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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_9/R^9 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_9 coefficient are given for the homonuclear alkali-metal dimers. The size of the C_9: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 $\mathrm{Li}_2(X\,^1\Sigma_g^+)$ and the $\mathrm{Li}_2(A\,^1\Sigma_u^+)$ 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,

$$V_{\mathrm{PA}}(R) = -\frac{C_3}{R^3} - \frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots . \qquad (1)$$

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 $^7\mathrm{Li}(2s)$-$^7\mathrm{Li}(2p)$ states gave a value of $C_3 = 11.0024(2)$ a.u. [8] that was 0.016% larger than the value of 11.0007 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 Ovsiannikov 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 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 supersede 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 $\mathrm{He}(1\,^1S^e)$-$\mathrm{He}(2\,^1P^o)$, $\mathrm{He}(2\,^1S^e)$-$\mathrm{He}(2\,^1P^o)$, and $\mathrm{He}(2\,^3S^e)$-$\mathrm{He}(2\,^3P^o)$ 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 expansion [16,26].

A. The multipole expansion

The dispersion interaction operator in the asymptotic region $R \gg 1\, a_0$ (a_0 is the Bohr radius) may be presented in the form of an expansion in power series of R^{-1} [27]:

$$V(\mathbf{R}) = \sum_{k=1}^{\infty}\sum_{k'=1}^{\infty} \frac{v_{kk'}(\hat{\mathbf{n}})}{R^{k+k'+1}}, \tag{2}$$

where

$$v_{kk'}(\hat{\mathbf{n}}) = (-1)^{k'} G_{kk'K}(\mathbf{C}^K(\hat{\mathbf{n}}) \cdot [\mathbf{Q}^k(\boldsymbol{\sigma}) \times \mathbf{Q}^{k'}(\boldsymbol{\rho})]^K). \tag{3}$$

The coefficient $G_{kk'K}$ is

$$G_{kk'K} = \left[\frac{(2K)!}{(2k)!(2k')!}\right]^{1/2}, \tag{4}$$

where $K = k + k'$, $\mathbf{Q}^k(\boldsymbol{\sigma}) = \sum_i \sigma_i^k \mathbf{C}^k(\hat{\boldsymbol{\sigma}}_i)$, and $\mathbf{Q}^k(\boldsymbol{\rho}) = \sum_j \rho_j^k \mathbf{C}^k(\hat{\boldsymbol{\rho}}_j)$ are the operator of atomic 2^k-pole electric moments for atoms (A) and (B), respectively, and the summation is from 1 to the number of electrons of each atom. The unit vector $\hat{\mathbf{n}} = \mathbf{R}/R$ points from the first atom (A) to the second atom (B). The $\mathbf{C}^k(\hat{\boldsymbol{\sigma}}_i)$ and $\mathbf{C}^k(\hat{\boldsymbol{\rho}}_j)$ are the spherical tensors [28] of angular variables of the ith or jth electron's position vector $\boldsymbol{\sigma}_i = \{\sigma_i,\theta_i,\varphi_i\}$ and $\boldsymbol{\rho}_j = \{\rho_j,\theta_j,\varphi_j\}$ of atoms (A) and (B), correspondingly. $\mathbf{C}^K(\hat{\mathbf{n}})$ is the interatomic unit vector $\hat{\mathbf{n}}$. Defining the quantization axis in the $\hat{\mathbf{n}}$ direction simplifies Eq. (3) to

$$\begin{aligned} v_{kk'}(\hat{\mathbf{n}}) &= (-1)^{k'} G_{kk'K}[\mathbf{Q}^k(\boldsymbol{\sigma}) \times \mathbf{Q}^{k'}(\boldsymbol{\rho})]_0^K \\ &= (-1)^{k'} G_{kk'K} \sum_{\mu} \langle k\, -\mu k' \mu | K 0\rangle Q_{-\mu}^k(\boldsymbol{\sigma}) Q_{\mu}^{k'}(\boldsymbol{\rho}). \end{aligned} \tag{5}$$

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,

$$\Psi^{(0)}(M) = \Psi_A(\boldsymbol{\sigma})\Psi_B(\boldsymbol{\rho}) = |n_a l_a m_a n_b l_b m_b\rangle, \tag{6}$$

with initial energy $E_{n_a n_b}^{(0)} = E_{n_a} + E_{n_b}$ and $M = m_a + m_b$. 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

$$\begin{aligned} \Delta E^{(3)} = &\sum_{n_c n_d}{}' \sum_{n_e n_f}{}' \frac{\mathcal{A}_1}{\left(E_{n_c n_d} - E_{n_a n_b}^{(0)}\right)\left(E_{n_e n_f} - E_{n_a n_b}^{(0)}\right)} \\ &- \Delta E^{(1)} \sum_{n_c n_d}{}' \frac{\mathcal{A}_2}{\left(E_{n_c n_d} - E_{n_a n_b}^{(0)}\right)^2}, \end{aligned} \tag{7}$$

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

$$\begin{aligned} \Delta E^{(1)} = &\sum_{kk'\mu} (-1)^{k+l_a-m_a+l_b-m_b} \frac{G_{kk'K}}{R^{K+1}} \begin{pmatrix} l_a & k & l_a \\ -m_a & -\mu & m_a' \end{pmatrix} \\ &\times \begin{pmatrix} l_b & k' & l_b \\ -m_b & \mu & m_b' \end{pmatrix} \begin{pmatrix} k & k' & K \\ -\mu & \mu & 0 \end{pmatrix} \mathcal{T}_{aa}^k \mathcal{T}_{bb}^{k'}, \end{aligned} \tag{8}$$

where $\mathcal{T}_{aa}^k$ and $\mathcal{T}_{bb}^{k'}$ are the reduced matrix elements, which comply with the style of the following formulas:

$$\mathcal{T}_{uv}^k = \langle n_u l_u \| \sum_i \sigma_i^k \mathbf{C}^k(\hat{\boldsymbol{\sigma}}_i) \| n_v l_v\rangle \quad (u,v = a,c,e), \tag{9}$$

$$\mathcal{T}_{uv}^k = \langle n_u l_u \| \sum_j \sigma_j^k \mathbf{C}^k(\hat{\boldsymbol{\rho}}_j) \| n_v l_v\rangle \quad (u,v = b,d,f). \tag{10}$$

In Eq. (7), $\mathcal{A}_1$ and $\mathcal{A}_2$ are

$$\begin{aligned} \mathcal{A}_1 = &\sum_{m_c m_d} \sum_{m_e m_f} \langle \Psi^{(0)}(M) | V(\mathbf{R}) | n_c l_c m_c n_d l_d m_d \rangle \\ &\times \langle n_c l_c m_c n_d l_d m_d | V(\mathbf{R}) | n_e l_e m_e n_f l_f m_f \rangle \\ &\times \langle n_e l_e m_e n_f l_f m_f | V(\mathbf{R}) | \Psi^{(0)}(M) \rangle, \end{aligned} \tag{11}$$

$$\begin{aligned} \mathcal{A}_2 = &\sum_{m_c m_d} \langle \Psi^{(0)}(M) | V(\mathbf{R}) | n_c l_c m_c n_d l_d m_d \rangle \\ &\times \langle n_c l_c m_c n_d l_d m_d | V(\mathbf{R}) | \Psi^{(0)}(M) \rangle, \end{aligned} \tag{12}$$

where $|n_c l_c m_c n_d l_d m_d\rangle$ and $|n_e l_e m_e n_f l_f m_f\rangle$ are two intermediate states with the energy eigenvalue $E_{n_c n_d} = E_{n_c} + E_{n_d}$ and $E_{n_e n_f} = E_{n_e} + E_{n_f}$, respectively. The prime in the summation of Eq. (7) indicates that the terms with $E_{n_c n_d} = E_{n_a n_b}^{(0)}$ and $E_{n_e n_f} = E_{n_a n_b}^{(0)}$ should be excluded. Using Eqs. (2)–(6) one obtains

$$\begin{aligned} \mathcal{A}_1 = &\sum_{k_1 k_1'} \sum_{k_2 k_2'} \sum_{k_3 k_3'} (-1)^{k_1+k_2+k_3} \frac{G_{k_1 k_1' K_1} G_{k_2 k_2' K_2} G_{k_3 k_3' K_3}}{R^{K_1+K_2+K_3+3}} \\ &\times \mathcal{U}_1 \mathcal{T}_{ac}^{k_1} \mathcal{T}_{ce}^{k_2} \mathcal{T}_{ea}^{k_3} \mathcal{T}_{bd}^{k_1'} \mathcal{T}_{df}^{k_2'} \mathcal{T}_{fb}^{k_3'}, \end{aligned} \tag{13}$$

$$\mathcal{A}_2 = \sum_{k_1 k_1'} \sum_{k_2 k_2'} (-1)^{k_1+k_2} \frac{G_{k_1 k_1' K_1} G_{k_2 k_2' K_2}}{R^{K_1+K_2+2}} \mathcal{U}_2 \mathcal{T}_{ac}^{k_1} \mathcal{T}_{ac}^{k_2} \mathcal{T}_{bd}^{k_1'} \mathcal{T}_{bd}^{k_2'}, \tag{14}$$

where $K_i = k_i + k_i'$ $(i = 1,2,3)$, and $\mathcal{U}_1$ and $\mathcal{U}_2$ are

$$\begin{aligned} \mathcal{U}_1 = &\sum_{\mu_1 \mu_2 \mu_3} \sum_{m_c m_d} \sum_{m_e m_f} \mathcal{F}_1 \begin{pmatrix} k_1 & k_1' & K_1 \\ -\mu_1 & \mu_1 & 0 \end{pmatrix} \begin{pmatrix} k_2 & k_2' & K_2 \\ -\mu_2 & \mu_2 & 0 \end{pmatrix} \begin{pmatrix} k_3 & k_3' & K_3 \\ -\mu_3 & \mu_3 & 0 \end{pmatrix} \begin{pmatrix} l_a & k_1 & l_c \\ -m_a & -\mu_1 & m_c \end{pmatrix} \\ &\times \begin{pmatrix} l_b & k_1' & l_d \\ -m_b & \mu_1 & m_d \end{pmatrix} \begin{pmatrix} l_c & k_2 & l_e \\ -m_c & -\mu_2 & m_e \end{pmatrix} \begin{pmatrix} l_d & k_2' & l_f \\ -m_d & \mu_2 & m_f \end{pmatrix} \begin{pmatrix} l_e & k_3 & l_a \\ -m_e & -\mu_3 & m_a' \end{pmatrix} \begin{pmatrix} l_f & k_3' & l_b \\ -m_f & \mu_3 & m_b' \end{pmatrix}, \end{aligned} \tag{15}$$

with the phase factor $\mathcal{F}_1 = (-1)^{l_a-m_a+l_b-m_b+l_c-m_c+l_d-m_d+l_e-m_e+l_f-m_f}$.

$$\mathcal{U}_2 = \sum_{\mu_1\mu_2}\sum_{m_cm_d} \begin{pmatrix} l_a & k_1 & l_c \\ -m_a & -\mu_1 & m_c \end{pmatrix} \begin{pmatrix} l_b & k_1' & l_d \\ -m_b & \mu_1 & m_d \end{pmatrix} \begin{pmatrix} l_c & k_2 & l_a \\ -m_c & -\mu_2 & m_a' \end{pmatrix} \begin{pmatrix} l_d & k_2' & l_b \\ -m_d & \mu_2 & m_b' \end{pmatrix} \times \begin{pmatrix} k_1 & k_1' & K_1 \\ -\mu_1 & \mu_1 & 0 \end{pmatrix} \begin{pmatrix} k_2 & k_2' & K_2 \\ -\mu_2 & \mu_2 & 0 \end{pmatrix}. \tag{16}$$

During the analysis it was noted that some $(-1)^k$ phase factors in Eqs. (13) and (14) were omitted during the algebraic development of the general expressions for the second-order dispersion interaction presented in [29,30]. For example, the first phase factor of Eqs. (13) and (14) in [29] should be $(-1)^{k_1+1+k_2}$, not $(-1)^{k_1'+1+k_2'}$. No impacts on the numerical values presented in those papers have been detected. The long-range interaction coefficients arising due to first-order effects are not affected since these always involve even multipoles of the spherical tensor. The second-order energy expressions involve two occurrences of the operator, $v_{kk'}(\hat{\mathbf{n}})$, and this also tends to cause phase errors to cancel.

Finally, in Eq. (8), let $k \to k_3$, $k' \to k_3'$, and $K \to K_3$, Substituting Eqs. (8), (13), and (14) into Eq. (7), one then obtains the third-order energy

$$\Delta E^{(3)} = \sum_{\substack{n\geqslant 3 \\ K_1+K_2+K_3=2n}} \frac{C_{2n+3}(M)}{R^{2n+3}}. \tag{17}$$

In the above, $C_{2n+3}(M)$ are the third-order dispersion coefficients,

$$\begin{aligned} C_{2n+3}(M) = {} & {\sum_{n_cn_d}}' {\sum_{n_en_f}}' \frac{(-1)^{k_1+k_2+k_3} G_{k_1k_1'K_1} G_{k_2k_2'K_2} G_{k_3k_3'K_3}}{\big(E_{n_cn_d} - E^{(0)}_{n_an_b}\big)\big(E_{n_en_f} - E^{(0)}_{n_an_b}\big)} \\ & \times \mathcal{F}_1 \mathcal{U}_1 \mathcal{T}^{k_1}_{ac} \mathcal{T}^{k_2}_{ce} \mathcal{T}^{k_3}_{ea} \mathcal{T}^{k_1'}_{bd} \mathcal{T}^{k_2'}_{df} \mathcal{T}^{k_3'}_{fb} \\ & - {\sum_{n_cn_d}}' \frac{(-1)^{k_1+k_2+k_3} G_{k_1k_1'K_1} G_{k_2k_2'K_2}}{\big(E_{n_cn_d} - E^{(0)}_{n_an_b}\big)^2} \\ & \times \mathcal{F}_2 \mathcal{U}_2{}' \mathcal{T}^{k_1}_{ac} \mathcal{T}^{k_2}_{ac} \mathcal{T}^{k_3}_{aa} \mathcal{T}^{k_1'}_{bd} \mathcal{T}^{k_2'}_{bd} \mathcal{T}^{k_3'}_{bb}, \end{aligned} \tag{18}$$

where $\mathcal{F}_2$ and $\mathcal{U}_2{}'$ are

$$\mathcal{F}_2 = (-1)^{l_a-m_a+l_b-m_b}, \tag{19}$$

$$\mathcal{U}_2{}' = \sum_{\mu} \begin{pmatrix} l_a & k_3 & l_a \\ -m_a & -\mu & m_a' \end{pmatrix} \begin{pmatrix} l_b & k_3' & l_b \\ -m_b & \mu & m_b' \end{pmatrix} \times \begin{pmatrix} k_3 & k_3' & K_3 \\ -\mu & \mu & 0 \end{pmatrix} \mathcal{U}_2. \tag{20}$$

C. The coupled third-order matrix element

In the molecular representation, the initial state is written as the coupled state, that is,

$$\begin{aligned} \Psi^{(0)}(LM) &= |n_al_an_bl_bLM\rangle \\ &= \sum_{m_am_b} \langle l_am_al_bm_b|LM\rangle |n_al_am_an_bl_bm_b\rangle \\ &= \sum_{m_am_b} (-1)^{l_a-l_b-M} \hat{L} \begin{pmatrix} l_a & l_b & L \\ m_a & m_b & -M \end{pmatrix} \\ & \quad \times |n_al_am_an_bl_bm_b\rangle, \end{aligned} \tag{21}$$

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

$$\begin{aligned} \Delta E^{(3)} = {} & {\sum_{n_cn_d}}' {\sum_{n_en_f}}' \frac{\mathcal{B}_1}{\big(E_{n_cn_d} - E^{(0)}_{n_an_b}\big)\big(E_{n_en_f} - E^{(0)}_{n_an_b}\big)} \\ & - \Delta E^{(1)} {\sum_{n_cn_d}}' \frac{\mathcal{B}_2}{\big(E_{n_cn_d} - E^{(0)}_{n_an_b}\big)^2}, \end{aligned} \tag{22}$$

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

$$\Delta E^{(1)} = \sum_{kk'} (-1)^{L-M+k} \frac{\hat{L}\hat{L}' G_{kk'K}}{R^{K+1}} \begin{pmatrix} L & K & L' \\ -M & 0 & M \end{pmatrix} \times \begin{Bmatrix} l_a & l_b & L \\ l_a & l_b & L' \\ k & k' & K \end{Bmatrix} \mathcal{T}^{k}_{aa} \mathcal{T}^{k'}_{bb}. \tag{23}$$

In Eq. (22), $\mathcal{B}_1$ and $\mathcal{B}_2$ are

$$\begin{aligned} \mathcal{B}_1 = {} & \sum_{L_1L_2} \sum_{M_1M_2} \langle \Psi^{(0)}(LM)|V(\mathbf{R})|n_cl_cn_dl_dL_1M_1\rangle \\ & \times \langle n_cl_cn_dl_dL_1M_1|V(\mathbf{R})|n_el_en_fl_fL_2M_2\rangle \\ & \times \langle n_el_en_fl_fL_2M_2|V(\mathbf{R})|\Psi^{(0)}(L'M)\rangle, \end{aligned} \tag{24}$$

$$\begin{aligned} \mathcal{B}_2 = {} & \sum_{m_cm_d} \langle \Psi^{(0)}(LM)|V(\mathbf{R})|n_cl_cn_dl_dL_1M_1\rangle \\ & \times \langle n_cl_cn_dl_dL_1M_1|V(\mathbf{R})|\Psi^{(0)}(L'M)\rangle. \end{aligned} \tag{25}$$

Using Eqs. (2) and (21), together with the Wigner-Eckart theorem, $\mathcal{B}_1$ can be expanded as

$$\begin{aligned} \mathcal{B}_1 = {} & \sum_{L_1L_2} \sum_{k_1k_1'} \sum_{k_2k_2'} \sum_{k_3k_3'} (-1)^{k_1+k_2+k_3} \frac{\hat{L}\hat{L}'\hat{L}_1^2\hat{L}_2^2}{R^{K_1+K_2+K_3+3}} \\ & \times G_{k_1k_1'K_1} G_{k_2k_2'K_2} G_{k_3k_3'K_3} \mathcal{U}_3 \mathcal{T}^{k_1}_{ac} \mathcal{T}^{k_2}_{ce} \mathcal{T}^{k_3}_{ea} \mathcal{T}^{k_1'}_{bd} \mathcal{T}^{k_2'}_{df} \mathcal{T}^{k_3'}_{fb}. \end{aligned} \tag{26}$$

Using the graphical methods [31], the factor $\mathcal{U}_3$, which contains all the $3j$ symbols, can be reduced to

$$\mathcal{U}_3 = \sum_X \hat{X}^2(-1)^{l_a+l_b+l_e+l_f+L+L_2}\begin{pmatrix} K_2 & X & K_3 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \begin{pmatrix} L_1 & X & L' \\ M & 0 & -M \end{pmatrix}\begin{pmatrix} L_1 & K_1 & L \\ M & 0 & -M \end{pmatrix}\begin{Bmatrix} L & K_3 & L_2 \\ K_2 & L_1 & X \end{Bmatrix}$$
$$\times \begin{Bmatrix} l_a & l_b & L \\ l_c & l_d & L_1 \\ k_1 & k_1' & K_1 \end{Bmatrix}\begin{Bmatrix} l_c & l_d & L_1 \\ l_e & l_f & L_2 \\ k_2 & k_2' & K_2 \end{Bmatrix}\begin{Bmatrix} l_a & l_b & L \\ l_e & l_f & L_2 \\ k_3 & k_3' & K_3 \end{Bmatrix}. \tag{27}$$

Substituting Eq. (27) into Eq. (26) gives rise to the final expression for $\mathcal{B}_1$,

$$\mathcal{B}_1 = \sum_X (-1)^{L+L_2}\begin{pmatrix} K_2 & X & K_3 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L_1 & X & L' \\ M & 0 & -M \end{pmatrix}\mathcal{D}_X, \tag{28}$$

where $\mathcal{D}_X$ is

$$\mathcal{D}_X = \sum_{L_1L_2}\sum_{k_1k_1'}\sum_{k_2k_2'}\sum_{k_3k_3'}(-1)^{k_1+k_2+k_3+l_a+l_b+l_e+l_f}\frac{\hat{L}\hat{L}'\hat{L}_1^2\hat{L}_2^2\hat{X}^2}{R^{K_1+K_2+K_3+3}}$$
$$\times G_{k_1k_1'K_1}G_{k_2k_2'K_2}G_{k_3k_3'K_3}\mathcal{T}_{ac}^{k_1}\mathcal{T}_{ce}^{k_2}\mathcal{T}_{ea}^{k_3}$$
$$\times T_{bd}^{k_1'}\mathcal{T}_{df}^{k_2'}\mathcal{T}_{fb}^{k_3'}\begin{pmatrix} L_1 & K_1 & L \\ M & 0 & -M \end{pmatrix}\begin{Bmatrix} L & K_3 & L_2 \\ K_2 & L_1 & X \end{Bmatrix}$$
$$\times \begin{Bmatrix} l_a & l_b & L \\ l_c & l_d & L_1 \\ k_1 & k_1' & K_1 \end{Bmatrix}\begin{Bmatrix} l_c & l_d & L_1 \\ l_e & l_f & L_2 \\ k_2 & k_2' & K_2 \end{Bmatrix}\begin{Bmatrix} l_a & l_b & L \\ l_e & l_f & L_2 \\ k_3 & k_3' & K_3 \end{Bmatrix}. \tag{29}$$

Performing a similar procedure for the $\mathcal{B}_2$ of Eq. (25), we have

$$\mathcal{B}_2 = \sum_X (-1)^{L'-M}\begin{pmatrix} L & X & L' \\ -M & 0 & M \end{pmatrix}\mathcal{W}_X, \tag{30}$$

with $\mathcal{W}_X$ being

$$\mathcal{W}_X = -\sum_{k_1k_1'}\sum_{k_2k_2'}\sum_{L_1}(-1)^{k_1+k_2+l_a+l_b+l_c+l_d}\frac{\hat{L}\hat{L}'\hat{L}_1^2\hat{X}^2}{R^{K_1+K_2+2}}G_{k_1k_1'K_1}$$
$$\times G_{k_2k_2'K_2}\mathcal{T}_{ac}^{k_1}\mathcal{T}_{ac}^{k_2}\mathcal{T}_{bd}^{k_1'}\mathcal{T}_{bd}^{k_2'}\begin{pmatrix} k_1 & k_2 & X \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \begin{Bmatrix} L & K_1 & L_1 \\ K_2 & L' & X \end{Bmatrix}\begin{Bmatrix} l_a & l_b & L \\ l_c & l_d & L_1 \\ k_1 & k_1' & K_1 \end{Bmatrix}\begin{Bmatrix} l_c & l_d & L_1 \\ l_a & l_b & L' \\ k_2 & k_2' & K_2 \end{Bmatrix}. \tag{31}$$

In Eq. (23) of $\Delta E^{(1)}$, making $k \to k_3$ and $k' \to k_3'$, 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,

$$\Delta E^{(3)} = \sum_{\substack{n\geqslant 3 \\ K_1+K_2+K_3=2n}}\frac{C_{2n+3}(L,M)}{R^{2n+3}}, \tag{32}$$

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

$$C_{2n+3}(L,M)$$
$$= \sum_{n_cn_d}{}'\sum_{n_en_f}{}'\sum_{L_1L_2X}\frac{(-1)^{L+L_2+k_1+k_2+k_3}\hat{L}\hat{L}'\hat{L}_1^2\hat{L}_2^2\hat{X}^2}{\left(E_{n_cn_d}-E_{n_an_b}^{(0)}\right)\left(E_{n_en_f}-E_{n_an_b}^{(0)}\right)}\mathcal{D}_X'$$
$$-\sum_{n_cn_d}{}'\sum_{L_1X}\frac{(-1)^{L+L'+k_1+k_2+k_3}\hat{L}^2\hat{L}'^2\hat{L}_1^2\hat{X}^2}{\left(E_{n_cn_d}-E_{n_an_b}^{(0)}\right)^2}\mathcal{W}_X', \tag{33}$$

where $\mathcal{D}_X'$ and $\mathcal{W}_X'$ are

$$\mathcal{D}_X' = (-1)^{l_a+l_b+l_e+l_f}G_{k_1k_1'K_1}G_{k_2k_2'K_2}G_{k_3k_3'K_3}\mathcal{T}_{ac}^{k_1}\mathcal{T}_{ce}^{k_2}\mathcal{T}_{ea}^{k_3}\mathcal{T}_{bd}^{k_1'}\mathcal{T}_{df}^{k_2'}\mathcal{T}_{fb}^{k_3'}\begin{pmatrix} K_2 & X & K_3 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L_1 & X & L' \\ M & 0 & -M \end{pmatrix}$$
$$\times \begin{pmatrix} L_1 & K_1 & L \\ M & 0 & -M \end{pmatrix}\begin{Bmatrix} L & K_3 & L_2 \\ K_2 & L_1 & X \end{Bmatrix}\begin{Bmatrix} l_a & l_b & L \\ l_c & l_d & L_1 \\ k_1 & k_1' & K_1 \end{Bmatrix}\begin{Bmatrix} l_c & l_d & L_1 \\ l_e & l_f & L_2 \\ k_2 & k_2' & K_2 \end{Bmatrix}\begin{Bmatrix} l_a & l_b & L \\ l_e & l_f & L_2 \\ k_3 & k_3' & K_3 \end{Bmatrix}, \tag{34}$$

$$\mathcal{W}_X' = (-1)^{1+l_a+l_b+l_c+l_d}G_{k_1k_1'K_1}G_{k_2k_2'K_2}G_{k_3k_3'K_3}\mathcal{T}_{ac}^{k_1}\mathcal{T}_{ac}^{k_2}\mathcal{T}_{aa}^{k_3}\mathcal{T}_{bd}^{k_1'}\mathcal{T}_{bd}^{k_2'}\mathcal{T}_{bb}^{k_3'}\begin{pmatrix} L & K & L' \\ -M & 0 & M \end{pmatrix}$$
$$\times \begin{pmatrix} L & X & L' \\ -M & 0 & M \end{pmatrix}\begin{pmatrix} k_1 & k_2 & X \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} L & K_1 & L_1 \\ K_2 & L' & X \end{Bmatrix}\begin{Bmatrix} l_a & l_b & L \\ l_c & l_d & L_1 \\ k_1 & k_1' & K_1 \end{Bmatrix}\begin{Bmatrix} l_c & l_d & L_1 \\ l_a & l_b & L' \\ k_2 & k_2' & K_2 \end{Bmatrix}\begin{Bmatrix} l_a & l_b & L \\ l_a & l_b & L' \\ k_3 & k_3' & K_3 \end{Bmatrix}. \tag{35}$$

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

$$\Psi^{(0)}(n_a,n_b,M) = \sum_{m_a=-l_a}^{l_a} \sum_{m_b=-l_b}^{l_b} \delta_{m_a+m_b,M} C_{m_a,m_b} \times \Psi(n_a l_a m_a n_b l_b m_b,M), \tag{36}$$

where Ψ_{n_a} has an energy eigenvalue of E_{n_a}, Ψ_{n_b} has an energy eigenvalue of E_{n_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

$$\Psi^{(0)}(n_a,n_b) = \Psi(n_a,m_a = 0,n_b,m_b = 0,M = 0). \tag{37}$$

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

$$\Psi^{(0)}(n_a,n_b,M) = [\Psi(n_a 0 n_b M,M) + \beta\Psi(n_b M n_a 0,M)]/\sqrt{2}. \tag{38}$$

The factor $\beta = \pm 1$ can be related to the fundamental symmetries of the states by $\beta = (-1)^{l_a+l_b}(-1)^S p$, 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 ${}^1\Sigma_u^+$ state has $\beta = +1$, while the ${}^1\Sigma_g^+$ 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.,

$$V^{(3)} = [\langle n_a 0 n_b M,M|V|n_a 0 n_b M,M\rangle + \beta\langle n_a 0 n_b M,M|V|n_b M n_a 0,M\rangle]/2. \tag{39}$$

E. The C_9 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_3/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

$$V^{(3)} = \beta\langle n_a 0 n_b M,M|V|n_b M n_a 0,M\rangle. \tag{40}$$

III. STRUCTURE CALCULATIONS

A. Hamiltonian and Hylleraas coordinates

The He and Li atoms are three- and four-body Coulomb systems. Since the Hylleraas method for computing the He and Li wave functions is quite similar, only the Li case is discussed. Treating the nuclear mass as infinite, the nonrelativistic Hamiltonian for Li can be written

$$H_0 = -\sum_{i=1}^{3}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{3}\frac{Z}{r_i} + \sum_{i>j\geqslant 1}^{3}\frac{1}{r_{ij}}, \tag{41}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between electrons i and j, and Z is the nuclear charge. In our calculation the wave functions are expanded in terms of the explicitly correlated basis set in Hylleraas coordinates,

$$\phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1-\beta r_2-\gamma r_3} \times \mathcal{Y}^{LM_L}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_3)\chi(1,2,3), \tag{42}$$

where $\mathcal{Y}^{LM_L}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_3)$ is the vector-coupled product of spherical harmonics to form an eigenstate of total angular momentum L and component M_L,

$$\mathcal{Y}^{LM_L}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_3) = \sum_{\text{all } m_i}\langle \ell_1 m_1 \ell_2 m_2|\ell_{12} m_{12}\rangle \times\langle \ell_{12} m_{12} \ell_3 m_3|L M_L\rangle Y_{\ell_1 m_1}(\hat{\mathbf{r}}_1) \times Y_{\ell_2 m_2}(\hat{\mathbf{r}}_2) Y_{\ell_3 m_3}(\hat{\mathbf{r}}_3), \tag{43}$$

and $\chi(1,2,3)$ is the three-electron spin-1/2 wave function. The variational wave function is a linear combination of antisymmetrized basis functions ϕ. With some truncations to avoid potential numerical linear dependence, all terms in Eq. (42) are included such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leqslant \Omega, \tag{44}$$

where Ω is an integer. The computational details for evaluating the necessary Hamiltonian matrix elements can be found in [33]. The convergence for the energies and other expectation values is studied by increasing Ω progressively. The basis sets are essentially the same as the two earlier Hylleraas calculations of the static polarizabilities [34,35]. The uncertainty in the final value of any quantity is usually estimated to be equal to the size of the extrapolation from the largest explicit calculation.

It should be noted that Hylleraas calculations for He and Li of finite nuclear masses have been performed recently [34]. However, there is a tendency for finite nuclear mass effects to lead to ground-state polarizabilities and dispersion coefficients to increase in size. On the other hand, relativistic effects cause the polarizabilities and dispersion coefficients to decrease in size [15]. The two effects tend to almost cancel each other in Li. Accordingly, we only present results for infinite nuclear masses in this paper, otherwise it would be questionable whether the use of a finite nuclear mass Hamiltonian would produce numerical values which are closer to the true values.

B. The semiempirical approach

The transition arrays for the alkali-metal atoms are those which were used in calculations of the dispersion interactions between these atoms and the ground states of hydrogen and helium [29]. These are computed by diagonalizing the fixed core Hamiltonian in a large basis of Laguerre-type orbitals. The core Hamiltonian is based upon a Hartree-Fock (HF) description of the core with a semiempirical core-polarization potential tuned to reproduce the energies of a low-lying 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

$$H = -\tfrac{1}{2}\nabla^2 + V_{\rm dir}(\mathbf{r}) + V_{\rm exc}(\mathbf{r}) + V_{p1}(\mathbf{r}), \qquad (45)$$

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

$$V_{p1}(\mathbf{r}) = -\sum_{\ell m} \frac{\alpha_{\rm core} g_\ell^2(r)}{2r^4} |\ell m\rangle\langle \ell m|. \qquad (46)$$

In the above, the coefficient $\alpha_{\rm core}$ is the static dipole polarizability of the core and $g_\ell^2(r) = 1 - \exp(-r^6/\rho_\ell^6)$ is a cutoff function designed to make the polarization potential finite at the origin. In these calculations, the cutoff parameters ρ_ℓ 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 $C_{11} = -3474.898\,038$ a.u., $C_{13} = -3.269\,869\,240 \times 10^5$ a.u., and $C_{15} = -2.839\,558\,063 \times 10^7$ 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 He(1 $^1S^e$)-He(1 $^1S^e$) 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.

(N_S,N_P,N_D,N_F)	C_{11}	C_{13}
(68,70,53,60)	−76.734140	−3808.62838
(140,168,146,105)	−76.725890	−3808.32822
(250,330,310,252)	−76.725730	−3808.32604
(406,440,425,360)	−76.725724	−3808.32592
Extrapolated	−76.72571(1)	−3808.3254(5)
Przybytek [22–24]	−76.74(4)	−3806(1)

TABLE II. Convergence of the Hylleraas calculations of C_9 for the He(1 $^1S^e$)-He(2 $^1P^o$) and He(2 $^1S^e$)-He(2 $^1P^o$) combinations. Values are given for $\beta = 1$. Values for $\beta = -1$ can be obtained by multiplying C_9 by −1.

$(N_S,N_P,N_{P'},N_D)$	$M_b = 0$	$M_b = \pm 1$
	He(1 $^1S^e$)-He(2 $^1P^o$)	
(68,70,44,53)	−270.7714	76.59798
(100,112,68,92)	−271.2254	76.74983
(140,168,100,146)	−271.2281	76.75505
(190,240,140,218)	−271.2257	76.74236
(250,330,190,310)	−271.2449	76.76323
Extrapolated	−271.25(1)	76.764(1)
Zhang *et al.* [38]	−271.24449(2)	76.76195(2)
	He(2 $^1S^e$)-He(2 $^1P^o$)	
(68,70,44,53)	1.716995×10^6	-3.654470×10^5
(100,112,68,92)	1.719162×10^6	-3.660414×10^5
(140,168,100,146)	1.719227×10^6	-3.661189×10^5
(190,240,140,218)	1.719528×10^6	-3.658259×10^5
(250,330,190,310)	1.719885×10^6	-3.662254×10^5
Extrapolated	$1.7199(1) \times 10^6$	$-3.6623(1) \times 10^5$
Zhang *et al.* [38]	$1.719978(5) \times 10^6$	$-3.662611(5) \times 10^5$

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 III. Convergence of the Hylleraas calculations of $10^{-5}C_9$ for the He(2 $^3S^e$)-He(2 $^3P^o$) combinations. Values are given for $\beta = 1$. Values for $\beta = -1$ can be obtained by multiplying C_9 by −1.

$(N_S,N_P,N_{P'},N_D)$	$M_b = 0$	$M_b = \pm 1$
(44,70,70,44)	5.110069	−1.168104
(100,112,100,119)	5.118769	−1.170238
(190,240,190,262)	5.119765	−1.170506
(322,330,322,364)	5.120391	−1.170679
(406,440,504,490)	5.120544	−1.170722
Extrapolated	5.12058(4)	−1.17073(1)
Zhang *et al.* [14]	5.12059227(6)	−1.17073536(2)

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.

(N_S,N_P,N_D,N_F)	C_{11}	C_{13}
(120,55,55,52)	-40.407906×10^6	-1.100112×10^{10}
(256,138,138,132)	-40.382372×10^6	-1.102884×10^{10}
(502,306,306,302)	-40.389347×10^6	-1.103513×10^{10}
(918,622,622,636)	-40.388211×10^6	-1.103784×10^{10}
Extrapolated	$-40.386(2) \times 10^6$	$-1.1039(2) \times 10^{10}$
CICP [39]	-40.44×10^6	-1.105×10^{10}

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_3, 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_8 and C_{10} coefficients. The C_8 coefficients are $9.90895(5) \times 10^5$ and $0.485648(5) \times 10^5$ for the Σ and Π states with $\beta = -1$ [34]. The C_{10} coefficients are 1.2113×10^8 and 9.1839×10^5 for the Σ and Π states with $\beta = -1$ [40]. The C_8 coefficients are $2.74079(2) \times 10^5$ and $1.03044(2) \times 10^5$ for the Σ and Π states with $\beta = +1$ [34]. The C_{10} coefficients are 3.0096×10^8 and 8.9295×10^5 for the Σ and Π states with $\beta = +1$ [40]. The third-order C_9 coefficients are roughly the same size as the second-order C_8 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(2$p_{1/2}$) transition, namely, $C_3 = 11.00241(23)$ [8]. This value was derived from the $A(^1\Sigma_u^+)$ state ($\beta = 1$) 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 $170a_0$. The interatomic potential can be described by a purely dispersive form past about $25a_0$ [41]. At this separation, the size of the C_9 to C_3 potential ratio is $2.2 \times 10^5/(11 \times 25^6) = 0.000082$. 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 $25a_0$. 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.

TABLE V. Convergence of C_9 for the Li(2s)-Li(2p) dimer using Hylleraas basis sets. Values are given for $\beta = 1$. Values for $\beta = -1$ can be obtained by multiplying C_9 by -1.

$(N_S,N_P,N_{P'},N_D)$	$10^{-5}C_9$ ($M_b = \pm 1$)	$10^{-5}C_9$ ($M_b = 0$)
(120,55,36,55)	-0.516749	2.296186
(256,138,108,138)	-0.516610	2.288464
(502,306,264,306)	-0.516932	2.287301
(918,622,568,622)	-0.517170	2.287505
(1589,1174,1106,1174)	-0.517255	2.287809
Extrapolated	$-0.5173(1)$	2.2880(2)
CICP	-0.5152	2.279

TABLE VI. C_3, C_9, and C_{11} for $X(ns)$-$X(np)$ homonuclear alkali-metal dimers. These coefficients were computed using the CICP matrix elements, except for the first four rows where the Hylleraas matrix elements were used.

Molecule	β	C_3	$C_9 \times 10^{-5}$	$C_{11} \times 10^{-7}$
		Hylleraas		
Li Σ	1	11.0007 [15]	2.2880(2)	-5.930
	-1	-11.0007 [15]	$-2.2880(2)$	-50.321
Li Π	1	-5.5004 [15]	$-0.5173(1)$	-9.924
	-1	5.5004 [15]	0.5173(1)	2.652
		CICP		
Li Σ	1	11.008	2.279	-5.976
	-1	-11.004	-2.279	-50.32
Li Π	1	-5.504	-0.5152	-9.925
	-1	5.504	0.5152	2.640
Na Σ	1	12.44	2.839	-30.27
	-1	-12.44	-2.839	-147.0
Na Π	1	-6.221	-0.5993	-28.64
	-1	6.221	0.5993	4.772
K Σ	1	16.82	13.05	-132.1
	-1	-16.82	-13.05	-7.325
K Π	1	-8.412	-2.318	-143.2
	-1	8.412	2.318	27.42
Rb Σ	1	17.73	19.72	-224.2
	-1	-17.73	-19.72	-121.1
Rb Π	1	-8.864	-3.552	-235.8
	-1	8.864	3.552	42.27
Cs Σ	1	19.91	35.00	-520.9
	-1	-19.91	-35.00	-255.1
Cs Π	1	-9.955	-53.23	-494.7
	-1	9.955	53.23	802.6

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_9 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_9 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_9 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_9 coefficient should be included as a matter of course in any analysis of photoassociation spectra aimed at deriving a value for the the C_3 parameter.

The C_{10} and C_{11} coefficients for lithium are roughly equal in magnitude. For example, the $\beta = 1$ Σ-state values of C_{10} and C_{11} are 3.01×10^7 [40] and -5.929×10^7, 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_9 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_9 dispersion coefficients occur in the interaction potentials for homonuclear dimers when one of the atoms is in a dipole excited state. The C_9: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_9 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_9/R^9 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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