Relativistic many-body calculations of van der Waals coefficients for Yb-Li and Yb-Rb dimers

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We derive the relativistic formulas for the van der Waals coefficients of Yb–alkali-metal dimers that correlate to ground and excited separated-atom limits. We calculate C_6 and C_8 coefficients of particular experimental interest. We also derive a semiempirical formula that expresses the C_8 coefficient of heteronuclear $A + B$ dimers in terms of the C_6 and C_8 coefficients of homonuclear dimers and the static dipole and quadrupole polarizabilities of the atomic states A and B. We report results of calculation of the C_6 coefficients for the Yb-Rb $^3P^o_1 + 5s\ ^2S_{1/2}$ and $^1S_0 + 5p\ ^2P^o_{1/2}$ dimers, and the C_8 coefficients for the Yb-Li $^1S_0 + 2s\ ^2S_{1/2}$ and Yb-Rb $^1S_0 + 5s\ ^2S_{1/2}$ dimers. Uncertainties are estimated for all predicted properties.

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I. INTRODUCTION

The subject of long-range interactions of Yb atoms and Yb–alkali-metal atoms has recently became of much interest owing to study of quantum gas mixtures [1–19], development of optical lattice clocks [20,21], study of fundamental symmetries [22], quantum computing [23], and practical realization of quantum simulation proposals [24–26]. Yb is a particularly suitable candidate for all of these applications owing to its five bosonic and two fermionic stable isotopes in natural abundance, the $^1S_0$ ground state, the long-lived metastable $6s6p\ ^3P^o_0$ state, and transitions at convenient wavelengths for laser cooling and trapping.

Presently there is much interest in forming cold molecules with both electric and magnetic dipole moments because of the greater possibilities for trapping and manipulation [2,6,17,18,27]. Unlike ultracold alkali-metal dimer molecules [28] with largely diamagnetic ground states, the alkali-metal–Yb dimers possess unpaired electron spin, and thereby can be controlled by both electric and magnetic fields. This added control enlarges the class of many-body Hamiltonians that can be simulated with ultracold molecules [24]. The characterization of Yb interactions with alkali-metal atoms is crucial for selecting efficient pathways for assembling Yb–alkali-metal molecules via photo- or magnetoassociation techniques [2,3]. Predictions of magnetically tunable Feshbach resonance positions and widths were recently reported for Yb-Li, Yb-Rb, and Yb-Cs [2,3].

Quantum degenerate mixtures of Li and Yb were realized in [8,9] using sympathetic cooling of Li atoms by evaporatively cooled Yb atoms. Controlled production of ultracold YbRb* molecules by photoassociation in a mixture of Rb and Yb gases was recently reported in [17,18]. In particular, Ref. [17] explored production of ultracold Yb-Rb $^1S_0 - 5p\ ^2P^o_{1/2}$ dimers by photoassociation in a mixture of Rb and Yb gases. The spectroscopic investigation of vibrational levels in the electronic ground state of the ^{176}Yb^{87}Rb molecule was recently carried out in [18]. Unusually strong interactions in a thermal mixture of ^{87}Rb and ^{174}Yb ultracold atoms which caused a significant modification of the spatial distribution were observed in [19].

This brings urgency to understanding the collisional interactions of Yb, both among its various isotopes and with other atoms, in particularly Li [2,6,8–10] and Rb [3,17–19]. Knowledge of the C_6 and C_8 long-range interaction coefficients in Yb–alkali-metal dimers is critical to understanding the physics of dilute gas mixtures for the applications mentioned above. Recently we evaluated the C_6 and C_8 coefficients for the Yb-Yb ($^1S_0 + {}^1S_0$) dimer and found them to be $C_6 = 1929(39)$ [29] and $C_8 = 1.88(6) \times 10^5$ [30], in excellent agreement with the experimental results $C_6 = 1932(35)$ and $C_8 = 1.9(5) \times 10^5$ [15]. However, the expressions for the C_6 and C_8 coefficients used there cannot be applied to calculations for the Yb-Rb ($^3P^o_1 + 5s\ ^2S_{1/2}$) and ($^1S_0 + 5p\ ^2P^o_{1/2}$) dimers due to the presence of the Yb $^3P^o_1 - {}^1S_0$ and Rb $5p\ ^2P^o_{1/2} - 5s\ ^2S_{1/2}$ decay channels and different angular couplings.

In this work we derive relativistic expressions for the C_6 coefficients of heteronuclear dimers involving excited state atoms with strong decay channels to the ground state. The nonrelativistic formalism has been described in Refs. [31–33]. We apply the resulting formulas to evaluate the C_6 coefficients for the ($^3P^o_1 + 5s\ ^2S_{1/2}$) and ($^1S_0 + 5p\ ^2P^o_{1/2}$) dimers. We also evaluate the C_8 coefficients for the Yb-Li ($^1S_0 + 2s\ ^2S_{1/2}$) and Yb-Rb ($^1S_0 + 5s\ ^2S_{1/2}$) dimers.

For the case when A and B are the spherically symmetric atomic states and there are no downward transitions from either of these states, we derive a semiempirical formula for the C_8 coefficient of heteronuclear $(A + B)$ dimers following a method suggested by Tang [34]. The resulting expression allows us to evaluate this property using the C_6 and C_8 coefficients of both homonuclear $(A + A)$ and $(B + B)$ dimers and static dipole $\alpha_1(0)$ and quadrupole $\alpha_2(0)$ polarizabilities of the atoms A and B. We find that this semiempirical formula gives the same value of C_8 for Yb-Li and Yb-Rb as our *ab initio* numerical calculation within our estimated uncertainties.

We have evaluated the uncertainties of all quantities calculated in this work. The results obtained here can be used for the analysis of existing measurements and for planning future experiments. The expressions for the C_6 and C_8 coefficients derived in this work as well as the methodology of calculations

can be used for evaluation of van der Waals coefficients in similar systems.

The paper is organized as follows. In Secs. II and III we present the general formalism and derive the analytical expressions for the C_6 coefficients for the $(^3P_1^o + 5s\ ^2S_{1/2})$ and $(^1S_0 + 5p\ ^2P_{1/2}^o)$ dimers. In Sec. IV we briefly describe the method of calculations. Section V is devoted to discussion of the results and Sec. VI contains concluding remarks.

Unless stated otherwise, we use atomic units (a.u.) for all matrix elements and polarizabilities throughout this paper: the numerical values of the elementary charge $|e|$, the reduced Planck constant $\hbar = h/2\pi$, and the electron mass m_e are set equal to 1. The atomic unit for polarizability can be converted to SI units via $\alpha/h[\mathrm{Hz/(V/m)^2}] = 2.48832 \times 10^{-8}\alpha$ (a.u.), where the conversion coefficient is $4\pi\epsilon_0 a_0^3/h$ and the Planck constant h is factored out in order to provide direct conversion into frequency units; a_0 is the Bohr radius and ϵ_0 is the electric constant.

II. GENERAL FORMALISM

We investigate the molecular potentials that asymptotically correlate to separated $|A\rangle$ and $|B\rangle$ atomic states. The general formalism for homonuclear dimers has been discussed in [30] and we only give a brief outline here. We take the Rb atom to be in the state $|J_A M_A\rangle$ and the Yb atom to be in the state $|J_B M_B\rangle$. The model space for treatment of Yb-Rb dimer consists of the product states

$$\Psi_\Omega = |J_A M_A\rangle\,|J_B M_B\rangle, \tag{1}$$

where $\Omega = M_A + M_B$ is the sum of the projections of the total angular momenta M_A and M_B on the internuclear axis. We assume that Ω is a good quantum number for all Yb-Rb dimers studied here, i.e., the coupling scheme can be described by the Hund's case (c). The correct molecular wave functions can be obtained by diagonalizing the molecular Hamiltonian

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{V}(R) \tag{2}$$

in the model space, where $\hat{H}_A$ and $\hat{H}_B$ represent the Hamiltonians of the two noninteracting atoms. $\hat{V}(R)$ is the residual electrostatic potential defined as the full Coulomb interaction energy of the dimer excluding interactions of the atomic electrons with their parent nuclei.

The multipole expansion of the potential $V(R)$ is given by

$$V(R) = \sum_{l,L=0}^{\infty} V_{lL}/R^{l+L+1}, \tag{3}$$

where V_{lL} are given in general form in [35]. We restrict our consideration by the dipole-dipole and dipole-quadrupole interactions in the second-order perturbation theory. The first two terms of the expansion given by Eq. (3) are

$$V_{dd}(R) = -\frac{1}{R^3}\sum_{\mu=-1}^{1} w_\mu^{(1)}(d_\mu)_A(d_{-\mu})_B, \tag{4}$$

$$V_{dq}(R) = \frac{1}{R^4}\sum_{\mu=-1}^{1} w_\mu^{(2)}[(d_\mu)_A(Q_{-\mu})_B - (Q_\mu)_A(d_{-\mu})_B], \tag{5}$$

where d and Q are the dipole and quadrupole operators, respectively. The dipole and quadrupole weights are

$$\begin{aligned} w_\mu^{(1)} &\equiv 1 + \delta_{\mu 0}, \\ w_\mu^{(2)} &\equiv \frac{6}{\sqrt{(1-\mu)!\,(1+\mu)!\,(2-\mu)!\,(2+\mu)!}}. \end{aligned} \tag{6}$$

Numerically $w_{-1}^{(2)} = w_{+1}^{(2)} = \sqrt{3}$ and $w_0^{(2)} = 3$.

The resulting dispersion potential can be approximated as

$$U(R) \approx -\frac{C_6(\Omega)}{R^6} - \frac{C_8(\Omega)}{R^8}, \tag{7}$$

where the second-order corrections, associated with the C_6 and C_8 coefficients, are given by

$$\frac{C_6(\Omega)}{R^6} = \sum_{\Psi_i \neq \Psi_\Omega} \frac{\langle\Psi_\Omega|\hat{V}_{dd}|\Psi_i\rangle\langle\Psi_i|\hat{V}_{dd}|\Psi_\Omega\rangle}{E_i - \mathcal{E}}, \tag{8}$$

$$\frac{C_8(\Omega)}{R^8} = \sum_{\Psi_i \neq \Psi_\Omega} \frac{\langle\Psi_\Omega|\hat{V}_{dq}|\Psi_i\rangle\langle\Psi_i|\hat{V}_{dq}|\Psi_\Omega\rangle}{E_i - \mathcal{E}}. \tag{9}$$

and the intermediate molecular state $|\Psi_i\rangle$ with unperturbed energy E_i runs over a *complete* set of two-atom states, excluding the model-space states, Eq. (1). The energy $\mathcal{E}$ is given by $\mathcal{E} \equiv E_A + E_B$, where E_A and E_B are the atomic energies of the $|A\rangle$ and $|B\rangle$ states. The complete set of doubled atomic states meets the condition $\sum_{\Psi_i} |\Psi_i\rangle\langle\Psi_i| = 1$.

Using Eqs. (1), (4), and (8) we separate the angular and radial parts of the C_6 coefficient and, after some transformations, arrive at the expression

$$C_6(\Omega) = \sum_{j=|J_A-1|}^{J_A+1} \sum_{J=|J_B-1|}^{J_B+1} A_{jJ}(\Omega)\, X_{jJ}, \tag{10}$$

where

$$A_{jJ}(\Omega) = \sum_{\mu m M} \left\{ w_\mu^{(1)} \begin{pmatrix} J_A & 1 & j \\ -M_A & \mu & m \end{pmatrix} \times \begin{pmatrix} J_B & 1 & J \\ -M_B & -\mu & M \end{pmatrix} \right\}^2, \tag{11}$$

with $\Omega = M_A + M_B = m + M$.

The quantities X_{jJ} are given by

$$X_{jJ} = \sum_{\gamma_n,\gamma_k} \frac{|\langle A||d||\gamma_n, J_n = j\rangle|^2\,|\langle B||d||\gamma_k, J_k = J\rangle|^2}{E_n - E_A + E_k - E_B}, \tag{12}$$

where the total angular momenta of the intermediate atomic states J_n and J_k are assumed to be fixed and equal to j and J, respectively; γ_n and γ_k include all the quantum numbers except the total angular momenta J_n and J_k.

If A and B are spherically symmetric atomic states and there are no downward transitions from either of them, we can apply the Casimir-Polder identity,

$$\frac{1}{x+y} = \frac{2}{\pi}\int_0^\infty d\omega \frac{x}{x^2+\omega^2}\frac{y}{y^2+\omega^2}; \quad x > 0,\ y > 0, \tag{13}$$

to simplify the general expressions. For the $(A+B)$ dimer we obtain the well known C_6 and C_8 coefficient formulas (see, e.g., [36])

$$\begin{aligned} C_6^{AB} &= C^{AB}(1,1), \\ C_8^{AB} &= C^{AB}(1,2) + C^{AB}(2,1), \end{aligned} \tag{14}$$

where the coefficients $C^{AB}(l,L)$ $(l,L=1,2)$ are quadratures of electric-dipole $\alpha_1(i\omega)$ and electric-quadrupole $\alpha_2(i\omega)$ dynamic polarizabilities at an imaginary frequency:

$$C^{AB}(1,1) = \frac{3}{\pi}\int_0^\infty \alpha_1^A(i\omega)\,\alpha_1^B(i\omega)\,d\omega, \tag{15}$$

$$\begin{aligned} C^{AB}(1,2) &= \frac{15}{2\pi}\int_0^\infty \alpha_1^A(i\omega)\,\alpha_2^B(i\omega)\,d\omega, \\ C^{AB}(2,1) &= \frac{15}{2\pi}\int_0^\infty \alpha_2^A(i\omega)\,\alpha_1^B(i\omega)\,d\omega. \end{aligned} \tag{16}$$

The derivation of formulas for the C_6 coefficients for the Yb-Rb $^1S_0 + 5p\,^2P^o_{1/2}$ and $^3P^o_1 + 5s\,^2S_{1/2}$ dimers, which have strong downward transitions, and final resulting expressions are given in Secs. V B and V C.

III. SEMIEMPIRICAL EXPRESSIONS FOR C_6 AND C_8 COEFFICIENTS

Using the method suggested by Tang [34], we are able to derive approximate formulas for the C_6^{AB} and C_8^{AB} coefficients. Following Tang, we express the dynamic 2^K-pole polarizability of a state X at the imaginary values of the frequency $i\omega$ as

$$\begin{aligned} \alpha_K^X(i\omega) &= \sum_n \frac{f_{nX}}{\omega_{nX}^2+\omega^2} \\ &= \sum_n \frac{f_{nX}}{\omega_{nX}^2}\,\frac{1}{1+(\omega/\omega_{nX})^2}, \end{aligned} \tag{17}$$

where f_{nX} are the oscillator strengths. Tang's procedure involves approximating Eq. (17) by

$$\alpha_K^X(i\omega) \approx \frac{\alpha_K^X(0)}{1+\left(\omega\,\phi_K^X\right)^2}. \tag{18}$$

Here ϕ_K^X is a free parameter that is determined below.

If we substitute Eq. (18) into (15) we find [34]

$$\phi_1^X = \frac{3}{4}\,\frac{\left(\alpha_1^X(0)\right)^2}{C_6^{XX}}, \tag{19}$$

where X is A or B. Using this expression we find that the C_6 coefficient for a heteronuclear dimer can be approximated by the following formula [34]:

$$C_6^{AB} \approx \frac{2\,\alpha_1^A(0)\,\alpha_1^B(0)\,C_6^{AA}\,C_6^{BB}}{C_6^{BB}\left(\alpha_1^A(0)\right)^2 + C_6^{AA}\left(\alpha_1^B(0)\right)^2}, \tag{20}$$

where $\alpha_1^A(0)$ and $\alpha_1^B(0)$ are the electric dipole static polarizabilities of the atomic states A and B, and C_6^{AA} and C_6^{BB} are the C_6 coefficients for the $(A+A)$ and $(B+B)$ dimers, respectively.

To derive the corresponding approximate formula for the C_8 coefficient, we use Eqs. (16), (18), and (13). We obtain

$$C_8^{AB} \approx \frac{15}{4}\left[\frac{\alpha_1^A(0)\,\alpha_2^B(0)}{\phi_1^A+\phi_2^B} + \frac{\alpha_2^A(0)\,\alpha_1^B(0)}{\phi_2^A+\phi_1^B}\right]. \tag{21}$$

The quantity ϕ_1^X is given by Eq. (19) and ϕ_2^X can be determined as follows. For a homonuclear $X+X$ dimer we have from Eq. (21)

$$C_8^{XX} \approx \frac{15}{2}\,\frac{\alpha_1^X(0)\,\alpha_2^X(0)}{\phi_1^X+\phi_2^X}. \tag{22}$$

If the C_8^{XX} coefficient is known, then we obtain from Eq. (22)

$$\begin{aligned} \phi_2^X &\approx \frac{15}{2}\,\frac{\alpha_1^X(0)\,\alpha_2^X(0)}{C_8^{XX}} - \phi_1^X \\ &= \frac{15}{2}\,\frac{\alpha_1^X(0)\,\alpha_2^X(0)}{C_8^{XX}} - \frac{3}{4}\,\frac{\left(\alpha_1^X(0)\right)^2}{C_6^{XX}}. \end{aligned} \tag{23}$$

Therefore, the heteronuclear C_8^{AB} coefficient can be obtained using Eq. (21) if one knows the following quantities: $\alpha_1^A(0)$, $\alpha_2^A(0)$, $\alpha_1^B(0)$, $\alpha_2^B(0)$, C_6^{AA}, C_8^{AA}, C_6^{BB}, and C_8^{BB}.

This approximate formula reproduces the result of the first-principle calculations carried out in this work within the uncertainty estimates, as discussed in Sec. V A. We suggest that the semiempirical formula can be used to estimate C_8 coefficients for other systems, such as the Yb-Cs dimer.

IV. METHOD OF CALCULATION

The dynamic electric-dipole and electric-quadrupole Rb polarizabilities, needed to carry out calculations of the C_6 and C_8 coefficients, were obtained elsewhere [37–39].

We calculated the Yb properties needed for this work using the method that combines configuration interaction (CI) and the coupled-cluster all-order approach (CI + all-order) that treats both core and valence correlation to all orders [40–42]. This approach has been demonstrated to give accurate results for energies, transition properties, and polarizabilities for a variety of divalent and trivalent neutral atoms and ions [29,41–44]. The application of this method for Yb has been discussed in [29,30] and we give only a brief outline below.

We start from solving the Dirac-Fock (DF) equations,

$$\hat{H}_0\,\psi_c = \varepsilon_c\,\psi_c,$$

where H_0 is the relativistic DF Hamiltonian [41,45] and ψ_c and ε_c are the single-electron wave functions and energies; the self-consistent procedure was carried out for the $[1s^2,\ldots,4f^{14}]$ closed core.

The wave functions and the low-lying energy levels are determined by solving the multiparticle relativistic equation for two valence electrons [46],

$$H_{\rm eff}(E_n)\Phi_n = E_n\Phi_n. \tag{24}$$

The effective Hamiltonian is defined as

$$H_{\rm eff}(E) = H_{\rm FC} + \Sigma(E), \tag{25}$$

where $H_{\rm FC}$ is the Hamiltonian in the frozen-core approximation and the energy-dependent operator $\Sigma(E)$ accounts for the virtual core excitations.

The CI space spans $6s$–$20s$, $6p$–$20p$, $5d$–$19d$, $5f$–$18f$, and $5g$–$11g$ orbitals and is effectively complete. The operator $\Sigma(E)$ is constructed using the linearized coupled-cluster single-double method [41]. For all-order terms evaluation we use a finite B-spline basis set, consisting of $N = 35$ orbitals for each partial wave with $l \leqslant 5$ and formed in a spherical cavity with radius 60 a.u.

The dynamic polarizability of the 2^K-pole operator $T^{(K)}$, $d_\mu \equiv T^{(1)}_\mu$, $Q_\mu \equiv T^{(2)}_\mu$, at imaginary argument is calculated as the sum of the valence and core polarizabilities

$$\alpha_K(i\omega) = \alpha^v_K(i\omega) + \alpha^c_K(i\omega). \tag{26}$$

The core polarizability $\alpha^c_K(i\omega)$ includes small vc part that restores the Pauli principle. The valence part of the dynamic polarizability $\alpha^v_K(i\omega)$ of an atomic state $|\Phi\rangle$ is determined by solving the inhomogeneous equation in the valence space [47]. The core contributions to multipole polarizabilities are evaluated in the relativistic random-phase approximation (RPA).

The uncertainties of the C_6 and C_8 coefficients may be expressed via uncertainties in the static multipole polarizabilities of the atomic states A and B ($A \neq B$) (see Refs. [30,38] for more detail):

$$\delta C^{AB}(l,L) = \sqrt{\left(\delta\alpha^A_l(0)\right)^2 + \left(\delta\alpha^B_L(0)\right)^2} \tag{27}$$

and

$$\begin{aligned} \Delta C^{AB}_6 &= \Delta C^{AB}(1,1), \\ \Delta C^{AB}_8 &= \sqrt{(\Delta C^{AB}(1,2))^2 + (\Delta C_{AB}(2,1))^2}. \end{aligned} \tag{28}$$

Here prefixes δ and Δ stand for the fractional and absolute uncertainties, respectively.

We discuss the results of calculations and evaluation of the uncertainties of the C_6 and C_8 coefficients in the next section. For brevity we use shorter notations for the Li ground state, $2s\ ^2S_{1/2} \equiv 2s$, and for the Rb ground and excited states, $5s\ ^2S_{1/2} \equiv 5s$ and $5p\ ^2P^o_{1/2} \equiv 5p_{1/2}$.

V. RESULTS AND DISCUSSION

A. Yb-Li ($6s^2\ ^1S_0 + 2s$) and Yb-Rb ($6s^2\ ^1S_0 + 5s$) dimers

The C_6 coefficient for the ground state case $^1S_0 + 5s$ was previously calculated in Ref. [29]. The C_8 coefficient is calculated in the present work. Since we are considering the dimers with Yb, Li, and Rb in the ground states, the C_6 and C_8 coefficients are given by Eqs. (14)–(16).

The integrals over ω needed for the evaluation of C_6 and C_8 are calculated using Gaussian quadrature of the integrand computed on a finite grid of discrete imaginary frequencies [37,54]. For example, the integral in the expression for C^{AB}_6 coefficient given by Eq. (15) is replaced by a finite sum

$$C^{AB}_6 = \frac{3}{\pi}\sum_{k=1}^{N_g} W_k\, \alpha^A_1(i\omega_k)\, \alpha^B_1(i\omega_k) \tag{29}$$

over values of $\alpha^A_1(i\omega_k)$ and $\alpha^B_1(i\omega_k)$ tabulated at certain frequencies ω_k yielding an N_g-point quadrature, where each term in the sum is weighted by factor W_k. In this work we use points and weights listed in Table A of Ref. [37] and $N_g = 50$.

The Li and Rb ground state dynamic electric-dipole and electric quadrupole polarizabilities at imaginary frequencies and the Li-Li ($2s + 2s$) and Rb–Rb ($5s + 5s$) C_6 and C_8 coefficients were determined earlier (see, e.g., [37,38], and references therein). The ground state Yb-Yb C_6 and C_8 coefficients as well as the dynamic electric dipole and electric quadrupole polarizabilities of the $^1S_0$ state at imaginary frequencies were obtained in our recent work [30]. These values are compiled in Table I for reference and comparison with selected other results [3,15,48,49,51]. We use the dynamic polarizabilities from these works to determine the van der Waals coefficients for Yb-Li ($^1S_0 + 2s$) and Yb-Rb ($^1S_0 + 5s$) dimers.

The $C_8(1,2)$ and $C_8(2,1)$ values as well as the final value of the C_8 coefficient for the Yb-Rb ($^1S_0 + 5s$) dimer are given in Table I. The final value of the C_8 coefficient for ($^1S_0 + 2s$) Yb-Li dimer is also listed in Table I. In an alternative approach we also carried out the calculation using the approximate formula Eq. (21) and obtained $C_8 \approx 1.27 \times 10^5$ a.u. and $C_8 \approx 3.20 \times 10^5$ a.u. for Yb-Li and Yb-Rb, respectively. These values are identical to our values obtained with Eqs. (14) and (16). Our C_6 value is in agreement with a very recent accurate analysis of the photoassociation data [53], while our C_8 result is lower by 3σ than the Ref. [53] value.

We substitute the static polarizability uncertainties listed in Table I into Eqs. (27) and (28) to estimate the uncertainty of the $C_8(^1S_0 + 5s)$ coefficient. The evaluation of the polarizability uncertainties was discussed in detail in Ref. [30]. The resulting uncertainties in the Yb-Li $C_8(^1S_0 + 2s)$ and Yb-Rb $C_8(^1S_0 + 5s)$ coefficients is estimated to be 2%.

B. Yb-Rb ($6s^2\ ^1S_0 + 5p_{1/2}$) dimer

The C_6 coefficient for the $6s^2\ ^1S_0 + 5p_{1/2}$ dimer cannot be calculated using Eqs. (14) and (15) due to the downward $5p_{1/2}$–$5s$ transition in Rb. We derive the expression for this C_6 coefficient below. In this subsection we designate $A \equiv 5p_{1/2}$ and $B \equiv {}^1S_0$.

We start from the general formula Eq. (10), which in this case is reduced to

$$C^{AB}_6(\Omega) = \sum_{j=1/2}^{3/2} A_{j1}(\Omega) X_{j1}. \tag{30}$$

Since the projection of the Rb total angular momentum $M_A = 1/2$ and the projection of the Yb total angular momentum $M_B = 0$, the only possible value of $\Omega = M_A + M_B = 1/2$. Substituting $J_A = M_A = 1/2$, $J_B = M_B = 0$, and $J = 1$ into Eq. (11) and setting $\Omega = 1/2$, we obtain $A_{j1}(\Omega = 1/2) = 1/3$ for both possible values $j = 1/2$ and $j = 3/2$.

TABLE I. The values of the static electric-dipole α_1 and electric-quadrupole α_2 polarizabilities (in a.u.) for the Li, Rb, and Yb ground states and the C_6 and C_8 coefficients for the Li-Li ($2s+2s$), Rb-Rb ($5s+5s$), Yb-Yb ($^1S_0+{}^1S_0$), Yb-Li ($^1S_0+2s$), and Yb-Rb ($^1S_0+5s$) dimers. The C_6 and C_8 coefficients for the Yb-Li ($^1S_0+2s$) and Yb-Rb ($^1S_0+5s$) dimers are found by (i) using the dynamic polarizabilities and Eqs. (14)–(16) and (ii) using the approximate formulas (20) and (21). The uncertainties are given in parentheses.

		(i) Numerical	(ii) Approximate	Other results
Li-Li	$\alpha_1(2s)$	164.0(1)[a]		164.1125(5)[b]
	$\alpha_2(2s)$	1424(4)[c]		1423.266(5)[d]
	$C_6(2s+2s)$	1389(2)[a]		1393.39(16)[d]
	$C_8(2s+2s)$	$8.34(4)\times10^4$[c]		$8.34258(4)\times10^4$[d]
Rb-Rb	$\alpha_1(5s)$	318.6(6)[a]		322(4)[e]
	$\alpha_2(5s)$	6520(80)[c]		6525(37)[e]
	$C_6(5s+5s)$	4690(23)[a]		
	$C_8(5s+5s)$	$5.77(8)\times10^5$[c]		
Yb-Yb	$\alpha_1(^1S_0)$	141(2)[f]		141(6)[g]
	$\alpha_2(^1S_0)$	2560(80)[h]		
	$C_6(^1S_0+{}^1S_0)$	1929(39)[f]		1932(35)[i]
	$C_8(^1S_0+{}^1S_0)$	$1.88(6)\times10^5$[e]		$1.9(5)\times10^5$[i]
Yb-Li	$C_6(^1S_0+2s)$	1551(31)[f]		1594[j]
	$C_8(^1S_0+2s)$	$1.27(3)\times10^5$	1.27×10^5	
Yb-Rb	$C_6(^1S_0+5s)$	2837(57)[f]	2814	2830[j]
				2837(13)[k]
	$C_8(^1S_0+5s)(1,2)$	$1.351(24)\times10^5$	1.335×10^5	
	$C_8(^1S_0+5s)(2,1)$	$1.848(57)\times10^5$	1.865×10^5	
	$C_8(^1S_0+5s)$	$3.200(65)\times10^5$	3.199×10^5	$4.9(6)\times10^5$[k]

[a]Reference [37].
[b]References [48,49].
[c]Reference [38].
[d]Reference [50].
[e]Reference [51].
[f]Reference [29].
[g]Reference [52].
[h]Reference [30].
[i]Reference [15].
[j]Reference [3], approximate formula.
[k]Reference [53].

Furthermore, all states with $j=3/2$ are above the $5p_{1/2}$ state, i.e., there are no downward transitions from the $5p_{1/2}$ state to any state with $j=3/2$. Then, using Eqs. (12) and (13) we obtain for $X_{\frac{3}{2}1}$:

$$X_{\frac{3}{2}1}=\frac{9}{\pi}\int_0^\infty \alpha^A_{1\frac{3}{2}}(i\omega)\,\alpha^B_1(i\omega)\,d\omega, \tag{31}$$

where $\alpha^A_{1j}(i\omega)$ is the part of the dynamic electric dipole $5p_{1/2}$ polarizability at the imaginary frequency with $J_n=j$:

$$\alpha^A_{1j}(i\omega)=\frac{1}{3}\sum_{\gamma_n}\frac{(E_n-E_A)|\langle\gamma_n J_n=j||d||A\rangle|^2}{(E_n-E_A)^2+\omega^2} \tag{32}$$

and α^B_1 is the dynamic electric-dipole polarizability of the $^1S_0$ state:

$$\alpha^B_1(i\omega)=\frac{2}{3}\sum_k\frac{(E_k-E_B)|\langle k||d||{}^1S_0\rangle|^2}{(E_k-E_B)^2+\omega^2}. \tag{33}$$

The case of $j=1/2$ is more complicated because there is the downward $5p_{1/2}$–$5s$ transition, precluding direct application of the Casimir-Polder identity (13). Using Eq. (12) we can separate out the contribution of the $5s$ state from the sum over n. Then we obtain

$$\begin{aligned}X_{\frac{1}{2}1}&\equiv X^{(1)}_{\frac{1}{2}1}+X^{(2)}_{\frac{1}{2}1}\\&=|\langle A||d||5s\rangle|^2\sum_k\frac{|\langle B||d||k\rangle|^2}{-\omega_{As}+\omega_{kB}}\\&\quad+\sum_{\gamma_n\neq5s,k}\frac{|\langle A||d||\gamma_nJ_n=1/2\rangle|^2\,|\langle B||d||k\rangle|^2}{\omega_{nA}+\omega_{kB}},\end{aligned} \tag{34}$$

where $\omega_{As}\equiv E_A-E_{5s}$, $\omega_{nA}\equiv E_n-E_A$ and $\omega_{kB}\equiv E_k-E_B$. Both frequencies ω_{nA} and ω_{kB} in the second term $X^{(2)}_{\frac{1}{2}1}$ are positive for any n and k. Using Eq. (13) we can represent this term by

$$\begin{aligned}X^{(2)}_{\frac{1}{2}1}=\frac{2}{\pi}\int_0^\infty d\omega\sum_{\gamma_n\neq5s}\frac{\omega_{nA}\,|\langle A||d||\gamma_nJ_n=1/2\rangle|^2}{\omega^2_{nA}+\omega^2}\\\times\sum_k\frac{\omega_{kB}\,|\langle B||d||k\rangle|^2}{\omega^2_{kB}+\omega^2}.\end{aligned} \tag{35}$$

Next, we add and subtract the term $|\gamma_n\rangle = |5s\rangle$ into the sum over γ_n under the integral in Eq. (35) and use again Eq. (13):

$$X^{(2)}_{\frac{1}{2}1} = \frac{9}{\pi}\int_0^\infty \alpha^A_{1\frac{1}{2}}(i\omega)\,\alpha^B_1(i\omega)\,d\omega + |\langle A||d||5s\rangle|^2 \sum_k \frac{|\langle B||d||k\rangle|^2}{\omega_{kB}+\omega_{As}}. \quad (36)$$

Combining $X^{(1)}_{\frac{1}{2}1}$ and $X^{(2)}_{\frac{1}{2}1}$ we arrive at

$$X_{\frac{1}{2}1} = \frac{9}{\pi}\int_0^\infty \alpha^A_{1\frac{1}{2}}(i\omega)\,\alpha^B_1(i\omega)\,d\omega + 3\,|\langle A||d||5s\rangle|^2\alpha^B_1(\omega_{As}), \quad (37)$$

where

$$\alpha^B_1(\omega_{As}) = \frac{2}{3}\sum_k \frac{\omega_{kB}|\langle k||d||B\rangle|^2}{\omega^2_{kB}-\omega^2_{As}}. \quad (38)$$

Taking into account that $A_{\frac{1}{2}1} = A_{\frac{3}{2}1} = 1/3$, and substituting the expressions for X_{j1} into Eq. (30), we arrive at the final expression for C_6^{AB} in the present case:

$$C_6^{AB} = \frac{3}{\pi}\int_0^\infty \alpha^A_1(i\omega)\,\alpha^B_1(i\omega)\,d\omega + |\langle 5p_{1/2}||d||5s\rangle|^2\,\alpha^B_1(\omega_{As}), \quad (39)$$

where $\alpha^A_1(i\omega)$ is the dynamic electric dipole polarizability of the $5p_{1/2}$ state at the imaginary argument $i\omega$.

The quantities needed to calculate the $C_6(^1S_0 + 5p_{1/2})$ coefficient and to evaluate its uncertainty are summarized in Table II. The Rb dynamic $5p_{1/2}$ polarizability was calculated in [39] in the framework of DF + MBPT approximation [45]. The Yb dynamic electric-dipole $^1S_0$ polarizabilities at the imaginary frequencies were calculated in [29]. Using experimental and theoretical data, the static electric-dipole polarizability of the $5p_{1/2}$ state was found to be 810.8(8) a.u. [39]. Using these polarizabilities and evaluating the integral using the finite sum Eq. (29), we obtain from Eq. (39)

$$\frac{3}{\pi}\int_0^\infty \alpha^A_1(i\omega)\,\alpha^B_1(i\omega)\,d\omega \approx 4336 \text{ a.u.} \quad (40)$$

We use the experimental value for the matrix element $|\langle 5p_{1/2}||d||5s\rangle| = 4.228(6)$ a.u. [55] in the the second term of Eq. (39). The quantity $\alpha^B_1(\omega_{As})$ is the electric-dipole ground-state Yb $^1S_0$ polarizability at the real frequency $\omega_{As} \equiv E_{5p_{1/2}} - E_{5s}$. Adding core and valence contributions (see [29] for detail) we obtain

$$\alpha^B_1(\omega_{As}) = \alpha^{B(\text{val})}_1 + \alpha^{B(\text{core})}_1 \approx 177 + 6 = 183 \text{ a.u.} \quad (41)$$

Thus, the contribution of the second term in Eq. (39) to the C_6 coefficient is

$$|\langle 5p_{1/2}||d||5s\rangle|^2\,\alpha^B_1(\omega_{As}) \approx 3271 \text{ a.u.}$$

We note that both terms are comparable in their magnitude. Adding these terms we obtain $C_6 \approx 7607$ a.u.

The uncertainty of this C_6 coefficient can be evaluated using Eqs. (27) and (28). Taking into account that the fractional uncertainty of the Rb static $5p_{1/2}$ polarizability 0.1% is negligible in comparison to the uncertainty of the Yb static $^1S_0$ polarizability 1.5%, the accuracy of the first term in Eq. (39) (4336 a.u.) is dominated by the the accuracy of the $^1S_0$ polarizability, i.e., 1.5%. In the second term (3271 a.u.) the fractional uncertainty of the matrix element $\langle 5p_{1/2}||d||5s\rangle$ 0.14% is negligible in comparison with the fractional uncertainty of the dynamic polarizability $\delta\alpha^B_1(\omega_{sp}) \approx \delta\alpha^B_1(0) \approx 1.5\%$. Thus we assume that the uncertainty in the second term is 1.5% and the final uncertainty for the C_6 coefficient is also 1.5%; $C_6 = 7607(114)$. The $C_6(^1S_0 + 5p_{1/2})$ coefficient is 33% larger than the value obtained from the fit of the photoassociation data with Leroy-Berstein method [17]. However, our $C_6(^1S_0 + 5s)$ ground-state value of 2837(57) a.u. is 14% larger than result of a similar fit that yielded 2485(21) a.u. [18]. Very recent accurate analysis of the photoassociation data gives 2837(13) a.u. [53], which is in perfect agreement with our central value. This may indicate that the uncertainties of the values obtained by the experimental data fit with the commonly used Leroy-Bernstein method may be larger than expected, especially for the excited states.

TABLE II. The quantities (in a.u.) used to calculate the $C_6(^1S_0 + 5p_{1/2})$ coefficient and to estimate its uncertainty. $\alpha_1(0)$ is the static polarizability, $\alpha_1(\omega_{As})$ is the Yb polarizability calculated at the real frequency $\omega_{As} \equiv E_{5p_{1/2}} - E_{5s}$. The uncertainties are given in parentheses.

	State	Quantity	Results	
Rb	$5p_{1/2}$	$\alpha_1(0)$	810.8(8)[a]	Theory + Expt.
		$\lvert\langle 5p_{1/2}\rvert\rvert d\rvert\rvert 5s\rangle\rvert$	4.228(6)[b]	Experiment
Yb	$^1S_0$	$\alpha_1(0)$	141(2)[c]	Theory
	$^1S_0$	$\alpha_1(\omega_{As})$	183(3)	This work
Yb-Rb	$^1S_0 + 5p_{1/2}$	C_6	7607(114)	This work
	$^1S_0 + 5p_{1/2}$	C_6	5684(98)[d]	Experiment

[a]Reference [39].
[b]Reference [55].
[c]Reference [29].
[d]Reference [17].

C. Yb-Rb ($6s6p\,^3P^o_1 + 5s$) dimer

This case also requires special attention because there is the downward $^3P^o_1$–$^1S_0$ transition in Yb. In this subsection we designate $A \equiv 5s$ and $B \equiv 6s6p\,^3P^o_1$.

The general expression for the C_6 coefficient, given by Eq. (10), leads to

$$C_6(\Omega) = \sum_{j=1/2}^{3/2}\sum_{J=0}^{2} A_{jJ}(\Omega)X_{jJ}.$$

Taking into account that $M_A = 1/2$ and $M_B = 0,1$, the possible values of Ω are $1/2$ and $3/2$, where $M_B = 0$ corresponds to $\Omega = 1/2$ and $M_B = 1$ corresponds to $\Omega = 3/2$.

The coefficients $A_{jJ}(\Omega)$ are given by Eq. (11). Their calculation is straightforward and numerical values are listed in Table III for different values of j, J, and Ω.

TABLE III. The values of the $A_{jJ}(\Omega)$ and X_{jJ} coefficients for different j, J, and Ω. The contributions to the C_6 coefficients are listed in the columns $C_6(\Omega = 1/2)$ and $C_6(\Omega = 3/2)$. The contributions of $\delta X_{1/2,0}$ and $\delta X_{3/2,0}$ are given in the rows $\delta_{1/2}$ and $\delta_{3/2}$; they are included in the terms $X_{1/2,0}$ and $X_{3/2,0}$, respectively. Final values of the C_6 coefficients and their uncertainties (in parentheses) are presented in the row labeled "Total."

		A_{jJ}			C_6	
j	J	$\Omega = 1/2$	$\Omega = 3/2$	X_{jJ}	$\Omega = 1/2$	$\Omega = 3/2$
$\delta_{1/2}$	0			−189		
1/2	0	2/9	0	680	151	0
1/2	1	1/18	1/9	4887	272	543
1/2	2	11/90	2/15	7419	907	989
$\delta_{3/2}$	0			−399		
3/2	0	2/9	1/12	1327	295	111
3/2	1	1/18	11/72	9671	537	1478
3/2	2	11/90	11/120	14675	1794	1345
Total					3955(160)	4466(180)

Starting from the general expression for X_{jJ} given by Eq. (12) and using the approach discussed in the previous subsection, we obtain

$$X_{jJ} = \frac{27}{\pi}\int_0^\infty \alpha^A_{1j}(i\omega)\,\alpha^B_{1J}(i\omega)\,d\omega + \delta X_{jJ}\,\delta_{J0}, \quad (42)$$

where $\alpha^A_{1j}(i\omega)$ is a contribution to the Rb $5s$ electric dipole polarizability given by Eq. (32) (with $A = 5s$) and $\alpha^B_{1J}(i\omega)$ is a contribution to the scalar part of the Yb electric-dipole $^3P^o_1$ polarizability, determined as

$$\alpha^B_{1J}(i\omega) = \frac{2}{9}\sum_{\gamma_k}\frac{(E_k - E_B)|\langle\gamma_k J_k = J||d||B\rangle|^2}{(E_k - E_B)^2 + \omega^2}. \quad (43)$$

The correction δX_{j0} to the X_{j0} term is due to the downward $^3P^o_1 \to {}^1S_0$ transition. One can show that it can be written as

$$\delta X_{j0} = 2\left|\left\langle {}^3P^o_1\right|\left|d\right|\left|{}^1S_0\right\rangle\right|^2 \times \sum_{\gamma_n}\frac{(E_n - E_A)\,|\langle\gamma_n, J_n = j||d||A\rangle|^2}{(E_n - E_A)^2 - \omega_0^2}, \quad (44)$$

where $\omega_0 \equiv E_{^3P^o_1} - E_{^1S_0}$ and the total angular momentum of the intermediate states J_n is fixed and equal to j. In our case, $j = 1/2$ or 3/2.

The Rb dynamic $5s$ polarizabilities at imaginary frequencies were obtained in Ref. [37]. We calculated δX_{j0} following the approach discussed in [38,39]. The calculation of the scalar part of the dynamic electric dipole $^3P^o_1$ polarizability was discussed in detail in [30]. The resulting contributions to C_6 coefficient are listed in Table III.

We note that $\delta X_{j0} < 0$ for both $j = 1/2$ and $j = 3/2$. As follows from Eq. (44), we need to calculate the dynamic $5s$ polarizability at the frequency $\omega_0 = E_{^3P^o_1} - E_{^1S_0} \approx 0.082$ a.u. to determine δX_{j0}. The dominant contribution to polarizability comes from the $5p_{1/2,3/2}$ states. Since $E_{5p_j} - E_{5s} \approx 0.057$ a.u., the energy denominators $(E_{5p_j} - E_{5s} - \omega_0)$ will be small and negative. It leads to the negative values of $\alpha^{5s}_{1j}(\omega_0)$ and, subsequently, δX_{j0}, for both $j = 1/2$ and $j = 3/2$.

Since the uncertainty of the Rb static $5s$ polarizability 0.2% is negligible in comparison with the uncertainty of the Yb static scalar $^3P^o_1$ polarizability (3.5%), the latter determines the uncertainty of the C_6 coefficient for the $(^3P^o_1 + 5s)$ dimer. Our final values are $C_6(\Omega = 1/2) = 3955(160)$ and $C_6(\Omega = 3/2) = 4466(180)$. Clearly at long range the $\Omega = 3/2$ potential is more attractive than the $\Omega = 1/2$ potential.

VI. CONCLUSION

To summarize, in this work we obtained accurate C_6 and C_8 values for the Yb-Rb and Yb-Li dimers of particular experimental interest which are needed for efficient production, cooling, and control of molecules. For the case when A and B are spherically symmetric atomic states and there are no downward transitions from either of these states, we derived a semiempirical formula for the C_8 coefficient of heteronuclear $(A + B)$ dimers. We evaluated the C_8 coefficient for the Yb-Li $^1S_0 + 2s$ and Yb-Rb $^1S_0 + 5s$ dimers using the exact and approximate expressions and found excellent agreement between these values. Our calculations of C_8 coefficients will allow accurate extraction of C_6 from the photoassociation spectra and may allow us to estimate contribution of the C_{10} in the interaction potential. We performed detailed uncertainty analysis and provided stringent bounds on all of the quantities calculated in this work to allow future benchmark tests of experimental methodologies and theoretical molecular models.

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