

QUADRATIC STARK CONSTANTS
OF NEUTRAL COPPER AND SILVER SPECTRAL LINES
IN THE COULOMB APPROXIMATION*

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Abstract: By using the LS-coupling-Coulomb approximation, quadratic Stark constants were calculated for several excited energy levels from the alkali part of the term diagrams of copper and silver atoms. Available experimental data for spectral lines were used for comparison.

1. Introduction

In showing the behaviour of the energy levels of an atom under the influence of an external field, quadratic Stark constants are of interest in plasma spectroscopy in the treatment of quasi-static broadening of spectral lines¹⁾.

As regards copper and silver there are no experimental data for quadratic Stark constants measured in a homogeneous external electric field. Thus theoretical values can be checked only by means of experimental values derived via Lindholm formula^{2,3)}. The situation is not so bad, because Coulomb approximation used in the calculation of the quadratic Stark constants will give satisfactory results when applied to the transition probabilities⁴⁾ of neutral copper and silver spectral lines with both the upper and lower levels lying in the alkali part of their term diagrams.

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2. Quadratic Stark constants

The energy of interaction between an atom and an external electric field is given by

$$V = -\vec{D}\vec{F}, \quad (1)$$

where \vec{D} is the electric dipol moment of the atom, and \vec{F} the homogeneous external electric field. Higher excited states have larger dipol moments and are therefore more strongly shifted. Shifts of energy levels can be calculated with the help of the time-independent theory by using the second order approximation (the first order approximation vanishes for all atoms except for hydrogen and hydrogen-like ions). If the external field is in the z -direction, then the shift of the level with the principal quantum number n is given by

$$\Delta E_{nJ} = F^2 \sum_{n'J'} \frac{|\langle nJM | D_z | n'J'M \rangle|^2}{E_{nJ} - E_{n'J'}}. \quad (2)$$

where J is the total angular momentum, M its projection on the z -axis, and E the excitation energy of the level. Summation is taken over all possible perturbing levels (marked with primes). In the theory of line broadening⁹⁾ the frequency shift of the level is expanded in the power series of the inverse distance between the source of the electric field (perturber) and the perturbed atom, i. e.

$$\Delta \nu = \sum_{\mu} \frac{C_{2\mu}}{r^{2\mu}} \quad (3)$$

where $C_{2\mu}$ are the Stark-constants. The coefficient in the second term of this series is the quadratic Stark-constant, which, with the help of Eqs. (2) and (3), is given explicitly by the following relation

$$C_{4nJM} = \frac{e^2}{h} \sum_{n'J'} \frac{|\langle nJM | D_z | n'J'M \rangle|^2}{E_{nJ} - E_{n'J'}}. \quad (4)$$

In essence, quadratic Stark-constants determine the magnitude of the shift of the energy levels in the atom which is under the influence of an external electric field.

The square of the matrix element in (4) may be expressed in the following way (assuming that the LS-coupling scheme is applicable in the case of an alkaline atom):

$$|\langle n J M | D_z | n' J' M \rangle|^2 = (2J + 1)(2J' + 1) \begin{pmatrix} J & 1 & J' \\ -M & 0 & M \end{pmatrix} l_{>} (4l_{>} - 1) \cdot W^2(J L J' L'; S 1) a_0^2 e^2 \sigma^2, \tag{5}$$

where we used the usual notation for the 3-*j* coefficient. $W^2(J L J' L'; S 1)$ denotes the square of Racah coefficient, L the total orbital angular momentum, S the total spin momentum, $l_{>}$ the larger of the two orbital angular momentums of the jumping electron, a_0 the Bohr radius, e the electron charge, and σ the radial part of the matrix element. σ is easily obtained with the tables of Bates and Damgaard⁶⁾ (in atomic units)

$$\sigma^2 = \frac{1}{4l_{>} - 1} \left[\int_0^\infty R_{n_l}(r) r R_{n'_l}(r) r^2 dr \right]^2, \tag{6}$$

where R_{n_l} is the radial wave function calculated in the Coulomb approximation.

The relation (5) is written with the assumption that only one electron is above the closed shell of other electrons. Therefore the same relation is valid for the alkali part of the term diagrams of neutral copper and silver atoms. From (5) it follows that summation in (4) may be taken only over the levels that satisfy the selection rules:

$$\begin{aligned} \Delta J &= 0, +1 \\ \Delta M &= 0 \\ \Delta S &= 0 \\ \Delta L &= +1 \\ \Delta L_1 &= 0, \end{aligned} \tag{7}$$

where ΔL_1 denotes the change of the total orbital quantum number of the parent ion.

From the definition of C_4 it follows that it depends on the structure of the energy diagram. Our calculations are restricted to the *s*, *p* and *d* levels of the alkali part of the term diagrams of the neutral copper and silver atoms. A comparison of the theoretical⁷⁾ and experimental⁸⁾ values of Lande factors will show that the LS-coupling is a reliable approximation. Furthermore, available experimental data^{4,9)} on transition probabilities show that the Coulomb approximation of Bates and Damgaard is also reliable. One may expect that it will not fail in application to higher levels, for which no measured transition probabilities are available.

Breaking the summation (4) into parts with different *J* values and calculating the constant factors on the left of σ^2 in (5), the explicit expression for the quadratic Stark-constants of the *s*, *p* and *d* levels may be written as follows

$$\begin{aligned}
C_4(n s^2 S_{1/2}^{1/2}) &= \frac{2}{3} \sum_{n'} \frac{\sigma^2(n s_{1/2}; n' p_{3/2})}{E_{ns_{1/2}} - E_{n'p_{3/2}}} + \frac{1}{3} \sum_{n'} \frac{\sigma^2(n s_{1/2}; n' p_{1/2})}{E_{ns_{1/2}} - E_{n'p_{1/2}}} \\
C_4(n p^2 P_{3/2}^{3/2}) &= \frac{12}{5} \sum_{n'} \frac{\sigma^2(n p_{3/2}; n' d_{5/2})}{E_{np_{3/2}} - E_{n'd_{5/2}}} + \frac{3}{5} \sum_{n'} \frac{\sigma^2(n p_{3/2}; n' d_{3/2})}{E_{np_{3/2}} - E_{n'd_{3/2}}} \\
C_4(n p^2 P_{3/2}^{1/2}) &= \frac{18}{5} \sum_{n'} \frac{\sigma^2(n p_{3/2}; n' d_{5/2})}{E_{np_{3/2}} - E_{n'd_{5/2}}} + \frac{1}{15} \sum_{n'} \frac{\sigma^2(n p_{3/2}; n' d_{3/2})}{E_{np_{3/2}} - E_{n'd_{3/2}}} + \\
&\quad + \frac{2}{3} \sum_{n'} \frac{\sigma^2(n p_{3/2}; n' s_{1/2})}{E_{np_{3/2}} - E_{n's_{1/2}}} \\
C_4(n p^2 P_{1/2}^{1/2}) &= \frac{10}{3} \sum_{n'} \frac{\sigma^2(n p_{1/2}; n' d_{3/2})}{E_{np_{1/2}} - E_{n'd_{3/2}}} + \frac{1}{3} \sum_{n'} \frac{\sigma^2(n p_{1/2}; n' s_{1/2})}{E_{np_{1/2}} - E_{n's_{1/2}}} \\
C_4(n d^2 D_{3/2}^{3/2}) &= \frac{28}{5} \sum_{n'} \frac{\sigma^2(n d_{3/2}; n' f_{5/2})}{E_{nd_{3/2}} - E_{n'f_{5/2}}} + \frac{3}{5} \sum_{n'} \frac{\sigma^2(n d_{3/2}; n' p_{3/2})}{E_{nd_{3/2}} - E_{n'p_{3/2}}} \\
C_4(n d^2 D_{3/2}^{1/2}) &= \frac{42}{5} \sum_{n'} \frac{\sigma^2(n d_{3/2}; n' f_{5/2})}{E_{nd_{3/2}} - E_{n'f_{5/2}}} + \frac{1}{15} \sum_{n'} \frac{\sigma^2(n d_{3/2}; n' p_{3/2})}{E_{nd_{3/2}} - E_{n'p_{3/2}}} + \\
&\quad + \frac{10}{3} \sum_{n'} \frac{\sigma^2(n d_{3/2}; n' p_{1/2})}{E_{nd_{3/2}} - E_{n'p_{1/2}}}
\end{aligned} \tag{8}$$

where σ^2 is expressed in atomic units, and excitation energies in cm^{-1} . In order to obtain the final dimension of C_4 one must include the factor $1.333 \cdot 10^{-12}$ for $[\text{cm}^4 \text{s}^{-1}]$ units or $1.82 \cdot 10^{-3}$ for $[(\text{kV}/\text{cm})^2 \text{cm}^{-1}]$ units. Because of the limited use of the Bates and Damgaard tables, we have taken only the first five terms in every sum in (8). In order to assess the omitted part of the summation, one should make use of the fact that the oscillator strengths of the higher members in a series are proportional to the inverse cube of the effective principal quantum number of the upper level of the transition. Because the oscillator strength and σ^2 differ only as regards the difference of energies between the perturbed and the perturbing levels, the same property is valid for σ^2 as well. This difference of energies may be chosen as a constant with the value $E_j - E_{\text{ion}}$, where E_{ion} is the ionization energy of the atom in an electric field. Summation over distant levels may be transformed into the integral:

Table 1

Level	C_i (cm ⁴ s ⁻¹)
5s ² S _{1/2} ^{1/2}	+ 4,44 · 10 ⁻¹⁵
6s ² S _{1/2} ^{1/2}	+ 4,38 · 10 ⁻¹⁴
4p ² P _{1/2} ^{1/2}	+ 2,72 · 10 ⁻¹⁶
4p ² P _{3/2} ^{1/2}	+ 1,9 · 10 ⁻¹⁶
4p ² P _{3/2} ^{3/2}	+ 3,77 · 10 ⁻¹⁶
5p ² P _{1/2} ^{1/2}	+ 4,92 · 10 ⁻¹⁴
5p ² P _{3/2} ^{1/2}	+ 5,47 · 10 ⁻¹⁴
5p ² P _{3/2} ^{3/2}	+ 4,25 · 10 ⁻¹⁴
6p ² P _{1/2} ^{1/2}	+ 3,07 · 10 ⁻¹³
6p ² P _{3/2} ^{1/2}	+ 1,83 · 10 ⁻¹³
6p ² P _{3/2} ^{3/2}	+ 1,59 · 10 ⁻¹³
4d ² D _{3/2} ^{1/2}	- 4,05 · 10 ⁻¹⁴
4d ² D _{3/2} ^{3/2}	- 0,44 · 10 ⁻¹⁴
5d ² D _{3/2} ^{1/2}	+ 1,36 · 10 ⁻¹²
5d ² D _{3/2} ^{3/2}	+ 1,07 · 10 ⁻¹²

Quadratic Stark-constants of several excited energy levels of neutral copper.

Table 2

Level	C_i (cm ⁴ s ⁻¹)
6s ² S _{1/2} ^{1/2}	+ 4,82 · 10 ⁻¹⁵
7s ² S _{1/2} ^{1/2}	+ 3,70 · 10 ⁻¹⁴
5p ² P _{1/2} ^{1/2}	+ 2,34 · 10 ⁻¹⁶
5p ² P _{3/2} ^{1/2}	+ 2,31 · 10 ⁻¹⁶
5p ² P _{3/2} ^{3/2}	+ 4,34 · 10 ⁻¹⁶
5d ² D _{3/2} ^{1/2}	- 5,23 · 10 ⁻¹⁴
5d ² D _{3/2} ^{3/2}	- 1,46 · 10 ⁻¹⁴
6d ² D _{3/2} ^{1/2}	+ 4,12 · 10 ⁻¹¹
6d ² D _{3/2} ^{3/2}	+ 2,79 · 10 ⁻¹¹

Quadratic Stark-constants of several excited energy levels of neutral silver.

$$\sum_k \frac{\sigma_{lk}^2}{E_l - E_k} \approx K \sum_{n^* = n^*_{\min}}^{\infty} \frac{1}{n^{*3}} \approx K \int_{n^*_{\min}}^{\infty} \frac{dn^*}{n^{*3}} = \frac{K}{2} \frac{1}{n^*_{\min}{}^2}, \tag{9}$$

where K is a constant, and n^*_{\min} the lowest effective principal quantum number for which the inverse cube approximation has been taken. As was

estimated, the approximative sum (9) makes a negligible contribution to the sum of the first five terms in every formula in (8) and was therefore omitted.

Tables 1 and 2 show the results of a few excited energy levels of the alkali part of the term diagrams in copper and silver atoms. Shifts for the 4p, 4d and 5d levels of copper were also calculated by means of the Coulomb approximation by Miyachi and Jaya Ram¹⁰. The objective of the present calculations was to evaluate the quadratic Stark-constants mainly for those levels from which isolated spectral lines may emerge. These spectral lines can be used for determining electron densities in plasmas^{4,5}. In a simple treatment averaged quadratic Stark-constants are used in studying the problem of the broadening of spectral lines in plasmas. The best averaging¹¹ over the Stark components of the energy level may be obtained by

$$C_4 = \sum_{k=1}^n p_k C_k, \quad (10)$$

with

$$\sum_{k=1}^n p_k = 1, \quad (11)$$

Table 3

λ (Å)	Transition	C_4 (cm ⁴ s ⁻¹)
8092	4p ² P _{3/2} ⁰ — 5s ² S _{1/2}	+ 4,44 · 10 ⁻¹³
7933	4p ² P _{1/2} ⁰ — 5s ² S _{1/2}	"
4530	4p ² P _{3/2} ⁰ — 6s ² S _{1/2}	+ 4,38 · 10 ⁻¹⁴
4480	4p ² P _{1/2} ⁰ — 6s ² S _{1/2}	"
5153	4p ² P _{1/2} ⁰ — 4d ² D _{3/2}	- 2,7 · 10 ⁻¹⁴
4022	4p ² P _{1/2} ⁰ — 5d ² D _{3/2}	+ 1,25 · 10 ⁻¹²
5105	4s ² ² D _{3/2} — 4p ² P _{3/2} ⁰	+ 2,6 · 10 ⁻¹⁶
5700	4s ² ² D _{3/2} — 4p ² P _{3/2} ⁰	"
5782	4s ² ² D _{3/2} — 4p ² P _{1/2} ⁰	+ 2,72 · 10 ⁻¹⁶
2618	4s ² ² D _{3/2} — 5p ² P _{3/2} ⁰	+ 5,01 · 10 ⁻¹⁴
2406	4s ² ² D _{3/2} — 6p ² P _{3/2} ⁰	+ 1,75 · 10 ⁻¹³
2294	4s ² D _{5/2} — 6p ² P _{3/2} ⁰	"
2392	4s ² ² D _{3/2} — 6p ² P _{1/2} ⁰	+ 3,07 · 10 ⁻¹³

Quadratic Stark-constants of some copper spectral lines.

Table 4

λ (Å)	Transition	C_4 (cm ⁴ s ⁻¹)
8273	5p ² P _{3/2} ⁰ — 6s ² S _{1/2}	+ 4,82 · 10 ⁻¹⁵
7687	5p ² P _{1/2} ⁰ — 6s ² S _{1/2}	"
4668	5p ² P _{3/2} ⁰ — 7s ² S _{1/2}	+ 3,70 · 10 ⁻¹⁴
4476	5p ² P _{1/2} ⁰ — 7s ² S _{1/2}	"
5209	5p ² P _{1/2} ⁰ — 5d ² D _{3/2}	- 3,82 · 10 ⁻¹⁴
4055	5p ² P _{1/2} ⁰ — 6d ² D _{3/2}	+ 3,62 · 10 ⁻¹¹

Quadratic Stark-constants of some silver spectral lines.

where p_k are the normed relative intensities of the n Stark components of the spectral line, which arise from the given energy level. If for the spectral line the shift of the lower energy level may be neglected in comparison with the shift of the higher level, the averaged quadratic Stark-constants of the latter may be interpreted as a quadratic Stark constant of this line. As can be seen from Tables 1 and 2, the shifts of the 4p level in neutral copper and 5p in neutral silver atoms, may be neglected in comparison with higher levels. Tables 3 and 4 show the quadratic Stark-constants of several spectral lines of the sharp and diffuse series of copper and silver atoms.

In calculating transition probabilities by means of the Coulomb approximation, both higher and lower levels have to lie in the alkali part of the term diagram. However, in calculations of the quadratic Stark-constant for the spectral line, only the higher energy level has to lie in the alkali part of the term diagram, provided that the shift of the lower level lying in the complex part of the term diagram is negligible. Thus in Table 3 we added the quadratic Stark-constants of several intercombination lines which connect excited np levels and very low lying metastable $4s^2$ levels. The constants in Tables 3 and 4 can be used for determining the electron density with the help of Lindholm's formula¹²⁾

$$\gamma = 38.8 C_4^{2/3} \nu^{1/3} N_e, \quad (12)$$

where γ is the half-width of the spectral line, ν the mean velocity of electrons, and N_e the electron density in plasma.

3. Discussion of results

An inspection of Tables 1 and 2 will show that the values of quadratic Stark-constants rise towards higher energy levels. The only serious fault of the copper values derives from the fact that the energy levels in the ²P series are strongly distorted¹³⁾ because of the configuration interaction with the

corresponding term 2P which lies in the complex part of the copper term diagram. This means that wave functions which represent 2P states in the alkali part are mixtures of two wave functions, only one of which can be calculated by means of the Coulomb approximation. In taking into calculation only the wave function from the Coulomb approximation we made a certain error. This error is certainly the greatest for the high lying 2S and 2P

Table 5

λ (Å)	C_2 (cm ⁴ s ⁻¹)	
	Coulomb approximation	experiment
5153	$2,69 \cdot 10^{-14}$	$5,2 \cdot 10^{-14}$ (?)
4530	$4,38 \cdot 10^{-14}$	$2,68 \cdot 10^{-14}$ (?)
4022	$1,25 \cdot 10^{-12}$	$1,1 \cdot 10^{-12}$ (?)

Comparison between experimental and theoretical quadratic Stark-constants of three copper spectral lines calculated by the Coulomb approximation.

levels. However, the calculated Stark-constants of the $4p$ levels are reliable, because of their great distance from the perturbing levels in the complex part of the copper term diagram. In the calculation of the quadratic Stark-constants of the 2D levels the major contribution comes from the 2F levels (except for $4d$ level), which are only slightly perturbed by the relevant term from the complex part of the term diagram.

In the case of silver there exists no strong configuration interaction and so the calculations are more reliable. The only question which arises here is the validity of the Coulomb approximation for such a heavy atom.

For copper there exist experimental data which have been obtained via the Lindholm formula by measuring the half-width of the spectral line and electron density in the copper arc under water²⁾ or in the free burning arc between copper electrodes³⁾. The comparison, shown by Table 5, is rather satisfactory.

4. Conclusion

The Coulomb approximation appears to be applicable to the higher excited states in the alkali part of the term diagrams of copper and silver atoms. Thus the calculation of the quadratic Stark-constants of highly excited energy levels by the use of the Coulomb approximation is justified and should be even more exact than the calculation of transition probabilities, because the latter includes low lying levels where the Coulomb approximation is less applicable. Tables 1 and 2 show some values of the quadratic Stark-constants, which show the behaviour of several excited energy levels of copper and

silver atoms under the influence of an external homogeneous electric field.

No data on measurements of quadratic Stark-constants of excited energy levels of copper and silver in a homogeneous electric field could be found for the purpose of comparison with the calculated values.

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KVADRATIČNE STARK KONSTANTE NEUTRALNIH BAKRENIH I SREBRNIH SPEKTRALNIH LINIJA U COULOMB-OVOJ APROKSIMACIJI

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Sadržaj

Upotrebom Coulomb-ove aproksimacije izračunate su kvadratične Stark konstante za nekoliko pobuđenih energetska nivoa iz alkalijskog dijela term dijagrama bakrenog i srebrnog atoma. Postignuto je zadovoljavajuće slaganje teoretskih vrijednosti s eksperimentalnim rezultatima za neke spektralne linije.