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High-accuracy relativistic many-body calculations of van der Waals coefficients C_6 for alkaline-earth-metal atoms

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Relativistic many-body calculations of van der Waals coefficients C_6 for dimers correlating to two ground-state alkaline-earth-metal atoms at large internuclear separations are reported. The following values and uncertainties were determined: $C_6=214(3)$ for Be, 627(12) for Mg, 2221(15) for Ca, 3170(196) for Sr, and 5160(74) for Ba in atomic units.

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INTRODUCTION

The realization of Bose-Einstein condensation (BEC) in dilute ultracold samples of hydrogen and alkali-metal atoms Li, Na, and Rb [1] has prompted a search for other atomic and molecular species where BEC can possibly be attained. Of non-alkali-metal atoms, so far the condensation was successful only with metastable helium [2,3]. Cooling and trapping experiments with alkaline-earth-metal (in particular Mg, Ca, and Sr) were recently reported (see, e.g., Refs. [4–6]) and prospects of achieving the condensation were also discussed [4,7]. Alkaline-earth-metal atoms possess several advantages over alkali-metal atoms. For example, utilization of the narrow spin-forbidden transition $^1S_0 \rightarrow {}^3P_1^0$ permits us to optically cool atoms down to the nano-Kelvin regime [5,8]. There are also a number of isotopes available with zero nuclear spin, so that the resulting molecular potentials are not complicated by hyperfine structure; this simplifies studies of trap losses and ultracold collisions [9].

We apply relativistic many-body methods to the determination of dispersion (van der Waals) coefficients C_6 for the interaction of two identical alkaline-earth-metal atoms in their ground states. The leading interaction of such atoms at large internuclear separations R is parametrized as $-C_6/R^6$. Knowledge of the dispersion coefficients is required, for example, in determination of scattering lengths governing properties of BEC of dilute samples [10].

We employ several atomic relativistic many-body methods of varying accuracy. The dominant contribution to C_6 was evaluated with the configuration-interaction (CI) method coupled with many-body perturbation theory (MBPT) [11,12]; smaller terms were computed using the relativistic random-phase approximation (RPA) and Dirac-Hartree-Fock (DHF) methods. The values were further adjusted with accurate theoretical and experimental data for electric-dipole matrix elements and energies of principal transitions. We tabulate the values of C_6 for Be, Mg, Ca, Sr, and Ba. We also estimate uncertainties to be on the order of 1–2 % for all alkaline-earth-metal atoms, except for a 5% accuracy for Sr.

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Method of calculations

The van der Waals coefficient may be expressed as [13]

$$C_6=6\sum_{ij}\frac{|\langle\Psi_g|D_z|\Psi_i\rangle|^2|\langle\Psi_g|D_z|\Psi_j\rangle|^2}{(E_i-E_g)+(E_j-E_g)}, \tag{1}$$

where Ψ_g and E_g are the wave function and energy of the atomic ground state, D_z is an electric-dipole operator, and the summation is over intermediate atomic states Ψ_i and Ψ_j with respective energies E_i and E_j. Atomic units $\hbar=|e|=m_e=1$ are used throughout. The above relation can be recast into the Casimir-Polder form

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

where $\alpha(i\omega)$ is the dynamic polarizability of imaginary argument defined as

$$\alpha(i\omega)=2\,\mathrm{Re}\sum_i\frac{\langle\Psi_g|D_z|\Psi_i\rangle\langle\Psi_i|D_z|\Psi_g\rangle}{(E_i-E_g)+i\omega}. \tag{3}$$

The intermediate states in the sum, Eq. (3), can be separated into valence and core-excited states. We write

$$\alpha(i\omega)=\alpha_v(i\omega)+\alpha_c(i\omega)+\alpha_{cv}(i\omega). \tag{4}$$

The valence contribution α_v is determined with the CI+MBPT method. Smaller contributions of core-excited states α_c are estimated using the RPA method for the atomic core. In this method, excitations of core electrons are allowed into the occupied valence shell and we introduce the correction α_{cv} to account for a subsequent violation of the Pauli exclusion principle.

Similar techniques were involved in our high-precision determination of C_6 coefficients for alkali-metal atoms [14,15]. Divalent atoms present an additional challenge due to a strong Coulomb repulsion of the valence electrons. This strong interaction is treated here with the configuration-interaction method and smaller residual corrections (like core polarization) are treated with the many-body perturbation theory. The method, designated as CI+MBPT, was developed in Refs. [11,12,16–19].

Here we recap the main features of the CI+MBPT method. The complete functional space for electronic wave

functions is partitioned in two parts: the model space spanning all possible excitations of the two valence electrons and an orthogonal space which adds various excitations of core electrons. The valence CI basis set is saturated; e.g., the Ba ground state wave function is represented as a combination of 1450 relativistic configurations in our calculations. Application of perturbation theory leads to effective operators encapsulating many-body effects and acting in the model space. For example, the CI wave functions are determined from the equation

$$H_{\rm eff}(E_n)|\Psi_n\rangle = E_n|\Psi_n\rangle, \tag{5}$$

with the effective Hamiltonian defined as

$$H_{\rm eff}(E) = H_0 + C + \Sigma(E). \tag{6}$$

Here H_0 is the lowest-order DHF Hamiltonian, C is the residual Coulomb interaction between valence electrons, and Σ is the energy-dependent self-energy operator corresponding to core-polarization effects in model-potential approaches. By the same token, one introduces an effective electric-dipole operator $D_{\rm eff}$ acting in the model space. We determine this effective operator using the random-phase approximation (RPA) [20,21]. Qualitatively, the RPA describes a shielding of the externally applied field by the core electrons.

The dynamic *valence* polarizability $\alpha_v(i\omega)$ was computed with the Sternheimer [22] or Dalgarno-Lewis [23] method implemented in the CI+MBPT+RPA framework. At the heart of the method is a solution of an inhomogeneous Schrödinger equation for a ''perturbed'' state $|\delta\Psi_\omega\rangle$

$$(H_{\rm eff} - E_g + i\omega)|\delta\Psi_\omega\rangle = (D_z)_{\rm eff}|\Psi_g\rangle, \tag{7}$$

so that

$$\alpha_v(i\omega) = 2\,{\rm Re}\langle\Psi_g|(D_z)_{\rm eff}|\delta\Psi_\omega\rangle. \tag{8}$$

In these expressions, the electric-dipole operator $D_{\rm eff}$ is calculated at the CI+MBPT+RPA level of approximation. The present approach is a frequency-dependent generalization of calculations of static dipole polarizabilities reported in [19,24]; technical details can be found in these works.

The overwhelming contribution (on the order of 90%) to the value of the van der Waals coefficient, Eq. (1), comes from the lowest-energy excited $nsnp\ ^1P_1^o$ state. Therefore, the calculated C_6 are mostly sensitive to accuracies of dipole matrix elements and energy separations of the principal $nsnp\ ^1P_1^o - ns^2\ ^1S_0$ transitions. We explicitly calculated these quantities using the same level of CI+MBPT+RPA approximation as employed in the solution of the inhomogeneous equation (7); these values are marked as CI+MBPT+RPA and CI+MBPT in Table I. We find a good agreement with more sophisticated *ab initio* [20,21] and experimental values [4,25–27] (see Table I). For Be we also computed additional many-body corrections; they can be neglected at the level of the quoted significant figures in Table I. We conservatively estimated an uncertainty in the matrix element for Be as a half of the difference between valence CI and correlated value.

TABLE I. Reduced matrix elements D and energy separations ΔE_p for transitions from the lowest-energy $nsnp\ ^1P_1^o$ to the ground $ns^2\ ^1S_0$ state.

	D		ΔE_p	
	CI+MBPT+RPA	Accurate	CI+MBPT	Expt.[a]
Be	3.26	3.26(1)[b]	0.194 291	0.193 942
Mg	4.03	4.03(2)[c]	0.159 173	0.159 705
Ca	4.93	4.967(9)[d]	0.107 776	0.107 768
Sr	5.31	5.28(9)[c]	0.098 508	0.098 866
Ba	5.52	5.466(23)[e]	0.082 891	0.082 289

[a]References [26,27].
[b]This work.
[c]References [20,21].
[d]Reference [4].
[e]Reference [25].

We correct the calculated dynamic polarizability by subtracting the *ab initio* CI+MBPT+RPA contribution of the principal transition

$$\alpha_p(i\omega) = \frac{2}{3}\frac{\Delta E_p}{(\Delta E_p)^2+\omega^2}|\langle ns^2\ ^1S_0\|D\|nsnp\ ^1P_1^0\rangle|^2 \tag{9}$$

from $\alpha(i\omega)$ and adding it back with experimental energies and high-accuracy matrix elements compiled in Table I.

The ''perturbed'' state $|\delta\Psi_\omega\rangle$ in Eq. (7) is comprised from all possible valence excitations from the ground state $|\Psi_g\rangle$. Contribution of core-excited states to the polarizability has to be added separately. We follow [14] and use the relativistic RPA [28] to determine the dynamic core polarizability as

$$\alpha_c(i\omega) = \sum_{\omega_\mu>0}\frac{f_\mu}{(\omega_\mu)^2+\omega^2}. \tag{10}$$

Here the summation is over particle-hole excitations from the ground state of the atomic core; ω_μ are excitation energies and f_μ are the corresponding electric-dipole oscillator strengths. Accounting for core excitations is essential in our accurate calculations, especially for heavier atoms. For example, for Ba they contribute as much as 15% to the total value of C_6. In the RPA, the particle-hole excitations include Pauli-principle violating excitations into the occupied valence shell. The counterterm $\alpha_{cv}(i\omega)$ may be written as

$$\alpha_{cv}(i\omega) = -\frac{2}{3}\sum_a \frac{|\langle a\|D\|ns\rangle|^2(\varepsilon_{ns}-\varepsilon_a)}{(\varepsilon_{ns}-\varepsilon_a)^2+\omega^2}, \tag{11}$$

where the principal quantum number $n=2$, 3, 4, 5, and 6 for Be, Mg, Ca, Sr, and Ba, respectively, and the summation is over core orbitals. This correction is computed with the DHF method.

Our polarizabilities satisfy two important relations: (i) $\alpha(\omega=0)$ is the ground-state static dipole polarizability and (ii) as a consequence of the nonrelativistic Thomas-Reiche-Kuhn sum rule, at large frequencies $\omega^2\alpha(i\omega)\to N$, where N

TABLE II. van der Waals coefficients C_6 for dimers correlating to ground states of alkaline-earth-metal atoms in a.u. Values marked *ab initio* were determined in the relativistic CI+MBPT+RPA framework. The values marked final are *ab initio* values adjusted for accurate dipole matrix elements and energies of principal transitions, compiled in Table I.

	Be	Mg	Ca	Sr	Ba
Ab initio	213	631	2168	3240	5303
Final	214(3)	627(12)	2221(15)	3170(196)	5160(74)
		Other works			
Stanton [31]	216	648	2042	3212	
Standard and Certain [32]	220	634	2735		
Maeder and Kutzelnigg [33]	208	618	2005		
Amusia and Cherepkov [34]	254		2370		
Stwalley [35]		683(35)			

is the number of atomic electrons. Indeed, for Ca we obtain $\alpha(0)=160$ a.u., while the experimental value [29] is 169(17) a.u. For Sr we obtain 199 a.u. which is in agreement with the measured value [30] of 186(15) a.u. And, finally, for Ba the computed static polarizability of 273 a.u. also compares well with the experimental value [30] of 268(22) a.u. Similarly, at large ω, in our *relativistic* calculations the product $\omega^2\alpha(i\omega)$ approaches 3.99 for Be, 11.9 for Mg, 19.71 for Ca, 37.1 for Sr, and 54.01 for Ba.

RESULTS AND THEORETICAL UNCERTAINTIES

The calculated van der Waals coefficients are presented in Table II. In this table, values marked *ab initio* were determined in the relativistic CI+MBPT+RPA framework. The values marked final are *ab initio* values adjusted for accurate matrix elements and energies of the principal transitions from Table I.

Different classes of intermediate states in Eq. (3) contribute at drastically different levels to the total values of C_6. For example, for Ca, the principal $4s4p\ ^1P_1^o-4s^2\ ^1S_0$ transition contributes 85%, remaining valence-valence excitations contribute 8%, core-excited states contribute 8%, and the counterterm α_{cv} modifies the final result only by -0.4%. To estimate dominant uncertainties, we approximate

$$C_6\simeq\frac{3}{\pi}\int_0^\infty[\alpha_p(i\omega)]^2d\omega+\frac{6}{\pi}\int_0^\infty\alpha_p(i\omega)\alpha_r(i\omega)d\omega$$
$$=C_6^{pp}+C_6^{pr}. \qquad (12)$$

Here α_p is a contribution of the principal transition Eq. (9), and $\alpha_r=\alpha_v'+\alpha_c$ is a contribution of the remaining valence states ($\alpha_v'=\alpha_v-\alpha_p$) and core-excited states. For Ca, this approximation recovers 99.3% of the C_6 obtained from the full expression (2). Based on Eq. (12), the sensitivity of C_6 to uncertainties δD in the matrix element D of the principal transition is

$$\delta_D C_6\approx(4C_6^{pp}+2C_6^{pr})\frac{\delta D}{D}. \qquad (13)$$

To evaluate the sensitivity of C_6 to uncertainties in the residual polarizability, we follow Ref. [36]. In the second term of Eq. (12), a narrow function $\alpha_p(i\omega)$ is integrated with a relatively broad distribution $\alpha_r(i\omega)$. Therefore,

$$\int_0^\infty\alpha_p(i\omega)\alpha_r(i\omega)d\omega\approx\alpha_r(0)\int_0^\infty\alpha_p(i\omega)d\omega \qquad (14)$$

and the sensitivity of C_6 is

$$\delta_{\alpha_r}C_6\approx C_6^{pr}\frac{\delta\alpha_r(0)}{\alpha_r(0)}. \qquad (15)$$

The uncertainty $\delta\alpha_r(0)$ is a sum of uncertainties in the contributions of valence states beyond the principal transition $\delta\alpha_v'(0)$ and core-excited states $\delta\alpha_c(0)$. The RRPA static dipole core polarizabilities for alkali-metal atoms are known [14] to be in a 1% agreement with those deduced from semiempirical analysis of Rydberg spectra; we approximate that $\delta\alpha_c(0)\approx0.01\alpha_c(0)$. Further, we estimate that $\delta\alpha_v'(0)\approx\delta\alpha_p(0)$, i.e., the difference of the contributions of the principal transition to static polarizability calculated with CI+MBPT+RPA and accurate values compiled in Table I.

The final error bars were calculated by adding the uncertainties $\delta_D C_6$ and $\delta_{\alpha_r}C_6$ in quadrature. The uncertainty in C_6 induced by errors in matrix elements of principal transition, $\delta_D C_6$, dominates over $\delta_{\alpha_r}C_6$. The total uncertainties are on the order of 1–2 % for all alkaline-earth-metal atoms, except for Sr, where the accuracy is 5%. Similar error analysis for alkali-metal atoms [14] has proven to be reliable; for example, for Cs the predicted $C_6=6851(74)$ a.u. was found to be in agreement with a value [37] of 6890(35) a.u. deduced from an analysis of magnetic-field-induced Feshbach resonances and photoassociation data. However, we emphasize that in the case of alkali metals a number of independent high-accuracy data was available for the dominant principal transitions ensuring reliability of derived dispersion coefficients. This is not the case for alkaline-earth-metal atoms. In our present calculation, we rely on the quoted uncertainties of accurate dipole matrix elements listed in Table I.

A comparison with other determinations of C_6 is presented in Table II. There is a reasonable agreement among different approaches for Be and Mg; results for Ca are less consistent due to a more significant role of correlations and core-excited states. Coupled-cluster calculations by Stanton

[31] were most elaborate among theoretical treatments. We find a good agreement with his predictions. Unfortunately, most of the authors do not estimate uncertainties of their methods. One of the exceptions is Ref. [32], where sum rules and Pade approximants were used to establish bounds on C_6. For Ca, they found $2740 \leqslant C_6 \leqslant 2830$ a.u. However, large uncertainties of underlying experimental data were not included in these bounds (see also Ref. [31]); this explains a significant deviation of our prediction for Ca, $C_6 = 2221(15)$ a.u., from constraints of Ref. [32].

CONCLUSION

We carried out relativistic many-body calculations of van der Waals coefficients C_6 for dimers correlating to two ground-state alkaline-earth-metal atoms at large internuclear separations. The values were adjusted with accurate theoretical and experimental data for the electric-dipole matrix elements and energies of the principal transitions. It is worth emphasizing that the dispersion coefficients depend sensitively on electric-dipole matrix elements of principal transitions. As more accurate data for the matrix elements become available, for example from photoassociation experiments with ultracold samples, the van der Waals coefficients can be constrained further within our many-body approach.

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