Pak. j. sci. ind. res., vol. 37, no. 12, December 1994

ON THE VALIDITY OF WEISSKOPF PHASE SHIFT IN THE PRESSURE BROADENING AND SHIFT OF SPECTRAL LINES

M.S. HELMI

Department of Physics, Faculty of Science, Alexandria Univeristy, Alexandria - Egypt

(Received April 3, 1994 ; revised October 17, 1994)

The classical theory of collisional broadening and shift parameter (β, δ) of an isolated spectral line is used to obtain simple analytical formulas for calculating both β and δ. These formulas are 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. The parameters β and δ depend on the Weisskopf phase shift $\eta_o = 1$. The obtained formulas are applied to both vandervaals and Lennard - jones model potentials for some atomic pair interactions. The obtained results are in close agreement with the numerical results obtained before. This verify the validity of both of the Weisskopf phase shift and the obtained analytical formulas.

Key words: Pressure broadening, Shift parameter, Spectral line.

Introduction

It has long been appreciated that measurements of the collision broadening and shift of spectral lines contain information concerning interatomic forces, and since the work of Wiesskopf [1], it has been possible to make quantitative estimates of interatomic force constants. Quantum mechanical formulation of the impact approximation to the theory of collision broadening and shift of spectral lines (Griem [2]) gives results which differ little from those of the classical theory of Lindholm [3] and Foley [4]. It seems worth while, 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 in the impact limit of line broadening theory have been calculated for Vanderwaals, Lennard Jones and Czuchaj Sienkiewicz [5] potentials by many authors Bielski *et al.* [6], Dygdala *et al.* [7] and DygdaLa *et al.* [8]. The results of these calculations are obtained by the numerical solution of the Lindholm and Foley impact theory of broadening developed by Hindmarh [9]. The aim of this work is to obtain 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 different and also to verify the validity of the Wiesskopf phase shift assumption $\eta_o = 1$.

Background. In the isolated line case the impact approximation yields alorentzain profile with half width γ and shift Δ given by

$$\gamma = 2N < v\, \sigma_b (v) > \quad \text{.....(1a)}$$

$$\Delta = N < v\, \sigma_s (v) > \quad \text{.....(Ib)}$$

N is the density number of perturbing gas, v is the relative velocity of the radiating and perturbing atoms, and the symbol <....> denotes the thermal average over the maxwellian distribution of velocities. $\sigma_b (v)$ and $\sigma_s (v)$ are the thermal averaging of effective cross sections for the broadening and shift respectively. Although the importance of the correct maxwellian averaging in (1) was suggested years ago by some authors (e.g Hindmarch [10]. In most theoretical interpretations of temperature dependence of line shape parameters the maxwellian averaging is omitted and the formula (1) are approximated by

$$\gamma\ (\bar{v}) = 2N\ \bar{v}\, \sigma_b (\bar{v}) \quad \text{.....(2a)}$$

$$\Delta (\bar{v}) = N \bar{v}\, \sigma_s (\bar{v}) \quad \text{.....(2b)}$$

in which v is replaced by the mean relative velocity $\bar{v} = [8\, kT/\pi\, \mu]^{1/2}$ where μ is the reduced mass of the radiator - perturber system and k is Boltzmann's constant. According to the adiabatic phase shift theory the effective cross sections $\sigma_b (v)$ and $\sigma_s (v)$ are given by

$$\sigma_b (v) = 2\pi \int_0^\infty \rho\, [\, 1 - \cos \eta\, (v, \rho)\,]\ d\rho \quad \text{.....(3a)}$$

$$\sigma_s (v) = 2\pi \int_0^\infty \rho \sin \eta\, (v, \rho)\ d\rho \quad \text{.....(3b)}$$

where $\eta\, (v,\rho)$ denotes the total phase shift caused by single collosion occuring at impact parameter ρ and relative velocity v. If the perturber follows a straight line trajectory then $\eta(v,\rho)$ can be written by Findeisen *et al.* [11] as:

$$\eta\, (v, \rho) = \frac{2}{hv} \int_\rho^\infty \frac{R\, \Delta v\, (R)}{R^2 - \rho^2}\, d\rho \quad \text{.....(4)}$$

Here R is the interatomic distance, $\Delta v\, (R)$ is the difference of

the adiabatic potentials describing the interaction between perturber and the emitting atom in its upper and lower states and ρ is the minimum interatomic distance.

For the simplest case of monotonic inverse-power potentials $\Delta v(R) = hcn R^{-n}$, the phase shift $\eta(v, \rho)$ takes the form

$$\eta(v_1, \rho) = \alpha_n Cn / v \rho^{n-1} \quad \text{..... (5)}$$

where

$$\alpha_n = \sqrt{\pi}\ \Gamma\left(\frac{n-1}{2}\right) / \Gamma(n/2)$$

The approximate formulas for γ and Δ. It follows from Sobelman [12] that the effective part for the broadening γ in (3a) comes from the near distances $(0 \rightarrow \rho_0)$ and the effective part for the shift Δ in (3b) comes from the far distances $(\rho_0 \rightarrow \infty)$. In this case (3a) and (3b) will take the form

$$\sigma_b(v) = 2\pi \int_0^{\rho_0} [1 - \cos \eta(\rho)]\, \rho \, . \, d\rho \quad \text{.....(6a)}$$

$$\sigma_s(v) = 2\pi \int_{\rho_0}^{\infty} \rho \sin \eta(\rho)\, d\rho \quad \text{.....(6b)}$$

It is seen from (5) that $\eta(\rho)$ will be large in the short range $(0 - \rho_0)$ and $\cos \eta(\rho)$ is quickly oscillating so that $\int \cos \eta(\rho) = 0$, while $\eta(\rho)$ will be very small in the long range $(\rho_0 \rightarrow \infty)$, so that $\sin \eta(\rho) \approx \eta(\rho)$. From this $\sigma_b(v)$ and $\sigma_s(v)$ are given as

$$\sigma_b(v) = 2\pi \int_0^{\rho_0} \rho\, d\rho = \pi \rho_0^2 \quad \text{.....(7a)}$$

$$\sigma_s(v) = 2\pi \int_{\rho_0}^{\infty} \rho\, \eta(\rho)\, d\rho \quad \text{.....(7b)}$$

Application to the potential. $\Delta v(R) = h\, Cn\, R^{-n}$. By introducing this potential in (4), then $\eta(v, \rho)$ is given by (5) and the effective cross section $\sigma_s(v)$ for shift is given from (7b) as:

$$\sigma_s(v) = 2\pi (\alpha_n C_n / v)(\rho_0^{3-n} / 3-n)$$

For the weisskopf these shift $\eta_0 = 1$, we have $\rho_0 = \left(\frac{\alpha\, n\, Cn}{v}\right)^{1/n-1}$ the broadening and shift parameters β and δ are given by

$$\beta = \gamma / N = 2v\ \sigma_b(v) = 2\pi v \left(\frac{\alpha\, n\, Cn}{v}\right)^{\frac{2}{n-1}} \quad \text{..... (8a)}$$

$$\delta = \Delta / N = 2v\ \sigma_s(v) = 2\pi v \left(\frac{\alpha\, n\, Cn}{v}\right)^{2/n-1} \frac{1}{n-3} \quad \text{.... (8b)}$$

so that the ratio between them is given by

$$\beta / \delta = n - 3 \quad \text{..... (9)}$$

the broadening and shift parameters β and δ are given from (3a) and (3b) without any approximations as:

$$\beta_n = 4\pi v \left(\frac{\alpha\, n\, Cn}{v}\right)^{2/n-1} \int_0^{\infty} \chi \left[1 - \cos \chi^{1-n}\right] d\chi \quad \text{.....(9a)}$$

$$\delta_n = 2\pi v \left(\frac{\alpha\, n\, Cn}{v}\right)^{2/n-1} \int_0^{\infty} \chi \sin \chi^{1-n}\, d\chi \quad \text{.....(9b)}$$

so that

$$\frac{\beta_n}{\delta_n} = \frac{2 \int_0^{\infty} \chi \left[1 - \cos \chi^{1-n}\right] d\chi}{\int_0^{\infty} \chi \sin \chi^{1-n}\, d\chi} \quad \text{.....(10)}$$

The approximated and numerical values for β_n, δ_n and also β_n / δ_n (in angular frequency units) for different values of n given by the formulas (8a,b), (9,10) are illustrated in Table 1.

Application to the Lennard-Jones potential. If the interaction energy $\Delta v(R)$ between the excited state of the radiating atom and the ground state of the perturbing atom is given by the Lennard-Jones model potential

$$\Delta v(R) = h C_{12} R^{-12} - h C_6 R^{-6} \quad \text{.....(11)}$$

where R is the distance between the atoms and the constants C_6 and C_{12} depend on the states of the colliding atoms. The pressure broadening β and shift δ parameter in the case of L.J. potential are given by Hindmarch [9] as:

$$\beta = 8\pi (3\pi/8)^{2/5} v^{3/5} / \Delta C_6{}^{/2/5} B(\alpha) \quad \text{.....(12a)}$$

$$\delta = 2\pi (3\pi/8)^{2/5} v^{3/5} / \Delta C_6{}^{/2/5} S(\alpha) \quad \text{.....(12b)}$$

Here the shift and broadening functions $S(\alpha)$ and $B(\beta)$ are defined by the following integrals

$$S(\alpha) = \int_0^{\infty} \chi \sin (\alpha \chi^{-11} - \chi^{-5})\, d\chi \quad \text{.....(13)}$$

TABLE 1.

β_n		δ_n		$(\gamma/\delta)_n$	
Formula (8a)	Formula (9a)	Formula (8b)	Formula (9b)	Formula (9)	Formula (10)
$\beta = 8.16$ $C_6^{2/5} v^{3/5}$	6.71 $C_6^{2/5} v^{3/5}$	$\delta_6 = 2.91$ $C_6^{2/5} v^{3/5}$	$\delta_6 = 2.24$ $C_6^{2/5} v^{3/5}$	$(\beta/\delta)_6 = 3$	$(\beta/\delta)_6 = 2.8$
				$(\beta/\delta)_4 = 1$	
$\beta_4 = 11.4$ $C_4^{2/3} v^{1/3}$	8.49 $C_4^{2/3} v^{1/3}$	$\delta_4 = 9.91$ $C_4^{2/3} v^{1/3}$	$\delta_4 = 8.49$ $C_4^{2/5} v^{3/5}$	--	$(\beta/\delta)_4 = 1.15$
$\beta_\infty = 19.74\, C_3$	$12.56\, C_3$	--	--	--	--

$$B(\alpha) = \int_0^\infty \chi \sin^2 \frac{1}{2}(\alpha\chi^{-11} - \chi^{-5})\, d\chi \quad \text{.....(14)}$$

where

$$\alpha = 0.536\, v^{6/5}\, \Delta C_{12}\, \Delta C_6^{-11/5} \quad \text{.....(15)}$$

Here ΔC_6 and ΔC_{12} denote the differences of potential parameters C_6 and C_{12} for the upper and lower states of the radiating-atom. For this potential the phase shift $\eta\ (v, \rho)$ is taken from (4) and (11) as

$$\eta\ (v_1, \rho) = \frac{\alpha_{12}\Delta C_n}{v}\, \rho^{-11} - \frac{\alpha_6 \Delta C_6}{v}\, \rho^{-5} \quad \text{.....(16)}$$

Following weisskopf $\eta\ (v, \rho) = 1$, then ρ_0 can be determined from

$$\frac{\alpha_{12}\Delta C_{12}}{v}\, \rho_o^{-11} - \frac{\alpha_6 \Delta C_6}{v}\, \rho_o^{-5} = 1 \quad \text{.....(17)}$$

By introducing (16) in (7b), the approximated analytical formulas for the broadening β and shift δ for L-J potential are given as

$$\beta = \gamma / N = v\, \rho_o^2 \quad \text{.....(18a)}$$

$$\delta = \Delta/N = v\left[\frac{\alpha_{12}\Delta C_{12}}{9v}\, \rho_o^{-9} - \frac{\alpha_6 \Delta C_6}{3v}\, \rho_o^{-3}\right] \quad \text{.....(18b)}$$

By knowing ρ_0 from (17), β and δ can be obtained from (18a) and (18b). To test the validity of the approximated formulas (18a) and (18b) with the weisskopf phase shift $\eta_0 = 1$ in case of L.J potential the (L.J) parameters ΔC_6 and ΔC_{12} for the transitions $3p^5\,4p - 3p^5\,6s$ in Ar and the resonance line of Th ($\lambda = 377.7$ nm) when the first is perturbed by He, Ne and Ar at T = 330°k and the second is perturbed by Ne and Ar at T = 860°k are taken from (Bielskie *et al.*, [6]), (Dygdala *et al.* [8]) respectively. These values in DHF approximation and the weisskopf radius ρ (in angstrom units) for the corresponding transitions are presented in Table 2.

The calculated values for the pressure broadening β and shift δ (in units of $10^{-20}\,cm^{-1}$) using the approximated formulas (18) for both Ar and Th lines are given in Table 3. These values are compared in the same table with the values obtained by the numerical solutions of (12a) and (12b) due to (Hindmarch [9]).

Results and Discussion

For the interaction potential $\Delta v(R) = hCnR^{-n}$ Table 1 illustrates that the approximated fromulas give very close values to the values obtained numerically for (δ, β and β/δ). Moreover the interaction potential can be so easily obtained from the measurments of the ratio β/δ, as it is linearly dependent on the integar number n.

It is seen from Table 2 that the Weisskopf radius ρ_0 is large for light radiating atoms while it is small for heavier atoms. It is seen also from Table 2 that ρ_0 decreases as the mass of the perturbing atom decrease while it is independent of mass of the perturbing atom in case of the heavy radiating atom.

For the L.J potential it is also seen from Table 3 that there is a close agreement between the values obtained by the two methods. There is some discrepancy especially for some shift values. It seems that the weisskopf phase shift $\eta(v_1, \rho_0) = 1$ may be not the appropriate value for the pressure shift of spectral lines.

From Tables 1 and 3, it can be seen that the approximated formulas give good results irrespective of the used potential so that they can be used for preliminary results especially for complicated interaction potential.

TABLE 2. ΔC_6 IN UNITS OF $10^{-31}\,cm^6$ RAD s^{-1} AND ΔC_{12} IN UNITS OF $10^{-74}\,cm^{12}$ RAD s^{-1} AND ρ_0 IN ANGSTROM UNIT.

Perturber	Ar			Ne			He		
Radiating atom	ρ_0(A°)	ΔC_6	ΔC_{12}	ρ_0(A°)	ΔC_6	ΔC_{12}	ρ_0	ΔC_6	ΔC_{12}
Ar $3P^5\,4P$-$3P^5\,6s$	18.18	53.18	83750	17.77	13	55866	16.56	7.05	48187
Th λ = 377.7 nm	7.21	5.87	15.25	7.21	1.43	6.58	--	--	--

TABLE 3.

Formula	Ar				Ne				He			
	β		δ		β		δ		β		δ	
	(18a)	(12a)	(18b)	(12b)	(18a)	(12a)	(18b)	(12b)	(18a)	(12a)	(18b)	(12b)
Ar/ $3P^5\,4P$-$3P^5\,6s$	6.51	7.04	-0.05	0.2	7.6	8.25	0.65	0.99	12.67	13.89	1.27	1.89
Th/ λ = 377.7 nm	1.3	1.89	-1.2	-1.18	1.73	1.83	-0.14	-0.09	--	--	--	--

It seems that for more close agreement between the approximated analytical formulas and the numerical solution of (3a) and (3b) the end parameter $\rho_{o\beta}$ for broadening may not be exactly equal to the starting parameter $\rho_{o\delta}$ for shift so that there is some interference between the two parameters and $\rho_{o\beta}$ must be larger than $\rho_{o\delta}$. (equations 7a and 7b).

References

1. V. Weisskopf, Phys. Z., **34**, 1 (1993).
2. H.R. Griem, *Plasma Spectroscopy* (McGraw Hill, New York, 1964).
3. E. Lindholm, Ark. Mat. Astr. Fys., **32**A (17) (1945).
4. H.M. Foley, Phys. Rev., **69**, 616, (1946).
5. E. Czuchaj and J. Sienkiewicz, Nature f, **39**a, 513, (1984).
6. A. Bielski, J. Wawrzynski and J. Wolnikowski, Acta physica polonica, A**67**, (3), 621 (1985).
7. R.S. Dygdala, E. Lisicki and J. Szudy, J. Phys. B: At. Mol. Phys., **20**, 3001, (1987).
8. R.S. Dygdala, R. Bobkowski and E.J. Lisicki, J. Phys. B: At. Mol. Opt. Phys., **22**, 1563, (1989).
9. W.R. Hindmarsh, A.D. Petford and G. Smith, Proc. Roy. Soc., A**297**, 296, (1967).
10. W.R. Hindmarsh, Lectures at the Winter College on Atoms, Molecules and Lasers, Trieste, (Vienna : IAEA, 1973), pp. 133-173.
11. M. Findeisen, T. Grycuk, A. Bielski, and J. Szudy, J. Phy. B: At Mol. Phys., **20**, 5997 (1987).
12. U.U. Sobelman, Introduction to the Theory of Atomic Spectra Moscow (1963).