

# High-Accuracy Calculations of Dipole, Quadrupole, and Octupole Electric Dynamic Polarizabilities and van der Waals Coefficients $C_6$ , $C_8$ , and $C_{10}$ for Alkaline-Earth Dimers

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**Abstract**—The static and dynamic electric dipole, quadrupole, and octupole polarizabilities of the alkaline-earth atoms (beryllium, magnesium, calcium, strontium, and barium) in the ground state were calculated. The dynamic polarizabilities obtained were used to calculate the van der Waals coefficients  $C_6$ ,  $C_8$ , and  $C_{10}$  of alkaline-earth metal dimers for the interaction of two like atoms in the ground state. The results are compared with other theoretical and experimental data.

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## 1. INTRODUCTION

Studies of the behavior of atoms at very low temperatures in magneto-optical traps are of the greatest current interest in modern atomic physics. Magneto-optical traps are used most extensively when atoms should be cooled to microkelvin or lower temperatures, because these are the temperatures at which several phenomena, virtually unstudied until recently, are observed. Quite a number of new directions in the field of atomic physics have been initiated to describe collisions of ultracold atoms, such as photoassociation and Feshbach resonance spectroscopy [1]. The use of magneto-optical traps has allowed the atomic condensate phenomenon to be observed for the first time. This phenomenon of the transition of bosonic atoms into the ground quantum-mechanical state at very low temperatures [2, 3] was predicted by Bose and Einstein as early as the 1930s. Another direction for using magneto-optical traps is the confinement of atoms in a trap at very low temperatures with the purpose of creating so-called “atomic optical clock,” that is, establishing a new standard of frequency based on one of the atomic transitions [4–6].

Until recently, the most important advances in studies of ultracold atomic collisions have been made with the use of alkali metal atoms. In particular, the Bose–Einstein condensate was for the first time obtained in 1995 for atomic rubidium. The interpretation of experimental data on alkali metal atoms is, however, very complex and ambiguous because of the presence of a fine structure in the ground state. Alkaline-earth atoms

in the ground state do not have this disadvantage. Their attractive feature is the existence of several isotopes with zero nuclear spins. The absence of hyperfine structure in them facilitates both theoretical and experimental studies of atomic interactions. Currently, magneto-optical traps have been obtained virtually for all alkaline-earth atoms (e.g., see [7–9]). This opens up new possibilities for studying interatomic interactions in them, which is necessary for understanding photoassociation phenomena and offers promise for preparing Bose–Einstein condensates.

The interaction of atoms in a cold trap at large interatomic distances is usually described in terms of dispersion (van der Waals) coefficients  $C_n$ . For two alkaline-earth atoms in the ground state, the long-range potential can be written as

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots, \quad (1)$$

where  $R$  is the distance between atomic nuclei.

We have already calculated the  $C_6$  coefficients [10]. The determination of  $C_6$  requires knowledge of the matrix elements of the E1 transitions from the ground  $^1S_0$  state to the intermediate states of the opposite parity  $^3,^1P_1^o$ . Recall that the equation for  $C_6$  contains the  $\langle ^3,^1P_1^o || d || ^1S_0 \rangle$  matrix elements raised to the fourth power. As the transition from the lower  $^1P_1^o$  state to the

ground  $^1S_0$  state is resonance in character (the corresponding E1 amplitude makes a  $\sim 90\%$  contribution to  $C_6$  [10]), it is clear that the E1 amplitude of this transition should be found with the highest accuracy possible. In [10], we used high-accuracy experimental lifetimes of low lying  $^1P_1^o$  states to determine the contribution of this amplitude to electric dynamic dipole polarizability and, accordingly, the  $C_6$  coefficient. However, in the past several years, new experimental lifetime data have been reported, and some of the earlier results have been revised by experimental physicists. This in particular resulted in a noticeable change in the  $C_6$  coefficient for Ca. The  $C_6$  coefficient for Sr can now be calculated much more accurately than previously. Since dispersion coefficients substantially influence the determination of scattering lengths necessary for describing the rate of cooling of low-temperature gases and condensate stability, it is in our view worthwhile to report new, more accurate values.

It follows from (1) that, apart from  $C_6$ , the long-range interaction potential is also characterized by the coefficients  $C_8$  and  $C_{10}$ . We used the relativistic method that combines configuration interaction (CI) and many-body perturbation theory (MBPT) to calculate these coefficients for Be, Mg, Ca, Sr, and Ba; estimated the accuracy of these values; and compared them with other theoretical and experimental results. Note that the  $C_8$  and  $C_{10}$  coefficients for Ba were calculated for the first time.

The paper is organized as follows. Section 2 contains general equations used in our calculations. The method for calculations is briefly described in Section 3, which also contains some technical details of constructing the wavefunctions that are necessary for the calculations. Section 4 presents a discussion of the results obtained and their comparison with literature data. The Conclusions contain a review of the modern state of the theoretical and experimental techniques and a discussion of possible improvements in the accuracy of calculations.

## 2. GENERAL FORMALISM

If two atoms  $a$  and  $b$  are in the ground spherically symmetrical state, their long-range interactions can conveniently be written as [11]

$$V(R) = - \sum_{n=3}^{\infty} \frac{C_{2n}^{ab}}{R^{2n}} \quad (2)$$

(we use the atomic system of units; that is,  $m = \hbar = |e| = 1$ ). It is easy to see that retaining the first three terms of this series leads to (1). The van der Waals coefficients for atoms in the ground state are given by

the equation [12]

$$C_{2n}^{ab} = \frac{(2n-2)!}{2\pi} \sum_{l=1}^{n-2} \frac{1}{(2l)!(2l)!} \times \int_0^{\infty} \alpha_l^a(i\omega) \alpha_l^b(i\omega) d\omega, \quad (3)$$

where  $l' = n - l - 1$  and  $\alpha_l^a(i\omega)$  and  $\alpha_{l'}^b(i\omega)$  are the  $2^l$ -pole and  $2^{l'}$ -pole dynamic polarizabilities of atoms  $a$  and  $b$ , respectively, defined as

$$\alpha_l(i\omega) = 2\text{Re} \sum_k \frac{\langle \Psi_{0l} | T_0^{(l)} | \Psi_k \rangle \langle \Psi_k | T_0^{(l)} | \Psi_0 \rangle}{(E_k - E_0) + i\omega}. \quad (4)$$

Here, the summation over intermediate states includes both discrete and continuous spectra and  $T_0^{(l)}$  stands for zero components of electric multipole operator tensors

$$T_m^{(l)} = \sum_{i=1}^N r_i^l C_m^{(l)}(\hat{\mathbf{r}}_i), \quad (5)$$

where  $C_m^{(l)}$  are the normalized spherical functions [13] and  $N$  is the number of electrons in the atom.

The  $C_6$ ,  $C_8$ , and  $C_{10}$  coefficients can conveniently be written as

$$\begin{aligned} C_6^{ab} &= C_{ab}(1, 1), \\ C_8^{ab} &= C_{ab}(1, 2) + C_{ab}(2, 1), \\ C_{10}^{ab} &= C_{ab}(2, 2) + C_{ab}(1, 3) + C_{ab}(3, 1), \end{aligned} \quad (6)$$

where the  $C_{ab}(l, l')$  values are, to within a factor, the integrals of the product of the  $2^l$ -pole and  $2^{l'}$ -pole dynamic polarizabilities. They are given by the equations

$$C_{ab}(1, 1) = \frac{3}{\pi} \int_0^{\infty} \alpha_1^a(i\omega) \alpha_1^b(i\omega) d\omega, \quad (7)$$

$$C_{ab}(1, 2) = \frac{15}{2\pi} \int_0^{\infty} \alpha_1^a(i\omega) \alpha_2^b(i\omega) d\omega, \quad (8)$$

$$C_{ab}(2, 2) = \frac{35}{\pi} \int_0^{\infty} \alpha_2^a(i\omega) \alpha_2^b(i\omega) d\omega, \quad (9)$$

$$C_{ab}(1, 3) = \frac{14}{\pi} \int_0^{\infty} \alpha_1^a(i\omega) \alpha_3^b(i\omega) d\omega. \quad (10)$$

If we consider the interaction of two like atoms in identical states, that is,  $a = b$ , the equations given above are simplified. It is, in particular, clear that  $C_{aa}(1, 2) = C_{aa}(2, 1)$  and  $C_{aa}(1, 3) = C_{aa}(3, 1)$ .

It follows from (7)–(10) that calculations of the coefficients require knowledge of the dipole  $\alpha_1(i\omega)$ , quadrupole  $\alpha_2(i\omega)$ , and octupole  $\alpha_3(i\omega)$  dynamic polarizabilities. Following [14, 15], the polarizability  $\alpha_l(i\omega)$  can conveniently be divided into three parts,

$$\alpha_l(i\omega) = \alpha_l^v(i\omega) + \alpha_l^c(i\omega) + \alpha_l^{cv}(i\omega), \quad (11)$$

where  $\alpha_l^v(i\omega)$  includes excitations of valence electrons;  $\alpha_l^c(i\omega)$ , excitations of core electrons; and  $\alpha_l^{cv}(i\omega)$  is a small correction to  $\alpha_l^c(i\omega)$ , which appears because of possible excitations of core electrons into the closed valence  $s$  shell, which is forbidden by the Pauli principle. The corresponding contribution should be subtracted from  $\alpha_l^c(i\omega)$ .

Note from the outset that  $\alpha_3^{cv}(i\omega) = 0$  for all atoms under consideration. Indeed, this contribution is caused by the excitation of  $f$  electrons into the valence  $s$  shell, whereas the alkaline-earth atoms do not have  $f$  electrons. As concerns  $\alpha_2(i\omega)$ , the main contribution to  $\alpha_2^{cv}(i\omega)$  is made by the excitations of core  $d$  electrons into the valence  $s$  shell. There are no core  $d$  electrons in Be, Mg, and Ca, and this contribution is therefore zero for them. For Sr and Ba, it is small to the extent that it can be ignored virtually without loss in accuracy. Lastly, the main contribution to  $\alpha_1^{cv}(i\omega)$  caused by the excitation of core  $p$  electrons is absent for Be only. For the other atoms, we include the  $\alpha_1^{cv}(i\omega)$  term into the final equation for  $\alpha_1(i\omega)$ .

The general approach to calculating the energies and various observables for atoms with several valence electrons has repeatedly been described; it is considered in detail in [16–18]. Recently, we applied it to calculate the multipole dynamic polarizabilities of alkali metal atoms [15]. Therefore, we shall only remind the reader of the main points here. All electrons of an atom are divided into two groups, one including core and the other, valence electrons. The valence electrons of alkaline-earth atoms are the two electrons on the highest energy level, whereas the other electrons constitute the core. Core–core and core–valence correlations are calculated using many-body perturbation theory, and the interaction between valence electrons, by the method of configuration interaction. Technically, this is done as

follows. An effective Hamiltonian is constructed in the space of valence electrons; it can be written as

$$H_{\text{eff}}(E_n)\Phi_n = E_n\Phi_n, \quad (12)$$

where

$$H_{\text{eff}}(E) = H_{FC} + \Sigma(E). \quad (13)$$

Here,  $H_{FC}$  is the Hamiltonian obtained in the frozen-core approximation and the energy-dependent correction  $\Sigma$  describes the virtual excitations of core electrons. In our approach, we fully took into account the second and, in part, higher perturbation theory orders. The latter should be considered separately. The matter is that, already at the stage of calculating second-order corrections to the Hamiltonian, we must, in addition to one-electron, calculate two-electron diagrams, which is a special feature of applying many-body perturbation theory to atoms with several valence electrons. The number of these diagrams is very large ( $>10^7$ ), and their calculations take enormous time even on modern supercomputers. Fortunately, there is no need to calculate all diagrams; the problem can usually be reduced to calculations of several hundred thousand diagrams virtually without loss in accuracy. Clearly, attempts at directly taking into account all third-order diagrams of many-body perturbation theory would cause great technical difficulties and can hardly be practicable. It is therefore more reasonable to include the higher orders of many-body perturbation theory partly and indirectly. According to [18], the quality of wavefunctions can be considerably improved by the introduction of energy shift  $\delta$  with the replacement  $\Sigma(E) \rightarrow \Sigma(E + \delta)$  in (13). The  $\delta$  parameter is selected to provide the best fit of the calculated energies to experiment. Practical calculations (e.g., see [10, 19, 20]) show that two or three  $\delta$  parameters are usually sufficient for reproducing both even and odd low-lying energy levels to high accuracy. Actually, the introduction of the  $\delta$  parameter corresponds to implicitly including the higher perturbation theory orders.

If the number of valence electrons is two or more, the method of configuration interaction explicitly describes their interactions with each other. This approach allows all types of interelectronic correlations to be included and increases the accuracy of level energy and various observable calculations by approximately one order of magnitude compared with the pure method of configuration interaction. Note that the approach under consideration is especially effective in high-accuracy calculations of divalent atoms. First, the presence of only two valence electrons allows “saturation” of the method of configuration interaction to be attained. The number of basis functions used is so large that the error arising from basis insufficiency can be ignored. These basis functions are used to construct all possible configurations in the valence space. This solves the problem of saturation in the method of con-

figuration interaction. No errors arise that are caused by not including all possible configurations within the framework of the basis sets constructed. Secondly, because of a more compact core, the convergence of perturbation theory series is better than, say, for alkali metal atoms. The second many-body perturbation theory order therefore gives high accuracy for both energies and E1 amplitudes.

In addition to the effective Hamiltonian, other effective operators that act in the model space of valence electrons can be constructed [17]. It is important that corrections for the screening of external electric fields by core electrons be taken into account. These corrections are introduced using the random phase approximation described in detail in [17, 21, 22].

After solving (12) by applying the approach described above, which combines the methods of configuration interaction and many-body perturbation theory (referred to as CI + MBPT for brevity), and obtaining the wavefunctions of the ground states, the dynamic polarizabilities  $\alpha_i^v(i\omega)$  are found by solving the inhomogeneous many-body Schrödinger equation with the use of the Sternheimer–Dalgarno–Lewis method [23, 24]. Let us introduce the wavefunction of intermediate states  $|\Psi_f\rangle$  defined as

$$\begin{aligned} |\Psi_f\rangle &= \text{Re} \left\{ \frac{1}{H_{\text{eff}} - E_0 + i\omega} \sum_i |\Psi_i\rangle \langle \Psi_i | (T_0^l)_{\text{eff}} | \Psi_0 \rangle \right\} \\ &= \text{Re} \left\{ \frac{1}{H_{\text{eff}} - E_0 + i\omega} (T_0^l)_{\text{eff}} | \Psi_0 \rangle \right\}, \end{aligned} \quad (14)$$

where  $\Psi_0$  and  $E_0$  are the wavefunction and energy of the ground state. The equation for  $\alpha_i^v(i\omega)$  then takes the simple form

$$\alpha_i^v(i\omega) = 2 \langle \Psi_0 | (T_0^l)_{\text{eff}} | \Psi_f \rangle. \quad (15)$$

Here,  $(T_0^l)_{\text{eff}}$  are the effective operators of electric multipole moments constructed by analogy with the effective Hamiltonian. We assume in what follows that these operators are constructed with the inclusion of self-energy corrections  $\Sigma$  and corrections calculated by the random phase approximation method.

As concerns the  $\alpha_i^c(i\omega)$  contribution, it is calculated by the relativistic random phase approximation method described in [21, 22]. The procedure does not differ basically from that applied in [15] to calculate similar contributions for alkali metal atoms.

### 3. METHOD OF CALCULATIONS

All the Be, Mg, Ca, Sr, and Ba atoms are treated as divalent, that is, as having two valence electrons above

the closed core. Beryllium has four core electrons  $[1s^2, 2s^2]$ , whereas the cores of the other atoms can be represented as  $[1s^2, \dots, np^6]$ , where  $n = 2, 3, 4,$  and  $5$  for Mg, Ca, Sr, and Ba, respectively. The scheme for constructing one-electron basis sets was approximately the same for all atoms. At the first stage, self-consistent solutions to the Hartree–Fock–Dirac equations for the configurations  $[1s^2, \dots, (n+1)s^2]$  ( $n = 1$  for Be) were obtained. As a result, the orbitals  $1s - (n+1)s$  were constructed in the  $V^N$  approximation. The next several orbitals (usually,  $(n+1)p$ ,  $nd$ , and  $(n+1)d$ ) were obtained in the  $V^{N-1}$  approximation. That is, the  $1s - (n+1)s$  orbitals were “frozen,” one electron was transferred from the valence  $s$  shell into one of the orbitals specified above, and the corresponding one-electron wavefunction was found by solving the Hartree–Fock–Dirac equations. Additional orbitals of the basis sets can be constructed as the products of one of the existing orbitals with powers of  $r$  or with  $\sin r$  with subsequent orthogonalization of the newly constructed orbital with respect to all the other. This recurrent scheme was described in detail in [25, 26]. Note that the number of orbitals in each partial wave for each atom was selected such that it ensured the numerical convergence of the method of configuration interaction. As a result, the one-electron basis sets used in calculations by the method of configuration interaction comprised the following orbitals:

Be, Mg, Ca:

$1s-13s, 2p-13p, 3d-12d, 4f-11f;$

Sr:

$1s-14s, 2p-14p, 3d-13d, 4f-12f, 5g-7g;$

Ba:

$1s-16s, 2p-16p, 3d-13d, 4f-13f, 5g-7g.$

(16)

At the stage of calculating self-energy corrections, we must include core electron excitations. Since we consider excitation of inner-shell electrons at this stage, and these shells may lie fairly deeply, we must take into account a large number of high-lying states. The corresponding basis sets should usually contain much more orbitals than the basis sets at the stage of configuration interaction. As is explained in detail in [16], this poses no problem, because different basis sets can be used for configuration interaction and performing many-body perturbation theory calculations, depending on the particular atom under consideration and the problem to be solved. In this work, extended basis sets necessary for calculating self-energy corrections included the orbitals  $1s-ks, 2p-kp, 3d-(k-1)d, 4f-(k-4)f,$  and  $5g-(k-8)g$ , where  $k = 18, 19, 20, 21,$  and  $22$  for Be, Mg, Ca, Sr, and Ba, respectively.

## 4. RESULTS AND DISCUSSION

### 4.1. Dipole Electric Polarizabilities

We begin with dipole electric polarizabilities. For alkaline-earth atoms in the ground  $^1S_0$  state,  $\alpha_1^\vee(i\omega)$  can conveniently be written in terms of reduced matrix elements as

$$\alpha_1^\vee(i\omega) = \frac{2}{3} \sum_a \frac{(E_a - E_{1S_0}) |\langle ns^2 1S_0 \| d \| a \rangle|^2}{(E_a - E_{1S_0})^2 + \omega^2}. \quad (17)$$

Here  $E_a$  and  $E_{1S_0}$  are the energies of intermediate and ground states and  $d \equiv (T^1)_{\text{eff}}$  denotes the effective electric dipole moment operator. Let us single out the term of (17) that characterizes the  $E1$  transition from the ground state to the lowest  $^1P_1^o$  state and makes the major contribution to the dipole electric polarizability of the ground state  $^1S_0$ . We can then write  $\alpha_1^\vee(i\omega)$  as the sum of two terms

$$\alpha_1^\vee(i\omega) = \alpha_{1,p}^\vee(i\omega) + \alpha_1^{\vee'}(i\omega), \quad (18)$$

where

$$\alpha_{1,p}^\vee(i\omega) = \frac{2}{3} \frac{\Delta E_p}{(\Delta E_p)^2 + \omega^2} \times |\langle ns^2 1S_0 \| d \| nsnp^1P_1^o \rangle|^2. \quad (19)$$

Here,

$$\Delta E_p \equiv E_{nps^1P_1^o} - E_{ns^2 1S_0},$$

and  $\alpha_1^{\vee'}(i\omega)$  includes all the other terms of the sum over  $a$  in (17); that is,

$$\alpha_1^{\vee'}(i\omega) = \alpha_1^\vee(i\omega) - \alpha_{1,p}^\vee(i\omega).$$

With the core contributions included, the total polarizability  $\alpha_1(i\omega)$  can be written as

$$\alpha_1(i\omega) = \alpha_{1,p}^\vee(i\omega) + \alpha_{1,r}(i\omega), \quad (20)$$

where

$$\alpha_{1,r}(i\omega) = \alpha_1^{\vee'}(i\omega) + \alpha_1^c(i\omega) + \alpha_1^{c\vee}(i\omega). \quad (21)$$

The reason for such partitioning is as follows. The  $\alpha_{1,p}^\vee(i\omega)$  term makes a determining contribution to  $\alpha_1(i\omega)$ . This contribution amounts to 90% even for Ba and 97% for Be. Accordingly, the accuracy of calculating  $\alpha_1(i\omega)$  is to a great extent determined by the accuracy of the  $\alpha_{1,p}^\vee(i\omega)$  value. For obtaining the highest

accuracy, it appears reasonable to correct dipole polarizabilities found by solving inhomogeneous equation (4).

We single out the  $\alpha_{1,p}^\vee$  contribution and recalculate it using the experimental energy levels from [27] and the most accurate matrix element  $\langle ^1P_1^o \| d \| ^1S_0 \rangle$  values published.

Table 1 summarizes the results obtained for static electric polarizabilities, that is, polarizabilities at  $\omega = 0$ . The table contains both final and recommended values. The former were obtained by numerically solving the inhomogeneous equation to obtain  $\alpha_1^\vee(0)$  and adding core contributions to this value. The recommended values were found by refining the results through using the values listed in Table 2 as ‘‘best.’’ In some instances, recommended values differ somewhat from final. In particular, we used the experimental high-accuracy lifetimes of the low-lying  $^1P_1^o$  states for Ca [28] and Sr [29] to obtain very accurate matrix element values,  $\langle ^1P_1^o \| d \| ^1S_0 \rangle = 4.905(22)$  au for Ca and  $\langle ^1P_1^o \| d \| ^1S_0 \rangle = 5.249(2)$  au for Sr. These values were used to calculate polarizabilities the most accurately.

As has been mentioned above, the error in  $\alpha_1(0)$  is largely determined by the error in  $\alpha_{1,p}^\vee(0)$ . As the level energies are known to a very high accuracy, they barely at all contribute to errors in the calculated  $\alpha_{1,p}^\vee(0)$  values, which are, therefore, almost fully determined by the uncertainties in the  $\langle ^1P_1^o \| d \| ^1S_0 \rangle$  matrix elements. The  $\alpha_1^{\vee'}$ (0),  $\alpha_1^c$ (0), and  $\alpha_1^{c\vee}$ (0) terms introduce additional errors into the final  $\alpha_1(0)$  value. It follows from (20) and (21) that, ignoring the small term  $\alpha_1^{c\vee}$ , the absolute error  $\Delta\alpha_1$  can be represented in the form

$$\Delta\alpha_1 = \{ (\alpha_{1,p}^\vee)^2 (\delta\alpha_{1,p}^\vee)^2 + (\alpha_1^{\vee'})^2 (\delta\alpha_1^{\vee'})^2 + (\alpha_1^c)^2 (\delta\alpha_1^c)^2 \}^{1/2}, \quad (22)$$

where  $\delta\alpha$  is the relative error defined as  $\delta\alpha = \Delta\alpha/\alpha$ .

Since the uncertainty in  $\langle ^1P_1^o \| d \| ^1S_0 \rangle$  is known, it is easy to find the error in  $\delta\alpha_{1,p}^\vee$ . As far as the second and third terms on the right-hand side of (22) are concerned, the method for calculating them was described in [10]. The  $\delta\alpha_1^{\vee'}$  value can be estimated as

$$\delta\alpha_1^{\vee'} \sim \frac{\alpha_{1,\text{num}}^\vee - \alpha_{1,\text{acc}}^\vee}{\alpha_{1,\text{num}}^\vee},$$

where  $\alpha_{1,\text{num}}^\vee$  is the  $\alpha_{1,p}^\vee$  term calculated with the  $\langle ^1P_1^o \| d \| ^1S_0 \rangle$  matrix element and the energies obtained

**Table 1.** Static dipole polarizabilities  $\alpha_1$  for the ground states of alkaline-earth atoms: valence contributions for CI and CI + MBPT, core contributions, final results including all terms according to (20), and recommended values (see text)

	Be	Mg	Ca	Sr	Ba
$\alpha_1^v$ (CI)	37.84	72.24	175.0	230.3	333.9
$\alpha_1^v$ (CI + MBPT)	37.71	70.89	155.9	196.6	262.2
$\alpha_1^c + \alpha_1^{vc}$	0.05	0.44	3.1	5.4	9.9
Final	37.76	71.33	159.0	202.0	272.1
Recommended	37.76(22)	71.3(7)	157.1(1.3)	197.2(2)	273.5(2.0)
Other theoretical works					
[30]	37.69	71.35	159.4	201.2	
[31]	37.9	72.0	152.7	193.2	
[32]		71.7	157		
[33]	36.7	70.5	153.7		
[34]	37.76				
[35]	37.3 (7)				
Experimental					
[36]		71.5 (3.1)			
[28]			168.7 (13.5)		
[37]				186 (15)	
[38]					268 (22)

**Table 2.** Reduced matrix elements  $|\langle nsn p^1 P_1^0 || d || ns^2 1 S_0 \rangle|$  for transitions from the ground state to the  $nsnp^1 P_1^0$  state

	$ \langle ^1 P_1^0    d    ^1 S_0 \rangle $		$E_{1P_1^0} - E_{1S_0}$	
	this work	the best value	this work	experimental <sup>a</sup>
Be	3.26	3.26(1) <sup>b</sup>	0.193928	0.193942
Mg	4.03	4.03(2) <sup>c</sup>	0.159743	0.159705
Ca	4.93	4.905(22) <sup>d</sup>	0.107776	0.107768
Sr	5.31	5.249(2) <sup>e</sup>	0.098508	0.098866
Ba	5.475	5.466(23) <sup>f</sup>	0.082313	0.082289

Note: Here,  $n = 2, 3, 4, 5,$  and  $6$  for Be, Mg, Cs, Sr, and Ba, respectively. The values obtained in this work and “the best literature values” from <sup>a</sup> [27], <sup>b</sup> [10], <sup>c</sup> [19, 20], <sup>d</sup> [28], <sup>e</sup> [29], and <sup>f</sup> [39] are given.

in this work and  $\alpha_{1,acc}^v$  is the  $\alpha_{1,p}^v$  term calculated using the best values (see Table 2). Lastly, the term containing  $\delta\alpha_1^c$  on the right-hand side of (22) is fairly small even for Ba (Table 1). It was shown in [10] that the error in its calculated values can be estimated at  $\delta\alpha_1^c \sim 0.01$  for alkaline-earth atoms.

The final results for the static dipole polarizabilities obtained in this work and other theoretical and experi-

mental data are listed in Table 1. As follows from the above discussion and seen from the table, the polarizabilities were determined most accurately for the light Be and Mg atoms and least accurately for Ba. This is a reasonable result for calculations by the methods of configuration interaction and many-body perturbation theory.

It has already been noted that the error of calculations at the stage of the configuration interaction was virtually zero because superposition was complete. At

**Table 3.** Contributions to static quadrupole polarizabilities  $\alpha_2$  for the ground states of alkaline-earth atoms: valence contributions for CI and CI + MBPT, core contributions, and final results (here, final is equivalent to recommended)

	Be	Mg	Ca	Sr	Ba
$\alpha_2^v$ (CI)	304.8	877.3	3632	5767	11235
$\alpha_2^v$ (CI + MBPT) $_{\delta=0}$	301.2	822.7	3028	4597	7530
$\alpha_2^v$ (CI + MBPT) $_{\delta \neq 0}$	300.6	811.5	3074	4613	8850
$\alpha_2^c$	0.015	0.5	6.9	17	46
Final	300.6(3)	812(6)	3081(23)	4630(8)	8900(650)
Other theoretical works					
[30]	300.7	813.9	3063	4577	
[32]		809.3	3016		
[33]	302.6	828	2717		
[34]	301.0				
[35]	298.8 (2.6)				

the stage of many-body perturbation theory calculations, second order of perturbation theory was included completely, and the higher orders, only partly. This was the main source of errors and limited the accuracy of calculations. Naturally, the heavier the atom, the larger the number of electrons that it has, the more important interelectronic core–core and core–valence interactions are, and the greater the role played by perturbation theory. Accordingly, the role played by the higher orders of perturbation theory increases as the number of electrons in the atom grows.

The above reasoning is illustrated in Table 1 by the results obtained using pure configuration interaction, configuration interaction combined with many-body perturbation theory, and the final equations for polarizabilities including the  $\alpha_1^c(0)$  and  $\alpha_1^{cv}(0)$  terms. The difference between the values obtained at the stages of configuration interaction and configuration interaction combined with many-body perturbation theory characterizes the role played by perturbation theory corrections for every atom and thereby the corresponding accuracy level.

A comparison of the results obtained in this work with other data shows that the lighter the atom, the closer the agreement of the results obtained by different theoretical groups. This is explained by a decrease in the role played by electron correlation as the number of electrons becomes smaller, because the accurate inclusion of electron correlation is usually a very nontrivial task. As a consequence, the accuracy of calculations increases for light atoms. Note that, in spite of the spread of theoretical results, they all agree with the experimental values to within measurement errors. The primary reason for this is the low accuracy of experi-

mental data. Since theoretical accuracy is in many cases superior to experimental, performing new experiments with the purpose of more accurately measuring static dipole polarizabilities is a topical problem of timely interest.

#### 4.2. Quadrupole and Octupole Electric Polarizabilities

Quadrupole and octupole electric polarizabilities were calculated by analogy with dipole electric polarizabilities by solving inhomogeneous many-body Schrödinger equation (4). The calculation results are listed in Tables 3 and 4. As distinct from dipole polarizabilities, transitions from the ground  $^1S_0$  state to low-lying excited states of the corresponding parity do not make determining contributions to quadrupole and octupole electric polarizabilities. In addition, the accuracy of determining the matrix elements is lower for the E2 and E3 transitions than for the electric dipole transitions.

At the same time, we determined the errors in these values following the same line of reasoning as with dipole polarizabilities, because the major contribution is, as previously, made by higher orders of perturbation theory included indirectly. On this assumption, the uncertainty in electric quadrupole polarizability can be approximately estimated as half the difference between the polarization values obtained with and without taking into account higher orders of perturbation theory; that is,

$$\Delta\alpha_2(0) \sim \frac{1}{2} |(\alpha_2(0))_{\delta=0} - (\alpha_2(0))_{\delta \neq 0}|. \quad (23)$$

**Table 4.** Contributions to static octupole polarizabilities divided by  $10^3$  for the ground states of alkaline-earth atoms: valence contributions for CI and CI + MBPT, core contributions, and final results (here, final is equivalent to recommended)

	Be	Mg	Ca	Sr	Ba
$\alpha_3^v$ (CI)	3.837	14.70	75.40	138.1	282.5
$\alpha_3^v$ (CI + MBPT) $_{\delta \neq 0}$	3.781	13.51	61.58	106.3	205.6
$\alpha_3^c$	$10^{-5}$	$10^{-3}$	0.034	0.11	0.41
Final	3.781	13.51	61.62	106.4	206.0
Other theoretical works					
[30]	3.955	14.02	65.12	107.2	
[31]	3.488	11.7	50.8	80.7	
[33]	4.126	14.74	61.51		

Here,  $(\alpha_2(0))_{\delta=0}$  is the static quadrupole polarizability of the ground state calculated at  $\delta = 0$ , which corresponds to disregarding higher orders of perturbation theory. The polarizability  $(\alpha_2(0))_{\delta \neq 0}$  was calculated at a certain nonzero  $\delta$  value, that is, implicitly including higher orders of perturbation theory. It should be borne in mind that we always selected the  $\delta$  value that most closely reproduced the energies of the ground and low-lying  $^1D_2$  states. This improved the corresponding wavefunctions and therefore refined the contribution of the E2 amplitude of the  $^1S_0 \rightarrow ^1D_2$  transition to quadrupole polarizability. The contribution of the other intermediate states was, however, appreciable, and the procedure specified did not result in improvement of the final result as clearly as with dipole polarizabilities.

Unfortunately, we were unable to find experimental data on static quadrupole polarizabilities of alkaline-earth atoms and can therefore only compare our results with those reported by other theoretical groups. Table 3 shows that the agreement between different calculations is quite satisfactory in spite of the problems mentioned above. Our results are especially close to those reported by Mitroy and Bromley [30], who included a large number of intermediate states in their calculations. Because none of the low-lying intermediate states made a predominant contribution to quadrupole polarizability, it was very important to accurately perform the summation over the whole spectrum. Intermediate states of both discrete and continuous spectra could accurately be included without formal summation over all intermediate states by solving the inhomogeneous Schrödinger equation. As far as we know, this method was used in the present work only, which allows us to claim high accuracy of the results obtained.

The results for octupole polarizabilities are listed in Table 4. Reasoning similar to that applied to quadrupole polarizabilities shows that the error in the calcu-

lated octupole polarizabilities does not exceed 10%. A more meticulous analysis of errors is, we believe, unnecessary. Indeed, the main goal of this work is calculations of the van der Waals coefficients that characterize long-range interatomic interaction potential. Equations (6)–(10) show that dynamic octupole polarizability appears in the  $C_{10}$  coefficient only. It is well known that van der Waals series (2) diverges, and high-accuracy calculations of  $C_{10}$  with neglect of the other series terms whose contribution to the potential is only slightly smaller than  $C_{10}/R^{10}$  does not make sense. The requirements on the accuracy of  $C_{10}$  and, accordingly, octupole polarizability calculations are therefore much lower than with  $C_6$  and  $C_8$ .

#### 4.3. The van der Waals Coefficients $C_6$ , $C_8$ , and $C_{10}$

Let us turn to the van der Waals coefficients  $C_6$ ,  $C_8$ , and  $C_{10}$ . Calculating them with the use of (6)–(10) poses no serious difficulties if we know the dynamic multipole polarizabilities. The  $C_6$  coefficients are listed in Table 5, which also contains the results obtained by other authors for comparison. In particular, our own results obtained several years ago are included. Comparison shows that the coefficient values remained unchanged for Be, Mg, and Ba; for Ca and Sr, the  $C_6$  coefficients and their uncertainties changed. For both atoms, this is the result of the refinement of the E1 amplitudes of transitions from the ground state into the odd low-lying  $^1P_1^o$  state. For Sr, the lifetime  $\tau$  of the  $5s5p\ ^1P_1^o$  state was measured in [29] with unprecedented accuracy to obtain  $\tau = 5.263(4)$  ns. This allowed us to calculate the matrix element of the E1 transition  $^1S_0 \rightarrow ^1P_1^o$  and, eventually, the  $C_6 = 3103(7)$  coefficient with accuracy no worse than 0.2%. As far as we



**Table 5.** Van der Waals coefficients  $C_6$  of alkaline-earth dimers comprising atoms in the ground state  $^1S_0$ 

Final	Be	Mg	Ca	Sr	Ba
	214(3)	627(12)	2121(35)	3103(7)	5160(74)
Other theoretical works					
[10]	214(3)	627(12)	2221(15)	3170(196)	5160(74)
[30]	213	629.5	2188	3249	
[41]	216	648	2042	3212	
[42]	220	634	2785		
[33]	208	618	2005		
[43]	254		2370		
Experimental					
[40]			2080(7)		
[44]		683(35)			

**Table 6.** Van der Waals coefficients  $C_8$  of alkaline-earth dimers comprising atoms in the ground state  $^1S_0$ ;  $10^{-4}C_8$  values are given

Final	Be	Mg	Ca	Sr	Ba
	1.023(6)	4.15(5)	22.3(3)	37.92(8)	77.2(4.6)
Other theoretical works					
[30]	1.022	4.164	22.6	38.54	
[42]	1.04–1.09	4.11–4.35	19.0–24.9		
Experimental					
[40]			28.5(5.0)		
[44]		3.8(8)			

know, such accuracy is unparalleled in calculations of van der Waals coefficients.

The situation with Ca is opposite to a degree. In 2003, Tiemann *et al.* (Germany) published new data on the probability of the transition from the  $4s4p\ ^1P_1^o$  state to the ground  $4s^2\ ^1S_0$  state,  $\gamma = 2.150(19) \times 10^8\ \text{s}^{-1}$  [28]. This value was different from  $\gamma = 2.205(8) \times 10^8\ \text{s}^{-1}$  reported by the same group earlier [8]. As a consequence, the matrix element of the E1 transition  $^1S_0 \rightarrow ^1P_1^o$  and the  $C_6$  coefficient also changed. Note that  $C_6 = 2121(35)$  obtained for Ca in this work is much closer to the experimental value 2080(7) [40] than our earlier result 2221(15) [10] based on less accurate experimental data from [8]. Note also that the new matrix element value,  $\langle 4s^2\ ^1S_0 || d || 4s4p\ ^1P_1^o \rangle = 4.905(22)$  au, obtained from the most recent data [28] became closer to our numerical result 4.93 au than previously.

The method for estimating errors in calculated  $C_6$  coefficients was discussed in detail in [10]. We shall therefore only briefly remind the reader that the largest

error is introduced in  $C_6$  by uncertainties in the  $\langle ns^2\ ^1S_0 || d || nsnp\ ^1P_1^o \rangle$  matrix elements. This is clearly seen from the results listed in Table 5 (especially the results obtained for Sr). In our view, new high-accuracy experimental measurements of, for instance, the lifetimes of low-lying  $^1P_1^o$  levels would improve the accuracy of determining the  $C_6$  coefficients for two alkaline-earth atoms that interact with each other in the ground state.

A comparison of our results with other data reveals a picture closely similar to that with polarizabilities. Agreement between the results reported by various groups is closer for light and less close for heavy atoms. Our results are closest to those reported by Mitroy and Bromley [30] for all atoms except strontium. For the latter, the value obtained in this work on the basis of the high-accuracy experimental data [29] is smaller by 4%.

The general approach to calculating errors in  $C_8$  and  $C_{10}$  was described in [15]; this approach was applied to alkali metal atoms. The same technique is equally applicable to alkaline-earth atoms. For this reason, we

**Table 7.** Van der Waals coefficients  $C_{10}$  of alkaline-earth dimers comprising atoms in the ground state  $^1S_0$ ;  $10^{-6}C_{10}$  values are given

Final	Be	Mg	Ca	Sr	Ba
	0.5043	2.757	21.32	42.15	101.4
Other theoretical works					
[30]	0.5165	2.817	22.00	42.50	
[42]	0.51–0.56	2.73–3.04	17.7–22.8		
Experimental					
[40]			13(10)		

shall omit details and write the final result right away. The uncertainty in the van der Waals coefficients is directly related to errors in dynamic multipole polarization calculations. It is easy to see from (7)–(10) that the  $C_{ab}(l, l')$  values are largely “built up” in the region  $\omega \approx 0$ . The errors in polarizabilities being known, the relative error in  $C_{ab}(l, l')$  can therefore be estimated as

$$\frac{\Delta C_{ab}(l, l')}{C_{ab}(l, l')} \approx \left\{ \left( \frac{\Delta \alpha_l(0)}{\alpha_l(0)} \right)^2 + \left( \frac{\Delta \alpha_{l'}(0)}{\alpha_{l'}(0)} \right)^2 \right\}^{1/2} \quad (24)$$

It follows that, for the interaction of two like atoms, the uncertainty in  $C_8$  can be written as

$$\frac{\Delta C_8^{aa}}{C_8} \approx \left\{ \left( \frac{\Delta \alpha_1(0)}{\alpha_1(0)} \right)^2 + \left( \frac{\Delta \alpha_2(0)}{\alpha_2(0)} \right)^2 \right\}^{1/2} \quad (25)$$

The final van der Waals coefficient values are listed in Tables 5–7.

## 5. CONCLUSIONS

Note in conclusion once more that, in this work, we calculated the electric dipole, quadrupole, and octupole dynamic polarizabilities of alkaline-earth atoms in the ground state. The static polarizabilities  $\alpha_1$ – $\alpha_3$  obtained from the dynamic polarizabilities at  $\omega = 0$  are listed in the tables and compared with other results found in the literature. Unfortunately, high-accuracy experimental data that might be used to test the calculation results are nearly absent at present. The dynamic polarizabilities found were used to calculate the  $C_6$ ,  $C_8$ , and  $C_{10}$  van der Waals coefficients; the errors in their values were estimated. Note that the  $C_8$  and  $C_{10}$  coefficients for barium were calculated for the first time.

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