

High-Precision Calculations of Dispersion Coefficients, Static Dipole Polarizabilities, and Atom-Wall Interaction Constants for Alkali-Metal Atoms

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The van der Waals coefficients for the alkali-metal atoms from Na to Fr interacting in their ground states are calculated using relativistic *ab initio* methods. The accuracy of the calculations is estimated by also evaluating atomic static electric-dipole polarizabilities and coefficients for the interaction of the atoms with a perfectly conducting wall. The results are in excellent agreement with the latest data from studies of magnetic field induced Feshbach resonances in ultracold collisions of Na and of Rb atoms. For Cs we provide critically needed data for ultracold collision studies. [S0031-9007(99)09020-1]

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The van der Waals interaction plays an important role in characterizing ultracold collisions between two ground-state alkali-metal atoms. While the calculation of interaction coefficients has been a subject of great interest in atomic, molecular, and chemical physics for a very long time, it is only very recently that novel cold collision experiments, photoassociation spectroscopy, and analyses of magnetic field induced Feshbach resonances have yielded strict constraints on magnitudes of the coefficients. Moreover, due to the extreme sensitivity of elastic collisions to the long-range part of the potentials, knowledge of the van der Waals coefficients influences predictions of signs and magnitudes of scattering lengths determining stability of Bose-Einstein condensates. Although many theoretical methods have been developed over the years to calculate van der Waals coefficients, persistent discrepancies remain.

In this paper, various relativistic *ab initio* methods are applied to determine the van der Waals coefficients for the alkali-metal dimers of Na to Fr [1]. As a check on our calculations, we also evaluate the atom-wall interaction constants and use them as a sensitive test of the quality of our wave functions. Furthermore, we calculate atomic polarizabilities and compare them to experimental data.

The van der Waals interaction is the leading term of the potential energy between two ground-state alkali-metal atoms at long range. It arises from the interaction between induced dipole moments and is represented as $-C_6/R^6$, where R is the distance between atoms. The dispersion coefficient C_6 can be conveniently expressed as an integral over dynamic polarizability at imaginary frequency $\alpha(i\omega)$ (cf. [2]),

$$C_6 = \frac{3}{\pi} \int_0^\infty d\omega [\alpha(i\omega)]^2. \quad (1)$$

The polarizability $\alpha(i\omega)$ for a valence state $|v\rangle$ can be written as a sum over intermediate states $|k\rangle$,

$$\alpha(i\omega) = \frac{2}{3} \sum_k \frac{E_k - E_v}{(E_k - E_v)^2 + \omega^2} |\langle v | \mathbf{R} | k \rangle|^2, \quad (2)$$

where the sum includes an integration over continuum states and $\mathbf{R} = \sum_{j=1}^N \mathbf{r}_j$ is the dipole operator for the N -electron atomic system. We use atomic units throughout. The coefficient C_3 of the Lennard-Jones interaction between an atom and a perfectly conducting wall is (cf. [3])

$$C_3 = \frac{1}{4\pi} \int_0^\infty d\omega \alpha(i\omega), \quad (3)$$

or, by explicit integration,

$$C_3 = \frac{1}{12} \langle v | \mathbf{R} \cdot \mathbf{R} | v \rangle. \quad (4)$$

Using the latter relation, we have previously [4] determined the values of C_3 coefficients for alkali-metal atoms using many-body methods.

The dipole operator \mathbf{R} , being a one-particle operator, can have nonvanishing matrix elements for intermediate states represented by two types of Slater determinant. First, the valence electron v can be promoted to some other valence state w . Second, one of the core orbitals a can be excited to a virtual state m , leaving the valence state v unchanged. In the language of second quantization, the first type of states is represented by $a_w^\dagger |0_c\rangle$ and the second type by $a_m^\dagger a_a |0_c\rangle$, where $|0_c\rangle$ describes the core. Correspondingly, we break the total polarizability α into three parts: the polarizability due to valence states α_v , the core polarizability α_c , and the valence-core coupling term α_{cv} , with

$$\alpha = \alpha_v + \alpha_c + \alpha_{cv}.$$

The last two terms arise from the summation over core excitations.

Various states contribute at drastically different levels to the dynamic polarizability. For example, 96% of the static polarizability of Cs is determined by the two intermediate valence states $6P_{1/2}$ and $6P_{3/2}$; other valence states contribute less than 1%. The core polarizability accounts for approximately 4% of the total value and the contribution of the core-valence coupling term is about -0.1% . The dynamic polarizability $\alpha(i\omega)$, given in Eq. (2), behaves as

$$\alpha(i\omega) \sim \sum_k f_{vk} / \omega^2 = N / \omega^2, \quad (5)$$

at large value of ω , where we used the nonrelativistic oscillator strength sum rule $S(0) = \sum f_{vk} = N$. Because the ratio α_c/α_v nonrelativistically is close to $N - 1$ we expect the core polarizability to give the major contribution at large ω and become increasingly important for heavier atoms.

Based on the above argument, we use several many-body techniques of varying accuracy to calculate the different contributions to the total polarizability. In particular, we employed the relativistic single-double (SD) all-order method to obtain the leading contribution from valence states [5]. The core polarizability is obtained from the relativistic random-phase approximation (RRPA) [6]. The core-valence coupling term and the nonleading contribution from valence states is estimated in the Dirac-Hartree-Fock approximation.

The relativistic SD all-order method has been previously used to obtain high-precision atomic properties for alkali-atom systems [5]. The results of theoretical SD matrix elements and comparison with experimental data are presented elsewhere [7]. Generally, the electric-dipole matrix elements for principal transitions agree with precise experimental data to better than 0.5% for all alkali-metal atoms; the calculations being more accurate for lighter elements. In the present work, for Na, K, Rb, and Cs, we used SD matrix elements for the first six lowest $P_{1/2}$ and $P_{3/2}$ levels. For Fr, we used SD matrix elements for a principal transition and matrix elements calculated with the third-order many-body perturbation theory (MBPT), described in [8], for the four other lowest $P_{1/2}$ and $P_{3/2}$ states. Unless noted otherwise, we used experimental values of energy levels from Ref. [9] and from the compilation of Dzuba *et al.* [10] for Fr.

The RRPA was used previously to obtain static core polarizabilities for all alkali-metal atoms except Fr in Ref. [6]. In the present calculations we reformulated the original differential equation method used in [6] in a manner similar to [11]. We reproduce the results of Ref. [6] and, in addition, obtain a value of 20.41 a.u. for the static dipole polarizability of the Fr^+ ion. Zhou and Norcross [12] find $\alpha_c(0) = 15.644(5)$ for the polarizability of Cs^+ , by fitting Rydberg states energies to a model potential for Cs, while the present RRPA calculations yield the value $\alpha_c(0) = 15.81$. Based on this comparison, we expect the RRPA method to give at least a few per cent accuracy in the calculation of $\alpha_c(i\omega)$.

To demonstrate the sensitivity of our results to errors in the core polarizability, we present the ratios of values calculated omitting α_c to the total values of $\alpha(0)$, C_3 , and C_6 in Table I. We see that while $\alpha(0)$ is affected at the level of a few per cent, the core contribution to C_6 becomes increasingly important for heavier systems. $\alpha_c(i\omega)$ contributes 2% to C_6 for Na and 23% for Fr. The constant C_3 , obtained with Eq. (3), is the most sensitive to the core contribution. Indeed, while α_c contributes 16% of C_3 for Na, it accounts for half of the total value for Fr.

TABLE I. Demonstration of the relative importance of the core contribution with increasing number of electrons N , where α^v , C_3^v , and C_6^v represent values calculated disregarding core excitations.

	Na	K	Rb	Cs	Fr
$\alpha^v(0)/\alpha(0)$	0.99	0.98	0.97	0.96	0.94
C_3^v/C_3	0.84	0.73	0.65	0.59	0.50
C_6^v/C_6	0.98	0.93	0.89	0.85	0.77

The tabulation of our results is presented in Tables II–IV. In method I we use high-precision experimental values, compiled in [7], for dipole matrix elements of the principal transition. In method II we use the theoretical SD matrix elements for the principal transition. We recommend using the values obtained with method I for $\alpha(0)$ and C_6 , since the accuracy of experimental data for the principal transitions is better than that of SD predictions.

In Table II we compare our calculations with experimental data for static polarizabilities. We find perfect agreement with a high-precision value for Na obtained in recent atom-interferometry experiments [13]. The experimental data for static polarizabilities of K, Rb, and Cs are known with the accuracy of about 2% [14,15]. While we agree with those experimental values, we believe that our theoretical approach gives more accurate results, mainly due to the overwhelming contribution of the principal transition to the sum over intermediate states. The theoretical error is estimated from the experimental accuracy of matrix elements from an estimated 5% error for the core polarizabilities, and 10% error for the remaining contributions to $\alpha(0)$.

A sensitive test of the quality of the present dynamic polarizability functions is obtained by calculating C_3 coefficients in two different ways: (i) by direct integration of $\alpha(i\omega)$ using Eq. (3) and (ii) by calculating the diagonal expectation value of \mathbf{R}^2 in Eq. (4). In the present work we extend calculations of the expectation value of \mathbf{R}^2 [4] in the SD formalism to obtain C_3 values for Rb, Cs, and Fr. In Table III, we compare the SD values for C_3 with those obtained in [4] using MBPT. The difference of 7% for Cs and 10% for Fr between SD and MBPT values is not surprising, since the MBPT [8] underestimates the line strength of principal transitions by a few per cent for Cs and Fr. To make a consistent comparison between the C_3 values obtained by integrating $\alpha(i\omega)$ and by calculating the expectation value, we have used SD energies and matrix elements in method II calculations in Table III. These C_3 values agree to about 0.6% for Na, 1% for K and Rb, 2.5% for Cs, and 3.4% for Fr. We assume that most of the error is due to the RRPA method used to calculate the core polarizability.

The error estimates in C_6 are based on the accuracy of experimental matrix elements for the principal transition, and by scaling the error of the core contribution from C_3 to C_6 , using Table I. The comparison of C_6 coefficients

TABLE II. Comparison of static dipole polarizabilities $\alpha(0)$ for alkali-metal atoms in atomic units. The entries in column 1 indicate either method I, utilizing high-accuracy experimental data for electric-dipole matrix elements for the principal transition, or method II, utilizing all-order SD values instead.

	Na	K	Rb	Cs	Fr
I ^a	162.6(3)	290.2(8)	318.6(6)	399.9(1.9)	317.8(2.4)
II	163.0	289.1	316.4	401.5	315.1
Expt.	162.7(8) ^b	293.6(6.1) ^c	319.9(6.1) ^c	403.6(8.1) ^c	

^aValues recommended from the present work.

^bRef. [13].

^cWeighted average of experimental data from Refs. [14,15].

with other calculations is presented in Table IV. The integration over $\alpha(i\omega)$ as in Eq. (1) has been used recently by Kharchenko *et al.* [16], by Marinescu, Sadeghpour, and Dalgarno [17], and by Patil and Tang [18]. Reference [16] utilized a combination of experimental and theoretical data constrained by oscillator strength sum rules yielding a function $\alpha(i\omega)$ satisfying Eq. (5). The present results are in good agreement with this calculation of C_6 for Na. In contrast to the present *ab initio* calculations, Refs. [17] and [18] employed model potentials. In addition, Ref. [17] used corrections to multipole operators to account for core polarization effects with parameters chosen to reproduce the experimental values of static polarizabilities, which for K, Rb, and Cs atoms are known with an accuracy of approximately 2%. The major contribution in the integration of Eq. (1) arises from the region of $\omega = 0$ and the integrand is quadratic in $\alpha(i\omega)$. Therefore, the predictions [17] of C_6 for K, Rb, and Cs have an inherent (experimental) accuracy of about 4%. Theoretical uncertainty of the method used in Ref. [17] is determined, among other factors, by the omitted contribution from core polarizability as discussed in Refs. [2,17]. Patil and Tang [18] used model-potential calculations with analytical representations of wave functions and with experimental energies. They used a direct summation method in Eq. (2). The contribution from the core excitations was not included as can be seen from Eq. (3.4) of Ref. [18]. In fact, this formulation does not result in a dynamic polarizability satisfying $\alpha(i\omega) \rightarrow N/\omega^2$, Eq. (5) in the limit of large ω . Therefore, the model-potential calculations generally underestimate the C_6 coefficients. Indeed, from the

comparison in Table IV, one can see that the C_6 values from Refs. [17] and [18] are systematically lower than our values.

Maeder and Kutzelnigg [19] used a method alternative to the integral Eq. (1) to calculate dispersion coefficients by minimizing a Hylleraas functional providing a lower bound. However, their prediction depended on the quality of the solution of the Schrödinger equation for the ground state. For alkali-metal atoms, model potentials were used to account for correlations. The predicted static polarizabilities are several per cent higher than experimental values and are not within the experimental error limits. However, for C_6 coefficients we generally find good agreement with the values of Maeder and Kutzelnigg [19].

Recently Marinescu *et al.* [20] presented calculations of dispersion coefficients for Fr, using a model-potential method similar to Ref. [17]. As shown in Table IV our result for Fr is significantly larger than the result of Ref. [20]. We believe this may be because the method of Ref. [20] does not completely take into account the contribution of the core polarizability, which accounts for 23% of C_6 for Fr.

Elastic scattering experiments and photoassociation spectroscopy have sensitively constrained the possible values of C_6 for Na and Rb. van Abeelen and Verhaar [21] reviewed spectroscopic and cold collision data for Na, including data from recent observations of magnetic field induced Feshbach resonances [22]. Our result for Na 1556(4) is in good agreement with their conclusion that $1539 < C_6 < 1583$. Photoassociation experiments [23] for Rb limit the C_6 coefficient to a range of

TABLE III. Comparison of atom-wall interaction constants C_3 for alkali-metal atoms in atomic units. Method I designates the use of high-accuracy experimental data for electric-dipole matrix elements and energies for principal transition. Method II designates the use of all-order SD values instead.

	Na	K	Rb	Cs	Fr
Method I, Eq. (3)	1.871	2.896	3.426	4.269	4.437
Method II, Eq. (3)	1.875	2.877	3.410	4.247	4.427
$\frac{1}{12}\langle R^2 \rangle$, SD ^{a,b} , Eq. (4)	1.8858	2.860	3.362	4.143	4.281
$\frac{1}{12}\langle R^2 \rangle$, MBPT [4], Eq. (4)	1.8895	2.838	3.281	3.863	3.870

^aValues recommended from the present work.

^bNa and K values are from Ref. [4]; those for Rb, Cs, and Fr are the present calculations.

TABLE IV. Tabulation and comparison of C_6 dispersion coefficients for alkali-metal atoms in atomic units. Method I designates the use of high-accuracy experimental data for electric-dipole matrix elements for principal transition. Method II designates the use of all-order SD values instead.

	Na	K	Rb	Cs	Fr
Method I ^a	1556(4)	3897(15)	4691(23)	6851(74)	5256(89)
Method II	1564	3867	4628	6899	5174
Ref. [16] ^b	1561				
Ref. [19]	1540	3945	4768	6855	
Ref. [17]	1539 ^c	3813	4426	6331	
Ref. [18]	1500	3796	4531	6652	
Ref. [20]					3934 ^d
Expt. [23]			4400–4900		
Expt. [24]			4700(50)		

^aValues recommended from the present work.

^bUtilizing a combination of experimental and theoretical data constrained by oscillator strength sum rules.

^cFor Na the value from Ref. [17] is 1472, obtained using the data from Ref. [14]. Using the same method, but with data from Ref. [13], the resulting value is 1539.

^dValue for 31_u molecular symmetry.

4400–4900 a.u. and even more recently [24] a study of a Feshbach resonance in elastic collisions of ^{85}Rb concluded $C_6 = 4700(50)$. Our value $C_6 = 4691(23)$ is in excellent agreement with this experiment. For Cs, knowledge of the value of C_6 is critical for predictions of the sign of the elastic scattering length [25], though it has been demonstrated the resulting cross sections are not particularly sensitive to the value of C_6 [26]. For Fr, the paucity of other dimer data constrains quantitative theoretical collisional studies for the near future.

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