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Long-range dispersion interactions. I. Formalism for two heteronuclear atoms

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A general procedure for systematically evaluating the long-range dispersion interaction between two heteronuclear atoms in arbitrary states is outlined. The C_6 dispersion parameter can always be written in terms of sum rules involving oscillator strengths only and formulas for a number of symmetry cases are given. The dispersion coefficients for excited alkali-metal atoms interacting with the ground-state H and He are tabulated.

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I. INTRODUCTION

In this paper a systematic approach to the calculation of the long-range interactions between two heteronuclear atoms in arbitrary atomic states is presented. For two spherically symmetric atoms, the long-range interaction is just the well known van der Waals interaction [1,2], e.g.,

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots . \tag{1}$$

The C_n parameters are the dispersion coefficients while R is the distance between the two nuclei. The procedures for determining the dispersion coefficients for two spherically symmetric atoms are well understood and there has been a lot of activity in calculating the van der Waals coefficients for alkali atoms [3–9]. Very recently, the dispersion coefficients for hydrogen were evaluated for all multipoles up to C_{30} including terms arising from the tenth order of perturbation theory [10].

When one of the atoms is in a state with nonzero angular momentum the van der Waals interaction depends on the angular momentum projections of the states. While there have been some investigations of the van der Waals coefficients for nonspherically symmetric states, the overall impression one gains is that calculations are performed in an ad hoc fashion with expressions for different configurations derived on a case by case basis [9,11–15]. One recent attempt to deal with the problem by a more formal process using tensor calculus was reported by Santra and Greene [16,17]. However, this work was confined to the investigation of the long-range interactions of the $5s5p\ {}^3P^o_2$ state of strontium. An earlier treatment by Ovsiannikov [18] developed expressions for the atomic representation (results in the present paper are given in the molecular representation).

The absence of a systematic procedure to determine the long-range interactions and its impact upon the existing research is best highlighted by reference to some recent studies of the spectra of MgH and CaH [19–21]. The dispersion coefficients were evaluated using the oscillator strength sum rules for spherically symmetric states, or used the London formula [19,22] without any reference to the symmetries of the molecular system. This is surprising since the lowest order C_6 dispersion parameter can be written as a sum over oscillator strengths even for the anisotropic case. However, we are unaware of any publication that systematically reports the details of the oscillator strength sum rules that are needed to compute the dispersion coefficients for the anisotropic case.

The present work describes a procedure that can be used to determine the long-range interaction between two atoms in arbitrary states. The method is then applied to a calculation of excited alkali-metal atoms interacting with the ground states of H and He. The interactions of alkali-metal atoms with He are of relevance for the modeling of atmospheres of brown dwarf stars [23–27]. Finally, expressions for the C_6 dispersion coefficient in terms of oscillator strength sum rules are presented. Extensive sets of formulas suitable for use with tabulations of oscillator strengths are also given.

II. THEORETICAL DEVELOPMENT

The general expression for the long-range interaction between two atoms has contributions from both first-order and second-order perturbation theory [28]. The general expression can be written

$$V(R) = -\sum_{s=1}^{\infty} \frac{C_{2s+4}}{R^{2s+4}} - \sum_{s=1}^{l_a+l_b-1} \frac{C_{2s+3}}{R^{2s+3}} \cdots . \tag{2}$$

The first summation arises from second-order perturbation theory and is always present. The second summation occurs as the result of the first-order interaction between two atomic states with nonzero angular momentum. The number of terms in the second sum is finite and depends on the angular momentum on the individual atoms.

The dispersion coefficients will be evaluated for states written as molecular states. In the case of degenerate states with the same molecular symmetry, the strategy will be to first diagonalize the leading term of the first-order quadrupole-quadrupole interaction to determine the molecular states. These are then used to determine the dispersion coefficients. All expressions are given for the case of two atoms each with a single active electron. These expressions can be trivially extended to the more general case since all atomic structure information is encapsulated in the reduced matrix elements.

The coefficients for the van der Waals interaction will be evaluated by evaluating the sum over intermediate states with a pseudostate expansion [5,29].

A. Multipole expansion

The dispersion interaction operator in the asymptotic region $R \gg a_0$ may be presented in the form of an expansion in the power series of R^{-1} [30] as follows:

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$$V(\mathbf{R}) = \sum_{k=1}^{\infty} \sum_{k'=1}^{\infty} \frac{v_{kk'}(\hat{\mathbf{n}})}{R^{k+k'+1}}, \tag{3}$$

where

$$v_{kk'}(\hat{\mathbf{n}}) = (-1)^{k'} \left[\frac{(2K)!}{(2k)!(2k')!} \right]^{1/2} (\mathbf{C}^K(\hat{\mathbf{n}}) \cdot [\mathbf{Q}^k(\mathbf{r}_a) \times \mathbf{Q}^{k'}(\mathbf{r}_b)]^K), \tag{4}$$

where $K=k+k'$, $\mathbf{Q}^k(\mathbf{r})=r^k\mathbf{C}^k(\mathbf{r})$ is the operator of the atomic 2^k-pole electric moment, and the unit vector $\hat{\mathbf{n}}=\mathbf{R}/R$ points from the first atom (a) to the second atom (b). The $\mathbf{C}^k(\theta,\varphi)$ and $\mathbf{C}^K(\hat{\mathbf{n}})$ are the spherical tensors [31] of angular variables of the atomic electron's position vector $\mathbf{r}=\{r,\theta,\varphi\}$ and those of the interatomic unit vector $\hat{\mathbf{n}}$, correspondingly. Defining the quantization axis in the $\hat{\mathbf{n}}$ direction simplifies Eq. (4) to

$$\begin{aligned} v_{kk'}(\hat{\mathbf{n}}) &= (-1)^{k'} \left[\frac{(2K)!}{(2k)!(2k')!} \right]^{1/2} [\mathbf{Q}^k(\mathbf{r}_a) \times \mathbf{Q}^{k'}(\mathbf{r}_b)]^K_0 \\ &= (-1)^{k'} \left[\frac{(2K)!}{(2k)!(2k')!} \right]^{1/2} \sum_{\mu} \langle k-\mu k'\mu | K0\rangle \\ &\quad \times Q^k_{-\mu}(\mathbf{r}_a) Q^{k'}_{\mu}(\mathbf{r}_b). \end{aligned} \tag{5}$$

B. First-order interaction

The general matrix element is evaluated between product states

$$\Psi^{(0)}(M) = \Psi_{n_a l_a m_a}(\mathbf{r}_a)\Psi_{n_b l_b m_b}(\mathbf{r}_b), \tag{6}$$

with $M=m_a+m_b$. The electron-electron operator, Eq. (3), conserves M but not m_a or m_b. The general matrix element is written as follows:

$$\begin{aligned} V^{(1)}_{m_a m_b m_a' m_b'} = \sum_{kk'\mu} \frac{(-1)^{k'}}{R^{K+1}} \left[\frac{(2K)!}{(2k)!(2k')!} \right]^{1/2} \langle k-\mu k'\mu | K0\rangle \\ \times \langle n_a l_a m_a n_b l_b m_b | Q^k_{-\mu} Q^{k'}_{\mu} | n_a l_a m_a' n_b l_b m_b'\rangle, \end{aligned} \tag{7}$$

which is expressed most conveniently as

$$\begin{aligned} V^{(1)}_{m_a m_b m_a' m_b'} &= \sum_{kk'} \frac{(-1)^{k'}}{R^{K+1}} \left[\frac{(2K+1)!}{(2k)!(2k')!} \right]^{1/2} \langle n_a l_a \| r^k \mathbf{C}^k \| l_a n_a\rangle \\ &\quad \times \langle n_b l_b \| r^{k'} \mathbf{C}^{k'} \| l_b n_b\rangle \\ &\quad \times \sum_{\mu} (-1)^{l_a - m_a + l_b - m_b} \begin{pmatrix} l_a & k & l_a \\ -m_a & -\mu & m_a' \end{pmatrix} \\ &\quad \times \begin{pmatrix} l_b & k' & l_b \\ -m_b & \mu & m_b' \end{pmatrix} \begin{pmatrix} k & k' & K \\ -\mu & \mu & 0 \end{pmatrix}. \end{aligned} \tag{8}$$

It is possible to write this expression in a coupled form [16]. Using the coupled state,

$$\Psi^{(0)}(LM) = \sum_{m_a, m_b} \langle l_a m_a l_b m_b | LM\rangle \Psi_{n_a l_a m_a}(\mathbf{r}_a)\Psi_{n_b l_b m_b}(\mathbf{r}_b) \tag{9}$$

gives

$$\begin{aligned} V^{(1)}_{LL'M} &= \sum_{kk'} \frac{(-1)^{k'}}{R^{K+1}} \left[\frac{(2K)!}{(2k)!(2k')!} \right]^{1/2} \langle n_a l_a n_b l_b LM | [\mathbf{Q}^k(\mathbf{r}_a) \\ &\quad \times \mathbf{Q}^{k'}(\mathbf{r}_b)]^K_0 | n_a l_a n_b l_b L' M\rangle \\ &= \sum_{K} (-1)^{L-M} \begin{pmatrix} L & K & L' \\ -M & 0 & M \end{pmatrix} U^K, \end{aligned} \tag{10}$$

where the reduced matrix element U^K is

$$\begin{aligned} U^K = \sum_{kk'} \frac{(-1)^{k'} \hat{L}\hat{L}'}{R^{K+1}} \left[\frac{(2K+1)!}{(2k)!(2k')!} \right]^{1/2} \begin{Bmatrix} l_a & l_b & L \\ l_a & l_b & L' \\ k & k' & K \end{Bmatrix} \\ \times \langle n_b l_b \| r^{k'} \mathbf{C}^{k'} \| l_b n_b\rangle \langle n_a l_a \| r^k \mathbf{C}^k \| l_a n_a\rangle. \end{aligned} \tag{11}$$

The notation $\hat{L}=\sqrt{(2L+1)}$ is adopted.

It is simple to show that the first-order interaction is zero if one of the atoms is in an S state. The first configuration leading to a nonzero quadrupole interaction is the $P-P$ case. Since the minimum value of k or k' leading to a nonzero reduced matrix element is 2, one gets $K=4$ and so in this case the first-order interaction transforms as a tensor of rank 4 [16]. The C_{K+1} coefficients are obtained from Eqs. (8) and (11) by multiplying by $-R^{K+1}$.

C. Second-order interaction

For the second-order interaction $V^{(2)}$, the general matrix element in uncoupled form is

$$\begin{aligned} V^{(2)}_{m_a m_b m_a' m_b'} &= -\sum_{k_1 k_1' \mu_1} \sum_{k_2 k_2' \mu_2} \sum_{\substack{n_c m_c \\ n_d m_d}} \frac{(-1)^{k_1' + k_2'}}{R^{K_1+K_2+2}} \\ &\quad \times \left[\frac{(2K_1)!(2K_2)!}{(2k_1)!(2k_1')!(2k_2)!(2k_2')!} \right]^{1/2} \\ &\quad \times \langle n_a l_a m_a n_b l_b m_b | Q^{k_1}_{-\mu_1} Q^{k_1'}_{\mu_1} | n_c l_c m_c n_d l_d m_d\rangle \\ &\quad \times \frac{\langle n_c l_c m_c n_d l_d m_d | Q^{k_2}_{-\mu_2} Q^{k_2'}_{\mu_2} | n_a l_a m_a' n_b l_b m_b'\rangle}{E_{n_c} + E_{n_d} - E_{n_a} - E_{n_b}} \\ &\quad \times \langle k_1 - \mu_1 k_1 \mu_1 | K_1 0\rangle \langle k_2 - \mu_2 k_2' \mu_2 | K_2 0\rangle. \end{aligned} \tag{12}$$

Applying the Wigner-Eckart theorem and collecting terms gives

$$\begin{aligned} V^{(2)}_{m_a m_b m_a' m_b'} &= -\sum_{k_1 k_1' \mu_1} \sum_{k_2 k_2' \mu_2} \sum_{n_c n_d, m_c m_d} \frac{(-1)^{k_1' + k_2'}}{R^{K_1+K_2+2}} \\ &\quad \times \left[\frac{(2K_1+1)!(2K_2+1)!}{(2k_1)!(2k_1')!(2k_2)!(2k_2')!} \right]^{1/2} \\ &\quad \times \frac{\langle n_a l_a \| r^{k_1} \mathbf{C}^{k_1} \| l_c n_c\rangle \langle n_a l_a \| r^{k_2} \mathbf{C}^{k_2} \| l_c n_c\rangle}{E_{n_c} + E_{n_d} - E_{n_a} - E_{n_b}} \\ &\quad \times \langle n_b l_b \| r^{k_1'} \mathbf{C}^{k_1'} \| l_d n_d\rangle \langle n_b l_b \| r^{k_2'} \mathbf{C}^{k_2'} \| l_d n_d\rangle \end{aligned}$$

$$\times \begin{pmatrix} l_a & k_1 & l_c \\ -m_a & -\mu_1 & m_c \end{pmatrix} \begin{pmatrix} l_b & k_1' & l_d \\ -m_b & \mu_1 & m_d \end{pmatrix}$$
$$\times \begin{pmatrix} l_c & k_2 & l_a \\ -m_c & -\mu_2 & m_a' \end{pmatrix} \begin{pmatrix} l_d & k_2' & l_b \\ -m_d & \mu_2 & m_b' \end{pmatrix}$$
$$\times \begin{pmatrix} k_1 & k_1' & K_1 \\ -\mu_1 & \mu_1 & 0 \end{pmatrix} \begin{pmatrix} k_2 & k_2' & K_2 \\ -\mu_2 & \mu_2 & 0 \end{pmatrix}. \quad (13)$$

The dispersion interaction can also be written in coupled form and one has

$$V^{(2)}_{LL'M} = -\sum_{k_1k_1'} \sum_{k_2k_2'} \sum_{cd,L_IM_I} \frac{(-1)^{k_1'+k_2'}}{R^{K_1+K_2+2}}$$
$$\times \left[\frac{(2K_1)!(2K_2)!}{(2k_1)!(2k_1')!(2k_2)!(2k_2')!} \right]^{1/2}$$
$$\times \frac{\langle n_a l_a n_b l_b LM | [\mathbf{Q}^{k_1}(\mathbf{r}_a) \times \mathbf{Q}^{k_1'}(\mathbf{r}_b)]^{K_1}_0 | n_c l_c n_d l_d L_I M_I \rangle}{E_{n_c} + E_{n_d} - E_{n_a} - E_{n_b}}$$
$$\times \langle n_c l_c n_d l_d L_I M_I | [\mathbf{Q}^{k_2}(\mathbf{r}_a) \times \mathbf{Q}^{k_2'}(\mathbf{r}_b)]^{K_2}_0 | n_a l_a n_b l_b L' M \rangle$$
$$= \sum_X (-1)^{L-M} \begin{pmatrix} L & X & L' \\ -M & 0 & M \end{pmatrix} W^X, \quad (14)$$

where

$$W^X = -\sum_{k_1k_1'} \sum_{k_2k_2'} \sum_{cd,L_I} \frac{(-1)^{k_1'+k_2'}}{R^{K_1+K_2+2}} (-1)^{L'-L} \hat{L} \hat{L}' \hat{L}_I^2$$
$$\times \left[\frac{(2K_1+1)!(2K_2+1)!}{(2k_1)!(2k_1')!(2k_2)!(2k_2')!} \right]^{1/2} (-1)^{l_c-l_a+l_d-l_b}$$
$$\times \frac{\langle n_a l_a \| r^{k_1} \mathbf{C}^{k_1} \| n_c l_c \rangle \langle n_a l_a \| r^{k_2} \mathbf{C}^{k_2} \| n_c l_c \rangle}{E_{n_c} + E_{n_d} - E_{n_a} - E_{n_b}}$$
$$\times \langle n_b l_b \| r^{k_1'} \mathbf{C}^{k_1'} \| n_d l_d \rangle \langle n_d l_d \| r^{k_2'} \mathbf{C}^{k_2'} \| n_d l_d \rangle \begin{Bmatrix} l_a & l_b & L \\ l_c & l_d & L_I \\ k_1 & k_1' & K_1 \end{Bmatrix}$$
$$\times \begin{Bmatrix} l_c & l_d & L_I \\ l_a & l_b & L' \\ k_2 & k_2' & K_2 \end{Bmatrix} \hat{X}^2 \begin{pmatrix} K_1 & K_2 & X \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & K_1 & L_I \\ K_2 & L' & X \end{Bmatrix} \quad (15)$$

is a tensor of rank X. The allowable tensor ranks are determined by the multipolarities of the transitions contributing to the dispersion coefficient. For the C_6 parameter, one has $K_1 = K_2 = 2$ and so X can assume the values 0, 2, or 4 [16]. This expression is most usefully applied if the wave functions for the molecular states are written as a linear combination of coupled states. The $C_{K_1+K_2+2}$ coefficients are obtained from Eqs. (13) and (15) by multiplying by $-R^{K_1+K_2+2}$.

III. MOLECULAR WAVE FUNCTIONS

A. General form of wave functions

The zeroth-order wave function for the combined system a-b for two unlike atoms a and b, in states with angular momentum l_a and l_b, with a total magnetic quantum number M can be written in the form

$$\Psi^{(0)}(M) = \sum_{m_a=-l_a}^{+l_a} \sum_{m_b=-l_b}^{+l_b} \delta_{m_a+m_b,M} C_{m_a,M}$$
$$\times \Psi_{n_a l_a, m_a}(\mathbf{r}_a) \Psi_{n_b l_b, m_b}(\mathbf{r}_b), \quad (16)$$

where Ψ_{n_a} has an energy eigenvalue of E_{n_a}, and Ψ_{n_b} has an energy eigenvalue of E_{n_b}. The expansion constant is $C_{m_a,M}$. When $M=0$ the wave function should only change by ±1 upon reflection through a plane containing the internuclear axis. In some cases, the wave function is trivial to construct. However, for a number of configurations there are a number of states with the same M value. In these instances, the long-range form of the wave function is determined by diagonalizing the leading term of the asymptotic interaction. This is the quadrupole-quadrupole term of the first-order interaction.

B. *S-L* case

If one of the atoms (say a) is in an S state, the wave function for any M is simply

$$\Psi^{(0)}(M) = \Psi_{n_a 0,0}(\mathbf{r}_a) \Psi_{n_b l_b, M}(\mathbf{r}_b). \quad (17)$$

C. *P-P* case

The overall values of M are 0, 1, or 2 (the -1 and -2 cases can be trivially deduced from $M=1,2$ by symmetry considerations). The Δ system is trivial since there is only one term that can appear in Eq. (16). There are two Π states that can occur and the wave function construction is listed in Table I.

However, there are three possible m combinations for the Σ symmetry from which two Σ^+ states (of + symmetry) and one Σ^- state (of − symmetry) can be formed. The states with $m_a = -m_b \neq 0$ come in pairs, that can be written most compactly as

$$\Psi^+ = \frac{1}{\sqrt{2}} (\Psi_{n_a l_a m_a} \Psi_{n_b l_b -m_a} + \Psi_{n_a l_a -m_a} \Psi_{n_b l_b m_a}),$$

$$\Psi^- = \frac{1}{\sqrt{2}} (\Psi_{n_a l_a m_a} \Psi_{n_b l_b -m_a} - \Psi_{n_a l_a -m_a} \Psi_{n_b l_b m_a}). \quad (18)$$

The $\Psi_{n_a, l_a, 0} \Psi_{n_b, l_b, 0}$ state is a Σ^+ state (has + symmetry). The properly normalized combinations of states that diagonalize the first-order interaction are given in Table I. The values of the first order interaction constant C_5 listed in Table I are expressed in terms of the $\langle n_a l_a \| r^k \mathbf{C}^k \| l_a n_a \rangle$ and $\langle n_b l_b \| r^{k'} \mathbf{C}^{k'} \| l_b n_b \rangle$ reduced matrix elements.

D. *P-D* case

The overall values of M are 0, 1, 2, or 3. The Φ system is trivial since there is only one term that can appear in Eq.

TABLE I. The electronic wave functions for a heteronuclear molecule in a $n_a l_a$-$n_b l_b$ configuration. The notation $|a^l_{m_l}\rangle$ indicates the radial quantum number n_a, the orbital angular momentum l_a, and its projection m_l. The notation $|abLM\rangle$ indicates the state obtained by coupling a and b to have total orbital angular momentum L with a projection of M. The coefficient in the C_5 column is the number by which $\langle n_a l_a \| r^k \mathbf{C}^k \| l_a n_a \rangle \langle n_b l_b \| r^{k'} \mathbf{C}^{k'} \| l_b n_b \rangle$ should be multiplied to give C_5.

Asymptote	M	Symmetry	C_5	Uncoupled representation
as-bl	M		0	$\lvert a^0_0 b^l_M\rangle$
ap-bp	2	$^{1,3}\Delta$	$-\frac{1}{5}$	$\lvert a^1_1 b^1_1\rangle$
ap-bp	1	(1) $^{1,3}\Pi$	$\frac{4}{5}$	$\frac{1}{\sqrt{2}}[\lvert a^1_0 b^1_1\rangle + \lvert a^1_1 b^1_0\rangle]$
ap-bp	1	(2) $^{1,3}\Pi$	0	$\frac{1}{\sqrt{2}}[\lvert a^1_0 b^1_1\rangle - \lvert a^1_1 b^1_0\rangle]$
ap-bp	0	$^{1,3}\Sigma^-$	0	$\frac{1}{\sqrt{2}}[\lvert a^1_1 b^1_{-1}\rangle - \lvert a^1_{-1} b^1_1\rangle]$
ap-bp	0	(1) $^{1,3}\Sigma^+$	0	$\frac{1}{\sqrt{3}}[-\lvert a^1_0 b^1_0\rangle + \lvert a^1_1 b^1_{-1}\rangle + \lvert a^1_{-1} b^1_1\rangle]$
ap-bp	0	(2) $^{1,3}\Sigma^+$	$-\frac{6}{5}$	$\frac{\sqrt{2}}{\sqrt{3}}\lvert a^1_0 b^1_0\rangle + \frac{1}{\sqrt{6}}[\lvert a^1_1 b^1_{-1}\rangle + \lvert a^1_{-1} b^1_1\rangle]$
ap-bd	3	$^{1,3}\Phi$	$-\frac{2}{5}\sqrt{\frac{3}{7}}$	$\lvert a^1_1 b^2_2\rangle$
ap-bd	2	(1) $^{1,3}\Delta$	$\frac{1}{2}\sqrt{\frac{3}{7}}\left(1+\frac{\sqrt{41}}{5}\right)$	$\frac{1}{\sqrt{41-3\sqrt{41}}}[4\lvert a^1_0 b^2_2\rangle + \frac{\sqrt{41}-3}{\sqrt{2}}\lvert a^1_1 b^2_1\rangle]$
ap-bd	2	(2) $^{1,3}\Delta$	$\frac{1}{2}\sqrt{\frac{3}{7}}\left(1-\frac{\sqrt{41}}{5}\right)$	$\frac{1}{\sqrt{41+3\sqrt{41}}}[4\lvert a^1_0 b^2_2\rangle - \frac{3+\sqrt{41}}{\sqrt{2}}\lvert a^1_1 b^2_1\rangle]$
ap-bd	1	(1) $^{1,3}\Pi$	0.3837930326	$-0.833244609\lvert n^1_1 m^2_0\rangle - 0.408698988\lvert n^1_0 m^2_1\rangle + 0.372382274\lvert n^1_{-1} m^2_2\rangle$
ap-bd	1	(2) $^{1,3}\Pi$	−0.0123119774	$0.551678682\lvert n^1_1 m^2_0\rangle - 0.569733166\lvert n^1_0 m^2_1\rangle + 0.609142636\lvert n^1_{-1} m^2_2\rangle$
ap-bd	1	(3) $^{1,3}\Pi$	−0.6333425233	$0.036797448\lvert n^1_1 m^2_0\rangle - 0.713000180\lvert a^1_0 b^2_1\rangle - 0.700197609\lvert a^1_{-1} b^2_2\rangle$
np-bd	0	$^{1,3}\Sigma^-$	$\frac{2}{5}\sqrt{\frac{3}{7}}$	$\frac{1}{\sqrt{2}}[\lvert a^1_1 b^2_{-1}\rangle - \lvert a^1_{-1} b^2_{+1}\rangle]$
ap-bd	0	(1) $^{1,3}\Sigma^+$	$-\frac{2\sqrt{7}}{35}(\sqrt{3}-\sqrt{5})$	$\frac{1}{\sqrt{5+\sqrt{15}}}(-\lvert a^1_0 b^2_0\rangle + \frac{\sqrt{5}+\sqrt{3}}{2}[\lvert a^1_1 b^2_{-1}\rangle + \lvert a^1_{-1} b^2_1\rangle])$
ap-bd	0	(2) $^{1,3}\Sigma^+$	$-\frac{2\sqrt{7}}{35}(\sqrt{3}+\sqrt{5})$	$\frac{1}{\sqrt{5-\sqrt{15}}}(\lvert a^1_0 b^2_0\rangle + \frac{\sqrt{5}-\sqrt{3}}{2}[\lvert a^1_1 b^2_{-1}\rangle + \lvert a^1_{-1} b^2_1\rangle])$
Asymptote	M	Symmetry	C_5	Coupled representation
as-bl	M		0	$\lvert ablM\rangle$
ap-bp	2	$^{1,3}\Delta$	$-\frac{1}{5}$	$\lvert ab22\rangle$
ap-bp	1	(1) $^{1,3}\Pi$	$\frac{4}{5}$	$\lvert ab21\rangle$
ap-bp	1	(2) $^{1,3}\Pi$	0	$\lvert ab11\rangle$
ap-bp	0	$^{1,3}\Sigma^-$	0	$\lvert ab10\rangle$
ap-bp	0	(1) $^{1,3}\Sigma^+$	0	$\lvert ab00\rangle$
ap-bp	0	(2) $^{1,3}\Sigma^+$	$-\frac{6}{5}$	$\lvert ab20\rangle$
ap-bd	3	$^{1,3}\Phi$	$-\frac{2}{5}\sqrt{\frac{3}{7}}$	$\lvert ab33\rangle$
ap-bd	2	(1) $^{1,3}\Delta$	$\frac{1}{2}\sqrt{\frac{3}{7}}\left(1+\frac{\sqrt{41}}{5}\right)$	$-\frac{\sqrt{3}}{3\sqrt{123+13\sqrt{41}}}[10\lvert ab22\rangle - \frac{13+3\sqrt{41}}{\sqrt{2}}\lvert ab32\rangle]$
ap-bd	2	(2) $^{1,3}\Delta$	$\frac{1}{2}\sqrt{\frac{3}{7}}\left(1-\frac{\sqrt{41}}{5}\right)$	$\frac{\sqrt{3}}{3\sqrt{123-13\sqrt{41}}}[10\lvert ab22\rangle - \frac{13-3\sqrt{41}}{\sqrt{2}}\lvert ab32\rangle]$
ap-bd	1	(1) $^{1,3}\Pi$	0.3837930326	$0.2488046425\lvert ab11\rangle - 0.6373372563\lvert ab21\rangle - 0.7293130134\lvert ab31\rangle$
ap-bd	1	(2) $^{1,3}\Pi$	−0.0123119774	$0.9583516810\lvert ab11\rangle + 0.2709996634\lvert ab21\rangle + 0.0901179113\lvert ab31\rangle$
ap-bd	1	(3) $^{1,3}\Pi$	−0.6333425233	$0.1402080789\lvert ab11\rangle - 0.7213601071\lvert ab21\rangle + 0.6782192053\lvert ab31\rangle$
ap-bd	0	$^{1,3}\Sigma^-$	$\frac{2}{5}\sqrt{\frac{3}{7}}$	$\lvert ab20\rangle$
ap-bd	0	(1) $^{1,3}\Sigma^+$	$-\frac{2\sqrt{7}}{35}(\sqrt{3}-\sqrt{5})$	$\frac{1}{\sqrt{5-\sqrt{15}}}[\lvert ab10\rangle + \frac{\sqrt{5}-\sqrt{3}}{\sqrt{2}}\lvert nb30\rangle]$
ap-bd	0	(2) $^{1,3}\Sigma^+$	$-\frac{2\sqrt{7}}{35}(\sqrt{3}+\sqrt{5})$	$-\frac{1}{\sqrt{5+\sqrt{15}}}[\lvert ab10\rangle - \frac{\sqrt{3}+\sqrt{5}}{\sqrt{2}}\lvert ab30\rangle]$

(16). There are two Δ states that can occur. There are three possible m combinations for the Π state. The eigenvectors, which diagonalize the quadrupole-quadrupole part (i.e., C_5) of the first-order interaction are expressed in terms of real numbers. The determination of the eigenvalues requires the solution of a cubic equation, which cannot be readily expressed as an exact solution.

There are three possible m combinations for the Σ symmetry from which two states of $+$ symmetry and one state of the $-$ symmetry can be formed. The representation given in Table I is the one that diagonalizes the quadrupole-quadrupole part of the first-order interaction. Diagonalizing the first-order quadrupole-quadrupole interaction is enough to ensure that the energy denominator in the second-order interaction will be finite for all terms up to C_{10}.

E. *D-D* case

The overall values of M are 0, 1, 2, 3, or 4 and there are a total of 15 distinct molecular states. The representations of the states that diagonalize the C_5 operator, and the values of C_5 for those states are listed in Table II.

Diagonalizing the first-order quadrupole-quadrupole interaction is enough to ensure that the energy denominator in the second-order interaction will be finite for all terms up to C_{10}.

F. Coupled representation

The molecular wave functions can also be written in terms of coupled states. In this case, one would write the zeroth-order wave function as

$$\Psi^{(0)}(M) = \sum_{L=|l_a-l_b|}^{l_a+l_b} C_{L,M}\Psi_{n_al_a,n_bl_b,LM}(\mathbf{r}_a,\mathbf{r}_b), \qquad (19)$$

where $\Psi_{n_al_a,n_bl_b,LM}(\mathbf{r}_a,\mathbf{r}_b)$ is given by Eq. (9). The molecular states are also listed in terms of coupled atomic states in Tables I and II. The representation for the *np-mp* cases is very simple since the quadrupole-quadrupole interaction is a tensor of rank 4 and so can only give a nonzero matrix element between for a coupled state with an angular momentum of 2.

IV. DISPERSION COEFFICIENT IN TERMS OF OSCILLATOR STRENGTHS

The absorption oscillator strength of multipole k for a transition from $0 \to n$ has been defined as

$$f_{0n}^{(k)} = \frac{2|\langle\psi_0;L_0\|r^k\mathbf{C}^k(\hat{\mathbf{r}})\|\psi_n;L_n\rangle|^2\Delta E_{n0}}{(2k+1)(2L_0+1)}, \qquad (20)$$

where $\Delta E_{n0}=E_n-E_0$. The general expression for the smallest multipole van der Waals coefficient C_6 can be rewritten solely in terms of oscillator strengths. Equation (13) becomes

$$V^{(2)}_{m_am_b,m'_am'_b} = -\sum_{n_cn_d}\frac{135}{2R^6}\frac{\hat{l}_a^2\hat{l}_b^2f_{ac}^{(1)}f_{bd}^{(1)}}{\Delta E_{ca}\Delta E_{db}(\Delta E_{ca}+\Delta E_{db})}$$
$$\times\sum_{\mu_1\mu_2}\sum_{m_cm_d}\begin{pmatrix}1 & 1 & 2\\ -\mu_1 & \mu_1 & 0\end{pmatrix}\begin{pmatrix}1 & 1 & 2\\ -\mu_2 & \mu_2 & 0\end{pmatrix}$$
$$\times\begin{pmatrix}l_a & 1 & l_c\\ -m_a & -\mu_1 & m_c\end{pmatrix}\begin{pmatrix}l_b & 1 & l_d\\ -m_b & \mu_1 & m_d\end{pmatrix}$$
$$\times\begin{pmatrix}l_c & 1 & l_a\\ -m_c & -\mu_2 & m'_a\end{pmatrix}\begin{pmatrix}l_d & 1 & l_b\\ -m_d & \mu_2 & m'_b\end{pmatrix}. \qquad (21)$$

Numerical values of the coefficients multiplying the oscillator strengths for a number of cases are given in Tables III and IV. These coefficients were determined by evaluating Eq. (21) numerically for the molecular representations. In Table IV we also list the coefficients for off-diagonal matrix elements between two different molecular states of the same symmetry. The molecular representation that diagonalizes the first-order interaction does not necessarily diagonalize the second-order interaction for two atoms in P states. The exact fractions given in Tables III and IV were easily identifiable from the floating point-representations. As an example of usage, the value of C_6 for the Π symmetry for an *ns-nd* configuration would be

$$C_6 = \sum_{\substack{n_cn_d\\ l_c=1\ l_d=1}}\frac{15f_{ac}^{(1)}f_{bd}^{(1)}}{8\Delta E_{ca}\Delta E_{db}(\Delta E_{ca}+\Delta E_{db})}$$
$$+\sum_{\substack{n_cn_d\\ l_c=1\ l_d=2}}\frac{9f_{ac}^{(1)}f_{bd}^{(1)}}{8\Delta E_{ca}\Delta E_{db}(\Delta E_{ca}+\Delta E_{db})}$$
$$+\sum_{\substack{n_cn_d\\ l_c=1\ l_d=3}}\frac{45f_{ac}^{(1)}f_{bd}^{(1)}}{28\Delta E_{ca}\Delta E_{db}(\Delta E_{ca}+\Delta E_{db})}. \qquad (22)$$

Explicit expressions for C_6 were also generated for the *P-D* and *D-D* configurations, but are not included in the present manuscript for reasons of brevity.

V. INTERACTIONS OF ALKALI-METAL EXCITED STATES WITH H AND He

The calculational technology is now applied to the determination of the long-range interactions of the low-lying excited states of the alkali-metal atoms with the hydrogen and helium ground states.

All the dispersion coefficients computed in this paper were computed by first diagonalizing the semiempirical Hamiltonian [5,34–37] in a large mixed Laguerre-type orbital (LTO) and Slater-type orbital basis set [5]. Next, various sum rules involving oscillator strengths or reduced matrix elements were summed over the set of physical and pseudo states.

The set of reduced matrix elements for hydrogen were obtained by diagonalizing the hydrogen ground state in a basis with 15 LTOs for each l [10]. The

TABLE II. The electronic wave functions for a heteronuclear molecule in an *ad-bd* configuration. The notation $|a^{l}_{m_l}\rangle$ indicates the radial quantum number n_a, the orbital angular momentum l, and its projection m_l. The notation $|abLM\rangle$ indicates the state obtained by coupling a and b to have total orbital angular momentum L with a projection of M. The coefficient in the C_5 column is the number by which $\langle n_a l_a \| r^k \mathbf{C}^k \| l_a n_a\rangle \langle n_b l_b \| r^{k'} \mathbf{C}^{k'} \| l_b n_b\rangle$ should be multiplied to give C_5.

M	Symmetry	C_5	Uncoupled representation
4	$^{1,3}\Gamma$	$-\frac{12}{35}$	$\|a^2_2 b^2_2\rangle$
3	(1) $^{1,3}\Phi$	$\frac{18}{35}$	$\frac{1}{\sqrt{2}}[\|a^2_1 b^2_2\rangle + \|a^2_2 b^2_1\rangle]$
3	(2) $^{1,3}\Phi$	$-\frac{6}{35}$	$\frac{1}{\sqrt{2}}[\|a^2_1 b^2_2\rangle - \|a^2_2 b^2_1\rangle]$
2	(1) $^{1,3}\Delta$	$\frac{2}{5}$	$\frac{1}{\sqrt{2}}[\|a^2_2 b^2_0\rangle - \|a^2_0 b^2_2\rangle]$
2	(2) $^{1,3}\Delta$	$\frac{13}{35}$	$\frac{1}{\sqrt{19}}[\sqrt{8}\|a^2_2 b^2_0\rangle + \sqrt{8}\|a^2_0 b^2_2\rangle + \sqrt{3}\|a^2_1 b^2_1\rangle]$
2	(3) $^{1,3}\Delta$	$-\frac{6}{35}$	$\frac{-\sqrt{3}}{\sqrt{38}}[\|a^2_2 b^2_0\rangle + \|a^2_0 b^2_2\rangle] + \frac{4}{\sqrt{19}}\|a^2_1 b^2_1\rangle$
1	(1) $^{1,3}\Pi$	$\frac{1}{35}(1+\sqrt{79})$	$-\sqrt{\frac{1}{4} - \frac{5}{4\sqrt{79}}}[\|a^2_1 b^2_0\rangle + \|a^2_0 b^2_1\rangle] + \sqrt{\frac{1}{4} + \frac{5}{4\sqrt{79}}}[\|a^2_2 b^2_{-1}\rangle + \|a^2_{-1} b^2_2\rangle]$
1	(2) $^{1,3}\Pi$	$-\frac{1}{35}(1-\sqrt{55})$	$-\sqrt{\frac{1}{4} - \frac{7}{4\sqrt{55}}}[\|a^2_1 b^2_0\rangle - \|a^2_0 b^2_1\rangle] + \sqrt{\frac{1}{4} + \frac{7}{4\sqrt{55}}}[\|a^2_2 b^2_{-1}\rangle - \|a^2_{-1} b^2_2\rangle]$
1	(3) $^{1,3}\Pi$	$-\frac{1}{35}(\sqrt{79}-1)$	$\sqrt{\frac{1}{4} + \frac{5}{4\sqrt{79}}}[\|a^2_1 b^2_0\rangle + \|a^2_0 b^2_1\rangle] + \sqrt{\frac{1}{4} - \frac{5}{4\sqrt{79}}}[\|a^2_2 b^2_{-1}\rangle + \|a^2_{-1} b^2_2\rangle]$
1	(4) $^{1,3}\Pi$	$-\frac{1}{35}(1+\sqrt{55})$	$\sqrt{\frac{1}{4} + \frac{7}{4\sqrt{55}}}[\|a^2_1 b^2_0\rangle - \|a^2_0 b^2_1\rangle] + \sqrt{\frac{1}{4} - \frac{7}{4\sqrt{55}}}[\|a^2_2 b^2_{-1}\rangle - \|a^2_{-1} b^2_2\rangle]$
0	(1) $^{1,3}\Sigma^-$	$-\frac{6}{35}(1-\sqrt{5})$	$\frac{-1}{\sqrt{5-\sqrt{5}}}[\|a^2_1 b^2_{-1}\rangle - \|a^2_{-1} b^2_1\rangle] + \frac{1}{\sqrt{5+\sqrt{5}}}[\|a^2_2 b^2_{-2}\rangle - \|a^2_{-2} b^2_2\rangle]$
0	(1) $^{1,3}\Sigma^+$	0.0967289162	$0.559343096[\|a^2_{-1} b^2_1\rangle + \|a^2_1 b^2_{-1}\rangle] - 0.43195704[\|a^2_2 b^2_{-2}\rangle + \|a^2_{-2} b^2_2\rangle] - 0.033118444\|a^2_0 b^2_0\rangle$
0	(2) $^{1,3}\Sigma^+$	−0.3016901699	$0.131587475[\|a^2_{-1} b^2_1\rangle + \|a^2_1 b^2_{-1}\rangle] + 0.206359062[\|a^2_2 b^2_{-2}\rangle + \|a^2_{-2} b^2_2\rangle] - 0.938190464\|a^2_0 b^2_0\rangle$
0	(2) $^{1,3}\Sigma^-$	$-\frac{6}{35}(1+\sqrt{5})$	$\frac{1}{\sqrt{5+\sqrt{5}}}[\|a^2_1 b^2_{-1}\rangle - \|a^2_{-1} b^2_1\rangle] + \frac{1}{\sqrt{5-\sqrt{5}}}[\|a^2_2 b^2_{-2}\rangle - \|a^2_{-2} b^2_2\rangle]$
0	(3) $^{1,3}\Sigma^+$	−0.6521816034	$0.412092268[\|a^2_{-1} b^2_1\rangle + \|a^2_1 b^2_{-1}\rangle] + 0.520412387[\|a^2_2 b^2_{-2}\rangle + \|a^2_{-2} b^2_2\rangle] + 0.344531306\|a^2_0 b^2_0\rangle$
M	Symmetry	C_5	Coupled representation
4	$^{1,3}\Gamma$	$-\frac{12}{35}$	$\|ab44\rangle$
3	(1) $^{1,3}\Phi$	$\frac{18}{35}$	$\|ab43\rangle$
3	(2) $^{1,3}\Phi$	$-\frac{6}{35}$	$\|ab33\rangle$
2	(1) $^{1,3}\Delta$	$\frac{2}{5}$	$\|ab32\rangle$
2	(2) $^{1,3}\Delta$	$\frac{13}{35}$	$\frac{1}{\sqrt{133}}[5\|ab22\rangle + 6\sqrt{3}\|ab42\rangle]$
2	(3) $^{1,3}\Delta$	$-\frac{6}{35}$	$-\frac{1}{\sqrt{133}}[6\sqrt{3}\|ab22\rangle - 5\|ab42\rangle]$
1	(1) $^{1,3}\Pi$	$\frac{1}{35}(1+\sqrt{79})$	$-\frac{1}{\sqrt{553-61\sqrt{79}}}\left[5\sqrt{\frac{3}{7}}\|ab21\rangle - \frac{7\sqrt{79}-61}{\sqrt{14}}\|ab41\rangle\right]$
1	(2) $^{1,3}\Pi$	$-\frac{1}{35}(1-\sqrt{55})$	$-\frac{1}{\sqrt{55-\sqrt{55}}}[3\sqrt{3}\|ab11\rangle + \frac{\sqrt{55}-1}{\sqrt{2}}\|ab31\rangle]$
1	(3) $^{1,3}\Pi$	$-\frac{1}{35}(\sqrt{79}-1)$	$\frac{1}{\sqrt{553+61\sqrt{79}}}\left[5\sqrt{\frac{3}{7}}\|ab21\rangle + \frac{7\sqrt{79}+61}{\sqrt{14}}\|ab41\rangle\right]$
1	(4) $^{1,3}\Pi$	$-\frac{1}{35}(1+\sqrt{55})$	$-\frac{1}{\sqrt{55+\sqrt{55}}}[3\sqrt{3}\|ab11\rangle - \frac{1+\sqrt{55}}{\sqrt{2}}\|ab31\rangle]$
0	(1) $^{1,3}\Sigma^-$	$-\frac{6}{35}(1-\sqrt{5})$	$\frac{\sqrt{2}}{\sqrt{5+\sqrt{5}}}\left[\frac{1+\sqrt{5}}{2}\|ab10\rangle - \|ab30\rangle\right]$
0	(1) $^{1,3}\Sigma^+$	0.0967289162	$0.9014568154\|ab00\rangle + 0.1450974868\|ab20\rangle - 0.4078263470\|ab40\rangle$
0	(2) $^{1,3}\Sigma^+$	−0.3016901699	$0.3526937901\|ab00\rangle - 0.7924274786\|ab20\rangle + 0.4976603075\|ab40\rangle$
0	(2) $^{1,3}\Sigma^-$	$-\frac{6}{35}(1+\sqrt{5})$	$\frac{1}{\sqrt{5-\sqrt{5}}}\left[\frac{\sqrt{5}-1}{\sqrt{2}}\|ab10\rangle + \sqrt{2}\|ab30\rangle\right]$
0	(3) $^{1,3}\Sigma^+$	−0.6521816034	$0.2509635439\|ab00\rangle + 0.5924570960\|ab20\rangle + 0.7655141338\|ab40\rangle$

TABLE III. Expressions for the C_6 dispersion coefficient in terms of absorption oscillator strengths for the case when one of the atoms is in an S state. The $f_{as\rightarrow ip}$ transition is common to all terms. The coefficient is the numerical factor multiplying the intermediate sum with the $f_{bl\rightarrow jl'}$ term.

Configuration	Symmetry	$f_{l\rightarrow(l-1)}$	$f_{l\rightarrow l}$	$f_{l\rightarrow(l+1)}$
as-bs	$^{1,3}\Sigma$	0	0	$\frac{3}{2}$
as-bp	$^{1,3}\Pi$	$\frac{3}{4}$	$\frac{15}{8}$	$\frac{57}{40}$
as-bp	$^{1,3}\Sigma$	3	$\frac{3}{4}$	$\frac{33}{20}$
as-bd	$^{1,3}\Delta$	$\frac{3}{4}$	$\frac{9}{4}$	$\frac{9}{7}$
as-bd	$^{1,3}\Pi$	$\frac{15}{8}$	$\frac{9}{8}$	$\frac{45}{28}$
as-bd	$^{1,3}\Sigma$	$\frac{9}{4}$	$\frac{3}{4}$	$\frac{12}{7}$
as-bf	$^{1,3}\Phi$	$\frac{3}{4}$	$\frac{39}{16}$	$\frac{19}{16}$
as-bf	$^{1,3}\Delta$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$
as-bf	$^{1,3}\Pi$	$\frac{39}{20}$	$\frac{15}{16}$	$\frac{27}{16}$
as-bf	$^{1,3}\Sigma$	$\frac{21}{10}$	$\frac{3}{4}$	$\frac{7}{4}$

reduced matrix elements for helium were derived from a Hylleraas calculation that gave an energy of −2.903 724 377 034 119 59(1) hartree, and a polarizability of α_d=1.383 192 174 455(1) a_0^3 ground state. Both these values agree with previous calculations to all quoted significant figures [9,38].

The details of the calculation for the alkali-metal atoms are very similar to those reported in [5,7,36,39] apart from some minor changes in the cutoff parameters and the use of an orbital basis of larger dimension. The polarization potentials were initially defined by tuning the potential to reproduce the *ns*, *np*, *nd*, and *nf* binding energies. The Hamiltonian was then diagonalized in a basis consisting of about 50 LTOs for each L. Expectation values for multipole operators were computed with a modified operator that allowed for polarization corrections [5,40,41].

The binding energies of the low-lying states of the alkali-metal atom are tabulated and compared with the experiment in Table V. The agreement between the present energies and the experimental energies is always within 10^{-4} hartree.

A. Oscillator strengths

The oscillator strengths between a number of the low-lying states are given in Table VI and compared with the results of other calculations. The most accurate calculations for Li are those of Yan and co-workers that use an explicitly correlated basis [42]. The present oscillator strengths agree with correlated calculations to 0.1% or better. A similar level of agreement is also achieved with the multiconfiguration Hartree-Fock (MCHF) calculation [43].

For Na and K, the most accurate *ab initio* oscillator strengths are the large MCHF [44] and relativistic many-body perturbation theory (MBPT) [45] calculations. The

TABLE IV. Expressions for the C_6 dispersion coefficient for the P-P case in terms of absorption oscillator strengths. The coefficient is the numerical factor multiplying the intermediate sum with the $f_{ap\rightarrow il_i}f_{bp\rightarrow jl_j}$ term. The column headings give the quantum numbers of the intermediate state. The off-diagonal coefficients connecting two states with the same symmetry, e.g., (1)-(2) $^{1,3}\Pi$ are also listed.

Symmetry	(is,js)	(is,jp)	(is,jd)	(ip,js)	(ip,jp)	(ip,jd)	(id,js)	(id,jp)	(id,jd)
$^{1,3}\Delta$	0	0	$\frac{27}{20}$	0	$\frac{9}{4}$	$\frac{81}{40}$	$\frac{27}{20}$	$\frac{81}{40}$	$\frac{27}{25}$
(1) $^{1,3}\Pi$	0	$\frac{81}{16}$	$\frac{27}{80}$	$\frac{81}{16}$	$\frac{9}{16}$	$\frac{81}{80}$	$\frac{27}{80}$	$\frac{81}{80}$	$\frac{837}{400}$
(2) $^{1,3}\Pi$	0	$\frac{9}{16}$	$\frac{243}{80}$	$\frac{9}{16}$	$\frac{9}{16}$	$\frac{153}{80}$	$\frac{243}{80}$	$\frac{153}{80}$	$\frac{81}{80}$
(1)-(2) $^{1,3}\Pi$	0	$\frac{27}{16}$	$\frac{81}{80}$	$-\frac{27}{16}$	0	$-\frac{27}{40}$	$-\frac{81}{80}$	$\frac{27}{40}$	0
(1) $^{1,3}\Sigma^+$	0	0	$\frac{27}{10}$	0	$\frac{9}{8}$	$\frac{81}{40}$	$\frac{27}{10}$	$\frac{81}{40}$	$\frac{189}{200}$
(2) $^{1,3}\Sigma^+$	$\frac{27}{2}$	0	$\frac{27}{20}$	0	$\frac{27}{8}$	0	$\frac{27}{20}$	0	$\frac{513}{200}$
(1)-(2) $^{1,3}\Sigma^+$	0	0	$-\frac{27\sqrt{2}}{20}$	0	$\frac{9\sqrt{2}}{8}$	0	$-\frac{27\sqrt{2}}{20}$	0	$\frac{27\sqrt{2}}{200}$
$^{1,3}\Sigma^-$	0	$\frac{9}{4}$	0	$\frac{9}{4}$	$\frac{9}{4}$	$\frac{63}{40}$	0	$\frac{63}{40}$	$\frac{81}{50}$

TABLE V. Theoretical and experimental energy levels (in hartree) of some of the low-lying states of the alkali-metal atoms. The energies are given relative to the energy of the ionized core. The experimental energies for the doublet states are averages with the usual $(2J+1)$ weighting factors. The experimental data are taken from [32,33]. The *md* level is the 3*d* level for Li, Na, and K while for Rb it is the 4*d* level.

Systems	Li		Na		K		Rb	
level	Theory	Experiment	Theory	Experiment	Theory	Experiment	Theory	Experiment
ns	−0.198141	−0.198142	−0.188855	−0.188858	−0.159520	−0.159516	−0.153509	−0.153507
np	−0.130239	−0.130235	−0.111563	−0.111547	−0.100183	−0.100176	−0.095473	−0.095471
md	−0.055611	−0.055606	−0.055938	−0.055936	−0.061396	−0.061393	−0.065372	−0.065317
$(n+1)s$	−0.074168	−0.074182	−0.071544	−0.071578	−0.063625	−0.063712	−0.061683	−0.061777
$(n+1)p$	−0.057228	−0.057236	−0.050927	−0.050934	−0.046888	−0.046912	−0.045190	−0.045217
$(m+1)d$	−0.031277	−0.031274	−0.031443	−0.031442	−0.034606	−0.034684	−0.036336	−0.036398

present calculations agree with these calculations at the 1–2 % level for the transitions with oscillator strengths close to 1, and at the 2–5 % level for the weaker transitions. Some transitions lack MBPT and MCHF results, and the critically assessed data from National Institute of Standards and Technology (NIST) [46] are quoted. The overall degree of consistency is excellent.

TABLE VI. Absorption oscillator strengths for various dipole transition lines of the alkali-metal atoms.

Transition	Present	Other
		Li
$f(2s\rightarrow 2p)$	0.7475	0.7470 Corr [42], 0.7471 MCHF [43]
$f(2s\rightarrow 3p)$	0.00469	0.00471 MCHF [43]
$f(2p\rightarrow 3s)$	0.1106	0.1105 MCHF [43]
$f(2p\rightarrow 3d)$	0.6388	0.6386 Corr [42], 0.6385 MCHF [43] 0.6385 [55]
$f(3d\rightarrow 4p)$	0.01807	0.0184 NIST [56]
$f(3d\rightarrow 4f)$	1.0153	1.0153 [57]
		Na
$f(3s\rightarrow 3p)$	0.9616	0.959 CI [58], 0.9640 MBPT [45]
$f(3s\rightarrow 4p)$	0.01281	0.01298 MBPT [45], 0.01211 MCHF [44]
$f(3p\rightarrow 4s)$	0.1710	0.1707 MBPT [45]
$f(3p\rightarrow 3d)$	0.8563	0.859 CI [58], 0.8492 MCHF [44]
$f(3d\rightarrow 4p)$	0.1183	0.1125 MCHF [44]
$f(3d\rightarrow 4f)$	1.002	1.00 NIST [46]
		K
$f(4s\rightarrow 4p)$	0.9983	0.962 [58], MBPT 0.9962 [45]
$f(4s\rightarrow 5p)$	0.00819	0.009026 MBPT [45]
$f(4p\rightarrow 5s)$	0.1859	0.1833 MBPT [45]
$f(4p\rightarrow 3d)$	0.8236	0.837 CI [58],
$f(3d\rightarrow 5p)$	0.1482	0.14 NIST [46]
$f(3d\rightarrow 4f)$	0.7513	0.75 NIST [46]
		Rb
$f(5s\rightarrow 5p)$	1.029	1.02 [58], 1.031 MBPT [45]
$f(5s\rightarrow 6p)$	0.01262	0.01457 MBPT [45]
$f(5p\rightarrow 4d)$	0.6544	0.639 [58], 0.6263 MBPT [59]
$f(5p\rightarrow 6s)$	0.2024	0.1988 MBPT [45]
$f(4d\rightarrow 6p)$	0.1059	0.08688 MBPT [59]
$f(4d\rightarrow 4f)$	0.6149	

There is a decrease in the level of agreement with the MBPT calculations for rubidium. There are differences of 20% for the $5s\rightarrow 6p$ and $4d\rightarrow 6p$ transitions. These differences are small in absolute terms since the transitions are both weak. The rubidium atom has a nuclear charge of $Z=37$ and so it is possible that relativistic effects are responsible for the differences in the weaker transitions.

B. Scalar and tensor polarizabilities

The definitions of the scalar and tensor polarizabilities for general states have been given in [47] and do not need to be repeated here. The static dipole, quadrupole, and octupole polarizabilities are given in Table VII. In addition, the tensor part of the polarizability for dipole excitations is also given.

The most precise information is that for the *np* states where a comparison may be made with experiment [48–52] and sophisticated relativistic MBPT calculations [53]. Agreement with the MBPT calculations is as good as could be expected when allowance is made for the fact that the present calculation does not include the spin-orbit interaction.

The model potential (ModP) of Magnier and Aubert-Frecon [54] was not constructed with the same attention to detail as the present semiempirical calculation. The ModP dispersion coefficients are expected to be less accurate than the present results and are included to demonstrate that there are no gross errors in the present set of results.

C. Dispersion interaction

The dispersion coefficients between the low-lying states of the alkali-metal atoms with H and He are given in Tables VIII–X. Lists of reduced matrix elements for the relevant states were generated from stand-alone atomic structure programs. These lists were then processed by a relatively compact program that evaluated Eq. (13) for all the molecular representations. The impact of excitations from the core were included using a procedure outlined previously [47,60].

Table IX gives the dispersion coefficients between the alkali-metal ground states and the H and He ground states. Values for the coefficients have been presented previously

TABLE VII. The scalar and tensor polarizabilities (in atomic units) of the low-lying states of the alkali-metal atoms. Values for the $np_{1/2}$ and $np_{3/2}$ states are given by the MBPT calculation with that for the $np_{1/2}$ state given first. The same is true for the experimental values. The numbers in the square brackets denote powers of ten.

Method	α_1	α_2	α_3	α_{2,L_0L_0}
	Na-3p			
Present	360.7	1.005[4]	1.069[6]	−87.89
ModP [54]	360			−87
MBPT [53]	359.7, 361.4			−88.0
Experiment ([48,49])	359.6(7), 360.7(8)			−88.4(4)
	Na-4s			
Present	3110	4.606[5]	4.114[7]	
Mod. [54]	3095			
	Na-3d			
Present	6396	1.241[5]	1.198[8]	−5073
ModP [54]	6408[4]			−5094
	K-4p			
Present	615.3	1.900[5]	2.561[6]	−107.9
MBPT [53]	605, 616			−111
ModP [54]	611			−102
Experiment [50,51]	610(6), 615(7)			−107(2)
	K-5s			
Present	4997	2.393[6]	9.756[7]	
ModP [54]	4940			
	K-4d			
Present	1419	−3.208[5]	3.086[7]	−679.2
ModP [54]	1392			−666
	Rb-5p			
Present	854.4	2.534[4]	3.844[6]	−160.5
MBPT [53]	807, 870			−171
ModP [54]	849			−149
Experiment ([50,52,52])	811(6), 858(7)			−163(3)
	Rb-6s			
Present	5202	−3.455[5]	1.233[8]	
ModP [54]	5270			
	Rb-4d			
Present	544.8	2.287[5]	1.466[7]	−33.29
ModP [54]	529			−1043

using essentially the same method [6]. The only changes are the usage of larger basis sets for the alkali-metal atoms, and the use of a Hylleraas rather than a CI basis to represent He and its excited states. The largest change in any of the dispersion parameters was less than 0.1%. Close to exact values of C_6 have been computed with correlated wave functions [9] for the interaction of the 2s state of Li with H and He. The present calculations agree with these values to better than 0.1%.

TABLE VIII. The dispersion coefficients between the resonant alkali-metal np excited state and the hydrogen and helium ground states. Data by other groups are identified by the citation in the first column (MBPT means many-body perturbation theory, while ModP means model potential). The numbers in the square brackets denote powers of ten.

System	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
	Hydrogen		
LiH $^{1,3}\Sigma$	160.1	2.404[4]	2.812[6]
Exact [64]	160.06		
LiH $^{1,3}\Pi$	85.43	1.143[3]	5.276[4]
Exact [64]	85.418		
NaH $^{1,3}\Sigma$	243.5	4.917[4]	7.333[6]
NaH $^{1,3}\Pi$	133.3	2.085[3]	1.236[5]
KH $^{1,3}\Sigma$	322.4	8.082[4]	1.440[7]
KH $^{1,3}\Pi$	182.8	3.416[3]	2.357[5]
RbH $^{1,3}\Sigma$	365.4	1.007[5]	1.947[7]
RbH $^{1,3}\Pi$	210.3	4.328[3]	3.179[5]
	Helium		
LiHe $^2\Sigma$	50.71	7.854[3]	9.143[5]
Exact [64]	50.686		
ModP [27]	50.75		
LiHe $^2\Pi$	28.27	305.5	1.486[4]
Exact [64]	28.267		
ModP [27]	28.31		
NaHe $^2\Sigma$	76.94	1.587[4]	2.368[6]
MBPT [53]	79.5		
ModP [27]	77.02		
NaHe $^2\Pi$	43.74	591.3	3.775[4]
MBPT [53]	43.4		
ModP [27]	43.72		
KHe $^2\Sigma$	103.3	2.590[4]	4.625[6]
MBPT [53]	116		
ModP [27]	105.6		
KHe $^2\Pi$	60.85	1.021[3]	7.455[4]
MBPT [53]	63.3		
ModP [27]	61.96		
RbHe $^2\Sigma$	117.8	3.219[4]	6.240[7]
MBPT [53]	120		
RbHe $^2\Pi$	70.56	1.322[3]	1.018[6]
MBPT [53]	68.0		

There is better than 1% agreement between the present and MBPT calculations [61] for the C_6 values of NaH, KH, and RbH ground states. Therefore it is surprising that the present calculations give C_6 values which are 2–3 % larger than the MBPT calculations of the ground states of the NaHe, KHe, and RbHe dimers [53] (note, the MBPT calculations use a frequency-dependent polarizability for He derived from a functions that came from a Hylleraas calculation). If the present calculations were to be giving C_6 values which are too large, then the f-value distribution assumed for the core would be the most likely reason. The present f-value

TABLE IX. The dispersion coefficients between the alkali-metal *ns* ground state and the lowest $(n+1)s$ excited state and the hydrogen and helium ground states. Data by other groups are identified by the citation in the first column (MBPT means many-body perturbation theory while ModP means model potential). The numbers in the square brackets denote powers of ten.

System	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
	Hydrogen-alkali *ns* ground state		
LiH $^{1,3}\Sigma$	66.54	3.282[3]	2.232[5]
Exact [9]	66.536	3.2800[3]	2.2302[5]
NaH $^{1,3}\Sigma$	74.18	4.012[3]	2.916[5]
MBPT [61]	73.83(9)	4.059[3]	
KH $^{1,3}\Sigma$	112.0	7.970[3]	7.344[5]
MBPT [61]	111.2(2)		
RbH $^{1,3}\Sigma$	124.6	9.540[3]	9.301[5]
MBPT [61]	124.3(3)		
	Hydrogen-alkali $(n+1)s$ excited state		
LiH $^{1,3}\Sigma$	514.9	1.336[5]	4.137[7]
PS [65]	512.1	1.326[5]	4.097[7]
NaH $^{1,3}\Sigma$	557.0	1.541[5]	5.073[7]
PS [65]	550.4	1.522[5]	4.996[7]
KH $^{1,3}\Sigma$	715.7	2.445[6]	9.831[7]
PS [65]	696.1	2.387[5]	9.558[7]
RbH $^{1,3}\Sigma$	768.5	2.772[5]	1.175[8]
PS [65]	740.8	2.690[5]	1.136[8]
	Helium-alkali *ns* ground state		
LiHe $^{2}\Sigma$	22.51	1.084[3]	7.266[4]
Exact [9]	22.507	1.0832[3]	7.2602[4]
ModP [27]	22.57		
NaHe $^{2}\Sigma$	25.76	1.328[3]	9.514[4]
MBPT [53]	25.1		
ModP [27]	26.33		
KHe $^{2}\Sigma$	39.46	2.623[3]	2.398[5]
MBPT [53]	38.3		
ModP [27]	42.44		
RbHe $^{2}\Sigma$	44.68	3.145[3]	3.037[5]
MBPT [53]	43.4		
	Helium-alkali $(n+1)s$ excited state		
LiHe $^{2}\Sigma$	160.7	4.190[4]	1.311[7]
PS [65]	158.8	4.145[4]	1.295[7]
NaHe $^{2}\Sigma$	174.3	4.829[4]	1.605[7]
PS [65]	170.5	4.751[4]	1.577[7]
KHe $^{2}\Sigma$	225.0	7.639[4]	3.097[7]
PS [65]	215.1	7.421[4]	3.001[7]
RbHe $^{2}\Sigma$	242.4	8.652[4]	3.698[7]
PS [65]	228.8	8.356[4]	3.562[7]

TABLE X. The dispersion coefficients between the lowest alkali-metal *nd* excited state and the hydrogen and helium ground states. The model potential data (ModP) by Mullamphy *et al.* are also included. The numbers in the square brackets denote powers of ten.

System	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
	Hydrogen		
LiH $^{1,3}\Sigma$	715.0	5.192[5]	2.944[8]
LiH $^{1,3}\Pi$	633.8	1.849[5]	1.652[7]
LiH $^{1,3}\Delta$	390.1	−2.683[4]	−5.161[5]
NaH $^{1,3}\Sigma$	702.9	5.031[5]	2.821[8]
NaH $^{1,3}\Pi$	623.3	1.792[5]	1.584[7]
NaH $^{1,3}\Delta$	384.4	−2.588[4]	−4.970[5]
KH $^{1,3}\Sigma$	506.0	2.912[5]	1.366[8]
KH $^{1,3}\Pi$	449.5	1.035[5]	7.760[6]
KH $^{1,3}\Delta$	278.0	−1.419[4]	−2.519[5]
RbH $^{1,3}\Sigma$	412.9	2.061[5]	8.596[7]
RbH $^{1,3}\Pi$	367.7	7.326[4]	4.943[6]
RbH $^{1,3}\Delta$	232.0	−9.417[3]	−1.587[5]
	Helium		
LiHe $^{2}\Sigma$	221.8	1.615[5]	9.240[7]
LiHe $^{2}\Pi$	196.9	5.835[4]	5.270[6]
LiHe $^{2}\Delta$	122.4	−8.693[3]	−1.328[5]
NaHe $^{2}\Sigma$	218.7	1.566[5]	8.856[7]
ModP [27]	218.7		
NaHe $^{2}\Pi$	194.3	5.655[4]	5.055[6]
ModP [27]	194.3		
NaHe $^{2}\Delta$	121.3	−8.393[3]	−1.281[5]
ModP [27]	121.2		
KHe $^{2}\Sigma$	160.1	9.084[4]	4.304[7]
KHe $^{2}\Pi$	142.8	3.284[4]	2.476[6]
KHe $^{2}\Delta$	90.90	−4.671[3]	−6.611[4]
RbHe $^{2}\Sigma$	132.9	6.445[4]	2.715[7]
RbHe $^{2}\Pi$	119.0	2.336[4]	1.576[6]
RbHe $^{2}\Delta$	77.35	−3.132[3]	−4.231[4]

distribution predicts a $C_3=\Sigma_n f_{0n}/(8\Delta E_{n0})=1.93$ [5] for the sodium ground state, while a more accurate estimate would be 1.89 [5,62,63]. The core f-value distribution is constructed by initially setting the oscillator strength from a given orbital as $f_{i,\text{core}}=N_i$, where N_i is the number of electrons in the orbital. Then the excitation energy for each subshell is set to the Koopman energy ϵ_i (i.e., the single-particle energy coming from a HF calculation) plus an energy shift. Then, the expression

$$\alpha_{\text{core}} = \sum_i \frac{N_i}{(\epsilon_i + \Delta)^2}, \tag{23}$$

is used to fix Δ so that the computed polarizability is equal to a core polarizability obtained independently. A numerical experiment was done in which the core f-value distribution for the $2p$ shell was split into two parts, one with an oscillator strength of 1.0 and one with an oscillator strength of 5.0.

$$\alpha_{\text{core}} = \sum_i \frac{N_i}{(\epsilon_i + \Delta_1)^2} + \frac{5}{(\epsilon_{2p} + \Delta_1)^2} + \frac{1}{(\epsilon_{2p} + \Delta_2)^2}. \tag{24}$$

Then the parameters Δ_1 and Δ_2 were adjusted to decrease the core contribution to C_3 by 0.04, while keeping α_d for the core constant. This resulted in the NaHe C_6 decreasing from 25.76 to 25.61 a.u. There is a reduction in C_6, but the remaining discrepancy is still larger than 2%.

Close to exact values of C_6 have been computed with correlated wave functions [64] for the interaction of the $2p$ state of Li with H and He. The present calculations agree with these values to better than 0.1%. Comparisons with the MBPT calculations of Zhu *et al.* [53] of C_6 for the ns-np case for helium reveal differences of 3% for NaHe, 12% for KHe, and 3% for RbHe. In this case, the MBPT values of C_6 are always larger than the present values. It is particularly hard to understand the 12% discrepancy for KHe as there is a 1–3 % agreement for the polarizabilities of the two calculations. Further, the calculation of Zhu *et al.* [53] did not allow for the possibility of an excitation of K to a $^1P^e$ state (formed by coupling the $^2P^o$ core excited state to the $4p$ valence state). Inclusion of this additional excitation pathway would increase the Zhu *et al.* dispersion coefficients by about 1%, leading to a larger difference.

One possible reason for the discrepancy is computation error. The present code gives almost perfect dispersion parameters for LiH and LiHe, and the present oscillator strengths for K originating from the $4p$ level agree quite well with the high precision calculations listed in Table VI. It would be more likely that Zhu *et al.* suffer from a computation error since they do not report any similar validation checks (e.g., determining the LiHe dispersion parameters). The other possible cause of discrepancy is that the MBPT calculation of the frequency-dependent polarizability for the alkali-metal atoms is capturing additional physics that is simply absent in the present model.

Values of C_6 for the alkali-metal np-He case have also been determined in the model potential of calculations of alkali-metal broadening by Mullamphy *et al.* [27]. These values cannot be used to resolve the discrepancy since not enough information about the details of the calculation of C_6 are presented.

The dispersion coefficients for the interaction of atoms in excited $(n+1)s$ states with hydrogen and helium are given in Table IX. The results of Proctor and Stwalley (PS) [65] are presented for comparison. The PS results were derived by using various constraints on oscillator strength sum rules (based on experimental and theoretical data) to determine the oscillator strength distribution as a function of excitation energy. Although PS quoted uncertainties, these are not given here since their uncertainties in many cases seem to be overoptimistic.

The most obvious feature of Table IX is that the present dispersion coefficients are all larger than those of PS. One reason for this is the contribution of the core; indeed PS state that their results for the alkali-metal atoms should be regarded as valence only dispersion coefficients. Therefore it would be expected that the differences from PS get larger as the size of the atom increases, and this is the case. The overall contribution of the core to C_6 for potassium was 6.3 a.u. out of 225.0 a.u. For rubidium, the core contribution to C_6 was 9.5 a.u. out of 242.4 a.u. Adding a core contribution to the PS data would give C_6 parameters closer to the present results. For example, the PS C_6 for KHe would increase to 221.4 a.u.

The dispersion coefficients involving alkali-metal atoms in their lowest d levels are given in Table X. We are not aware of any other calculations for most of the cases listed in the table. The one exception comes from the model potential of Mullamphy *et al.* [27,66], which gave C_6 values for NaHe amazingly close to the present values.

VI. CLOSE TO RESONANT COUPLING BETWEEN HETERONUCLEAR ATOMS

One of the perceived differences between homonuclear and heteronuclear systems is that the former admits a longer range C_3/R^3 interaction in cases where one of the atoms is in a P state and the other is in an S state [67–71]. This term is often called the resonant dipole interaction. This term is usually derived for a pair of homonuclear atoms by writing the symmetrized molecular wave functions down explicitly and demonstrating that the first-order interaction leads to the C_3/R^3 resonant dipole interaction [9,12,71–73].

However, it is also known that a resonant dipole interaction can occur between two heteronuclear systems whenever the excitation energy of one atom exactly or approximately cancels the deexcitation energy of another atom in an excited state [74–76]. This type of interaction will occur between alkali-metal atoms in two isotopes and was utilized in the photoassociation of the heteronuclear ^{6}Li-^{7}Li molecule [75].

Let us start the discussion by considering a pair of heteronuclear alkali-metal atoms of the same element, one in the nS ground state and the other in the lowest nP first excited state. The nS-nP excitation energy for these atoms will be almost the same except for an isotopic energy shift Δ. There are two nearly resonant states with

$$\Psi_1 = |nSnP1M\rangle, \quad E = E_0,$$

$$\Psi_2 = |nPnS1M\rangle, \quad E = E_0 + \Delta. \tag{25}$$

The near degeneracy between the two energies means that perturbation theory cannot be applied to treat the interaction between the two states. Accordingly, one diagonalizes the first-order Hamiltonian, e.g.,

$$H = \begin{bmatrix} E_0 & \dfrac{A_M|\langle nS\|r^k\mathbf{C}^k\|nP\rangle|^2}{R^3} \\ \dfrac{A_M|\langle nS\|r^k\mathbf{C}^k\|nP\rangle|^2}{R^3} & E_0+\Delta \end{bmatrix}, \tag{26}$$

where A_M is $-\frac{2}{3}$ for $M=0$ and A_M is $\frac{1}{3}$ for $M=\pm1$ between these states. Writing $C_3 = -A_M|\langle nS\|r^k\mathbf{C}^k\|nP\rangle|^2$, the eigenvalues are

$$F_1 = E_0 + \frac{\Delta}{2} + \frac{\sqrt{\Delta^2 + \dfrac{4C_3^2}{R^6}}}{2}, \tag{27}$$

$$F_2 = E_0 + \frac{\Delta}{2} - \frac{\sqrt{\Delta^2 + \dfrac{4C_3^2}{R^6}}}{2}, \tag{28}$$

and the eigenvectors

$$|\Phi_1\rangle = c_{11}|\Psi_1\rangle + c_{12}|\Psi_2\rangle, \tag{29}$$

$$|\Phi_2\rangle = -c_{12}|\Psi_1\rangle + c_{11}|\Psi_2\rangle, \tag{30}$$

where

$$c_{11} = -\frac{(2C_3)}{\sqrt{2}\mathcal{N}}, \tag{31}$$

$$c_{12} = \frac{(R^3\Delta + \sqrt{R^6\Delta^2 + 4C_3^2})}{\sqrt{2}\mathcal{N}}, \tag{32}$$

$$\mathcal{N} = \sqrt{R^6\Delta^2 + R^3\Delta\sqrt{R^6\Delta^2 + 4C_3^2} + 4C_3^2}. \tag{33}$$

Consider the case where $|C_3|/R^3 \gg \Delta$, the energies become

$$F_1 \approx E_0 + \frac{\Delta}{2} + \frac{|C_3|}{R^3} + \frac{R^3\Delta^2}{8|C_3|}, \tag{34}$$

$$F_2 \approx E_0 + \frac{\Delta}{2} - \frac{|C_3|}{R^3} - \frac{R^3\Delta^2}{8|C_3|}, \tag{35}$$

and the coefficients of their corresponding eigenvectors are

$$c_{11} \approx -\frac{1}{\sqrt{2}}\left(\frac{C_3}{|C_3|} - \frac{R^3\Delta}{4C_3}\right), \tag{36}$$

$$c_{12} \approx \frac{1}{\sqrt{2}}\left(1 + \frac{R^3\Delta}{4|C_3|}\right). \tag{37}$$

These results are compatible with the short description for dissimilar alkali-metal atoms given by Nikitin [76].

The near-degeneracy between the two states results in one molecular state of predominantly *gerade* type and another molecular state of *ungerade* type. This results in an attractive close to resonant dipole interaction between the two atoms. The dispersion interaction is then determined from $|\Phi_1\rangle$ and $|\Phi_2\rangle$.

This C_3/R^3 interaction will be dominant up to a range given by the identity $R_{C3} \approx \sqrt[3]{C_3/\Delta}$. The range of the resonant dipole interaction increases as the energy difference between them decreases. As an example, the isotope shift of the ^{22}Na-^{23}Na isotopes for the $3p$-$3s$ transition is about 1.15×10^{-7} hartree [77]. For the Σ state this corresponds to $R_{C3} \approx 480a_0$ (using a value of $C_3^{\Sigma} = 12.44$).

The above analysis was performed assuming two isotopes of a pair of alkali-metal-like atoms. However, the general principles apply to any pair of atoms which possess an accidental energy degeneracy for excitation (deexcitation); the off-diagonal coupling will then involve a product of the reduced matrix elements of two states. The coupled two-state analysis will most likely be necessary when the critical radius is larger than the LeRoy radius [78].

VII. CONCLUSIONS

A systematic approach to the determination of the dispersion parameters for two heteronuclear atoms has been developed. The most significant aspect of the present work is that the production of van der Waals coefficients in the heteronuclear case for almost any two low-lying atomic states has been reduced to a process that is purely mechanical. One simply generates files containing arrays of state and reduced matrix element information, and then feeds them into the dispersion coefficient program, which can currently handle all cases up to the *D*-*D* symmetry. For example, the determination of the dispersion coefficients for alkali-metal atom excited states and the rare gases was easily accomplished once a set of quadrupole and octupole pseudo-oscillator strengths for the rare gases was constructed [81]. Further, there is very little information available for the long-range interactions of alkaline-earth excited states with other atoms. It would not be very difficult to rectify this state of affairs. The explicit expressions for C_6 make it possible to determine this part of the dispersion interaction from oscillator strength tabulations.

The key to the algebraic reductions leading to the final expressions was the use of Eqs. (4) and (5). An alternate form of the electron-electron operator that is widely used [1,12,47,79] should be avoided since it makes the algebraic reduction much more complicated.

All considerations of electron spin have been omitted from this paper. The assumption has been made that the electron-electron operator does not change the overall spin state of the two atoms. So the van der Waals interactions between two atoms can be calculated without any reference to the spin state.

The results of the present calculations are in excellent agreement with previous high accuracy calculations by Yan and co-workers [9,64]. Agreement with the calculations by Zhu *et al.* [53], which used MBPT to compute the frequency-dependent polarizability of the alkali-metal excited state, was not so good and the differences between the dispersion parameters was generally 3% or larger. This is puzzling since previous comparisons with dispersion coefficients computed with the MBPT-type calculations have usually yielded agreement at the 1% level [5–7,80].

The expressions can also be applied to the homonuclear case with some restrictions. First, if the two atoms are in the same state, then the relations developed here will correctly evaluate the dispersion coefficients, e.g., the Li($2p$)-Li($2p$) case. Second, the present methodology can also be applied without modification when the two atoms have different spins, e.g., the He($2\,^1P$)-He($2\,^3P$) case. Indeed, it proved possible to reproduce the He($2\,^1P$)-He($2\,^1P$), He($2\,^1P$)-He($2\,^3P$), and the He($2\,^3P$)-He($2\,^3P$) dispersion parameters of Zhang *et al.* [82] to all digits by feeding lists of matrix elements into the program that evaluates Eq. (13).

Some qualifications are in order. First, only the diagonal part of the long-range interaction has been presented. A multichannel approach may be important in cases where the molecular representation admits a number of degenerate states with the same overall symmetry. The off-diagonal part of the dispersion interaction can be easily computed with the present approach. Secondly, the impact of the spin-orbit interaction has been ignored when the molecular representations were derived. Finally, the case of two isotopes of the same atom requires special treatment for most configurations due to the near degeneracy of the energies.

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