Theory of Resonance Broadening of Spectral Lines by Atom-Atom Impacts*

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The broadening of spectral lines due to dipole-dipole interactions with ground-state atoms of the same element is calculated with the impact and classical path approximations. Summation over all contributing intermediate states accounts for the multiplicity of the levels involved and results in a width proportional to the geometrical mean of absorption and emission oscillator strengths. Higher multipole interactions are shown to be almost always negligible, and for Lyman-α the iterated solution of the time-dependent Schrödinger equation describing the collisions is extended to fourth order. Estimated errors of its calculated width and of the widths of other lines are about 5% in the validity regime of the impact approximation, apart from any uncertainties in oscillator strengths and statistical weight factors.

1. INTRODUCTION

RESONANCE broadening (also called self-broadening) arises when upper or lower levels of the spectral line have allowed dipole transitions to the ground state, and when the radiating atom (radiator) is surrounded by like atoms in the ground state (perturbers). The problem of resonance broadening of spectral lines was first investigated, as early as 1925, by Holtsmark[1] who assumed the broadening to arise from the coupling of stationary harmonic oscillators through their dipole fields and obtained the linewidth from the rms deviation of the various frequencies from the unperturbed frequency. The first estimate of the effects of collisions (impacts) between radiators and perturbers on self-broadening was made by Weisskopf in 1933.[2] He assumed that only strong collisions cause line broadening, namely, those which result in phase shifts larger than 1 of the emitted radiation. Furssow and Wlassow,[3] in 1936, considered in addition the effects of weak (or distant) collisions which contributed 25% of the total width. Byron and Foley[4] recently calculated self-broadening widths using Anderson's impact theory.[5] They diagonalize the time integral of the interaction Hamiltonian rather than this Hamiltonian itself, using an especially convenient but time-independent coordinate system, a procedure similar to one which underestimates excitation-transfer cross sections[6] by about a factor of 1.5. (Calculations of excitation-relaxation cross sections[7] using irreducible tensors may well be subject to similar errors.) The present paper is based on recent impact-broadening theories[8,9] which in the case of Stark broadening (dipole-monopole interactions) have been found to give the best agreement with experiment.[9,10] In these theories weak interactions from distant collisions are treated exactly, and the necessary cutoff at small impact parameters and the contribution of close collisions are estimated in a self-consistent manner.

Holtsmark's approach to the problem has been continued by Mead and his co-workers[11,12] in the sense that actual results are only obtained in the limit of infinite atomic mass, which is equivalent to Holtsmark's quasi-static approximation. Theirs and the present work are therefore complementary, and it depends on the experimental situation which of the two theories is applicable. (Appropriate validity criteria are discussed in Sec. 5.) Reck *et al.* do account for the multiplicity of the levels (whose importance was first realized by Foley[13]) by considering spin-orbit interactions, but their contention that the binary collision treatment may never be valid near the line center of self-broadened lines is not borne out for pure impact broadening.

To disprove the validity of their contention for this special case consider a system consisting of two atoms described by a symmetrized wave function so that excited and ground-state atoms remain unspecified. (This description is adequate as long as Doppler effects can be neglected, because it then makes no difference whether or not the excited atom is, e.g., moving toward or away from the observer.) For the dipole-dipole interaction and the case of resonance the impact-broadening operator introduced in the next section can now be shown to have only diagonal matrix elements in the above representation. This follows because the operator as defined in Eq. (1) involves an average over relative

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orientations of the two atoms. With isotropic distributions of relative velocity vectors and distances of closest approach, application of the operator cannot result in a change of the orientation of the excited atom, i.e., in the magnetic quantum number of the excited state. Since the various accessible excited states are distinguished only by this quantum number, there are therefore indeed no off-diagonal matrix elements. Collisions in which excitation energy is exchanged between the two atoms thus need not be followed in detail because those involving changes in magnetic quantum numbers "average out" and because the others produce no change in the symmetrized wave function. (In the following calculation of the diagonal matrix element of the impact-broadening operator simple product wave functions will be used, which does not constitute any additional approximation.) Except in the Doppler core this disposes of the necessity to deal with processes[12] in which the excitation energy is carried through a whole chain of atoms in a series of subsequent collisions, before emission takes place, and justifies the usual binary-collision assumption for conditions where simultaneous multiple collisions are unlikely to occur.

2. APPROXIMATE CALCULATION OF THE IMPACT WIDTH

Profiles of impact-broadened lines are determined[8,9] by the matrix elements of an operator governing the relaxation of the system under consideration, namely,

$$\Phi=2\pi N\int vf(v)dv\int\rho d\rho\{S-1\}_{\rm av}=2\pi N\int vf(v)dv\int\rho d\rho \times\sum_{n=1}^{\infty}\left(\frac{1}{i\hbar}\right)^n\left\{\int_{-\infty}^{+\infty}dt_n\tilde{V}(t_n)\int_{-\infty}^{t_n}dt_{n-1}\tilde{V}(t_{n-1})\cdots \times\int_{-\infty}^{t_2}dt_1\tilde{V}(t_1)\right\}_{\rm av},\quad(1)$$

if written in the classical path approximation. Here N is the density of perturbers, v their velocity and ρ their impact parameter, and S is the S matrix for a single collision. Further, $\tilde{V}(t)$ is the interaction Hamiltonian (in the interaction representation) for a perturber whose time of closest approach is at $t=0$. The average (from now on just denoted by $\{\cdots\}$) is over angles associated with perturber positions ($\boldsymbol{\varrho}$) at $t=0$ and with their velocities ($\mathbf{v}$). In general, the $\tilde{V}(t)$ depend both on these angles and on the magnitudes of $\boldsymbol{\varrho}$ and $\mathbf{v}$, i.e., on ρ and v. The results must finally be averaged over the velocity distribution $f(v)$.

As mentioned in the preceding section, the operator Φ has only diagonal matrix elements for resonance dipole-dipole interactions. Then the line profiles are Lorentzian with (half) half-widths

$$w=-\mathrm{Re}\langle l|\Phi|l\rangle,\quad(2)$$

where l designates the upper or lower state of the line, whichever connects with the ground state via an allowed dipole transition. Shifts would be given by the imaginary part of $\langle l|\Phi|l\rangle$, but are zero for resonance dipole-dipole interactions. They would have to arise from terms with odd n in Eq. (1), whose matrix elements vanish for these interactions, or from nonresonant dipole-dipole (van der Waals) or higher multipole interactions.

To evaluate Eq. (1), the interaction Hamiltonian must be specified. For atoms the leading term in a multipole expansion of the complete electrostatic interaction Hamiltonian is the dipole-dipole interaction

$$V_{dd}=\left[\frac{\mathbf{d}_r\cdot\mathbf{d}_p}{|\mathbf{r}|^3}-3\frac{(\mathbf{d}_r\cdot\mathbf{r})(\mathbf{d}_p\cdot\mathbf{r})}{|\mathbf{r}|^5}\right].\quad(3)$$

Here $\mathbf{d}_r$ and $\mathbf{d}_p$ are dipole moment operators of radiating and perturbing atom electrons, respectively, and $\mathbf{r}$ is the position vector of the perturber relative to the radiator. Neglecting back reactions on the perturber, which must be negligible anyway for the impact approximation to be valid,[8,9] the position vector is in terms of impact parameter, velocity, and time (measured from the instant of closest approach),

$$\mathbf{r}(t)=\boldsymbol{\varrho}+\mathbf{v}t.\quad(4)$$

Required for Eq. (1) are time integrals of $\tilde{V}(t)$ over completed collisions. However, for resonance interactions there is no difference between the matrix elements of $V(t)$ and $\tilde{V}(t)$, as all states involved have the same energy. For the integral of $V(t)$ follows from Eqs. (3) and (4):

$$\int_{-\infty}^{+\infty}V_{dd}(t)dt=\frac{2}{v\rho^2}\left[\mathbf{d}_r\cdot\mathbf{d}_p-\frac{2}{\rho^2}(\mathbf{d}_r\cdot\boldsymbol{\varrho})(\mathbf{d}_p\cdot\boldsymbol{\varrho})-\frac{1}{v^2}(\mathbf{d}_r\cdot\mathbf{v})(\mathbf{d}_p\cdot\mathbf{v})\right].\quad(5)$$

Averaged over angles, this integral vanishes because of $\{\rho_x^2\}=\frac{1}{3}\rho^2$, $\{\rho_x\rho_y\}=0$, etc.

To calculate the second-order term in Eq. (1), consider now

$$\begin{aligned}&\langle l|\int_{-\infty}^{+\infty}dt_2\,V(t_2)\int_{-\infty}^{t_2}dt_1V(t_1)|l\rangle\\&=\tfrac{1}{2}\langle l|\int_{-\infty}^{+\infty}V(t_2)dt_2\int_{-\infty}^{+\infty}V(t_1)dt_1|l\rangle\\&=\frac{2}{v^2\rho^4}\langle l|\mathbf{d}_r\cdot\mathbf{d}_p-\frac{2}{\rho^2}(\mathbf{d}_r\cdot\boldsymbol{\varrho})(\mathbf{d}_p\cdot\boldsymbol{\varrho})-\frac{1}{v^2}(\mathbf{d}_r\cdot\mathbf{v})(\mathbf{d}_p\cdot\mathbf{v})|i\rangle\\&\times\langle i|\mathbf{d}_r\cdot\mathbf{d}_p-\frac{2}{\rho^2}(\mathbf{d}_r\cdot\boldsymbol{\varrho})(\mathbf{d}_p\cdot\boldsymbol{\varrho})-\frac{1}{v^2}(\mathbf{d}_r\cdot\mathbf{v})(\mathbf{d}_p\cdot\mathbf{v})|l\rangle,\quad(6)\end{aligned}$$

using Eq. (5) and inserting intermediate states. With additional relations for the averages like $\{\rho_x^4\}=\frac{1}{5}\rho^4$, $\{\rho_x^2\rho_y^2\}=\frac{1}{9}\rho^4$, etc., this can be averaged over angles, leading to

$$\left\{\langle l|\int_{-\infty}^{+\infty}dt_2\,V(t_2)|i\rangle\langle i|\int_{-\infty}^{t_2}dt_1 V(t_1)|l\rangle\right\}=(v^2\rho^4)^{-1}$$
$$\times\Big[(10/9)(\langle l_r|\mathbf{d}|i_r\rangle\cdot\langle i_r|\mathbf{d}|l_r\rangle)(\langle l_p|\mathbf{d}|i_p\rangle\cdot\langle i_p|\mathbf{d}|l_p\rangle)$$
$$-(2/9)(\langle l_r|\mathbf{d}|i_r\rangle\cdot\langle l_p|\mathbf{d}|i_p\rangle)(\langle i_r|\mathbf{d}|l_r\rangle\cdot\langle i_p|\mathbf{d}|l_p\rangle)\Big], \tag{7}$$

where now l_r and i_r designate initial and intermediate states of the radiator and l_p and i_p the corresponding states of the perturber. Also, matrix elements like $\langle l_r|d_x|i_r\rangle\langle l_p|d_z|i_p\rangle\langle i_r|d_z|l_r\rangle\langle i_p|d_x|l_p\rangle$ were omitted as they vanish on account of the usual selection rules for dipole transitions.

Equation (7) is of the form $|\mathbf{A}|^2|\mathbf{B}|^2(10/9-(2/9)\times\cos^2\theta)$ with θ being the angle between $\mathbf{A}$ and $\mathbf{B}$. Actually required is the sum of such an expression over intermediate states (magnetic quantum numbers), each term involving another angle. As there is no preferred direction in the problem, this amounts to replacing the term $(2/9)\cos^2\theta$ by its average over the sphere, i.e., by $2/27$, and then summing $(28/27)|\mathbf{A}|^2|\mathbf{B}|^2$. Furthermore, since l_r is the perturbed excited state and i_r the ground state, $\langle l_r|\mathbf{d}|i_r\rangle\cdot\langle i_r|\mathbf{d}|l_r\rangle$ is evidently proportional to the emission oscillator strength f_e of the line corresponding to this transition. On the other hand, l_p is the ground state and the i_p are all excited states of the same energy as the perturbed state so that $\langle l_p|\mathbf{d}|i_p\rangle\cdot\langle i_p|\mathbf{d}|l_p\rangle$ is proportional to the absorption oscillator strength f_a of the same line. With these considerations and using Eqs. (1), (2), and (7), the linewidth becomes to second order in the resonance dipole-dipole interaction

$$w\approx 2\pi N\int vf(v)dv\int\rho d\rho\left[\frac{7}{3}\frac{g_a}{g_e}\left(\frac{e^2f_a}{m\omega v\rho^2}\right)^2\right]. \tag{8}$$

The angular frequency ω is that of the resonance line, and f_e was expressed in terms of f_a and the statistical weights of "absorbing" and "emitting" states g_a and g_e, respectively. (See Ref. 5 for a more detailed derivation of the second-order term.)

The ρ integral diverges at small impact parameters. However, the bracketed term in Eq. (8) constitutes according to Eqs. (1) and (2) the first nonvanishing contribution to a sum representing $\{\langle l|1-S|l\rangle\}$, S being the S matrix for a single collision. For strong (close) collisions the magnitude of the sum may always be assumed to oscillate rapidly between 2 and 0 as ρ decreases. It is therefore customary to use the mean value, namely, $\{\langle l|1-S|l\rangle\}=1$ for strong collisions and the second-order result for weak collisions. The two regimes are separated by that value of ρ (Weisskopf radius) for which the second-order result (the bracketed term) assumes the value 1. In this manner follows approximately

$$w\approx 2\pi\left(\frac{7}{3}\frac{g_a}{g_e}\right)^{1/2}N\frac{e^2f_a}{m\omega}=3.06\pi\left(\frac{g_a}{g_e}\right)^{1/2}N\frac{e^2f_a}{m\omega}. \tag{9}$$

Weak and strong collisions contribute equally to this result, and the width is independent of the perturber velocity distribution, i.e., temperature. (Actually Weisskopf equated the magnitude of the first-order term to 1. The definition of the limiting radius in terms of the second-order term is due to Anderson.[5])

3. EFFECTS OF HIGHER MULTIPOLE INTERACTIONS

Within the framework of the impact approximation, there are two higher order effects which must be considered to assess the accuracy of the resonance widths estimated in the preceding section. (When extremely small oscillator strengths are involved, van der Waals broadening might also be important which, however, is not simply additive when caused by the same atoms.[4,7]) It is both necessary to estimate the corrections due to higher than second-order terms in the Dyson expansion in Eq. (1) and to discuss contributions to the broadening by higher multipole than dipole-dipole interactions. For the sake of concreteness, both of these corrections will be evaluated for Lyman-α. The conclusions are then generalized to arrive at a more accurate expression for the resonance width of any line, or are used to estimate remaining uncertainties in this width.

The next term in the multipole expansion for the interaction Hamiltonian following the dipole-dipole term in Eq. (3) is the dipole-quadrupole term. As a rule its matrix elements vanish because selection rules for dipole and quadrupole transitions and the condition of resonance between radiator and perturber states cannot be fulfilled simultaneously. However, for hydrogen the degeneracy of S and P states allows fulfillment of all these requirements, e.g., when initial and final radiator states and intermediate perturber states for the second-order term in Eq. (1) are 210 and 200, respectively, in the *nlm* representation. The radiator thus provides a dipole moment in the z direction which interacts with the quadrupole moment of the perturber. The relevant terms in the interaction Hamiltonian are accordingly

$$V_{dq}=-(3/e|\mathbf{r}(t)|^5)r_z(t)d_{rz}(d_{pz}^2+\tfrac{1}{2}|\mathbf{d}_p|^2), \tag{10}$$

where, e.g., d_{rz} is the z component of the radiator dipole-moment operator. Integrated over one collision this becomes

$$\int_{-\infty}^{+\infty}V_{dq}dt=-\frac{4}{e\rho^4v}\rho_z d_{rz}(d_{pz}^2+\tfrac{1}{2}|\mathbf{d}_p|^2), \tag{11}$$

using Eq. (4). With

$$\int_{-\infty}^{+\infty} dt_2\, V(t_2)\int_{-\infty}^{t_2} dt_1\, V(t_1)=\frac{1}{2}\int_{-\infty}^{+\infty} V(t)dt\int_{-\infty}^{+\infty} V(t)dt$$

and $\{\rho_z^2\}=\frac{1}{3}\rho^2$ the dipole-quadrupole contribution to the matrix elements of the second-order term in Eq. (1) can then be calculated from the appropriate atomic matrix elements as

$$\left\{\langle l|\int_{-\infty}^{+\infty} dt_2\, V_{dq}(t_2)\int_{-\infty}^{t_2} dt_1 V_{dq}(t_1)\,|\,l\rangle\right\}=\frac{2^{35}5^2}{3^{23}}\left(\frac{e^2a_0^3}{\rho^3 v}\right)^2. \quad (12)$$

This should be compared with Eq. (7) which gives for the dipole-dipole contribution

$$\left\{\langle l|\int_{-\infty}^{+\infty} dt_2 V_{dd}(t_2)\int_{-\infty}^{t_2} dt_1 V_{dd}(t_1)\,|\,l\rangle\right\}=\frac{2^{32}7}{3^{22}}\left(\frac{e^2a_0^2}{\rho^2 v}\right)^2, \quad (13)$$

when also the matrix elements there are expressed in terms of the Bohr radius a_0. The ratio of Eqs. (12) and (13) is

$$r=\frac{200}{21}\left(\frac{a_0}{\rho}\right)^2 \quad (14)$$

Typical values of ρ are of the order of the Weisskopf radius ρ_0 where Eq. (13) divided by $\hbar^2$ is about 1, i.e., can be estimated from

$$\left(\frac{\rho_0}{a_0}\right)^2\approx\frac{2^{16}7^{1/2}}{3^{11}}\frac{e^2}{\hbar v}\approx\frac{e^2}{\hbar v}. \quad (15)$$

Now atom velocities are never larger than about 10^6 cm/sec for conditions where resonance broadening is at all important. Therefore $(\rho/a_0)^2$ is typically larger than 2×10^2 and the dipole-quadrupole contribution remains according to Eq. (14) near or below 5% of the leading term from the dipole-dipole interaction. The corresponding correction to the half-width is about 1%, which can be shown using the same techniques that will be applied in the following section to calculate higher order effects from the dipole-dipole interactions, i.e., to derive Eq. (21). For Lyman-α the term $-\epsilon/6$ in this equation would have to be supplemented by $+\delta/4$, with $\delta=(3^{10}5^2/2^{13}7^{3/2})(\hbar v/e^2)$, to account for dipole-quadrupole interactions.

For other atoms without the l degeneracy the first correction would arise from quadrupole-quadrupole interactions and thus be still smaller. It is therefore safe to say that higher multipole interactions are not important in the resonance broadening of spectral lines through atom-atom impacts. (Possible exceptions are lines for which the relevant oscillator strengths for the transitions to the ground state are very small.) Since shifts by impact-type resonance interactions would also have to come from such higher multipole interactions contributing to terms with odd n in Eq. (1), these shifts will usually also be completely negligible.

4. IMPROVED CALCULATION OF THE IMPACT WIDTH

The matrix elements of the fourth-order term in Eq. (1) can be written as

$$\langle l|\int_{-\infty}^{+\infty} dt_4 V(t_4)\int_{-\infty}^{t_4} dt_3 V(t_3)\int_{-\infty}^{t_3} dt_2 V(t_2)\int_{-\infty}^{t_2} dt_1 V(t_1)\,|\,l\rangle$$
$$=\frac{1}{4!}\langle l|\int_{-\infty}^{+\infty} V(t)dt\int_{-\infty}^{+\infty} V(t)dt\int_{-\infty}^{+\infty} V(t)dt$$
$$\times\int_{-\infty}^{+\infty} V(t)dt\,|\,l\rangle=\frac{1}{4!}\sum_{i,j,k} A_{li}A_{ij}A_{jk}A_{kl}. \quad (16)$$

The indices of the matrix A designate always the excited states, either of the radiator or of the perturber, e.g., in the case of Lyman-α, the 211, 210, and 21-1 states. Numbering them states 1, 2, and 3, respectively, the A matrix for this line is from Eq. (5) and with the matrix elements now expressed in terms of ρ_0 from Eq. (15),

$$A=\frac{3\hbar}{7^{1/2}}\left(\frac{\rho_0}{\rho}\right)^2\begin{bmatrix} a_{11} & a_{12} & a_{13}\\ a_{12}^* & a_{22} & a_{12}\\ a_{13}^* & a_{12}^* & a_{11}\end{bmatrix}. \quad (17)$$

The individual matrix elements are

$$a_{11}=1-\frac{\rho_x^2+\rho_y^2}{\rho^2}-\frac{1}{2}\frac{v_x^2+v_y^2}{v^2},$$

$$a_{12}=-\sqrt{2}\frac{(i\rho_x+\rho_y)\rho_z}{\rho^2}-\frac{1}{\sqrt{2}}\frac{(iv_x+v_y)v_z}{v^2},$$

$$a_{13}=-\frac{(i\rho_x+\rho_y)^2}{\rho^2}-\frac{1}{2}\frac{(iv_x+v_y)^2}{v^2},\quad a_{22}=1-2\frac{\rho_z^2}{\rho^2}-\frac{v_z^2}{v^2}. \quad (18)$$

A straightforward though tedious calculation yields with relations for the required averages like

$$\{v_x^{2m}\}=\frac{1}{2m+1},$$

etc., for the fourth-order dipole-dipole contribution

$$\left\{\langle l|\int_{-\infty}^{+\infty} dt_4 V_{dd}(t)\int_{-\infty}^{t_4}\cdots\int_{-\infty}^{t_2} dt_1 V_{dd}(t_1)\,|\,l\rangle\right\}=0.62\hbar^4\left(\frac{\rho_0}{\rho}\right)^8\equiv\epsilon\hbar^4\left(\frac{\rho_0}{\rho}\right)^8. \quad (19)$$

In terms of the Weisskopf radius ρ_0 as defined by Eq. (15) the linewidth is thus from Eqs. (1), (2), (13), and (19)

$$w=\pi Nv\left[\rho_1^2+2\int_{\rho_1}^{\infty}\left(\frac{\rho_0^4}{\rho^4}-\epsilon\frac{\rho_0^8}{\rho^8}\right)\rho d\rho\right]$$
$$=2\pi Nv\rho_0^2\left[\frac{1}{2}\left(\frac{\rho_1}{\rho_0}\right)^2+\frac{1}{2}\left(\frac{\rho_0}{\rho_1}\right)^2-\frac{\epsilon}{6}\left(\frac{\rho_0}{\rho_1}\right)^6\right]. \quad (20)$$

Here the (nonessential) velocity average was omitted. Also, $\rho_1=\rho_0$ should be a rather good choice. (There $\{\langle l|1-S|l\rangle\}$ lies between $1-\epsilon$ and 1, which suggests that the strong collision term is overestimated, $\{\langle l|1-S|l\rangle\}$ at $\rho=\rho_0$ being below its mean value 1 for $\rho<\rho_0$, while the weak collision term is clearly underestimated.) An improved expression for the width is thus

$$w=2\pi Nv\rho_0^2(1-\tfrac{1}{6}\epsilon), \quad (21)$$

or, employing Eq. (9) for the approximate width, namely $w=2\pi Nv\rho_0^2$,

$$w=2.74\pi\left(\frac{g_a}{g_e}\right)^{1/2}N\frac{e^2f_a}{m\omega}. \quad (22)$$

(The appropriate f_a value for Lyman-α is $f_a=0.4162$, with $g_a/g_e=\frac{1}{3}$.)

Written in this form the improved formula for the resonance impact (half) half-width (in angular frequency units) should hold for any line, because the fourth-order term can be expressed in terms of oscillator strengths and statistical weight factors as well. One might perhaps expect a weak additional dependence on "angular" factors like the $\cos^2\theta$ term in the second-order term which was discussed below Eq. (7). However, even this term has only a minute influence on the half-width. Although it contributes $\frac{1}{5}$ of the $\{1-S\}$ matrix element, its effect on the width is less than 0.1%, i.e., entirely negligible. This can be seen from Eq. (20) for $\epsilon=0$, now using $(\rho_0/\rho_1)^4(1\pm1/15)=1$.

Inclusion of the fourth-order term has changed the impact width by 10%. Terms of still higher order should accordingly affect the result only by about 1%, while higher multipole interactions (see the preceding section) and any subtle details of the matrix elements, which cannot simply be expressed in terms of oscillator strengths and statistical weights, are still less critical. Combined errors of the numerical factor in Eq. (22) from these various sources are therefore probably below 2%. Uncertainties stemming from the somewhat arbitrary choice of ρ_1 might seem more serious. However, errors in weak and strong collision terms tend to compensate each other, as was discussed below Eq. (20), and ought to be of comparable magnitude. Remaining errors in the width should therefore be of the order of the error in the corrections to the weak collision term, leading one to believe that the total error in the coefficient of the impact formula, i.e., of Eq. (22), is probably near 5%. This error estimate is corroborated by a recent calculation[6] of the S-P excitation-transfer cross section which exceeds the value corresponding to Eq. (22) by 6%.

The small sensitivity to the actual choice of the Weisskopf radius is a particular feature of resonance broadening. Here errors in strong and weak collision terms from changes in the Weisskopf radius compensate each other to first order in this change, because both terms are equal to each other in the approximate theory.

5. VALIDITY CRITERIA AND COMPARISON WITH PREVIOUS RESULTS

The estimated theoretical accuracy of 5% for the width of resonance broadened lines as given by Eq. (22) and the representation of their profiles through unshifted Lorentzian shapes is subject to the condition that the impact approximation be valid. This requires fulfillment of two criteria,[8,9] first the time between effective collisions, which is of the order of the inverse of the linewidth (damping constant), must be much larger than the duration of an effective collision, which is estimated by the ratio of Weisskopf radius and thermal velocity v. Second, the times contributing to the Fourier integral which gives the line shape must be much larger than the duration of an effective collision. (These times are of the order of the inverse of the frequency separation $\Delta\omega$ from the line center.) Fulfillment of the first criterion implies that the average and long-time behavior of the time-dependent wave functions does not depend on the details of the collisions but rather only on the net change during a collision as described by the S matrix. The second criterion then decides that the line shape (or the interesting part of it) is indeed determined by this long-time behavior.

Both criteria can be combined into $(v/\rho_0)\gg\mathrm{Max}(w, |\Delta\omega|)$ with ρ_0 estimated by

$$\rho_0\approx\left(\frac{7g_a}{3g_e}\right)^{1/4}\left(\frac{e^2f_a}{m\omega v}\right)^{1/2}. \quad (23)$$

As a rule, resonance widths are so small that one is only interested in values of $\Delta\omega$ larger than w. The relevant (most restrictive) validity criterion is then

$$|\Delta\omega|\ll v/\rho_0\approx\left(\frac{g_e}{g_a}\right)^{1/4}\left(\frac{m\omega}{e^2f_a}\right)^{1/2}\left(\frac{kT}{M}\right)^{3/4}, \quad (24)$$

where M is the mass of the atoms and T their kinetic temperature.

As an example, consider the experiment of Kuhn and Vaughan[14] in which the resonance broadening of helium ($g_e/g_a=3$, $\omega\approx3\times10^{16}$ sec^{-1}, $f_a\approx0.3$, $M\approx6\times10^{-24}$ g) was measured in a liquid-helium-cooled discharge ($T\approx12$°K). Substitution of these parameters into Eq. (24) yields $|\Delta\omega|\ll10^{11}$ sec^{-1} or, in wave number units,

[14] H. G. Kuhn and J. M. Vaughan, Proc. Roy. Soc. (London) A277, 297 (1964).

$|\Delta\nu| \ll 0.5$ cm^{-1}. The values of $|\Delta\nu|$ covered by the measured profiles are about 0.1 cm^{-1}, i.e., the impact approximation is applicable, even though small errors from the only marginal fulfillment of the validity criterion cannot be ruled out.

Actually measured in this experiment were the profiles of a line whose lower level combined with the ground state and whose upper level was metastable. [The relevant oscillator strength, statistical weights, and frequency entering Eq. (22) are still those appropriate for the resonance line, though.] Besides resonance broadening, natural and Doppler broadening were assumed to be present. The latter was separated by analyzing the profiles in terms of Voigt functions. (This procedure is not strictly applicable, as resonance and Doppler broadening are not entirely independent of each other.) Then the width of the Lorentzian contribution plotted as function of density was interpreted as the sum of natural broadening (giving rise to a constant term) and resonance broadening (yielding a term linear in the density). Finally, oscillator strengths for the resonance line were deduced from both terms, namely $f_a = 0.38$ from the natural width and similar values from the resonance-broadening contribution. Using Eq. (22) the latter yields $f_a = 0.22$, i.e., taking mean values one obtains $f_a = 0.30$, which agrees rather well with theory[15] ($f_a = 0.276$).

No other experiments seem to exist in which resonance broadening could be well isolated and in which oscillator strengths and densities were known reasonably well. (Note also that in experiments with resonance lines proper, there is always considerable danger of self-absorption in boundary layers.) Detailed comparison with previous impact theories is probably not too meaningful either as they were based on overly simplified models. [The estimate in Ref. 9, Eq. (4-104), is an exception but could certainly not be claimed to be at all as accurate as the present result.] However, to demonstrate the amount of disagreement with previous calculations, it is instructive to compare numerical factors obtained by various authors corresponding to the factor 2.74 in Eq. (22). These factors are, e.g., 1.00, 1.33, and 1.81 in Refs. 2, 3, and 4, respectively. (Unsöld[16] estimates 1.57, and Ref. 9 gave 3.00.) Statistical weight factors were almost always neglected, except in Refs. 4 and 9. (As mentioned before, they had first been considered in Ref. 13 where, however, the above factor was much too large.)

Additional experiments in which resonance broadening of optically thin lines is a well-isolated mechanism and in which the required oscillator strengths, etc., are well known from theory or other experiments are needed to verify the estimated accuracy of the present calculations, i.e., of Eq. (22). Preferably they should span a range of conditions, both well in the validity regime of the impact approximation and near its limits of validity. Thereafter, and perhaps also meanwhile, the present results will quite likely find their most important application in the determination of resonance-line oscillator strengths from resonance widths of longer wavelength lines as in the experiments of Kuhn, Stacey, and Vaughan.[14,17] Special care should be exercised at low densities where Doppler and resonance broadening are comparable. Then the mean free path between excitation transfer collisions is of the same order as the wavelength of the emitted radiation so that Doppler effects may give a contribution to the Lorentzian width.[18] These excitation transfer collisions do not result in any phase shifts of the emitted radiation for resonance dipole-dipole interactions, but tend to change its polarization. Depending on multiplicities, therefore, only a more or less important fraction of these collisions need be considered as causing collisional narrowing of the Doppler core and enhancing the Lorentzian component through Doppler effects.

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