High-Precision Calculations of the $^{3,1}P_1^o \to {}^1S_0$ E1 Amplitudes for Magnesium, Calcium, and Strontium

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High-precision calculations of the $^{3,1}P_1^o (nsnp) \longrightarrow {}^1S_0(ns^2)$ E1 amplitudes were carried out for magnesium, calcium, and strontium ($n = 3, 4$, and 5, respectively). The following results are obtained for the reduced matrix element $\langle {}^{3,1}P_1^o \| d \| {}^1S_0 \rangle$ of electric dipole moment operator: 4.03(2) au for Mg, 4.91(7) au for Ca, and 5.28(9) au for Sr. These matrix elements are necessary for calculating the van der Waals coefficients C_6, which are used in the evaluation of the atomic scattering lengths. The latter determine the dynamics and stability of Bose–Einstein condensate. © 2000 MAIK "Nauka/Interperiodica".

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In this work, high-precision calculations of the $^{3,1}P_1^o (nsnp) \longrightarrow {}^1S_0(ns^2)$ E1 amplitudes were carried out for magnesium, calcium, and strontium ($n = 3, 4$, and 5, respectively). The computations were motivated by the following reasons. First, in recent years a considerable success has been achieved in the development of magneto-optic traps. Atomic capture followed by atom cooling makes it possible to study the atomic interactions at ultralow temperatures. Most experiments were carried out with alkali atoms, for which it is possible to achieve high densities and low temperatures and observe Bose–Einstein condensate. However, the interpretation of the experimental data for these systems is quite complicated and ambiguous, in particular, because of the presence of ground-state hyperfine structure in alkali atoms. For example, the authors of recent works [1, 2] draw antithetical conclusions about the possibility of obtaining Bose–Einstein condensate for cesium.

An attractive feature of the bivalent atoms is that they have several isotopes with zero nuclear spin. The absence of the hyperfine structure in these atoms facilitates both experimental and theoretical study of atomic interactions. Since the cold traps were already obtained for magnesium, calcium, and strontium, the new possibilities of studying their interatomic interactions and the prospects for achieving Bose–Einstein condensate of these atoms have been actively discussed, e.g., in [3–5].

The dispersion (van der Waals) coefficient C_6 is one of the main parameters characterizing the dipole–dipole interaction of atoms in a cold trap. This coefficient is necessary for evaluating the atomic scattering lengths, which determine the dynamics and stability of the Bose–Einstein condensate. To calculate the C_6 coefficient, one should know the matrix elements for the E1

transitions from the low-lying odd-parity states to the ground state (see, e.g., [6, 7]). It is worth noting that the expression for C_6 contains the fourth power of matrix elements $\langle {}^{3,1}P_1^o \| d \| {}^1S_0 \rangle$ and, considering the resonant character of the $^1P_1^o \longrightarrow {}^1S_0$ transition (the contribution of the corresponding E1 amplitude to $C_6 \sim 90\%$ [8]), it becomes clear that the E1 amplitude of this transition should be determined with the highest possible accuracy.

Another motive is as follows. Despite the fact that the oscillator strengths and lifetimes of the $^3P_1^o$ and $^1P_1^o$ states were repeatedly determined both theoretically and experimentally [4, 9–12], the results for all three atoms are quite contradictory. In particular, the discrepancies between the data of different experimental groups are as great as 70%. Therefore, high-precision calculations of the above-mentioned E1 amplitudes appear to be well-timed and topical.

We used a method combining the configuration interaction (CI) and the many-body perturbation theory (MPT). This method was developed by our group over several recent years and successfully applied to the energies of low-lying levels and various observables in some atoms [13]. Since the method is described in detail in the cited papers, we only outline its basic positions. The MPT is used to construct effective operators (Hamiltonian, electric dipole moment operator, etc.) for valence electrons. In doing so, the interaction between valence and core electrons is taken into account. Next, if the number of valence electrons is two or more, the CI is used to account for the interaction between them. This approach describes both the interaction between valence electrons and the valence–core

correlations and, thereby, improves the accuracy of calculating level energies and various observables by an order of magnitude, as compared to the pure CI method. It should be noted that this method is particularly efficient in the high-precision calculations of bivalent atoms. First, the presence of only two valence electrons allows one to apply full CI. In this case, the number of basis functions is taken to be so large that the error introduced by the incomplete basis set is negligible. Therefore, the problem of unsaturated CI (typical of the systems with many valence electrons) does not arise. Second, due to the compact core, the perturbation series converges better than for the alkali atoms. Because of this, even the second-order MPT provides a good accuracy for both energies and $E1$ amplitudes.

The aforesaid indicates that the combination of CI and MPT (CI+MPT) is highly appropriate for our calculations. We omit the detailed description of the computational procedure (it will be given elsewhere) and pass on to the numerical results for the reduced matrix elements $\langle ^{3,1}P_1^o \| d \| ^1S_0 \rangle$ for Mg, Ca, and Sr. For comparison, we present the results obtained for all three atoms by two methods, pure CI and CI+MPT. In the latter case, we took into complete account the second order and partially included the higher-order MPT corrections. As regards these latter, the following should be pointed out. Specific to the MPT for the atoms with several valence electrons, both one- and two- electron diagrams need to be calculated at the step of obtaining the second-order corrections to the Hamiltonian. There are great many of such diagrams ($>10^7$), whose evaluation is a rather time-consuming procedure even for modern supercomputers. Fortunately, there is no need to calculate all the diagrams and one usually restricts oneself to the evaluation of several hundred of thousands of diagrams practically without any loss in accuracy. However, it is clear that an attempt at taking account of all the third-order diagrams will face immense technical obstacles and is hardly feasible in practice.

In this connection, a variant with partial inclusion of high- order diagrams in an indirect way seems to be more reasonable. One such method is used in this paper. This method was proposed in [14], where, in particular, it was demonstrated that the agreement between the calculated and experimental spectra of many-electron atoms can be substantially improved by choosing an optimal one-electron Hamiltonian. Below, the optimized effective Hamiltonian is used for calculating the atomic observables. When constructing the effective electric dipole moment operator and at the step of $E1$ amplitude calculations, the RPA equations were solved and one- and two-particle corrections to the RPA were evaluated (including corrections for the normalization of wave functions and for the structure emission). This procedure is described in detail in [15]. Note that, when solving the RPA equations, we effectively sum a certain subsequence of all-order MPT diagrams. The RPA

equations were solved at frequency $\omega = E(^1P_1^o) - E(^1S_0)$ for all three atoms. Both length (L) and velocity (V) gauges were used in the calculations. This allowed the control of computational accuracy and was helpful in the estimation of theoretical error. The results are presented in the table.

One can see that the difference between the L- and V-gauge results for the $E1$-allowed $^1P_1^o \longrightarrow {}^1S_0$ transition is 0.3% for Mg, 0.5% for Ca, and 0.8% for Sr. For the $^1P_1^o \longrightarrow {}^1S_0$ transition, the corresponding $E1$ amplitudes are small. This transition is accompanied by a change in the total spin S and, hence, its amplitude is suppressed. Mathematically, this is a result of multiple mutual cancellations of the major contributions that come from the one-electron matrix elements $\langle np_{1/2} \| d \| ns \rangle$ and $\langle np_{3/2} \| d \| ns \rangle$ ($n = 3$, 4, and 5 for Mg, Ca, and Sr, respectively). This, naturally, impairs the computational accuracy. Nevertheless, the corresponding L- and V-gauge results coincide at a 6% level and are quite satisfactory. The V-gauge matrix element of electric dipole moment operator is written as (atomic units $\hbar = e = m = 1$ are used)

$$\langle f | \mathbf{d} | i \rangle = ic \langle f | \alpha | i \rangle / (E_i - E_f).$$

Here, c is the speed of light, E_i and E_f are the energies of the initial and final states, respectively, and α are the Dirac matrices. Hence, a good result for the V gauge can be obtained if not only the matrix elements of dipole moment operator but also the transition energies are properly calculated. For all three atoms, the $^3P_1^o$, $^1P_1^o$, and $^1S_0$ energies were reproduced with a very high accuracy ($\leq 0.1\%$).

It is worth noting that, for all six transitions (see table), the V-gauge values obtained at the CI step are closer to the final results than the corresponding L-gauge values. Unfortunately, this fact does not imply that the V gauge is more trustworthy in this case. Although the contribution of MPT to the final result is lesser for the velocity gauge, this is so because of multiple cancellations of various perturbative corrections, each being several times larger in magnitude than for the length gauge. As a result, the V gauge is much more sensitive to the high-order MPT corrections than the L gauge is. For this reason, the length-gauge values are taken as the final results of our calculations.

Note that the major error in the results is caused by the fact that all-order MPT cannot be realized. As was mentioned above, the CI is saturated and does not introduce any additional errors. Therefore, the smaller the MPT corrections the smaller the resultant error. In addition, the computational error was estimated with allowance made for the proximity of the L- and V-gauge results. The MPT yields the following corrections to the

L- and *V*-gauge reduced matrix elements $|\langle ^{1,3}P_1^\circ \| d \| ^1S_0 \rangle|$ (au) calculated for Mg, Ca, and Sr

Transition	Mg		Ca		Sr	
	CI	CI + MPT	CI	CI − MPT	CI	CI + MPT
$^1P_1^\circ \longrightarrow {}^1S_0$						
L gauge	4.09	4.03	5.20	4.91	5.63	5.28
V gauge	4.07	4.04	5.11	4.89	5.48	5.32
Resultant value	4.03(2)		4.91(7)		5.28(9)	
Experiment	4.15(10) [9]		4.967(9) [4]		5.57(6) [10]	
	4.06(10) [17]		4.99(4) [10]		5.40(8) [18]	
	4.12(6) [19]		4.93(11) [20]			
$^3P_1^\circ \longrightarrow {}^1S_0$						
L gauge	0.0055	0.0064	0.027	0.034	0.123	0.161
V gauge	0.0062	0.0062	0.030	0.032	0.133	0.172
Resultant value	0.0064(7)		0.034(4)		0.161(16)	
Experiment	0.0053(3) [21]		0.0357(4) [22]		0.1555(16) [23]	
	0.0056(4) [24]		0.0352(10) [25]		0.1510(18) [25]	
	0.0061(10) [26]		0.0357(16) [27]		0.1486(17) [28]	

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L-gauge $^1P_1^o \longrightarrow {}^1S_0$ *E*1 amplitudes: 1.6% for Mg, 5.5% for Ca, and 6.4% for Sr (table).

Our final $|\langle ^1P_1^o \| d \| ^1S_0 \rangle|$ values, which can be used for the subsequent calculations (e.g., of the C_6 coefficients), are as follows: 4.03(2) for Mg, 4.91(7) for Ca, and 5.28(9) for Sr. Note that the $P_1 \longrightarrow {}^1S_0$ transition probability in Ca was recently experimentally found to be $2.205(8) \times 10^8$ s^{-1} [4]. Being recalculated to the corresponding transition amplitude, this gives 4.967(9) au. The experimental accuracy of 0.2% is unprecedented for the *E*1 amplitude and far exceeds the accuracy of our calculation. At the same time, this enables us to check the reliability of the estimated computational accuracy. As for Mg and Sr, the accuracy of our results is higher than the experimental accuracy for the former and is at a level of the best experimental results for the latter.

The MPT contributions to the $^3P_1 \longrightarrow {}^1S_0$ transitions are considerably greater for the *L* gauge, which we believe to be more reliable than the *V* gauge. In addition, due to multiple cancellations (reaching 99%, e.g., for magnesium) of the major contributions, the role of high-order corrections is much greater for these transitions. In particular, it was demonstrated in [16] that the inclusion of Breit interaction reduces by ~5% the $^3P_1 \longrightarrow {}^1S_0$ transition amplitude for magnesium. For this reason, we estimate the computational error for this E1 amplitude at a level of 10–12% for all three atoms.

In conclusion, note once more that we have calculated the $\langle ^3P_1^o \| d \| ^1S_0 \rangle$ and $\langle ^1P_1^o \| d \| ^1S_0 \rangle$ matrix elements with emphasis on high-precision calculations of the singlet–singlet transitions. As expected, the best accuracy is obtained for Mg (0.5%) and it equals 1.4% for Ca and 1.7% for Sr. The accuracy obtained for magnesium is the best in the world and the results for calcium and strontium are the best among the theoretical works. As pointed out above, the major error in our calculations is due to the incomplete inclusion of high-order MPT terms. Since the second-order MPT is usually overstate the correlation corrections to various observables, we assume that our results are slightly lower than the true value for the singlet–singlet amplitudes and higher than the singlet–triplet ones. This agrees well with the experimental data on the singlet–singlet amplitudes. One can see in the table that the amplitudes calculated for all three atoms proved to be less than the experimental values. Subsequently, we intend to use the results of this work for calculating the C_6 coefficients for magnesium, calcium, and strontium.

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