High-accuracy relativistic many-body calculations of van der Waals coefficients, $C_6$, for alkaline-earth 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 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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a. Introduction. The realization of Bose-Einstein condensation (BEC) in dilute ultracold samples of hydrogen and alkali-metal atoms Li, Na, and Rb has prompted a search for other atomic and molecular species where BEC can possibly be attained. Of non-alkali atoms, so far the condensation was successful only with metastable helium [1, 2]. Cooling and trapping experiments with alkaline-earth atoms (in particular Mg, Ca, and Sr) were recently reported (see, e.g., Ref. [3]) and prospects of achieving the condensation with alkaline-earth atoms were also discussed [4, 5]. Ultracold alkaline-earth atoms possess several advantages over alkali-metal atoms. For example, utilization of the narrow spin-forbidden transition $^1S_0 \rightarrow ^3P_1^0$ permits to optically cool atoms down to nano–Kelvin regime [6, 7]. There is also a number of isotopes available with zero nuclear spin, so that the resulting molecular potentials are not complicated by the “spaghetti” of hyperfine-structure states; this simplifies studies of trap losses and ultracold collisions [8].

Here 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 atoms in their respective ground states. The leading interaction of two ground-state atoms at large internuclear separations $R$ is parameterized as $-C_6/R^6$. Knowledge of the dispersion coefficients is required, for example, in determination of scattering lengths governing properties of Bose-Einstein condensates of dilute samples [9].

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 less accurate relativistic random-phase approximation (RRPA) 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 atoms, except for a 5% accuracy for Sr.

b. Method of calculations. The dispersion coefficient $C_6$ describes a second-order correction to energies of molecular terms related to the interaction of atomic dipoles induced by molecular fields. Due to large inter-nuclear separations involved, the two-center molecular-structure problem is reduced to the determination of atomic properties. The van der Waals coefficient may be expressed as

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

where $\Psi_g$ and $E_g$ are the wavefunction and energy of the atomic ground state, $D_z$ is an electric-dipole operator, and the summation is over intermediate atomic states $\Psi_i$ and $\Psi_j$ 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

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

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

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

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

$$\alpha(i\omega) = \alpha_v(i\omega) + \alpha_c(i\omega) + \alpha_{vc}(i\omega).$$

To determine the valence contribution $\alpha_v$ we employ combined relativistic configuration interaction method and many-body perturbation theory (CI+MBPT). Smaller contributions of core-excited states $\alpha_c$ are estimated with the relativistic random-phase approximation for the atomic core. In this method excitations of core electrons are allowed into the occupied valence shell and we introduce the correction $\alpha_{vc}$ to account for a subsequent violation of the Pauli exclusion principle; this
small correction is evaluated using the Dirac-Hartree-Fock method.

Similar relativistic many-body techniques were involved in our previous high-precision determination of van der Waals coefficients for atoms with one valence electron outside a closed core [14, 15]. Divalent atoms, considered here, 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 Ref. [1, 2, 3, 7, 8, 13].

Here we briefly recap the main features of the CI+MBPT method. The complete functional space for electronic wavefunctions 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 wavefunction 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 valence wavefunctions are determined from the Schrödinger equation

\[ H_{\text{eff}}(E_n) |\Psi_n\rangle = E_n |\Psi_n\rangle, \]  

with the effective Hamiltonian defined as

\[ H_{\text{eff}}(E) = H_0 + C + \Sigma(E). \]  

Here \( H_0 \) is the lowest-order Dirac-Fock Hamiltonian, \( C \) is the residual Coulomb interaction between valence electrons, and \( \Sigma \) is the energy-dependent self-energy operator corresponding to core-polarization effects in model-potential approaches. The operator \( \Sigma \) completely accounts for the second order of perturbation theory. By the same virtue, one introduces an effective (dressed) electric-dipole operator \( D_{\text{eff}} \) acting in the model space. We determine this effective operator using the random-phase approximation (RPA) [21, 22]. Qualitatively, the RPA describes a shielding of the externally applied field by the core electrons.

The dynamic valence polarizability \( \alpha_v(\omega) \) 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 \( |\Psi_\omega\rangle \)

\[ (H_{\text{eff}} - E_g + i\omega)|\Psi_\omega\rangle = (D_\omega)|\Psi_\omega\rangle, \]  

so that

\[ \alpha_v(\omega) = 2\text{Re}(\langle D_\omega |\Psi_\omega\rangle). \]  

In these expressions the electric-dipole operator \( D_{\text{eff}} \) is calculated at the CI+MBPT+RPA level of approximation. 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. (5), comes from the lowest-energy excited \( nsnp^1P^0 \) state. Therefore the calculated \( C_6 \) are mostly sensitive to accuracies of dipole matrix elements and energy separations of the principal \( nsnp^1P^0 - ns^2 \) \( 1S_0 \) 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 \( \text{ab initio} \) [20, 21] and experimental values [1, 25, 26, 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.

Due to the enhanced sensitivity of \( C_6 \) to uncertainties in the dipole matrix element and the energy separation \( \Delta E_p \) of principal transitions, we further correct the calculated dynamic polarizability by subtracting the \( \text{ab initio} \) CI+MBPT+RPA contribution of the principal transition

\[ \alpha_p(\omega) = \frac{2}{3} \frac{\Delta E_p}{(\Delta E_p)^2 + \omega^2} |\langle ns^2 \ 1S_0 || D || nsnp^1P^0 \rangle|^2 \]  

from \( \alpha(\omega) \) 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. (6) is defined in the model space of the valence electrons, i.e., it is comprised from all possible valence excitations from the ground state \( |\Psi_g\rangle \). Since the core-excited states do not enter the model space, their contribution to the polarizability has to be added separately. Here we follow our work [14, 25] and use the relativistic random-phase approximation to determine the dynamic core polarizability as

\[ \alpha_c(\omega) = \sum_{\omega_p > 0} \frac{f_\mu}{(\omega_\mu)^2 + \omega^2}. \]  

Here the summation is over particle-hole excitations from the ground state of the atomic core; \( \omega_\mu \) are excitation en-
TABLE II: van der Waals coefficients for dimers correlating to ground states of alkaline-earth atoms in a.u. Values marked \textit{ab initio} were determined in the relativistic CI+MBPT+RPA framework. The values marked final are \textit{ab initio} values adjusted for accurate dipole matrix elements and energies of principal transitions, compiled in Table I.

|          | Be | Mg | Ca | Sr | Ba |
|----------|----|----|----|----|----|
| \textit{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 |
|          | S&K [32] | 220 | 634 | 2785 |
|          | MAK [33] | 208 | 618 | 2005 |
|          | Ak&Ch [34] | 254 | 2370 |
| Stwalley [35] | 683(35) |

**energies and \( f_\mu \) 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 \( C_6 \).

The particle-hole excitations summed over in Eq. (10) include Pauli-principle violating excitations into the occupied valence shell. We explicitly subtract their contribution; this small correction \( \alpha_{\text{vp}}(i\omega) \) is computed with the Dirac-Hartree-Fock method.

Our calculated dynamic 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 \( N \) is the total number of atomic electrons. Indeed, for Ca we obtain \( \alpha(0) = 160 \) a.u., while the experimental value [23] is 169(17) a.u. For Sr we obtain 199 a.u. which is in agreement with the measured value [31] of 186(15) a.u. And, finally, for Ba the computed static polarizability of 273 a.u. also compares well with experimental value [31] of 268(22) a.u. Similarly, at large \( \omega \), in our 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; these asymptotic relativistic values are slightly smaller than the exact nonrelativistic limits.

c. Results and theoretical uncertainties. We combine various parts of the dynamic polarizability, Eq. (1), and then obtain dispersion coefficients \( C_6 \) with a quadrature, Eq. (2). The resulting values of van der Waals coefficients are presented in Table I. In this Table, values marked \textit{ab initio} were determined in the relativistic CI+MBPT+RPA framework. The values marked final are \textit{ab initio} values adjusted for accurate dipole matrix elements and energies of principal transitions, compiled in Table I.

Different classes of intermediate states in Eq. (1) contribute at drastically different levels to the total values of dispersion coefficients. For example, for Ca, the principal \( 4s^4p^1 \bar{1}P^0 - 4s^2 \bar{1}S_0 \) transition contributes 85\% to the values of \( C_6 \), remaining valence-valence excitations contribute 8\%, core-excited states contribute 8\%, and the counter term \( \alpha_{\text{ct}} \) modifies the final result only by -0.4\%. To estimate dominant theoretical uncertainties we approximate \( C_6 \) as

\[
C_6 \approx \frac{3}{2} \int_0^\infty |\alpha_p(i\omega)|^2 d\omega + \frac{6}{\pi} \int_0^\infty \alpha_p(i\omega) \alpha_r(i\omega) d\omega
\]

\[
= C_6^{pp} + C_6^{pr} .
\]

Here \( \alpha_p \) is a contribution of the principal transition Eq. (3), and \( \alpha_r = \alpha_r' + \alpha_r'' \) is a contribution of the remaining valence states \( (\alpha_r' = \alpha_r - \alpha_p) \) and core-excited states. From a direct calculation for Ca we find that this approximation recovers 99.3\% of the \( C_6 \) obtained from the full expression (3). Based on Eq. (11) the sensitivity of \( C_6 \) to uncertainties \( \delta D \) in the matrix element \( D \) of the principal transition is

\[
\delta_D C_6 \approx (4C_6^{pp} + 2C_6^{pr}) \frac{\delta D}{D} .
\]

To evaluate the sensitivity of \( C_6 \) to uncertainties in the residual polarizability we follow Ref. [36]. In the second term of Eq. (11) a narrow function \( \alpha_p(i\omega) \) is integrated with a relatively broad distribution \( \alpha_r(i\omega) \). Therefore we can approximate that

\[
\int_0^\infty \alpha_p(i\omega) \alpha_r(i\omega) d\omega \approx \alpha_r(0) \int_0^\infty \alpha_p(i\omega) d\omega
\]

and the sensitivity of \( C_6 \) is

\[
\delta_C C_6 \approx C_6^{pr} \frac{\delta \alpha_r(0)}{\alpha_r(0)} .
\]

The uncertainty in the residual static polarizability \( \delta \alpha_r(0) \) is a sum of uncertainties in the contributions of valence states beyond principal transition \( \delta \alpha_r'(0) \) and core-excited states \( \delta \alpha_{r''}(0) \). The RRPA static dipole core polarizabilities for alkali-metal atoms are known [23] to be in a 1\% agreement with those deduced from semiempirical analysis of Rydberg spectra; we approximate that \( \delta \alpha_r(0) \approx 0.01 \alpha_r(0) \). Further we estimate that \( \delta \alpha_r'(0) \approx \delta \alpha_p(0) \), 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 error bars of the final values of dispersion coefficients in Table I were calculated by adding the uncertainties \( \delta \omega C_6 \) and \( \delta_C C_6 \) in quadrature. For all considered alkaline-earth atoms the uncertainty in \( C_6 \) induced by errors in matrix elements of principal transition, \( \delta \omega C_6 \), dominates over \( \delta_C C_6 \). The estimated total uncertainties are in the order of 1-2\% for all alkaline-earth atoms, except for Sr where the accuracy is 5\%. Similar error analysis for alkali-metal atoms [23] 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 [27] 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 atoms. In our present calculation we rely on the quoted uncertainties of accurate dipole matrix elements listed in Table I.

A comparison with other theoretical and semiempirical determinations 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 $2740 \leq C_6 \leq 2830$ 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].

d. Conclusion. We carried out relativistic many-body calculations of van der Waals coefficients $C_6$ for dimers correlating to two ground state alkaline-earth 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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