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The phase shifts leading to the broadening and shift of spectral lines

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ABSTRACT

The classical theory of collisional broadening and shift parameters (β, δ) of an isolated spectral line was used to obtain simple analytical formulas for calculating both β and δ. These formulas were obtained on the assumption that the short range interaction is effective only in the broadening while the long range is effective in the shift of the spectral line. These parameters β and δ depend on the limiting phase shifts responsible for broadening η_b and shift $\eta\delta$. It was found that the values of η_b and η_δ are not equal to each other as was proposed by Weisskopf $\eta_\mathrm{b} = \eta_\delta = 1$. The maximum and average values of η_b ($\eta_{\mathrm{b\,max}}$, $\eta_{\mathrm{b\,av}}$) and η_δ ($\eta_{\delta\,\mathrm{max}}$, $\eta_{\delta\,\mathrm{av}}$) were obtained by numerical evaluation, using different inverse power potentials. By introducing these parameters into the approximated formulas for β and δ using Van der Waals and Lennard-Jones potential, it was found that the results of calculations for (β and δ) with different atomic transitions perturbed by different inert gases are in close agreement with earlier results. Those results, obtained earlier, were based on the Lindholm–Foley theory especially with the average values of η_b [$\eta_{\mathrm{b\,av}} = 0.6057$] and the maximum values of η_δ [$\eta_{\delta\,\mathrm{max}} = 1.57625$]. The impact parameters ρ_b and ρ_δ leading to the broadening and shift of the spectral line were also obtained for different interactions. It was found that the end parameter for the broadening ρ_b is not equal to the starting parameter for the shift ρ_δ.

1. Introduction

The collision broadening β and shift δ of atomic spectral lines represent important fundamental processes which are strongly related to the interaction potentials between radiating and perturbing atoms. It is well established that for low densities the impact approximation is justified and the line shape can be described by the Lorentzian profile with half width and shift proportional to the density of the perturbing gas [1]. Quantum mechanical formulation of the impact approximation to the theory of collision broadening and shift of spectral lines [2] gives results which differ little from those of the classical theory of Lindholm [3] and Foley [4]. It seems worthwhile, therefore, to use the classical theory of collision broadening and shift developed for any interaction potential. To interpret the experimental data, the theoretical values of broadening and shift parameters obtained in the impact limit of line broadening theory have been calculated for Van der Waals, Lennard-Jones and Czuchaj Sienkiewicz [5] potentials by many authors Bielski et al. [6], Dygdala and Dygdala et al. [7,8]. The results of these calculations are obtained by the numerical solution of the Lindholm and Foley impact theory of broadening developed by Hindmarsh [9]. In a previous work, Helmi [10] obtained a simple analytical formulas based on the assumption that the ranges of the interaction potential, responsible for the broadening and shift of the spectral line, are

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different, but the end parameter for broadening ρ_b is equal to the starting parameter ρ_δ for shift, i.e $\rho_b = \rho_\delta = \rho_0$. The value of ρ_0 depends on the Weisskopf phase shift $\eta_0 = 1$ [11]. Helmi and Roston [12] made some correction in both Weissskopf phase shift η_0 and the impact parameters for the broadening ρ_b and the shift ρ_δ. In this work we present the accurate values for the Weisskopf phase shift leading to the broadening and shift of the spectral lines η_b and η_δ and also the broadening and shift impact parameters ρ_b and ρ_δ, respectively. The calculated values are based on the use of the Lindholm–Foley theory [4] for the broadening and shift of spectral lines.

It was shown in [10] that the values of the broadening β and shift δ parameters obtained from the approximated formulas using the Weisskopf phase shift $\eta_0 = 1$ are inconsistent with the Hindmarsh [9] values. This is not due to the inadequacy of the approximate formulas given by [10], but due to the unreliable value of the Weisskopf phase shift $\eta_0 = 1$ which has no basis. Thus we devote this work to obtain the accurate values for the phases η_b and η_δ of the broadening and shift parameters.

2. Background

The impact approximation yields for the isolated line a Lorentzian profile with half width γ and Δ given by:

$$\gamma = 2N\hat{\upsilon}\sigma_b(\hat{\upsilon}) \tag{1a}$$

$$\Delta = N\hat{\upsilon}\sigma_s(\hat{\upsilon}) \tag{1b}$$

where $\hat{\upsilon}$ is the mean relative velocity and $\sigma_b(\hat{\upsilon})$ and $\sigma_s(\hat{\upsilon})$ are the effective cross sections for the broadening and shift, given by:

$$\sigma_b(\hat{\upsilon}) = 2\pi \int_0^\infty \rho[1 - \cos\eta(\hat{\upsilon},\rho)]\,d\rho \tag{2a}$$

$$\sigma_s(\hat{\upsilon}) = 2\pi \int_0^\infty \rho \sin\eta(\hat{\upsilon},\rho)\,d\rho \tag{2b}$$

where $\eta(\hat{\upsilon},\rho)$ denotes the total phase shift caused by a single collision occurring at the impact parameter ρ and relative velocity $\hat{\upsilon}$. If the perturber follows a straight line trajectory $\eta(\hat{\upsilon},\rho)$ can be written by Findeisen et al. [13] as:

$$\eta(\hat{\upsilon},\rho) = \frac{2}{\hbar\hat{\upsilon}} \int_0^\infty \frac{R\Delta V(R)}{[R^2 - \rho^2]^{1/2}}\,dR \tag{3}$$

Here R is the interatomic separation, $\Delta V(R)$ is the difference between the adiabatic potentials describing the interaction between the perturber and emitting atom in its upper and lower states.

For the simplest case of monatomic inverse-power potentials $\Delta V(R) = \hbar C_n R^{-n}$, the phase shift $\eta(\hat{\upsilon},\rho)$ takes the form

$$\eta(\hat{\upsilon},\rho) = \frac{\alpha_n C_n}{\hat{\upsilon}\rho^{n-1}} \tag{4}$$

A_n is a constant. For more details see [12].

2.1. The approximate formulas for γ and Δ

If we assume that the effective part for broadening γ in (2a) comes from the near distances ($0 - \rho_b$) and the effective part for the shift Δ in (2b) comes from the far distances ($\rho_\delta \to \infty$), in this case (2a) and (2b) will take the form

$$\sigma_b(\hat{\upsilon}) = 2\pi \int_0^{\rho_b} \rho[1 - \cos\eta(\hat{\upsilon},\rho)]\,d\rho \tag{5a}$$

$$\sigma_s(\hat{\upsilon}) = 2\pi \int_{\rho_\delta}^\infty \rho \sin\eta(\hat{\upsilon},\rho)\,d\rho \tag{5b}$$

It is seen from (4) that $\eta(\hat{\upsilon},\rho)$ will be large in the short range (0–ρ_b) and $\cos\eta(\hat{\upsilon},\rho)$ is quickly oscillating so that $\int \cos\eta(\hat{\upsilon},\rho) = 0$ [Fig. 1(a)], while $\eta(\hat{\upsilon},\rho)$ will be very small in the long range ($\rho_\delta \to \infty$) [Fig. 1(b)].

As $\sin\eta(\hat{\upsilon},\rho)$ can be expanded in a series, which may be written as

$$\sin(\hat{\upsilon},\rho) \approx \eta(\hat{\upsilon},\rho) - \frac{\eta(\hat{\upsilon},\rho)^3}{6} + \frac{\eta(\hat{\upsilon},\rho)^5}{120}$$

Then if we take only the first three terms of this series, the values of δ_b and δ_s given by (5a) and (5b) will be written as

$$\sigma_b(\hat{\upsilon}) = 2\pi \int_0^{\rho_b} \rho\,d\rho = \pi\rho_b^2 \tag{6a}$$