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Transition amplitudes, polarizabilities, and energy levels within optical wavelength of highly charged ions Sm^{14+} and Sm^{13+}

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We discuss the possible search for optical transitions in Sm^{13+} and Sm^{14+} using *ab initio* calculations of differential dynamic polarizability. We calculate dynamic polarizability for $M1$ transition between first and second excited states of Sm^{14+}. Transition amplitudes and energies within the optical range for states that contribute to the polarizability of the mentioned transition are presented. Employing simple analytical formula for polarizability data in the vicinity of a resonance and assuming that several values of the polarizability for different laser frequencies will be measured one can find the accurate position of the resonance. Results of similar calculations of amplitudes and energies of states that contribute to the polarizability of the $M1$ transition between ground and first excited states of Sm^{13+} are also presented.

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I. INTRODUCTION

The physics of highly charged ions (HCIs) has a long and rich history due to the role the ions play in studying laboratory and cosmic plasma. Recently, the interest to the subject was further elevated due to proposals to use HCIs for the exceptionally accurate atomic clock [1,2] and for laboratory search for possible time variation of the fine-structure constant [3–6]. The latter proposal suggests the use of HCIs with optical transitions between states of different configurations. The existence of such transitions is due to level crossing while moving from Madelung to Coulomb level ordering along an isoelectronic sequence with increasing nuclear charge Z [7]. One of the main obstacles in the use of HCI with optical transitions is the absence of experimental data on the spectra of the ions. Theoretical calculations are also difficult just because of level crossing. Level crossing means that the energy interval between states of different configurations is very small ($\sim 10^{-2}$–10^{-3}) compared to the total ionization energy of valence electrons. As a result, the relative theoretical error in this interval is enhanced $\sim 10^{2}$–10^{3} times. For example, different calculations give different ground states for Sm^{14+}, Eu^{14+}, etc. [7,8].

Experimental study of the optical transitions is likely to have problems as well. All these transitions are very weak magnetic dipole ($M1$), electric quadrupole ($E2$) or strongly suppressed electric dipole ($E1$) transitions. This is because level crossing in HCIs happens mostly between s and f levels or p and f levels. The s-d crossing happens for low ionization degree and there is no level crossing consistent with selection rules for electric dipole transitions. However, electric dipole optical transitions are still possible between many-valence-electron states of HCIs due to configuration mixing. These transitions are suppressed because leading configurations do not contribute to the amplitude and small admixture of appropriate configurations make the electric dipole transition possible. In this paper we suggest to employ dynamic Stark shift of single known transition for recovering other optically accessible transitions.

We consider optically accessible transitions in Sm^{14+} and Sm^{13+} ions. For these ions it is reasonable to consider $M1$ transitions between first and second exited states (the first exited state is metastable) for Sm^{13+} and ground- to first-exited-state transition in Sm^{14+}. If differential dynamic Stark shift of such transitions in external laser field is measured for different frequencies of light the information about ion spectra can be extracted. The value of the dynamic Stark shift is determent by $E1$ or $M1$ transitions from these two states to other states. Therefore, studying the dependence of the shift on frequency of the laser field can reveal the positions of theses other states. It is important that in contrast to direct scanning we do not have to come close to the resonance while its position can be found with very high accuracy. This may have a significant advantage in searching for weak transitions in considered HCIs.

II. CALCULATIONS

A. Energy levels

The results of calculations presented in this paper rely on the method described in detail in [9–11]. A brief description of this method is presented below.

We use the V^{N-M} approximation [10]. The core electron states were obtained in Hartree-Fock approximation for $N-M$ electrons, where N and M are the total number of electrons and number of electrons above closed shells ("valence electrons"). The Hartree-Fock (HF) Hamiltonian of the system has the form

$$\hat{H}_{\mathrm{HF}} = \sum_{i=1}^{M} c\alpha\hat{\mathbf{p}}_{\mathbf{i}} + (\beta - 1)mc^2 - \frac{Ze^2}{r_i} + V^{N-M}(r_i), \qquad (1)$$

where $\hat{\mathbf{p}}_{\mathbf{i}}$ and $\mathbf{r}_{\mathbf{i}}$ are the operator of momentum and coordinate of electron, V^{N-M} is the self-consistent HF potential.

The configuration-interaction method combined with the many-body perturbation theory (the CI + MBPT method [12]) is used to construct the many-electron states for valence

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electrons. The effective CI Hamiltonian has the form

$$\hat{H}^{\text{CI}} = \sum_{i=1}^{M} \hat{h}_1(r_i) + \sum_{j>i=1}^{M} \hat{h}_2(r_i,r_j), \tag{2}$$

where $\hat{h}_1(r)$ is the single-electron operator and $\hat{h}_2(r_i,r_j)$ is the two-electron operator. The single electron operator $\hat{h}_1(r)$ differs from (1) by an extra operator $\Sigma_1(r)$,

$$\hat{h}_1(r_i) = c\alpha\hat{\mathbf{p}}_\mathbf{i} + (\beta - 1)mc^2 - \frac{Ze^2}{r_i} + V^{N-M}(r_i) + \Sigma_1(r_i). \tag{3}$$

This Σ_1 operator represents the correlation interaction between a particular valence electron and electrons in the core. The two-electron part of (2) is given by

$$\hat{h}_2(r_i,r_j) = \frac{e^2}{|\mathbf{r_i} - \mathbf{r_j}|} + \Sigma_2(r_i,r_j), \tag{4}$$

where Σ_2 accounts for the screening of Coulomb interaction between valence electrons by core electrons. We calculate the Σ_1 and Σ_2 operators in the lowest, second order of the MBPT.

The CI many-electron wave function is written in a form

$$\Psi = \sum_k c_k \Phi_k(r_1,\ldots,r_M), \tag{5}$$

where Φ_k are determinants made of single electron eigenfunctions of (1) combined in a way to have the appropriate value of total angular moment J. The expansion coefficients c_k and corresponding energies are found by solving the matrix eigenvalue problem

$$H^{\text{CI}}\Psi = E\Psi \tag{6}$$

for the lowest states of definite J and parity.

B. Transition amplitudes and dynamic polarizabilities

Electric dipole transition amplitudes are calculated using the time-dependent Hartree-Fock method [13] (equivalent to the well-known random-phase approximation) and the CI technique,

$$\langle a|E1|b\rangle = \langle \Psi^{(a)}|d_z + \delta V_{ij}^{N-M}|\Psi^{(b)}\rangle, \tag{7}$$

where $d_z = -ez$ is the z component of the dipole moment operator and δV^{N-M} is the correction to core potential due to its polarization by external electric field. Electron wave functions $\Psi^{(a)}$ and $\Psi^{(b)}$ were obtained using the CI + MBPT techniques described in the previous section.

Dynamic Stark shift is considered in the Appendix. For our analysis we need scalar polarizability given by (A2). Its calculation involves summation over the complete set of intermediate many-electron states. We use the Dalgarno-Lewis method [14] to reduce this summation to solving a system of linear equations with the CI matrix. The polarizability is rewritten as

$$\alpha(\omega) = \frac{2}{3(2J+1)} \sum_{J'=J,J\pm 1} \left\langle \delta\Psi_{J'}^{(a)} \middle| |\mathbf{d}| \middle| \Psi_J^{(a)} \right\rangle, \tag{8}$$

where J is the total angular momentum of the state a. The correction $\delta\Psi_{J'}^{(a)}$ to the wave function $\Psi_J^{(a)}$ due to the laser electric field is found from the equation

$$(H^{\text{CI}} - E_a)\delta\Psi_{J'}^{(a)} = -(d_z + \delta V^{N-M})\Psi_J^{(a)}. \tag{9}$$

The same formulas can be used to calculate energy shift in laser magnetic field. Note that in our calculations we use relativistic form of $M1$ and $E1$ (r gauge) operators.

III. ENERGY LEVELS OF Sm^{14+} AND Sm^{13+}

All optical $E1$ transitions in highly charged ions are narrow. This is because these transitions are in the optical range due to s-f or p-f level crossing [7]. The f states are not connected to either s or p states by electric dipole operator. However, if the number of valence electrons is larger than 1, the electric dipole transition might be possible due to the mixing with appropriate configuration. This mixing is small due to large energy intervals between the states in HCIs. For example, the f^2-sf electric dipole transition might be possible if the second state is mixed with the df configuration. This mixing is small because it is inversely proportional to the d-f energy interval which is large in HCIs.

Let us consider in detail the search for electrical dipole optical transitions in the Sm^{14+} ion. It has two valence electrons above the Xe-like core. There is a $4f$-$5s$ level crossing for this ion [7] which means that all lower states of the ion are dominated by the $4f^2$, $4f5s$, and $5s^2$ configurations and intervals between them are in optical range. It makes this ion a candidate for optical clocks and for experimental search of time variation of the fine-structure constant. The experimental spectrum of this ion is not known and we use *ab initio* calculations to find all the data we need. The results for energy levels and g factors are presented in Table II. Note that due to the level crossing energy intervals between states of Sm^{14+} are small compared to total two-electron removal energy. Therefore, they are very sensitive to accurate treatment of correlation and relativistic effects. For example, estimations of Ref. [7] give a different order of states than those presented in Table II. The most accurate calculations for Sm^{14+} will be published elsewhere [8]. Preliminary results of [8] indicate the same order of states as in the present work.

We consider a differential dynamic polarizability in the $M1$ transition between the first and second excited states of Sm^{14+}. These states are shown in Table II in bold. Both states are very long-living states. Although, there is an allowed $E1$ transition from the second exited state to the ground state we expect it to be very weak for reasons discussed above (see also calculated $E1$-transition amplitudes in Table I). The first excited state can decay to the ground state only via $E3$ transition. Due to its high order and small frequency the probability of the transition is extremely small.

Figure 1 presents results of calculation of differential polarizability of $M1$ transition between the first and second exited states in Sm^{+14} (reference transition). Energy levels within the optical range which contribute to the polarizability of the reference transition are listed in Table I.

The results for the relative position of the levels given by Eq. (A5) are presented in Fig. 2. The presence of horizontal regions (the same value of ΔE for different values of ω) indicates the existence of frequency intervals where one resonance strongly dominates. The fitting of the dynamic

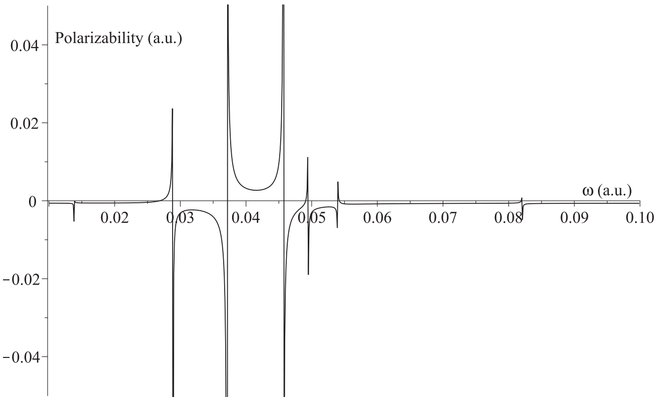

FIG. 1. Difference of the scalar polarizabilities (A2) for Sm^{+14} $M1$ transition. The resonances appear for ω equal to 0.0139; 0.0288; 0.0371; 0.0456; 0.0494; 0.0539; 0.0820.

polarizability using (A5) in these frequency intervals recovers the positions of the energy levels which are in good agreement with direct calculations. This means that such approximation for differential polarizability is valid near resonances. The error for detecting level position is of the order of 10^{-4} a.u.

There is an additional uncertainty in the fitting procedure which needs to be discussed. When differential polarizability is considered and energy distance to the resonance ΔE is found from the fitting procedure, it is not known to which energy of the two states this ΔE should be added to find the position of the resonance level. There is also a question about the sign of ΔE. The sign is always positive for the ground-state polarizability. For differential polarizability of excited states the sign of ΔE must be consistent with the sign of A [see (A5)]. This is evident from comparing (A3) and (A4). If $A < 0$ then the energy of the resonance state is either $E_e + \Delta E$ or $E_g - \Delta E$. If $A > 0$ then the energy is $E_e - \Delta E$ or $E_g + \Delta E$. The actual choice between these two possibilities is easy when the calculated spectrum is available. Note that the accuracy of the calculations does not have to be very high since we only need to choose between two very distinct possibilities.

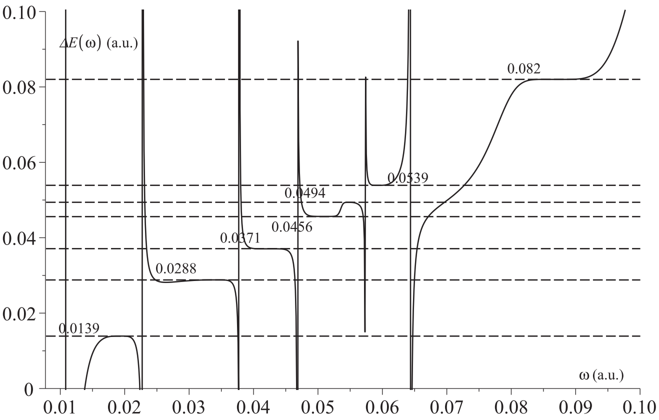

FIG. 2. Energy-level position ΔE given by (A5) relative to one of the reference transition levels, as a function of external laser frequency ω_1. Dashed lines correspond to resonances in polarizability presented in Fig. 1. For small values of $\Delta\omega$ there is no sensitivity to $\Delta\omega$.

Table III illustrates reconstruction of the energy levels of Sm^{14+} from the data on the dynamic scalar polarizability of the $M1$ transition (Fig. 1). The first two columns present the values of ΔE and A obtained from (A5) using the values of the polarizabilities close to corresponding resonance. The last column of the table shows the recovering of the energies of the resonance states using presumably known energies of the states for which polarizability is measured and ΔE from the first column. The right choice of the sign of ΔE and the energy to which of the two states it should be added is shown in bold. The resulting energies agree well with calculated energies of Table II. Note that the energies of the states which contribute to polarizabilities of both considered states are found twice.

The third column in Table III presents the squared reduced matrix element of the electric dipole transition which can be compared with the parameter A. In a single-resonance approximation they are related by $|A| = \langle g||E1||e\rangle^2/2(3J+1)$. One can see from the table that they are really close in value. Some small difference illustrates the accuracy of fitting by (A4). The data in Table III show that in the frequency

TABLE I. $E1$- and $M1$-allowed transitions within the optical wavelengths from one of the reference levels of Sm^{14+}.

Initial state		Final state		Transition energy (a.u.)	Matrix element $\langle i\|\|E1\|\|f\rangle(a_0)$	Partial width, Γ (a.u.)
J_i	E_i (cm^{-1})	J_f	E_f (cm^{-1})			
2	1243	2	9337	0.0371	1.1×10^{-2}	6.3×10^{-16}
2	1243	3	13070	0.0539	-2.1×10^{-3}	7.2×10^{-17}
3	3053	2	9337	0.0288	-6.6×10^{-3}	7.6×10^{-17}
3	3053	3	13070	0.0456	-1.2×10^{-2}	1.0×10^{-15}
3	3053	4	0	0.0139	-0.95×10^{-3}	1.8×10^{-19}
3	3053	4	13891	0.0494	3.9×10^{-3}	1.0×10^{-16}
3	3053	4	21048	0.0820	1.4×10^{-3}	6.22×10^{-17}
Initial state		Final state		Transition energy (a.u.)	Matrix element $\langle i\|\|M1\|\|f\rangle(a_0)$	Partial width, Γ (a.u.)
J_i	E_i (cm^{-1})	J_f	E_f (cm^{-1})			
2	1243	3	14603	0.0609	-2.9×10^{-3}	9.4×10^{-17}
3	3053	3	14603	0.0526	-8.3×10^{-4}	5.0×10^{-18}
3	3053	4	8092	0.0230	9.0×10^{-3}	3.8×10^{-17}

TABLE II. Energy spectrum of Sm^{+14}. The results were obtained using configuration-interaction method and include up to second order of many-body perturbation theory. States of the clock transition are shown in bold, measurement of its dynamic Stark shift gives necessary a differential polarizability can be obtained. Star symbol indicates levels that contribute to differential polarizability of reference transition and therefore can be calculated using proposed method.

Configuration	J	Parity	ΔE (cm^{-1})	g factor
$4f^{2*}$	4	e	0	0.8
$5s4f$	**2**	**o**	**1243**	**0.67**
$5s4f$	**3**	**o**	**3053**	**1.07**
$4f^2$	5	e	5409	1.0
$5s4f^*$	4	o	8092	1.25
$4f^{2*}$	2	e	9377	0.67
$4f^2$	6	e	10877	1.16
$4f^{2*}$	3	e	13070	1.0
$4f^{2*}$	4	e	13891	1.14
$5s4f^*$	3	o	14611	1.0
$4f^{2*}$	4	e	21048	1.1
$5s^2$	0	e	30908	0.0

intervals where the fitting formula (A4) works well it can be used to recover not only the energy positions of the resonance states but also the values of electric dipole transition amplitudes.

The procedure considered above implies dynamic Stark shift of reference transition energy in the external electric field of a laser. This shift is suppressed due to small values of electric dipole transition amplitudes. The amplitudes are small because the transitions cannot go between leading configurations and appear only due to configuration mixing. On the other hand, there are magnetic dipole transitions which are not suppressed because they go between states of the same configuration. In this situation magnetic dipole transitions can give significant contribution to the dynamic polarizability. To check this we have performed calculations of the $M1$ amplitudes for transitions which may affect the energy shift of the reference transition. The results are presented in the lower lines of Table I. To present $M1$ amplitudes we use the relation Bohr magneton $\mu_B = \alpha/2 \approx 3.65 \times 10^{-3}$ a.u. As one can notice the values of $M1$ and $E1$ amplitudes are of the same order of magnitude. Therefore, they should be included in the calculation of the total-energy shift. The shift is described by the same equations as ones presented in the Appendix after replacing electric field with magnetic field in (A1) and $E1$ with $M1$ amplitudes in (A2). The analysis based on formula (A4) is still the same. There are going to be extra peaks on the graph of the energy shift as a function of external frequency. This complicates the analysis, however the positive side of this is that it allows us to see more levels. Theoretical calculations might be used to help identify the states where the resonances originate from.

TABLE III. Energy levels of Sm^{14+} recovered from data on Fig. 2. ΔE and A are the interpolation parameters in Eq. (A4). Sign of A together with theoretical calculation results allows to pick correct one (bold) of two possible values of E_k - exited energy level, that contributes to reference transition differential polarizability.

ΔE (a.u.)	$A/2(3J+1)$ (a_0^2)	$\langle i\|\|E1\|\|f\rangle^2$ (a_0^2)	E_k (cm^{-1})
0.0139	$+9.07 \times 10^{-7}$	9.02×10^{-7}	**3053 − 3052=1** 1243 + 3052=4295
0.0288	-4.34×10^{-5}	4.36×10^{-5}	**3053 + 6324=9377** 1243 − 6324= −5081
0.0371	$+1.22 \times 10^{-4}$	1.21×10^{-4}	**1243 + 8146=9389** 3053 − 8146= −5093
0.0456	-1.39×10^{-4}	1.44×10^{-4}	**3053 + 10013=13066** 1243 − 10013= −8830
0.0494	-1.52×10^{-5}	1.50×10^{-5}	**3053 + 10847=13900** 1243 − 10847= −9604
0.0539	$+4.43 \times 10^{-6}$	4.41×10^{-6}	**1243 + 11835=13078** 3053 − 11835= −8782
0.0820	-2.03×10^{-6}	1.96×10^{-6}	**3053 + 18005=21058** 1243 − 18005= −16762

TABLE IV. $E1$-allowed transitions within the optical wavelengths from one of the reference levels of Sm^{13+}.

Initial state		Final state		Transition energy (a.u.)	Matrix element $\langle i\|\|E1\|\|f\rangle$ (a_0)
$5s^24f^1$, odd		$5s^14f^2$, even			
J_i	E_i (cm^{-1})	J_f	E_f (cm^{-1})		
2.5	0	1.5	31974	0.1457	-3.5×10^{-5}
2.5	0	1.5	59831	0.2726	-7.9×10^{-3}
2.5	0	1.5	63794	0.2907	-3.4×10^{-3}
2.5	0	2.5	33648	0.1533	-3.2×10^{-3}
2.5	0	2.5	47679	0.2172	-1.4×10^{-2}
2.5	0	2.5	59004	0.2688	-5.9×10^{-4}
2.5	0	3.5	22824	0.1040	-2.1×10^{-3}
2.5	0	3.5	35940	0.1638	3.0×10^{-3}
2.5	0	3.5	44036	0.2006	1.1×10^{-2}
2.5	0	3.5	53901	0.2456	2.3×10^{-3}
3.5	6787	2.5	33648	0.1224	0.3×10^{-3}
3.5	6787	2.5	47679	0.1863	-2.5×10^{-3}
3.5	6787	2.5	59004	0.2379	6.8×10^{-3}
3.5	6787	3.5	22824	0.0731	0.3×10^{-3}
3.5	6787	3.5	35940	0.1328	2.0×10^{-3}
3.5	6787	3.5	44036	0.1697	-6.9×10^{-3}
3.5	6787	3.5	53901	0.2147	1.4×10^{-2}
3.5	6787	4.5	25357	0.0846	-3.0×10^{-3}
3.5	6787	4.5	37041	0.1378	1.2×10^{-2}
3.5	6787	4.5	39687	0.1499	3.0×10^{-4}
3.5	6787	4.5	46921	0.1829	1.7×10^{-2}

The same relation between optical $E1$ and $M1$ transitions is expected to be valid for many HCIs with more than one valence electron. In such systems electric dipole transition amplitudes are small because they cannot go between leading configurations and appear only due to configuration mixing. On the other hand, there are always states of the same configuration where $M1$ amplitudes are of the order of Bohr magneton.

Table IV presents the results of similar calculations for the Sm^{13+} ion. This ion has one extra electron above closed shells which leads to a much larger number of transitions within the optical range. The reference transition is the $M1$ transition between the ground and first exited states with the energy of 6787 cm^{-1}. The last column of the table represents the amplitudes that can be used to reduce the number of fitting parameters.

For this ion there are only two levels of odd parity (reference transition) within the optical range. Therefore for the Sm^{13+} ion there will be no extra resonances in energy shift due to laser magnetic field as it was for the Sm^{14+} ion.

Unfortunately, the authors are unaware of any experimental data on energies and transition amplitudes for the investigated HCI. In order to estimate the accuracy similar calculations have been carried out for several atoms and ions like neutral barium and radium, ions of lutetium. In all these cases the error in energies and amplitudes was under a few percent of their total magnitude. The error is due to the incomplete basis set for the CI calculations. Nevertheless, in HCIs the energy intervals are much larger; we would expect much better accuracy due to faster saturation of the CI basis. Comparing our calculations to the ones done by other groups [8] we expect predicted energy intervals to be accurate up to 2000 cm^{-1} and transition amplitudes up to 2% of the presented values.

IV. CONCLUSIONS

It has been shown that the analysis of the dynamic Stark shift for a single transition in HCIs can be used to recover a significant part of the spectrum of this ion as well as the values of the electric dipole transition amplitudes between the shifted states and states which contribute to their polarizabilities. Highly charged ions Sm^{14+} and Sm^{13+} considered in the paper are of particular interest since they are candidates for atomic clocks and for the search for time variation of the fine-structure constant. The ions have relatively simple electron structure with two and three valence electrons above closed shells. This makes it easier to base the analysis on the theoretical calculations of the polarizabilities. However, similar analysis based on experimental data is not limited to ions with simple electron structure and can be useful for experimental study of the wide range of the HCIs.

ACKNOWLEDGMENT

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APPENDIX: STARK SHIFT NEAR RESONANCE

Energy shift of atomic levels in the presence of external electric field $\mathcal{E}$ of linearly polarized light with frequency ω can be written as [15,16]

$$\Delta\varepsilon_{nJM} = -\left[\alpha^S_{nJ}(\omega) + \alpha^T_{nJ}(\omega)\frac{3M^2 - J(J+1)}{J(2J-1)}\right]\frac{\mathcal{E}^2}{4}, \quad \text{(A1)}$$

where $n,\ J,\ M$ are the main quantum number, the total electron angular momentum, and its projection respectively and $\alpha^S_{nf}(\omega)$ and $\alpha^T_{nf}(\omega)$ are scalar and tensor dynamic polarizabilities of the state n,J. Averaging over all total angular momentum projections cancels out tensor polarizability, therefore for simplicity we will consider only scalar polarizability. It can be written as

$$\alpha^S_{nJ}(\omega) = \frac{2}{3(2J+1)}\sum_{n',J'=J-1}^{J'=J+1}\frac{\Delta E\langle nJ||\mathbf{d}||n'J'\rangle^2}{\Delta E^2 - \omega^2}, \quad \text{(A2)}$$

where $\Delta E = E_n - E_{n'}$, $\mathbf{d} = -e\mathbf{r}$ is the electric dipole operator and the summation goes over the complete set of intermediate states. The above equation has singular points at $\omega = E_n - E_{n'}$, which corresponds to the resonances. If frequency ω of the laser light is close to a resonance it is convenient to rewrite (A2) in the following form:

$$\alpha^S_{nJ}(\omega) = -\frac{2}{3(2J+1)}\left(\frac{1}{2}\frac{\langle nJ||\mathbf{d}||kJ'\rangle^2}{(E_n - E_k) - \omega} + \frac{1}{2}\frac{\langle nJ||\mathbf{d}||kJ'\rangle^2}{(E_n - E_k) + \omega} + \sum_{n'\neq k}\frac{(E_n - E_{n'})\langle nJ||\mathbf{d}||n'J'\rangle^2}{(E_n - E_{n'})^2 - \omega^2}\right). \quad \text{(A3)}$$

Since ω is close to resonance energy $\Delta E = |E_n - E_k|$ the first or second term in brackets determines the behavior of $\alpha_0(\omega)$ depending on the sign of ΔE. Hence for differential polarizability $\alpha^S(\omega) = \alpha^S_{n_1J_1}(\omega) - \alpha^S_{n_2J_2}(\omega)$ of the reference transition near resonance a simple analytical formula containing a single resonance term and some simple approximation for the rest of the sum can be employed:

$$\Delta\alpha^S_{nJ}(\omega) = -\left(\frac{A}{\Delta E - \omega} + K\omega + C\right). \quad \text{(A4)}$$

Here nJ is one of the two states n_1J_1 or n_2J_2 which satisfy the resonance condition $\omega \approx |E_{n'J'} - E_{nJ}|$; A, K, C, and ΔE are fitting parameters. It is assumed that $\Delta E > 0$. Comparing (A4) to (A2) one can see that the parameter A is related to the electric dipole transition amplitude between the resonance states nJ and $n'J'$ by $A = \pm\langle nJ||\mathbf{d}||n'J'\rangle^2/3(2J+1)$. The plus sign corresponds to the case when $E_{n'J'} > E_{nJ}$, the minus sign is when $E_{n'J'} < E_{nJ}$. Fitting the measured differential Stark shift of the frequency of the reference transition as a function of the laser frequency using (A4) allows one to find the position of the resonance (ΔE) and the value of the electric dipole transition amplitude between the states involved in the resonance (A). Note that there is still uncertainty due to the fact that it is still not known which of the two reference states n_1J_1 or n_2J_2 is involved in the resonance. Fitting by (A4) does not distinguish between the two possibilities. One has to compare with the calculations or use some other considerations. For example, if $A < 0$ then the state nJ cannot be the ground state. More generally, it cannot be the state from which there is no electric dipole transition to the lower states.

It can be useful to have the formulas for the parameters ΔE, A, K, and C in (A4) for the case when the differential polarizability is known at four values of laser frequency, ω_1, ω_2, ω_3, and ω_4 separated by equal frequency intervals $\Delta\omega$. The formulas are

$$\Delta E = \frac{\omega_4 - Q\omega_1}{1 - Q},$$
$$Q = \frac{\alpha^S_{nJ}(\omega_1) - 2\alpha^S_{nJ}(\omega_2) + \alpha^S_{nJ}(\omega_3)}{\alpha^S_{nJ}(\omega_2) - 2\alpha^S_{nJ}(\omega_3) + \alpha^S_{nJ}(\omega_4)},$$
$$A = -\frac{\alpha^S_{nJ}(\omega_1) - 2\alpha^S_{nJ}(\omega_2) + \alpha^S_{nJ}(\omega_3)}{\Delta\omega^2}\frac{3(2J+1)}{4} \times (\Delta E - \omega_1)(\Delta E - \omega_2)(\Delta E - \omega_3). \quad \text{(A5)}$$

[1] A. Derevianko, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. Lett. **109**, 180801 (2012).
[2] V. A. Dzuba, A. Derevianko, and V. V. Flambaum, Phys. Rev. A **86**, 054501 (2012); **87**, 029906(E) (2013).
[3] J. C. Berengut, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. Lett. **105**, 120801 (2010).
[4] J. C. Berengut, V. A. Dzuba, V. V. Flambaum, and A. Ong, Phys. Rev. Lett. **106**, 210802 (2011).
[5] J. C. Berengut, V. A. Dzuba, V. V. Flambaum, and A. Ong, Phys. Rev. Lett. **109**, 070802 (2012).
[6] V. A. Dzuba, A. Derevianko, and V. V. Flambaum, Phys. Rev. A **86**, 054502 (2012).
[7] J. C. Berengut, V. A. Dzuba, V. V. Flambaum, and A. Ong, Phys. Rev. A **86**, 022517 (2012).
[8] M. S. Safronova, V. A. Dzuba, V. V. Flambaum, U. I. Safronova, and M. G. Kozlov (to be published).
[9] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **54**, 3948 (1996).
[10] V. A. Dzuba, Phys. Rev. A **71**, 032512 (2005).
[11] V. A. Dzuba and J. S. M. Ginges, Phys. Rev. A **73**, 032503 (2006).
[12] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **54**, 3948 (1996); JETP Lett. **63**, 882 (1996).
[13] V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, J. Phys. B **20**, 1399 (1987).
[14] A. Dalgarno and J. T. Lewis, Proc. R. Soc. London A **233**, 70 (1955).
[15] N. L. Manakov, V. D. Ovsiannikov, and L. P. Rapoport, Phys. Rep. **141**, 320 (1986).
[16] N. L. Manakov and V. D. Ovsiannikov, Phys. Rep. **75**, 803 (1978).