are the reduced matrix elements, which comply with the style of the following formulas:

\[
T_{2,2}^{\mu \mu} = \sum_j \frac{\beta_j^\mu \beta_j^\mu}{\beta_j^\mu n^{\mu}(\nu, \nu)},
\]

\[
T_{2,2}^{\mu \mu} = \sum_j \frac{\beta_j^\mu \beta_j^\mu}{\beta_j^\mu n^{\mu}(\nu, \nu)},
\]

In Eq. (7), \( A_1 \) and \( A_2 \) are

\[
A_1 = \sum_{m_a, m_b, m_{a1}} \sum_{m_{a2}} \sum_{m_{b1}} \sum_{m_{b2}} (\Psi^{(0)}(M) \mid \Psi(n_{a1} n_{a2} n_{b1} n_{b2}))(M \mid \Psi(n_{a1} n_{a2} n_{b1} n_{b2})),
\]

\[
A_2 = \sum_{m_a, m_b, m_{a1}} \sum_{m_{a2}} \sum_{m_{b1}} \sum_{m_{b2}} (\Psi^{(0)}(M) \mid \Psi(n_{a1} n_{a2} n_{b1} n_{b2}))(M \mid \Psi(n_{a1} n_{a2} n_{b1} n_{b2})),
\]

where \( A_1 \) and \( A_2 \) are two intermediate states with the energy eigenvalue \( E_{n_{a1} n_{a2} n_{b1} n_{b2}} = E_{a_1} + E_{a_2} + E_{b_1} + E_{b_2} \) and \( E_{n_{a1} n_{a2} n_{b1} n_{b2}} = E_{a_1} + E_{a_2} + E_{b_1} + E_{b_2} \). The prime in the summation of Eq. (7) indicates that the terms with \( E_{n_{a1} n_{a2} n_{b1} n_{b2}} = E_{n_{a1} n_{a2} n_{b1} n_{b2}} \) and \( E_{n_{a1} n_{a2} n_{b1} n_{b2}} = E_{n_{a1} n_{a2} n_{b1} n_{b2}} \) should be excluded. Using Eqs. (2)–(6) one obtains

\[
A_1 = \sum_{k_i, k_i'} \sum_{k_j, k_j'} \sum_{k_{i+1}, k_{i+1}'} \sum_{k_{j+1}, k_{j+1}'} (-1)^{k_i + k_{i+1} + k_{i+1}'} G_{k_i k_i'} G_{k_j k_j'} G_{k_{i+1} k_{i+1}'} G_{k_{j+1} k_{j+1}'} \times T_{2,2}^{k_i, k_i'} T_{2,2}^{k_j, k_j'} T_{2,2}^{k_{i+1}, k_{i+1}'} T_{2,2}^{k_{j+1}, k_{j+1}'}
\]

\[
A_2 = \sum_{k_i, k_i'} \sum_{k_j, k_j'} \sum_{k_{i+1}, k_{i+1}'} \sum_{k_{j+1}, k_{j+1}'} (-1)^{k_i + k_{i+1} + k_{i+1}'} G_{k_i k_i'} G_{k_j k_j'} G_{k_{i+1} k_{i+1}'} G_{k_{j+1} k_{j+1}'} \times T_{2,2}^{k_i, k_i'} T_{2,2}^{k_j, k_j'} T_{2,2}^{k_{i+1}, k_{i+1}'} T_{2,2}^{k_{j+1}, k_{j+1}'}
\]

where \( K_i = k_i + k_i' \) (i = 1, 2, 3), and \( \bar{t}_1 \) and \( \bar{t}_2 \) are
with the phase factor \[ \mathcal{F}_1 = (-1)^{l_a-l_b-M} \hat{L} \hat{L} \hat{L} G_{kk'kk} G_{\mu\mu\mu} \]
\[ \times |n_a l_a m_a l_b m_b|, \]  
(21)  

where \( \hat{L} = \sqrt{2L+1} \). According to perturbation theory, the third-order energy correction is

\[ \Delta E^{(3)} = \sum_{n,n_d} \left( \sum_{n_d} E_{n,n_d} - E_{n,n_d}^{(0)} \left| E_{n,n_d} - E_{n,n_d}^{(0)} \right| \right) \]
\[ \times \frac{B_1}{E_{n,n_d} - E_{n,n_d}^{(0)}} \left( L K L' \right) \]
\[ \times \left| \frac{\hat{L}}{R^{2k+1}} \right|^2, \]  
(22)  

where \( \Delta E^{(1)} \) is the first-order energy correction, whose expression in the molecular representation is

\[ \Delta E^{(1)} = \sum_{n,n_d} \left( \sum_{n_d} E_{n,n_d} - E_{n,n_d}^{(0)} \left| E_{n,n_d} - E_{n,n_d}^{(0)} \right| \right) \]
\[ \times \frac{B_1}{E_{n,n_d} - E_{n,n_d}^{(0)}} \left( L K L' \right) \]
\[ \times \left| \frac{\hat{L}}{R^{2k+1}} \right|^2, \]  
(23)  

In Eq. (22), \( B_1 \) and \( B_2 \) are

\[ B_1 = \sum_{L,1,\ldots,2,L_1} \left( \Psi^{(0)}(LM) | V(\mathbf{R}) | n_1 l_1 n_2 l_2 L_1 M_1 \right) \]
\[ \times \left( n_1 l_1 n_2 l_2 L_1 M_1 | V(\mathbf{R}) | n_1 l_1 n_2 l_2 L_2 M_2 \right), \]  
(24)  

\[ B_2 = \sum_{L,1,\ldots,2,L_1} \left( \Psi^{(0)}(LM) | V(\mathbf{R}) | n_1 l_1 n_2 l_2 L_1 M_1 \right) \]
\[ \times \left( n_1 l_1 n_2 l_2 L_1 M_1 | V(\mathbf{R}) | \Psi^{(0)}(LM') \right), \]  
(25)  

Using Eqs. (2) and (21), together with the Wigner-Eckart theorem, \( B_1 \) can be expanded as

\[ B_1 = \sum_{L,1,\ldots,2,L_1} \left( \sum_{n_1 l_1 n_2 l_2 L_1 M_1} \frac{\hat{L}^L \hat{L'}^L \hat{L}^L}{R^{k+1}} \right) \]
\[ \times \left( n_1 l_1 n_2 l_2 L_1 M_1 | V(\mathbf{R}) | \Psi^{(0)}(LM') \right), \]  
(26)
Using the graphical methods [31], the factor $U_3$, which contains all the $3j$ symbols, can be reduced to:

$$U_3 = \sum_x \hat{X}^2 (-1)^{y_i + j_b + j_c + L_j + L_j + L_j} \left( \begin{array}{ccc} K_2 & X & K_3 \\ 0 & 0 & 0 \end{array} \right)$$

$$\times \left( \begin{array}{c} L_1 & X & L' \\ M & 0 & -M \end{array} \right) \left( \begin{array}{c} L_1 & K_1 & L \\ M & 0 & -M \end{array} \right) \left( \begin{array}{c} K_2 & L_1 & X \end{array} \right)$$

$$\times \left\{ \begin{array}{c} l_a & l_b & L \\ l_c & l_d & L_1 \\ k_1 & k'_1 & K_1 \end{array} \right\} \left\{ \begin{array}{c} l_c & l_d & L_1 \\ l_e & l_f & L_2 \\ k_2 & k'_2 & K_2 \end{array} \right\} \left\{ \begin{array}{c} l_e & l_f & L_2 \\ k_3 & k'_3 & K_3 \end{array} \right\}.$$

(27)

Substituting Eq. (27) into Eq. (26) gives rise to the final expression for $B_1$:

$$B_1 = \sum_x (-1)^{L_2} \left( \begin{array}{ccc} K_2 & X & K_3 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{c} L_1 & X & L' \\ M & 0 & -M \end{array} \right) D_x,$$

(28)

where $D_x$ is:

$$D_x = \sum_{L_1 L_2 K_1 K_2 K_3} \sum_{k_1 k'_1 \ldots k_3 k'_3} (-1)^{k_1 + k_2 + k_3 + L_1 + L_2 + L_3} \hat{L}_1 \hat{L}_2 \hat{L}_3 \hat{X}^2 \frac{R_{K_1 K_2 K_3}}{R_{K_1 K_2 K_3}}$$

$$\times G_{k_1 k_2 K_1} G_{k_3 K_3 K_3} T_{ac}^{k_1} T_{ce}^{k_2} T_{ed}^{k_3}$$

$$\times T_{bd}^{k_1} \frac{1}{L_1 L_2 L_3}$$

$$\left\{ \begin{array}{c} l_a & l_b & L \\ l_c & l_d & L_1 \\ k_1 & k'_1 & K_1 \end{array} \right\} \left\{ \begin{array}{c} l_c & l_d & L_1 \\ l_e & l_f & L_2 \\ k_2 & k'_2 & K_2 \end{array} \right\} \left\{ \begin{array}{c} l_e & l_f & L_2 \\ k_3 & k'_3 & K_3 \end{array} \right\}.$$

(29)

Performing a similar procedure for the $B_2$ of Eq. (25), we have:

$$B_2 = \sum_x (-1)^{L' - M} \left( \begin{array}{ccc} L & X & L' \\ -M & 0 & M \end{array} \right) \mathcal{W}_X,$$

(30)

with $\mathcal{W}_X$ being:

$$\mathcal{W}_X = -\sum_{k_1 k'_1 K_1} \sum_{k_2 k'_2 K_2} (-1)^{k_1 + k_2 + L_1 + L_2 + L_3} \hat{L}_1 \hat{L}_2 \hat{X}^2 \frac{R_{K_1 K_2 K_3}}{R_{K_1 K_2 K_3}}$$

$$\times G_{k_1 k_2 K_1} T_{ac}^{k_1} T_{ac}^{k_2} T_{bd}^{k_1} T_{bd}^{k_2} \left( \begin{array}{c} k_1 \ k_2 \ X \\ 0 \ 0 \ 0 \end{array} \right)$$

$$\times \left\{ \begin{array}{c} l_a & l_b & L \\ l_c & l_d & L_1 \\ k_1 & k'_1 & K_1 \end{array} \right\} \left\{ \begin{array}{c} l_c & l_d & L_1 \\ l_e & l_f & L_2 \\ k_2 & k'_2 & K_2 \end{array} \right\} \left\{ \begin{array}{c} l_e & l_f & L_2 \\ k_3 & k'_3 & K_3 \end{array} \right\}.$$

(31)

In Eq. (23) of $\Delta E^{(3)}$, making $k \rightarrow k_3$ and $k' \rightarrow k'_3$, combined with Eqs. (22), (28), and (30), the third-order energy correction can finally be written as a sum of powers of $1/R$ in the molecular representation,

$$\Delta E^{(3)} = \sum_{k_1 k_2 k_3 k_4 = 3} \frac{C_{2n+3}(L, M)}{R^{2n+3}},$$

(32)

where $C_{2n+3}(L, M)$ are the dispersion coefficients,

$$C_{2n+3}(L, M) = \frac{\sum_{n,n_{ij}} \sum_{L_1 L_2 X} (-1)^{L_1 + L_2 + k_1 + k_2 + k_3} \frac{L_1 L_2 \hat{X}^2}{R_{K_1 K_2 K_3}}}{\sum_{L_1 L_2 X} (-1)^{L_1 + L_2 + k_1 + k_2 + k_3} \frac{L_1 L_2 \hat{X}^2}{R_{K_1 K_2 K_3}}},$$

(33)

where $D_x$ and $\mathcal{W}_X$ are:

$$D_x = (-1)^{L_1 + L_2 + L_3} G_{k_1 k_2 K_1} G_{k_3 k_4 K_3} T_{ac}^{k_1} T_{ce}^{k_2} T_{ed}^{k_3} T_{bd}^{k_1} T_{bd}^{k_2} \left( \begin{array}{ccc} K_2 & X & K_3 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{c} L_1 & X & L' \\ M & 0 & -M \end{array} \right)$$

$$\times \left\{ \begin{array}{c} l_a & l_b & L \\ l_c & l_d & L_1 \\ k_1 & k'_1 & K_1 \end{array} \right\} \left\{ \begin{array}{c} l_c & l_d & L_1 \\ l_e & l_f & L_2 \\ k_2 & k'_2 & K_2 \end{array} \right\} \left\{ \begin{array}{c} l_e & l_f & L_2 \\ k_3 & k'_3 & K_3 \end{array} \right\}.$$

(34)

$$\mathcal{W}_X = (-1)^{L_1 + L_2 + L_3} G_{k_1 k_2 K_1} G_{k_3 k_4 K_3} G_{k_5 k_6 K_5} T_{ac}^{k_1} T_{ac}^{k_2} T_{bd}^{k_1} T_{bd}^{k_2} \left( \begin{array}{c} L & K & L' \\ -M & 0 & M \end{array} \right)$$

$$\times \left\{ \begin{array}{c} l_a & l_b & L \\ l_c & l_d & L_1 \\ k_1 & k'_1 & K_1 \end{array} \right\} \left\{ \begin{array}{c} l_c & l_d & L_1 \\ l_e & l_f & L_2 \\ k_2 & k'_2 & K_2 \end{array} \right\} \left\{ \begin{array}{c} l_e & l_f & L_2 \\ k_3 & k'_3 & K_3 \end{array} \right\}.$$

(35)
D. Molecular representation for homonuclear dimers

For two atoms A and B, the zeroth-order wave function for the combined system A-B, in a state with angular momentum $l_a$ and $l_b$, and the total magnetic quantum number $M$, can be written most generally in the form

$$\Psi^{(0)}(n_a, n_b, M) = \sum_{m_a, m_b} \sum_{m} \delta_{m_a+m, m_b} M C_{m_a, m_b} \times \Psi(n_a \ell_a, n_b \ell_b, m_a m_b, M),$$

(36)

where $C_{m_a, m_b}$ has an energy eigenvalue of $E_{m_a}$, $\Psi_{m_b}$ has an energy eigenvalue of $E_{m_b}$, and the expansion coefficients are $C_{m_a, m_b}$. The evaluation of the third-order van der Waals coefficients is confined to two cases in the present work. When both atoms are in an S state and $n_a = n_b$, one can simply write

$$\Psi^{(0)}(n_a, n_b) = \Psi(n_a, m_a = 0, n_b, m_b = 0, M = 0).$$

(37)

The van der Waals interaction is the same in the atomic and molecular representations. The second case is when two like atoms have $l_a = 0$ and $l_b > 0$. When one of the atoms (A) is in an S state and the other is in a different state, one has $m_b = M$ and the zeroth-order wave function is

$$\Psi^{(0)}(n_a, n_b, M) = [\Psi(n_a \ell_a, M) + \beta \Psi(n_b M n_a 0, M)]/\sqrt{2}.$$

(38)

The factor $\beta = \pm 1$ can be related to the fundamental symmetries of the states by $\beta = (-1)^{s+1+1}(-1)^p$, where $S$ is the total spin and $p = +1$ for even (g) and $p = -1$ for odd (u) molecular states. Consider an alkali-metal dimer dissociating into $X(ns) - X(np)$ states. The $^1\Sigma^+_g$ state has $\beta = +1$, while the $^1\Sigma^+_u$ state has $\beta = -1$. The van der Waals interaction in the molecular representation leads to what can be called the direct and interchange contributions to the matrix elements, e.g.,

$$V^{(3)} = [\langle n_a \ell_a, M | V | n_b \ell_b, M \rangle + \beta \langle n_a \ell_a, M | V | n_b M n_a 0, M \rangle]/2.$$

(39)

E. The C₉ term for the homonuclear case

For heteronuclear molecules the first term in the third-order dispersion interaction is the $C_{11}/R^{11}$ interaction. This term is well known [18–21]. Homonuclear molecules allow for the possibility of a $C_9/R^9$ interaction when the two asymptotic atomic states are connected by a dipole transition. This term arises from the excitation transfer between the two identical atoms. The excitation transfer can lead to a first-order dipole interaction with the form $C_9/R^3$ which is sometimes called the resonant van der Waals interaction [30,32]. The interchange matrix element for the case of $l_a = 0$ and $l_b > 0$ is written

$$V^{(3)} = \beta \langle n_a \ell_a, M | V | n_b \ell_b, M \rangle.$$
spectrum. This approach to the determination of atomic structure is referred to as the configuration-interaction plus core-polarization (CICP) method in the remainder of this paper.

The effective Hamiltonian for the active electron is written

$$H = -\frac{1}{2} \nabla^2 + V_{\text{dir}}(r) + V_{\text{exc}}(r) + V_{\text{p1}}(r),$$

where the direct $V_{\text{dir}}(r)$ and the exchange $V_{\text{exc}}(r)$ interactions of the valence electron with the HF core are calculated exactly and the $\ell$-dependent polarization potential $V_{\text{p1}}(r)$ is semiempirical in nature with the functional form

$$V_{\text{p1}}(r) = - \sum_{\ell m} \frac{a_{\text{core}} g_\ell^2(r)}{2 r^4} |\ell m\rangle \langle \ell m|.\quad (46)$$

In the above, the coefficient $a_{\text{core}}$ is the static dipole polarizability of the core and $g_\ell^2(r) = 1 - \exp(-r/\rho_\ell^2)$ is a cutoff function designed to make the polarization potential finite at the origin. In these calculations, the cutoff parameters $\rho_\ell$ are tuned to reproduce the binding energies of the low-lying states. All the reduced transition matrix elements needed for the $C_n$ sums are computed with multipole operators modified with core-polarization corrections [26,36,37].

IV. RESULTS FOR SPECIFIC MOLECULES

A. Hydrogen

The first test calculations are for the third-order $C_{11,13,15}$ coefficients of the $H(1s)$-$H(1s)$ dimer. A number of highly accurate results for these coefficients exist in the literature [18–21]. Our calculations using the formulas presented here give rise to $C_{11} = -3474.898038$ a.u., $C_{13} = -3.269869240 \times 10^3$ a.u., and $C_{15} = -2.839558063 \times 10^7$ a.u. These are in perfect agreement with the previously reported values [18,19].

B. Helium

1. The ground-state dimer

The convergence of $C_{11}$ and $C_{13}$ for the ground-state helium dimer is tabulated in Table I. The only values available for comparison are those of Przybytek [22–24]. The better than 0.1% agreement with the Przybytek $C_{11}$ and $C_{13}$ calculations validates the analytic expressions developed for the evaluation of $C_{11}$ and $C_{13}$. The present values of $C_{11}$ and $C_{13}$ are converged to six and seven significant digits.

### TABLE I. Convergence of the $C_{11}$ and $C_{13}$ coefficients for the $\text{He}(1\,1S)$-$\text{He}(1\,1S)$ dimer. The number of $s$-, $p$-, $d$-, and $f$-type states in the Hylleraas basis are given in the $(N_S,N_P,N_D,N_F)$ column.

<table>
<thead>
<tr>
<th>$(N_S,N_P,N_D,N_F)$</th>
<th>$C_{11}$</th>
<th>$C_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(68,70,53,60)</td>
<td>-76.734140</td>
<td>-3808.62838</td>
</tr>
<tr>
<td>(140,168,146,105)</td>
<td>-76.725890</td>
<td>-3808.32822</td>
</tr>
<tr>
<td>(250,330,310,252)</td>
<td>-76.725730</td>
<td>-3808.32604</td>
</tr>
<tr>
<td>(406,440,425,360)</td>
<td>-76.725724</td>
<td>-3808.32592</td>
</tr>
<tr>
<td>Extrapolated</td>
<td>-76.72571(1)</td>
<td>-3808.32545(5)</td>
</tr>
<tr>
<td>Przybytek [22–24]</td>
<td>-76.74(4)</td>
<td>-3808(1)</td>
</tr>
</tbody>
</table>

Zhang et al. [38] 3.658259 $\times$ 10$^5$

2. $C_9$ values for dimers with one atom in an excited state

Tables II and III present $C_9$ for helium dimers with one atom in a dipole excited state. The calculation of $C_9$ includes contributions from unnatural parity states which are not present in the calculation of $C_{11}$ for the ground-state dimer. The Hylleraas calculations of $C_9$ have been previously reported by atoms by Zhang et al. [14,38] and the current values were mainly computed as a validation exercise since the values of Zhang et al. were obtained using larger Hylleraas basis sets and are therefore more precise. The present values of $C_9$ are consistent with those of Zhang et al. [14,38].

V. THE LITHIUM DIMER

A. The ground-state dimer

Table IV presents a convergence study for $C_{11}$ and $C_{13}$ of the ground-state Li dimer. The convergence is slower than the He ground-state dimer, where $C_{11}$ is converged only to four significant digits. The difference between the CICP and Hylleraas values of $C_{11}$ is less than 0.2%. The CICP calculation did not include any contributions from the core.

### TABLE II. Convergence of the Hylleraas calculations of $C_9$ for the $\text{He}(2\,1S)$-$\text{He}(2\,1S)$ and $\text{He}(2\,1S)$-$\text{He}(2\,1S)$ combinations. Values are given for $\beta = 1$. Values for $\beta = -1$ can be obtained by multiplying $C_9$ by $-1$.

<table>
<thead>
<tr>
<th>$(N_S,N_P,N_D,N_F)$</th>
<th>$M_9 = 0$</th>
<th>$M_9 = \pm 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He(2,1S)He(2,1S)</td>
<td>3.654470 $\times$ 10$^5$</td>
<td>3.661189 $\times$ 10$^5$</td>
</tr>
<tr>
<td>(100,112,100,119)</td>
<td>3.660441 $\times$ 10$^5$</td>
<td>3.662254 $\times$ 10$^5$</td>
</tr>
<tr>
<td>(140,168,100,146)</td>
<td>3.661189 $\times$ 10$^5$</td>
<td>3.6623(1) $\times$ 10$^5$</td>
</tr>
<tr>
<td>Extrapolated</td>
<td>3.66211(5) $\times$ 10$^5$</td>
<td></td>
</tr>
</tbody>
</table>

Zhang et al. [38] 3.658259 $\times$ 10$^5$

<table>
<thead>
<tr>
<th>$(N_S,N_P,N_D,N_F)$</th>
<th>$M_9 = 0$</th>
<th>$M_9 = \pm 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(44,70,44,60)</td>
<td>5.110069</td>
<td>-1.168104</td>
</tr>
<tr>
<td>(100,112,100,119)</td>
<td>5.118769</td>
<td>-1.170238</td>
</tr>
<tr>
<td>(190,240,190,262)</td>
<td>5.119765</td>
<td>-1.170506</td>
</tr>
<tr>
<td>(322,330,322,364)</td>
<td>5.120391</td>
<td>-1.170679</td>
</tr>
<tr>
<td>(406,440,504,490)</td>
<td>5.120544</td>
<td>-1.170722</td>
</tr>
<tr>
<td>Extrapolated</td>
<td>5.12058(4)</td>
<td>-1.17073(1)</td>
</tr>
<tr>
<td>Zhang et al. [14]</td>
<td>5.12059227(6)</td>
<td>-1.170735(6)</td>
</tr>
</tbody>
</table>
TABLE IV. Convergence of the $C_{11}$ and $C_{13}$ coefficients for the Li(2s)-Li(2s) dimer. The number of s-, p-, d-, and f-type states in the Hylleraas basis are given in the $(N_s,N_p,N_d,N_f)$ column.

<table>
<thead>
<tr>
<th>$(N_s,N_p,N_d,N_f)$</th>
<th>$C_{11}$</th>
<th>$C_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(120,55,55,52)</td>
<td>$-0.40407906 \times 10^6$</td>
<td>$-1.100112 \times 10^{10}$</td>
</tr>
<tr>
<td>(256,138,138,132)</td>
<td>$-0.383272 \times 10^6$</td>
<td>$-1.102884 \times 10^{10}$</td>
</tr>
<tr>
<td>(502,306,306,302)</td>
<td>$-0.389347 \times 10^6$</td>
<td>$-1.103513 \times 10^{10}$</td>
</tr>
<tr>
<td>(918,622,622,636)</td>
<td>$-0.388211 \times 10^6$</td>
<td>$-1.103784 \times 10^{10}$</td>
</tr>
<tr>
<td>Extrapolated</td>
<td>$-0.386(2) \times 10^6$</td>
<td>$-1.1039(2) \times 10^{10}$</td>
</tr>
<tr>
<td>CICP [39]</td>
<td>$-0.44 \times 10^6$</td>
<td>$-1.105 \times 10^{10}$</td>
</tr>
</tbody>
</table>

B. The Li(2s)-Li(2p) case

The convergence of $C_9$ for the Li(2s)-Li(2p) dimer using the Hylleraas calculation is listed in Table V. However, the convergence of $C_{11}$ is slow and no rigorous estimate of the uncertainty is available (see Table VI). Comparisons for $C_5$, $C_9$, and $C_{11}$ between the Hylleraas and CICP calculations are made in Table VI. The agreement between the Hylleraas and CICP calculations is better than 1%. The CICP calculation does not include any contribution involving core excitations.

The relative importance of the $C_9$ coefficient can be estimated by comparison with the $C_3$ and $C_{10}$ coefficients. The $C_9$ coefficients are 9.908 95(5) × 10¹ and 0.485 64(8) × 10¹ for the Σ and Π states with $β = -1$ [34]. The $C_{10}$ coefficients are 1.2113 × 10⁴ and 9.1839 × 10³ for the Σ and Π states with $β = -1$ [40]. The $C_9$ coefficients are 2.740 79(2) × 10³ and 1.030 44(2) × 10³ for the Σ and Π states with $β = +1$ [34]. The $C_{10}$ coefficients are 3.0096 × 10⁵ and 8.9295 × 10⁵ for the Σ and Π states with $β = +1$ [40]. The third-order $C_9$ coefficients are roughly the same size as the second-order $C_9$ coefficients.

The $C_9$ coefficients have potential applications in the analysis of photoassociation spectra for homonuclear dimers [2,4,8]. The $C_3$ and $C_9$ values for a given molecular state will typically have the same sign (see Table VI). Omission of the $C_9$ dispersion interaction from the analysis of the photoassociation spectrum could potentially lead to the analysis having an inherent tendency to overestimate the magnitude of $C_3$ and thus the transition rate.

At present, the most precise atomic transition rate ever measured is that of the Li(2s)-Li(2p1/2) transition, namely, $C_3 = 11.002 41(23)$ [8]. This value was derived from the $A(1\Sigma_u^+)$ state ($β = 1$) of the $^7$Li dimer. This transition rate is about 0.016% larger than the best theoretical estimate of $C_3 = 11.0007$ using Hylleraas wave functions [15]. The Hylleraas estimate of $C_3 = 11.0007$ was made for $^7$Li and incorporated an estimate of the relativistic correction. The experimental analyses use rovibrational data that sample the potential out to an internuclear separation of about 170 a₀. The interatomic potential can be described by a purely dispersive form past about 25 a₀ [41]. At this separation, the size of the $C_9$ to $C_3$ potential ratio is $2.2 \times 10^5/(11 \times 25) = 0.000 082$. The magnitude of this ratio is about the same size as the relative uncertainty in the experimental value of $C_3$. However, the ratio of the $C_9$ to $C_8$ interaction is 0.034 at 25 a₀. Formal considerations suggest the third-order $C_9$ interaction should probably be included in an attempt to construct the potential of the $A(1\Sigma_u^+)$ state. However, it would appear that the inclusion of the $C_9$ term in the potential would change the values of $C_3$ by an amount that would be less than the quoted uncertainty and is therefore unlikely to resolve the current discrepancy between the best experimental and theoretical values of $C_3$.

C. The heavier alkali-metal atoms

Table VI shows $C_9$ and $C_{11}$ for the heavier alkali-metal atoms computed with CICP wave functions. For all the dimers from Li to Rb it is seen that the magnitude of $C_9$ is larger for the Σ state than for the Π state. Core excitations were
not included in the calculations. Calculations of the $C_6$ values for the homonuclear alkali-metal dimers show that the core contributions are less than 1% for Li and 12% for Rb [26].

Table VI also includes values of $C_{6}$ and $C_{11}$ for Cs. These values were computed with a nonrelativistic structure model designed along the same lines as the CICP models for Li to Rb [26]. This model results in 397.5 for the polarizability and 6732 for the ground-state $C_6$ value. More sophisticated calculations based on relativistic perturbation theory give 398.4(7) [42] for the polarizability and 6851 for $C_6$ [43,44]. The large spin-orbit splitting for the $6p$ levels is of course omitted from the present calculations. We would estimate an uncertainty in the present $C_6$ and $C_{11}$ values of about 20%. The estimated $C_6$ values for the $6s-6p$ asymptotic state are 18 323 for the state with $M = 0$ and 12 342 for the state with $M = 1$.

Table VI shows that the relative importance of $C_6$ with respect to $C_3$ increases as the alkali-metal atoms increase in size. Most analyses of molecular spectra that take long-range dispersion forces into account typically include $C_6$, $C_8$, and $C_{10}$. Therefore it would seem reasonable that the $C_6$ coefficient should be included as a matter of course in any analysis of photoassociation spectra aimed at deriving a value for the $C_3$ parameter.

The $C_{10}$ and $C_{11}$ coefficients for lithium are roughly equal in magnitude. For example, the $\beta = 1$ $\Sigma$-state values of $C_{10}$ and $C_{11}$ are $3.01 \times 10^7$ [40] and $-5.929 \times 10^7$, respectively. The third-order $C_{11}$ dispersion interaction would be an order of magnitude smaller than the $C_{10}$ term of the second-order dispersion interaction at an internuclear distance of 25a$_0$.

VI. SUMMARY

In this paper, the general matrix elements for the third-order dispersion interaction between two atoms have been derived and calculations performed for the hydrogen and helium dimers, and for the alkali-metal atom dimers. The third-order dispersion coefficients have been computed previously for hydrogen and helium dimers [14,18,19,38]. Perfect agreement has been achieved with the earlier calculations of $C_{11}$ for the ground-state hydrogen dimer. For helium dimers with one atom in a dipole excited state, the agreement of $C_6$ with the previous calculations [14,38] has indicated the algebraic correctness of our derivations. For the ground-state helium dimer, improved results have also been obtained for $C_{11}$ and $C_{13}$.

The $C_6$ dispersion coefficients occur in the interaction potentials for homonuclear dimers when one of the atoms is in a dipole excited state. The $C_6$:$C_3$ ratio increases for the heavier alkali-metal dimers. This term has potential application in the analysis of photoassociation spectra for homonuclear dimers [2,4,8].

At the present time, the best theoretical estimate of the Li(2s)-Li(2p) transition rate [15] is incompatible with an analysis of the potential curves asymptoting to the Li(2s)-Li(2p) state [8]. While the discrepancy is only 0.016%, it is larger than the theoretical and experimental error limits. This discrepancy is highly significant and should be taken very seriously since the Hylleraas calculation [15] represents the theoretical state of the art and the analysis of the Li(2s)-Li(2p) potential curve likewise represents a landmark in diatomic spectral analysis [8].

This discrepancy has relevance to cold-atom physics and the new generation of optical frequency atomic clocks. The blackbody radiation shift is looming as the potential source of the largest systematic error [45–49]. It is possible to compensate for this error if the polarizabilities of the two states in the clock transition are known. One way the polarizabilities can be determined is to measure polarizability ratios of two atoms in an atom interferometer [50]. This requires that the polarizability of one atom be known to high precision so it can serve as a reference standard. From the theoretical perspective the lithium atom is the preferred atom to serve as such a standard [49].

The current conflict between the most precise theoretical and experimental estimates of the resonance lifetimes limits the accuracy of any working polarizability standard based on $^7$Li.

Inclusion of the $C_6$ interaction will probably have only a very small impact on the value of the Li $C_3$ determined from a potential fit to the photoassociation data. It could be more important for the heavier alkali-metal atoms, which do not have spectroscopic data going out to the very large internuclear separations as occurs for the Li dimer. However, the wealth of spectroscopic data available from high-precision photoassociation experiments does raise the possibility of determining atomic lifetimes with a precision superior to 0.01%. The potential analysis required will need to account for a number of small corrections, possibly including magnetic interactions, finite mass effects, spin-orbit, retardation, and other effects. The relative importance of all these terms will need to be determined by systematic computational investigation as a necessary prelude. As part of any effort to achieve $C_3$ precisions significantly better than 0.01% it will be necessary to include the $C_6/R^6$ potential in the analysis just as current analyses of diatomic spectra aiming at determining dissociation energies need to include the $C_6/R^6$ potential [51].

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