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Resonance Broadening of Spectral Lines

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A general treatment of the collision of an excited atom with an unexcited one shows that the three principal methods of calculating collision broadening are all justified as approximations to the complete treatment. When the fine structure of the lines is taken into account it follows that all members of a Russell-Saunders multiplet are broadened to the same extent. The calculated broadening turns out to be $\Delta\nu=(\frac{3}{2})^{\frac{1}{2}}NS(J, J')/\hbar(2J+1)(2J'+1)$, which is less by a factor of five than that observed in the work of Hughes and Lloyd.

THE broadening of spectral lines which accompanies an increase in the pressure of the absorbing or emitting gas has been the subject of a large number of theoretical investigations from various points of view.[1] Usually the principal attention has been given to the broadening produced by a foreign gas, and most of the reliable experimental work has been of this kind. The broadening in a homogeneous gas, known as resonance broadening, is very much greater, but its study has been accompanied with such technical difficulties that until recently very few dependable measurements have been made on it. The recent work of Hughes and Lloyd,[2] however, provides experimental data of some reliability, and it is therefore of interest to examine again the theoretical predictions as to the absolute magnitude of the effect, and as to the relative broadening of the components of a multiplet.

The various theoretical points of view from which this subject has been treated show considerable diversity. Some of them have been definitely shown to be wrong, but there remain several others which have sometimes been thought to be distinct, even though they lead to approximately the same results. Furthermore, in all of the work which has been published there appears to be no examination of the relative broadening of the different members of a multiplet, although it might be surmised on general grounds that all such lines would be broadened to the same extent. It is proposed to show here, first, that the various methods of approach which have been used on this problem are merely different approximations to the complete treatment; and, second, that the broadening can be expressed in such a way as to show that the different members of a Russell-Saunders multiplet are broadened to the same extent.

The theoretical points of view from which this problem has been treated may be classified under three headings as follows:

1. Furssow and Wlassow[3] have emphasized the fact that when an excited atom passes by an unexcited atom of the same kind there is a finite probability that the energy of excitation will be transferred from the first to the second atom, without the intervention of radiation. This results in a reduction of the lifetime of the excited atom and a corresponding broadening of the line radiation emitted. Although this statement is in terms of an emission line, the conclusion applies to an absorption line as well.

2. A second method of treatment is closely related to the Lorentz theory of collision broadening in which the phase of a classical oscillator is regarded as being changed in a random way during a collision. From this point of view the problem is to compute the amount of the change of phase in terms of the forces of interaction and the closeness of approach. The Fourier analysis of this interrupted oscillation gives the familiar dispersion curve. In the quantum mechanical treatment the Fourier analysis is made of exp $(i/\hbar)(E'-E)t$, where E' is the energy of the excited atom and E is the energy of the ground state. The quantity E' is considered to vary

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[1] For summaries of the theoretical work see: Margenau and Watson, Rev. Mod. Phys. **8**, 22 (1936); V. Weisskopf, Physik. Zeits. **34**, 1 (1933).

[2] Hughes and Lloyd, Phys. Rev. **52**, 1215 (1937).

[3] Furssow and Wlassow, Physik. Zeits. der Sowjetunion **10**, 379 (1936). The criticism of Weisskopf's work contained in this paper does not appear to be justified.

during the collision, by an amount which can be computed, and so to produce a change in phaes. This method has been extensively used by Weisskopf and by Lenz.[4]

3. A third method of treatment is to consider the motion of the atomic nuclei under the attractive or repulsive force due to the electronic interaction between the two atoms. If the stationary states of this motion are found, and if it is assumed that the electronic motion is essentially unchanged during the collision, it is possible to compute the probability of transition, from the excited to the ground state, with the emission of radiation and a change in the kinetic energy of the atoms. This method shows much more clearly than the others that the conservation of energy is made possible through the change in the kinetic energy of the atomic motion; and Weisskopf has shown that this treatment leads, at least approximately, to the same result as the method of Fourier analysis. This method has recently been treated extensively by Jablonski.[5]

Since all three of these methods lead to roughly the same result, it is easy to suppose that they are really equivalent. On the other hand, and especially since the result seems to be considerably smaller than required by experiment, it might be supposed that these are three effects which, in the first approximation, are independent and must therefore be added together. A complete analysis, however, shows that they are merely three approximations to the exact quantum mechanical treatment.

General Theory of a Collision

The theory as usually treated, and as treated here, applies to the case of low pressures only. Pressures are low when the mean free time between collisions is considerably greater than the duration of a collision. Under these circumstances it is sufficient to treat simple collisions between two atoms only, and to add together the effects of the different collisions. This has as a consequence that the broadening will be proportional to the number of molecules per unit volume.

Consider then two identical atoms which for simplicity will be treated as having only two electronic states. They will be capable of occupying a continuum of states of translational motion, but apart from the translational states there will be three important electronic states.

$$\begin{aligned} U_a &= u_0(1)u_1(2) \\ U_b &= u_0(2)u_1(1) \\ U_0 &= u_0(1)u_0(2). \end{aligned} \tag{1}$$

The state u_0 is the ground state and the state u_1 the excited state. The arguments of these functions are the electronic coordinates of the first and second atoms respectively. The states U_a and U_b differ with respect to the number of the atom which is excited, but they have the same energy.

To treat the problem of the emission of radiation, the state of the radiation field must also be taken into account. It may be assumed that when the atomic state is U_a or U_b there is no radiation in the field, and when the atomic state is U_0 there is one quantum of energy $h\nu$. Let the function describing the field in the first case be F_0 and in the second case be F_ν. Then the three states of importance are

$$\begin{aligned} \psi_a &= U_a v_1(R, t) F_0 \exp\left[-(i/\hbar)E_1 t\right] \\ \psi_b &= U_b v_1(R, t) F_0 \exp\left[-(i/\hbar)E_1 t\right] \\ \psi_0 &= U_0 v_0(R, t) F_\nu \exp\left[-(i/\hbar)(E_0+h\nu)t\right]. \end{aligned} \tag{2}$$

The function $v(R, t)$ is a function of the distance between the atomic nuclei and the time; $v_1(R, t)$ and $v_0(R, t)$ represent the nuclear motion before and after the collision, respectively. For certain methods of treatment these functions will represent wave packets and for others they will be functions corresponding to a precise value of the translational energy. They could, of course, be written as functions of the coordinates of the two atoms separately, but a function of the relative coordinate R gives all of the generality which is of importance.

The Hamiltonian function for this system will contain terms which represent the atomic energies, the translational energy, and the energy of the radiation field. In addition there will be a term $V(R)$, which represents the dipole interaction energy between the two atoms and is a function of their separation R, and another term S which represents the interaction between the electrons and the radiation field.

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[4] W. Lenz, Zeits. f. Physik **80**, 422 (1932).

[5] A. Jablonski, Acta Physica Polonica **6**, 371 (1937).

Let the general solution of the problem be

$$\Psi = a\psi_a + b\psi_b + c\psi_0, \tag{3}$$

where a, b, and c are functions of the time. Substitution of this form into the Schrödinger equation leads to

$$\begin{aligned} \dot{a} &= -(i/\hbar)(a|V|b)b \\ &\quad -(i/\hbar)(a|S|c)c \exp\left[(i/\hbar)(E_1-E_0-h\nu)t\right] \\ \dot{b} &= -(i/\hbar)(b|V|a)a \\ &\quad -(i/\hbar)(b|S|c)c \exp\left[(i/\hbar)(E_1-E_0-h\nu)t\right] \\ \dot{c} &= -(i/\hbar)(c|S|a)a \exp\left[-(i/\hbar)(E_1-E_0-h\nu)t\right] \\ &\quad -(i/\hbar)(c|S|b)b \exp\left[-(i/\hbar)(E_1-E_0-h\nu)t\right]. \end{aligned} \tag{4}$$

For the cases of interest the matrix elements of V are of more importance than those of S. This corresponds to the fact that the broadening due to pressure is greater than the natural width of the lines. Hence, to find an approximate solution, neglect at first the matrix elements of S altogether. The remaining two equations can then be solved for a and b. The solution is

$$\begin{aligned} a &= A \exp\left[-(i/\hbar)\textstyle\int (a|V|b)dt\right. \\ &\qquad + B \exp\left[(i/\hbar)\textstyle\int (a|V|b)dt\right] \\ b &= A \exp\left[-(i/\hbar)\textstyle\int (a|V|b)dt\right. \\ &\qquad - B \exp\left[(i/\hbar)\textstyle\int (a|V|b)dt\right], \end{aligned} \tag{4a}$$

where $|A|^2+|B|^2=\frac{1}{2}$.

According to the treatment given by Furssow and Wlassow the motion of the atoms is fixed and no account is taken of changes in it. The initial conditions are made such that at the initial time the atom 1 is excited and atom 2 is not. This condition requires as initial values, $a=0$, $b=1$, so the above solutions become

$$\begin{aligned} a &= -i \sin (1/\hbar)\int_{t_0}^{t} (a|V|b)dt, \\ b &= \cos (1/\hbar)\int_{t_0}^{t} (a|V|b)dt. \end{aligned} \tag{5}$$

Since the nuclear motion is to be described classically, the functions representing it will consist of a compact wave packet for each atom, and the distance between the atoms will have a precise value which is a function of the time. The matrix elements will be functions of R and will have the form

$$(a|V|b) = \alpha/R^3 = \alpha/(p^2+v^2t^2)^{\frac{3}{2}}, \tag{6}$$

where α is a constant which depends upon the electronic functions, p is the distance of closest approach, and v is the relative velocity of the atoms. The zero of time is taken at the time of closest approach. This expression can be integrated so that

$$\begin{aligned} a &= -i \sin \{(\alpha t/\hbar p^2 v)/(p^2/v^2+t^2)^{\frac{1}{2}} \\ &\qquad -(\alpha t_0/\hbar p^2 v)/(p^2/v^2+t_0^2)^{\frac{1}{2}}\}, \\ b &= \cos \{(\alpha t/\hbar p^2 v)/(p^2/v^2+t^2)^{\frac{1}{2}} \\ &\qquad -(\alpha t_0/\hbar p^2 v)/(p^2/v^2+t_0^2)^{\frac{1}{2}}\}. \end{aligned} \tag{7}$$

Most of the change in these functions occurs near the time $t=0$, and the whole change in phase between $t=-\infty$ and $t=+\infty$ is $2\alpha/\hbar p^2 v$. Hence the effect of a collision at the velocity v and the distance of closest approach p is to make the coefficients

$$a = -i \sin (2\alpha/\hbar p^2 v), \quad b = \cos (2\alpha/\hbar p^2 v). \tag{8}$$

This represents a probability of $\sin^2 (2\alpha/\hbar p^2 v)$ that the energy of excitation has been transferred to atom 2 during the collision. Since the collisions occur frequently during the lifetime of an excited state the coefficient b may be approximated by a decreasing exponential, $e^{-\mu t}$, which, substituted into the equation for c, gives the familiar resonance curve for the probability of radiation.

On the other hand one may insert the general solution, Eq. (4a), into the equation for c. This gives c as a function of ν by a Fourier analysis of $\exp\{(i/\hbar)\int (a|V|b)dt-(i/\hbar)(E_1-E_0)t\}$. The evaluation of this integral is just the method of Weisskopf and Lenz. Instead of treating the exact analysis, it is possible to consider the phase as changing abruptly by the amount $(2\alpha/\hbar p^2 v)$ at each collision.

In neither of these approximations is the mechanism of the conservation of energy obvious, because of the assumption of constraints which cause the atoms to move past each other in straight lines at uniform velocity. To give a treatment in which this motion is allowed to change under the influence of the atomic interaction it is necessary to make the functions $v_1(R, t)$ and $v_0(R, t)$ characteristic of the energy of translation. When this is done the matrix elements $(a|V|b)$ are constants whose magnitude depends upon the translational energy but which vanish as the relative duration of the collision decreases. When the corresponding values for a

and b are inserted in the equation for c, the integral shows a secular increase of c only when $(E_1+T_1-E_0-T_0)=h\nu$. T_1 and T_0 are the kinetic energies before and after the impact respectively. The square of the absolute value of c will be proportional to $|(c|S|a)|^2$ which will depend upon ν through the difference (T_1-T_0). This, as shown by Weisskopf, gives approximately the same distribution of radiation as the previous methods.

The conclusion is that all three methods are essentially equivalent, and that one is to be preferred over another only if the computation seems simpler or if it can be shown that the approximation to the exact solution is better. Thus far no outstanding superiority of one method over the others seems to have been demonstrated, but for the following treatment of multiplets the point of view of Furssow and Wlassow has been adopted.

Broadening of the Members of a Multiplet

To take into account the multiplet structure consider the ground state to have the inner quantum number J and the excited state to have the inner quantum number J'. When the atoms are held at a fixed distance apart there are $2(2J+1)(2J'+1)$ stationary states of the dipole interaction energy. Each of these states represents a definite value of the angular momentum about the line connecting the atoms. Positive and negative values of this angular momentum have the same value of the energy. Half of the states are symmetric and half of them are antisymmetric in the two atoms, and the corresponding symmetric and antisymmetric states have energies of equal magnitude but of opposite sign. Furthermore, in each class of states the sum of the interaction energies is zero.

Let the $2(2J+1)(2J'+1)$ states be designated as follows

$$\begin{aligned}\psi(p, M, M')&=u(\alpha', J', M'; 1)\\&\qquad\times u(\alpha, J, M; 2)v_1(R, t)e^{-(i/\hbar)E_1t}\\ \psi(q, M, M')&=u(\alpha', J', M'; 2)\\&\qquad\times u(\alpha, J, M; 1)v_1(R, t)e^{-(i/\hbar)E_1t}.\end{aligned}\quad(9)$$

The quantum numbers α', J', M' represent the excited state and α, J, M, the ground state. The designations p and q refer respectively to states in which the excitation energy is in atom 1 and to those in which it is in atom 2. These are not the symmetric and antisymmetric states which are characteristic of the interaction energy, but are selected to conform to the treatment of Furssow and Wlassow. If the interaction with the radiation field is neglected, as above, the equations to be solved are

$$\begin{aligned}\dot{a}(p, M, M')&=-(i/\hbar)\sum_{\mu,\,\mu'}\\&\qquad\times(p, M, M'|V|q, \mu, \mu')a(q, \mu, \mu')\\ \dot{a}(q, M, M')&=-(i/\hbar)\sum_{\mu,\,\mu'}\\&\qquad\times(q, M, M'|V|p, \mu, \mu')a(p, \mu, \mu').\end{aligned}\quad(10)$$

If the assumed motion of the atoms is such that the nuclei move past each other in straight lines and that the angular momentum around the line connecting the atoms remains constant, the equations can be solved. This involves the application to each atom of a torque as well as a force. To find the solution let

$$\begin{aligned}a(p, M, M')&=A(p, M, M')e^{i\omega(t)},\\ a(q, M, M')&=A(q, M, M')e^{i\omega(t)}.\end{aligned}\quad(11)$$

Substitution into Eqs. (10) gives a set of simultaneous equations for the A's whose coefficients contain the $\dot{\omega}$. The values of $\dot{\omega}$ which permit the solution of the equations are just $(i/\hbar)$ times the characteristic values of the interaction energy. Let these be α_j/R^3. The solution will then have the form

$$\begin{aligned}a(p, M, M')&=\sum_j A_j(p, M, M')\\&\qquad\times\exp\left[(i\alpha_j/\hbar)\textstyle\int dt/R^3\right].\end{aligned}\quad(12)$$

In accord with the method of Furssow and Wlassow all of the $a(q, M, M')$ must be set equal to zero at the initial time. After a single collision

$$\begin{aligned}a(p, M, M')&=\sum_j A_j\cos(2\alpha_j/hp^2v),\\ a(q, M, M')&=i\sum_j A_j\sin(2\alpha_j/hp^2v),\end{aligned}\quad(13)$$

where the sum is taken over only those values of j which represent either the symmetric or the antisymmetric states. This solution assumes a definite constant orientation of the angular momentum vectors with reference to the line connecting the atoms and this orientation determines the relative values of the coefficients A_j. To include all possibilities it is necessary to average over all sets of initial and final states. This may be done by considering that there are $(2J+1)(2J'+1)$ states in which the system might be before collision, and the same number into which it might be thrown by the collision. The transition probability to many of these is zero, but the sum of the transition probabilities must be divided by the total number of possibilities. This leads to a resultant transition probability of

$$P=(1/(2J+1)^2(2J'+1)^2)\sum_j \sin^2(2\alpha_j/\hbar p^2 v), \qquad (14)$$

that the excitation energy has been transferred to the second atom. Collisions closer than those for which the probability becomes equal to unity can be regarded as collisions in the sense of the Lorentz. To determine the value of this distance, p_0, the sine may be replaced by its argument. Then

$$\frac{4}{\hbar^2 p_0^4 v^2(2J+1)^2(2J'+1)^2}\sum_j \alpha_j^2 = \frac{8S^2(J,J')}{3\hbar^2 p_0^4 v^2(2J+1)^2(2J'+1)^2}, \qquad (15)$$

where $S(J, J')$ is the strength of the line as defined by Condon and Shortly.[6] The half-width at half-maximum due to collisions of this kind is then

$$\begin{aligned}\mu_1 &= N\pi p_0^2 v\\ &= (8/3)^{\frac{1}{2}}\pi S(J,J')/\hbar(2J+1)(2J'+1) \qquad (16)\end{aligned}$$

in angular units.

For the more distant collisions the contributions of a large number of impacts must be added together to get the probable rate of loss of energy. Let this rate be $2\mu_2$.

$$\begin{aligned}2\mu_2 &= \frac{8NvS^2(J,J')2\pi}{3\hbar^2 v^2(2J+1)^2(2J'+1)^2}\int_{p_0}^{\infty}\frac{dp}{p^3}\\ &= \left(\frac{2}{3}\right)^{\frac{1}{2}}\frac{2\pi S(J,J')N}{\hbar(2J+1)(2J'+1)}. \qquad (17)\end{aligned}$$

The rate at which the probability amplitude decreases is just half of this so that the total half-width at half-maximum in angular measure is

$$\mu=\mu_1+\mu_2=\frac{6^{\frac{1}{2}}\pi S(J,J')}{\hbar(2J+1)(2J'+1)}N. \qquad (18)$$

From the definition of $S(J, J')$ it follows that this width is the same for all members of a Russell-Saunders multiplet.

COMPARISON WITH EXPERIMENT

The work of Hughes and Lloyd[2] showed the equality of the broadening of the two members of the first doublet of the principal series of potassium, and also showed the proportionality of the width with N. The measurement of the width showed that

$$\Delta\nu_{\text{obs}}=16\times 10^{-8}N\text{cm}^{-1}.$$

For this doublet the line strength is[7]

$$\text{S}(\tfrac{1}{2},\tfrac{1}{2})=e^2h/4\pi^2 m\nu=1.09\times 10^{-34}.$$

This leads to a theoretical half-width at half-maximum of

$$\Delta\nu_{\text{calc}}=6^{\frac{1}{2}}Ne^2/16\pi m\nu=3.16\times 10^{-8}N\text{cm}^{-1}.$$

A possible explanation of this discrepancy of a factor of five lies in the uncertainty with respect to the vapor pressure of potassium as a function of temperature. The value used by Lloyd was extrapolated by means of a formula from a region where there was already considerable divergence among different observations. It is hard to believe that the theoretical approximations used could account for as much as a factor of two.

It is an honor and a privilege to be permitted at this time to pay my respects publicly to Professor Sommerfeld on the occasion of his seventieth birthday. His influence on physics and physicists will long endure.

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[6] Condon and Shortley, *The Theory of Atomic Spectra*, p. 98.

The fact that $\sum_j \alpha_j^2=\frac{2}{3}S^2$ can be derived by writing down the expression for the matrix elements of the dipole interaction energy and summing the squares of the absolute values. This gives the diagonal sum of the matrix of the square of this energy.

[7] This assumes the f value of the first doublet to be unity which is correct to about one percent.