

## Long-range potentials for two-species alkali-metal atoms

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We address a growing interest in trapping and cooling of mixed-species alkali-metal atoms. Long-range coefficients that arise in the multipole expansion of molecular potentials for unlike alkali-metal dimers are calculated. The coefficients for the heteronuclear alkali-metal dimers corresponding to different molecular symmetries that separate to  $nS-n'S, nS-n'P, nS-n'D$ , and  $nP-n'P$  atomic levels are computed with high precision. We consider cases where in the infinite separation limit, one atom is in the ground state and the other is in one of the lowest  $S$ ,  $P$ , and  $D$  excited states and both atoms are in their lowest excited  $P$  states. We find the long-range potentials for  $\text{Rb}(5S)\text{-Cs}(6S)$ ,  $\text{Rb}(6S)\text{-Cs}(6S)$ ,  $\text{K}(4S)\text{-Rb}(5P)^{1,3}\Sigma$ ,  $\text{K}(4P)\text{-Cs}(6P)^{1,3}\Sigma$ , and  $\text{Rb}(5S)\text{-Na}(3D)^{1,3}\Sigma$  molecules to be the most attractive. The  $\text{K}(4S)\text{-Rb}(5P)$  dimer represents the best candidate molecule for ultracold photoassociative spectroscopy. We also find the  $\text{K}(4P)\text{-Cs}(6P)$  and  $\text{Rb}(5S)\text{-K}(4P)$  dimers to form, respectively, the most attractive and the most repulsive long-range potentials. The present calculation is in good agreement with experimentally determined value for the  $1/R^6$  van der Waals coefficient for the interaction between  $\text{Cs}(6S)$  and  $\text{Li}(2P)$  atoms. [S1050-2947(99)07101-2]

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### I. INTRODUCTION

Our understanding of the collisional interaction between bosonic atoms operating at ultracold temperatures has advanced manifold in recent years [1–3]. The creation of like alkali-metal Bose-Einstein condensates [4–6] has provided the impetus for the burst in theoretical activities. As the level of sophistication in manipulating trapped atoms rises and new techniques for probing the interatomic properties at the macroscopic level are developed [7,8], theory is being directed toward understanding the atomic interactions in mixed-isotope and mixed-species alkali-metal condensates [9–14]. It is also possible to study the ultracold photoassociative spectroscopic features of heteronuclear alkali-metal systems [15,16]. Mixed-species (heteronuclear) atoms in a single trap offer the possibility of stabilizing formerly unstable condensates [6]. From a spectroscopic point of view, ultracold collisions between two unlike atoms offer unique opportunities. For instance, whereas the collision between two optically pumped like alkali-metal atoms proceeds via the long-range resonant dipole interaction, the photoassociative spectroscopy of two similarly arranged unlike alkali-metal atoms is driven by the much shorter range van der Waals forces.

That binary elastic collisions, the so-called good collisions, between atoms are responsible for the thermalization of bosonic atoms in magnetic traps is established [1,2,17]. These ultracold atoms interact via large distances inside the traps. A practical and extremely meaningful parameter in describing the short-range collisional properties of cold interacting atoms is the scattering length. It is also well known

that the scattering length demonstrates extreme sensitivity to the form of the long-range part of the dimer potential [1,2]. This has been the chief driving force behind the recent theoretical push in obtaining precise values for the long-range interaction between two neutral bosonic atoms [20–23]. In collisions between mixed-species condensates, a crucial parameter is the interspecies scattering length [24]. As with the intraspecies cases, the interspecies scattering length, in both sign and magnitude, will be sensitive to the long-range form of the heteronuclear molecular potential-energy curves.

The long-range interactions between two atoms, where the exchange forces become ineffective [18,19], are of the electrostatic type. It is possible to expand the dimer adiabatic Born-Oppenheimer potential in the small parameter  $1/R$ , where  $R$  is the internuclear distance. The coefficients appearing in front of each term in the series expansion in  $1/R$  describe the different electric multipole interactions between atoms correlated at large distances. Coefficients in inverse powers of  $1/R^n$  with  $n \geq 6$ , the so-called dispersion coefficients, can be computed in the second order of degenerate perturbation theory, where the perturbation is given by the Coulomb interaction between the atomic charge distributions [21,23]. Second-order optical transitions, the dynamic response of atoms and molecules to weak external electric fields, are needed for the calculation of various properties in dispersive media such as the refractive index and light scattering.

Calculations of atomic properties of alkali-metal atoms are facilitated by recognizing that each atom has a single active electron outside a closed core. The motion of this valence electron can be modeled with high precision with an angular-momentum-dependent, radial local potential. Such a model potential whose parameters were optimized to yield known atomic energy levels and static dipole polarizabilities

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was used to calculate ground-state dispersion coefficients for alkali-metal dimers [20]. We emphasize that the atomic energy levels and static polarizabilities are calculated to experimental precision. The valence electron model includes the core effects such as the core polarization and screening. In calculating the transition matrix elements, we “dress” the electric dipole operator to include the effect of the core polarization, which can become significant for heavier alkali metals. Extensions of the method to more complex situations in calculating the long-range interaction potentials correlating to  $nS-n'S$ ,  $nS-n'P$ ,  $nS-n'D$ , and  $nP-nP$  dissociation limits for the homonuclear alkali-metal dimers were recently carried out [21–23].

In this work we study the long-range forces between two unlike alkali-metal atoms. We consider the following cases: both atoms in the ground state, one atom in the ground state and the other in an  $S$ , a  $P$ , or a  $D$  excited state, and both atoms in a  $P$  excited state.

For large internuclear distances, the potential-energy curves associated with the  $nS-n'S$  asymptotes may be expressed as

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots, \quad (1.1)$$

where  $C_n$  for  $n=6,8,10$  are the dispersion coefficients. The expressions for the  $C_6, C_8$ , and  $C_{10}$  coefficients when both atoms are in their ground states and when one of the atoms is in an  $S$  excited state are presented in Sec. II.

For the  $nS-n'P$  and  $nS-n'D$  asymptotes, the long-range potential-energy curves are given by

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \dots \quad (1.2)$$

The formal theory of the dispersion coefficients involved when one atom is in its ground state and the other atom is in an excited  $P$  or  $D$  state is presented in Secs. III and IV, respectively. We mention that in contrast to the homonuclear case, the multipole terms with  $n=3$  and  $n=5$ , namely, the  $C_3$  and  $C_5$  coefficients, for molecular symmetries dissociating to  $nS-n'P$  and  $nS-n'D$  limits, respectively, vanish because no resonant dipole or quadrupole excitation between two unlike atoms is possible.

For the  $nP-n'P$  asymptote, the long-range potential-energy curves are given by

$$V(R) = -\frac{C_5}{R^5} - \frac{C_6}{R^6} - \frac{C_8}{R^8} - \dots \quad (1.3)$$

The expressions for the  $C_5, C_6$ , and  $C_8$  coefficients associated with different molecular symmetries dissociating to the  $nP-n'P$  limit are presented in Sec. V. Numerical results for the long-range coefficients of heteronuclear alkali-metal dimers are presented in Sec. VI. Throughout this paper we use atomic units ( $\hbar = m_e = e = 1$ ).

## II. DISPERSION COEFFICIENTS FOR THE $nS-n'S$ ASYMPTOTE

We denote the two interacting atoms by  $A$  and  $B$ . At infinite separations, the atoms  $A$  and  $B$  can be in their unperturbed ground  $S$  states represented by the set of quantum numbers  $\nu_A = \{n_A 00\}$  and  $\nu_B = \{n_B 00\}$ , respectively. The other atomic excited states are denoted by  $\nu'_X = \{n'_X l'_X m'_X\}$ , where  $X=A, B$ .

The dispersion coefficients  $C_6, C_8$ , and  $C_{10}$  are obtained in the second order of the perturbation theory. Here the perturbation is given by the Coulomb interaction between the atomic charge distributions [21,25–27] and the unperturbed wave function is given by the product of the atomic wave functions  $|n_A 00\rangle |n_B 00\rangle$ . Following a procedure similar to that presented in [21], we find the following expressions for the dispersion coefficients:

$$C_6 = \frac{2}{3} S_1^0, \quad (2.1)$$

$$C_8 = S_2^0 + S_3^0, \quad (2.2)$$

$$C_{10} = \frac{14}{5} S_4^0 + \frac{4}{3} (S_5^0 + S_6^0), \quad (2.3)$$

where

$$S_1^0 = \sum_{n'_A, n'_B} \frac{(n_A S | r | n'_A P)^2 (n_B S | r | n'_B P)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B P} - E_{n_B S})}, \quad (2.4)$$

$$S_2^0 = \sum_{n'_A, n'_B} \frac{(n_A S | r | n'_A P)^2 (n_B S | r^2 | n'_B D)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B D} - E_{n_B S})}, \quad (2.5)$$

$$S_3^0 = \sum_{n'_A, n'_B} \frac{(n_A S | r^2 | n'_A D)^2 (n_B S | r | n'_B P)^2}{(E_{n'_A D} - E_{n_A S}) + (E_{n'_B P} - E_{n_B S})}, \quad (2.6)$$

$$S_4^0 = \sum_{n'_A, n'_B} \frac{(n_A S | r^2 | n'_A D)^2 (n_B S | r^2 | n'_B D)^2}{(E_{n'_A D} - E_{n_A S}) + (E_{n'_B D} - E_{n_B S})}, \quad (2.7)$$

$$S_5^0 = \sum_{n'_A, n'_B} \frac{(n_A S | r | n'_A P)^2 (n_B S | r^3 | n'_B F)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B F} - E_{n_B S})}, \quad (2.8)$$

$$S_6^0 = \sum_{n'_A, n'_B} \frac{(n_A S | r^3 | n'_A F)^2 (n_B S | r | n'_B P)^2}{(E_{n'_A F} - E_{n_A S}) + (E_{n'_B P} - E_{n_B S})}. \quad (2.9)$$

$E_{n_X l'_X}$  denotes the energy levels of the atom  $X$  with principle quantum number  $n_X$  and angular momentum  $l'_X$  and  $(||)$  is a radial matrix element. Equations (2.4)–(2.9) are quite general, available for any  $nS-n'S$  asymptote. We are interested in studying cases when both atoms are in their ground states (“ground-ground” case) and when one of the atoms, say  $B$ , is in the first  $S$  excited state (“ground-excited” case). Below, we provide expressions for  $S_j$ , suitable for numerical computation.

### A. Ground-ground case

The sums in Eqs. (2.4)–(2.9) span the discrete and continuum Rydberg manifolds. A convenient scheme for computing the matrix elements  $S_j^0$  for  $j=1, \dots, 6$  is to factor them into individual contributions of each atom by using the integral representation [28]

$$\frac{1}{a+b} = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re} \left( \frac{1}{a+i\omega} \right) \operatorname{Re} \left( \frac{1}{b+i\omega} \right). \quad (2.10)$$

Note that Eq. (2.10) holds only for positive values of  $a$  and  $b$ . For cases where both atoms are in their ground states, the integral representation in Eq. (2.10) may be applied directly to the denominators in Eqs. (2.4)–(2.9), where  $a$  and  $b$  are both positive. The expressions in Eqs. (2.4)–(2.9) can now be written as integrals over dynamic polarizabilities

$$S_1^0 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re} [(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \\ \times \operatorname{Re} [(n_B S | r g_P(E_{n_B S} + i\omega) r | n_B S)], \quad (2.11)$$

$$S_2^0 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re} [(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \\ \times \operatorname{Re} [(n_B S | r^2 g_D(E_{n_B S} + i\omega) r^2 | n_B S)], \quad (2.12)$$

$$S_3^0 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re} [(n_A S | r^2 g_D(E_{n_A S} + i\omega) r^2 | n_A S)] \\ \times \operatorname{Re} [(n_B S | r g_P(E_{n_B S} + i\omega) r | n_B S)], \quad (2.13)$$

$$S_4^0 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re} [(n_A S | r^2 g_D(E_{n_A S} + i\omega) r^2 | n_A S)] \\ \times \operatorname{Re} [(n_B S | r^2 g_D(E_{n_B S} + i\omega) r^2 | n_B S)], \quad (2.14)$$

$$S_5^0 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re} [(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \\ \times \operatorname{Re} [(n_B S | r^3 g_F(E_{n_B S} + i\omega) r^3 | n_B S)], \quad (2.15)$$

$$S_6^0 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re} [(n_A S | r^3 g_F(E_{n_A S} + i\omega) r^3 | n_A S)] \\ \times \operatorname{Re} [(n_B S | r g_P(E_{n_B S} + i\omega) r | n_B S)], \quad (2.16)$$

where  $g_l$  is the atomic radial Green's functions with angular momentum  $l$ . The two-center molecular integral is now reduced to an integral over one-center atomic polarizabilities. Equations (2.11)–(2.16) may be rewritten in terms of the atomic multipole polarizabilities at imaginary frequency by employing the identity

$$\alpha_l(i\omega) = \frac{2}{2l+1} \operatorname{Re} [(n S | r^l g_l(E_{n S} + i\omega) r^l | n S)]. \quad (2.17)$$

$S_1^0$  is due to dipole-dipole interaction,  $S_2^0$  and  $S_3^0$  are due to dipole-quadrupole interaction,  $S_4^0$  is due to quadrupole-quadrupole interaction, and  $S_5^0$  and  $S_6^0$  are due to dipole-octupole interactions.

### B. Ground-excited case

When one of the atoms is in an  $S$  excited state, the factoring technique in Eq. (2.10) must be used with caution since the denominators in the  $S_j^0$  sums (2.4)–(2.9) may not always be written as a sum of two positive quantities. For these cases where  $a > 0$  and  $b < 0$ , we replace  $1/(a+b)$  by

$$\frac{1}{a+b} + \frac{1}{a-b} + \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re} \left[ \frac{1}{a+i\omega} \right] \operatorname{Re} \left[ \frac{1}{b+i\omega} \right], \quad (2.18)$$

where the last two terms in Eq. (2.18) cancel each other. This substitution preserves the completeness of the sums over the atomic states in the integral.

Whether  $a < 0$  or  $b < 0$  depends on the succession of the excited atomic levels for alkali-metal atoms. Suppose that atom  $A$  is in its ground state and atom  $B$  is in the first  $S$  excited state. Then we distinguish two cases. When the atom  $B$  is Li, Na, or K, there exists one  $P$  intermediate level between the ground state and the first  $S$  excited state and when atom  $B$  is Rb or Cs, there are one  $P$  and one  $D$  intermediate levels between the ground state and the first  $S$  excited state. Thus, using Eqs. (2.10) and (2.18), the  $S_j^0$  sums (2.4)–(2.9) for the Li(2*S*)-Na(4*S*), Li(2*S*)-K(5*S*), Na(3*S*)-Li(3*S*), Na(3*S*)-K(5*S*), K(4*S*)-Li(3*S*), K(4*S*)-Na(4*S*), Rb(5*S*)-Li(3*S*), Rb(5*S*)-Na(4*S*), Rb(5*S*)-K(5*S*), Cs(6*S*)-Li(3*S*), Cs(6*S*)-Na(4*S*), and Cs(6*S*)-K(5*S*) asymptotes become

$$S_1^0 = S_1^0 + (n_B - 1P | r | n_{B S})^2 [(n_A S | r g_P(E_{n_A S} - E_{n_B S} \\ + E_{n_{B-1P}}) r | n_A S) + (n_A S | r g_P(E_{n_A S} + E_{n_B S} \\ - E_{n_{B-1P}}) r | n_A S)], \quad (2.19)$$

$$S_3^0 = S_3^0 + (n_B - 1P | r | n_{B S})^2 [(n_A S | r^2 g_D(E_{n_A S} - E_{n_B S} \\ + E_{n_{B-1P}}) r^2 | n_A S) + (n_A S | r^2 g_D(E_{n_A S} + E_{n_B S} \\ - E_{n_{B-1P}}) r^2 | n_A S)], \quad (2.20)$$

$$S_6^0 = S_6^0 + (n_B - 1P | r | n_{B S})^2 [(n_A S | r^3 g_F(E_{n_A S} - E_{n_B S} \\ + E_{n_{B-1P}}) r^3 | n_A S) + (n_A S | r^3 g_F(E_{n_A S} + E_{n_B S} \\ - E_{n_{B-1P}}) r^3 | n_A S)] \quad (2.21)$$

and  $S_2^0, S_4^0$ , and  $S_5^0$  are as before, in Eqs. (2.12), (2.14), and (2.15). On the right-hand side (rhs) of Eqs. (2.19)–(2.21), the  $S_j^0$  terms, with  $j=1, 3$ , and  $6$ , are given by Eqs. (2.11), (2.13), and (2.16), respectively.  $n_A$  takes on values 2, 3, 4, 5, and 6 and  $n_B$  takes on values 3, 4, 5, 6, and 7 for Li, Na, K, Rb, and Cs, respectively.

For the Li(2*S*)-Rb(6*S*), Li(2*S*)-Cs(7*S*), Na(3*S*)-Rb(6*S*), Na(3*S*)-Cs(7*S*), K(4*S*)-Rb(6*S*), K(4*S*)-Cs(7*S*),

Rb(5*S*)-Cs(7*S*), and Cs(6*S*)-Rb(6*S*) asymptotes,  $S_1^0, S_3^0$ , and  $S_6^0$  are given by Eqs. (2.19)–(2.21), respectively, and

$$S_2^0 = S_2^0 + (n_B - 2D|r^2|n_B S)^2 [(n_A S|r g_P(E_{n_A S} - E_{n_B S} + E_{n_B - 2D})r|n_A S) + (n_A S|r g_P(E_{n_A S} + E_{n_B S} - E_{n_B - 2D})r|n_A S)], \quad (2.22)$$

$$S_4^0 = S_4^0 + (n_B - 2D|r^2|n_B S)^2 [(n_A S|r^2 g_D(E_{n_A S} - E_{n_B S} + E_{n_B - 2D})r^2|n_A S) + (n_A S|r^2 g_D(E_{n_A S} + E_{n_B S} - E_{n_B - 2D})r^2|n_A S)], \quad (2.23)$$

where on the rhs of Eqs. (2.22) and (2.23),  $S_2^0$  and  $S_4^0$  are given by Eqs. (2.12) and (2.14), respectively.  $S_5^0$  remains unchanged as in Eq. (2.15). The extra terms outside the integrals in the expressions for  $S_j^0$  for  $j=1,2,3,4$ , and 6 stem from the first two terms of Eq. (2.18).

### III. DISPERSION COEFFICIENTS FOR THE $NS-N'P$ ASYMPTOTES

In contrast with the homonuclear case, the  $1/R^3$  term for the heteronuclear dimers, namely,  $C_3$ , is zero since no resonant dipole excitation between unlike atoms is allowed by the energy conservation rule. Therefore, the series expansion in  $1/R$  for the  $S$ - $P$  asymptotes for heteronuclear dimers begins with  $C_6/R^6$ . The zeroth-order wave functions  $|n_A 00\rangle|n_B 1 m_B\rangle$  (assuming atom  $A$  is in the ground state and atom  $B$  is in a  $P$  excited state). Given the cylindrical symmetry of the total Hamiltonian, the projection of the total angular momentum along the internuclear axis  $\Lambda = m_B$  is conserved.  $\Lambda = 0$  corresponds to electronic states with  $^{1,3}\Sigma^+$  symmetries and  $\Lambda = \pm 1$  corresponds to electronic states with  $^{1,3}\Pi$  symmetries. In the long-range limit, the singlet and triplet states are degenerate. This degeneracy is removed by considering the exchange energy, which is neglected here [19]. Unlike the homonuclear case, the symmetry under the exchange of nuclear centers is broken. Following a procedure similar to that presented in [21], we obtain expressions for the dispersion coefficients.

For the  $^{1,3}\Sigma^+$  symmetries we have

$$C_6 = \frac{4}{9}S_1^1 + \frac{22}{45}S_2^1, \quad (3.1)$$

$$C_8 = \frac{18}{25}S_3^1 + \frac{129}{175}S_4^1 + \frac{3}{5}S_5^1 + \frac{18}{25}S_6^1 + \frac{48}{35}S_7^1 \quad (3.2)$$

and for the  $^{1,3}\Pi$  symmetries we have

$$C_6 = \frac{1}{9}S_1^1 + \frac{19}{45}S_2^1, \quad (3.3)$$

$$C_8 = \frac{6}{25}S_3^1 + \frac{93}{175}S_4^1 + \frac{1}{5}S_5^1 + \frac{16}{25}S_6^1 - \frac{24}{35}S_7^1, \quad (3.4)$$

where

$$S_1^1 = \sum_{n'_A, n'_B} \frac{(n_A S|r|n'_A P)^2 (n_B P|r|n'_B S)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B S} - E_{n_B P})}, \quad (3.5)$$

$$S_2^1 = \sum_{n'_A, n'_B} \frac{(n_A S|r|n'_A P)^2 (n_B P|r|n'_B D)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B D} - E_{n_B P})}, \quad (3.6)$$

$$S_3^1 = \sum_{n'_A, n'_B} \frac{(n_A S|r|n'_A P)^2 (n_B P|r^2|n'_B P)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B P} - E_{n_B P})}, \quad (3.7)$$

$$S_4^1 = \sum_{n'_A, n'_B} \frac{(n_A S|r|n'_A P)^2 (n_B P|r^2|n'_B F)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B F} - E_{n_B P})}, \quad (3.8)$$

$$S_5^1 = \sum_{n'_A, n'_B} \frac{(n_A S|r^2|n'_A D)^2 (n_B P|r|n'_B S)^2}{(E_{n'_A D} - E_{n_A S}) + (E_{n'_B S} - E_{n_B P})}, \quad (3.9)$$

$$S_6^1 = \sum_{n'_A, n'_B} \frac{(n_A S|r^2|n'_A D)^2 (n_B P|r|n'_B D)^2}{(E_{n'_A D} - E_{n_A S}) + (E_{n'_B D} - E_{n_B P})}, \quad (3.10)$$

$$S_7^1 = \sum_{n'_A, n'_B} \frac{(n_A S|r|n'_A P)^2 (n_B P|r|n'_B D)(n'_B D|r^3|n_B P)}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B D} - E_{n_B P})}. \quad (3.11)$$

The algebraic coefficients that enter in the expressions for the  $C_6$  and  $C_8$  coefficients are the same as those for the homonuclear  $C_6$  and  $C_8$  coefficients [21], although in the expression for the  $C_8$  coefficient for the homonuclear dimers there are three additional terms, strictly related to the gerade and ungerade symmetries.

The computation of the  $S_j^1$  sums, with  $j=1, \dots, 7$ , may be carried out in a similar fashion outlined in Sec. II, by using the integral representations in Eqs. (2.10) and (2.18). When, at infinite separations, atom  $A$  is in the ground state and atom  $B$  in the first  $P$  excited state, we have

$$S_1^1 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S|r g_P(E_{n_A S} + i\omega)r|n_A S)] \times \operatorname{Re}[(n_B P|r g_S(E_{n_B P} + i\omega)r|n_B P)] + (n_B S|r|n_B P)^2 [(n_A S|r g_P(E_{n_A S} - E_{n_B P} + E_{n_B S})r|n_A S) + (n_A S|r g_P(E_{n_A S} + E_{n_B P} - E_{n_B S})r|n_A S)], \quad (3.12)$$

$$S_2^1 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S|r g_P(E_{n_A S} + i\omega)r|n_A S)] \times \operatorname{Re}[(n_B P|r g_D(E_{n_B P} + i\omega)r|n_B P)], \quad (3.13)$$

$$S_3^1 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S|r g_P(E_{n_A S} + i\omega)r|n_A S)] \times \operatorname{Re}[(n_B P|r^2 g'_P(E_{n_B P} + i\omega)r^2|n_B P)] + (n_B P|r^2|n_B P)^2 (n_A S|r g_P(E_{n_A S})r|n_A S), \quad (3.14)$$

$$S_4^1 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \\ \times \operatorname{Re}[(n_B P | r^2 g_F(E_{n_B P} + i\omega) r^2 | n_B P)], \quad (3.15)$$

$$S_5^1 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r^2 g_D(E_{n_A S} + i\omega) r^2 | n_A S)] \\ \times \operatorname{Re}[(n_B P | r g_S(E_{n_B P} + i\omega) r | n_B P)] \\ + (n_B S | r | n_B P)^2 [(n_A S | r^2 g_D(E_{n_A S} - E_{n_B P} \\ + E_{n_B S}) r^2 | n_A S) + (n_A S | r^2 g_D(E_{n_A S} + E_{n_B P} \\ - E_{n_B S}) r^2 | n_A S)], \quad (3.16)$$

$$S_6^1 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r^2 g_D(E_{n_A S} + i\omega) r^2 | n_A S)] \\ \times \operatorname{Re}[(n_B P | r g_D(E_{n_B P} + i\omega) r | n_B P)], \quad (3.17)$$

$$S_7^1 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \\ \times \operatorname{Re}[(n_B P | r g_D(E_{n_B P} + i\omega) r^3 | n_B P)], \quad (3.18)$$

where  $g'$  in Eq. (3.14) denotes the radial Green's function reduced relative to the real part of the energy argument, i.e., the term  $E = E_{n_B P}$  is excluded from the summation.  $n_A$  and  $n_B$  take on values 2, 3, 4, 5, and 6 for Li, Na, K, Rb, and Cs, respectively.

#### IV. DISPERSION COEFFICIENTS FOR THE $NS-N'D$ ASYMPTOTE

The  $C_5$  coefficient, present in the multipole expansion in inverse powers of  $R$  for the homonuclear dimers, is zero in the case of heteronuclear molecules since no resonant quadrupole excitation between different atoms is allowed. Thus the dispersion series begins with  $C_6/R^6$ . We distinguish the electronic states with  $^{1,3}\Sigma^+$  symmetries ( $\Lambda=0$ ),  $^{1,3}\Pi$  symmetries ( $\Lambda=1$ ), and  $^{1,3}\Delta$  symmetries ( $\Lambda=2$ ). The degeneracy between the singlet and triplet states can be removed by taking in consideration the exchange interactions and are neglected here.

For the  $^{1,3}\Sigma^+$  symmetries we have

$$C_6 = \frac{2}{5} S_1^2 + \frac{16}{35} S_2^2, \quad (4.1)$$

$$C_8 = \frac{3}{5} S_3^2 + \frac{2}{7} S_4^2 + \frac{24}{35} S_5^2 + \frac{14}{25} S_6^2 + \frac{117}{175} S_7^2 + \frac{24}{35} S_8^2 + \frac{88}{105} S_9^2, \quad (4.2)$$

for the  $^{1,3}\Pi$  symmetries we have

$$C_6 = \frac{1}{3} S_1^2 + \frac{3}{7} S_2^2, \quad (4.3)$$

$$C_8 = \frac{1}{5} S_3^2 + \frac{10}{49} S_4^2 + \frac{146}{245} S_5^2 + \frac{12}{25} S_6^2 + \frac{111}{175} S_7^2 - \frac{8}{35} S_8^2 + \frac{16}{45} S_9^2, \quad (4.4)$$

and for the  $^{1,3}\Delta$  symmetries we have

$$C_6 = \frac{2}{15} S_1^2 + \frac{12}{35} S_2^2, \quad (4.5)$$

$$C_8 = \frac{18}{49} S_4^2 + \frac{17}{49} S_5^2 + \frac{6}{25} S_6^2 + \frac{93}{175} S_7^2 - \frac{4}{35} S_8^2 - \frac{244}{315} S_9^2, \quad (4.6)$$

where

$$S_1^2 = \sum_{n'_A, n'_B} \frac{(n_A S | r | n'_A P)^2 (n_B D | r | n'_B P)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B P} - E_{n_B D})}, \quad (4.7)$$

$$S_2^2 = \sum_{n'_A, n'_B} \frac{(n_A S | r | n'_A P)^2 (n_B D | r | n'_B F)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B F} - E_{n_B D})}, \quad (4.8)$$

$$S_3^2 = \sum_{n'_A, n'_B} \frac{(n_A S | r | n'_A P)^2 (n_B D | r^2 | n'_B S)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B S} - E_{n_B D})}, \quad (4.9)$$

$$S_4^2 = \sum_{n'_A, n'_B} \frac{(n_A S | r | n'_A P)^2 (n_B D | r^2 | n'_B D)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B D} - E_{n_B D})}, \quad (4.10)$$

$$S_5^2 = \sum_{n'_A, n'_B} \frac{(n_A S | r | n'_A P)^2 (n_B D | r^2 | n'_B G)^2}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B G} - E_{n_B D})}, \quad (4.11)$$

$$S_6^2 = \sum_{n'_A, n'_B} \frac{(n_A S | r^2 | n'_A D)^2 (n_B D | r | n'_B P)^2}{(E_{n'_A D} - E_{n_A S}) + (E_{n'_B P} - E_{n_B D})}, \quad (4.12)$$

$$S_7^2 = \sum_{n'_A, n'_B} \frac{(n_A S | r^2 | n'_A D)^2 (n_B D | r | n'_B F)^2}{(E_{n'_A D} - E_{n_A S}) + (E_{n'_B F} - E_{n_B D})}, \quad (4.13)$$

$$S_8^2 = \sum_{n'_A, n'_B} \frac{(n_A S | r | n'_A P)^2 (n_B D | r | n'_B P) (n'_B P | r^3 | n_B D)}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B P} - E_{n_B D})}, \quad (4.14)$$

$$S_9^2 = \sum_{n'_A, n'_B} \frac{(n_A S | r | n'_A P)^2 (n_B D | r | n'_B F) (n'_B F | r^3 | n_B D)}{(E_{n'_A P} - E_{n_A S}) + (E_{n'_B F} - E_{n_B D})}. \quad (4.15)$$

The algebraic coefficients that enter in the expressions for the  $C_6$  coefficients are the same as those for the homonuclear cases [21], although for the homonuclear dimers another term, related to the gerade and ungerade symmetries, is present.

At infinite separations, when atom  $A$  is in the ground state and atom  $B$  is in the first  $D$  excited state, we distinguish three cases, according to the particular sequences of the excited levels for alkali-metal atoms. When atom  $B$  is either Rb or Cs, there exists one  $P$  intermediate level between the ground

and the first excited states. When atom  $B$  is either Na or K, there are one  $S$  and one  $P$  intermediate levels between the ground and the first  $D$  excited state. Finally, when atom  $B$  is Li, there exist one  $S$  and two  $P$  intermediate levels between

the ground and the first  $D$  excited state. Thus, for the Li(2S)-Rb(4D), Na(3S)-Rb(4D), K(4S)-Rb(4D), Cs(6S)-Rb(4D), Li(2S)-Cs(5D), Na(3S)-Cs(5D), K(4S)-Cs(5D), and Rb(5S)-Cs(5D) asymptotes, we obtain

$$S_1^2 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \operatorname{Re}[(n_B D | r g_P(E_{n_B D} + i\omega) r | n_B D)] \\ + (n_B D | r | n_{g_B P})^2 [(n_A S | r g_P(E_{n_A S} - E_{n_B D} + E_{n_{g_B P}}) r | n_A S) + (n_A S | r g_P(E_{n_A S} + E_{n_B D} - E_{n_{g_B P}}) r | n_A S)], \quad (4.16)$$

$$S_2^2 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \operatorname{Re}[(n_B D | r g_F(E_{n_B D} + i\omega) r | n_B D)], \quad (4.17)$$

$$S_3^2 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \operatorname{Re}[(n_B D | r^2 g_S(E_{n_B D} + i\omega) r^2 | n_B D)] + (n_B D | r^2 | n_{g_B S})^2 \\ \times [(n_A S | r g_P(E_{n_A S} - E_{n_B D} + E_{n_{g_B S}}) r | n_A S) + (n_A S | r g_P(E_{n_A S} + E_{n_B D} - E_{n_{g_B S}}) r | n_A S)], \quad (4.18)$$

$$S_4^2 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \operatorname{Re}[(n_B D | r^2 g'_D(E_{n_B D} + i\omega) r^2 | n_B D)] \\ + (n_B D | r^2 | n_B D)^2 (n_A S | r g_P(E_{n_A S}) r | n_A S), \quad (4.19)$$

$$S_5^2 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \operatorname{Re}[(n_B D | r^2 g_G(E_{n_B D} + i\omega) r^2 | n_B S)], \quad (4.20)$$

$$S_6^2 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r^2 g_D(E_{n_A S} + i\omega) r^2 | n_A S)] \operatorname{Re}[(n_B D | r g_P(E_{n_B D} + i\omega) r | n_B D)] + (n_B D | r | n_{g_B P})^2 \\ \times [(n_A S | r^2 g_D(E_{n_A S} - E_{n_B D} + E_{n_{g_B P}}) r^2 | n_A S) + (n_A S | r^2 g_D(E_{n_A S} + E_{n_B D} - E_{n_{g_B P}}) r^2 | n_A S)], \quad (4.21)$$

$$S_7^2 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r^2 g_D(E_{n_A S} + i\omega) r^2 | n_A S)] \operatorname{Re}[(n_B D | r g_F(E_{n_B D} + i\omega) r | n_B D)], \quad (4.22)$$

$$S_8^2 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \operatorname{Re}[(n_B D | r g_P(E_{n_B D} + i\omega) r^3 | n_B D)] + (n_B D | r | n_{g_B P}) (n_{g_B P} | r^3 | n_B D) \\ \times [(n_A S | r g_P(E_{n_A S} - E_{n_B D} + E_{n_{g_B P}}) r | n_A S) + (n_A S | r g_P(E_{n_A S} + E_{n_B D} - E_{n_{g_B P}}) r | n_A S)], \quad (4.23)$$

$$S_9^2 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A S | r g_P(E_{n_A S} + i\omega) r | n_A S)] \operatorname{Re}[(n_B D | r g_F(E_{n_B D} + i\omega) r^3 | n_B D)], \quad (4.24)$$

where  $n_A$  takes on values 2, 3, 4, 5, and 6 for Li, Na, K, Rb, and Cs, respectively, while  $n_B$  takes on values 4 and 5 and  $n_{g_B}$  takes on values 5 and 6 for Rb and Cs, respectively. For the Li(2S)-Na(3D), K(4S)-Na(3D), Rb(5S)-Na(3D), Cs(6S)-Na(3D), Li(2S)-K(3D), Na(3S)-K(3D), Rb(5S)-K(3D), and Cs(6S)-K(3D) asymptotes, the  $S_j^2$  have the same expressions as in the previous case except that  $S_3^2$  becomes

$$S_3^2 = S_3^2 + (n_B D | r | n_{g_B + 1S})^2 \\ \times [(n_A S | r g_P(E_{n_A S} - E_{n_B D} + E_{n_{g_B + 1S}}) r | n_A S) \\ + (n_A S | r g_P(E_{n_A S} + E_{n_B D} - E_{n_{g_B + 1S}}) r | n_A S)], \quad (4.25)$$

where on the rhs of Eq. (4.25), the  $S_3^2$  term is given by Eq.

TABLE I. Dispersion coefficients for the ground state of heteronuclear alkali-metal dimers, in a.u. The numbers in square brackets denote powers of ten.

Molecule	$C_6$	$C_8$	$C_{10}$	Reference
Li(2 <i>S</i> )-Na(3 <i>S</i> )	1.4594[3]	9.8060[4]	9.1279[6]	
	1.440[3]	9.485[4]	8.859[6]	[30]
	1.452[3]	9.781[4]	9.058[6]	[31]
	1.527[3]	8.800[4]		[32]
	1.4601[3]			[33]
	1.470[3]			[34]
Li(2 <i>S</i> )-K(4 <i>S</i> )	2.2933[3]	1.9249[5]	2.0730[7]	
	2.290[3]	1.852[5]	1.949[7]	[30]
	2.238[3]	1.911[5]	2.139[7]	[31]
	2.550[3]	1.753[5]		[32]
	2.3338[3]			[33]
	2.240[3]			[34]
Li(2 <i>S</i> )-Rb(5 <i>S</i> )	2.4683[3]	2.2825[5]	2.5645[7]	
	2.500[3]	2.190[5]	2.356[7]	[30]
	2.807[3]	2.272[5]		[32]
	2.440[3]			[34]
Li(2 <i>S</i> )-Cs(6 <i>S</i> )	2.9338[3]	3.1253[5]	3.7627[7]	
	3.015[3]	3.049[5]	3.379[7]	[30]
	3.596[3]	3.450[5]		[32]
	3.000[3]			[34]
Na(3 <i>S</i> )-K(4 <i>S</i> )	2.4000[3]	2.1947[5]	2.4873[7]	
	2.367[3]	2.082[5]	2.303[7]	[30]
	2.336[3]	2.174[5]	2.553[7]	[31]
	2.803[3]	2.015[5]		[32]
	2.4430[3]			[33]
	2.390[3]			[34]
Na(3 <i>S</i> )-Rb(5 <i>S</i> )	2.5815[3]	2.5815[5]	3.0567[7]	
	2.582[3]	2.444[5]	2.773[7]	[30]
	3.085[3]	2.602[5]		[32]
	2.600[3]			[34]
Na(3 <i>S</i> )-Cs(6 <i>S</i> )	3.0593[3]	3.4907[5]	4.4378[7]	
	3.106[3]	3.355[5]	3.948[7]	[30]
	3.940[3]	3.930[3]		[32]
	3.180[3]			[34]
K(4 <i>S</i> )-Rb(5 <i>S</i> )	4.1065[3]	4.7599[5]	6.3524[7]	
	4.149[3]	4.531[5]	5.724[7]	[30]
	5.200[3]	4.907[5]		[32]
	4.000[3]			[34]
K(4 <i>S</i> )-Cs(6 <i>S</i> )	4.9011[3]	6.3606[5]	9.0399[7]	
	5.016[3]	6.162[5]	8.077[7]	[30]
	6.677[3]	7.272[5]		[32]
	4.940[3]			[34]
Rb(5 <i>S</i> )-Cs(6 <i>S</i> )	5.2840[3]	7.3052[5]	1.0831[8]	
	5.483[3]	7.111[5]	9.629[7]	[30]
	7.353[3]	8.870[5]		[32]
	5.370[3]			[34]

(4.18).  $n_A$  takes on values 2, 3, 4, 5, and 6 for Li, Na, K, Rb, and Cs, respectively,  $n_B = 3$ , and  $n_{gB}$  takes on values 3 and 4 for Na and K, respectively. The additional term in Eq. (4.25) is due to the presence of an  $S$  intermediate level between the ground and the first excited  $D$  states for Na and K. For the Na(3*S*)-Li(3*D*), K(4*S*)-Li(3*D*), Rb(5*S*)-Li(3*D*),

TABLE II. Dispersion coefficients for the  $nS$ - $n'S$  asymptote of heteronuclear alkali-metal dimers, where in the dissociation limit one atom is the ground state and other in the first  $S$  excited state, in a.u.

Molecule	$C_6$	$C_8$	$C_{10}$
Li(2 <i>S</i> )-Na(4 <i>S</i> )	2.1041[4]	4.6830[6]	1.4266[9]
Li(2 <i>S</i> )-K(5 <i>S</i> )	2.5920[4]	7.6198[6]	2.8252[9]
Li(2 <i>S</i> )-Rb(6 <i>S</i> )	2.7415[4]	8.6940[6]	3.4006[9]
Li(2 <i>S</i> )-Cs(7 <i>S</i> )	3.0254[4]	1.0824[7]	4.6359[9]
Na(3 <i>S</i> )-Li(3 <i>S</i> )	1.9650[4]	4.2353[6]	1.2536[9]
Na(3 <i>S</i> )-K(5 <i>S</i> )	2.5177[4]	7.9005[6]	3.0110[9]
Na(3 <i>S</i> )-Rb(6 <i>S</i> )	2.6738[4]	8.9899[6]	3.6129[9]
Na(3 <i>S</i> )-Cs(7 <i>S</i> )	2.9615[4]	1.1144[7]	4.9007[9]
K(4 <i>S</i> )-Li(3 <i>S</i> )	7.2026[4]	7.6334[6]	2.2762[9]
K(4 <i>S</i> )-Na(4 <i>S</i> )	4.0374[4]	8.8202[6]	2.7857[9]
K(4 <i>S</i> )-Rb(6 <i>S</i> )	5.0609[4]	1.6112[7]	6.4682[9]
K(4 <i>S</i> )-Cs(7 <i>S</i> )	5.5453[4]	1.9984[7]	8.7520[9]
Rb(5 <i>S</i> )-Li(3 <i>S</i> )	1.1736[5]	8.6022[6]	2.5892[9]
Rb(5 <i>S</i> )-Na(4 <i>S</i> )	4.4861[4]	9.8939[6]	3.1608[9]
Rb(5 <i>S</i> )-K(5 <i>S</i> )	5.3224[4]	1.5776[7]	6.0817[9]
Rb(5 <i>S</i> )-Cs(7 <i>S</i> )	6.0858[4]	2.2184[7]	9.8113[9]
Cs(6 <i>S</i> )-Li(3 <i>S</i> )	-1.5369[4]	1.1834[7]	3.4076[9]
Cs(6 <i>S</i> )-Na(4 <i>S</i> )	6.3643[4]	1.3036[7]	4.1468[9]
Cs(6 <i>S</i> )-K(5 <i>S</i> )	7.1651[4]	2.0483[7]	7.9087[9]
Cs(6 <i>S</i> )-Rb(6 <i>S</i> )	7.3673[4]	2.3203[7]	9.4367[9]

and Cs(6*S*)-Li(3*D*) asymptotes, the presence of an additional  $P$  intermediate level between the ground and first excited  $D$  states of Li affects the expressions for the  $S_1^2$ ,  $S_6^2$ , and  $S_8^2$  sums in the following manner:

$$S_1^2 = S_1^2 + (n_B D |r| n_{gB} + 1P)^2 [(n_A S |r g_P (E_{n_A S} - E_{n_B D} + E_{n_{gB}+1P}) r | n_A S) + (n_A S |r g_P (E_{n_A S} + E_{n_B D} - E_{n_{gB}+1P}) r | n_A S)], \quad (4.26)$$

$$S_6^2 = S_6^2 + (n_B D |r| n_{gB} + 1P)^2 [(n_A S |r^2 g_D (E_{n_A S} - E_{n_B D} + E_{n_{gB}+1P}) r^2 | n_A S) + (n_A S |r^2 g_D (E_{n_A S} + E_{n_B D} - E_{n_{gB}+1P}) r^2 | n_A S)], \quad (4.27)$$

$$S_8^2 = S_8^2 + (n_B D |r| n_{gB} + 1P) (n_{gB} + 1P |r^3 | n_B D) \times [(n_A S |r g_P (E_{n_A S} - E_{n_B D} + E_{n_{gB}+1P}) r | n_A S) + (n_A S |r g_P (E_{n_A S} + E_{n_B D} - E_{n_{gB}+1P}) r | n_A S)]. \quad (4.28)$$

On the rhs of Eqs. (4.26)–(4.28), the  $S_j^2$ , with  $j = 1, 6$ , and  $8$ , terms are given by Eqs. (4.16), (4.21), and (4.23), respectively. The expressions for the  $S_j^2$ , with  $j = 2, 4, 5, 7$ , and  $8$ , terms are given by Eqs. (4.17), (4.19), (4.20), (4.22), and (4.24), respectively, while  $S_3^2$  is given by Eq. (4.25).  $n_A$  takes on values 3, 4, 5, and 6 for Na, K, Rb, and Cs, respectively, while  $n_B = 3$  and  $n_{gB} = 2$ .

TABLE III. Dispersion coefficients for the lowest  $nS-n'P$  asymptote of the heteronuclear alkali-metal dimers, in a.u.

Molecule	$1,3\Sigma^+$		$1,3\Pi$		Reference
	$C_6$	$C_8$	$C_6$	$C_8$	
Li(2S)-Na(3P)	-1.0648[4]	1.3333[6]	-1.0849[3]	1.1990[5]	
	-1.1405[4]	1.2400[6]	-1.367[3]	7.620[4]	[32]
Li(2S)-K(4P)	2.7751[4]	2.2371[6]	9.2765[3]	1.5318[5]	
	2.9650[4]	2.3420[6]	9.738[3]	-4.370[4]	[32]
Li(2S)-Rb(5P)	2.6744[4]	2.8089[6]	9.4312[3]	1.7135[5]	
	3.0115[4]	3.4550[6]	1.1078[4]	-2.8440[5]	[32]
Li(2S)-Cs(6P)	2.2416[4]	3.6187[6]	8.9016[3]	1.8926[5]	
	2.6960[4]	4.3520[6]	1.1287[4]	-3.670[5]	[32]
Na(3S)-Li(2P)	1.6829[4]	6.9559[5]	5.1409[3]	9.5887[4]	
	1.7314[4]	6.7300[5]	5.237[3]	5.5200[4]	[32]
Na(3S)-K(4P)	1.7822[4]	2.3743[6]	6.8777[3]	1.9560[5]	
	1.9470[4]	2.5700[6]	7.405[3]	-3.830[4]	[32]
Na(3S)-Rb(5P)	1.8621[4]	2.9641[6]	7.4845[3]	2.2030[5]	
	2.1878[4]	3.7910[6]	9.351[3]	-3.0130[5]	[32]
Na(3S)-Cs(6P)	1.8353[4]	3.7927[6]	7.9598[3]	2.4778[5]	
	2.3060[4]	4.7600[6]	1.0724[4]	-3.8680[5]	[32]
K(4S)-Li(2P)	-1.8781[4]	1.4233[6]	-3.2455[3]	2.8306[5]	
	-2.0670[4]	1.3650[6]	-3.663[3]	1.8960[5]	[32]
K(4S)-Na(3P)	-5.3678[3]	2.9107[6]	1.2805[3]	4.8260[5]	
	-6.488[3]	2.7840[6]	1.130[3]	3.3450[5]	[32]
K(4S)-Rb(5P)	2.3247[5]	5.3744[6]	6.2776[4]	5.8355[5]	
	3.0585[5]	6.9240[6]	8.3070[4]	-2.7600[5]	[32]
K(4S)-Cs(6P)	6.4292[4]	6.8132[6]	2.1731[4]	6.3629[5]	
	8.5992[4]	8.6860[6]	2.9987[4]	-3.8840[5]	[32]
Rb(5S)-Li(2P)	-1.6506[4]	1.8187[6]	-2.5677[3]	4.1208[5]	
	-1.8340[4]	1.7000[6]	-2.930[3]	2.9320[5]	[32]
Rb(5S)-Na(3P)	-4.6163[3]	3.9298[6]	1.6714[3]	8.0545[5]	
	-5.462[3]	3.5620[6]	1.665[3]	5.6590[5]	[32]
Rb(5S)-K(4P)	-2.1118[5]	5.0124[6]	-4.8538[4]	7.0665[5]	
	-2.8011[5]	5.5610[6]	-6.5250[4]	2.7200[5]	[32]
Rb(5S)-Cs(6P)	8.2377[4]	7.6901[6]	2.6721[4]	8.3844[5]	
	1.1006[5]	9.9620[6]	3.6900[4]	-2.0120[5]	[32]
Cs(6S)-Li(2P)	-1.0349[4]	-7.2314[6]	-7.4299[2]	-2.6182[6]	
	-1.1980[4]	-1.3830[6]	-8.80[2]	-7.8200[5]	[32]
	-9.898[3]	-1.1369[7]	-9.00[2]	-3.9547[6]	[35]
Cs(6S)-Na(3P)	-1.7758[3]	1.8326[6]	2.9296[3]	4.7920[4]	
	-1.952[3]	3.5100[6]	3.418[3]	4.1950[5]	[32]
Cs(6S)-K(4P)	-3.8865[4]	8.6801[6]	-4.5843[3]	1.7915[6]	
	-5.3166[4]	8.4980[6]	-7.125[3]	8.7220[5]	[32]
Cs(6S)-Rb(5P)	-5.3516[4]	9.7072[6]	-7.2791[3]	1.7715[6]	
	-6.9116[4]	1.1573[7]	-7.890[3]	4.1250[5]	[32]

### V. LONG-RANGE COEFFICIENTS FOR THE $NP-N'P$ ASYMPTOTE

The interaction between two excited  $P$  alkali-metal atoms is of interest in spectroscopy of excited molecules. The

asymptotic molecular designation for these molecules are  $\nu_A = \{n_A 1 m_A\}$  and  $\nu_B = \{n_B 1 m_B\}$ . According to the possible values of the projection of the total angular momentum along the internuclear axis  $\Lambda = m_A + m_B$ , we distinguish six types



TABLE IV. Dispersion coefficients for the lowest  $nS-n'D$  asymptote of heteronuclear alkali-metal dimers, in a.u.

Molecule	$1,3\Sigma^+$		$1,3\Pi$		$1,3\Delta$		Reference
	$C_6$	$C_8$	$C_6$	$C_8$	$C_6$	$C_8$	
Li(2S)-Na(3D)	3.6685[4]	1.8505[7]	3.1601[4]	4.5943[6]	1.6348[4]	-7.7675[5]	
Li(2S)-K(3D)	2.0579[4]	9.2864[6]	1.7822[4]	2.4911[6]	9.5529[3]	-2.9399[5]	
Li(2S)-Rb(4D)	1.5217[4]	5.8713[6]	1.3195[4]	1.5770[6]	7.1308[3]	-1.5547[5]	
Li(2S)-Cs(5D)	7.4423[3]	1.1240[7]	6.4663[3]	3.6246[6]	3.5382[3]	-7.5012[3]	
	3.413[3]	4.7610[6]	2.948[3]	1.5070[6]	1.551[3]	3.9400[4]	[32]
Na(3S)-Li(3D)	7.5094[4]	2.4149[7]	6.3660[4]	3.4752[6]	2.9357[4]	-1.5091[6]	
Na(3S)-K(3D)	1.9260[4]	9.0298[6]	1.6745[4]	2.6598[6]	9.1978[3]	-2.0489[5]	
Na(3S)-Rb(4D)	1.4610[4]	5.1948[6]	1.2708[4]	1.5062[6]	7.0014[3]	-9.6581[4]	
Na(3S)-Cs(5D)	7.3888[3]	4.0150[6]	6.4338[3]	1.2711[6]	3.5688[3]	1.7725[4]	
	3.528[3]	2.0140[6]	3.053[3]	6.0920[5]	1.627[3]	5.1300[4]	[32]
K(4S)-Li(3D)	2.3285[4]	2.9048[7]	2.1209[4]	1.1364[7]	1.4980[4]	2.7880[5]	
K(4S)-Na(3D)	1.2938[5]	4.3615[7]	1.0958[5]	5.4897[6]	5.0170[4]	-2.4173[6]	
K(4S)-Rb(4D)	2.8705[4]	1.1454[7]	2.4789[4]	3.1564[6]	1.3040[4]	-7.7364[3]	
K(4S)-Cs(5D)	1.3310[4]	1.3728[6]	1.1532[4]	3.2307[5]	6.1957[3]	1.4086[5]	
	6.780[3]	1.3490[6]	5.843[3]	3.0500[5]	3.030[3]	1.1090[5]	[32]
Rb(5S)-Li(3D)	2.6838[4]	3.2636[7]	2.4318[4]	1.2976[7]	1.6758[4]	6.8198[5]	
Rb(5S)-Na(3D)	2.0541[5]	5.7941[7]	1.7308[5]	3.0614[6]	7.6091[4]	-4.0139[6]	
Rb(5S)-K(3D)	4.5668[4]	1.9884[7]	3.9290[4]	5.2694[6]	2.0158[4]	-1.0143[5]	
Rb(5S)-Cs(5D)	1.4527[4]	2.2641[6]	1.2579[4]	6.5738[5]	6.7375[3]	2.1526[5]	
	7.520[3]	1.8350[6]	6.479[3]	4.8400[5]	3.354[3]	1.5800[5]	[32]
Cs(6S)-Li(3D)	3.8277[4]	3.9099[7]	3.4277[4]	1.3766[7]	2.2275[4]	-1.3979[5]	
Cs(6S)-Na(3D)	-8.5119[4]	2.1951[7]	-6.8613[4]	2.3199[7]	-1.9093[4]	4.9099[6]	
Cs(6S)-K(3D)	6.6785[4]	2.7277[7]	5.7148[4]	6.7612[6]	2.8236[4]	1.0793[5]	
Cs(6S)-Rb(4D)	4.2725[4]	1.7136[7]	3.6734[4]	4.8093[6]	1.8762[4]	3.8947[5]	

of electronic states: one corresponding to the  $1,3\Delta$  symmetries, two corresponding to the  $1,3\Pi$  symmetries, one corresponding to the  $1,3\Sigma^-$  symmetries, and two corresponding to the  $1,3\Sigma^+$  symmetries. The singlet and triplet states are again assumed to be degenerate. The  $C_5$  coefficient results from the first order of degenerate perturbation theory while the  $C_6$  and  $C_8$  coefficients are obtained in the second order of perturbation. Following a procedure similar to that outlined in [23], we find the following expressions for the long-range coefficients.

For the  $1,3\Delta$  symmetries, we have

$$C_5 = -\frac{6}{25}(n_A P|r^2|n_A P)(n_B P|r^2|n_B P), \quad (5.1)$$

$$C_6 = \frac{2}{15}(S_2 + S_3) + \frac{16}{75}S_4, \quad (5.2)$$

$$C_8 = \frac{27}{125}(S_6 + S_{10}) + \frac{6}{35}(S_7 + S_{11}) + \frac{246}{875}(S_8 + S_{12}) - \frac{4}{35}(S_{13} + S_{15}) - \frac{76}{175}(S_{14} + S_{16}). \quad (5.3)$$

For the  $1,3\Pi$  symmetries, we have for the first set of electronic states

$$C_5 = \frac{24}{25}(n_A P|r^2|n_A P)(n_B P|r^2|n_B P), \quad (5.4)$$

$$C_6 = \frac{1}{30}(S_2 + S_3) + \frac{31}{75}S_4, \quad (5.5)$$

$$C_8 = \frac{6}{25}(S_5 + S_9) + \frac{3}{25}(S_6 + S_{10}) + \frac{3}{175}(S_7 + S_{11}) + \frac{3}{5}(S_8 + S_{12}) - \frac{8}{35}(S_{13} + S_{15}) + \frac{4}{25}(S_{14} + S_{16}) \quad (5.6)$$

and for the second set of electronic states

$$C_5 = 0, \quad (5.7)$$

$$C_6 = \frac{3}{10}(S_2 + S_3) + \frac{1}{5}S_4, \quad (5.8)$$

$$C_8 = \frac{63}{125}(S_6 + S_{10}) + \frac{3}{7}(S_7 + S_{11}) + \frac{219}{875}(S_8 + S_{12}) + \frac{36}{175}(S_{14} + S_{16}). \quad (5.9)$$

For the  $1,3\Sigma^-$  symmetries, we have

$$C_5 = 0, \quad (5.10)$$

$$C_6 = \frac{8}{25}S_4, \quad (5.11)$$

TABLE V. Long-range coefficients for the lowest  $nP$ - $n'P$  asymptote of heteronuclear alkali-metal dimers, in a.u.

Molecule	Symmetry	$C_5$	$C_6$	$C_8$
Li(2P)-Na(3P)	$1^3\Delta$	-2.6091[2]	-2.0460[4]	2.3200[6]
	$1^3\Pi$	1.0436[3]	-2.4576[3]	3.1143[6]
	$1^3\Pi$		-4.8103[4]	2.5651[6]
	$1^3\Sigma^-$		2.3622[3]	-2.0401[4]
	$1^3\Sigma^+$		-4.2692[4]	2.1203[6]
	$1^3\Sigma^+$	-1.5654[3]	-2.8525[4]	-1.0925[7]
Li(2P)-K(4P)	$1^3\Delta$	-3.4187[2]	5.0303[3]	8.0278[6]
	$1^3\Pi$	1.3675[3]	5.1398[3]	1.8411[6]
	$1^3\Pi$		8.2987[3]	2.1876[7]
	$1^3\Sigma^-$		3.4508[3]	-2.6867[4]
	$1^3\Sigma^+$		7.4724[3]	2.1146[7]
	$1^3\Sigma^+$	-2.0512[3]	-5.2700[4]	9.9573[6]
Li(2P)-Rb(5P)	$1^3\Delta$	-3.8417[2]	6.5618[3]	-1.8430[6]
	$1^3\Pi$	1.5367[3]	6.1659[3]	1.7324[6]
	$1^3\Pi$		1.1244[4]	-2.5382[6]
	$1^3\Sigma^-$		4.0227[3]	-2.3540[4]
	$1^3\Sigma^+$		1.0107[4]	-3.4418[6]
	$1^3\Sigma^+$	-2.3050[3]	-9.0214[4]	3.9927[6]
Li(2P)-Cs(6P)	$1^3\Delta$	-4.3638[2]	1.3421[3]	8.3839[5]
	$1^3\Pi$	1.7455[3]	5.7141[3]	2.7150[6]
	$1^3\Pi$		-1.1635[3]	3.0653[6]
	$1^3\Sigma^-$		4.7810[3]	2.0888[4]
	$1^3\Sigma^+$		-9.0146[2]	1.9049[6]
	$1^3\Sigma^+$	-2.6183[3]	4.5691[4]	-1.2484[5]
Na(3P)-K(4P)	$1^3\Delta$	-5.0773[2]	-2.7418[4]	3.4166[6]
	$1^3\Pi$	2.0309[3]	3.9113[2]	1.2188[7]
	$1^3\Pi$		-6.7326[4]	5.5002[6]
	$1^3\Sigma^-$		6.4406[3]	-8.4867[4]
	$1^3\Sigma^+$		-5.9667[4]	3.9838[6]
	$1^3\Sigma^+$	-3.0464[3]	-4.0016[4]	5.0616[6]
Na(3P)-Rb(5P)	$1^3\Delta$	-5.7056[2]	-5.0200[4]	3.6550[6]
	$1^3\Pi$	2.2822[3]	-3.9804[3]	1.4840[7]
	$1^3\Pi$		-1.1962[5]	1.7770[6]
	$1^3\Sigma^-$		7.6175[3]	-9.5416[4]
	$1^3\Sigma^+$		-1.0611[5]	-1.1070[5]
	$1^3\Sigma^+$	-3.4234[3]	-6.8294[4]	-1.2852[7]
Na(3P)-Cs(6P)	$1^3\Delta$	-6.4810[2]	5.0316[4]	-5.2855[6]
	$1^3\Pi$	2.5924[3]	2.3008[4]	-1.1129[6]
	$1^3\Pi$		1.0510[5]	-5.7709[5]
	$1^3\Sigma^-$		9.2699[3]	-3.6371[4]
	$1^3\Sigma^+$		9.3679[4]	-3.0324[6]
	$1^3\Sigma^+$	-3.8886[3]	1.6783[4]	2.8237[7]
K(4P)-Rb(5P)	$1^3\Delta$	-7.4760[2]	-1.1948[5]	5.4658[7]
	$1^3\Pi$	2.9904[3]	-1.6280[4]	1.0072[8]
	$1^3\Pi$		-2.7941[5]	2.1665[7]
	$1^3\Sigma^-$		1.2081[4]	-2.3737[5]
	$1^3\Sigma^+$		-2.4803[5]	1.8438[7]
	$1^3\Sigma^+$	-4.4856[3]	-1.3056[5]	-2.8400[8]
K(4P)-Cs(6P)	$1^3\Delta$	-8.4920[2]	-4.9098[3]	1.5655[9]
	$1^3\Pi$	3.3968[3]	1.5887[4]	1.7710[8]
	$1^3\Pi$		-2.4359[4]	3.9176[9]
	$1^3\Sigma^-$		1.5213[4]	-2.3360[5]
	$1^3\Sigma^+$		-2.1229[4]	3.9133[9]
	$1^3\Sigma^+$	-5.0952[3]	-7.2025[4]	1.2826[9]
Rb(5P)-Cs(6P)	$1^3\Delta$	-9.5429[2]	3.6307[3]	2.1725[7]
	$1^3\Pi$	3.8171[3]	2.2221[4]	6.4698[6]
	$1^3\Pi$		-8.4082[3]	6.2326[7]
	$1^3\Sigma^-$		1.8945[4]	-4.0705[5]
	$1^3\Sigma^+$		-6.9477[3]	5.6837[7]
	$1^3\Sigma^+$	-5.7257[3]	1.7188[4]	4.2982[6]

$$C_8 = \frac{9}{125}(S_6 + S_{10}) + \frac{342}{875}(S_8 + S_{12}) - \frac{72}{175}(S_{14} + S_{16}). \quad (5.12)$$

For the  $1,3\Sigma^+$  symmetries, the first set of electronic states gives

$$C_5 = 0, \quad (5.13)$$

$$C_6 = \frac{4}{15}(S_2 + S_3) + \frac{14}{75}S_4, \quad (5.14)$$

$$C_8 = \frac{12}{25}(S_6 + S_{10}) + \frac{3}{7}(S_7 + S_{11}) + \frac{36}{175}(S_8 + S_{12}) - \frac{32}{175}(S_{14} + S_{16}), \quad (5.15)$$

and the second set of electronic states gives

$$C_5 = -\frac{36}{25}(n_A P|r^2|n_A P)(n_B P|r^2|n_B P), \quad (5.16)$$

$$C_6 = \frac{2}{3}S_1 + \frac{2}{15}(S_2 + S_4) + \frac{38}{75}S_4, \quad (5.17)$$

$$C_8 = \frac{18}{25}(S_5 + S_9) + \frac{21}{125}(S_6 + S_{10}) + \frac{24}{175}(S_7 + S_{11}) + \frac{648}{875}(S_8 + S_{12}) + \frac{24}{35}(S_{13} + S_{15}) + \frac{128}{175}(S_{14} + S_{16}). \quad (5.18)$$

The  $S_j$  sums, with  $j = 1, \dots, 16$ , are given as

$$S_1 = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A S)^2 (n_B P|r|n'_B S)^2}{(E_{n'_A S} - E_{n_A P}) + (E_{n'_B S} - E_{n_B P})}, \quad (5.19)$$

$$S_2 = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A S)^2 (n_B P|r|n'_B D)^2}{(E_{n'_A S} - E_{n_A P}) + (E_{n'_B D} - E_{n_B P})}, \quad (5.20)$$

$$S_3 = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A D)^2 (n_B P|r|n'_B S)^2}{(E_{n'_A D} - E_{n_A P}) + (E_{n'_B S} - E_{n_B P})}, \quad (5.21)$$

$$S_4 = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A D)^2 (n_B P|r|n'_B D)^2}{(E_{n'_A D} - E_{n_A P}) + (E_{n'_B D} - E_{n_B P})}, \quad (5.22)$$

$$S_5 = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A S)^2 (n_B P|r^2|n'_B P)^2}{(E_{n'_A S} - E_{n_A P}) + (E_{n'_B P} - E_{n_B P})}, \quad (5.23)$$

$$S_6 = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A D)^2 (n_B P|r^2|n'_B P)^2}{(E_{n'_A D} - E_{n_A P}) + (E_{n'_B P} - E_{n_B P})}, \quad (5.24)$$

$$S_7 = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A S)^2 (n_B P|r^2|n'_B F)^2}{(E_{n'_A S} - E_{n_A P}) + (E_{n'_B F} - E_{n_B P})}, \quad (5.25)$$

$$S_8 = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A D)^2 (n_B P|r^2|n'_B F)^2}{(E_{n'_A D} - E_{n_A P}) + (E_{n'_B F} - E_{n_B P})}, \quad (5.26)$$

$$S_9 = \sum_{n'_A, n'_B} \frac{(n_A P|r^2|n'_A P)^2 (n_B P|r|n'_B S)^2}{(E_{n'_A P} - E_{n_A P}) + (E_{n'_B S} - E_{n_B P})}, \quad (5.27)$$

$$S_{10} = \sum_{n'_A, n'_B} \frac{(n_A P|r^2|n'_A P)^2 (n_B P|r|n'_B D)^2}{(E_{n'_A P} - E_{n_A P}) + (E_{n'_B D} - E_{n_B P})}, \quad (5.28)$$

$$S_{11} = \sum_{n'_A, n'_B} \frac{(n_A P|r^2|n'_A F)^2 (n_B P|r|n'_B S)^2}{(E_{n'_A F} - E_{n_A P}) + (E_{n'_B S} - E_{n_B P})}, \quad (5.29)$$

$$S_{12} = \sum_{n'_A, n'_B} \frac{(n_A P|r^2|n'_A F)^2 (n_B P|r|n'_B D)^2}{(E_{n'_A F} - E_{n_A P}) + (E_{n'_B D} - E_{n_B P})}, \quad (5.30)$$

$$S_{13} = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A D)(n'_A D|r^3|n_A P)(n_B P|r|n'_B S)^2}{(E_{n'_A D} - E_{n_A P}) + (E_{n'_B S} - E_{n_B P})}, \quad (5.31)$$

$$S_{14} = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A D)(n'_A D|r^3|n_A P)(n_B P|r|n'_B D)^2}{(E_{n'_A D} - E_{n_A P}) + (E_{n'_B D} - E_{n_B P})}, \quad (5.32)$$

$$S_{15} = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A S)^2 (n_B P|r|n'_B D)(n'_B D|r^3|n_B P)}{(E_{n'_A S} - E_{n_A P}) + (E_{n'_B D} - E_{n_B P})}, \quad (5.33)$$

$$S_{16} = \sum_{n'_A, n'_B} \frac{(n_A P|r|n'_A D)^2 (n_B P|r|n'_B D)(n'_B D|r^3|n_B P)}{(E_{n'_A D} - E_{n_A P}) + (E_{n'_B D} - E_{n_B P})}. \quad (5.34)$$

If atoms  $A$  and  $B$  are identical, then  $S_2=S_3$ ,  $S_5=S_9$ ,  $S_6=S_{10}$ ,  $S_7=S_{11}$ ,  $S_8=S_{12}$ ,  $S_{13}=S_{15}$ , and  $S_{14}=S_{16}$  and the expressions for the  $C_6$  and  $C_8$  coefficients become the same as those in [23]. The  $S_j$  sums, with  $j=1, \dots, 16$ , may be

transformed to integral representations in a similar fashion as in the previous sections, by using Eqs. (2.10) and (2.18). When both alkali-metal atoms are in their lowest excited  $P$  state, we obtain

$$S_1 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r g_S(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r g_S(E_{n_B P} + i\omega) r | n_B P)] + (n_B P | r | n_B S)^2 \\ \times [(n_A P | r g_S(E_{n_A P} - E_{n_B P} + E_{n_B S}) r | n_A P) + (n_A P | r g_S(E_{n_A P} + E_{n_B P} - E_{n_B S}) r | n_A P)] + (n_A P | r | n_A S)^2 \\ \times [(n_B P | r g_S(E_{n_B P} - E_{n_A P} + E_{n_A S}) r | n_B P) + (n_B P | r g_S(E_{n_B P} + E_{n_A P} - E_{n_A S}) r | n_B P)], \quad (5.35)$$

$$S_2 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r g_S(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r g_D(E_{n_B P} + i\omega) r | n_B P)] + (n_A P | r | n_A S)^2 \\ \times [(n_B P | r g_D(E_{n_B P} - E_{n_A P} + E_{n_A S}) r | n_B P) + (n_B P | r g_D(E_{n_B P} + E_{n_A P} - E_{n_A S}) r | n_B P)], \quad (5.36)$$

$$S_3 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r g_D(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r g_S(E_{n_B P} + i\omega) r | n_B P)] + (n_B P | r | n_B S)^2 \\ \times [(n_A P | r g_D(E_{n_A P} - E_{n_B P} + E_{n_B S}) r | n_A P) + (n_A P | r g_D(E_{n_A P} + E_{n_B P} - E_{n_B S}) r | n_A P)], \quad (5.37)$$

$$S_4 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r g_D(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r g_D(E_{n_B P} + i\omega) r | n_B P)], \quad (5.38)$$

$$S_5 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r g_S(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r^2 g'_P(E_{n_B P} + i\omega) r^2 | n_B P)] + (n_A P | r | n_A S)^2 \\ \times [(n_B P | r^2 g_P(E_{n_B P} - E_{n_A P} + E_{n_A S}) r^2 | n_B P) + (n_B P | r^2 g_P(E_{n_B P} + E_{n_A P} - E_{n_A S}) r^2 | n_B P)] \\ + (n_B P | r^2 | n_B S)^2 (n_A P | r g_S(E_{n_A P}) r | n_A P), \quad (5.39)$$

$$S_6 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r g_D(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r^2 g'_P(E_{n_B P} + i\omega) r^2 | n_B P)] \\ + (n_B P | r^2 | n_B S)^2 (n_A P | r g_D(E_{n_A P}) r | n_A P), \quad (5.40)$$

$$S_7 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r g_S(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r^2 g_F(E_{n_B P} + i\omega) r^2 | n_B P)] + (n_A P | r | n_A S)^2 \\ \times [(n_B P | r^2 g_F(E_{n_B P} - E_{n_A P} + E_{n_A S}) r^2 | n_B P) + (n_B P | r^2 g_F(E_{n_B P} + E_{n_A P} - E_{n_A S}) r^2 | n_B P)], \quad (5.41)$$

$$S_8 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r g_D(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r^2 g_F(E_{n_B P} + i\omega) r^2 | n_B P)], \quad (5.42)$$

$$S_9 = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r^2 g'_P(E_{n_A P} + i\omega) r^2 | n_A P)] \operatorname{Re}[(n_B P | r g_S(E_{n_B P} + i\omega) r | n_B P)] + (n_B P | r | n_B S)^2 \\ \times [(n_A P | r^2 g_P(E_{n_A P} - E_{n_B P} + E_{n_B S}) r^2 | n_A P) + (n_A P | r^2 g_P(E_{n_A P} + E_{n_B P} - E_{n_B S}) r^2 | n_A P)] \\ + (n_A P | r^2 | n_A S)^2 (n_B P | r g_S(E_{n_B P}) r | n_B P), \quad (5.43)$$

$$S_{10} = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r^2 g'_P(E_{n_A P} + i\omega) r^2 | n_A P)] \operatorname{Re}[(n_B P | r g_D(E_{n_B P} + i\omega) r | n_B P)] \\ + (n_A P | r^2 | n_A S)^2 (n_B P | r g_D(E_{n_B P}) r | n_B P), \quad (5.44)$$

$$S_{11} = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r^2 g_F(E_{n_A P} + i\omega) r^2 | n_A P)] \operatorname{Re}[(n_B P | r g_S(E_{n_B P} + i\omega) r | n_B P)] + (n_B P | r | n_B S)^2 \\ \times [(n_A P | r^2 g_F(E_{n_A P} - E_{n_B P} + E_{n_B S}) r^2 | n_A P) + (n_A P | r^2 g_F(E_{n_A P} + E_{n_B P} - E_{n_B S}) r^2 | n_A P)], \quad (5.45)$$

$$S_{12} = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r^2 g_F(E_{n_A P} + i\omega) r^2 | n_A P)] \operatorname{Re}[(n_B P | r g_D(E_{n_B P} + i\omega) r | n_B P)], \quad (5.46)$$

$$S_{13} = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r^3 g_D(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r g_S(E_{n_B P} + i\omega) r | n_B P)] + (n_B P | r | n_B S)^2 \\ \times [(n_A P | r^3 g_D(E_{n_A P} - E_{n_B P} + E_{n_B S}) r | n_A P) + (n_A P | r^3 g_D(E_{n_A P} + E_{n_B P} - E_{n_B S}) r | n_A P)], \quad (5.47)$$

$$S_{14} = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r^3 g_D(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r g_D(E_{n_B P} + i\omega) r | n_B P)], \quad (5.48)$$

$$S_{15} = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r g_S(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r^3 g_D(E_{n_B P} + i\omega) r | n_B P)] + (n_A P | r | n_A S)^2 \\ \times [(n_B P | r^3 g_D(E_{n_B P} - E_{n_A P} + E_{n_A S}) r | n_B P) + (n_B P | r^3 g_D(E_{n_B P} + E_{n_A P} - E_{n_A S}) r | n_B P)], \quad (5.49)$$

$$S_{16} = \frac{2}{\pi} \int_0^\infty d\omega \operatorname{Re}[(n_A P | r g_D(E_{n_A P} + i\omega) r | n_A P)] \operatorname{Re}[(n_B P | r^3 g_D(E_{n_B P} + i\omega) r | n_B P)]. \quad (5.50)$$

$n_A$  and  $n_B$  take on values 2, 3, 4, 5, and 6 for Li, Na, K, Rb, and Cs, respectively. While Eqs. (5.19)–(5.34) are general, available for any  $nP$ - $n'P$  asymptote, Eqs. (5.35)–(5.50) are valid only for the lowest  $nP$ - $n'P$  asymptote. They provide an efficient method for calculating the dispersion coefficients. We mention that similar relations exist for computing the dispersion coefficients for the homonuclear dimers [23].

## VI. NUMERICAL RESULTS AND DISCUSSION

The main task in calculating long-range dispersion coefficients consists of numerical evaluation of the atomic matrix elements involving Green's functions at real and complex energies. Our approach, outlined in detail elsewhere [20,21], is based on an efficient algorithm for solving a set of coupled-channel inhomogeneous differential equations. We follow in the spirit the Dalgarno-Lewis method [29].

Table I presents the dispersion coefficients for the ground state of heteronuclear alkali-metal dimers, together with other published results [30–34]. Our results agree well with previous computations. More precise agreement is found with the results of Patil and Tang [30]. For LiNa, LiK, and NaK dimers we obtain excellent agreement with the results of Spelsberg *et al.* [31], which were obtained using a configuration interaction approach.

The dispersion coefficients when one atom is in the ground state and the other is in the first  $S$  excited state are presented in Table II. To the best of our knowledge, there are no equivalent results in the literature. Note that the  $C_6$  coefficient for the Cs(6S)-Li(3S) asymptote is negative, leading to a repulsive form for the interaction in the long-range limit. This peculiar feature is due to the fact that the 3S-2P transition in Li is nearly resonant with the transition in Cs (the

6S-6P transition). Therefore, the first term in the  $S_1^0$  sum in Eq. (2.4) [or the second term in the square bracket on the rhs of Eq. (2.19)] has a strong resonant character. Since the energy spacing between the 3S and the 2P energy levels of Li is greater than the energy spacing between the 6S and the 6P energy levels of Cs, an overall negative value for  $S_j^0$  results.

A similar anomaly, but leading to a strong attractive interaction in the long-range limit, occurs for the Rb(5S)-Li(3S) asymptote, where the 3S-2P transition in Li is almost resonant with the 5S-5P transition in Rb. Since the

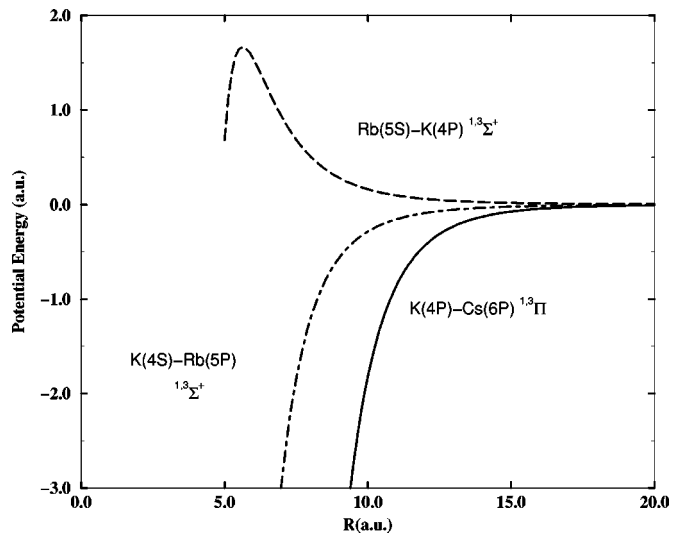


FIG. 1. The most attractive and the most repulsive asymptotic potential energy curves for the heteronuclear alkali-metal dimers. The K(4S)-Rb(5P) molecule is the most likely candidate for ultra-cold photoassociative spectroscopy.

transition energy in Li,  $E_{2P}-E_{3S}$ , is smaller than the energy spacing between the  $5S$  and  $5P$  energy levels in Rb, the contribution from the first term in the  $S_1^0$  sum is large and positive. Therefore, the  $C_6$  coefficient for the Rb( $5S$ )-Li( $3S$ ) asymptote has the largest value among all the heteronuclear alkali-metal dimers.

Table III presents our results for the dispersion coefficients when one atom is in the ground state and the other is in the first  $P$  excited state, together with the numerical results from Bussery *et al.* [32] and the experimental predictions of Vadla *et al.* [35]. Our results for the  $\Sigma$  symmetries are only in qualitative agreement with those of Bussery *et al.* [32], while for the  $\Pi$  symmetries the agreement is only occasional. Major discrepancies exist not only in absolute magnitude, but in the form of the attraction potentials. Bussery *et al.* predict that nearly one-half of the  $1/R^8$  coefficients in the  $nS-n'P$  interaction between unlike alkali-metal atoms are repulsive. The largest absolute errors are about 30–40%. Similar discrepancies were also reported in [21], between our calculations and that of [36] for the homonuclear dimers. The results from [32] and [36] were obtained from diagonalizing the long-range Born-Oppenheimer Hamiltonian in a set of molecular basis functions constructed from noninteracting atomic functions.

The strongest attractive long-range potential results from the interaction between K( $4S$ ) and Rb( $5P$ ) and the most repulsive long-range potential is found in the interaction between Rb( $5S$ ) and K( $4P$ ). We mention that our numerical results for the  $C_6$  coefficients for the Cs( $6S$ )-Li( $2P$ ) asymptote are in good agreement with the experimental values from [35] and we confirm the repulsive character of the Cs( $6S$ )-Li( $2P$ ) asymptote found in [35]. The experimental values for the van der Waals coefficients for Cs( $6S$ )-Li( $2P$ ) were determined from the wavelength dependence of the wings of the Li resonance lines broadened by Cs ground-state atoms.

Table IV present our numerical values for the dispersion coefficients for the cases when one atom is in the ground state and the other is in the first  $D$  excited state, together with the results from [32]. We find a factor of 2 discrepancy in our results for the  $C_6$  coefficients and those calculated in [32] and our values for  $C_8$  are also in disagreement with those from [32]. We find the largest attractive long-range potential in the case of the Rb( $5S$ )-Na( $3D$ ) interaction and

the largest repulsive potential in the case of the Cs( $6S$ )-Na( $3D$ ) interaction.

The long-range coefficients for the  $nP-n'P$  asymptote, where in the dissociation limit both atoms are in the first  $P$  excited state, are presented in Table V. To the best of our knowledge, these results represent the first such calculations. The most attractive long-range potential is formed between K( $4P$ )-Cs( $6P$ ) in a  $\Pi$  molecular symmetry and the most repulsive long-range potential forms also between Rb( $5P$ )-Cs( $6P$ ), but in a  $\Sigma$  symmetry. We notice the unpredictable nature of the sign of the  $C_6$  and  $C_8$  coefficients, which was also mentioned in [23] for homonuclear alkali-metal dimers.

In Fig. 1, we show the most attractive and the most repulsive asymptotic potential curves that form in the interaction of two-species alkali-metal atoms. The dashed curve gives the most optimal heteronuclear candidate molecule for photoassociative spectroscopy.

## VII. SUMMARY

In this work we have calculated the coefficients of the long-range multipole expansion of the Born-Oppenheimer dimer potentials for two-species alkali-metal atoms for various molecular symmetries that correlate to ground and excited atomic levels. The calculations are based on an efficient numerical algorithm that solves for the response of the dimer system to electric multipole excitations and results when the infinite sums in the second order of perturbation theory are transformed into coupled inhomogeneous differential equations. We have calculated the heteronuclear dimer potential energies for the Rb( $5S$ )-Cs( $6S$ ), Rb( $6S$ )-Cs( $6P$ ), K( $4P$ )-Cs( $6P$ )  $\Sigma$ , Rb( $5S$ )-Na( $3D$ )  $\Sigma$ , and K( $4S$ )-Rb( $5P$ )  $\Sigma$  molecules to have the largest attractive interactions in the long range, of which the last dimer presents the best opportunity for ultracold photoassociation. Our calculated value of the van der Waals coefficient for Cs( $6S$ )-Li( $2P$ ) agrees well with the experimentally determined  $C_6$  coefficient.

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