doi:10.14311/ppt.2017.3.277
Plasma Physics and Technology **4**(3):277–280, 2017

PROGRAM PROCESSING DATABASE DATA FOR CALCULATION OF SPECTRAL LINES WIDTH AND SHIFT IN PLASMA

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Abstract. Electric and magnetic fields cause splitting of energy levels in an atom. Transition of electrons among these levels could be seen as broadening and shift of spectral lines. We recognize various types of effects, the most important is Stark effect. We developed a program for calculations of temperature dependence linear coefficients of Stark broadening and shift of spectral lines. Our results were calcutated for temperatures usual for SF_6 circuit breaker.

Keywords: spectral line broadening, spectral line shift, Stark effect, Van der Waals effect.

1. Introduction

The article is about database data processing to be able to calculate width and shift of spectral lines. There are a lot of information about studying object in the spectral line. Spectroscopic observation of spectral lines brings unique information which is not available by any other physical method. Analysis of spectral line position, width, deformation and intensity brings information about plasma density, temperature, pressure and kind of matter or mixture of matter.

We are able to investigate electric and magnetic properties of an object thanks to Stark and Zeeman effects present in spectral lines. Elaboration and theoretical understanding of demanding physical processes, where information is available thanks to spectral lines, are the only way to gain knowledge about processes where direct measurements are not feasible, ie. processes on distant stars.

2. Spectral lines properties

Hot plasma is described by a degree of ionization. The degree of ionization is determined by ionized to all neutral particles ratio in observed volume. The degree of ionization is an important factor which describes plasma behaviour. The degree of ionization for plasma of once ionized atoms in local thermodynamic equilibrium can be calculated by the equation which was invented by Indian scientist M. N. Saha in the twentieth years of the past century.

Spectral lines in radiation belong to discrete frequencies. The broadening of these lines is caused by natural atomic effects as well as external effects. Next important factor is temperature broadening of spectral lines which is caused by temperature motion of absorbing atoms. There is no line exactly monochromatic, but the line is broadened with maximum at wavelength predicted by quantum mechanics. Broadening and shift of the spectral line could be calculated:

$$\delta = \delta_{\mathrm{S}} + \delta_{\mathrm{R}} + \delta_{\mathrm{V}} + \delta_{\mathrm{N}}, \tag{1}$$

$$d = d_{\mathrm{S}} + d_{\mathrm{V}}, \tag{2}$$

where index S stands for Stark, R for resonance, V for Van der Waals and N for natural broadening or shift repectively.

2.1. Stark broadening and shift

External electric field belongs among external effects which cause spectral lines broadening due to splitting energy layers in atom – Stark broadening. Stark broadening effect could be either in linear or quadratic form. The form of Stark broadening effect depends on external electric field intensity. Stark effect is very significant during plasma arcs when there are high degree of plasma ionization. This phenomenon is used in spectroscopy as the most precise method for measurements of vibrational and rotational states of molecules.

There are several ways how to calculate Stark broadening of spectral line, we can calculate the broadening:

$$\delta_S = F\left(T, p\right)\left(P + Q\right), \tag{3}$$

where

$$P = \sum_{J''} \frac{S\left(J'', J\right)}{2J+1} g_{se}\left(X_{J''J}\right), \tag{4}$$

$$Q = \sum_{J''} \frac{S\left(J'', J'\right)}{2J'+1} g_{se}\left(X_{J''J'}\right) \tag{5}$$

and function F is defined:

$$F\left(T, p\right) = 16\left(\frac{\pi}{3}\right)^{2/3} cR_\infty a_0^3 N_{\mathrm{e}} \left(\frac{hcR_\infty}{k_B T}\right)^{1/2}, \tag{6}$$

where Rydberg constant $R_\infty = 109737.3\,\mathrm{cm}^{-1}$, a_0 is the Bohr radius, variable N_{e} is the electron density,

$S\left(J^{''}, J^{*}\right)$ is the line strength of transition between states with quantum numbers $J^{''}$, J^{*}: $J^{''} \rightarrow J^{*}$, this line strength is available in NIST database [1]. $J^{''}$, J^{*} are quantum numbers of total momentum of atom [2].

Stark effect also causes shift of spectral line:

$$d_S = F\left(T, p\right)\left(R - S\right), \tag{7}$$

where

$$R = \sum_{J^{''}} \frac{\Delta E_{J^{''}J}}{\left|\Delta E_{J^{''}J}\right|} \frac{S\left(J^{''}, J\right)}{2J+1} g_{sh}\left(X_{J^{''}J}\right), \tag{8}$$

and

$$S = \sum_{J^{''}} \frac{\Delta E_{J^{''}J^{'}}}{\left|\Delta E_{J^{''}J^{'}}\right|} \frac{S\left(J^{''}, J^{'}\right)}{2J^{'}+1} g_{sh}\left(X_{J^{''}J^{'}}\right). \tag{9}$$

Kramers-Gaunt g_{se} and g_{sh} factors are used for necessary corrections when using classical physics approach in areas on the border of quantum mechanics. These factors were published by Gaunt in 1930 and they were made more accurate by Hummer 1988, Hoof 2014 [3].

Stark broadening and shift depend on temperature. There could be calculated linear coefficients a, b resp. A, B for temperature dependence of width resp. shift of spectral line.

2.2. Van der Waals broadening and shift

Van der Waals broadening occurs during neutral particles interactions. Firstly we have to calculate effective main qunatum number:

$$n_k^{*} = Z\sqrt{\frac{R_\infty}{I_p - E_k}}, \tag{10}$$

where I_p is ionization potential and E_k is energy of electron state. Then we have to calculate mean matrix elements:

$$\bar{R}_k^2 = \frac{\left(n_k^{*}\right)^2}{2Z^2} \cdot \left[5\left(n_k^{*}\right)^2 + 1 - 3l_k\left(l_k+1\right)\right], \tag{11}$$

where l_k is orbital angular momentum quantum number of electron. Van der Waals broadening is given by:

$$\delta_V = \frac{a_0^2}{2}\left[\frac{9\pi\alpha c}{4}\right]^{2/5} \cdot \left(\bar{R}_{\mathrm{up}}^2 - \bar{R}_{\mathrm{low}}^2\right)^{2/5} \cdot \sum_{p\neq a}\left(\frac{R_\infty}{E_p}\right)^{4/5} \cdot V_{\mathrm{p}}^{3/5} \cdot N_1^{\mathrm{p}}, \tag{12}$$

where α is the polarisability, $\bar{R}_{\mathrm{up}}^2$ and $\bar{R}_{\mathrm{low}}^2$ are averaged radial matrix elements of upper and lower energy states of the i-th spectral line of species a, V_{p} is the realtive velocity of the perturber and N_1 is the population density of the ground state of the perturbing species [4].

3. Program for computation of spectral lines properties

There are spectroscopic databases available on the internet. I would like to mention some free access databases: american institute NIST database, professor Kurucz database (from Harvard University) and international database The Opacity Project.

We used the NIST database in our program. NIST is commercial database, but some of the spectra of selected substances can be accessed for free for noncommercial purposes. There was once ionized sulphur atoms taken as an example. This sulphur ion is produced during the quenching mechanism in SF_6 circuit breaker.

We used Eclipse environment and C programming language due to speed of calculation and compatibility with Linux and Windows operating systems. Our program loads data from NIST database, it fills internal fields of variables with these data. The program adds increments from equivalent energy levels to broadening and shift of spectral line. There are linear coefficients a, b resp. A, B counted for spectral lines broadening and their shift in temperature range 5000 K – 50 000 K. We use a linear approximation for thermal dependence for width and also for shift:

$$y = kx + q, \tag{13}$$

where $k = a$ and $q = b$ for thermal dependence of spectral line width, resp. $k = A$ and $q = B$ for thermal dependence of spectral line shift. There are thirteen parameters in the output of the program describing absorption spectral lines, the most important is the width according to Stark and according to Van der Waals.

4. Results

There are various types of broadening and shift of spectral lines. We have taken into consideration external as well as internal factors and sum up their influence. We calculate linear coefficients a, b resp. A, B necessary for calculation of spectral lines broadening resp. shift in the whole temperature range 5000 K – 50 000 K. The chosen temperature range covers the whole range needed for study of spectral effects connected with SF6 circuit breakers functioning. SF_6 molecule begins to react with used construction materials at temperature of 550 K, thermal dissociation of SF_6 gas starts about 2000 K and final temperature before quenching of an arc could exceed 20 000 K according to circuit breaker type [6].

Selected results are presented in table 1 and comparison with literature in table 2. We need to obtain function F, after that Stark broadening and shift of spectral lines can finally be calculated.

5. Conclusion

Observed spectrosocopic microsecond effects during burning and quenching of an arc in SF_6 circuit break-

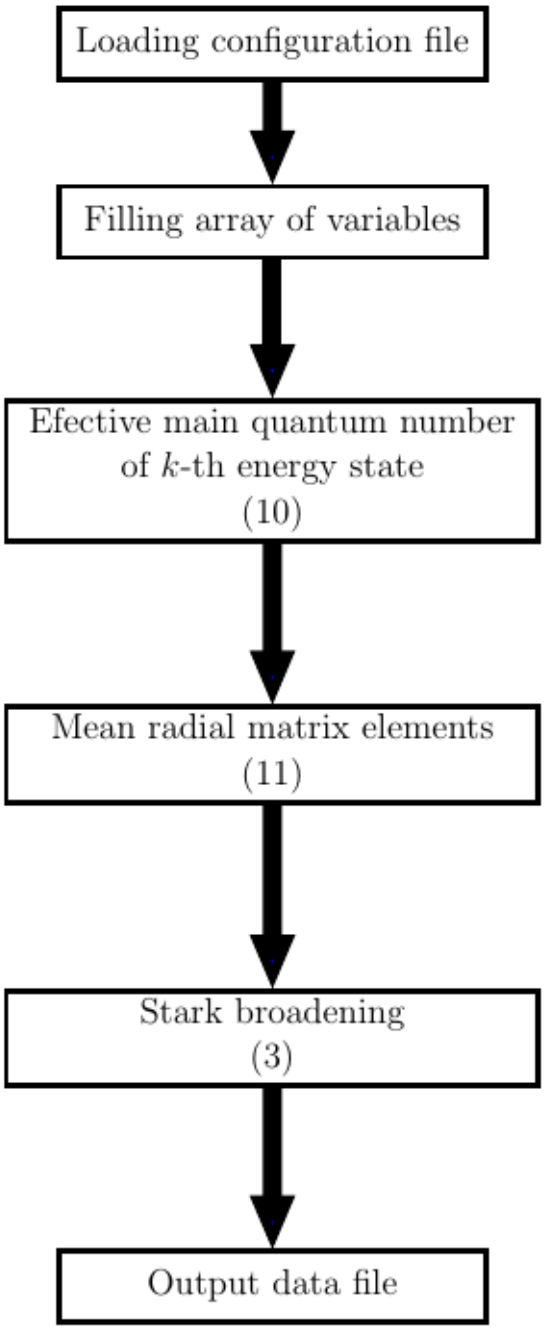

Figure 1. Block diagram of our program.

```
/* lower energy level */
if ( (Euj == El) && (semaphore1 == 0) ) {
  semaphore1 = 1;
  C4ini = C4ini+foscj*pow((lambdaj*1e-7),2.0); /* parameter Stark France */
  Aeml = 6.6702e13*glj*foscj/(guj*lambdaj*lambdaj); /* natural broadening low */
  Dnl = Dnl+Aeml;
  for ( cntK=0; cntK<6; cntK++ ) {
    gJD[cntK] = 0.275664*log(1+0.012854*pow(T[cntK],1.5)/(z*abs(Elj-El)));
    AJD[cntK]=gJD[cntK]*Sj/gl;
    DHni[cntK]=DHni[cntK]+AJD[cntK];
    gsJD[cntK]=0.001391*pow(T[cntK],1.5)/(z*abs(Elj-El));  /* shift */
    BJD[cntK]=gsJD[cntK]*Sj*(Elj-El)/(gl*abs(Elj-El));
    DHd[cntK]=DHd[cntK]+BJD[cntK];
  }
}
```

Figure 2. Example of code from our program. The segment calculates Gaunt factors.

λ nm	width a $s^{-1}K^{-1}$	width b s^{-1}	shift A $s^{-1}K^{-1}$	shift B s^{-1}
267.0604	1.50×10^{-4}	-1.55×10^{-1}	-3.22×10^{-5}	1.94×10^{-1}
386.1224	2.66×10^{-4}	-2.21×10^{-2}	3.93×10^{-5}	-2.37×10^{-1}
421.8370	2.65×10^{-4}	-2.50×10^{-1}	5.12×10^{-5}	-3.08×10^{-1}
470.1519	2.50×10^{-4}	-1.86×10^{-1}	7.12×10^{-5}	-4.29×10^{-1}
545.5371	2.50×10^{-4}	-2.29×10^{-1}	1.68×10^{-5}	-1.01×10^{-1}
560.7707	1.89×10^{-4}	-1.79×10^{-1}	-3.89×10^{-5}	2.35×10^{-1}
564.8587	2.22×10^{-4}	-1.65×10^{-1}	3.16×10^{-5}	-1.90×10^{-1}
630.7227	2.00×10^{-4}	-1.92×10^{-1}	-5.65×10^{-5}	3.41×10^{-1}
631.4431	1.62×10^{-4}	-1.50×10^{-1}	-2.60×10^{-5}	1.57×10^{-1}
727.5214	2.49×10^{-4}	-1.95×10^{-1}	3.29×10^{-6}	-1.98×10^{-2}

Table 1. Linear coefficients a, b resp. A, B for Stark broadening resp. shift of S^+.

Transition array	Multiplet or Term	λ nm	w_{MSE} nm	T 10^3K	N_e $10^{23}m^3$	J	J'	δ_λ nm
$3p^2 3d - 3p^2 4p$	$^4F - {}^4D^0$	560.7707	0.0304	23.5	1.0	9/2	7/2	0.019
	$^4D - {}^4P^0$	630.7227	0.0963	23.5	1.0	7/2	5/2	0.025
	$^2F - {}^2D^0$	631.4431	0.103	23.5	1.0	5/2	3/2	0.020
$3p^2 4s - 3p^2 4p$	$^4P - {}^4D^0$	545.5371	0.0301	28.5	1.0	5/2	7/2	0.026
			0.050	32.6	0.7	5/2	7/2	0.019
	$^2P - {}^2D^0$	564.8587	0.0424	27.0	0.67	1/2	3/2	0.016
			0.0374	34.0	1.02	1/2	3/2	0.028

Table 2. Comparison of calculated Stark broadening of spectral lines of S^+ with literature [5].

ers lead to possibilities of theoretical modelling of these effects. Pressure at burning arc has direct influence on spectral lines broadening and also thermal effects in SF6 gas plays an important role. SF_6 gas gradually thermally dissociates about temperature of 2000 K and rapidly cools down the arc. SF_6 circuit breaker has great advantage against air circuit breakers because of lower dissociation temperature. The thermal dissociation of air begins about 7000 K [6].

Emission spectrum changes over time due to gradual thermal heating of circuit breaker components. At the end of burning of the arc there are usually emission lines of eletrodes' material found in the emitted spectrum. We designed a program for calculation of spectral properties of various ions. We calculated data for ionized sulphur atoms in this article, selected results for S^+ ion are in table 1. In table 2, comparison of our results with calculation of other authors [5] is presented. In [5], modified semi–empirical approach is used; the difference with our results occurs due to the fact that in [5] the Stark widths of whole multiplets have been calculated.

Thorough theoretical study of spectra could bring new ways for design of electrodes shapes in order to avoid soon arc cutoff, improve cooling down mechanisms or to find new alloys for electrodes. As a result of these studies should be increased number of working cycles and improved safety of high voltage devices.

Acknowledgements

This work was supported by the Internal Grant Agency of Brno University of Technology, grant No. FEKT-S-17-4626 and by the Czech Science Foundation under project No. 15-14829S.

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