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# High-precision calculations of dispersion coefficients, static dipole polarizabilities, and atom-wall interaction constants for alkali-metal atoms

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## Abstract

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 ultra-cold collisions and from studies of magnetic field induced Feshbach resonances in Na and Rb. For Cs we provide critically needed data for ultra-cold collision studies.

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The van der Waals interaction plays an important role in characterizing ultra-cold 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. 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, which have recently been calculated by other methods, 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, where available.

The dynamic polarizability at imaginary frequency $\alpha(i\omega)$ for a valence state $|v\rangle$ can be represented as a sum over intermediate states $|k\rangle$

$$\alpha\left(i\omega\right)=\frac{2}{3}\sum_{k}\frac{E_k-E_v}{\left(E_k-E_v\right)^2+\omega^2}\langle v|\mathbf{R}|k\rangle\cdot\langle k|\mathbf{R}|v\rangle\,, \tag{1}$$

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 dispersion coefficient $C_6$ of the van der Waals interaction between two identical atoms is

$$C_6=\frac{3}{\pi}\int_0^\infty d\omega\,\left[\alpha(i\omega)\right]^2. \tag{2}$$

The coefficient $C_3$ of the interaction between an atom and a perfectly conducting wall is

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

or alternatively

$$C_3=\tfrac{1}{12}\,\langle v|\mathbf{R}\cdot\mathbf{R}|v\rangle\,. \tag{4}$$

Using the latter relation, we have previously [2] 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 non-vanishing matrix elements for intermediate states represented by two types of Slater determinant. Firstly, the valence electron $v$ can be promoted to some other valence state $w$. Secondly, 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 $a_m^\dagger a_a a_v^\dagger|0_c\rangle$, where $|0_c\rangle$ describes the core. These states will be referred to as "valence" and "autoionizing" states, respectively.

In accordance with such a classification, we break the total polarizability $\alpha$ into three parts: the polarizability due to valence states $\alpha_v$, the core polarizability $\alpha_c$, and the valence-core coupling term $\alpha_{cv}$, with

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

The last two terms arise from the summation over autoionizing states. In evaluating the core polarizability we permit excitations into all possible states outside the core. The term $\alpha_{cv}$ is a counter term accounting for the consequent violation of the Pauli principle.

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 relative sizes of contributions to the static polarizabilities for the other alkali-metal atoms are similar. The dynamic polarizability $\alpha(i\omega)$, given in Eq. (1), behaves as

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

at large value of $\omega$, where we have used the nonrelativistic oscillator strength sum rule $S\,(0) = \sum f_{vk} = N$. Because the ratio $\alpha_c/\alpha_v$ nonrelativistically is close to $N-1$ we expect the core polarizability to give the major contribution at large $\omega$. Therefore, the core polarizability becomes 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 [3]. The core polarizability is obtained from the relativistic random-phase approximation (RRPA) [4]. The core-valence coupling term and the non-leading contribution from valence states is estimated in the Dirac-Hartree-Fock approximation by a direct summation over basis set functions [5].

The relativistic single-double (SD) all-order method has been previously used to obtain high-precision atomic properties for the first few excited states in alkali-atom systems [3]. The results of theoretical SD matrix elements and comparison with experimental data are presented elsewhere [6]. 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 have used SD matrix elements for the first six lowest $P_{1/2}$ and $P_{3/2}$ levels. For Fr, we have used SD matrix elements for a principal transition and matrix elements calculated with the third-order many-body perturbation theory (MBPT), described in [7], for four other lowest $P_{1/2}$ and $P_{3/2}$ states. Unless noted otherwise, we have used experimental values of energy levels from Ref. [8] and from the compilation of Dzuba *et al.* [9] for Fr.

The relativistic random-phase approximation (RRPA) was used previously to obtain static core polarizabilities for all alkali-metal atoms except Fr in Ref. [4]. In the present calculations we reformulated the original differential equation method used in [4] in terms of basis sets [5], in a manner similar to [10]. We reproduce the results of Ref. [4] and, in addition, obtain a value of 20.41 a.u. for the static dipole polarizability of the $\mathrm{Fr}^+$ ion. Zhou and Norcross [11] find $\alpha_c(0) = 15.644(5)$ for the polarizability of $\mathrm{Cs}^+$, 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 $\alpha_c(iw)$.

To demonstrate the sensitivity of our results to errors in the core polarizability, we present the ratios of values calculated omitting $\alpha_c$ 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. $\alpha_c(iw)$ contributes 2% to $C_6$ for Na and 23% for Fr. The atom-wall interaction constant $C_3$, obtained with Eq. (3), is the most sensitive to the core contribution. Indeed, while $\alpha_c$ contributes 16% of $C_3$ for Na, it accounts for the half of the total value of $C_3$ for Fr.

The tabulation of our results for static dipole polarizabilities, atom-wall interaction constants $C_3$, and $C_6$ dispersion coefficients is presented in Tables II–IV. In Method I we use high-precision experimental values [12] for dipole matrix elements of the principal transition. We used a weighted average of experimental data if there were several measurements for a particular 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 electric-dipole matrix elements for principal transitions are known typically at the level 0.1% accuracy for all alkalis. The theoretical error is estimated from the experimental accuracy of matrix elements [12], 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 $\mathbf{R}^2$ [2] in the SD formalism to obtain $C_3$ values for Rb, Cs, and Fr. In the Table III, we compare the SD values for $C_3$ with those obtained in [2] using MBPT. The difference of 7% for Cs and 10% for Fr between SD and MBPT values is not surprising, since the MBPT [7] 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. At present, it appears no experimental data are available for comparison. We assume that most of the error is due to the RRPA method used to calculate the core polarizability. Therefore, the error estimates in $C_6$ are based on the accuracy of experimental matrix elements for the principal transition [12], and by scaling the error of core contribution from $C_3$ to $C_6$, using Table I.

The comparison of $C_6$ coefficients with other calculations is presented in the Table IV. For Na the results are in good agreement with a semi-empirical determination [16]. The integration over $\alpha(i\omega)$ as in Eq. (2) has been most recently used by Marinescu, Sadeghpour, and Dalgarno [17] and by Patil and Tang [18]. In contrast to the present *ab initio* calculations, both works 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 from experimental measurements with an accuracy of approximately 2%. The major contribution in the integration of Eq. (2) arises from the region of $\omega = 0$ and the integrand is quadratic in $\alpha(i\omega)$. Therefore, until more accurate experimental values for static polarizabilities are available, 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. [17,19]. 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. (1). The contribution from the core polarizability was not included as can be seen from Eq. (3.4) of Ref. [18]. In fact, this formula in the limit of large $\omega$ results in $\alpha(i\omega) \rightarrow 1/\omega^2$ instead of the correct limit $\alpha(i\omega) \rightarrow N/\omega^2$, which follows from the oscillator strength sum rule. 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 Ref. [17] and Ref. [18] are systematically lower than our values.

Maeder and Kutzellnigg [20] used a method alternative to the integral Eq. (2) 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 Kutzellnigg [20].

Recently Marinescu *et al.* [21] presented calculations of dispersion coefficients of different molecular symmetries 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. [21]. We believe this may be because the method of Ref. [21] 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 [22] reviewed spectroscopic and cold-collision data for Na, including data from recent observations of magnetic field induced Feshbach resonances [23]. They considered values for Na of $1539 < C_6 < 1583$ and concluded that $C_6 = 1539$ gave the best consistency between data sets. Our result for Na using Method I is in particularly good agreement with this value. Photoassociation experiments [24] for Rb limits the $C_6$ coefficient to a range 4400-4900 a.u. and even more recently [25] 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 [26], though it has been demonstrated the resulting cross sections are not particularly sensitive to the value of $C_6$ [27]. For Fr, the paucity of other dimer data constrains quantitative theoretical collisional studies for the near future. As photoassociation experiments move beyond the alkali-metal atoms to other atoms with many electrons such as Sr [28] and Cr [29], it will be important to have reliable *ab initio* methods for calculation of atomic properties. The approaches presented here could, in principle, be applied to Sr and perhaps with some significant effort to Cr.

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# TABLES

TABLE I. Demonstration of the relative importance of the contribution of autoionizing states with increasing number of electrons $N$, where $\alpha^v$, $C_3^v$, and $C_6^v$ represent values calculated disregarding autoionizing states.

| | 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 |

TABLE II. Comparison of static dipole polarizabilities $\alpha(0)$ 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] | 162.6(3) | 290.2(8) | 318.6(6) | 399.9(1.9) | 317.8(2.4) |
| Method II | 163.0 | 289.1 | 316.4 | 401.5 | 315.1 |
| Expt. [13] | 162.7(8) | | | | |
| Expt. [14,15][b] | | 293.6(6.1) | 319.9(6.1) | 403.6(8.1) | |

[a] Values recommended from the present work.

[b] Weighted average of experimental data from Refs. [14,15].

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 | 2.887 | 3.410 | 4.247 | 4.427 |
| $\frac{1}{12}\langle R^2\rangle$, SD[ab], Eq. (4) | 1.8858 | 2.860 | 3.362 | 4.143 | 4.281 |
| $\frac{1}{12}\langle R^2\rangle$, MBPT [2], Eq. (4) | 1.8895 | 2.838 | 3.281 | 3.863 | 3.870 |

[a] Values recommended from the present work.

[b] The values for Na and K are from Ref. [2], and 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. [20] | 1540 | 3945 | 4768 | 6855 | |
| Ref. [17] | 1539[c] | 3813 | 4426 | 6331 | |
| Ref. [18] | 1500 | 3796 | 4531 | 6652 | |
| Ref. [21] | | | | | 3934[d] |
| Expt. [24] | | | 4400-4900 | | |
| Expt. [25] | | | 4700(50) | | |

[a] Values recommended from the present work.

[b] Semiempirical method.

[c] For 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 [19].

[d] Value for $^{3}1_u$ molecular symmetry. Values for other symmetries are $C_6(^{1}0_g^+) = 3929$, and $C_6(^{1}0_u^-) = 3947$.

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