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

M. Soltanolkotabi

Department of Physics, University of Isfahan, Isfahan, Islamic Republic of Iran

Abstract

Quadratic Stark constants of neutral copper spectral lines for all s,p, and d levels are calculated using the Coulomb approximation. These results are compared with existing data and, generally, good agreement is observed.

Introduction

In showing the behavior of the energy levels of an atom under the influence of an external electric field, quadratic Stark constants are of interest in plasma spectroscopy in the treatment of quasi-static broadening of spectral lines [1-3]. In particular, Stark broadening data are important for radiative transfer calculations and diagnostics of both laboratory and astrophysical plasmas [4].

To the best of our knowledge, no experimental data are available for quadratic Stark constants measured in a homogeneous external electric field. The Coulomb approximation used in the calculation of the quadratic Stark constants will give satisfactory results when applied to the transition probabilities [5-7] and lifetimes [5,7-9] of neutral copper spectral lines with consideration of filled core atom. Although the quadratic Stark effect has been evaluated for the hydrogen atom [9-11], no similar calculation has been carried out for the copper atom (as far as we know) except for a few levels [12].

Quadratic Stark Constants

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

$$W = -D.\xi \qquad (1)$$

where D is the electric dipole moment of the atom, and ξ is the homogeneous external electric field. Higher excited states have larger dipole moments and are therefore more strongly shifted.

Shifts of energy levels can be calculated with the help of time-independent perturbation theory by using the second order approximation (the first order approximation vanishes) [14]. If the external field is in the z-direction, then the shift of the level with the principal quantum number n is given by

$$\Delta E_{nj} = E^2 \sum_{n'j'} \frac{|\langle njM| D_z |n'j'M\rangle|^2}{E_{nj} - E_{n'j'}} \qquad (2)$$

where j is the total angular momentum, M is its projection on the z-axis and E is the excitation energy of the level. The summation is taken over all possible perturbing levels which are marked with primes. In the theory of line broadening [2], 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.

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

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 Equations (2) and (3), is given explicity by the following relation

$$C_{4njM} = \frac{e^2}{h} \sum_{n'j'} \frac{|\langle njM|\, D_z \,|n'j'M\rangle|^2}{E_{nj} - E_{n'j}} \qquad (4)$$

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) with the help of LS coupling approximation may be expressed in the following way [5]:

$$|\langle njM|\, D_z \,|n'j'M\rangle|^2 = (2j+1)\,(2j'+1)\, C^2(jlj';\, -MOM)\, (j\,\|D_z\|\,j')^2 l_>\,(4l_>^2 - 1)\, W^2(jLj\,'L';\, Sl)\, a_0^2 e^2 \sigma^2 \qquad (5)$$

where C and W denote the Clebsch-Gordan and Racah coefficients, respectively. L shows the total angular momentum, S the total spin momentum, $l_>$ the larger of the two orbital angular momenta of the jumping electron, a_0 the Bohr radius, e the electron charge, and σ the radial part of the matrix element which is given by

$$\sigma^2 = \frac{1}{4l_>^2 - 1} \left(\int_0^{\infty} R_{nl}(r)\, R_{n'l'}(r)\, r^2\, dr \right)^2 \qquad (6)$$

where R_{nl} is the radial wavefunction calculated in the Coulomb approximation [5, 15].

The relation (5) is written with the assumption that only one electron is above the closed shell of other electrons. From (5) it follows that the summation in (4) may be taken only over the levels that satisfy the selection rules:

$$\begin{aligned} &\Delta j = 0,1 \\ &\Delta M = 0 \\ &\Delta S = 0 \\ &\Delta l = +1 \\ &\Delta L_1 = 0 \end{aligned} \qquad (7)$$

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. It was shown that both the LS coupling approximation and the Coulomb approximation are reliable [5,6,13,15]. We used these approximations.

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

$$C_4(ns^2\, S_{1/2}^{1/2}) = 2/3 \sum_{n'} \frac{\sigma^2(ns_{1/2};\, n'p_{3/2})}{E_{ns_{1/2}} - E_{n'p_{1/2}}} + 1/3 \sum_{n'} \frac{\sigma^2(ns_{1/2};\, n'p_{1/2})}{E_{ns_{1/2}} - E_{n'p_{1/2}}}$$

$$C_4(np^2\, P_{3/2}^{3/2}) = 12/5 \sum_{n'} \frac{\sigma^2(np_{3/2};\, n'd_{5/2})}{E_{np_{3/2}} - E_{n'd_{5/2}}} + 3/5 \sum_{n'} \frac{\sigma^2(np_{3/2};\, n'd_{3/2})}{E_{np_{3/2}} - E_{n'd_{3/2}}}$$

$$C_4(np^2\, P_{3/2}^{1/2}) = 18/5 \sum_{n'} \frac{\sigma^2(np_{3/2};\, n'd_{5/2})}{E_{np_{3/2}} - E_{n'd_{5/2}}} + 1/15 \sum_{n'} \frac{\sigma^2(np_{3/2};\, n'd_{3/2})}{E_{np_{3/2}} - E_{n'd_{3/2}}} + 2/3 \sum_{n'} \frac{\sigma^2(np_{3/2};\, n's_{1/2})}{E_{np_{3/2}} - E_{n's_{1/2}}}$$

$$C_4(np^2\, P_{1/2}^{1/2}) = 10/3 \sum_{n'} \frac{\sigma^2(np_{1/2};\, n'd_{3/2})}{E_{np_{1/2}} - E_{n'd_{3/2}}} + 1/3 \sum_{n'} \frac{\sigma^2(np_{1/2};\, n's_{1/2})}{E_{np_{1/2}} - E_{n's_{1/2}}}$$

$$C_4(nd^2\, D_{3/2}^{3/2}) = 28/5 \sum_{n'} \frac{\sigma^2(nd_{3/2};\, n'f_{5/2})}{E_{nd_{3/2}} - E_{n'f_{5/2}}} + 3/5 \sum_{n'} \frac{\sigma^2(nd_{3/2};\, n'p_{3/2})}{E_{nd_{3/2}} - E_{n'p_{3/2}}}$$

$$C_4(nd^2\, D_{3/2}^{1/2}) = 42/5 \sum_{n'} \frac{\sigma^2(nd_{3/2};\, n'f_{5/2})}{E_{nd_{3/2}} - E_{n'f_{5/2}}} + 1/15 \sum_{n'} \frac{\sigma^2(nd_{3/2};\, n'p_{3/2})}{E_{nd_{3/2}} - E_{n'p_{3/2}}}$$

$$+10/3 \sum_{n'} \frac{\sigma^2 (nd_{3/2} ; n' p_{1/2})}{E_{nd_{3/2}} - E_{n' p_{1/2}}} \quad (8)$$

where σ is expressed in Å and excitation energies in cm^{-1}. In order to obtain the final dimension of C_4, one must include the factor 1.12×10^{-12} for [$cm^4 sec^{-1}$] units. Excitation energies were taken from Moore's table [16] which is limited. Thus, we used the available terms in every sum in (8). The revised computer program stated in ref. [5] was used for these calculations.

Table I. Quadratic Stark constant of copper atom

Level	C_4 ($cm^4 sec^{-1}$) this work	C_4 ($cm^4 sec^{-1}$) Ref. (13)
5s $^2S_{1/2}$	-4.16×10^{-16}	4.44×10^{-15}
6s $^2S_{1/2}$	-6.48×10^{-15}	4.38×10^{-14}
7s $^2S_{1/2}$	-3.83×10^{-14}	———
8s $^2S_{1/2}$	-1.27×10^{-10}	———
9s $^2S_{1/2}$	-3.43×10^{-13}	———
4p $^2P_{1/2}$	-3.01×10^{-15}	2.72×10^{-16}
4p $^2P_{1/2}$	-4.41×10^{-15}	1.9×10^{-16}
4p $^2P_{3/2}$	-1.81×10^{-15}	3.77×10^{-16}
5p $^2P_{1/2}$	-4.9×10^{-14}	4.92×10^{-14}
5p $^2P_{3/2}$	-8.25×10^{-14}	5.47×10^{-14}
5p $^2P_{3/2}$	-2.15×10^{-14}	4.25×10^{-14}
6p $^2P_{1/2}$	-1.8×10^{-13}	———
6p $^2P_{3/2}$	-7.35×10^{-14}	———
6p $^2P_{3/2}$	-7.02×10^{-14}	———
7p $^2P_{1/2}$	-4.56×10^{-13}	———
7p $^2P_{3/2}$	-4.47×10^{-12}	———
7p $^2P_{3/2}$	-3.26×10^{-13}	———
8p $^2P_{1/2}$	-1.49×10^{-11}	———
8p $^2P_{3/2}$	-1.49×10^{-11}	———
8p $^2P_{3/2}$	-8.20×10^{-13}	———
9p $^2P_{1/2}$	-1.69×10^{-12}	———
9p $^2P_{3/2}$	-2.04×10^{-12}	———
9p $^2P_{3/2}$	-1.63×10^{-12}	———
10p $^2P_{3/2}$	-3.45×10^{-12}	———
10p $^2P_{3/2}$	-2.3×10^{-12}	———
4d $^2D_{3/2}$	$+2.29\times10^{-12}$	-4.05×10^{-14}
4d $^2D_{3/2}$	$+0.39\times10^{-12}$	-0.44×10^{-14}
5d $^2D_{3/2}$	$+8.94\times10^{-12}$	$+1.36\times10^{-12}$

Results and Discussion

Table I shows the quadratic Stark constant of this work. Column 3 shows the only available data using the same method, namely the Coulomb approximation [13]. Generally, good agreement can be seen. However, there are some differences which are described as follows: (i) The signs are opposite, except for 5d. As relation (8) shows, the only places that sign plays a role are the energies in the denominators in which, in general, the higher principal quantum number, n, corresponds to higher energy. Therefore, one expects to obtain negative signs for all C_4's. However, there are exceptions (such as effective principal quantum number) in which higher n may correspond to lower energy compared with initial state. This may make the sign for C_4's positive. (ii) One can not rely on the results of this reference, because of several mistakes which were observed (formulas (5) & (6) of this reference). Furthermore, this reference made use of the tables of Bates and Damgaard [17] which are limited. On the other hand, the Coulomb approximation gives statisfactory results with regard to the transition probabilities and lifetimes as mentioned earlier. Therefore, one expects reliable results for quadratic Stark constants. Due to the difficulties both in calculations and in

experiments, no other data, to the best of our knowledge, exist. A more accurate energy level is needed. This can be achieved using the latest laser spectroscopy techniques.

One may use the Weisskopf formula in plasma to deduce the electron density by applying the quadratic Stark constant, C_4

$$\gamma = 8.46 N_e v^{\frac{1}{3}} (C_4)^{\frac{2}{3}} \qquad (9)$$

where γ is the half-width of spectral line, v the mean velocity of electrons, and N_e the electron density [2]. Stark broadening has been measured by various investigators [3]. Some of these results are tabulated by N. Konjevic *et al.* [4]. Stark broadening parameters for several CuI multiplets were also calculated by R. Konjevic *et al.* [18]. Large discrepancies are reported by these authors. As far as we know, no direct measurement of the quadratic Stark constant has been reported.

References

1. Griem, H.R. *Plasma spectroscopy*. McGraw-Hill, New York, (1964).
2. Sobel'man, I.I. *Introduction to the theory of atomic spectra*. Pergamon Press, (1972).
3. Fleurier, C. In *Spectral line shapes*, Vol. III, (ed. R.J. Exton and A. Deepak), p. 67. Pub. Hampton, Va, (1987).
4. Konjevic, N. and Wiese, W.L. "Experimental Stark widths and spectral lines of neutral and ionized atoms". *J. Chem. Ref. Data*, **19**, (6), 1307, (1990).
5. Soltanolkotabi, M. "Calculations of oscillator strengths and lifetimes of CuI, AgI and AuI using Coulomb approximation". *J. Sci. I.R.Iran.*, **1**, (1), 68, (1989).
6. Laughlin, C. "On the accuracy of the Coulomb approximation and a model-potential method for atomic transition probabilities in alkali-like systems". *Physica Scripta*, **45**, 238, (1992).
7. Hannaford, P. and Lowe, R.M. "Some recent developments in atomic lifetime determination". *Aust. J. Physics*, **39**, 829, (1988) and references therein.
8. Carlsson, J., Donszelmann, A., Lundberg, H., Persson, A., Sturesson, L. and Svanberg, S. "Natural radiative lifetimes in the $^2S_{1/2}$ and $^2D_{3/2, 5/2}$ sequences of neutral copper". *Z. Phys. D, Atoms, Molecules and Clusters*, **6**, 125, (1987).
9. Carlsson, J., Sturesson, L. and Svanberg, S. "Accurate time-resolved laser spectroscopy on sputtered metal atoms". *Ibid.*, **11**, 287, (1989).
10. Adkins, G.S. and Hood, R.F. "Use of the Schrödinger-Coulomb Green function in the evaluation of the quadratic Stark effect". *Eur.J.Phys.*, **10**, 61, (1989).
11. Imbo, T. and Sukhatme, U. "Logarithmic perturbation expansions in nonrelativistic quantum mechanics". *Am. J.Phys.*, **52**, 140, (1984).
12. Tang, A.Z., Liber, M. and Chan, F.T. "Simple example in second-order perturbation theory". *Ibid.*, **53**, 595, (1985).
13. Pichler, G. "Quadratic Stark constant of neutral copper lines in the Coulomb approximation". *Fizika*, **4**, 235, (1972).
14. Schiff, L.I. *Quantum mechanics*, (3rd edn). McGraw-Hill, (1981).
15. Pichler, G. "Properties of the oscillator strengths of CuI and AgI spectral lines". *Fizika*, **4**, 179, (1972).
16. Moore, C.E. *Atomic energy levels*, NBS, Circular No. 467 (US Government Publication Office), (1958).
17. Bates, D.R. and Damgaard, A. "The calculation of the absolute strengths of spectral lines". *Phil. Trans. Roy. Soc.*, London, (1949).
18. Konjevic, R. and Konjevic, N. "Stark broadening and shift of neutral copper spectral lines". *Fizika*, **18**, (4), 324, (1986).