ASTRONOMY
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Electron-impact shifts of ion lines: modified semiempirical approach

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Summary. A simple method for calculation of ion line shifts produced by electron impacts, based on the modified (Dimitrijević and Konjević, 1980) semiempirical (Griem, 1968) approach is presented. Obtained relations have been applied to a number of Be II, Mg II, Al II, Ar II and Ca II lines and the results are compared with semiclassical and semiempirical values as well as with critically selected experiments.

Key words: Stark broadening – line shift

1. Introduction

Stark shift is the dominant pressure line shift in atmospheres of hot stars and white dwarfs. Since, in spectra of some of them, like O and B stars, ion lines dominate, the knowledge of the Stark broadening and shift parameters for a large number of elements in several ionization stages is very important. Even in relatively cool stellar atmospheres, as in the solar one, where line broadening caused by collisions with neutral perturbers is significantly larger than the Stark broadening, in some cases the Stark shift could be of the same order of magnitude as the neutral atom-impact shift (Vince et al., 1985a). In accordance with that fact, Stark shift is also one of the causes of the stellar spectral line asymmetries (Vince et al., 1985b), therefore it can serve for more precise determination of other causes of asymmetry (e.g. granular motion). In the case of white dwarfs and other stars where relativistic effects are pronounced, knowledge of the Stark shift theory can make possible accurate determination of the gravitational red shifts (Wiese and Kelleher, 1971; Grabowski et al., 1986).

Quantum mechanical or semiclassical theories are able to provide data of high accuracy but they require considerable labour and knowledge of numerous atomic data. Astrophysicists often require Stark-broadening data for a large number of transitions in many atoms. For large scale calculations high accuracy of every particular line is not so important. One requires only a reasonable accuracy for the large number of lines. In such cases, tedious calculations can be avoided if one uses simple approximative formulae with good average accuracy, e.g. the semiempirical method (Griem, 1968) or the modified semiempirical method (Dimitrijević and Konjević, 1980; 1981a) for Stark widths

of ion lines, and a simple method for widths and shifts of neutral atom lines by the same authors (1986).

The modified semiempirical approach (Dimitrijević and Konjević, 1980) was tested several times (Dimitrijević and Konjević, 1981a,b,c; Dimitrijević, 1982a,b; 1983; Konjević et al., 1984) and on the average gives a satisfactory agreement with experiments.

The aim of this paper is to present analogous improvements of the semiempirical theory for the electron-impact shift as well as to test the results obtained, by comparison with other theories and available experiments.

2. Theory

Starting from Baranger's (1958) quantum mechanical expression for the width of an isolated ion line within the impact approximation, together with Bethe's (1930) relation for the inelastic cross-section, as well as from the semiempirical effective Gaunt factor, g_{se} (the Gaunt factor is a measure of the probability for the incident electron to change kinetic energy from the value before the collision to the value after it), suggested by Seaton (1962) and Van Regemorter (1962), Griem (1968) derived semiempirical formulae for the width and the shift of ion lines. At the same time, he assumed that contributions of the elastic collisions can be neglected for high electron temperatures, in accordance with the Bethe-Born approximation (valid for allowed dipole transitions only). In the case of low temperatures, contributions of elastic collisions were taken into account by extrapolation of the threshold value of the inelastic cross-section into the region below the threshold (Gailitis, 1963). Griem's (1968) formula for the shift is

$$d = N \frac{4\pi}{3} \frac{\hbar^2}{m^2} \left(\frac{2m}{\pi kT} \right)^{1/2} \frac{\pi}{\sqrt{3}} \cdot \sum_{i,i'} \left[\frac{\Delta E_{i'i}}{|\Delta E_{i'i}|} \mathbf{R}_{i'i}^2 g_{sh}\left(\frac{E}{|\Delta E_{i'i}|} \right) \right.$$
$$\left. - \frac{\Delta E_{f'f}}{|\Delta E_{f'f}|} \mathbf{R}_{f'f}^2 g_{sh}\left(\frac{E}{|\Delta E_{f'f}|} \right) \right] \tag{1}$$

In this expression $\mathbf{R}_{j'j}^2$ (in units of the Bohr radius a_0^2) is the square of the coordinate operator matrix element summed over all components of the operator and the magnetic substates of total angular momentum J', and averaged over the magnetic substates of J, $E = 3kT/2$ is the energy of the perturbing electron; $\Delta E_{j'j}$ is the energy difference between perturbing level j' and perturbed level j; indexes i and f denote initial (upper) and final (lower) level of the transition, respectively; and N is the electron density.
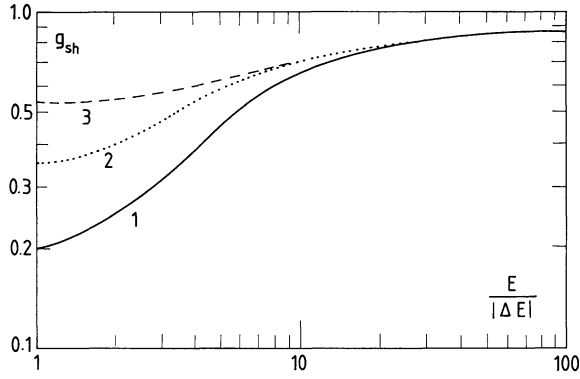
Fig. 1. Semiempirical effective Gaunt factors for shifts: $1 - g_{sh}$ from Griem (1968); $2 - \tilde{g}_{sh}$ for $\Delta n = 0$, for singly charged ions; $3 - \tilde{g}_{sh}$ for $\Delta n = 0$, for doubly charged ions

The Gaunt factor for the shift, g_{sh}, was obtained by Griem from g_{se}, solving the Cauchy integral dispersion relation

$$g_{sh}(x) = \frac{x}{\pi} \mathscr{P} \int_0^\infty \frac{g_{se}(x')}{x'(x - x')} dx' \qquad (2)$$

Here, $x = E/|\Delta E_{j'j}|$ and $\mathscr{P}$ denotes the principal value of the integral. For $x < 2$ the solution of Eq. (2) is the semiconvergent series

$$g_{sh}(x) = \sum_{n=0}^\infty A_n x^n = A_0 + 0.332 \left(\frac{x}{10}\right) + 0.305 \left(\frac{x}{10}\right)^2 + 0.550 \left(\frac{x}{10}\right)^3 + 1.36 \left(\frac{x}{10}\right)^4 \qquad (3)$$

According to the GBKO theory (Griem et al., 1962) one can obtain

$$g_{sh}(x) \approx \frac{\sqrt{3}}{\pi} b(y_{\min}) \qquad (4)$$

Here $b(y)$ denotes the Stark broadening function for straight perturber paths. From the relation (4) Griem (1968) derived $g_{sh}(x)$ for large values of x, by obtaining a best fit with the semiclassical calculations made in the same paper. Starting from the same relation, Griem also concluded that to typical perturber energies at threshold ($x = 1$) corresponds $g_{sh} \approx 0.20$, the value identical to

$g_{se}(1)$. According to this value, one can obtain $A_0 = 0.163$. The $g_{sh}(x)$ function (Griem, 1968) is shown in Fig. 1 and Table 1.

Using the Coulomb-Born II approximation (Van Regemorter, 1960), Bely (1966b) calculated the cross-sections for excitation due to electron impacts of lithium-like ions. The threshold values of the Gaunt factor obtained from these cross-sections are significantly larger than 0.2 for the resonant transitions, while for the transitions with changes in principal quantum number, the values can be even less than 0.2. Blaha (1969), on the basis of less refined calculations, obtained similar results. According to Bely's (1966,a,b) results, Kobzev (1971) suggested the following relation for the threshold value of the Gaunt factor in the case of transitions with $\Delta n = 0$ (n is the principal quantum number):

$$g_{th} = 0.9 - 1.1/Z \qquad (5)$$

where Z is the residual ionic charge. It is seen from the calculations of Bely and Petrini (1970) that g_{th} for transitions with $\Delta n \neq 0$, depending on the type of transition, can be either larger or less than 0.2. But since the differences are not as large as in the case $\Delta n = 0$, it seems that $g_{th} = 0.2$ can be retained as a mean value for the transitions with $\Delta n \neq 0$. The dependence of the Gaunt factor on Z for these transitions (Bely and Petrini, 1970) is significantly weaker than for $\Delta n = 0$ transitions, so a reasonable approximation is to neglect it.

The cross-sections obtained from experiments confirm in general (Kunze, 1972) the characteristics of Gaunt factors described above.

In modifying formula (1) we had two intentions: first, to improve the accuracy, by taking into account (5); and second, to make the method easier for applications, by avoiding the necessity of knowing the complete set of perturbing energy levels.

For the transitions with $\Delta n = 0$ we calculated the new $g_{sh}(x)$ functions for singly, doubly and triply charged ions.

Starting from the semiempirical Gaunt factor for $\Delta n = 0$ transitions $\tilde{g}_{se}(x)$ introduced by Dimitrijević and Konjević (1980) on the basis of Eq. (5)

$$\tilde{g}_{se}(x) = 0.7 - 1.1/Z + g_{se}(x) \qquad (6)$$

Eq. (2) becomes

$$\tilde{g}_{sh}(x) = \tilde{g}_{sh}(0) + \frac{x}{\pi} \mathscr{P} \int_0^\infty \frac{g_{se}(x') - g_{se}(0)}{x'(x' - x)} dx' \qquad (7)$$

Table 1. Values for effective Gaunt factors g_{sh} and $\tilde{g}_{sh}$ as a function of $x = E/|\Delta E_{j'j}|$ and Z

x		$\leqslant 1$	2	3	4	5	6	7	8	9	10	20	30	40	60	80	100
g_{sh}		.20	.25	.32	.41	.45	.51	.56	.60	.63	.66	.78	.82	.84	.85	.86	.87
$\tilde{g}_{sh}$	Z=2	.35	.40	.47	.53	.58	.61	.64	.66	.68	.70	.78	.82	.84	.85	.86	.87
	Z=3	.53	.54	.57	.59	.62	.64	.66	.67	.69	.70	.78	.82	.84	.85	.86	.87
	Z=4	.62	.62	.63	.64	.65	.66	.67	.68	.69	.70	.78	.82	.84	.85	.86	.87
	Z>4	.88-1.1/Z+.01x/Z															

with the solution

$$g_{sh}(x) = \tilde{A}_0 + 0.332\left(\frac{x}{10}\right) + 0.305\left(\frac{x}{10}\right)^2 + 0.550\left(\frac{x}{10}\right)^3$$
$$+ 1.36\left(\frac{x}{10}\right)^4 \tag{8}$$

for $x < 2$.

According to the semiclassical theory with hyperbolic perturber paths (see e.g. Sahal-Bréchot, 1969a,b, or Griem, 1974)

$$g_{sh}(x) = \frac{\sqrt{3}}{\pi} b(\delta, \xi) \tag{9}$$

where $\delta = (\varepsilon_{\min} - 1)\xi$, $\xi = \sqrt{E_H/E}(Z - 1)/2x$, ε is the eccentricity of the hyperbolic path and E_H is the ionization energy of hydrogen. Using

$$\varepsilon_{\min} \approx 1 + \frac{E_n^2}{(Z - 1)ZE_H} \tag{10}$$

(Griem, 1974, Eq. 500) one obtains

$$\delta \approx \frac{n^2}{2Zx} \sqrt{\frac{E}{E_H}} \tag{11}$$

Taking into account that the semiempirical Gaunt factor g_{se} agrees best with the quasiclassical calculations for $2n^2/Z = 10$ (see Griem, 1968, Eq. 34), for typical perturber energies $E \approx 3kT/2 \approx 2\,\text{eV}$ (the majority of experiments for doubly and triply charged ion lines has been performed at 2–$2.5\,\text{eV}$ (Konjević et al., 1984)) we obtain

$$g_{sh}(x) = \frac{\sqrt{3}}{\pi} b\left(\frac{0.959}{x}, \frac{1.304(Z - 1)}{x}\right) \tag{12}$$

We estimated the threshold values for the $\tilde{g}_{sh}(x)$ functions according to Eq. 5 ($g_{th} = 0.35$ for singly and 0.53 for doubly charged ions). The $\tilde{A}_0$ values can be obtained from Eqs. 6 and 8 (e.g. $\tilde{A}_0 = 0.313$ and 0.493 for singly and doubly charged ions, respectively). In order to determine $\tilde{g}_{sh}(x)$ we used Eq. 3 with the corresponding $\tilde{A}_0$ values for $x \leq 5$ and Eq. 12 for $5 < x \leq 7$. Since we estimated that for $x \geq 7$ the typical difference between straight path and hyperbolic path calculations is less than 10%, for $7 < x \leq 50$ we used Eq. 4 with $y_{\min} \approx 5/x$ (see Griem, 1968), and for $x > 50$, the $\tilde{g}_{sh}(x)$ functions converge to the value $\tilde{g}_{sh} = \sqrt{3}/2$ obtained from the GBKO (Griem et al., 1962) high temperature limit. The best fit values for $Z = 2$, 3 and 4 are presented in Table 1 and Fig. 1. For $Z > 4$, we can use as rough estimate the expression

$$\tilde{g}_{sh}(x) \approx 0.88 - 1.1/Z + 0.01x/Z, \quad x < 100$$
$$\tilde{g}_{sh}(x) = \sqrt{3}/2, \quad x \geq 100 \tag{12a}$$

connecting threshold values with the high temperature limit. The high temperature limit value $g_{sh} = \sqrt{3}/2$ is also a good estimate for $\Delta n = 0$ transitions for higher Z values since eventual differences are of the order of 10% for $Z > 7$.

For the transitions with $\Delta n \neq 0$, g_{sh} according to Griem (1968) is retained.

Assuming the LS coupling approximation, separating the transitions with $\Delta n = 0$, and estimating the energy distance to the nearest perturbing level from

$$|\Delta E_{n,n+1}| \approx 2Z^2 E_H/n^{*3} \tag{13}$$

(n^* is the effective principal quantum number given by the relation $n^* = [E_H Z^2/(E_{\text{ion}} - E_n)]^{1/2}$, where E_{ion} is the ionization energy of the emitter, and E_n is the energy of the considered level) one can suggest the following expression for the ion line shift:

$$d = N \frac{4\pi}{3} \frac{\hbar^2}{m^2}\left(\frac{2m}{\pi kT}\right)^{1/2} \frac{\pi}{\sqrt{3}} \cdot \left\{ \mathbf{R}_{l_i,l_i+1}^2 \tilde{g}_{sh}(x_{l_i,l_i+1}) \right.$$
$$- \mathbf{R}_{l_i,l_i-1}^2 \tilde{g}_{sh}(x_{l_i,l_i-1}) - \mathbf{R}_{l_f,l_f+1}^2 \tilde{g}_{sh}(x_{l_f,l_f+1})$$
$$+ \mathbf{R}_{l_f,l_f-1}^2 \tilde{g}_{sh}(x_{l_f,l_f-1}) + \sum_{i'}(\mathbf{R}_{i'i}^2)_{\Delta n \neq 0} g_{sh}(x_{n_i,n_i+1})$$
$$- 2 \sum_{i', \Delta E_{i'i} < 0} \left[(\mathbf{R}_{i'i}^2)_{\Delta n \neq 0} g_{sh}(x_{i'i})\right]$$
$$- \sum_{f'}(\mathbf{R}_{f'f}^2)_{\Delta n \neq 0} g_{sh}(x_{n_f,n_f+1})$$
$$\left. + 2 \sum_{f', \Delta E_{f'f} < 0} \left[(\mathbf{R}_{f'f}^2)_{\Delta n \neq 0} g_{sh}(x_{f'f})\right] + \sum_k \delta_k \right\} \tag{14}$$

where $x_{j'j} = E/|\Delta E_{j'j}|$. (All transitions with $\Delta n \neq 0$ are firstly summed and the corresponding matrix elements are treated lumped together. From the sum obtained we have subtracted the group of transitions with $\Delta E_{j'j} < 0$.)

The sum $\sum_k \delta_k$ is not equal to zero only if perturbing levels strongly violating the assumed approximations exist, i.e. if there are levels with $|\Delta E_{j'j}| \ll |\Delta E_{n,n+1}|$. Contribution of each such level should be calculated as

$$\delta_i = \pm(\mathbf{R}_{i'i}^2)\left[g_{sh}(x_{i'i}) \mp g_{sh}(x_{n_i,n_i+1})\right]$$

or

$$\delta_f = \mp(\mathbf{R}_{f'f}^2)\left[g_{sh}(x_{f'f}) \mp g_{sh}(x_{n_f,n_f+1})\right] \tag{15}$$

where lower sign corresponds to $\Delta E_{j'j} < 0$.

Relevant matrix elements can be calculated using the Coulomb approximation of Bates and Damgaard (1949)

$$\mathbf{R}_{j'j}^2 \approx \left(\frac{3n_l^*}{2Z}\right)^2 \frac{l}{2l_j + 1}(n_l^{*2} - l^2)\phi^2(n_{l-1}^*, n_l^*, l) \tag{16}$$

$$\sum_{j'}(\mathbf{R}_{j'j}^2)_{\Delta n \neq 0} \approx \left(\frac{3n_j^*}{2Z}\right)^2 \frac{1}{9}(n_j^{*2} + 3l_j^2 + 3l_j + 11), \quad j = i,f \tag{17}$$

Here, l_j is the orbital quantum number of the valence electron, l is max $(l_{j'}, l_j)$ and ϕ^2 is the Bates-Damgaard factor (tabulated e.g. in Oertel and Shomo's (1968) paper. The cases where the one-electron model (i.e. only one energy level for each nl electron) assumed in Eqs. 16 and 17 is not satisfied are analysed in detail by Dimitrijević (1982c). E.g., for a multiplet as a whole, $\mathbf{R}_{i',i}^2$ should be multiplied by $R_{\text{mult}}^2(2l + 1)/(2L + 1)$. The multiplet factor R_{mult}^2 can be found in Tables of Shore and Menzel (1965).

3. Results and discussion

Results of our computations of line shifts of singly charged ions are compared in Figs. 2–9 with other theoretical approaches and with available experimental data.

Generally, the possibilities of theory in the case of shifts are considerably smaller than for the line widths (Dimitrijević et al., 1981; Griem, 1974). The only quantum mechanical (strong coupling) calculation in the case of ion line shifts was performed by Barnes and Peach (1970) for the resonant lines of Ca II. Extensive tables of semiclassical line shift calculations for the singly charged ions have been made by Jones et al. (1971) (given also
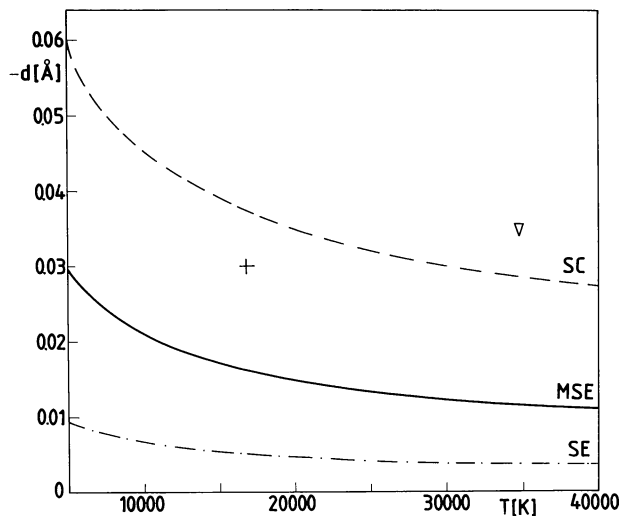
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Fig. 2. Stark shifts for Be II $2s^2S$-$2p^2P^0$ multiplet. Calculations: MSE – modified semiempirical; SE – semiempirical according to Griem (1968); SC – semiclassical, Jones et al. (1971); QM – quantum mechanical, Barnes and Peach (1970). Experimental points: +-Purić and Konjević (1972); ▽-Hažiomerspahić et al. (1973); △-Roberts and Barnard (1972); ○-Fleurier et al. (1977); ×-Lakićević et al. (1981); ●-Blandin et al. (1968); ▼-Labat et al. (1974); ▲-Morris and Morris (1970); □-Helbig and Kusch (1972); ■-Hühn and Kusch (1973)

Fig. 4. Stark shifts for Ca II $4s^2S$-$4p^2P^0$ multiplet. Notation is the same as in Fig. 2

Fig. 3. Stark shifts for Mg II $3p^2P^0$-$4s^2S$ multiplet. Notation is the same as in Fig. 2
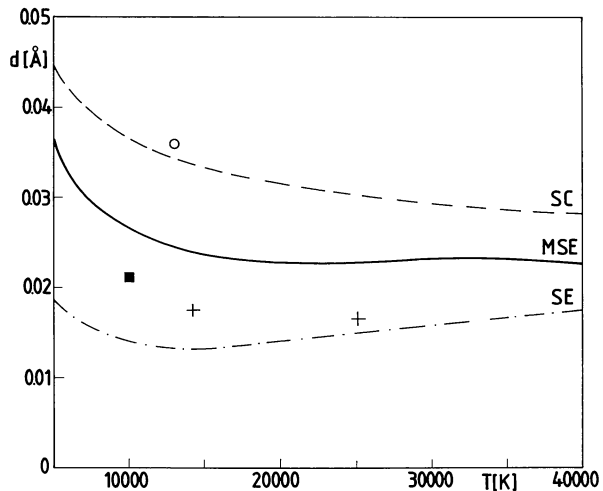
Fig. 5. Stark shifts for Ca II $4p^2P^0$-$5s^2S$ multiplet. Notation is the same as in Fig. 2

paper; calculations were performed by the authors;

SC – semiclassical theory; results of Jones et al. (1971);

QM – quantum mechanical calculations by Barnes and Peach (1970).

Experimental results were taken from the critical reviews of experimental data by Konjević and Wiese (1976) and Konjević et al. (1984). We have not taken into account experiments with lowest accuracy (accuracy denoted by D in the mentioned reviews). According to the fact that our calculations were made for the multiplet as a whole, experimental data for different lines within a multiplet (if they exist) were also averaged.

On the basis of the figures presented, in spite of the fact that the proposed method is considerably simpler than the semiclassical one, the agreement with experimental results is comparable with more sophisticated approaches. Moreover, the results obtained using modified semiempirical method are closer to the semiclassical results than the semiempirical ones.

by Griem, 1974). Experimental data exist almost exclusively for singly charged ions.

Theoretical approaches presented in Figs. 2–9 are the following:

MSE – modified semiempirical formula, Eq. 14;

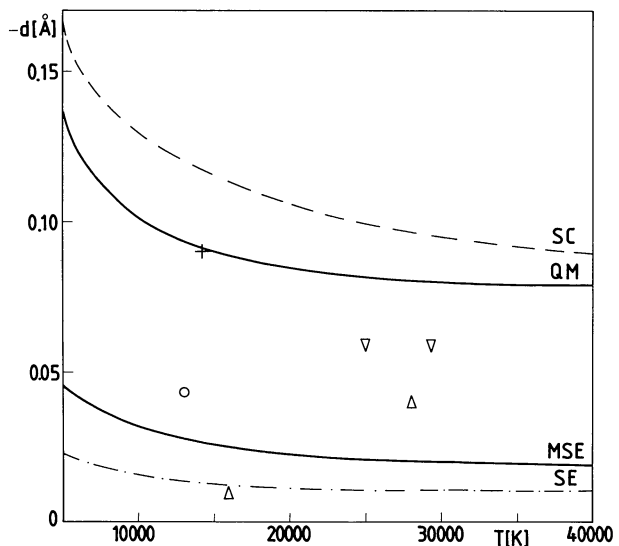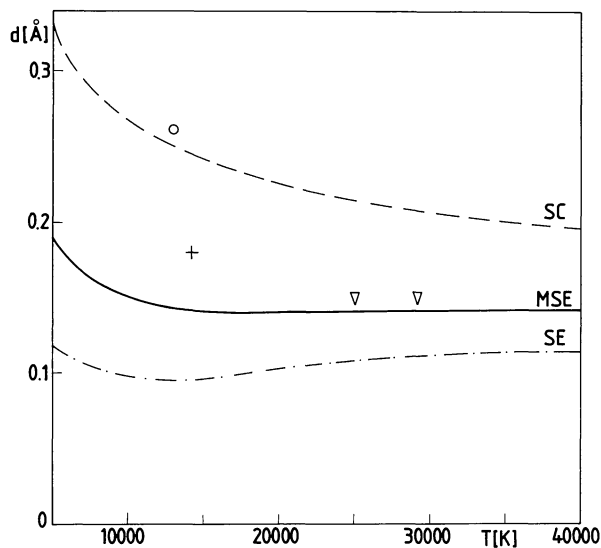SE – semiempirical formula of Griem (1968) – Eq. 1 in this

Fig. 6. Stark shifts for Ca II $4p^2P^0$-$4d^2D$ multiplet. Notation is the same as in Fig. 2
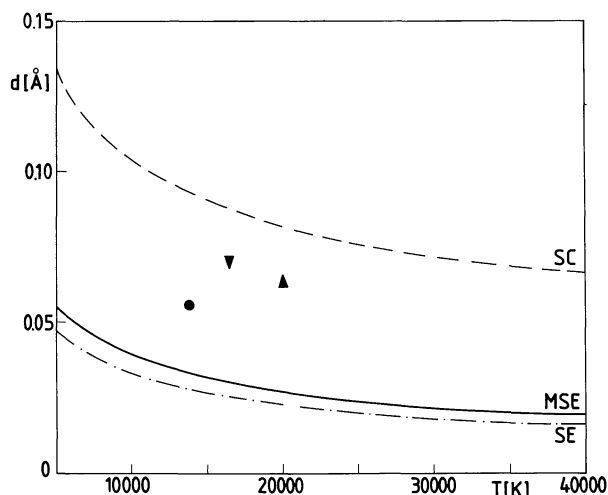

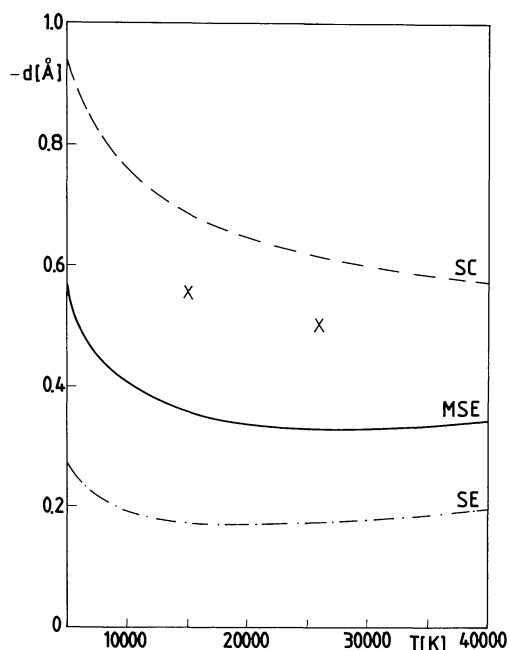**Fig. 8.** Stark shifts for Ar II $3d^4D$-$4p^4P^0$ multiplet. Notation is the same as in Fig. 2

Fig. 7. Stark shifts for Al II $4s^3S$-$4p^3P^0$ multiplet. Notation is the same as in Fig. 2
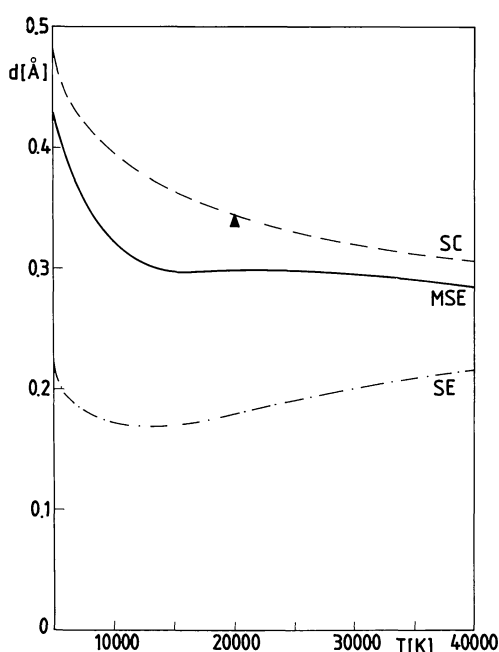

Fig. 9. Stark shifts for Ar II $4p^4P^0$-$5s^4P$ multiplet. Notation is the same as in Fig. 2

One should also emphasize that the calculating procedure is simple and extremely fast. Unlike the semiempirical formula (1), the present method does not require the knowledge of the complete set of perturbing energy levels.

The agreement between the present modified semiempirical theory and both experimental and more sophisticated theoretical values is very encouraging and it indicates that this simple method can be useful in calculating Stark shifts in astrophysical and physical problems.

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