High-precision determination of transition amplitudes of principal transitions in Cs from van der Waals coefficient C_6

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A method for determination of atomic dipole matrix elements of principal transitions from the value of dispersion coefficient C_6 of molecular potentials correlating to two ground-state atoms is proposed. The method is illustrated on atomic Cs using C_6 deduced from high-resolution Feshbach spectroscopy. The following reduced matrix elements are determined $\langle 6S_{1/2}||D||6P_{1/2}\rangle = 4.5028(60)\,|e|a_0$ and $\langle 6S_{1/2}||D||6P_{3/2}\rangle = 6.3373(84)\,|e|a_0$ ($a_0 = 0.529177 \times 10^{-8}$ cm.) These matrix elements are consistent with the results of the most accurate direct lifetime measurements and have a similar uncertainty. It is argued that the uncertainty can be considerably reduced as the coefficient C_6 is constrained further.

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The leading long-range interaction of two atoms in their respective spherically-symmetric ground states is described in terms of van der Waals coefficient C_6 [?]. Studies of magnetic-field induced Feshbach resonances and photoassociation in ultracold atomic samples allow to constrain this coefficient. Several highly-accurate determinations of C_6 for alkali-metal dimers were recently reported [? ? ? ? ?]. Here we propose a method for determination of electric-dipole matrix elements (or lifetimes) of principal transitions from these coefficients.

The method is illustrated for atomic Cs. In recent years the most accurate lifetimes for alkali-metal atoms were derived using photoassociation spectroscopy of ultracold atomic samples reviewed in Refs. [? ?]. Unfortunately, this approach was not as successful for Cs because of peculiarities of molecular potentials of the Cs dimer [?]. We consider an alternative method. Based on the van der Waals coefficient C_6 deduced from ultracold collision data, the calculations reported here lead to the matrix elements for Cs with an uncertainty similar to the best direct lifetime measurements. We note that the determined high-precision dipole matrix element for $6S_{1/2} - 6P_{1/2}$ transition in Cs [?] is crucial for an interpretation of the most accurate measurement [?] of atomic parity nonconservation (PNC). Atomic PNC [? ?] provides powerful constraints on possible extensions (e.g. extra Z-bosons) to the standard model of elementary particles.

For Cs, ?] deduced $C_6 = 6890(35)$[1] using results of high-resolution Feshbach spectroscopy [?]. Recently more Feshbach resonances due to higher angular momenta were identified by Chu and co-workers and this value has been constrained further to $C_6 = 6859(25)$ [?].

The dispersion coefficient C_6 characterizes a second-order dipole response of atoms to molecular fields at large internuclear separations. It can be expressed as a quadrature of dynamic polarizability [?]

$$C_6 = \frac{3}{\pi} \int_0^\infty d\omega \ [\alpha(i\omega)]^2 \ , \tag{1}$$

where

$$\alpha(i\omega) = \frac{2}{3} \sum_{|i\rangle} \frac{\Delta E_i}{(\Delta E_i)^2 + \omega^2} |\langle v|D|i\rangle|^2 \ . \tag{2}$$

Here $|v\rangle$ is an atomic ground state ($6S_{1/2}$ for Cs), ΔE_i are energies of intermediate states $|i\rangle$ taken with respect to the ground state, and D are electric-dipole matrix elements. For Cs almost 85% of C_6 is accumulated from intermediate states $6P_{1/2}$ and $6P_{3/2}$. We exploit this strong dependence to deduce matrix elements of principal transitions by calculating residual contributions using *ab initio* methods. We separate the contribution of $6P_J$ states to dynamic polarizability and write

$$\alpha(i\omega) = \alpha_p(i\omega) + \alpha_r(i\omega) \ ,$$

where α_r combines contributions of other intermediate states. These polarizabilities are shown in Fig. 1. Introducing reduced matrix elements $D_J = \langle 6S_{1/2}||D||6P_J\rangle$ and a ratio $R = (D_{3/2}/D_{1/2})^2$,

$$\alpha_p(i\omega) = \frac{1}{3} D_{1/2}^2 \left(\frac{\Delta E_{1/2}}{\Delta E_{1/2}^2 + \omega^2} + \frac{\Delta E_{3/2}}{\Delta E_{3/2}^2 + \omega^2} R \right) \ . \tag{3}$$

Energies ΔE_J of $6P_J$ states are known experimentally with a high accuracy and the ratio of matrix elements $R = 1.9809(9)$ has been measured with a 0.05% precision by ?]. This accuracy is much better than the errors in individual matrix elements due to a cancellation of systematic uncertainties.

Since

$$C_6 = \frac{3}{\pi} \int_0^\infty d\omega \ \left[\alpha_p(i\omega)^2 + 2\alpha_p(i\omega)\alpha_r(i\omega) + \alpha_r(i\omega)^2 \right] \ , \tag{4}$$
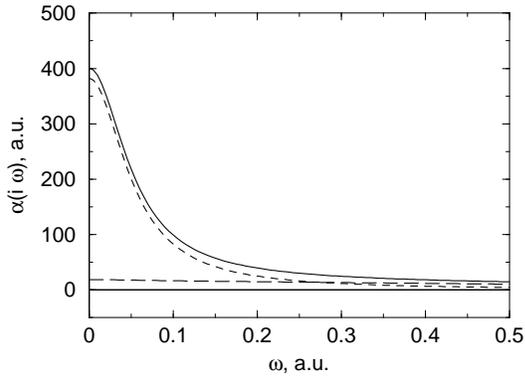
TABLE I: Breakdown of various *ab initio* contributions to static dipole polarizability from the intermediate states beyond $6P_J$.

	States	Value	Method
$\alpha_v(0)$	$7P_J$	1.50	CCSD[a]
	$8P_J$	0.18	CCSD[a]
	$9\cdots\infty P_J$	0.33	DHF
	Total	2.01	
$\alpha_{cv}(0)$		-0.47	DHF
$\alpha_c(0)$		15.81	RRPA
$\alpha_r(0)$		17.35	

[a] *ab initio* matrix elements and experimental energies.

TABLE II: Characteristic accuracy of *ab initio* methods in calculations of contribution of principal transitions to static polarizability of Cs ground state. Accuracy of DHF and CCSD methods is defined with respect to the experimental value (third row).

Method	Value	Accuracy
DHF	644	70%
CCSD[a]	378.6	0.7%
Expt.	381.2	0.2%[b]

[a] *ab initio* matrix elements and experimental energies.
[b] Based on experimental error bars in matrix elements from Ref. [?]

FIG. 3: Sample Brueckner-Goldstone diagram illustrating coupling of a doubly excited core state (double horizontal line) to the many-body ground state of a closed-shell core through a one-body dipole matrix element (wavy line). Such contribution is possible only in a combination with correlation part of the wavefunction of the ground state (first order correction is shown, with Coulomb interaction represented by dashed line.)

polarizability $\alpha_r(0)$. We present a breakdown of various contributions to this polarizability in Table I.

The error bars of the derived matrix elements depend sensitively on the uncertainty of ξ_x. To estimate this uncertainty, it is instructive to discuss characteristic accuracies of various relativistic many-body methods. As a test case we consider contribution of principal transitions to the static dipole polarizability

$$\alpha_p(0) = \frac{1}{3}\left(\frac{D_{1/2}^2}{\Delta E_{1/2}} + \frac{D_{3/2}^2}{\Delta E_{1/2}}\right). \quad (13)$$

We calculate this quantity in (i) Dirac-Hartree-Fock (DHF) approximation, (ii) linearized coupled-cluster singles-doubles (CCSD) method [?], and (iii) using experimental energies [?] and matrix elements [?]. The results are presented in Table II. It is clear that the Hartree-Fock approximation has a 70% error and the CCSD values have an accuracy in the order of 1%. Based on this example we assign a 1% uncertainty to CCSD contributions from $7P_J$ and $8P_J$ intermediate states and a 70% uncertainty to the corrections from the rest of the valence state and 70% to core-valence coupling term. We further replace the RPA value for the static polarizability of the core with accurate semiempirical value 15.644(5) [?] and obtain $\alpha_r^{s.e.}(0) = 17.18(40)$. Almost entire error comes from the uncertainty of the Hartree-Fock method. It is worth noting that the overall accuracy of the $\alpha_v(0)$ and the derived matrix elements can be further improved using, for example, linear-response coupled-cluster method [?]. Based on Eq. (12) we improve the accuracy of the parameter ξ_x by rescaling the *ab initio* value of the integral, Eq. (7), with the semiempirical $\alpha_r^{s.e.}(0)$. The final value for the quantity ξ_x is 46.0(1.0).

The overwhelming contribution to parameter ξ_r comes from the dynamic core polarizability $\alpha_c(i\omega)$. In summation over core-excited states we employ relativistic random-phase approximation (RPA), described in Refs. [? ?] with an obvious extension for frequency-dependence. Because of the equivalence of length- and velocity-forms of dipole matrix elements in RPA, the calculated dynamic polarizability of the core satisfies an important Thomas–Reiche–Kuhn (TRK) sum rule

$\lim_{\omega\to\infty} \alpha_c(i\omega) = N_c/\omega^2$, N_c being the number of core electrons ($N_c = 54$ for Cs.) This property is illustrated in Fig. 1 of Ref. [?]. The static ($\omega = 0$) core polarizability obtained with RPA is $\alpha_c(0) = 15.81$. This result is in a 1% agrement with a value of 15.644(5) deduced from semiempirical fitting of Rydberg spectrum of Cs [?]. The RPA accounts only for a correlated contribution of particle-hole excitations. However, the correction from multiple core excitations is expected to be strongly suppressed because they can couple only to the first-order many-body correction to the core wavefunction (see Fig. 3). In addition, the effect of multiple core excitations is reduced by larger energy denominators in the expression for polarizability.

Overall the RPA approximation results in a dynamic core polarizability differing from the high-precision value by 1% at $\omega = 0$ and at large frequencies recovering the exact TRK limit [?]. The parameter ξ_r calculated including only core polarizability, $\xi_r = 137.2$, is slightly increased by inclusion of valence states and the core-valence coupling term α_{cv} to 138.0. Based on the above discussion we assign a 2% uncertainty to ξ_r and arrive at $\xi_r = 138.0(2.8)$. It should be noted that more conservative error bar of 5% for ξ_r does not significantly affect the resulting precision of derived matrix elements.

Employing $C_6 = 6859(25)$ [?] and the calculated parameters ξ we determine the matrix element $D_{1/2}$, and, using the ratio R [?], the matrix element $D_{3/2}$. The obtained values are given in Eq. (10). The uncertainty in matrix element calculated from Eq. (9) can be param-

eterized as

$$\left(\frac{\delta D_{1/2}}{D_{1/2}}\right)^2 = A_{C_6}\left(\frac{\delta C_6}{C_6}\right)^2 +$$

$$+\ A_x\left(\frac{\delta\xi_x}{\xi_x}\right)^2 + A_r\left(\frac{\delta\xi_r}{\xi_r}\right)^2 + A_R\left(\frac{\delta R}{R}\right)^2\ ,$$

where $A_{C_6} = 7.5\times 10^{-2}$, $A_r = 3.0\times 10^{-5}$, $A_x = 1.4\times 10^{-3}$, and $A_R = 9.4\times 10^{-2}$. Combining estimated uncertainties we obtain an error bound of 0.13% for matrix elements. This accuracy is similar to that of the best direct lifetime measurements by **?**]. The reader is referred to Ref. [**?**] for an extensive comparison with other measurements and theoretical predictions. Our result is most sensitive to the errors in the van der Waals coefficient and parameter ξ_x. Provided that C_6 is known exactly, the uncertainty in the matrix elements can be reduced to 0.07% with the current technique for estimation of ξ_x. It is worth noting that the precision of calculation for ξ_x can be substantially improved, for example, using linear-response coupled-cluster method [**?**].

Conclusion. — We exploited a strong dependence of the van der Waals coefficient C_6 on matrix elements of principal transitions. We deduced these matrix elements by calculating small residual contributions using *ab initio* methods. The proposed method was applied to Cs atom and the derived matrix elements are consistent with the best direct lifetime measurements [**?**] and have a similar uncertainty.

In anticipation of high-precision measurements of static dipole polarizability $\alpha(0)$ of the ground state of Cs with atom interferometry [**?**], we note that 96% of the polarizability is due to the contribution of the principal transitions $\alpha_p(0)$ [**?**]. Subtracting the residual contribution $\alpha_r^{\mathrm{s.e.}}(0) = 17.18(40)$ from the measured $\alpha(0)$ one can also determine matrix elements of principal transitions to an accuracy of 0.05% from Eq. (3).

We employed the 0.36%-accurate value of the van der Waals coefficient C_6 deduced by **?**] from high-resolution Feshbach spectroscopy of ultracold Cs atoms [**?**]. According to Ref. [**?**] the precision of this dispersion coefficient can be potentially improved to 0.03%. If such a precision is achieved, the method proposed here, augmented with more accurate *ab initio* calculations and better measurements of the ratio R, can lead to determination of matrix elements of principal transitions with an unprecedented 0.01% accuracy.