Resonance line broadening due to self-pressure in the nonbinary region

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The spectral distribution of a resonance line in the presence of self-pressure broadening in the nonbinary region is calculated for the case in which one or more broadening particles is found in the Weiskopf sphere. It is shown that transition to the nonbinary region leads to a significant narrowing of the line and change of sign of the shift. The absence of a static limit is predicted.

1. INTRODUCTION

Broadening of spectral lines by self-pressure is caused by resonant transfer of excitation during the course of collisions of identical particles. As a rule, resonant transfer of excitation takes place as a result of dipole-dipole interaction and has a significant cross section, 10^{-13} cm^2. The problem of self-pressure broadening has been investigated since the 1930's,[1,2] however, there is still no complete theory of this type of spectral line broadening.

Like any other broadening mechanism, self-pressure broadening is characterized by a binarity parameter

$$h=4\pi N\rho_W{}^3/3. \tag{1}$$

where N is the density of the identical particles, ρ_W is the Weiskopf radius, which for the dipole-dipole interaction is equal to

$$\rho_W \approx \frac{D}{(v\hbar)^{1/2}}. \tag{2}$$

In formula (2) D is the dipole moment of the particles and v is their velocity. If $h \ll 1$, the broadening is binary. In this limit the main questions of self-pressure broadening have been answered.[2-6] There are detailed calculations of the collision widths and shifts for line broadening of a number of metal atoms,[4] and a closed theory of absorption and scattering spectra has been constructed, including the case of an intense electromagnetic field.[6] As for the other limiting case $h \geqslant 1$, here the behavior of the spectrum of a line broadened by self-pressure (not necessarily a resonance line) remains unknown, even qualitatively. Efforts at an analytic consideration of the quasistatic limit[7] in self-pressure broadening have not led to any well-founded results. In recent studies of thin layers ($\leqslant 100$ Å), Langmuir films, etc., directed at the development of new technologies,[8] interest has arisen, generally speaking, in nonbinary processes of resonant (or quasiresonant) excitation exchange and its optical manifestations. For this reason, the classical problem of nonbinary self-pressure broadening has acquired a special significance from the viewpoint of achieving an understanding of the physics of such processes.

In the present paper self-pressure broadening is analyzed on the basis of the density-matrix formalism. We consider gas particles, identical two-level systems corresponding to resonant $\Delta m = 0$ transitions, which exchange excitation via dipole-dipole interaction, of the internuclear axis. The equation for the density matrix is solved numerically, assuming rectilinear motion of the particles in a box with dimensions $a_x \times a_y \times a_z$ and specularly reflecting walls. The spectral transition function is calculated from the relation for the work of the field.[6]

2. FORMULATION OF THE PROBLEM

The equation for the density matrix of a system of identical particles has the form

$$\frac{\partial\rho}{\partial t}=\left[\sum_i (H_{0i}-\mathbf{D}_i\mathbf{E})+\sum_{ij} U_{ij},\rho\right]+\Gamma\rho; \tag{3}$$

here ρ is the density matrix of the entire system, H_{0i} is the Hamiltonian of the ith particle, $\mathbf{E}$ is the intensity of the resonant electromagnetic field, U_{ij} is the interaction operator of the ith and jth particles, and $\Gamma\rho$ is an operator that describes other types of relaxation of the system.

For the dipole interaction the operator U_{ij} has the form

$$U_{ij}=[\mathbf{DD}'-3(\mathbf{Dn})(\mathbf{D}'\mathbf{n})]/R_{ij}^3. \tag{4}$$

In Eq. (4) R_{ij} is the distance between the ith and jth particles. We should note an important fact. If the ith particle is the test particle and the remaining particles are distributed uniformly around it, the mean potential of the interaction of the ith particle with all the remaining particles is equal to zero. This means that the dipole interaction like the Coulomb interaction has a vector character, and in particular the multiparticle broadening theory of Anderson[9] is also inapplicable in this case.

The transition spectral function can be found from the expression for the work of the field

$$Q=\mathbf{E}\frac{\partial\mathbf{P}}{\partial t}, \tag{5}$$

where $\mathbf{P} = \mathrm{Sp}(\mathbf{D}\rho)$ is the polarization of the medium.

3. THE BINARY REGION ($h \ll 1$)

In the binary region only two particles participate in each collision, therefore there is no need to consider the entire ensemble of particles as a whole.

If ρ_a is the single-particle density matrix, then the equation for it, taking into account only pairwise collisions, has the form[6]

$$\frac{d\rho_a}{dt}=-i[H_a-\mathbf{DE},\rho_a]+(d\rho_a/dt)_{sp}+(d\rho_a/dt)_{col}, \tag{6}$$

where

$$\left(\frac{d\rho_a}{dt}\right)_{sp}=\lambda[-D\rho_a D^+ +{}^1/_2(DD^+\rho_a+\rho_a DD^+)] \tag{7}$$

is the spontaneous-relaxation operator of an isolated atom,

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D is the dipole-moment operator,[10]

$$\left(\frac{d\rho}{dt}\right)_{col}=\left\langle \int d\tau \,\mathrm{Sp}'\Big[U,-i\rho\times\rho'(t)+\int S^{+}(t,t')[U(t'),\rho\times\rho']S(t,t')dt'\Big]\right\rangle \tag{8}$$

is the binary collision integral,[6,11] U is the dipole-interaction operator (5), S is the evolution operator of the atom a and the atom a', satisfying the equation

$$i\frac{dS}{dt}=-S(H_a\times 1'-\mathbf{DE}\times 1'+1\times H_a'-1\times\mathbf{D}'\mathbf{E}+U), \tag{9}$$

$$S^{+}(t,t)=S(t,t)=1\times 1'.$$

The sign "$\times$" denotes the direct product, Sp' is the race operator over all the states of one of the atoms, and τ is the collision time.

By introducing a kinetic time, which corresponds to the completed-collision approximation, the collision integral (9) reduces to the form[6]

$$\left(\frac{d\rho}{dt}\right)_{col}=\langle\langle(\Gamma_{ij})^{lm}_{i'j'}\rangle_b\rho_{lm}(t,\mathbf{v}')\rangle_{\mathbf{v}'}\rho_{i'j'}(t,\mathbf{v}), \tag{10}$$

where the quantities Γ do not depend on time. In Eq. (10) b is the impact parameter, and repeated indices indicates summation.

Solution of the equation for the density matrix with collision integral (10), followed by its substitution in the expression for the absorbed power, leads to the following form of the line spectrum of a two-level system:

$$S(\omega)=\frac{1}{\pi}\frac{\gamma k_1+\Delta\omega k_2}{(k_1^2+k_2^2)\delta^2}, \tag{11}$$

where

$$k_1=1+\gamma\Delta/\delta^2,\quad k_2=\Delta\omega\Delta/\delta^2,\quad \delta^2=(\Delta\omega+\Delta)^2+\gamma^2,$$

$$\gamma+i\Delta=\frac{Nv}{4}\int U(\tau)d\tau\int d\tau' U(\tau')\exp\Big[-i\int(\Delta\omega-U)dt\Big].$$

Contour (11) coincides with the Lorentzian only in the absence of a shift; in real situations $\Delta\sim\gamma$. For a two-level system with

$$U\approx D_{12}^2/2R^3$$

the collisional linewidth is equal to

$$\gamma\approx 1{,}5\pi e^2 fN/m\omega.$$

Here f and ω are the oscillator strength and the transition frequency.

4. THE NONBINARY LIMIT ($h\geqslant 1$)

In the nonbinary limit, naturally, one cannot isolate a single atom as a subsystem. It is necessary to consider the equation for the entire set of identical particles. Taking only the dipole-dipole interaction into account, relaxation of the system of identical particles in an electromagnetic field is described by the equations

$$i\hbar\frac{\partial\rho}{\partial t}=\Big[\sum(H_{a_i}-\mathbf{D}_i\mathbf{E})+U,\rho\Big], \tag{12}$$

where ρ is the density matrix of the entire system. Note that H and D are single-particle operators, and U is a two-particle operator.

In the weak-field approximation for a resonance line, it is sufficient to consider Eq. (12) for two-level particles in a basis of states of the compound system of the form

$$\begin{aligned}|0\rangle&=|0_1,\ldots 0_i,\ldots,0_N\rangle,\\ |1\rangle&=|1_1,\ldots 0_i,\ldots 0_N\rangle,\\ |N\rangle&=|0_1,\ldots 0_i,\ldots,1_N\rangle,\end{aligned} \tag{13}$$

where N is the number of particles, 0_i means that the ith particle is in the ground state, and 1_i means that the ith particle is located in the excited state.

In a weak field $\langle i|\rho|i\rangle\ll\langle 0|\rho|0\rangle\approx 1$, and Eq. (13) has the form

$$i\hbar\frac{\partial\rho_{0i}}{\partial t}=-DE_0e^{-i\Delta\omega t}+\sum U_{ij}(t)\rho_{0j}, \tag{14}$$

$$\rho_{0i}(0)=0,$$

where $\rho_{oi}=\langle 0|\rho|i\rangle$, E_0 is the amplitude of the electromagnetic field, $\Delta\omega$ is the frequency detuning of the field, and $U_{ij}(t)$ is the matrix element (4) for the interaction of the ith and jth particles. In what follows we will consider the transition $\Delta m=0$ (m is the magnetic quantum number), which corresponds to taking account in Eq. (4), in the coordinate system associated with the two particles, only of the z projection of the dipole moment

$$U_{ij}=D_z^2(1-3\cos^2(\theta))/R_{ij}^3. \tag{15}$$

(The model can describe the behavior of identical atoms in a strong magnetic field.) In Eq. (15) θ is the angle between the internuclear axis and the z axis of the laboratory system. Note that interaction (15) corresponds to the condition of vectorality, which is easy to verify directly.

The expression for the absorbed power has in this notation the form

$$Q\propto s(\omega)=\frac{2}{T}\int_0^T dt\sum_i\frac{1}{N}\,\mathrm{Im}(\rho_{0i}e^{i\Delta\omega t}). \tag{16}$$

The summation in Eq. (16) corresponds to averaging the result over all the particles, and the integration—to calculating the trace over the states of all the particles save one.

Equations (14)–(16) determine completely the spectrum of the resonance line. In the binary limit the solution of Eq. (14) can be easily found recognizing that all the ρ_{0i} are identical (the approximation of independence of binary processes). Taking into account interaction with only one particle, it is easy to obtain the well-known expression in the theory of line broadening for the line spectrum

$$s(\omega)=2\sum\frac{1}{N}\int_0^T dt\int d\tau\exp\Big\{i\Delta\omega\tau-\int\sum U_{ij}dt'\Big\}\frac{1}{T}\Big|_{T\to\infty}, \tag{17}$$

in which averaging over the states of all the particles corresponds to the limit $T\to\infty$. Here averaging over the impact parameters and velocities of the broadening particles is automatic.[12]

In the static limit the approximation $\rho_{0i}(t)\cong\rho_{0j}(t)$ is in principle inapplicable; nevertheless, let us consider the consequences which its use in Eq. (17) leads to. Setting U_{ij} constant in Eq. (17) and carrying out the integration over time, we obtain

$$s(\omega)=\left\langle \delta\left(\Delta\omega-\sum U_{ij}\right)\right\rangle, \qquad (18)$$

where $\langle\ldots\rangle$ denotes averaging over the ensemble of particles. Calculating in the same way as for static broadening by ionic microfields in a plasma (the Holtsmark approximation) for the potential

$$U_{ij}=\frac{D^2(1-3\cos^2\theta)}{r^3}$$

we obtain a Lorentz contour (a sum of two Lorentz contours with zero shifts) with a width differing from the collision width only by the numerical factor

$$\gamma\approx\frac{4\pi D^2N}{3\hbar}.$$

However, this result is fundamentally invalid. For an accurate analysis of the quasistatic limit, we must change over in Eq. (14) to a continuous distribution of the particles in space. Here, since $U(t,\mathbf{r})=U(\mathbf{r})$, we can seek the solution in the form $\rho=\rho' e^{-i\Delta\omega t}$. Dropping the unimportant normalization factor DE, we obtain the equation

$$1+\Delta\omega\rho'(\mathbf{r})-i\int d\mathbf{r}'U(\mathbf{r},\mathbf{r}')\rho'(\mathbf{r}')=0, \qquad (19)$$

$$s(\omega)=\operatorname{Im}\rho'.$$

[Note the fundamental difference of Eq. (19) from the case of broadening by ionic microfields in a plasma.] By virtue of the property of the interaction potential

$$\int d\mathbf{r}'U(\mathbf{r},\mathbf{r}')\equiv 0$$

the solution of Eq. (19) is apparent at once

$$\rho'=-\frac{1}{\Delta\omega}, \qquad s(\Delta\omega)=\delta(\Delta\omega).$$

The same solution can be obtained exactly by taking the Fourier transform. Thus, use of approximation (19) demonstrates the absence of a static limit in self-pressure broadening. According to Eq. (19), in the static limit the resonance line spectrum should have a sharp peak against the background of binary quasistatic broadening.

5. RESULTS OF NUMERICAL CALCULATIONS

The calculations of Eqs. (14)–(16) were carried out on the basis of the method of particles in a box. T particles are introduced into a box of dimensions $(a_x)\times(a_y)\times(a_z)$ with a random uniform distribution over the box and the directions of motion. Reflection from the walls of the box is taken to be specular. The interaction potentials of the particles (15) are calculated at every moment in the laboratory coordinate system, and the system is solved numerically (by the implicit one-step method) for the nondiagonal elements of the density matrix (14). The spectral function is calculated directly (16). The integration step varied from 1/200 to 1/50 of the inverse Weiskopf frequency, the number of particles T was varied from 5 to 50, and the dimensions of the box were chosen such that $N=T/a_xa_ya_z$, where the density N is determined by the binarity parameter h and the particle velocity v.

The calculations were carried out for a fixed number of particles and a few ($k=5$) initial random values of the coordinates and projections of the velocities of the particles, which made it possible to control the error of the calculation. By choosing the limits of variation of the integration step in time, the calculation error was reduced to a value substantially smaller than the statistical error associated with a finite number of particles. The value of the statistical error was determined by comparing the calculations of the spectral function for various values of the number of particles, but fixed density. The relative variation of the linewidths and shifts in this case was inversely proportional to the cube root of the number of particles, thus: $\varepsilon=\lambda/N^{1/3}$, where $\lambda=0.4$. One can expect that for $\mathcal{N}=50$ the calculational error will not exceed 10%.

Some results of the calculations, illustrating the behavior of the spectrum of a resonance line broadened by self-pressure are shown in Figs. 1 and 2. The results are normalized to the quantity

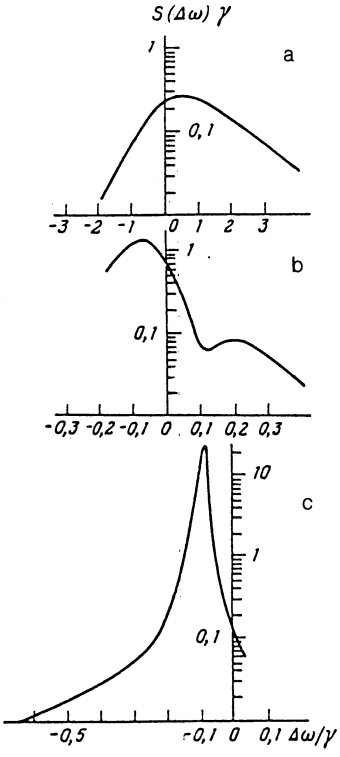

FIG. 1. Resonance line spectra in the presence of self-pressure broadening for various values of the binarity parameter h for $v=10^4$ cm/s: a) $N=4\cdot10^{16}$ cm^{-3}, $h=0.064$; b) $N=3.4\cdot10^{17}$ cm^{-3}, $h=0.5$; c) $N=2.53\cdot10^{18}$ cm^{-3}, $h=3.7$; $\gamma=\pi D^2N/h$ ($D=1$ a.u. $\approx2.3\cdot10^{-18}$).

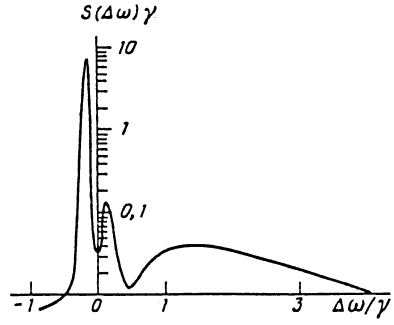

FIG. 2. The same as for Fig. 1, except $v=10^3$ cm/s and $N=7.7\cdot10^{16}$ cm^{-3}, $h=3.6$.

$$\gamma = \frac{\pi D^2 N}{\hbar},$$

which coincides with the linewidth in the collision limit. Such a normalization allows one to make out with greater clarity the differences in the behavior of the line shape in the static and binary limits.

As can be seen from Fig. 1a in the binary limit $h = 0.064 \ll 1$ the line shape is in good agreement with the analytical line shape. The linewidth grows linearly with growth of the density of the gas, and the line shift is equal to roughly half the linewidth. The situation changes abruptly with approach to the nonbinary limit. Already at $h = 0.5$ it appears as if there are two lines shapes, the first similar to a binary line shape shifted in the positive direction, and the second, which does not have an analog, shifted to the left. Comparing Fig. 1b with 1c, it is easy to see that the width of the second line shape depends weakly on the density, whereas its shift (in the negative direction) depends linearly on the density and is roughly equal to 0.1γ. This line shape, in the limit, tends toward a δ-function.

Figure 2 presents the results of a calculation of the resonance line shape for another value of the velocity $v = 10^3$ cm/s. As can be seen, the qualitative behavior of the line shape is independent of particle velocity. Interesting is the complicated structure of the line, associated with the appearance of an additional peak in the line spectrum. A discussion of this fact goes beyond the scope of this paper.

6. CONCLUSION

The results pertain here directly to resonance lines. Regarding the resonance lines of gases, observation of nonlinear behavior of the spectral line is hampered by reabsorption. Nevertheless, our conclusions regarding the behavior of the line shift apply in full measure to transitions to an upper resonance level, which makes it possible to investigate these dependences directly. The behavior of the width of a line broadened by self-pressure in the nonbinary region can be investigated only in structures with dimensions < 1 μm (surfaces, films, clusters).

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