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High-precision calculations of van der Waals coefficients for heteronuclear alkali-metal dimers

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van der Waals coefficients for the heteronuclear alkali-metal dimers of Li, Na, K, Rb, Cs, and Fr are calculated using relativistic *ab initio* methods augmented by high-precision experimental data. We argue that the uncertainties in the coefficients are unlikely to exceed about 1%.

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Considerable attention has been given to the determination of the coefficients of the leading term of the van der Waals attractions of two alkali-metal atoms because of their importance in the simulation, prediction, and interpretation of experiments on cold atom collisions, photoassociation, and fluorescence spectroscopy [1–6]. There is strong interest in heteronuclear molecules formed by pairs of different alkali-metal atoms. Experiments have been carried out on trap loss in mixtures of Na with K [7,8], Rb [9,10], and Cs [11] and on optical collisions [12] in a Na-Cs mixture and on molecular formation [13]. The mixtures of magnetically trapped alkali-metal atoms, Na-Cs and Na-K, have been proposed [14] as a means to search for evidence of an electric dipole moment to test for violation of parity and time-reversal symmetry. We extend here previous studies [15] of the van der Waals coefficient between pairs of identical ground state alkali-metal atoms to unlike ground-state atoms.

The leading term of the van der Waals interaction is given at an atom separation R by [16,17],

$$V^{AB}(R)=-\frac{C_6^{AB}}{R^6}, \tag{1}$$

where C_6^{AB} is the van der Waals coefficient. We use atomic units throughout.

The van der Waals coefficient may be expressed as

$$C_6^{AB}=\frac{2}{3}\sum_{st}\frac{|\langle v_A|D_A|s_A\rangle|^2|\langle v_B|D_B|t_B\rangle|^2}{(E_s^A-E_v^A)+(E_t^B-E_v^B)}, \tag{2}$$

where $|v_A\rangle$ is the ground-state atomic wave function of atom A with energy E_v^A, and similarly for atom B, and $|s_A\rangle$ and $|t_B\rangle$ represent complete sets of intermediate atomic states with, respectively, energies E_s^A and E_t^B. The electric dipole operators are $D_A=\sum_{i=1}^{N_A}\mathbf{r}_i^A$, where $\mathbf{r}_i^A$ is the position vector of electron i measured from nucleus A, N_A is the total number of atomic electrons for atom A, and similarly for atom B.

At this point the two-center molecular-structure problem is reduced to the determination of *atomic* matrix elements and energies. The dependence on one-center atomic properties becomes explicit when Eq. (2) is cast into the Casimir-Polder form

$$C_6^{AB}=\frac{3}{\pi}\int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega)d\omega, \tag{3}$$

where $\alpha_A(i\omega)$ is the dynamic polarizability of imaginary argument for atom A given by

$$\alpha_A(i\omega)=\frac{2}{3}\sum_s\frac{(E_s^A-E_v^A)|\langle v^A|\mathbf{D}_A|s^A\rangle|^2}{(E_s^A-E_v^A)^2+\omega^2}, \tag{4}$$

and $\alpha(\omega=0)$ is the ground-state static dipole polarizability. In the limit of infinite frequency the function $\alpha_A(i\omega)$ satisfies

$$\alpha_A(i\omega)\rightarrow\frac{N_A}{\omega^2}, \tag{5}$$

as a consequence of the nonrelativistic Thomas-Reiche-Kuhn sum rule.

Modern all-order many-body methods are capable of predicting electric dipole matrix elements for principal transitions and energies in alkali-metal atoms to within errors approaching 0.1% [18]. Many-body methods augmented by high-precision experimental data for principal transitions, similar to those employed in parity violation calculations [19], have led to a high-precision evaluation of dynamic dipole polarizabilities for alkali-metal atoms [15]. The values of C_6 previously calculated for *homonuclear* dimers [15] are in excellent agreement with analyses of cold-atom scattering of Na [20], Rb [2], and Cs [6,21]. Here we employ the same methods to compute the van der Waals coefficients for heteronuclear alkali-metal dimers.

Precise nonrelativistic variational calculations of C_6 for Li_2 have been carried out [22]. They provide a critical test of our procedures. We separate the dynamic polarizability into valence and core contributions, which correspond, respectively, to valence-electron and core-electron excited intermediate states in the sum, Eq. (4). In our calculations for Li we employ high-precision experimental values for the principal transition $2s-2p_J$, all-order many-body data and experimental energies for $3p_J$ and $4p_J$ intermediate states, and Dirac-Hartree-Fock values for higher valence-electron excitations. The high-precision all-order calculations were performed using the relativistic linearized coupled-cluster method truncated at single and double excitations from a reference determinant [18,23]. Contributions of valence-excited states above $4p_J$ were obtained by a direct summa-

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tion over a relativistic B-spline basis set [24] obtained in the ''frozen-core'' (V^{N-1}) Dirac-Hartree-Fock potential. Core excitations were treated with a highly accurate relativistic configuration-interaction method applied to the two-electron Li^+ ion. For the heavier alkali metals [15] the random-phase approximation [25] was used to calculate this contribution.

The principal transition $2s-2p_J$ accounts for 99% of the static polarizability and 96% of the Li_2 dispersion coefficient. In accurate experiments, McAlexander *et al.* [26] reported a lifetime of the $2p$ state of 27.102(9) ns (an accuracy of 0.03%) and Martin *et al.* [27] reported 27.13(2) ns. In our calculations we employ the more precise value from Ref. [26]; in the subsequent error analysis we arbitrarily assigned an error bar of twice the quoted value of Ref. [26], so that the two experiments are consistent.

The dynamic core polarizability of Li was obtained in the framework of the relativistic configuration-interaction (CI) method for heliumlike systems. This CI setup is described by Johnson and Cheng [28], who used it to calculate precise relativistic static dipole polarizabilities. We extended their method to calculate the *dynamic* polarizability $\alpha(i\omega)$ for two-electron systems. The numerical accuracy was monitored by comparison with results of Ref. [28] for the static polarizability of Li^+ and with the sum rule, Eq. (5), in the limit of large frequencies. Core-excited states contribute only 0.5% to C_6 and 0.1% to $\alpha(0)$ for Li. Their contribution becomes much larger for heavier alkali metals.

We calculated static and dynamic polarizabilities and used quadrature, Eq. (3), to obtain the dispersion coefficient. The results are $C_6=1390$ and $\alpha(0)=164.0$. There are two major sources of uncertainties in the final value of C_6 — experimental error in the dipole matrix elements of the principal transition, and theoretical error related to higher valence-electron excitations. The former results in a uncertainty of 0.12%, and the latter much less. The result $C_6=1390(2)$ is in good agreement with the *nonrelativistic* variational result of Yan *et al.* [22], $C_6=1393.39$. The slight discrepancy between the two values may arise because in our formulation, the correlations of the core-excited states with the valence electron were disregarded as were intermediate states containing simultaneous excitation of the valence electron with one or both core electrons. On the other hand, Ref. [22] did not account for relativistic corrections. Relativistic contractions lead to a smaller value of C_6 and to better agreement between the present result and that of Ref. [22]. Similar error analysis for the static polarizability of Li leads to $\alpha(0)=164.0(1)$, which agrees with the numerically precise nonrelativistic result of 164.111 [22]. An extensive comparison with other published data for the values of $\alpha(0)$ and C_6 for lithium is given in Ref. [22]. For the heavier alkali-metal atoms, we followed the procedures of Ref. [15] to calculate $\alpha(i\omega)$. The results for Cs are illustrated in Fig. 1. They indicate that while most of the contribution to C_6 comes from the resonant transition at $\omega\sim 0.05$ a.u., the core excitations are significant.

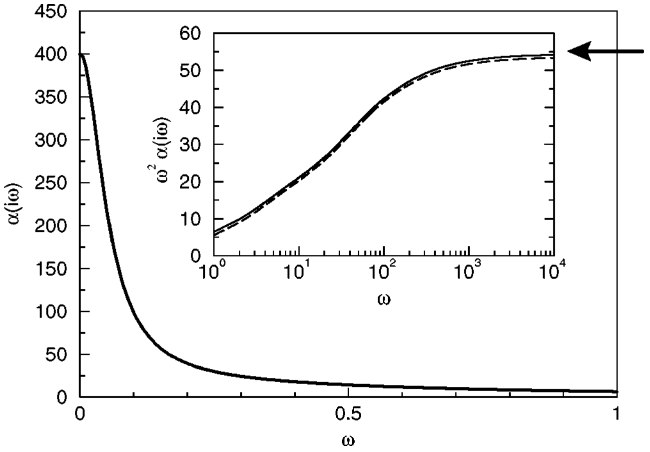

FIG. 1. The dependence of the dynamic dipole polarizability $\alpha(i\omega)$ with frequency ω for Cs. The inset illustrates the behavior of the quantity $\omega^2\alpha(i\omega)$ at asymptotically large ω, where the dashed line represents the contribution of the core-excited states to the total $\omega^2\alpha(i\omega)$ (solid line) and the arrow marks the nonrelativistic limit $N=55$ following from the sum rule, Eq. (5). All quantities are in atomic units.

RESULTS AND CONCLUSIONS

We evaluated the dispersion coefficients for various heteronuclear alkali-metal dimers with the quadrature Eq. (3). The calculated values are presented in Table I. Most of the contributions to C_6^{AB} come from the principal transitions of each atom. An analysis of the dispersion coefficient of unlike atoms yields the approximate formula

$$C_6^{AB}\approx\frac{1}{2}\sqrt{C_6^{AA}C_6^{BB}}\frac{\Delta E_A+\Delta E_B}{\sqrt{\Delta E_A\Delta E_B}}, \tag{6}$$

where the energy separations of the principal transitions are designated as ΔE_A and ΔE_B. Equation (6) combined with the high-accuracy values of C_6 for homonuclear dimers [15]

TABLE I. Dispersion coefficients C_6 and their estimated uncertainties (parentheses) for alkali-metal atom pairs in atomic units. Coefficients for Na_2, K_2, Rb_2, Cs_2, and Fr_2 are from Ref. [15].

	Li	Na	K	Rb	Cs	Fr
Li	1389(2)	1467(2)	2322(5)	2545(7)	3065(16)	2682(23)
Na		1556(4)	2447(6)	2683(7)	3227(18)	2842(24)
K			3897(15)	4274(13)	5159(30)	4500(39)
Rb				4691(23)	5663(34)	4946(44)
Cs					6851(74)	5968(60)
Fr						5256(89)

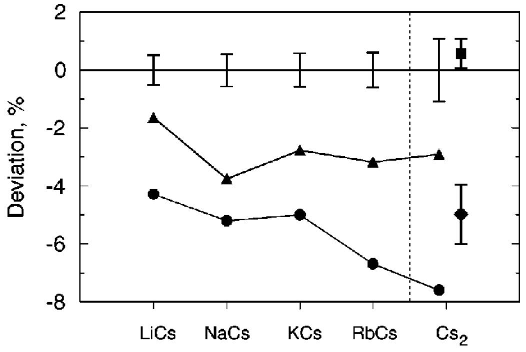

FIG. 2. Percentage deviation of results of recent calculations Refs. [35,37] from our values for van der Waals coefficients C_6 for Cs-Li, Cs-Na, Cs-K, Cs-Rb, and Cs-Cs. The values with error bars placed along the horizontal line at 0 correspond to our results with the estimated uncertainties. Circles represent the results of Ref. [35] and triangles the results of Ref. [37]. For Cs-Cs, to the right of the vertical-dotted line, we show the difference between our prediction [15] and the values deduced from cold-collision data in Ref. [6] (square) and Ref. [30] (diamond).

gives accurate approximations to our results based on Eq. (3). For example, Eq. (6) overestimates our accurate value from Table I for Li-Na by 0.4% and for Cs-Li by 2%. We may use Eq. (6) to estimate the uncertainties δC_6^{AB} in the heteronuclear cases from the uncertainties δC_6^{AA} and δC_6^{BB} in the homonuclear dispersion coefficients,

$$\frac{\delta C_6^{AB}}{C_6^{AB}} \approx \frac{1}{2}\left[\left(\frac{\delta C_6^{AA}}{C_6^{AA}}\right)^2 + \left(\frac{\delta C_6^{BB}}{C_6^{BB}}\right)^2\right]^{1/2}.$$

The accuracy of C_6 for homonuclear dimers was assessed in Ref. [15] and a detailed discussion for the Rb dimer is given in Ref. [29]. Analyzing the error in this manner by using the quoted coefficients and their uncertainties from Ref. [15], we find that most of the dispersion coefficients reported here have an estimated uncertainty below 1%. The corresponding values are given in parentheses in Table I.

In Fig. 2 we present, for the dispersion coefficients of the dimers involving Cs, a comparison between our calculated values and the most recent determinations [6,30]. We give the percentage deviation from our calculations. It is apparent that the other calculations that employed one-electron model potentials and accordingly omitted contributions from core-excited states yield values systematically smaller than ours.

The discrepancies are most significant for Cs$_2$ where the number of electrons is greatest. Figure 2 also compares the values for the Cs$_2$ dimer with values deduced from ultracold-collision data [6,30]. The agreement of our prediction 6851(74) [15] with their values for C_6 in Cs$_2$ is close. Core-excited states contribute 15% [31,15] to the value of the C_6 coefficient for the Cs dimer and are needed to fulfill the oscillator strength sum rule, Eq. (5). In the present approach the contributions of core-excited states to dynamic polarizabilities are obtained using the random-phase approximation, which nonrelativistically satisfies the oscillator strength sum rule exactly [25]. In the inset of Fig. 1, it is illustrated that our calculated $\alpha(i\omega)$ approaches N/ω^2 as ω becomes asymptotically large, where $N=55$ for Cs. While the deviation between the present calculations and the model potential calculations are smaller for dimers involving lighter atoms, an accurate accounting of core-excited states is essential to achieve high accuracy in dispersion coefficient calculations for heavy atoms [31–33].

TABLE II. Comparision of present theoretical and experimental values for the dispersion coefficient for NaK.

Reference	C_6
This paper	2447(6)
Russier-Antoine *et al.* [34]	2519(10) [a]
Ishikawa *et al.* [38]	2646(31) [a]
Ross *et al.* [39]	2669.4(20) [a]

[a] Experiment.

Few experimental data are available for comparison in the heteronuclear case, except for NaK. The results from investigations of NaK molecular potentials based on spectral analysis [34] are compared to our value in Table II. Our value is smaller than the experimental values. Earlier theoretical calculations of dispersion coefficients for NaK have been tabulated and evaluated by Marinescu and Sadeghpour [35], Zemke and Stwalley [36], and Patel and Tang [37]. Those values are generally lower than our value of 2447(6) except for that of Maeder and Kultzelnigg [32] who give 2443.

The present paper extends the application of modern relativistic atomic structure methods to calculations of ground-state van der Waals coefficients of Li$_2$ and of the heteronuclear alkali-metal atoms [37]. We argue that the uncertainty of the coefficients is unlikely to exceed 1%. Additional experimental data from future cold-collision experiments or spectroscopy would provide further tests of the present calculations.

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