Semiempirical Formulas for the Electron-Impact Widths and Shifts of Isolated Ion Lines in Plasmas*

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Using the Bethe-Born approximation for excitation and deexcitation cross sections with semiempirical effective Gaunt factors as proposed by Van Regemorter and Seaton, and extrapolating to below threshold energies, an "optical" cross section is obtained which agrees on the average to within a factor of 1.5 with measured Stark widths for ratios of initial electron energies to threshold energies from about 0.5 to 50. At low values of this ratio, inelastic collisions causing allowed dipole transitions are almost negligible, indicating that most of the broadening is then due to elastic collisions and, probably to a lesser extent, also to superelastic collisions and inelastic collisions involving higher multipole interactions. Comparison of this semiempirical cross section with quasiclassical estimates shows that the dependence on two parameters (namely, the Coulomb parameter and the relative size of the dipole matrix elements) not accounted for in the semiempirical effective Gaunt factors is generally weak in line-broadening applications. Line shifts are estimated from the widths using a dispersion relation, and from an expression valid for large perturber energies. Over the whole energy range considered, the ratio of the shift d of the maximum to the (half) half width w is found to vary between about 0.7 and 1.4 for lines where there is no cancellation between contributions to the shift from various levels. For other lines this ratio is smaller, in reasonable agreement with experiments. The measurements are also consistent (though not conclusively) with the existence of an additional blue shift (plasma polarization shift) corresponding typically to $\Delta(d/w)\approx 0.15$.

1. INTRODUCTION

WITH the impact approximation, i.e., assuming that various perturbers interact separately with the perturbed atom or ion and that only the net changes in the perturbed system are significant, Baranger[1] derived the following formula for the width (angular frequency separation of half intensity points from peak of Lorentz profile) of an isolated line (whose width is much smaller than separations between relevant unperturbed energy levels),

$$w_{if}=\tfrac{1}{2}N\left\{v\left[\sum_{i'}\sigma_{i'i}+\sum_{f'}\sigma_{f'f}+\int|f_i(\theta,\phi)-f_f(\theta,\phi)|^2 d\Omega\right]\right\}_{\rm av}. \quad (1)$$

Here N is the perturber (free electron) density and v the electron velocity, over which Eq. (1) must be averaged. The $\sigma_{i'i}$ and $\sigma_{f'f}$ are the inelastic cross sections for collisional transitions to levels i', f' from initial (i) and final (f) levels, respectively, of the optical transition, and the f_i, f_f are elastic scattering amplitudes for the two states of the perturbed system. The integral is over scattering angles, $d\Omega$ being the element of solid angle.

Because all of the cross sections and scattering amplitudes required to implement the above general expression for the impact width of isolated lines are next to impossible to obtain from *ab initio* calculations or direct measurements, further approximations are necessary in practical calculations. A very successful approximation is often provided by the classical path assumption for the perturbing electrons, as was first demonstrated in the case of neutral helium lines.[2] Similar calculations[3] were found to be almost equally reliable ($\sim\pm 20\%$) in many other neutral atom spectra,[4,5] in spite of the somewhat larger uncertainties in atomic wave functions. However, for ion lines, all but one[6] of nine experiments[7–14] yielded widths that were larger than the (straight) classical path results[3] by factors of 2 to 10. Most of this disagreement can be removed[15] by using hyperbolic trajectories and assuming that for so-called strong collisions certain additional terms appear which are absent in the case of weakly interacting systems.[16] Whether or not perturbed ions and perturbing electrons can be assumed to be weakly interacting on the average depends on the representa-

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tion.[17] In the completely quantum-mechanical description, it suffices that the spread in photon energies, i.e., the linewidth w, be much smaller than kT. However, for the usual classical-path approximation to be valid, also the relevant energy-level separations must be much less than kT. The latter is not the case for many isolated ion lines, in contrast to typical neutral-atom lines, a fact which makes classical-path calculations somewhat questionable even when Seaton's symmetrization[18] with respect to initial and final electron velocities is employed to account for some quantum-mechanical effects.

The reason[19] that the classical-path approximation works so well for neutral-atom lines is that most of the broadening is then due to rather high l partial waves ($l \gtrsim 10$) so that summations over l can be replaced by integrals and the WKB approximation can be employed to obtain the complex phase shifts. This results in the classical-path approximation which is, as mentioned above, only valid when in addition the energy exchange is relatively small. That the latter is the case follows for neutrals from an adiabaticity argument[19] which sets an upper limit for the relative change in electron energy of about $2/l$. For (singly-charged) ions, on the other hand, l values are smaller (~ 5), and, moreover, the adiabaticity argument is invalidated by the acceleration in the Coulomb field, which leads to the large (if not maximum) cross sections just above threshold.[20] In spite of the much improved agreement between modified classical-path calculations[15] and experiments[7–14] quantum mechanical calculations, based more directly on Baranger's general formula[1] [Eq. (1)], would be clearly more convincing, especially because the additional terms introduced in Ref. 15 are difficult to evaluate quantitatively. (Arguments[16] that they should be negligible also in the classical path approximation can be refuted on the basis of rather general considerations.[17])

2. SEMIEMPIRICAL AND QUASICLASSICAL INELASTIC CROSS SECTIONS

At high perturber energies, most of the contribution to the width comes from the inelastic terms in Eq. (1). The need, therefore, first arises for inelastic cross sections for electrons interacting with the various excited states of the ion. A suitable first approximation to these cross sections is provided by the Born approximation and by replacing the actual interaction by the dipole-monopole interaction. In this limit Bethe[21] obtained, e.g.,

$$\sigma_{i'i}=\frac{8\pi^2}{3^{3/2}}\frac{E_H}{E}|\langle i'|\mathbf{r}|i\rangle|^2 g, \tag{2}$$

where E_H is the hydrogen ionization energy, E the initial energy of the colliding electron, $\mathbf{r}$ the bound electron position operator, and g the Gaunt factor, which depends on initial and final electron energies. For electron energies much larger than the threshold energy $E_{i'}-E_i \equiv \Delta E_{i'i}$, the Bethe-Born approximation is undoubtedly the proper limit for allowed dipole transitions. Furthermore, since large l partial waves dominate then, the Gaunt factor is in the validity range of Eq. (2) obtained here essentially from classical considerations.

Following Seaton[18] we write

$$\sigma_{i'i}\approx 2\pi\int P_{i'i}\rho d\rho$$

$$\approx 2\pi\int_0^\infty (1/\hbar^2)\left|\langle i'|\int_{-\infty}^{+\infty}\tilde{V}(t)dt|i\rangle\right|^2\rho d\rho, \tag{3}$$

where $P_{i'i}$ is the probability that the transition occurs for a collision at impact parameter ρ, and $\tilde{V}$ is the classical path perturbation Hamiltonian in the interaction representation. For an electron whose radius vector is $\mathbf{r}(t)$ and assuming for the time being $|\Delta E_{i'i}| \ll \hbar v/\rho$ (i.e., $\tilde{V}\approx V$, V being the perturbation Hamiltonian in the Schrödinger picture), the transition probability is therefore approximately

$$P_{i'i}\approx(1/\hbar^2)\left|\langle i'|\int_{-\infty}^{+\infty}\frac{e^2\mathbf{r}\cdot\mathbf{r}(t)}{|\mathbf{r}(t)|^3}dt|i\rangle\right|^2$$

$$=(m/z\hbar)^2|\langle i'|\mathbf{r}\cdot[\mathbf{v}(+\infty)-\mathbf{v}(-\infty)]|i\rangle|^2$$

$$=\tfrac{4}{3}(mv/z\hbar)^2\sin^2\alpha/2|\langle i'|\mathbf{r}|i\rangle|^2, \tag{4}$$

when it is recognized[22] that $-ze^2\mathbf{r}(t)|\mathbf{r}(t)|^{-3}$ is the Coulomb force between an ion of charge z and the electron, and when the scattering angle α is introduced

[17] To make the usual classical-path approximation it is necessary to construct wave-packet states having small spatial spreads and to assume that the perturber trajectories are essentially fixed regardless of the interactions. In this case the perturber density matrix remains indeed diagonal, as in the fully quantum mechanical treatment. However, for those ion lines for which deviations between measurements and straight classical path calculations are large, typical level splittings are of the order of thermal electron energies. The "back reaction" on the perturber therefore is then large, and the perturber density matrix cannot be assumed diagonal in the wave-packet representation required for an extended classical-path approximation, even though it could still be diagonal in a less compact wave-packet representation sufficient for a fully quantum-mechanical theory. Since the arguments presented in Ref. 16, that the additional terms introduced in Ref. 15 (which involve off-diagonal S-matrix elements) are negligible, were based on a diagonal perturber density matrix also in the classical-path limit, they must therefore be considered invalid for the lines showing large deviations between measurements and straight classical-path calculations. These arguments are valid, on the other hand, for situations where relevant level splittings are small compared with thermal energies and where therefore Coulomb effects are small, such that the straight classical-path approximation employed in Ref. 3 yields reliable results.

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and an average over angles is performed. With the classical relation between scattering angle α, velocity v, and impact parameter ρ for a Coulomb field,

$$\rho=\frac{ze^2}{mv^2}\cot\tfrac{1}{2}\alpha=\frac{zE_Ha_0}{E}\cot\tfrac{1}{2}\alpha, \tag{5}$$

Eqs. (3) and (4) finally result in

$$\sigma_{i'i}\approx\frac{8\pi}{3}\frac{E_H}{E}|\langle i'|\mathbf{r}|i\rangle|^2\ln\left[\frac{\sin(\frac{1}{2}\alpha_{\max})}{\sin(\frac{1}{2}\alpha_{\min})}\right], \tag{6}$$

$\alpha_{\max}$ and $\alpha_{\min}$ being the limits of the α integral.

Comparison of Eqs. (2) and (6) yields for the quasiclassical effective Gaunt factor

$$\bar{g}\approx\frac{\sqrt{3}}{\pi}\ln\frac{\sin(\frac{1}{2}\alpha_{\max})}{\sin(\frac{1}{2}\alpha_{\min})}. \tag{7}$$

The cutoff parameters $\alpha_{\max}$ and $\alpha_{\min}$ must be determined by examination of the various approximations. The lower limit corresponds to large impact parameters at which the approximation $\tilde{V}\approx V$ fails. If during the collision the ratio of the perihelion velocity v' and distance ρ' does not exceed $|\Delta E_{i'i}|/\hbar$, no transition would be possible, i.e., a maximum impact parameter is estimated by

$$\rho_{\max}\approx\rho'\frac{v'}{v}\approx\frac{\hbar v'}{|\Delta E_{i'i}|}\frac{v'}{v}=\frac{\hbar v}{|\Delta E_{i'i}|}\left(\frac{v'}{v}\right)^2, \tag{8}$$

where use was made of angular momentum conservation in the Coulomb field ($v'\rho'=v\rho$). Invoking also conservation of energy for the unperturbed classical path ($\frac{1}{2}mv'^2=\frac{1}{2}mv^2+ze^2/\rho_{\max}$) and Eq. (5), these considerations result in

$$\sin\tfrac{1}{2}\alpha_{\min}\approx\frac{1}{2}\frac{ze^2}{\hbar v}\frac{|\Delta E_{i'i}|}{E}\left[1-\frac{ze^2}{\hbar v}\frac{|\Delta E_{i'i}|}{E}+\cdots\right]$$

$$\equiv\epsilon(1-2\epsilon+\cdots)\equiv\frac{\epsilon}{F(\epsilon)}. \tag{9}$$

In principle, $\sin\frac{1}{2}\alpha_{\max}$ could be as large as 1. However, usually the perturbation theory used in estimating the probability $P_{i'i}$ fails already at smaller values of $\sin\alpha_{\max}$. With the somewhat arbitrary requirement $\sum P_{i'i}\lesssim\frac{1}{2}$ and the estimate $\sum|\langle i'|\mathbf{r}|i\rangle|^2\approx\frac{5}{2}n_i^4a_0^2/(z+1)^2$ in Eq. (4), summed over i', the condition on $\sin\frac{1}{2}\alpha_{\max}$ is therefore

$$\sin\tfrac{1}{2}\alpha_{\max}\approx\min\left[1,\frac{(z+1)ze^2}{4n_i^2\hbar v}\right]. \tag{10}$$

In case of excitation (which is usually more important than deexcitation), the Coulomb parameter

$$\eta\equiv\frac{ze^2}{\hbar v}=z\left(\frac{E_H}{E}\right)^{1/2} \tag{11}$$

is certainly smaller than its value at threshold,

$$\eta_{\max}=z\left|\frac{E_H}{\Delta E}\right|^{1/2}, \tag{12}$$

which is about 10 or less for typical isolated ion lines. For excited states ($n^2\gg1$), therefore, only the second option in Eq. (10) is relevant here, and the quasiclassical effective Gaunt factor allowing for weak collisions ($\alpha<\alpha_{\max}$) becomes, accordingly, dropping indices,

$$\bar{g}_w\approx\frac{\sqrt{3}}{\pi}\ln\left[\frac{(z+1)E}{2n^2|\Delta E|}\left(1+\eta\frac{|\Delta E|}{E}+\cdots\right)\right]$$

$$=\frac{\sqrt{3}}{\pi}\ln\left(\frac{(z+1)E}{2n^2|\Delta E|}F(\epsilon)\right). \tag{13}$$

Clearly, cross sections based on this relation cannot be expected to be reliable unless the argument of the logarithm is large. To extend the validity range of quasiclassical calculations toward lower electron energies, it is customary to add a strong collision term to the cross section, which is at least for the more probable transitions of the order $\frac{1}{2}\pi\rho'^2_{\min}$, with $\rho'_{\min}$ corresponding to that $\alpha'_{\max}$ which results in $P_{i'i}\approx\frac{1}{2}$. This procedure results, with Eqs. (4) and (5), in a "strong collision" Gaunt factor

$$\bar{g}_s\approx\frac{\sqrt{3}}{2\pi}\cos^2\alpha'_{\max}\approx\frac{\sqrt{3}}{2\pi}\left(1-\left[\frac{(z+1)ze^2}{4n^2\hbar v}\right]^2\right), \tag{14}$$

using the second option in Eq. (10) in the factor $\cos^2\alpha'_{\max}$.

At very low energies, $\alpha_{\min}$ may become larger than $\alpha_{\max}$, indicating the breakdown of the assumption $\tilde{V}\approx V$ even for strong collisions. Such a situation would manifest itself by the logarithm turning negative. Excluding this case for the time being, the total quasiclassical effective Gaunt factor is finally estimated by the sum of Eqs. (13) and (14),

$$\bar{g}_{qc}\approx\frac{\sqrt{3}}{\pi}\left\{\tfrac{1}{2}-\tfrac{1}{2}\left[\frac{(z+1)\eta}{4n^2}\right]^2+\ln\left[\frac{(z+1)E}{2n^2|\Delta E|}F(\epsilon)\right]\right\}. \tag{15}$$

It is therefore a function of three parameters, namely $E/|\Delta E|$ as in Van Regemorter[23] and Seaton's[20] approximation and, in addition, of $2n^2/(z+1)$ and (mainly)

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through

$$\epsilon=\frac{1}{2}\frac{ze^2}{\hbar v}\frac{|\Delta E|}{E}=\tfrac{1}{2}\eta\frac{|\Delta E|}{E} \tag{16}$$

also of the Coulomb parameter η. The latter varies typically from 3 to 10 [see Eq. (11) with $E\approx\min(|\Delta E|,kT)$] in line broadening applications, while $2n^2/(z+1)$ tends to be between 5 and 15 for reasonably intense isolated ion lines (using effective quantum numbers and $z=1$ as appropriate for singly charged ions). The function $F(\epsilon)$ obeys according to the considerations leading to Eq. (9)

$$F(\epsilon)=\epsilon\left[\frac{5+4\epsilon+\epsilon^2}{\frac{1}{2}+2\epsilon+\epsilon^2-\frac{1}{2}(1+8\epsilon)^{1/2}}\right]^{1/2} \tag{17}$$

and provides a measure of the change in the adiabatic limit due to Coulomb interactions. As can be seen from Fig. 1, this effect is appreciable for all $\epsilon\gtrsim 0.5$.

Effective Gaunt factors obtained from Eq. (15) are shown in Fig. 2. At high ratios $E/|\Delta E|$ of initial electron to threshold energies, they are practically independent of the Coulomb parameter η and only weakly dependent on the parameter $2n^2/(z+1)$, which is a measure of the magnitude of the dipole matrix elements. At lower $E/|\Delta E|$, the parameters η and $2n^2/(z+1)$ enter more strongly, and the curves terminate when the logarithm in Eq. (15) vanishes. Also included in Fig. 2 is the semiempirical effective Gaunt factor $\bar{g}_{se}$ proposed by Seaton[20] and Van Regemorter[23] as deduced by comparison with some experiments and a few direct calculations. Its most notable feature is the threshold value $\bar{g}_{se}\approx 0.2$ and the fact that it is not a function of η and $2n^2/(z+1)$. Similar values at threshold can actually be estimated by returning to Eq. (7), the perturbation theory result, which is valid here since the corresponding transition probabilities $P_{i'i}$ are small. Therefore $\sin\frac{1}{2}\alpha_{max}$ can now be assumed to be close to 1,

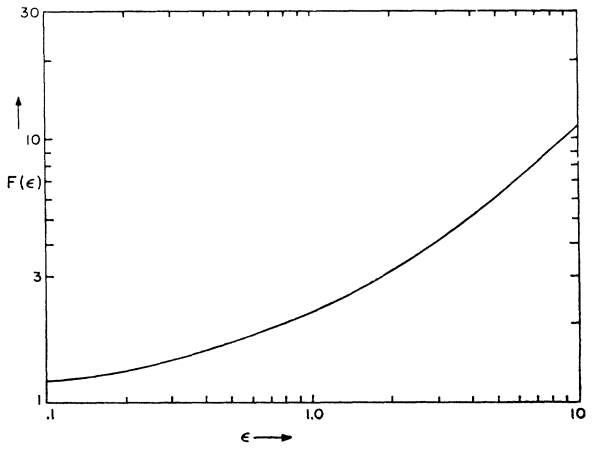

FIG. 1. The function $F(\epsilon)$ accounting for Coulomb effects on the adiabatic limit.

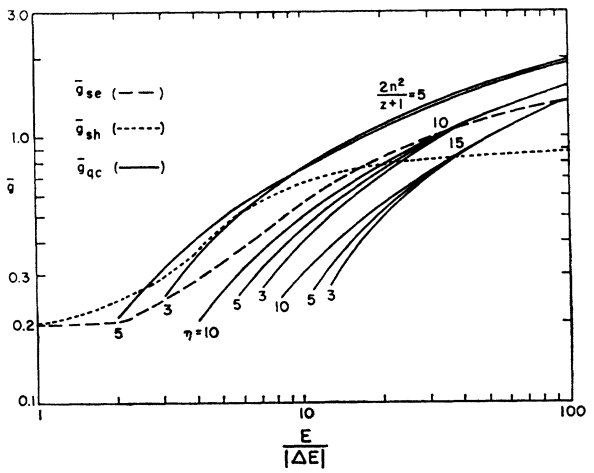

FIG. 2. Semiempirical effective Gaunt factors for widths ($\bar{g}_{se}$) (from Refs. 20 and 23) and shifts ($\bar{g}_{sh}$) and some quasiclassical estimates ($\bar{g}_{qc}$).

and $\sin\frac{1}{2}\alpha_{min}$ can be related to the adiabatic limit ρ_{max} as estimated by Eq. (8) with the maximum velocity being close to $v'=(2ze^2/m\rho_{max})^{1/2}$, since the initial kinetic energy is usually negligible for near threshold collisions. From Eq. (8) follows therefore

$$\rho_{max}\approx\left(\frac{2ze^2\hbar}{|\Delta E|mv}\right)^{1/2}=2\left(\eta\left|\frac{E_H}{\Delta E}\right|\right)^{1/2}a_0 \tag{18}$$

and with Eq. (5) accordingly at $E=|\Delta E|$

$$\sin\tfrac{1}{2}\alpha_{min}\approx\left(1+\frac{4\eta}{z^2}\left|\frac{\Delta E}{E_H}\right|\right)^{-1/2}. \tag{19}$$

This quasiclassical estimate for the threshold value of the effective Gaunt factor finally yields with Eqs. (7) and (12)

$$\bar{g}_{th}\approx\frac{\sqrt{3}}{\pi}\ln\frac{1}{\sin(\frac{1}{2}\alpha_{min})}\approx\frac{\sqrt{3}}{2\pi}\ln\left(1+\frac{4}{z}\left|\frac{\Delta E}{E_H}\right|^{1/2}\right). \tag{20}$$

Numerical values of $\bar{g}_{th}$ range from 0.16 to 0.29 for $z=1$ and $|\Delta E|$ between 0.5 and 3 eV. (For much smaller values of $|\Delta E|$ the threshold behavior does not matter for line broadening because most electrons have then considerably higher initial energies, and transitions over larger energy gaps tend to be negligible.) This may be considered an indication that the semiempirical threshold value $\bar{g}_{se}\approx 0.2$ is probably correct to within a factor of 1.5. A similar or better accuracy of the semiempirical effective Gaunt factor is suggested at higher energies (where the present quasiclassical approximation becomes more reliable) by the rather satisfactory agreement between quasiclassical and semiempirical Gaunt factors on Fig. 2; only for $2n^2/(z+1)=15$ and $E/|\Delta E|<25$ do deviations exceeding a factor of 1.5 occur. For the corresponding levels $|\Delta E|$ tends to be

small ($\sim$0.3 eV), while mean energies of the perturbing electrons are $\frac{3}{2}kT\approx 3$ eV, i.e., $E/|\Delta E|\approx 10$, for which $\bar{g}_{se}\approx 2\bar{g}_{qc}$. However, much of this deviation may well be due to an underestimate of the strong collision term in $\bar{g}_{qc}$ which dominates in this region. It therefore seems unlikely that the use of the semiempirical Gaunt factor would entail errors larger than a factor of 1.5 in line broadening calculations for any of the values of $E/|\Delta E|$, $\eta=z|E_H/E|^{1/2}$ and $2n^2/(z+1)$ relevant for singly-charged ions.

3. SEMIEMPIRICAL OPTICAL CROSS SECTIONS AND LINEWIDTHS

While the discussion in the preceding section demonstrates that quasiclassical considerations are usually sufficient to obtain the inelastic cross sections needed to calculate line widths from Eq. (1), the same cannot be said of the elastic terms which probably dominate below threshold for allowed dipole transitions. Nevertheless, it is helpful to consider the classical-path approximation for the line width[2] in terms of the classical path S-matrix elements,

$$w_{cp}=N\left\{2\pi v\int \rho d\rho(1-\mathrm{Re}S_iS_f^*)\right\}_{av}$$

$$\approx N\Big\{2\pi v\int \rho d\rho(1/\hbar^2)\,\mathrm{Re}\sum_{i',f'}\Big[\langle i|\int_{-\infty}^{+\infty}\tilde{V}(t)dt|i'\rangle\langle i'|$$

$$\times\int_{-\infty}^{t}\tilde{V}(t')dt'|i\rangle-\langle i|\int_{-\infty}^{+\infty}\tilde{V}(t)dt|i\rangle\langle f|$$

$$\times\int_{-\infty}^{+\infty}\tilde{V}^*(t)dt|f\rangle+\langle f|\int_{-\infty}^{+\infty}\tilde{V}^*(t)dt|f'\rangle\langle f'|$$

$$\times\int_{-\infty}^{t}\tilde{V}^*(t')dt'|f\rangle+\cdots\Big]\Big\}_{av}. \quad (21)$$

The first-order terms in the Dyson series can be omitted, because they vanish on the average over directions (indicated by $\{\cdots\}_{av}$), also for higher multipole interactions; the (negative) interference term vanishes for isolated lines if one replaces the actual interaction by the dipole-monopole term.

With the additional approximation $\tilde{V}\approx V$, Eq. (21) is then easily seen to agree with Eq. (1), if the quasiclassical inelastic cross sections from Eq. (3), etc., are used and the elastic terms are omitted, but the velocity average is extended over all velocities, including those below threshold. These observations strongly suggest adopting "optical" cross sections as given by Eq. (2) with an effective Gaunt factor $\bar{g}$ like that proposed by Seaton[20] and Van Regemorter,[23] but extrapolated to below threshold energies. Inspection of Fig. 2 reveals that the only reasonable extrapolation leads to $\bar{g}\approx 0.20$ for $E/|\Delta E|<1$, while quasiclassical estimates of the second order terms in Eq. (21) analogous to those performed in the preceding section for the threshold value of the inelastic cross section would result in

$$\bar{g}_{el}\approx\frac{\sqrt{3}}{2\pi}\ln\left[1+\frac{4}{z}\frac{E}{|\Delta E|}\left(\frac{E}{E_H}\right)^{1/2}\right]. \quad (22)$$

Well below threshold, this is considerably less than the inelastic threshold value estimated in Eq. (20), and the above extrapolation of the semiempirical Gaunt factor therefore (if correct) accounts for the first truly quantum-mechanical effect in electron impact broadening.

Short of *ab initio* calculations for the elastic terms, it now seems most reasonable to write the width with Eqs. (1) and (2), assuming the electron velocity distribution to be Maxwellian as

$$w_{se}\approx 8\left(\frac{\pi}{3}\right)^{3/2}\frac{h}{ma_0}N\left(\frac{E_H}{kT}\right)^{1/2}$$

$$\times\sum_{i',f'}\left[|\langle i'|\mathbf{r}|i\rangle|^2\bar{g}_{se}\left(\frac{\bar{E}}{|\Delta E_{i'i}|}\right)\right.$$

$$\left.+|\langle f'|\mathbf{r}|f\rangle|^2\bar{g}_{se}\left(\frac{\bar{E}}{|\Delta E_{f'f}|}\right)\right], \quad (23)$$

using $\bar{E}=\frac{3}{2}kT$ and the effective Gaunt factor $\bar{g}_{se}$ as plotted on Fig. 2 but continued toward $E=0$ as a constant. (Since this Gaunt factor is only a weak function of its argument, it is sufficient to employ there $\frac{1}{2}mv^2\approx\frac{3}{2}kT$.) Often the nearest perturbing levels to which dipole transitions are allowed dominate in the sum. The actual $|\Delta E|$ may then be replaced by those corresponding to these levels, say, $|\Delta E_i|$ and $|\Delta E_f|$. Summing over states i' and f', the semiempirical expression for the (half) half width of an isolated ion line broadened by electron impacts is in such cases (in angular frequency units)

$$w_{se}\approx 8\left(\frac{\pi}{3}\right)^{3/2}\frac{h}{ma_0}N\left(\frac{E_H}{kT}\right)^{1/2}\left[\langle i|r^2|i\rangle\bar{g}_{se}\left(\frac{3kT}{2|\Delta E_i|}\right)\right.$$

$$\left.+\langle f|r^2|f\rangle\bar{g}_{se}\left(\frac{3kT}{2|\Delta E_f|}\right)\right]. \quad (24)$$

For the matrix elements of r^2 the hydrogenic ion value, i.e.,

$$\langle i|r^2|i\rangle=\frac{n_i^2}{2(z+1)^2}[5n_i^2+1-3l_i(l_i+1)]a_0^2, \quad (25)$$

should normally provide a very good estimate for the present purposes when n_i is the effective principal quantum number calculated from the empirical excitation (E_i) and ionization (I) energies through

$$n_i^2=(z+1)^2E_H/(I-E_i). \quad (26)$$

The orbital quantum number l_i is that of the bound valence electron and, as noted before, $z=1$ for singly charged ions, etc. [In case of doubly excited states, the ionization energy of the corresponding configuration should be employed. Also, when the nearest level only contributes a small fraction of $\langle i|r^2|i\rangle$, e.g., in case of the highest l_i for a given n_i, the sum over i' should be calculated according to Eq. (23) using Eq. (36) below for the atomic matrix elements.]

4. ESTIMATED SEMIEMPIRICAL LINE SHIFTS

Since electron impact widths and shifts are essentially given by the real and imaginary part of the same complex function [for example, in the classical path approximation, the shift d of the maximum of the Lorentz profile is given by a relation like Eq. (21) with Re replaced by $-\mathrm{Im}$], they are related to each other by a Cauchy integral (dispersion) relation.[24] In terms of effective Gaunt factors ($\bar{g}_{\mathrm{sh}}$ for the shift and, e.g., $\bar{g}_{\mathrm{se}}$ for the width) as functions of the variable $x=E/\Delta E$, this relation is for $x>0$

$$\bar{g}_{\mathrm{sh}}(x)=\frac{x}{\pi}P\int_0^\infty \frac{\bar{g}_{\mathrm{se}}(x')}{x'(x'-x)}dx', \tag{27}$$

ignoring questions of the proper sign for the time being. Because of the singularity at $x'=0$, Eq. (27) has to be rewritten as

$$\bar{g}_{\mathrm{sh}}(x)=\bar{g}_{\mathrm{sh}}(0)+\frac{x}{\pi}P\int_0^\infty \frac{\bar{g}_{\mathrm{se}}(x')-\bar{g}_{\mathrm{se}}(0)}{x'(x'-x)}dx' \tag{28}$$

for our particular choice of $\bar{g}_{\mathrm{se}}(x)$. Actually the principal value integral then only begins at $x'=2$, and for $x<2$ the following expansion is certainly appropriate:

$$\begin{aligned}\bar{g}_{\mathrm{sh}}(x)=\bar{g}_{\mathrm{sh}}(0)&+\frac{1}{\pi}\sum_{n=1}^{\infty}x^n\\ &\times\int_2^\infty\frac{\bar{g}_{\mathrm{se}}(x')-\bar{g}_{\mathrm{se}}(0)}{x'^{n+1}}dx'\equiv\sum_{n=0}^{\infty}A_n x^n\\ =A_0&+0.332(x/10)+0.305(x/10)^2\\ &+0.550(x/10)^3+1.36(x/10)^4+\cdots\end{aligned} \tag{29}$$

which, however, as a semiconvergent series, should represent $\bar{g}_{\mathrm{sh}}$ also for $x>2$.

It remains to estimate $\bar{g}_{\mathrm{sh}}(0)=A_0$. Straight classical-path calculations[2] yield

$$\bar{g}_{\mathrm{sh}}(x)\approx\frac{\sqrt{3}}{\pi}\int_{\rho_{\min}}^\infty B(y)\frac{d\rho}{\rho}=\frac{\sqrt{3}}{\pi}b(y_{\min}) \tag{30}$$

with

$$y\equiv\frac{|\Delta\omega|\rho}{v}=\frac{1}{2}\frac{m\rho v}{\hbar x}. \tag{31}$$

Two limits are of interest here. For small velocities, i.e., large y, $B(y)$ is well approximated by the adiabatic limit, $B(y)\approx\pi/(4y)$, and Eq. (30) then becomes

$$\bar{g}_{\mathrm{sh}}(x)\approx\frac{\sqrt{3}}{2}\frac{\hbar x}{m\rho_{\min}v}\approx\frac{\sqrt{3}}{4}\frac{xhv}{ze^2}=\frac{\sqrt{3}}{4z}\left(\frac{E}{E_H}\right)^{1/2}x, \tag{32}$$

when $\rho_{\min}$ is chosen near the Coulomb cutoff as $\rho_{\min}\approx ze^2/(\frac{1}{2}mv^2)$, because for smaller impact parameters there would be a much reduced contribution to the integral in Eq. (30), if the curvature of the classical path were taken into account. At threshold ($x=1$) for typical perturber energies $E\approx\frac{3}{2}kT\approx 3$ eV, this estimate therefore yields $\bar{g}_{\mathrm{sh}}\approx 0.20$ for singly charged ions. It is more appropriate to employ Eq. (30) for high velocities, for which Coulomb effects are negligible and for which the cutoff impact parameter is necessitated by the breakdown of perturbation theory. According to Eqs. (5) and (10) this criterion results in

$$\rho_{\min}\approx\frac{2n^2}{z+1}\frac{\hbar}{mv} \tag{33}$$

or

$$y_{\min}\approx\frac{n^2}{z+1}\frac{1}{x}\approx\frac{5}{x}, \tag{34}$$

observing that the semiempirical Gaunt factor $\bar{g}_{\mathrm{se}}$ on Fig. (2) agrees best with the quasiclassical calculations for $2n^2/(z+1)=10$.

The Gaunt factor $\bar{g}_{\mathrm{sh}}$, calculated from Eqs. (30) and (34) for $x=E/|\Delta E|\gtrsim 5$ and using recently corrected values[25] of $b(y)$, is also plotted on Fig. (2) and is seen to join smoothly with the dispersion relation result from Eq. (29) for $x\lesssim 5$ when the constant term is chosen as $A_0=0.163$, a choice which is consistent with the above estimate of $\bar{g}_{\mathrm{sh}}(1)\approx 0.20$ from Eq. (32). With the present choice of the semiempirical effective Gaunt factor for width calculations, there is therefore not much of an ambiguity in the determination of the corresponding factor for the shifts. One might argue that neglecting Coulomb effects for $x\gtrsim 5$ leads to an overestimate of $\bar{g}_{\mathrm{sh}}$ in this region, and consequently also for all $x\lesssim 5$. However, these Coulomb effects should be much less important than in the case of the widths, because the shifts are primarily caused by distant collisions and the widths by close collisions. Furthermore, at $x\approx 5$ ($y_{\min}\approx 1$), Eq. (30) is probably a slight underestimate (for neutral atoms) anyway, there being at least some contributions from strong collisions as well.

The above discussion suggests that relative values of $\bar{g}_{\mathrm{se}}$ and $\bar{g}_{\mathrm{sh}}$ as shown on Fig. 2 are more reliable than their absolute values, which should according to the considerations toward the end of Sec. 2 be within a factor of about 1.5 of the true value in most line broadening applications. For lines which are broadened and shifted essentially only due to interactions with one

[24] H. R. Griem and C. S. Shen, Phys. Rev. **125**, 196 (1962).

[25] G. K. Oertel (private communication).

perturbing level, and approximately also for lines where all contributions to the shifts are in one direction, the ratio of shifts and (half) half widths is simply given by $\bar{g}_{sh}/\bar{g}_{se}$, which according to Fig. 2 varies between about 0.7 and 1.4. In general, the shifts would have to be calculated from a formula analogous to Eq. (23), i.e.,

$$d\approx -8\left(\frac{\pi}{3}\right)^{3/2}\frac{h}{ma_0}N\left(\frac{E_H}{kT}\right)^{1/2}\times\sum_{i',f'}\left[\frac{\Delta E_{i'i}}{|\Delta E_{i'i}|}|\langle i'|\mathbf{r}|i\rangle|^2\bar{g}_{sh}\left(\frac{3kT}{2|\Delta E_{i'i}|}\right)-\frac{\Delta E_{f'f}}{|\Delta E_{f'f}|}|\langle f'|\mathbf{r}|f\rangle|^2\bar{g}_{sh}\left(\frac{3kT}{2|\Delta E_{f'f}|}\right)\right], \quad (35)$$

where, e.g., $\Delta E_{i'i}=E_{i'}-E_i$ is the difference in excitation energies of perturbing level i' and *upper* level i of the line. (For a formal derivation of the signs for the various terms, the singularities in the complex plane of the function whose real and imaginary parts on the real axis yield widths and shifts, respectively, must be located. The paths of the contour integrals leading to the Cauchy integral formula are then chosen accordingly, which results in a factor $+1$ or -1 preceding the principal value integrals.) Unless the sum in Eq. (35) is dominated by a single term or at least all contributions have the same sign, taking averages of $\Delta E_{i'i}$, etc., and summing over i', f' to obtain a relation analogous to Eq. (24) for the widths would not be justified. However, the atomic matrix elements can still be estimated using approximate wave functions, notably those from the Coulomb approximation of Bates and Damgaard.[26] In that case one has, e.g.,

$$|\langle i'|\mathbf{r}|i\rangle|^2\approx\frac{l}{2l_i+1}\left(\frac{3}{2}\frac{n_l}{(z+1)}\right)^2\times(n_l^2-l^2)\phi^2(n_{l-1},n_l,l)a_0^2, \quad (36)$$

where l_i is the orbital quantum number of the valence electron, l the larger of l_i and $l_{i'}$; n_l and n_{l-1} are effective quantum numbers to be estimated from Eq. (26), and ϕ is a tabulated correction factor.[26] (The values of $\Delta E_{i'i}$ have to be averaged over fine structure levels or, still better, $|\langle i'|\mathbf{r}|i\rangle|^2$ has to be divided according to the appropriate coupling scheme before summing over i'.)

5. COMPARISON WITH EXPERIMENT

Widths and to a lesser extent also shifts of isolated ion lines have been measured recently in a number of experiments,[6–14] in which electron densities and temperatures were determined independently. Measured ratios of shifts of the intensity maxima and (half) half widths are compared in Table I with calculated values obtained from Eqs. (23) and (35), using Coulomb approximation matrix elements.

TABLE I. Comparison of measured and calculated shift to width ratios.

Multiplet	Reference	$(d/w)_{meas}$	$(d/w)_{calc}$	$\Delta(d/w)$
Ar II(6)	7	0.5	0.2	0.3
Ar II(6)	10	0.5	0.2	0.3
Ar II(7)	10	0.25	0.2	0.05
Ar II(14)	10	0.15	0.2	−0.05
Ar II(31)	10	0.2	−0.1	0.3
Ca II(1)	9	0.35	0.15	0.2
Si II(5)	14	−1.0	−1.15	0.15

The values for the N II(4,5,18,29,30,40,58,59) multiplets[6] were omitted because a comparison of measured and calculated widths suggests some systematic error, the origin of which is still unknown. Measured values for N II(4) to N II(30) are all about $d/w\approx -1$, while the calculations yield typically $d/w\approx -0.3$ for these lines. (Since on the average measured widths in this experiment are smaller by a factor of 1.7 than calculated here, removal of such a possible systematic error in the width might result in ratios of $d/w\approx -0.6$.) For the higher multiplets, measured values are much smaller in magnitude, $d/w\approx 0.2$, while Eq. (35) yields $d/w\approx 0.5$. In these cases Debye shielding may have led to a reduction, especially of the shifts,[2] because the relevant energy differences $|\Delta E_{ii'}|$ are no longer much larger than $\hbar\omega_p$, where ω_p is the plasma frequency.

Whereas the evidence from the N II data is therefore inconclusive, the comparison in Table I lends some support to the notion of an additional blue shift of relative magnitude $\Delta(d/w)\approx 0.2$, even though one should certainly not overlook the possibility of errors of the same order in the calculated ratios. Such an excessive blue shift might be due to the presence of a small excess negative average space charge in the neighborhood of a positive ion immersed in a plasma, which partially shields the potential acting upon the orbiting electron and thus causes an increase in the energies, especially of highly excited levels. (The impact theory only accounts for fluctuations in the perturbing charge density.) The initial estimate[27] of this plasma polarization effect was based on entirely classical arguments and turned out to be about an order of magnitude larger than a corresponding quantum theoretical estimate,[28] in which the plasma electrons are considered to be in highly excited states of the atom or ion preceding the emitting ion in the ionization sequence. The latter estimate combined with Eq. (24) yields for the ratio of plasma polarization shift and

[26] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc London, A242, 101 (1949).

[27] H. F. Berg, A. W. Ali, R. Lincke, and H. R. Griem, Phys. Rev. 125, 199 (1962).

[28] H. R. Griem, *Proceedings of the Seventh International Conference on Phenomena in Ionized Gases* (Gradevinska Knjiga Publishing House, Belgrade, 1966), Vol. II, 551.

electron-impact width

$$\frac{d_p}{w}\approx\frac{z^{3/2}(z+1)^{3/2}}{5}\frac{E_H}{kT}\left(\frac{n_i-n_f}{\bar{g}_i n_i^4+\bar{g}_f n_f^4}\right), \qquad (37)$$

which is about $d_p/w\approx 0.15$ for all lines listed in Table I. [$\bar{g}_i\equiv\bar{g}_{se}(\frac{3}{2}kT/|\Delta E_i|)$, $\langle i|r^2|i\rangle\approx 2n_i^4a_0^2/(z+1)^2$]. This therefore very closely corresponds to the average excess blue shift, and could thus provide a semiquantitative explanation for the differences $\Delta(d/w)$ between measured and calculated values in Table I, were these differences indeed real. This question cannot be answered on the basis of the present data, because for all but one of the multiplets listed in Table I calculated electron-impact shift to width ratios are rather small, indicating substantial cancellation between the contributions to the shift from various levels and therefore strong sensitivity to the various approximations made.

Many more experimental data are available for widths of isolated ion lines. Using Eq. (24) and measured electron densities and temperatures, ratios of measured to calculated widths were calculated for all 50 cases of different lines or different plasma conditions for which such data have been reported. As can be seen from Fig. 3, there is agreement within a factor of 2 in almost all cases over the whole range (0.5 to 50) in the parameter $kT/|\Delta E_i|$, where ΔE_i is the energy separation between upper and nearest perturbing level fulfilling dipole selection rules. The rms deviation between measured and calculated widths is only about a factor 1.5, and the spread of this ratio for multiplets measured in different experiments indicates that much of this scatter is experimental. The mean value of the ratio is 0.81 with a probable error of ± 0.12 when Eq. (24) is used for all lines, or 0.95 with a probable error of ± 0.07 when Eqs. (23) and (36) are used for those lines where the approximation leading from Eq. (23) to Eq. (24) causes an overestimation of the width by more than 20%.

6. SUMMARY AND DISCUSSION

Judged on the basis of available measurements,[6–14] the semiempirical relation for the width [i.e., Eq. (23) in conjunction with Eqs. (26) and (36) and the semiempirical Gaunt factor $\bar{g}_{se}$ on Fig. 2] is on the average and for $z=1$ certainly reliable to within a factor of 1.5, but may well be more accurate than that. Also, no significant dependence is discernable on the additional parameters $\eta=ze^2/\hbar v\approx\mathrm{Min}[z(E_H/|\Delta E|)^{1/2},\ z(E_H/kT)^{1/2}]$, and $2n^2/(z+1)$ appearing in the quasiclassical estimates of the effective Gaunt factor on Fig. 2. Apart from these apparently rather weak dependences, quasiclassical considerations are sufficient to account for the broadening effect of electrons having above threshold energies for allowed dipole transitions. The extrapolation of a constant effective Gaunt factor to below threshold, however, has no quasiclassical explanation. Whether it

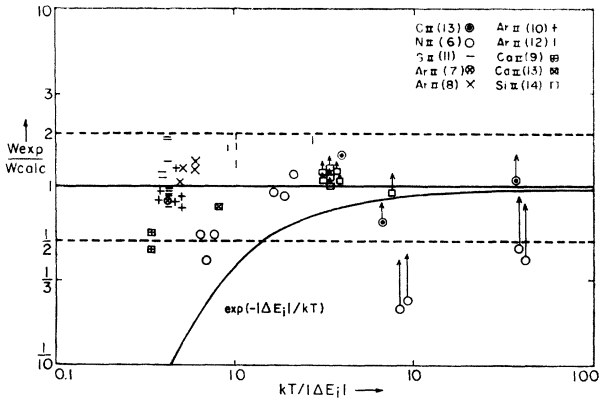

FIG. 3. Ratios of measured and calculated linewidths. Numbers associated with the various data points correspond to the experimental references, and the vertical arrows reflect changes in calculated widths when contributions from various perturbing levels are treated individually rather than lumped together. The abscissa in all cases corresponds to the perturbing level closest to the upper level of the line, and the exponential curve gives an estimate of the inelastic contribution.

can be justified by *ab initio* calculations of the elastic scattering amplitudes appearing in Eq. (1) remains to be seen, even though there is little question that this must be possible to within, say, a factor of 2 for the following reasons: there is not much of a deterioration in the agreement between measured and calculated widths on Fig. 3 toward small values of $kT/|\Delta E_i|$. Furthermore, the inelastic contribution is here smaller than the total width by a factor of about $\exp(-|\Delta E_i|/kT)$, which is below 0.1 for some of the lines, in severe disagreement[29] with a recent calculation.[30] [This factor would arise in Eq. (24) if the velocity integration were begun only at threshold energies, assuming the perturbing levels to be above the initial and final states of the line, respectively, which is the usual situation.]

One might argue that for $kT/|\Delta E_i|<1$ superelastic collisions inducing dipole transitions or collisions involving higher multipole interactions dominate. That the former is not the case for most lines follows because perturbing levels tend to be above perturbed levels. Also, the latter seem not important, because the relevant impact parameters contributing to the width (if the latter is written as $w\approx\pi N v\rho^2$) are according to the

[29] The principal claim in Ref. 30 is that practically all the broadening can be accounted for by inelastic collisions calculated using Coulomb excitation (perturbation) theory for small velocities and the straight classical-path approximation for large velocities. The limiting velocity between these two regimes was determined by the equality of Coulomb cutoff and straight classical-path strong-collision-impact parameters. This procedure leads to S-matrix elements considerably larger than would be consistent with unitarity for velocities below the above limit, because Coulomb effects remove effectively the adiabatic limitation on the transition probabilities. Because of this inconsistency, the fair agreement between such inelastic cross sections (with $\bar{g}\gtrsim 1.0$ rather than $\bar{g}\gtrsim 0.2$) and measured widths is only fortuitous.

[30] J. Cooper and G. K. Oertel, Phys. Rev. Letters 18, 985 (1967).

present estimates in Eqs. (23) to (25) and with $\bar{g}_{\text{eff}} \approx 0.2$

$$\rho \approx \frac{2n^2}{z+1}\frac{h}{mv} \approx \frac{2n^2 a_0}{z+1}\left(\frac{E_H}{kT}\right)^{1/2}. \tag{38}$$

This is for $z=1$ typically a factor of five larger than excited state Bohr radii, namely $n^2a_0/(z+1)$, and even though perihelion distances are somewhat smaller, quadrupole interactions which contribute in the ratio of the inverse square of such a suitably reduced factor will therefore almost always be negligible. The observation that quadrupole transitions often involve smaller energy differences (including zero) does not change this conclusion for any practical purposes, because the acceleration in the Coulomb field removes the so-called adiabatic cutoff to sufficiently large impact parameters.

Only for multiply ionized systems ($z=2, 3 \cdots$) would relevant impact parameters according to Eq. (38) come close to excited state Bohr radii, because kT is then usually comparable to or even larger than E_H. For $kT \approx 50$ eV the Bohr radius would actually be the larger of the two, and any multipole expansion would be useless. Furthermore, as indicated by the first version of Eq. (38), contributing angular-momentum quantum numbers are of the order $2n^2/(z+1)$ and tend therefore to be rather small for multiply ionized systems (especially their resonance lines). For such situations the quasiclassical arguments advanced in Sec. 2 are no longer applicable, but it should not be overlooked that any gross quantum-mechanical effects are accounted for in the semiempirical Gaunt factor of Van Regemorter[23] and Seaton[20] by fitting it, e.g., to the Coulomb-Born approximation[31] for the $1s$-$2p$ transition in high z hydrogenic ions. As far as allowed dipole transitions are concerned, this procedure should also take care of higher multipole interactions (which were included in the Coulomb-Born approximation calculations), and the semiempirical formulas for widths and shifts proposed here may therefore be applicable for high z systems as well (though probably less accurate than for $z=1$), because higher multipole transition rates never seem to become larger than allowed dipole transition rates.[20]

[31] A. Burgess, Mem. Soc. Roy. Sci. Liege 4, 299 (1961).

In regard to applications of semiempirical effective Gaunt factors to the calculation of excitation and de-excitation cross sections for allowed dipole transitions, the evidence from the (ion) line-broadening experiments[6–14] and from a comparison of line-broadening calculations for neutral helium atoms[32] using semiempirical "optical" cross sections[33] with classical-path calculations[2] supports Van Regemorter[23] and Seaton's[20] error estimate of a factor of 2 for near threshold energies and suggests a much better accuracy than that at intermediate initial electron energies, at least for the strong transitions. (Note that the width is given by the sum of such transition rates.) However, the quasiclassical estimates in Sec. 2 as shown on Fig. 2 do indicate that the high-energy limit adopted by Van Regemorter and Seaton is not generally correct, even for neutrals. (The practical consequences of this are minor, because cross sections at, say, more than 100 times the threshold energy are rarely required.)

Finally, in applications of the present formulas, e.g., to opacity calculations, errors from using semiempirical damping constants will be rather small, especially since errors in individual lines would tend to average out. Similarly, if electron densities are to be determined from measured ion-line Stark widths, averaging over the results obtained, say, from about 5 or 6 lines will typically result in a $\pm 20\%$ measurement of the electron density, which is comparable to the situation for neutral atom lines.[4] (The broadening by perturbing ions, while often a significant correction in case of neutral atoms, is usually negligible for ion lines.[3]) Electron-density determinations from measured shifts will generally be afflicted with a considerably larger theoretical error, at least when the ratio of shift to width is small. Exploition of the temperature dependence of these ratios for electron-temperature measurements[34] also does not seem very promising, as the ratios are only weakly dependent on temperature.

[32] H. R. Griem, paper to be presented at the Eighth International Conference on Phenomena in Ionized Gases, Vienna, 1967 (unpublished).

[33] In this case, the effective Gaunt factor is also $g_n' \approx 0.20$ at threshold, but then rises smoothly to merge with Van Regemorter and Seaton's value at about 30 times the threshold energy.

[34] D. D. Burgess and J. Cooper, Proc. Phys. Soc. (London) 86, 1333 (1965).