

LOW DENSITY APPROXIMATIONS IN THE ADIABATIC THEORY OF PRESSURE BROADENING*

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Various low density approximations, including that recently proposed by Szudy and Baylis, are discussed and compared between each other and with the Anderson-Baranger theory, by means of numerical calculations using a square well frequency perturbation. It is concluded that the Szudy-Baylis approximation is the most accurate, in addition to being the simplest *unified* low density approximation available. In the theoretical development, we retain the possible variation of the dipole moment *amplitude* during collisions.

1. Introduction

Jabłoński [1] was the first to give a fully quantum-mechanical theory of pressure broadening of spectral lines, by considering the radiating and perturbing atoms as constituting a single large molecular system. In order to obtain tractable results, Jabłoński showed that at sufficiently low densities and in the line wings, the N -perturber spectrum is well approximated by N times the spectrum that would result if there were a single perturber in the containing volume. This widely used one-perturber, or nearest-neighbor approximation, when supplemented by the impact approximation [2, 3] in the line center, provides a complete description of low density spectral profiles (of isolated lines). However, the fact that *two* different expressions must be used to cover the relevant frequency range constitutes a somewhat annoying feature of that description.

A *unified* quantum theory, describing both line center and wings by means of a single, *calculable* expression, was formulated by Baranger [4], who applied to the general approach and ideas of Jabłoński the correlation function method, which had been used by Anderson [5] for establishing a classical unified theory of pressure broadening. Later, Fano [6], using methods developed by Zwanzig [7], gave a different type of unified theory, which, although in some ways more restrictive than the Anderson-Baranger theory, has the advantage of being applicable to the case of mutually overlapping lines [8].

* Dedicated to Professor Aleksander Jabłoński on the occasion of his 80th birthday.

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Both the Anderson-Baranger and Fano theories (applied to an isolated line) involve substantially more computation than does the combination of impact and one-perturber approximations. Recently however, Szudy and Baylis [9] derived from the Anderson-Baranger theory a low density unified approximation which contains only quantities already present in the impact and one-perturber expressions, and yet describes the complete frequency range by means of a single expression. This remarkably simple approximation, termed "Unified-Frank-Condon" by its originators, we shall prefer to call "Szudy-Baylis approximation", as its applicability transcends the framework of the Franck-Condon approximation (it can in fact be applied to the case of degenerate levels, rotational or otherwise).

The purpose of the present paper is to study and compare the various low density approximations mentioned above. We do this mostly by means of numerical calculations of the classical profiles for a square well frequency perturbation, for which case many of the relevant quantities can be evaluated in closed form. We take the Anderson-Baranger profile as our "exact" reference, since all the other low density profiles can be viewed as approximations thereof. The general conclusion is that the Szudy-Baylis approximation (more precisely an improved version of it) is surprisingly good, better in addition to being simpler in general, than the other approximations studied, both in the line center and wings.

The paper first presents a rapid review of the adiabatic theory of pressure broadening, with derivations of the various low density approximations. In particular, a derivation is given of the Szudy-Baylis approximation, simpler than the original one [9]. Another novel feature is that we allow for variation of the *amplitude* of the dipole moment during collisions.

Sections 2 and 3 deal with the basic Anderson-Baranger theory, appropriately modified so as to accommodate a variable dipole moment amplitude. In Section 4, an expansion of the spectrum is given which brings out its structure, and from which the one-perturber and impact approximations are deduced. In Section 5 we derive the memory function approximation of Fano, adapted to the adiabatic theory. In Section 6, the Szudy-Baylis approximation is obtained. Section 7 presents numerical comparisons of the various low density approximations with the Anderson-Baranger result, for the case of a square well frequency perturbation. We conclude with a short discussion in Section 8.

2. Basic theory

Following Jabłoński [1], we consider the radiating and perturbing atoms as constituting a single large molecule. In the Born-Oppenheimer approximation, the total wave function $\Psi_{e,n} = \chi_e \phi_{e,n}$ is a product of electronic χ_e and nuclear $\phi_{e,n}$ components, the latter describing the motion of the nuclei in an effective potential V_e . The line shape corresponding to transitions between two non-degenerate electronic states $e = i$ and $e = f$ is given by (neglecting Doppler effect):

$$P(\omega) = \sum_{n,n'} P_{i,n} |\langle \phi_{f,n'} | D | \phi_{i,n} \rangle|^2 \delta(\omega - E_{f,n'} + E_{i,n}) \quad (2.1)$$

where D is the matrix element of the total dipole moment operator between initial and final electronic states, and $P_{i,n} \sim e^{-\beta E_{i,n}}$ is the relative probability for the initial state $\phi_{i,n}$. (2.1) can be rewritten as

$$P(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} C(\tau), \quad (2.2)$$

where

$$C(\tau) = \text{Tr } P_i D e^{i\tau H_f} D e^{-i\tau H_i} \quad (2.3)$$

$$= \langle D(0) \exp [i \int_0^\infty dt U(t)] D(\tau) \rangle_{Av} \quad (2.4)$$

is the dipole moment autocorrelation function. In (2.3), $H_{f,i} = T_{\text{nuc}} + V_{f,i}$ where T_{nuc} is the sum of nuclear kinetic energies, and $P_i = e^{-\beta H_i} / (\text{Tr } e^{-\beta H_i})$. In (2.4), $U = V_f - V_i$, $A(t) = e^{itH_i} A e^{-itH_i}$ for $A = U$ or D , $\langle (\) \rangle_{Av}$ signifies $\text{Tr } P_i (\)$ and the exponential is time-ordered. Note that because P_i commutes with H_i , and in view of the invariance of the trace under cyclic permutation of its arguments, one can time translate all quantities inside $\langle \ \rangle_{Av}$ by the same amount (time translation invariance under $\langle \ \rangle_{Av}$).

The classical spectrum is obtained if the time evolutions in (2.4) are regarded as classical, and $\langle \ \rangle_{Av}$ as the average over initial positions and velocities of all atoms. Physical arguments which will be given in reference to the classical picture, also apply to the quantum case if one thinks in terms of wave packet expansions or of the Feynman path-integral representation.

(2.4) represents an enormously complicated many-atom problem. Yet, the many-body aspect can be entirely solved if the following assumptions are made [4, 5] (i) the radiator is stationary, (ii) the perturbers move independently of each other and their interactions with the radiator are additive,

$$V_{f,i}(r_1 \dots r_N) = \sum_{j=1}^N v_{f,i}(r_j), \quad U(r_1 \dots r_N) = \sum_j u(r_j) \equiv \sum_j u_j, \quad (2.5)$$

where N is the total number of perturbers and $r_1 \dots r_N$ their position coordinates relative to the radiator; (iii) the dipole matrix element D factorises:

$$D(r_1 \dots r_N) = D_0 \prod_{j=1}^N d(r_j) \equiv \prod_j d_j, \quad (2.6)$$

where $d(r) \rightarrow 1$ as $r \rightarrow \infty$, D_0 being the dipole moment of the isolated radiator. $u(r)$ and $d(r)$ differ appreciably from 0 and 1 respectively only inside some finite *interaction volume* about the radiator. With the above assumptions (2.4) becomes

$$C(\tau) = D_0^2 \langle \prod_{j=1}^N d_j(0) \exp [i \int_0^\tau dt u_j(t)] d_j(\tau) \rangle_{Av} \quad (2.7)$$

$$= D_0^2 [C_1(\tau)]^N, \quad (2.8)$$

where

$$C_1(\tau) = \langle d(0) \exp \left[i \int_0^\tau dt u(t) \right] d(\tau) \rangle_{Av} \quad (2.9)$$

is $C(\tau)$ corresponding to the presence of a single perturber in the containing volume V .

Let us define the one-perturber quantity

$$g_1(\tau) = \lim_{V \rightarrow \infty} V [C_1(\tau) - 1] = \langle d(0) \exp \left[i \int_0^\tau dt u(t) \right] d(\tau) - 1 \rangle, \quad (2.10)$$

where

$$\langle \rangle \equiv \lim_{V \rightarrow \infty} V \langle \rangle_{Av} \quad (2.11)$$

sums over initial positions and averages over initial velocities of the perturber. Note that the sum $\langle \rangle$ in (2.10) is finite, since the summand differs from zero only for initial positions sufficiently close to the radiator that the perturber will interact with it during $(0, \tau)$ (roughly $r(t=0)$ must lie inside a sphere of radius $v\tau$, for each velocity v). We can now write, in the limit $N \rightarrow \infty$, $V \rightarrow \infty$, with $N/V = n$ the perturbing gas density:

$$[C_1(\tau)]^N = [1 - N^{-1}(N/V)V(C_1 - 1)]^N \rightarrow e^{ng_1(\tau)}. \quad (2.12)$$

It is convenient to define $g(\tau) = g_1(\tau) - g_1(0)$, i. e.

$$g(\tau) = \langle d(0) \exp \left[i \int_0^\tau dt u(t) \right] d(\tau) - d(0)^2 \rangle \quad (2.13)$$

and introduce the *normalised* line shape function

$$J(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} e^{ng(\tau)}. \quad (2.14)$$

($\int_{-\infty}^{\infty} d\omega J(\omega) = e^{ng(0)} = 1$ since $g(0) = 0$). We thus have (note that $g_1(0) = \langle d^2 - 1 \rangle$)

$$P(\omega) = D_0^2 e^{n\langle d^2 - 1 \rangle} J(\omega). \quad (2.15)$$

The density dependent factor $e^{n\langle d^2 - 1 \rangle}$ expresses the fact that the total intensity radiated increases or decreases according as the dipole moment is increased or decreased, on average, by the proximity of perturbers.

The fundamental result (2.14), expressing the many perturber spectrum in terms of the single perturber quantity $g(\tau)$, was first obtained by Anderson [5] and Baranger [4] in the classical and quantum cases respectively, assuming $d(r) \equiv 1$. The underlying assumptions, (i)–(iii) above, are best justified at densities sufficiently small that the radiator essentially interacts with a single perturber at a time, for which case (2.5) and (2.6) are automatically satisfied. Nevertheless, the model defined by these assumptions constitutes a good first approximation for dealing with higher densities, and line shape calculations based on (2.14) seem to correctly reproduce at least the main features of observed spectral lines, even at fairly large densities [10]. Corrections to (2.14) can be written down, but they seem extremely difficult to evaluate [11].

Let us now consider the quantity $g(\tau)$ in some detail.

3. Probabilities of $g(\tau)$

It is convenient to express $g(\tau)$ in terms of its second derivative $\ddot{g}(\tau)$, which is much easier to analyse and calculate. We have, noticing that $g(0) = 0$:

$$g(\tau) = \dot{g}(0)\tau + \int_0^\tau dt(\tau-t)\ddot{g}(t). \quad (3.1)$$

We observe that

$$\dot{g}(0) = \langle d(0)w(0) \rangle \quad (3.2)$$

where we defined

$$w(t) = iu(t)d(t) + \dot{d}(t). \quad (3.3)$$

Also, $\ddot{g}(\tau)$ has the expression

$$\ddot{g}(\tau) = -\langle w(0) \exp \left[i \int_0^\tau dt u(t) \right] w(\tau) \rangle \quad (3.4)$$

obtained from (2.13) by applying $d/d\tau$, translating by $-\tau$, applying again $d/d\tau$, and retranslating by $+\tau$.

Because $w(t)$ is appreciable during only a finite time interval (the collision duration), it is evident from (3.4) that $\ddot{g}(\tau) \rightarrow 0$ as $\tau \rightarrow \infty$, since then at least one of $w(0)$ and $w(\tau)$ tends to zero. This in turn implies $g(\tau)$ asymptotically linear in τ . Explicitly we have, using $\int_0^\tau = \int_0^\infty - \int_\tau^\infty$ in (3.1) (we consider the case $\tau > 0$; for negative τ we use $g(-\tau) = g(\tau)^*$):

$$g(\tau) = \alpha + \beta\tau + \tilde{g}(\tau), \quad (3.5)$$

where

$$\tilde{g}(\tau) = \int_\tau^\infty dt(t-\tau)\ddot{g}(t) \quad (3.6)$$

and

$$\begin{aligned} \alpha &= ia - c = - \int_0^\infty t dt \ddot{g}(t) = -\tilde{g}(0), \\ \beta &= id - b = \dot{g}(0) + \int_0^\infty dt \ddot{g}(t) = \dot{g}(\infty), \end{aligned} \quad (3.7)$$

a, b, c, d real. Clearly $\tilde{g}(\tau)$ vanishes as $\tau \rightarrow \infty$, whence the asymptotic behavior

$$g(\tau) \sim g_{as}(\tau) = \alpha + \beta\tau. \quad (3.8)$$

This is the basis of the impact approximation, obtained by approximating $g(\tau)$ by the asymptotically dominant term $\beta\tau$, with the result

$$J_{\text{imp}}(\omega) = \pi^{-1}nb/[(\omega - nd)^2 + (nb)^2]. \quad (3.9)$$

A better approximation is obtained if $g(\tau)$ is approximated by the complete $g_{as}(\tau)$, resulting in the Anderson-Talman-Traving profile [12, 13]

$$J_{as}(\omega) = \pi^{-1} e^{-nc} [nb \cos(na) + (\omega - nd) \sin(na)] / [(\omega - nd)^2 + (nb)^2]. \quad (3.10)$$

The Lindholm-Foley constant β has a long history, and its physical origin is well understood [2, 3]. The constant $\alpha = ia - c$ is less famous, and to get some feeling of its physical origin, let us consider the strong collision limit, wherein $u(r)$ is assumed large inside some volume V_0 , and nul, together with $d(r) = 1$, outside V_0 . Returning to expression (2.4), we break the operation $\langle \rangle_{Av}$ into a sum $\langle \rangle_{0,\tau} + \langle \rangle_{1,\tau} + \langle \rangle_{2,\tau} \dots$ where $\langle \rangle_{k,\tau}$ sums over only those initial states such that k and only k perturbors meet V_0 during $(0, \tau)$. All the terms $\langle D(0) e^{i\Phi(0,\tau)} D(\tau) \rangle_{k,\tau}$, $k \neq 0$, vanish, for the phases $\Phi(0, \tau) = \int_0^\tau dt U(t)$ are large and $e^{i\Phi(0,\tau)}$ is a rapidly oscillating function of initial states, averaging to zero. There remains

$$C(\tau) = \langle D(0) e^{i\Phi(0,\tau)} D(\tau) \rangle_{0,\tau} = \langle 1 \rangle_{0,\tau}. \quad (3.11)$$

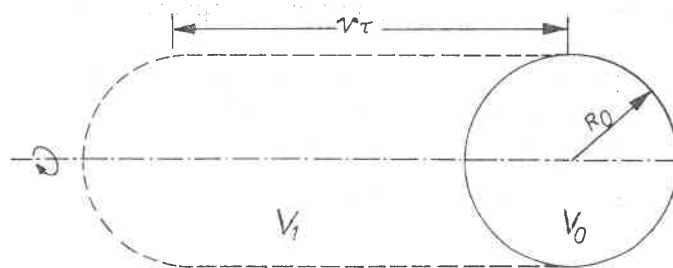


Fig. 1. For a given velocity v , a perturbation lying initially inside the volume $V_{0,\tau} = V_0 + V_1$, $V_1 = \pi R_0^2 v \tau$, meets or will meet the interaction volume V_0 during the time interval $(0, \tau)$

$\langle 1 \rangle_{0,\tau}$, the probability that no perturbation meet V_0 during $(0, \tau)$, equals the probability that there be no perturbation inside a volume $V_{0,\tau} = V_0 + \sigma v \tau$, $\sigma = \pi R_0^2$ (see Fig. 1) at time zero, i. e. $\langle 1 \rangle_{0,\tau} = e^{-nV_{0,\tau}}$ (Poisson distribution). We thus have in the strong collision limit:

$$C(\tau) = e^{-n(V_0 + \sigma v \tau)} = e^{-nV_0 - v \tau}, \quad (3.12)$$

where $v = n\sigma v$ is the collision frequency. Here then,

$$\alpha = -c = -V_0, \quad \beta = -b = -\sigma v; \quad (3.13)$$

we thus recover the well known strong collision result for β , while the value of α expresses the finiteness of the interaction volume¹. As we get away from the strong collision limit, both α and β acquire, in general, an imaginary part.

¹ The interaction volume is effectively assumed nul in the pure impact picture, where collisions are punctual in time, implying, so to speak, an interaction region in the form of a flat disc of area πR_0^2 and nul thickness, instantaneously perpendicular to the velocity of each perturbation with which it collides.

In general, β arises from trajectories which completely traverse the interaction volume (completed collisions) during $(0, \tau)$, α from trajectories either starting or ending inside V_0 , and $\tilde{g}(\tau)$ from those both starting and ending inside V_0 . Since $d(r) = 1$ outside the interaction volume, we may expect that β is independent of $d(r)$, as we now demonstrate. We first notice that (by time translation invariance)

$$\beta = \dot{g}(\infty) = \langle m(0, \infty) \rangle = \langle m(-\infty, 0) \rangle, \quad (3.14)$$

where we defined

$$m(t, \tau) = (d/d\tau)d(t)e^{i\phi(t, \tau)}d(\tau) = d(t)e^{i\phi(t, \tau)}\dot{w}(\tau), \quad (3.15)$$

where

$$\phi(t, \tau) = \int_t^\tau dt' u(t'). \quad (3.16)$$

Now, $\langle m(-\infty, 0) \rangle$ is of the general form $\langle F\{r(\cdot)\} \rangle$ where $F\{r(\cdot)\}$ denotes a functional of the trajectory $r(t)$, the dot representing the multitime dependence. We can reexpress $\langle F \rangle$ in the form

$$\langle F\{r(\cdot)\} \rangle = \int_{-\infty}^{\infty} dx_0 \langle [v/v(x_0)] F\{r(x_0, \varrho, v, \cdot)\} \rangle_{\varrho, v}. \quad (3.17)$$

Here, $r(x_0, \varrho, v, t)$ denotes motion along a trajectory of impact parameter ϱ , asymptotic velocity v , the initial position being at a distance x_0 from the point of closest approach, measured along the trajectory; $v(x_0)$ is the speed at x_0 and $\langle \rangle_{\varrho, v}$ sums over impact parameters and averages over asymptotic velocities. Defining a time variable s by $ds = dx_0/v(x_0)$ and $s = 0$ at $x_0 = 0$, we get

$$\langle F\{r(\cdot)\} \rangle = \int_{-\infty}^{\infty} ds \langle v F\{r(\varrho, v, \cdot + s)\} \rangle_{\varrho, v}, \quad (3.18)$$

where it is understood that the time of closest approach of $r(\varrho, v, t)$ is $t = 0$. With (3.18) we can write

$$\begin{aligned} \beta &= \langle m(-\infty, 0) \rangle = \int_{-\infty}^{\infty} ds \langle v m(-\infty, s) \rangle_{\varrho, v} = \langle v [d(-\infty) e^{i\phi(-\infty, s)} d(s)]_{s=-\infty}^{\infty} \rangle_{\varrho, v} \\ &= \langle v [e^{i\phi(-\infty, \infty)} - 1] \rangle_{\varrho, v}, \end{aligned} \quad (3.19)$$

where we used $d(\pm\infty) = 1$. This well known Lindholm-Foley expression of β [2, 3] is independent of $d(r)$, as was expected. In the quantum case, the sum over ϱ in (3.19) becomes a sum over angular momenta l , and in $\phi(-\infty, \infty) = \int_{-\infty}^{\infty} dt u(t)$, $u(t) = e^{i\hbar h_{l,1} t} u e^{-i\hbar h_{l,1} t}$, where $h_{l,1} = -(\hbar^2/2m)\nabla^2 + v_l(r) + \hbar^2 l(l+1)/(2mr^2)$, the exponential in (3.19) being time-ordered.

4. One-perturber approximation

We now seek low density approximations to the spectrum as given by (2.14). A natural procedure would be to expand $J(\omega)$ in powers of the density n , i. e. set $e^{ng(\tau)} = 1 + ng(\tau) + \frac{1}{2}n^2g(\tau)^2 + \dots$ in (2.14) and Fourier transform term by term. This however yields terms that diverge as $\omega \rightarrow 0$, in consequence of $g(\tau)^k \sim \tau^k$ as $\tau \rightarrow \infty$. So, referring to (3.5), we rather expand only the part $e^{n\tilde{g}(\tau)}$ and thereby obtain

$$J(\omega) = J_{as}(\omega) + J_{as}(\omega) * [n\tilde{h}(\omega) + \frac{1}{2}n^2\tilde{h}^{*2}(\omega) + \dots] \quad (4.1)$$

where $J_{as}(\omega)$ is defined in (3.10),

$$\tilde{h}(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} \tilde{g}(\tau) \quad (4.2)$$

and $*$ denotes convolution products: $f(\omega) * g(\omega) = \int_{-\infty}^{\infty} d\omega' f(\omega') g(\omega - \omega')$. Because $\tilde{g}(\tau) \rightarrow 0$ as $\tau \rightarrow \infty$, $\tilde{h}(\omega)$ is bounded, as well as all the terms in (4.1).

Before deducing low density approximations from (4.1), let us first try to interpret that expansion. Consider

$$h(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} g(\tau) = \tilde{h}(\omega) + \pi^{-1}(b\omega^{-2} + a\omega^{-1}), \quad (4.3)$$

the second equality by (3.5). In view of (2.13), we see that $h(\omega)$ is V times the spectrum that would result from the presence of a single perturber in the containing volume V (except at $\omega = 0$ where $h(\omega)$ contains an additional term $-n \langle d^2 \rangle \delta(\omega)$). Thus $\tilde{h}(\omega)$, the fluctuating part of the one-perturber spectrum $h(\omega)$ about a smooth behavior $\pi^{-1}(b\omega^{-2} + a\omega^{-1})$, can be interpreted as the spectrum radiated by the "molecule" formed by the radiator and a single perturber in *close* interaction. Likewise, the convolution power $\tilde{h}^{*k}(\omega)$ is the spectrum of a molecule consisting of the radiator and k nearby perturbers. All these "molecular spectra" are folded into $J_{as}(\omega)$, which means that they are broadened and shifted in roughly the same manner as the central line, as density increases: this represents their pressure broadening by the rest of the gas. Expansion (4.1) thus appears as very physical, breaking the spectrum into a sum of contributions from elementary collision processes. This interpretation cannot be taken too literally however, for the "molecular spectra" $\tilde{h}^{*k}(\omega)$ are not positive definite. It is in strong collision cases that it applies best, for then the negative parts are rather un conspicuous (see Fig. 8).

Let us now form a low density approximation by treating the second term in (4.1) to lowest order in n , and setting $J_{as}(\omega) \approx J_{as}^{(1)}(\omega) = \pi^{-1}(nb + \omega na)/[(\omega - nd)^2 + (nb)^2]$. We get

$$J(\omega) \approx J_{as}^{(1)}(\omega) + n\tilde{h}(\omega) \quad (4.4)$$

$$= J_{as}^{(1)}(\omega) - \pi^{-1}n(b\omega^{-2} + a\omega^{-1}) + n\tilde{h}(\omega). \quad (4.5)$$

One can see that $J_{as}^{(1)}(\omega) \approx \pi^{-1}n(b\omega^{-2} + a\omega^{-1})$ if $|\omega| \gg nb$, that is, in the wings, $J_{as}^{(1)}(\omega)$ just cancels the middle term in (4.5), leaving only the one-perturber spectrum $n\tilde{h}(\omega)$. In

the line center, we get from (4.4), $J(\omega) \approx J_{as}^{(1)}(\omega) \approx J_{imp}(\omega)$, provided n is sufficiently small. We thus recover the combination of impact and one-perturber approximations. Note that for small enough n , $J_{as}(\omega)$ passes smoothly into $nh(\omega)$, both quantities being equal to $\pi^{-1}n(b\omega^{-2} + a\omega^{-1})$ in the transition region.

The one-perturber spectrum $h(\omega)$ is not a very convenient quantity to calculate (this is tied to its divergent behavior at $\omega = 0$). A much easier quantity to compute is²

$$\ddot{h}(\omega) = -(2\pi)^{-1} \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} \ddot{g}(\tau). \quad (4.6)$$

We may then obtain $h(\omega)$ by using

$$h(\omega) = \omega^{-2} \ddot{h}(\omega) \quad (4.7)$$

which follows by Fourier transforming (3.1).

5. Memory function approximation

The memory function formalism was first applied to pressure broadening by Fano [6], and the ensuing low density approximation has been useful for dealing with mutually overlapping spectral lines [8]. We will here discuss this approximation in the simpler context of the adiabatic theory. We first derive it in a manner which shows clearly its physical meaning.

Let us return to expression (2.7) and rewrite it, using (3.15):

$$\begin{aligned} C(\tau) = D_0^2 \langle \prod_j [d_j(0)^2 + \int_0^\tau dt m_j(0, t)] \rangle_{Av} = D_0^2 \langle \prod_j d_j^2 + \sum_{j=1}^N \prod_{k \neq j} d_k^2 \int_0^\tau dt m_j(0, t) \\ + \frac{1}{2} \sum_{i \neq j} \prod_{k \neq i, j} d_k^2 \int_0^\tau dt \int_0^\tau dt' m_i(0, t) m_j(0, t') + \dots \rangle_{Av}. \end{aligned} \quad (5.1)$$

Using $\langle \prod_{j=1}^{N-k} d_j^2 \rangle_{Av} \rightarrow e^{n\langle d^2 - 1 \rangle}$ as $N, V \rightarrow \infty$, k finite, and $\int_0^\tau dt_1 \int_0^\tau dt_2 \dots \int_0^\tau dt_k = k! \int_0^\tau dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{k-1}} dt_k$, we find

$$I(\tau) = \langle 1 + \sum_j \int_0^\tau dt m_j(0, t) + \sum_{i \neq j} \int_0^\tau dt \int_0^\tau dt' m_i(0, t') m_j(0, t) + \dots \rangle_{Av}, \quad (5.2)$$

where we defined $I(\tau)$ by $C(\tau) = D_0^2 e^{n\langle d^2 - 1 \rangle} I(\tau)$ for $\tau > 0$, and $I(\tau < 0) = 0$, so that the line shape

$$J(\omega) = \pi^{-1} \text{Re } I(\omega) = \pi^{-1} \text{Re} \int_0^\infty d\tau e^{-i\omega\tau} I(\tau). \quad (5.3)$$

² $\ddot{h}(\omega)$ has an expression similar to that of $P(\omega)$ in Eq. (2.1), but with D replaced by $h_f d - dh_f = ud - (\hbar^2/2m) [\nabla^2, d]$, and all quantities pertaining to a single perturber.

Let us consider the quantity

$$m_1(0, t_1)m_2(0, t_2) = d_1(0)e^{i\phi_1(0, t_1)}w_1(t_1)d_2(0)e^{i\phi_2(0, t_2)}w_2(t_2). \quad (5.4)$$

This vanishes unless perturber 1 is near the radiator at time t_1 , or else $w_1(t_1) = 0$, and likewise for perturber 2 at t_2 . If for a given multi-perturber trajectory, the collisions of the radiator with perturbers 1 and 2 do not overlap in time, then, either (5.4) vanishes, or, 2 does not interact with the radiator prior to time t_1 at which 1 is still interacting (for (5.4) not to vanish), that is, $d_2(t) = 1$ and $u_2(t) = 0$ for $t < t_1$; we may then write $d_2(0) = 1 = d_2(t_1)$, $\phi_2(0, t_2) = \phi_2(t_1, t_2)$ that is, $m_2(0, t_2) = m_2(t_1, t_2)$ in (5.4). If now it is the case that the perturbing gas density n is low enough that collisions of the radiator with different perturbers are (almost) always disjoint in time, we can make the *binary collision approximation* $\langle m_1(0, t_1)m_2(0, t_2) \rangle_{Av} \approx \langle m_1(0, t_1)m_2(t_1, t_2) \rangle_{Av}$, and more generally

$$\begin{aligned} \langle m_1(0, t_1)m_2(0, t_2) \cdots m_k(0, t_k) \rangle_{Av} &\approx \langle m_1(0, t_1)m_2(t_1, t_2) \cdots m_k(t_{k-1}, t_k) \rangle_{Av} \\ &= V^k \dot{g}(t_1)\dot{g}(t_2 - t_1) \cdots \dot{g}(t_k - t_{k-1}). \end{aligned} \quad (5.5)$$

Expansion (5.2) thereby becomes a sum of convolution products, the Fourier-Laplace transform of which yields (after resummation)

$$I_M(\omega) = [i\omega - i\omega n \dot{g}(\omega)]^{-1} = [i\omega + \omega^2 n g(\omega)]^{-1}, \quad (5.6)$$

(M for *memory*), where we defined $\{g(\omega), \dot{g}(\omega), \ddot{g}(\omega)\} = \int_0^\infty d\tau e^{-i\omega\tau} \{g(\tau), \dot{g}(\tau), \ddot{g}(\tau)\}$, and used $\dot{g}(\omega) = i\omega g(\omega)$. The resulting spectrum is, by (5.3), a ‘‘Lorentzian’’

$$J_M(\omega) = \pi^{-1} n B(\omega) / [(\omega - n D(\omega))^2 + (n B(\omega))^2] \quad (5.7)$$

with

$$B(\omega) = \omega^2 \operatorname{Re} g(\omega) = \omega^2 \pi h(\omega) = \pi \hbar(\omega) \quad (5.8)$$

$$D(\omega) = -\omega^2 \operatorname{Im} g(\omega). \quad (5.9)$$

By applying $\int_0^\infty d\tau e^{-i\omega\tau}$ on (3.1), we have in analogy with (4.7), $g(\omega) = -\omega^{-2} [\dot{g}(0) + \ddot{g}(\omega)]$, so $-\omega^2 g(\omega)|_{\omega=0} = \dot{g}(0) + \int_0^\infty d\tau \ddot{g}(\tau) = \dot{g}(\infty) = \beta$, that is

$$B(\omega = 0) = b, \quad D(\omega = 0) = d. \quad (5.10)$$

It follows that in the line center, (5.7) reduces to the impact profile. In the wings, $J_M(\omega) \sim \pi^{-1} n B(\omega) / \omega^2 = n h(\omega)$, i. e. we get the one-perturber spectrum.

The physical meaning of approximation (5.7) is clear: it is obtained by suppressing the simultaneous interaction of the radiator with several perturbers, which is justified if the density is low enough that anyhow only one perturber at a time interacts with the radiator.

Eq. (5.6) may be obtained in a more straightforward, though physically less motivated manner, by setting a priori $I(\omega) = [i\omega - M(\omega)]^{-1}$, deducing the density expansion of $M(\omega)$ from that of $I(\omega)$, and retaining the first term only. This latter approach is an example of a general method for obtaining low density approximations [14], that

is: express $J(\omega)$ in terms of a quantity whose density expansion contains no unbounded terms (at least in the first few orders), contrarywise to the expansion of $J(\omega)$ itself, and retain only the first (or first few) terms in that expansion. We will now use this method to derive the Szudy-Baylis approximation.

6. Szudy-Baylis approximation

Basically, the Szudy-Baylis approximation [9] scheme consists in setting

$$J(\omega) = e^{-nc} G(\omega - nd) / [(\omega - nd)^2 + (nb)^2], \quad (6.1)$$

expanding $G(v)$, $v = \omega - nd$, in powers of n , and truncating. A convenient expression for $G(v)$ is, from (4.1),

$$G(v) = \pi^{-1} [(nb) \cos(na) + v \sin(na)] + [v^2 + (nb)^2] J'_{as} [n\tilde{h}(v) + \frac{1}{2} n^2 \tilde{h}^{*2}(v) + \dots], \quad (6.2)$$

where J'_{as} equals J_{as} , Eq. (3.10), but with $c = d = 0$. To first order in n , $G(v)$ equals

$$G^{(1)}(v) = \pi^{-1} (nb + vna) + v^2 n \tilde{h}(v) \quad (6.3)$$

$$= v^2 n \tilde{h}(v) = n \dot{h}(v). \quad (6.4)$$

The Szudy-Baylis approximation is thus

$$J_{SB}(\omega) = e^{-nc} n \dot{h}(\omega - nd) / [(\omega - nd)^2 + (nb)^2]. \quad (6.5)$$

At small $v = \omega - nd$, $G^{(1)}(v) \approx \pi^{-1} nb$, from (6.3), so $J_{SB}(\omega) \approx e^{-nc} J_{imp}(\omega)$. In the wings, $|v| \gg nb$, $J_{SB}(\omega) \approx e^{-nc} n \dot{h}(\omega - nd)$, that is the one-perturber spectrum, pressure shifted³ by nd and multiplied by e^{-nc} .

Since (6.5) applies to low densities, we could replace e^{-nc} by 1, which further simplifies the approximation by eliminating the necessity of calculating c (in the original approximation given by Szudy and Baylis [9], e^{-nc} does not appear, and $\dot{h}(\omega - n\langle u \rangle)$ appears instead of $\dot{h}(\omega - nd)$ in (6.5)). However, by retaining e^{-nc} , we considerably extend the range in density for which $J_{SB}(\omega)$ is a good approximation (see Figs. 2-10). This may be understood in part from the fact that in the strong collision limit, $J(\omega) \rightarrow e^{-nc} J_{imp}(\omega)$ whatever the density, as was seen in Section 3. Note that $J_{SB}(\omega)$ equals $e^{-nc} J_M(\omega)$ with the denominator in (5.7) replaced by its value at $\omega = 0$.

7. Square well frequency perturbation

To illustrate the discussion of the preceding sections, we performed numerical calculations of the classical line shapes for the case that $d(r) \equiv 1$, and $u(r)$ has the shape of a square well:

$$\begin{aligned} u(r) &= U, r < R_0 \\ &= 0, r > R_0. \end{aligned} \quad (7.1)$$

³ We could also retain the pressure broadening of the one-perturber spectrum by the rest of the gas, by retaining $J'_{as} \tilde{h}(v)$ in (6.3) rather than just $\tilde{h}(v)$. This however would destroy the beautiful simplicity of the approximation.

We assume the perturbers to follow rectilinear trajectories of uniform velocity v , so that $g(\tau)$ has the expression (we do not average over v)

$$g(\tau) = \int_{-\infty}^{\infty} dx_0 \int_0^{\infty} 2\pi \rho d\rho \left\{ \exp \left[i \int_0^{\tau} dt u \left[(x_0 + vt)^2 + \rho^2 \right]^{1/2} \right] - 1 \right\}. \quad (7.2)$$

With $u(r)$ given by (7.1), $g(\tau)$, $\tilde{h}(\omega)$, etc., as well as all the terms of expansion (4.1), are calculable in closed form. We choose units such that $V_0 = 4\pi R_0^3/3 = 1$ and $\tau_c = 1$, where

$$\tau_c = 2R_0/v \quad (7.3)$$

is the maximum duration of collisions. Here then, the density n equals the average number of perturbers in the interaction volume V_0 , while the well depth U and frequency ω are in units of τ_c^{-1} .

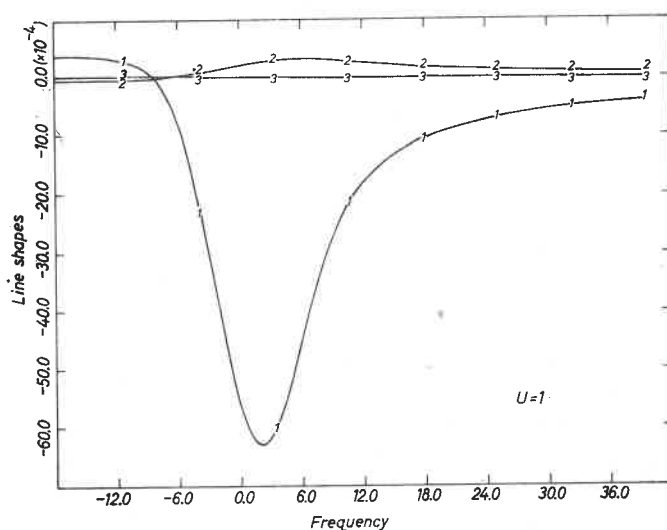


Fig. 2. The functions $\tilde{h}^{*k}(\omega)$, $k = 1, 2, 3$, for the case $U = 1$

The numerical results are shown in Figs. 2 to 10. We chose three different values of U : 1, 6 and 25, so as to illustrate weak, intermediate and strong collision conditions, respectively. In each case, we first give the "molecular spectra" $\tilde{h}^{*k}(\omega)$, which help to understand the structures of the line-shapes plotted⁴. In the figures, "exact" refers to the profiles obtained via the Anderson-Baranger expression (2.14), while "one-perturber" stands for $e^{-nc}h(\omega)$, i. e. the one-perturber spectrum multiplied by e^{-nc} , and ATT means Anderson-Talman-Traving, approximation (3.10). We use the Anderson expression (2.14)

⁴ The small oscillations in $\tilde{h}(\omega)$ for the case $U = 25$, Fig. 8, arise from the sharp edges of the square well, and represent an effect analogous to optical diffraction.

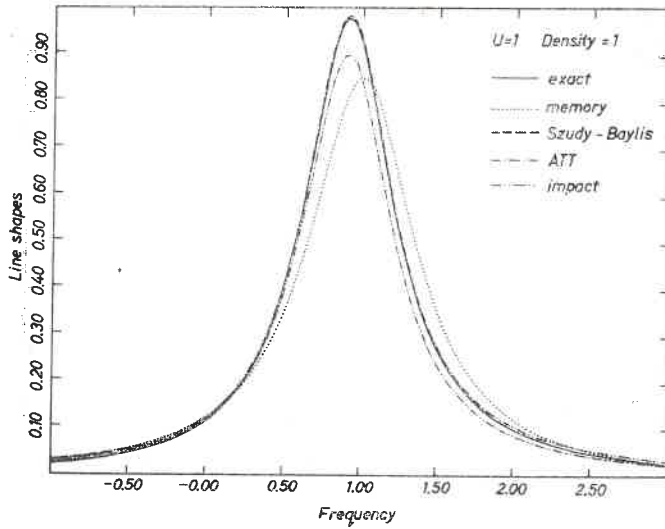


Fig. 3

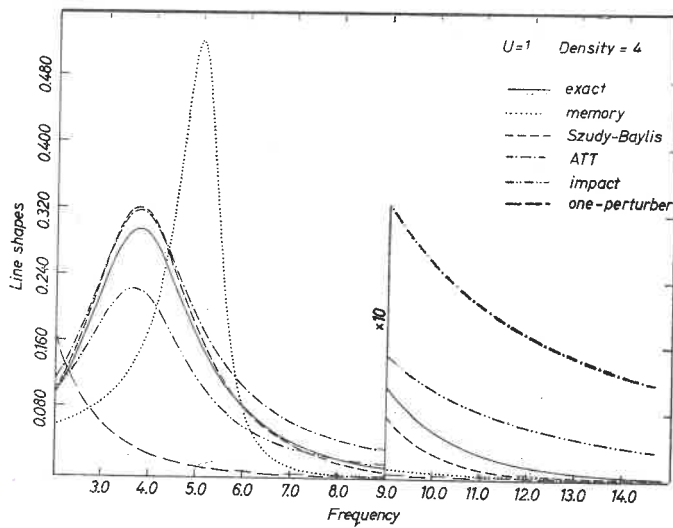


Fig. 4

Figs. 3 and 4. Exact and approximate profiles for $U = 1$. In Fig. 3, $J_{SB}(\omega)$ is indistinguishable from the exact profile, except near the peak maximum where it coincides with $J_{as}(\omega)$ (ATT). Note the scale change in Fig. 4. At $U = 1$, the constants a, b, c, d have the values: $a = 0.0396$, $b = 0.355$, $c = -0.0896$, $d = 0.903$

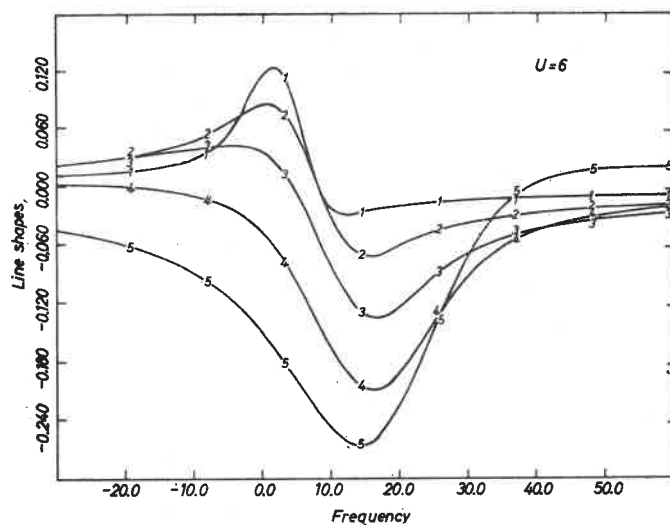


Fig. 5. The functions $\tilde{h}^{*k}(\omega)$, $k = 1$ to 5, for $U = 6$

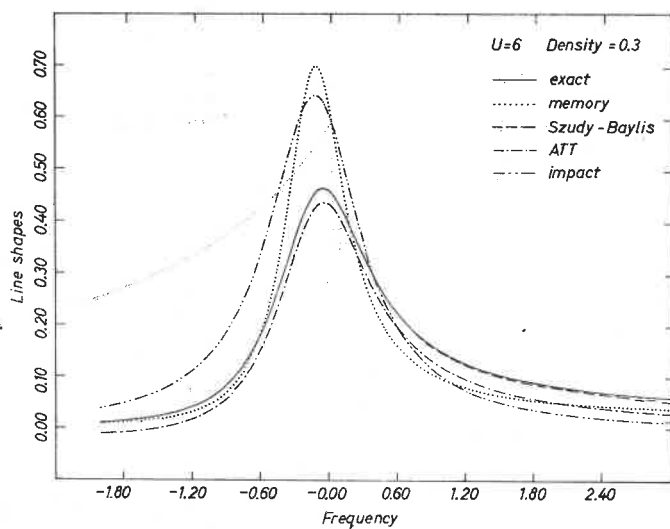


Fig. 6

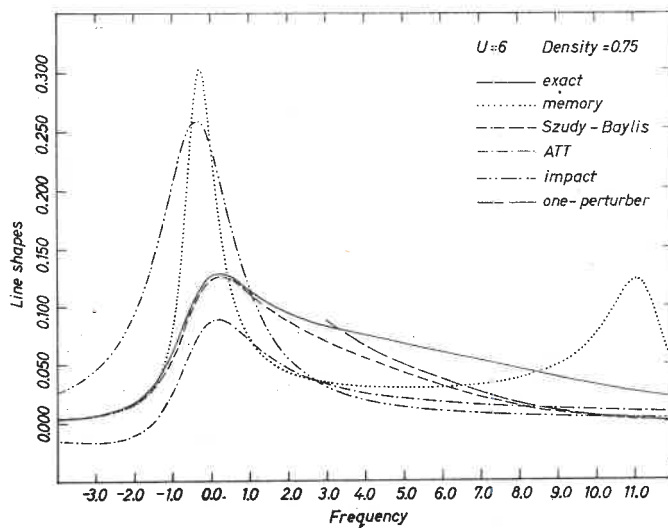


Fig. 7

Figs. 6 and 7. Exact and approximate profiles for $U = 6$. Here, $a = 1.07$, $b = 1.64$, $c = 1.20$, $d = -0.503$

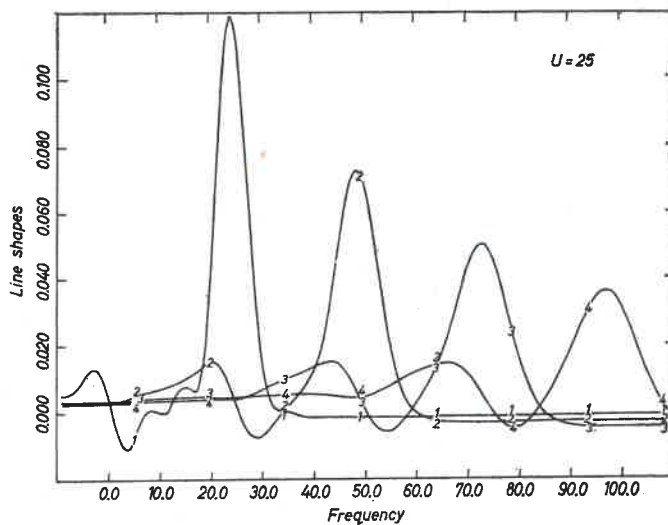


Fig. 8. The functions $\tilde{h}^{*k}(\omega)$, $k = 1$ to 4, for $U = 25$

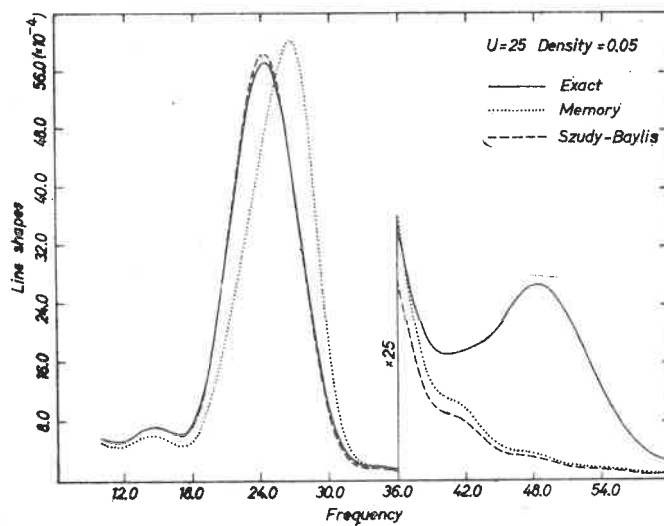


Fig. 9

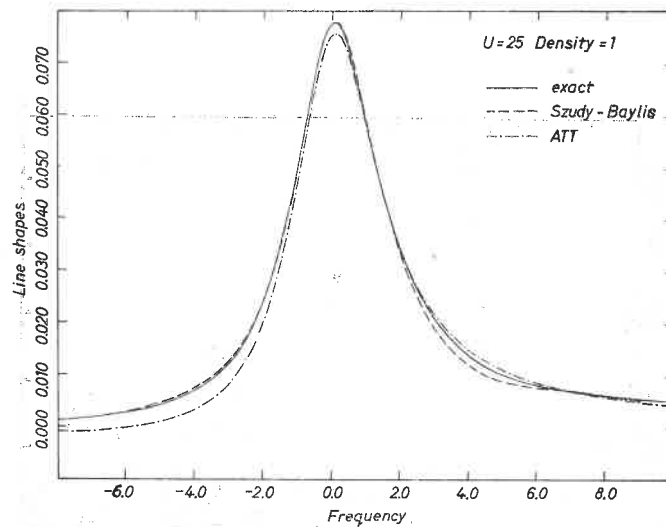


Fig. 10

Figs. 9 and 10. Exact and approximate profiles for $U = 25$, wings and line center respectively. In Fig. 9, the "one-perturber" $e^{-nch(\omega)}$ is indistinguishable from $J_{SB}(\omega)$; note the change of scale. In Fig. 10, we did not represent $J_M(\omega)$, which rises much higher than $J(\omega)$. Here, $a = 0.241$, $b = 1.52$, $c = 1.00$, $d = -0.120$

as our exact reference, as it is the exact solution to a well defined physical model (defined by assumptions (i)–(iii) of Section 2), with all the low density approximations discussed here being approximations to it.

One can see from the figures that the Szudy-Baylis approximation is surprisingly good, much better than any of the other approximations. Note that the presence of the factor e^{-nc} in it is essential to its good fit (at the densities considered). The memory approximation is accurate at densities much lower than those at which $J_{SB}(\omega)$ is. We observe on Fig. 7 that the memory approximation can produce extraneous “satellites”, around frequency = 10.5 in the present case, arising from the quantity $\omega - nD(\omega)$ getting small in the denominator of (5.7). In Fig. 9, we have a clear illustration of the fact that $J_M(\omega)$ and $J_{SB}(\omega)$ do not contain multiple collision effects, in that they do not reproduce the satellite at $\omega \approx 2U = 50$, arising from the simultaneous presence of two perturbers in the interaction volume (note that the exact $J(\omega)$ has satellites at $\omega = 25, 50, 75 \dots$, corresponding to the simultaneous presence of 1, 2, 3 ... perturbers in V_0 , as is readily inferred from considering the $\tilde{h}^{*k}(\omega)$ in Fig. 8). We have here an instance where, due to the rapid decrease of the one-perturber spectrum beyond the first satellite, multiple collision effects may dominate the far wings even at very low densities.

8. Discussion

The purpose of the present paper was to discuss and compare various low density approximations in the adiabatic theory of pressure broadening. Principally, we were interested in assessing the accuracy of the Szudy-Baylis approximation, which is deduced in a very simple manner from the Anderson-Baranger theory, but has no clear physical meaning, as does for instance the memory approximation of Fano. The numerical comparisons in Section 7 show $J_{SB}(\omega)$ to be accurate over a much wider range of frequencies and densities than is $J_M(\omega)$. This conclusion is also reached in a more theoretical manner by analysing the shape parameters, shift, width and asymmetry, resulting from each approximation: Recently [15], we deduced density expansions for these parameters from the Anderson-Baranger expression (2.14). The same can be done for the shape parameters corresponding to $J_{SB}(\omega)$ and $J_M(\omega)$. We find that $J_{SB}(\omega)$ gives the correct shift, width and asymmetry to 3rd, 3rd and 2nd orders in the density n , respectively, while for $J_M(\omega)$, the corresponding orders are only 1, 1 and 0 (for $J_{as}(\omega)$, they are 3, 2 and 2).

Finally, let us mention that although in the present paper we developed the theory for the explicit case of non-degenerate lines, so as to simplify the exposition, most of it also applies to the case of an isolated line in general, whether degeneracy, rotational or otherwise, is involved or not. The theory for such cases was given in a previous paper [14] where use was made of an adiabatic *representation*: for a general isolated line, one also obtains expression (2.14), but with $g(\tau)$ slightly complicated by degeneracy. Since the formal derivations of the various low density approximations discussed in the present paper do not depend on the explicit form of $g(\tau)$, apart from its asymptotic behavior, which is the same in the general case, it follows that these approximations, including the Szudy-Baylis approximation, can also be made in the

general case of an isolated line. In fact, it is not even necessary to pass through the intermediary of the Anderson-Baranger expression (2.14), with its concurrent assumptions, to derive these low density approximations: one only needs the first two terms of the formal density expansion of $J(\omega)$, which is given in a very general form in Ref. [14]. Let us end with the suggestion that perhaps an approximation of the Szudy-Baylis type, both better and simpler than the memory approximation, also exists for the case of overlapping lines.

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