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General Theory of Pressure Broadening of Spectral Lines

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A new, more consistent, shape has been given to the theory of pressure broadening of spectral lines recently published by the author. In contradistinction to other theories, the present theory constitutes a very close analogy to the theory of intensity distribution in molecular spectra. There is no doubt that both phenomena are due to the same cause, i.e., to the relative movements of atomic nuclei. Thus, the theoretical treatment of both must be identical as far as possible. The method used by James and Coolidge for the calculations of intensity distribution in H_2 and D_2 continuous spectra can be adapted to the calculations of the profiles of broadened lines. In this case, presumably, it will not be possible to represent the intensity distribution in a closed form. In order to obtain a closed form, Condon's method (the quantum mechanical form of the Franck-Condon principle) is applied, and the Wentzel-Kramers-Brillouin approximate eigenfunctions are used for nuclear motions. The limitations of applicability of this approximation are discussed (the same limitations apply *a fortiori* to the applicability of every theory based on the classical description of nuclear motions). Because of the above simplifications, the resulting intensity distribution formula must be considered as an asymptotic one only, valid in a restricted region of frequencies of the broadened line and only in the case of heavy atoms and high temperatures (it certainly fails in the case of broadening by light gases such as He and H_2 or electrons), though it still constitutes a better approximation than that previously published. Apart from a correction which is in most cases insignificant, it is identical with Kuhn's intensity distribution obtained on the basis of the primitive form of the Franck-Condon principle. The present paper is drafted so as to be comprehensible to the reader without knowledge of the preceding papers of the author, the main results of which are being included here.

I. INTRODUCTION

SINCE 1937 I have developed in several papers[1] a theory of pressure broadening of spectral lines differing from other theories inasmuch as it constitutes a close analogy to the quantum-mechanical treatment of intensity distribution of molecular spectra. The causes which induced me to publish one more paper on this subject are these: a new, more consistent, and, I hope, more digestible form is given to the theory; a better approximation is reached in the approximate final formula; the limitations of its applicability are discussed (these limitations apply *a fortiori* to all other theories published hitherto); and the way to still better approximations is indicated. Besides, it seemed necessary to emphasize once more the close analogy between the mechanism of pressure broadening and of the production of molecular spectra. This analogy is overlooked in most of the papers published recently. There is a predominating tendency to keep as close as possible to the classical collision damping theories.[2] These theories, although their aesthetic value must not be underestimated, cannot give better information about pressure broadening of spectral lines than does the classical treatment of molecular spectra[3] (consisting of Fourier analysis of electronic frequencies modulated by nuclear vibrations) about intensity distribution in molecular spectra. Since the quantum-mechanical procedure, in which the nuclear motions are described by eigenfunctions, leads to very satisfactory results in the case of molecular spectra,[4] one can reasonably expect that the same procedure applied to pressure broadening of spectral lines will give good results as well. After all, both phenomena are due to the same cause, that is, to the relative move-

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[1] A. Jabłoński, Acta Phys. Pol. **6**, 371 (1937) (henceforth designated by J.1); Acta Phys. Pol. **7**, 196 (1938) (J.2); Physica **8**, 541 (1940) (J.3). One more paper published in Acta Phys. Pol. is not accessible and will not be quoted here.

[2] H. A. Lorentz, Proc. Amst. Acad. **8**, 591 (1906); W. Lenz, Zeits. f. Physik **25**, 299 (1924); **80**, 423 (1933); **83**, 139 (1933); V. Weisskopf, Zeits. f. Physik **75**, 287 (1932) and Physik. Zeits. **34**, 1 (1933) (henceforth designated by W.1 and W.2 respectively).

[3] W. Lenz, Zeits. f. Physik **25**, 299 (1924); H. Sponer and E. Teller, Rev. Mod. Phys. **13**, 75 (1941), (henceforth quoted as S.T.).

[4] S. W. Brown, Zeits. f. Physik **82**, 768 (1933); A. S. Coolidge, H. M. James and R. D. Present, J. Chem. Phys. **4**, 193 (1936); H. M. James and A. S. Coolidge, Phys. Rev. **55**, 184 (1939); A. S. Coolidge, Phys. Rev. **65**, 236 (1944). (The last three papers will be quoted henceforth by C.J.P., J.C. and C. respectively).

ments of nuclei. It is expedient to recall briefly the main outlines of molecular theory,[5] which can have direct application to the pressure broadening theory.

According to Born and Oppenheimer,[6] an eigenfunction ψ_{rel}, which arises from the relative movement of all constituents (electrons and nuclei) of a molecule can in most cases be written approximately as

$$\psi_{\text{rel}}=\psi_{\text{el}}\psi_{\text{nucl}}, \tag{1}$$

where ψ_{el} denotes the electronic eigenfunction, depending upon electronic and nuclear positions, and ψ_{nucl} is the vibrational eigenfunction, depending upon the relative positions of nuclei only. The total eigenfunction of a molecule can be obtained by multiplying ψ_{rel} by the rotational eigenfunction ψ_{rot} (for restrictions cf. S.T.). Since the last function is unimportant in our problem,[7] we shall omit it in further considerations. The energy corresponding to ψ_{rel} is approximately equal to the sum of electronic energy, E_{el}, and translational energy of the nuclei E_{nucl}:

$$E_{\text{rel}}=E_{\text{el}}+E_{\text{nucl}}. \tag{2}$$

The transition probabilities are proportional to D^2 (square of matrix elements); D being given by:

$$\begin{aligned}D&=\int\int\psi'^*_{\text{rel}}M\psi''_{\text{rel}}d\tau_{\text{el}}d\tau_{\text{nucl}}\\&=\int\int\psi'^*_{\text{el}}\psi'^*_{\text{nucl}}M\psi''_{\text{el}}\psi''_{\text{nucl}}d\tau_{\text{el}}d\tau_{\text{nucl}}\\&=\int\mathfrak{M}\psi'^*_{\text{nucl}}\psi''_{\text{nucl}}d\tau_{\text{nucl}},\end{aligned} \tag{3}$$

where M is the variable part of electric moment of the molecule.

Further simplification is obtained by expanding $\mathfrak{M}$ (depending on normal coordinates ξ_i) in power series

$$\mathfrak{M}=\mathfrak{M}_0+\sum_i\mathfrak{M}_i\xi_i+\sum_{kl}\mathfrak{M}_{kl}\xi_k\xi_l+\cdots, \tag{4}$$

and neglecting all the terms but, say, the first two. If only the first term $\mathfrak{M}_0$ is taken into account, there results Condon's approximation (the quantum-mechanical form of the Franck-Condon principle); the integral (3) becomes:

$$D=\mathfrak{M}_0\int\psi'^*_{\text{nucl}}\psi''_{\text{nucl}}d\tau_{\text{nucl}}=\mathfrak{M}_0A, \tag{5}$$

where

$$A=A_{v'v''}=\int\psi'^*_{\text{nucl}}\psi''_{\text{nucl}}d\tau_{\text{nucl}}, \tag{6}$$

$A^2_{v'v''}$ being the probability of a change of the vibrational state, say from v'' to v', accompanying the electronic transition in the molecule.[8]

For qualitative estimations of $A^2_{v'v''}$ the classical form of the Franck-Condon principle (F.C.P.) can be very useful. It can be formulated as follows:[9]

If there occurs an electronic transition in a system of N atoms (as in an N-atomic molecule), no one of the N nuclei makes any considerable instantaneous change in its position or momentum while the transition occurs. There is an instantaneous change of mutual potential energy only, the last being dependent on the electronic state of the system (or its constituents).

If rotational energy is omitted, the emitted or absorbed energy quantum is (in each of the above approximations)

$$\hbar\omega=E'_{\text{rel}}-E''_{\text{rel}}=E'_{\text{el}}-E''_{\text{el}}+E'_{\text{nucl}}-E''_{\text{nucl}}. \tag{7}$$

Each of the above approximations can be adapted to the theory of pressure broadening of spectral lines, but, so far, only the primitive form of the F.C.P.[10] and its quantum-mechanical form[11] have actually been used.

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[5] Cf. S. T., reference 3.

[6] M. Born and R. Oppenheimer, Ann. d. Physik **84**, 457 (1927); Cf. S.T., reference 3.

[7] Cf. J.1.

[8] E. U. Condon, Phys. Rev. **32**, 825 (1928). It can be easily shown that $\sum_{v'}A^2_{v'v''}=1$, if summation is carried out over all the existing states v'. Eventually, integration over continuous states has to be carried out. The same relation holds for transitions from one particular state v' to all existing states v'': $\sum_{v''}A^2_{v'v''}=1$. (Cf. A. Jabłoński, Acta Phys. Pol. **6**, 360 (1937).)

[9] A. Jabłoński, Zeits. f. Physik **73**, 281 (1931).

[10] A. Jabłoński, Zeits. f. Physik **70**, 723 (1931); H. Margenau, Phys. Rev. **40**, 387 (1932); M. Kulp, Zeits. f. Physik **79**, 495 (1932); H. Kuhn, Phil. Mag. **18**, 987 (1934) and Proc. Roy. Soc. A158 and 212 (1937). (The last paper will be henceforth designated by K.) For further literature see H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1937).

[11] W.1 and W.2, reference 2; J.1, J.2, and J.3, reference 1.

If the law of conservation of energy is taken into account, the primitive F.C.P. leads to

$$E'_{\text{nucl}} - E''_{\text{nucl}} = V'(\xi) - V''(\xi), \tag{8}$$

(the difference of potential energies in two electronic states, in relative positions of the nuclei occupied during the electronic transition) and (7) becomes

$$\hbar\omega = E_{\text{el}}' - E_{\text{el}}'' + V'(\xi) - V''(\xi). \tag{9}$$

Equation (9) constitutes the starting point of pressure broadening theories, based on the classical F.C.P. (statistical or potential theories).

The classical theories[2] are based on the assumption that atoms or molecules emit a wave train of variable frequency (the frequency being dependent on the positions of moving nuclei). The intensity distribution is calculated by means of Fourier analysis of variable frequency (and eventually of variable amplitude too). The classical theories of intensity distribution in molecular spectra as well as those of pressure broadening of spectral lines cannot claim to describe the phenomena adequately (unless it is rigorously demonstrated). The same applies to theories, which, though based on Dirac's theory of radiation, describe the nuclear motion classically by considering merely the electronic energy levels as functions of time (their variability being assumed caused by the nuclear movements).[12]

An attempt to bridge the gulf between the classical and quantum-mechanical treatment of the problem has been made by Weisskopf.[2] Because of excessive simplifications his demonstration cannot be considered as convincing. Actually he has shown that, for the case of rectilinear motion of a radiating or absorbing atom in a potential field, the integral (6) can be transformed into an integral of the Fourier type, if Wentzel-Kramers-Brillouin (W.K.B.) eigenfunctions are used. The Fourier integral is then identical with that constituting the starting point of the classical pressure broadening theories. The assumption of rectilinear motion is incompatible with the fact that the atomic collision problem is a central force problem. The difficulty arising from the failure of W.K.B. approximation in the region of the point of closest approach of the colliding atoms (classical turning point) is not surmounted by Weisskopf's treatment, but merely completely camouflaged. As will be shown further, this difficulty is quite a serious one. In addition, Weisskopf treats the continuous translational energy spectrum as a discrete one should be treated, thus omitting an important factor in the final intensity distribution formula.[13] Moreover, there is no justification in the case of a gas consisting, say, of n atoms for replacing the nuclear eigenfunction, which can be approximately written as a product of eigenfunctions of the particular nuclei

$$\psi = \prod_{i}^{n} \psi_i$$

merely by means of a single eigenfunction describing the rectilinear motion of the absorbing (or emitting) atom in a fixed potential field. Further simplifications have been introduced by Weisskopf in order to obtain the classical collision damping formula. Weisskopf neglects all the collisions with impact parameters ρ larger than a certain optical collision radius ρ_0, the effect produced by those with $\rho < \rho_0$ being assumed independent of ρ. Thus, Weisskopf's theory cannot possibly describe the phenomena adequately.

A theory concerning the particular case of broadening of resonance lines by intrinsic pressure was developed by Houston.[14] There is no reason, however, to suppose that the present theory cannot embrace this particular case too.

But the last word belongs, of course, to experiment. This word, however, seems not yet to have been pronounced. One of the causes is

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[12] H. Margenau and W. W. Watson, reference 10; L. Spitzer, Jr., Phys. Rev. **55**, 699 (1939); **56**, 39 (1939); and **58**, 348 (1940). I do not share the opinion expressed by L. Spitzer that a formula obtained in this way would represent the "true" intensity distribution.

[13] In the case of continuous eigenvalues, eigendifferentials instead of eigenfunctions must be used. If, by using a limited space, the continuous spectrum is transformed into a discrete one, a factor, denoting the density of energy levels, appears in the intensity distribution formula. This factor being omitted in Weisskopf's considerations, an incorrect dependence of the width of the line on energy of collision (i.e., of the temperature of the gas) is obtained.

[14] W. V. Houston, Phys. Rev. **54**, 884 (1938). In this theory too, the nuclear motion is treated classically. The papers of Furssow and Wlasow, mentioned by Houston, were not accessible to the writer. The same applies to the paper by E. Lindholm (Ark. Math. Astr. Fys. **28B**, 1, No. 3 (1943)).

the lack of knowledge of the exact form of potential curves,[15] which prevents theoretical results sufficiently accurate for experimental distinction between different competing theories from being obtained. Experimental difficulties and the difficulties of exact numerical computations constitute the other causes. Yet, one can assert that the primitive form of Lorentz-Weisskopf-Lenz collision damping theory is certainly incompatible with experimental results. Except in the case of broadening by dipole interaction (observed by Rompe and Schulz), the intensity distribution does not result from the above theory. But even the case of dipole interaction cannot be considered as a proof of the collision damping theory, because in this particular case the observed dispersion intensity distribution results not only from the above theory but also from the statistical ones.[16]

According to Unsöld[17] the variation of equivalent breadths throughout the Mg series 3^1P-n^1D in the solar spectrum agrees well with collision damping theory if it is assumed that the lines are broadened by the Stark effect caused by electrons and ions. However, the theoretical values used by Unsöld in his calculations do not agree at all with the later experimental results of Eckarth.[18] If the experimental values of Stark effect constants are put into Unsöld's formulae, the agreement disappears entirely. Thus, Unsöld's results too by no means confirm the Lorentz-Weisskopf-Lenz theory.

As shown by Kuhn,[19] Minkowski,[20] and Rühmkorf[21] the intensity distribution in a certain range of frequencies within the broadened lines agrees well with that predicted by statistical theories. The same distribution (apart from a factor, constituting as a rule only an insignificant correction) results from the present theory for the asymptotic case of heavy atoms having large kinetic energy.[20] The limitations of its applicability are discussed in IX. These experiments thus support the present theory as well. The experiments of Horodniczy and the writer,[21] though perhaps not very precise ones, show that any influence of the temperature, that is, of the number of collisions per second, is much less pronounced than was to be expected according to Weisskopf and can also be considered as supporting rather the statistical theories (and thus the present theory as well).

Although below merely an asymptotic distribution is obtained (mainly because of the difficulties of more exact calculations of integral (6)), the way is still open to more precise calculations. The most suitable way seems to be the use of a differential analyser for calculations of eigenfunctions describing the nuclear movements and the integrals (6) or eventually, if necessary, (3). This method was used very successfully by Coolidge, James, and Present[22] for calculations of intensity distribution in H_2 and D_2 continuous spectra.

II. ON THE PROBABILITY DISTRIBUTION OF A QUANTITY COMPOSED OF A SUM OF QUANTITIES WITH PROBABILITY DISTRIBUTIONS OF A PARTICULAR FORM INDEPENDENT OF ONE ANOTHER

The problem we shall consider here has a direct application to the theory of pressure broadening. Although it does not constitute a characteristic feature of this particular theory, nevertheless its solution is essential for estimation of the conditions in which the single transits of atoms past each other are so predominant that the multiple transits can be neglected. Moreover, this makes it possible eventually to take into account also the multiple transits.

The problem is: The probability distributions $P_1(x_1)$, $P_2(x_2)$, $\cdots P_n(x_n)$ of certain quantities x_1, x_2, $\cdots x_n$ being given, calculate the probability distribution $P(X)$ of

$$X=\sum_{i=1}^{n} x_i$$

on the assumption that the $P_i(x_i)$ are independent of one another.

The general case, when $P_i(x_i)$ are not specified,

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[15] Cf. e.g., L. Gropper, Phys. Rev. **55**, 1095 (1939).

[16] K, reference 10.

[17] A. Unsöld, Zeits. f. Astrophys. **12**, 56 (1936).

[18] H. Eckarth, Zeits. f. Physik **107**, 182 (1937).

[19] K. reference 9; R. Minkowski, Zeits. f. Physik **93**, 731 (1935) and H. A. Rühmkorf, Ann. d. Physik [5] **33**, 21 (1938).

[20] The distribution obtained in J.3 (reference 1) differs by a factor 2 from the statistical distribution of Kuhn. The present formula constitutes a better approximation.

[21] H. Horodniczy and A. Jabłoński, Nature **142**, 1122 (1938) and **144**, 594 (1939).

[23] C.J.P.; J.C., reference 4.

is of little interest and is trivial. When the probability distribution

$$P_{1,2,\cdots(n-1)}\left(\sum_{i=1}^{n-1} x_i\right)$$

of an algebraic sum of $n-1$ quantities is known, one obtains the probability distribution $P(X)$ of

$$X=\sum_{i=1}^{n} x_i=\sum_{i=1}^{n-1} x_i+x_n$$

by forming a product of probabilities

$$P_{1,2,\cdots n-1}\,(X-x_n)P_n(x_n)$$

and integrating[23] over the whole range of variability of x_n, say, from $-\infty$ to $+\infty$:

$$P(X)=\int_{-\infty}^{+\infty} P_{1,2\cdots(n-1)}(X-x_n)\cdot P_n(x_n)dx_n. \tag{10}$$

By means of this procedure, one can calculate the probability distribution of a sum of any number of quantities by calculating successively the probability distribution of a sum of two quantities, then that of three, and so on, until all the quantities are taken into account.

The particular form of probability distribution we shall consider here is that of

$$\int_{\Delta x_i} P_i(x_i)dx_i=\int_{\Delta x_i}[(1-\epsilon)\delta(x_i)+W(x_i)]dx_i, \tag{11}$$

where Δx_i can be arbitrarily small. Thus, we assume that the probability of $x_i=0$ is $1-\epsilon$ and for $x_i\neq 0$ the probability of x_i being within Δx_i is

$$\int_{\Delta x_i} W(x_i)dx_i\approx W(x_i)\Delta x_i.$$

For our purposes it will suffice to consider the simplest case, when $P_1(x_1)=P_2(x_2)=\cdots P_n(x_n)$ for $x_1=x_2=\cdots x_n$.[24] Since

$$\int_{-\infty}^{+\infty} P_i(x_i)dx_i$$
$$=\int_{-\infty}^{+\infty}[(1-\epsilon)\delta(x_i)+W(x_i)]dx_i=1, \tag{12}$$

ϵ must be given by

$$\epsilon=\int_{-\infty}^{+\infty} W(x_i)dx_i. \tag{13}$$

Here, ϵ denotes the probability of $x_i\neq 0$.

Now we shall show that if all $P_i(x_i)$ are identical and of the type (11), the probability distribution

$$\int_{\Delta X} P(X)dX \text{ of } X=\sum_{i=1}^{n} x_i$$

is:

$$\int_{\Delta X} P(X)dX=\int_{\Delta X}\Bigg[\delta(X)(1-\epsilon)^n$$
$$+\sum_{\nu=1}^{n}\binom{n}{\nu}W^{(\nu)}(X)(1-\epsilon)^{n-\nu}\Bigg]dX, \tag{14}$$

where $W^{(1)}(X)$ is identical with $W(x_i)$ in (11). The integral $\int_{\Delta X} W^{(\nu)}(X)dX$ denotes the probability that the sum of ν quantities, none of which vanish, lies between X and $X+\Delta X$. $W^{(\nu)}(X)$ is obtained from $W^{(\nu-1)}(X)$ by a procedure analogous to that given by (10):

$$W^{(\nu)}(X)=\int_{-\infty}^{+\infty} W^{(\nu-1)}(X-x_i)W^{(1)}(x_i)dx_i.^{25} \tag{15}$$

For $n=2$ (14) can be verified immediately by means of (10) and (15):

$$\int_{\Delta X}\int_{-\infty}^{+\infty}[\delta(X-x_j)(1-\epsilon)+W^{(1)}(X-x_j)]$$
$$\times[\delta(x_j)(1-\epsilon)+W^{(1)}(x_j)]dXdx_j$$
$$=\int_{\Delta X}\int_{-\infty}^{+\infty}[\delta(X-x_j)\delta(x_j)(1-\epsilon)^2$$
$$+W^{(1)}(X-x_j)\delta(x_j)(1-\epsilon)$$
$$+\delta(X-x_j)(1-\epsilon)W^{(1)}(x_j)$$
$$+W^{(1)}(X-x_j)W^{(1)}(x_j)]dXdx_j$$
$$=\int_{\Delta X}\Bigg[\delta(X)(1-\epsilon)^2$$
$$+\binom{2}{1}W^{(1)}(X)(1-\epsilon)+W^{(2)}(X)\Bigg]dX, \tag{16}$$

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[23] We assume that the x_i are continuous.

[24] The more general case of $P_1(x_1)\neq P_2(x_2)\neq\cdots P_n(x_n)$ for $x_1=x_2=x_3=\cdots x_n$ is treated in J.1, reference 1.

[25] For example, $W^{(2)}(X)=\int_{-\infty}^{+\infty}W^{(1)}(X-x_i)W^{(1)}(x_i)dx_i$, where $X=x_i+x_j$.

which is identical with (14) for $n=2$

$$\left(W^{(2)}(X)=\int_{-\infty}^{+\infty}W^{(1)}(X-x_j)W^{(1)}(x_j)dx_j\right).$$[25]

In order to prove the expression (14), we need now show merely that if it is admitted to be true for n quantities, it will prove to be true for $n+1$ quantities as well. This can be done by applying the procedure (10) to (14) and taking into account (15):

$$\begin{aligned}
&\int_{\Delta X}\int_{-\infty}^{+\infty}\left[\delta(X-x_{n+1})(1-\epsilon)^n+\sum_{\nu=1}^{n}\binom{n}{\nu}W^{(\nu)}(X-x_{n+1})(1-\epsilon)^{n-\nu}\right][\delta(x_{n+1})(1-\epsilon)+W^{(1)}(x_{n+1})]dXdx_{n+1}\\
&=\int_{\Delta X}\left[\delta(X)(1-\epsilon)^{n+1}+\sum_{\nu=1}^{n}\binom{n}{\nu}W^{(\nu)}(X)(1-\epsilon)^{n+1-\nu}+W^{(1)}(X)(1-\epsilon)^n+\sum_{\nu=1}^{n}\binom{n}{\nu}W^{(\nu+1)}(X)(1-\epsilon)^{n-\nu}\right]dX\\
&=\int_{\Delta X}\left[\delta(X)(1-\epsilon)^{n+1}+\sum_{\nu=1}^{n}\binom{n}{\nu}W^{(\nu)}(X)(1-\epsilon)^{n+1-\nu}\right.\\
&\qquad\qquad\left.+W^{(1)}(X)(1-\epsilon)^n+\sum_{\nu=2}^{n+1}\binom{n}{\nu-1}W^{(\nu)}(X)(1-\epsilon)^{n+1-\nu}\right]dX\\
&=\int_{\Delta X}\left[\delta(X)(1-\epsilon)^{n+1}+\sum_{\nu=1}^{n+1}\binom{n+1}{\nu}W^{(\nu)}(X)(1-\epsilon)^{n+1-\nu}\right]dX, \qquad (17)
\end{aligned}$$

since

$$\binom{n}{\nu}+\binom{n}{\nu-1}=\binom{n+1}{\nu}.$$

Equation (17) being of the same form as (14) and (14) being proved true for $n=2$ (by Eq. (16)), the expression (14) is thus established.

In the limiting case of $\epsilon=1$ all the terms in (14) except the last one vanish. For $\epsilon\ll 1$ Eq. (14) can be written as:

$$\int_{\Delta X}P(X)dX=\int_{\Delta X}\left[\delta(X)e^{-\epsilon n}+\sum_{\nu=1}^{n}\binom{n}{\nu}W^{(\nu)}(X)e^{-\epsilon(n-\nu)}\right]dX. \qquad (14a)$$

Equation (14) or (14a) can be immediately applied to the pressure broadening of spectral lines[26] if changes of translational energy of the particular perturbers (perturbing atoms or molecules) due to an electronic transition in the radiator (radiating or absorbing atom) can be considered as independent of one another. The mutual collisions of perturbers with one another are practically irrelevant. In this case $\int_{\Delta X}P(X)dX$ is the probability distribution of the changes X of the total translational energy of the whole gas (n perturbers+radiator), $\int_{\Delta X_i}W^{(1)}(x_i)dx_i$—the probability that the translational energy of a particular nucleus changes its value by an amount x_i and $1-\epsilon$ the probability that this energy remains unchanged.

X is related directly to the frequency actually absorbed or emitted by the radiator. The absorbed frequency ω is

$$\omega=\omega_0+X/\hbar, \qquad (18)$$

and the emitted frequency

$$\omega=\omega_0-X/\hbar, \qquad (18a)$$

where ω_0 denotes the frequency of the unperturbed line. Obviously X can be both positive (increase of translational energy) and negative (decrease of translational energy). Thus, the intensity distribution is directly given by probability distribution (14).

It is now clear that if the independence of nuclear movements is assumed,[27] it is sufficient to know $W^{(1)}(X)$ (which can be considered as intensity distribution in the case when only one radiator and one perturber are present in the container), in order to calculate successively $W^{(2)}(X)$, $W^{(3)}(X)$, $\cdots W^{(n)}(X)$, and thus the

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[26] The same considerations could be applied with slight modifications to a system of atoms (e.g., molecule) with nuclear movements described by means of normal coordinates.

[27] This assumption may, however, not always correspond to the real conditions.

total intensity distribution $P(X)$ resulting from the action of n perturbers present in the container. The first term of (14) then denotes that part of the intensity which survives from the original intensity of the unperturbed line in its exact position ω_0 (the line being assumed for the sake of simplicity as infinitely narrow). The term containing $W^{(1)}(X)$ gives the contribution of single transits, $W^{(2)}(X)$ of double, $W^{(3)}(X)$ of triple, $\cdots W^{(\nu)}(X)$ of ν fold transits to the intensity in ω given by (18).

Because of the assumption of infinite narrowness of original spectral line and additivity of the effects produced by separate perturbers, formula (14) must be considered as an approximate one.

$$\epsilon=\int_{-\infty}^{+\infty} W^{(1)}(X)dX$$

cannot be calculated without exact knowledge of $W^{(1)}(X)$ in the whole range of X, and its computation may prove a hard task. Nevertheless, if one assumes that the effect produced by the transits with impact parameters ρ larger than a certain $\rho_{\max}$ can be practically neglected;[28] i.e., if one assumes a finite sphere of action of interatomic forces, ϵ can be estimated roughly even without relying on the quantum-mechanical theory developed below. It is of the order of magnitude of $(\rho_{\max}/R)^3$, where R denotes the radius of the container (which we suppose for the sake of simplicity to be spherical). Thus, e.g., for $\rho_{\max}=10^{-7}$ cm and $R=1$ cm, $\epsilon\sim 10^{-21}$. For $n\epsilon\ll 1$, $(1-\epsilon)^{n-\nu}\approx e^{-\epsilon(n-\nu)}\approx 1$, and the factors $(1-\epsilon)^{n-\nu}$ can be omitted in (14). In the above case of $\rho_{\max}=10^{-7}$ cm and $R=1$ cm, this can be done if $n\ll 10^{21}$.

As was shown (J.1, reference 1),

$$\int_{-\infty}^{+\infty} W^{(1)}(X)dX:\int_{-\infty}^{+\infty} W^{(2)}(X)dX:\cdots \int_{-\infty}^{+\infty} W^{(\nu)}(X)dX=\epsilon:\epsilon^2:\cdots\epsilon^\nu,$$

i.e.,

$$\epsilon\int_{-\infty}^{+\infty} W^{(\nu)}(X)dX=\int_{-\infty}^{+\infty} W^{(\nu+1)}(X)dX.$$

Since the $W^{(\nu)}(X)$ are essentially positive, there must always exist a region of X in which $W^{(\nu+1)}(X)/W^{(\nu)}(X)$ is of the order of magnitude of ϵ.[29] Thus, the ratio of any two neighboring terms in (14), say, of that containing $W^{(\nu+1)}(X)$ to that containing $W^{(\nu)}(X)$,

$$\frac{n-\nu}{\nu+1}\frac{W^{(\nu+1)}(X)}{W^{(\nu)}(X)}\frac{1}{1-\epsilon}$$

is, in this region, of the order of $[(n-\nu)/(\nu+1)]\times[\epsilon/(1-\epsilon)]$. If

$$\frac{n-\nu}{\nu+1}\frac{\epsilon}{1-\epsilon}\ll 1,$$

only single transits are relevant and all the terms in (14) but the first two can be neglected. The importance of further terms becomes appreciable at higher densities of gas. The higher the density of the gas, the farther away from the beginning of the sum (14) does the most important term of the sum lie.

III. GENERAL FORM OF $W^{(1)}(X)$

Now we have to proceed to calculate $W^{(1)}(X)$.

The assumption of independence of the movements of the nuclei of a gaseous system consisting of a radiator and n perturbers is equivalent to the assumption that the total eigenfunction of the system ψ_{nucl} can be represented as a product of eigenfunctions $\psi_{\text{nucl}\ i}$ representing the movements of separate nuclei

$$\psi_{\text{nucl}}=\prod_i^n \psi_{\text{nucl}\ i},$$

and the corresponding total translational energy E_t as the sum of translational energies E_i of separate nuclei

$$E_t=\sum_{i=1}^n E_i.$$

In this case (14) can be applied to the calculation of intensity distribution within a broadened line if $W^{(1)}(X)$ is calculated first for a single couple of

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[28] Strictly speaking this is never the case, the interatomic forces being in principle of infinite range.

[29] It is, however, not generally true that, if the $W^{(\nu)}(X)$ are decreasing functions of $|X|$, $W^{(\nu+1)}(X)$ must decrease more rapidly than $W^{(\nu)}(X)$ does (as sometimes assumed). So, e.g., if $W^{(1)}(X)$ has the form of a dispersion curve (and thus all the $W^{(\nu)}(X)$ have the same form as well but with half width ν times the half width of $W^{(1)}(X)$), $W^{(\nu+1)}(X)/W^{(\nu)}(X)$ is an *increasing* function of $|X|$.

atoms consisting of a radiator and a perturber.[30] In order to make possible the application to our problem of molecular theory as described in paragraph I, we suppose the above couple of atoms to be enclosed in a container of finite volume thus forcing the states of nuclear motion to become discrete and, in addition, making it easier to normalize the corresponding eigenfunctions. Thus (3) or (5) and (6) can be immediately used, the role of vibrational eigenfunctions now being played by nuclear eigenfunctions. These eigenfunctions are solutions of Schrödinger's equation for the two-body problem in relative coordinates r, which result when the motion of the mass center is separated. They are discrete if boundary conditions $\psi_{\mathrm{nucl}}(R)=0$ are imposed at the walls of the container (which it is convenient to regard as a sphere of radius R with radiator at its center). Thus we obtain two sets of nuclear eigenfunctions for two combining electronic states as functions of r. Only the radial eigenfunctions are relevant in our problem (cf. J.1). The shape of this function depends not only upon relative kinetic energy and mutual potential energy of the couple, but upon its angular momentum as well. Let v' and v'' be the radial quantum numbers (the number of nodes of the radial eigenfunction), and l' and l'' the angular momentum (rotational) quantum numbers of the states of nuclear motion in both electronic states respectively. The radial eigenfunctions $\psi_{v'l'}$ and $\psi_{v''l''}$ corresponding to the states with quantum numbers v' and l' (upper electronic state of the radiator) and v'' and l'' (lower electronic state of the radiator) respectively are solutions of Schrödinger equations:

$$\frac{d\psi_{v'l'}}{dr}+\frac{2\mu}{\hbar^2}\left(E_{v'l'}-V'(r)-\hbar^2\frac{l'(l'+1)}{2\mu r^2}\right)\psi_{v'l'}=0 \quad (19)$$

and

$$\frac{d\psi_{v''l''}}{dr}+\frac{2\mu}{\hbar^2}\left(E_{v''l''}-V''(r)-\hbar^2\frac{l''(l''+1)}{2\mu r^2}\right)\psi_{v''l''}=0 \quad (19a)$$

respectively, where μ denotes the reduced mass of the couple, $V'(r)$ and $V''(r)$ the mutual potential energy of the couple of atoms corresponding to the upper and lower electronic state, $E_{v'l'}$ and $E_{v''l''}$ the relative energy values of nuclear motion in quantum states v', l' and v'', l'' which may be found by taking into account the boundary conditions. We need not treat in detail the rotational eigenfunctions, the only effect of which is that in our approximation, only transitions between nuclear motion states v', $l' \leftrightarrow v''$, l'' with unchanged angular momentum $l'=l''$ are allowed. This follows from the orthogonality of rotational eigenfunctions. If instead of the radial eigenfunctions, we substitute the total nuclear eigenfunctions; i.e., $\psi_{vl}\psi_{\mathrm{rot}}$ in the integrals (3) or (6) and integrate over the whole range of variability of respective angles, only those integrals do not vanish for which $l'=l''$.[31] Apart from this "selection rule," the angular momentum comes to light in the centrifugal potential $\hbar^2 l(l+1)/2\mu r^2$ in Eqs. (19) and (19a) and thus in the radial eigenfunctions. The centrifugal potential induces the dependence on l of the matrix elements $D_{v'v''l}$ (cf. (3), (5) and (6)). For very large l's, the eigenfunctions of both sets become practically identical and thus orthogonal. Hence, practically no transitions $v' \leftrightarrow v''$ with $v' \neq v''$ will occur between states with sufficiently large l's. For smaller values of l, the dependence of $D_{v'v''l}$ on l becomes very marked. Classically speaking, the effect on spectral lines produced by collisions depends very markedly on impact parameter. Thus, it is by no means justifiable to assume that all the collisions with impact parameters smaller than a certain "optical collision radius" ρ_0 are equally effective, and those with larger impact parameter are entirely ineffective.

Let us now assume that the couple is in a state v'', l'' (lower electronic state) and consider all the possible transitions from this state v'',

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[30] Cf. J.1, reference 1. The applicability of this procedure to the calculations involving multiple collisions is limited to the cases when the mutual potential energy of the radiator and all the perturbers can be represented as a sum of the mutual potential energies of separate perturbers and the radiator. This generally seems to be at best only very roughly the case; the different orientations of angular momenta of the atoms relative to the axis joining the nuclei of the couple lead to different potential curves; these orientations may be disturbed by the presence of additional perturbers.

[31] Cf. J.1, reference 1.

$l'' \to v'$, l' (absorption line). In order to obtain the relative intensity distribution in energy scale, we have to multiply $D^2_{v'v''l}$ by the density of nuclear motion energy levels in the upper electronic state dv'/dE_v. For sufficiently large R, the energy states are dense enough to be treated v' as a continuous function of $E_{v'}$. The resulting intensity (or frequency) scale is proportional to $D^2_{v'v''l}(dv'/dE_{v'})$, except, however, for $D^2_{v'v''l}$ with $v'=v''$, i.e., for the position ω_0 of the original unperturbed line. In this position there will be always a discontinuity because, obviously, $D_{v'v''l}$ with $v'=v''$ is very much larger than any matrix element with $v' \neq v''$. The chance of an electronic transition without change of translational energy of the nuclei of the couple is very much larger than that with any change; this follows both from the above estimate of ϵ and from considerations on the product of nuclear eigenfunctions in the integral (3). This situation remains practically unchanged by the fact that, strictly speaking, $E_{v'}$ is not quite exactly equal to $E_{v''}$ for $v'=v''$, $E_{v'}$ and $E_{v''}$ being dependent slightly on mutual potential energy of the atoms different in two electronic states under consideration.

We may, instead of considering the case of a particular fixed l, allow the l's to be distributed at random according to a certain partition law $Q(l)$. $Q(l)$, denoting the probability of occurence of a rotational quantum number l, has to be calculated later. That is, if we consider the transitions from the levels with a certain fixed v'' and the l's distributed according to $Q(l)$ to all existing levels v'' with unchanged l's (except that one with $v'=v''$), the probability distribution of the changes of the nuclear motion energy of the couple (in energy scale) becomes:

$$W^{(1)}(X)=W^{(1)}(E_{v'}-E_{v''})$$

$$=\sum_{l=0}^{l_{\max}} Q(l)\frac{D^2_{v'v''l}}{\sum\limits_{v'=1}^{\infty} D^2_{v'v''l}}\,\frac{dv'}{dE_{v'}}$$

$$\approx\int_0^{l_{\max}} Q(l)\frac{D^2_{v'v''l}}{S}\,\frac{dv'}{dE_{v'}}dl \qquad (20)$$

and correspondingly, for the case of an emission line:

$$W^{(1)}(X)=W^{(1)}(E_{v'}-E_{v''})$$

$$=\sum_{l=0}^{l_{\max}} Q(l)\frac{D^2_{v'v''l}}{S}\,\frac{dv}{dE}$$

$$\approx\int_0^{l_{\max}} Q(l)\frac{D^2_{v'v''l}}{S}\,\frac{dv''}{dE_{v''}}dl. \qquad (21)$$

The upper limit $l_{\max}$ denotes the largest l occurring in $Q(l)$ or eventually the largest l relevant in our calculations. For very large $l_{\max}$ the sums can be approximately replaced by integrals. The strength

$$S=\sum_{v'=1}^{\infty} D^2_{v'v''l}=\sum_{v''=1}^{\infty} D^2_{v'v''l}$$

of the electronic transition under consideration is put in the denominators of (20) and (21) to secure proper normalization of $W^{(1)}(X)$ as expressing the probability of occurrence of $X=E_{v'}-E_{v''}$. Expressions (20) or (21) substituted in (14) (or (14a)) lead to the intensity distribution normalized so as to give the total intensity of the line equal to unity. Thus, the absolute intensity of $\omega=\omega_0+(X/\hbar)$ will be equal to that given by (14) multiplied by the total intensity of the unperturbed line. For the sake of simplicity we have supposed that the width of the unperturbed line is infinitely small. To obtain the true intensity distribution with full accuracy, we should impose on that calculated in the above way the natural and Doppler distributions. Generally the corrections for these effects can be neglected in the wings of the broadened line. The expressions (20) and (21) may be used for the most exact calculations. They become much simpler if Condon's approximation is considered sufficient (presumably, this will usually be so). Since in this case

$$S=\mathfrak{M}_0{}^2=\sum_{v'=1}^{\infty} D^2_{v'v''l}=\sum_{v''=1}^{\infty} D^2_{v'v''l}$$

and $D_{v'v''l}=\mathfrak{M}_0 A_{v'v''l}$ [cf. (5) and (6)], (20) and (21) become:

$$W^{(1)}(X)\approx\int_0^{l_{\max}} Q(l)A^2_{v'v''l}\frac{dv'}{dE_{v'}}dl$$

(absorption line), (20a)

and

$$W^{(1)}(X)\approx\int_0^{l_{\max}} Q(l)A^2_{v'v''l}\frac{dv''}{dE_{v''}}dl$$

(emission line). (21a)

The calculations of $W^{(1)}(X)$ can be carried out conveniently by the aid of a differential analyzer.[32]

Usually there is more than a single potential curve in each electronic state. Instead of the above simple $W^{(1)}(X)$ one must use then

$$W^{(1)}(X)=a_1W_1^{(1)}(X)+a_2W_2^{(1)}(X)+\cdots$$
$$=\sum_i a_iW_i^{(1)}(X). \quad (22)$$

Here, a_i denotes the relative abundance of transitions between two particular potential curves. a_i must fulfill the condition $\sum_i a_i=1$. Each $W_i^{(1)}(X)$ must be calculated separately, $D_{v'v''l}$ or $A_{v'v''l}$ being dependent on the shape of different potential curves in both electronic states. The multiplicity of potential curves causes a serious difficulty if multiple encounters come into play, i.e., at higher densities of gas. Equation (22) must not be forgotten while calculations for a particular line and gas mixture are carried out.

For the case $n\epsilon\ll 1$ the intensity distribution far enough from the unperturbed frequency ω_0 of the line, and, in any case, outside the half value width of the natural and Doppler intensity distribution is according to (14) and (22) simply:

$$I(\omega)=nh\sum_i a_iW_i^{(1)}(X)$$
$$=nh\sum_i a_iW_i^{(1)}(\hbar(\omega_0-\omega))$$
$$=(4/3)\pi R^3\hbar N\sum_i a_iW_i^{(1)}(\hbar\Delta\omega), \quad (23)$$

with $W_i''(X)$ calculated as indicated above. $Q(l)$ and dv/dE can be calculated easily with sufficient accuracy. Because of difficulties of exact calculation of $D_{v'v''l}$ or even $A_{v'v''l}$, we shall restrict ourselves to calculation of the asymptotic expressions of $A_{v'v''l}$ valid in the case of heavy nuclei with large kinetic energies in a limited spectral region of the broadened line and even then only approximately.

IV. CALCULATION OF $Q(l)$

In our case $Q(l)$ is simply proportional to the statistical weight $2l+1$ of the state l:

$$Q(l)=g\cdot(2l+1). \quad (24)$$

The factor g may be evaluated by comparison of (24) with the classical probability distribution of the impact parameters for large l's. The classical value of the impact parameter corresponding to the angular momentum $\hbar[l(l+1)]^{\frac{1}{2}}$ is:

$$\rho=\hbar[l(l+1)/2\mu E]^{\frac{1}{2}}, \quad (25)$$

where μ is the reduced mass of the couple and E its relative translational energy. For large l's, $Q(l)dl\approx Q'(\rho)d\rho$, i.e., is equal to the chance of the occurrence of impact parameter within the limits ρ and $\rho+d\rho$. For the case of a spherical container with radius R the classical calculation gives:

$$Q'(\rho)d\rho=\frac{3}{R^3}(R^2-\rho^2)^{\frac{1}{2}}\rho d\rho,$$

or for the only important case $\rho\ll R$

$$Q'(\rho)d\rho=\frac{3}{R^2}\rho d\rho=\frac{3}{2R^2}d\rho^2. \quad (26)$$

From (25) and (26) we obtain

$$Q'(\rho)d\rho=\frac{3\hbar^2}{4R^2\mu E}(2l+1)dl. \quad (27)$$

Thus[33]

$$Q(l)=\frac{3\hbar^2}{4R^2\mu E}(2l+1). \quad (28)$$

V. THE DENSITY OF TRANSLATIONAL ENERGY LEVELS[34]

The asymptotic solutions of Schrödinger Eqs. (19) and (20) for $r\rightarrow\infty$ (i.e., for $V(r)\rightarrow 0$ and $\hbar^2l(l+1)/2\mu r^2\rightarrow 0$) have the form

$$\overset{(A)}{\psi}_{\text{nucl }vl}(r)=(2/R)^{\frac{1}{2}}\cos\left[(2\mu E_v)^{\frac{1}{2}}r/\hbar+\delta\right], \quad (29)$$

where $(2/R)^{\frac{1}{2}}$ is the normalization factor securing the condition

$$\int_0^R \overset{(A)}{\psi}{}^2_{\text{nucl }vl}(r)dr=1$$

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[32] Cf. C.J.P. and J.C., reference 4; the writer had no opportunity of using this method.

[33] In the previous papers the angular momentum was treated classically.

[34] Cf. J.1, reference 1.

and δ a phase constant. Imposing the boundary condition $\overset{(A)}{\psi}_{\text{nucl}\, vl}(R)=0$ on (29) we have:

$$\frac{(2\mu E_v)^{\frac{1}{2}}}{\hbar}R+\delta=\frac{2v+1}{2}\pi, \tag{30}$$

(v integral) and hence the density of translational energy levels is given by

$$\frac{dv}{dE_v}=\frac{\mu^{\frac{1}{2}}R}{\pi\hbar(2E_v)^{\frac{1}{2}}}=\frac{\mu R}{\pi\hbar p_v(\infty)}, \tag{31}$$

where $p_v(\infty)=p_{\underset{r=\infty}{v}}(r)$ is the value of the radial component of the relative momentum of the couple for $r\rightarrow\infty$.

VI. APPROXIMATE CALCULATION OF $A_{v'v''l}$ BY MEANS OF WENTZEL-KRAMERS-BRILLOUIN EIGENFUNCTIONS

In order to calculate approximately the integral (6), we shall apply the solutions of Schrödinger's Eqs. (19) and (19a) in the form of the Wentzel-Kramers-Brillouin approximation. They can be written as follows:

$$\psi_{vl}=\left(\frac{2}{R}\right)^{\frac{1}{2}}\left[\frac{2\mu E_{vl}}{2\mu(E_{vl}-V(r))-\hbar^2\frac{l(l+1)}{r^2}}\right]^{\frac{1}{4}}$$
$$\times\cos\left\{\frac{1}{\hbar}\int_{r_0}^{r}\left[2\mu(E_{vl}-V(r))-\hbar^2\frac{l(l+1)}{r^2}\right]^{\frac{1}{2}}dr+\delta\right\}=\left(\frac{2p(\infty)}{Rp(r)}\right)^{\frac{1}{2}}\cos\left[\frac{1}{\hbar}\int_{r_0}^{r}p(r)dr+\delta\right], \tag{32}$$

where $p(r)=[2\mu(E_{vl}-V(r))-\hbar^2 l(l+1)/r^2]^{\frac{1}{2}}$ is the radial component of relative momentum of the couple with reduced mass μ and angular momentum $\hbar[l(l+1)]^{\frac{1}{2}}$. The normalization factor $(2p(\infty)/R)^{\frac{1}{2}}$ follows from the asymptotic form (29) of the solution. Equation (32) is valid only for $r>r_t$ (r_t the distance of closest approach or classical turning point has to be found from the equation $p(r_t)=0$) and fails in the region of r_t. We refrain temporarily from discussion of the phase constant δ (δ depends on the lower limit of the integral involved in (32) for which we have put r_t).

The integral (6) with eigenfunctions (32) becomes:

$$A_{v'v''l}\approx\frac{2}{R}\int_0^R\left\{\left(\frac{p'(\infty)}{p'(r)}\right)^{\frac{1}{2}}\cos\left[\int_{r_t}^{r}\frac{p'(r)}{\hbar}dr+\delta'\right]\left(\frac{p''(\infty)}{p''(r)}\right)^{\frac{1}{2}}\cos\left[\int_{r_t}^{r}\frac{p''(r)}{\hbar}dr+\delta''\right]\right\}dr$$
$$=\frac{1}{R}\int_{r_t}^{R}\left(\frac{p'(\infty)p''(\infty)}{p'(r)p''(r)}\right)^{\frac{1}{2}}\left[\cos\left(\int_{r_t}^{r}\frac{p'(r)-p''(r)}{\hbar}dr+\delta'-\delta''\right)\right.$$
$$\left.+\cos\left(\int_{r_t}^{r}\frac{p'(r)+p''(r)}{\hbar}dr+\delta'+\delta''\right)\right]dr. \tag{33}$$

The second cosine term is a very rapidly oscillating function of r and thus its contribution to the value of the integral (33) can be neglected. As to the first cosine term, the most important region of r is that in the neighborhood of $r=r_c$ for which $p'(r)=p''(r)$. It contributes most to the value of the integral (33) because the oscillation of the first cosine term becomes slowest there (apart, presumably, from the region of the classical turning point, which, however, we are compelled to omit here). r_c is just that distance in which, according to the classical form of F.C.P., the transition $p'(r_c)\leftrightarrow p''(r_c)$ takes place. Hence, the correspondence between the classical and quantum-mechanical form of F.C.P. becomes apparent. The square of the integral (33) ($A^2_{v'v''l}$) is the probability of change of translational energy by $X=E_{v'}-E_{v''}$ equal to that resulting from the classical F.C.P. for the transition in r_c:

$$X=V'(r_c)-V''(r_c)=\hbar(\omega_0-\omega)=\hbar\Delta\omega. \tag{34}$$

Neglecting the second term in (33) and developing the integrand involved in the first term in series in the neighborhood of r_c we obtain:

$$A_{v'v''l}=\frac{1}{R}\int_{r_t}^{R}\left[\frac{p'(\infty)p''(\infty)}{p'(r)p''(r)}\right]^{\frac{1}{2}}\cos\left\{\frac{1}{\hbar}\int_{r_t}^{r_c}(p'(r)-p''(r))dr+\delta'-\delta''\right.$$
$$\left.+\frac{1}{\hbar}\int_{r_c}^{r}\left[p'(r_c)-p''(r_c)+\left[\frac{d}{dr}(p'(r)-p''(r))\right]_{r=r_c}(r-r_c)+\cdots\right]dr\right\}dr. \quad (35)$$

Putting $r-r_c=\xi$ and neglecting all the terms of the series but the two first, we obtain instead of (35) (if the equality $p'(r_c)=p''(r_c)=p(r_c)$ is taken into account and the factor of the cosine term brought before the sign of integration and its value at $r=r_c$ attributed to it):[35]

$$A_{v'v''l}=\frac{(p'(\infty)p''(\infty))^{\frac{1}{2}}}{Rp(r_c)}\int_{-\infty}^{+\infty}\cos\,(\alpha\pm\beta\xi^2)d\xi=\frac{(p'(\infty)p''(\infty))^{\frac{1}{2}}}{Rp(r_c)}\left(\frac{\pi}{|\beta|}\right)^{\frac{1}{2}}\cos\left(\alpha\pm\frac{\pi}{4}\right), \quad (36)$$

where

$$\alpha=\frac{1}{\hbar}\int_{r_0}^{r_c}(p'(r)-p''(r))dr+\delta'-\delta''$$

and

$$\beta=\frac{1}{2\hbar}\left[\frac{d}{dr}(p'(r)-p''(r))\right]_{r=r_c}=\frac{1}{2\hbar}\left[\frac{-\mu\dfrac{dV'(r)}{dr}}{\left[2\mu(E_{v'l}-V'(r))-\hbar^2\dfrac{l(l+1)}{r^2}\right]^{\frac{1}{2}}}-\frac{-\mu\dfrac{dV''(r)}{dr}}{\left[2\mu(E_{v''l}-V''(r))-\hbar^2\dfrac{l(l+1)}{r^2}\right]^{\frac{1}{2}}}\right]_{r=r_t}=-\frac{1}{2\hbar}\frac{\mu\left(\dfrac{dU(r)}{dr}\right)_{r=r_c}}{p(r_c)}, \quad (37)$$

with $U(r)=X=V'(r)-V''(r)$ (cf. Eq. (34)). (The restrictions of applicability of (37), mentioned in J.3, are groundless). Thus (34) becomes:

$$A_{v'v''l}=A_X=\frac{1}{R}\left(\frac{p'(\infty)p''(\infty)2\pi\hbar}{p(r_c)\mu|dU/dr|_{r=r_c}}\right)^{\frac{1}{2}}\cos\left(\alpha\pm\frac{\pi}{4}\right)=\frac{1}{R}\left(\frac{p'(\infty)p''(\infty)2\pi\hbar}{p(r_c)\mu|dX/dr|_{r=r_c}}\right)^{\frac{1}{2}}\cos\left(\alpha\pm\frac{\pi}{4}\right). \quad (38)$$

The limitations of applicability of this approximate formula will be discussed in paragraph IX.

VII. ASYMPTOTIC INTENSITY DISTRIBUTION DUE TO THE SINGLE ENCOUNTERS

We now proceed to calculate the $W^{(1)}(X)$. From (20a), (28), (31) and (38) we obtain for the case of an absorption line:

$$W^{(1)}(X)=\int_0^{l_1}\frac{3}{4}\frac{\hbar^2}{\mu E_{v''}R^2}(2l+1)\frac{\mu Rp'(\infty)p''(\infty)}{\pi\hbar p'(\infty)R^2p(r_c)}\frac{2\pi\hbar}{\mu|dX/dr|_{r=r_c}}\cos^2\left(\alpha\pm\frac{\pi}{4}\right)dl+\zeta(X,l_t)$$
$$=\frac{3}{4}\frac{\hbar^2}{\mu E_{v''}R^3|dX/dr|_{r=r_c}}\int_0^{l_1}\frac{(2l+1)2\cos^2\left(\alpha\pm\dfrac{\pi}{4}\right)}{\left(1-\dfrac{V''(r_c)}{E_{v''l}}-\hbar^2\dfrac{l(l+1)}{2\mu E_{v''l}r_c{}^2}\right)^{\frac{1}{2}}}dl+\zeta(X,l_t)$$
$$=\frac{3}{2}\frac{r_c{}^2\left(1-\dfrac{V''(r_c)}{E_{v''l}}\right)^{\frac{1}{2}}}{l_t(l_t+1)R^3|dX/dr|_{r=r_c}}\int_0^{l_1}\frac{(2l+1)2\cos^2\left(\alpha\pm\dfrac{\pi}{4}\right)}{\left(1-\dfrac{l(l+1)}{l_t(l_t+1)}\right)^{\frac{1}{2}}}dl+\zeta(X,l_t), \quad (39)$$

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[35] The treatment of $p'(r)$ and $p''(r)$ in the factor of the cosine term as constants equal $p(r_c)$, i.e., equal to their value in the most important region of integration, constitutes a crude approximation which must not be used if r_c does not lie sufficiently far away from the turning point r_t.

where l_t has to be found from

$$2\mu(E_{v''l}-V''(r_c))-\hbar^2\frac{l_t(l_t+1)}{r^2}=p''^2(r_c)=0;$$

thus $l=l_t$ is the value of l for which $r_c=r_t$, i.e., the classical turning point. For the upper limit of integration we have put a provisionally unspecified l_1. One could conjecture that the integration should be extended at least over all $l\leqq l_t$ corresponding to all collisions with impact parameters ρ smaller than r_c (i.e., smaller than the distance in which according to classical F.C.P. the transition actually takes place) thus neglecting the region of r outside the classical range of motion. Because of the failure of W.K.B. approximation in the region of $l=l_t$ it is safer to put $l_1<l_t$ as the upper limit of integration and add a correction term $\zeta(X,l_t)$ (depending on X and l_t) which order of magnitude we shall estimate very roughly later. The more accurate calculations involving eigenfunctions valid in the regions of turning points and outside the classical range of motion would be very tedious unless carried out by the aid of the differential analyzer.

A further simplification arises if cos $(\alpha\pm\pi/4)$ is a sufficiently rapidly oscillating function[36] of l. Apart from l, α depends on $E_{v'}$ and $E_{v''}$. In this case $\cos^2(\alpha\pm\pi/4)$ can be replaced by its average value $\langle\cos^2(\alpha\pm\pi/4)\rangle_{\text{Av}}=\frac{1}{2}$. Equation (39) becomes then:

$$W^{(1)}(X)=\frac{3}{2}\frac{r_c^2\left(1-\dfrac{V''(r_c)}{E_{v''}}\right)^{\frac{1}{2}}}{l_t(l_t+1)R^3|dX/dr|_{r=r_c}}\int_0^{l_1}\frac{2l+1}{\left[1-\dfrac{l(l+1)}{l_t(l_t+1)}\right]^{\frac{1}{2}}}dl+\zeta(X,l_t)$$

$$=\frac{3r^2}{R^3|dX/dr|_{r=r_c}}\left(1-\frac{V''(r_c)}{E_{v''}}\right)^{\frac{1}{2}}\left[1-\left(1-\frac{l_1(l_1+1)}{l_t(l_t+1)}\right)^{\frac{1}{2}}\right]+\zeta(X,l_t),\quad(40)$$

and correspondingly for the case of an emission line

$$W^{(1)}(X)=\frac{3r_c^2}{R^3|dX/dr|_{r=r_c}}\left(1-\frac{V'(r_c)}{E_{v'}}\right)^{\frac{1}{2}}\left[1-\left(1-\frac{l_1(l_1+1)}{l_t(l_t+1)}\right)^{\frac{1}{2}}\right]+\zeta(X,l_t).\quad(40a)$$

The asymptotic forms $W_A^{(1)}(X)$ of $W^{(1)}(X)$ are

$$W_A^{(1)}(X)=\frac{3r_c^2(1-V''(r_c)/E_{v''})^{\frac{1}{2}}}{R^3|dX/dr|_{r=r_c}}\text{ (absorption line),}\quad(41)$$

and

$$W_A^{(1)}(X)=\frac{3r_c^2(1-V'(r_c)/E_{v'})^{\frac{1}{2}}}{R^3|dX/dr|_{r=r_c}}\text{ (emission line).}\quad(41a)$$

Before we proceed to discuss (40) and (40a), we shall show that (41) and (41a) lead in the case of $V(r_c)/E_v\ll 1$ to Kuhn's intensity distribution derived from the classical form of F.C.P.

VIII. THE ASYMPTOTIC INTENSITY DISTRIBUTION

According to (34)

$$X=V'(r_c)-V''(r_c)=\hbar(\omega-\omega_0)=\hbar\Delta\omega,$$

where ω is the frequency resulting from the classical F.C.P. Hence, one can get immediately the asymptotic form of the intensity distribution. Since $\Delta\omega$ is a function of r_c, r_c can be represented as a function of $\Delta\omega$, say $r_c=f(\Delta\omega)$. Substituting $X=\hbar(\Delta\omega)$ and $r_c=f(\Delta\omega)$ in (41) or (41a), and $n=(4/3)\pi R^3N$, where N denotes the number of perturbers per 1 cm³, in (23), we obtain from (23) and (41) or (41a):

$$I_A(\omega)=\sum_i a_i4\pi Nf^2(\Delta\omega)\frac{\left(1-\dfrac{V''(r_c)}{E_{v''}}\right)^{\frac{1}{2}}}{|d\Delta\omega/dr_c|}$$

(absorption line) (42)

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[36] The necessary condition is, that $|X|=|E_{v'}-E_{v''}|$ is sufficiently large, or, in other words, the region of frequencies under consideration far enough from the center of the unperturbed line.

TABLE I. Values of l_t and κ corresponding to $r_c=3.3$ AU for Hg+A and Hg+He.

Perturber \ T	1000°K		300°K	
	l_t	κ	l_t	κ
A	158	2.7	86	2.3
He	25	1.5	14	1.2

and

$$I_A(\omega)=\sum_i a_i 4\pi N f^2(\Delta\omega)\frac{\left(1-\dfrac{V''(r_c)}{E_{v''}}\right)^{\frac{1}{2}}}{|d\Delta\omega/dr_c|}\quad\text{(emission line)}.\qquad(42\text{a})$$

$I_A(\omega)$ should be, strictly speaking, averaged over all E occurring in the gas under consideration, but since usually the factor in brackets constitutes a small correction only (at least in a certain range of frequencies), we shall put simply $E=\frac{3}{2}kT$. $I_A(\omega)$ depends on the temperature only through this factor and the dependence is usually only very slight. This dependence may, however, become much more prominent in the region of the line arising from transitions in the repulsive branches of potential curves and particularly at the points at which $V\approx E$. Apart from the above factor, (42) and (42a) are identical with the equation constituting the starting point of the statistical theories.

For the case of two single potential curves of the form

$$V'(r_c)=-C'/r_c^{\eta}\quad\text{and}\quad V''(r_c)=-C''/r_c^{\eta}\qquad(43)$$

we have

$$\Delta\omega=\frac{1}{\hbar}\frac{C'-C''}{r_c^{\eta}}=\frac{K}{r_c^{\eta}},\quad r_c=f(\Delta\omega)=\left(\frac{K}{\Delta\omega}\right)^{1/\eta}$$

and

$$V''(r_c)=\frac{C''}{K}\Delta\omega;$$

thus (42) becomes:

$$I_A(\omega)=\frac{4\pi NK^{3/\eta}}{\eta(\Delta\omega)^{(\eta+3)/\eta}}\left(1+\frac{2C''\Delta\omega}{3KkT}\right)^{\frac{1}{2}},\qquad(44)$$

which is identical with Kuhn's[37] distribution for $2c''\Delta\omega/3KkT\ll 1$.

Thus, the intensity distribution resulting from the primitive form of F.C.P. has found its justification on the basis of the quantum-mechanical theory.

IX. LIMITATIONS OF THE APPLICABILITY OF THE ASYMPTOTIC INTENSITY DISTRIBUTION

The main cause of inaccuracy of the asymptotic intensity distribution is the failure of the W.K.B. approximation in the region of the upper limit of the integration with respect to l in (40) and (40a). The condition of validity of the W.K.B. approximation is:

$$dp(r)/dr\ll p^2(r)/\hbar,\qquad(45)$$

or

$$\hbar^2\frac{l(l+1)}{r^3}-\mu\frac{dV}{dr}\ll\frac{1}{\hbar}\left[2\mu(E-V)-\hbar^2\frac{l(l+1)}{r^2}\right]^{\frac{3}{2}}.\qquad(46)$$

Let us consider the case

$$|\hbar^2 l(l+1)/r^3|\gg|\mu(dV/dr)|.$$

Instead of (46) we have then:

$$\hbar^2[l(l+1)]^{\frac{3}{2}}\ll 2\mu(E-V)r^2-\hbar^2 l(l+1).\qquad(47)$$

Obviously (47) can be satisfied only by $l<l_t$, since the right side vanishes for $l=l_t$ and the left side is always positive. Considering $r=r_c$ as fixed, let us develop the right side of (47) in series in the neighborhood of l_t. Putting $l_t-l=\Delta l$ and neglecting all the terms but the first two, we have

$$\hbar^2[l(l+1)]^{\frac{3}{2}}\ll(2l_t+1)\Delta l,\qquad(48)$$

since the first term of the series vanishes for $l=l_t$. Hence,

$$\Delta l\gg\frac{[l_t(l_t+1)]^{\frac{3}{2}}}{2l_t+1}=\kappa(l_t).\qquad(49)$$

Since (39)–(41a) are derived by use of W.K.B. approximation, the extension of integration involved there beyond the limit $l_1=l_t-\Delta l$ appears unjustified. Unfortunately, (49) gives no information how much larger Δl must be than $\kappa(l_t)$ in order to obtain the desired accuracy and how large is the error committed. Should we assume that $\Delta l=10\kappa(l_t)$ secures a sufficient margin of

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[37] The intensity distribution derived in J.3 (reference 1) differs from Kuhn's formula by a factor two; it constitutes, however, a worse approximation than the present one.

The second term in brackets is positive if the initial state corresponds to an attraction potential curve; otherwise it is negative.

safety, Δl would become 18 for $l_t=100$ and 11 for $l_t=10$. Table I is given to illustrate the conditions in the case of Hg.

Thus it is clear that the asymptotic distribution (42) cannot be applied to the cases of light perturbers (or radiators or both) such as H_2 or He (and still more in the case of electrons as perturbers). Its application to the heavy atoms still involves a considerable amount of uncertainty, which may be very roughly estimated.

Presumably, $W_A{}^{(1)}(X)$ is always larger than would be the true $W^{(1)}(X)$, since $W_A{}^{(1)}(X)$ is obtained by extension of the integration involved in (41) or (41a) up to the region of $l=l_t$, where the W.K.B. eigenfunctions and thus $A^2_{v'v''l}$ become infinite. This could never be the case if exact eigenfunctions, which must be finite everywhere, were used; moreover, obviously, the true value of $A^2_{v'v''l}$ can never exceed unity and for $X\neq 0$ must be actually $A^2_{v'v''l}\ll 1$. In order to get an idea, if not of the error itself involved in $I_A(\omega)$ but, at least, of the order of magnitude of the proportion of $I_A(\omega)$ which may be reasonably considered as uncertain we may proceed as follows. We assume that we can obtain the right order of magnitude of $\zeta(X, l_t)$ (cf. (40)) if we suppose that in the region $l_1\leqq l\leqq l_t$ the value of $A^2_{v'v''l}$ remains constant and equal to that at l_1. That is, l in the denominator of the integrand in (40) may have the value $l=l_1$ in this whole region. We now carry out the integration involved in the first term between the above limits (l_1, l_t) under this assumption. This procedure may lead to a value of $W_A{}^{(1)}(X)$ which is too small since the true $W^{(1)}(X)$ grows probably when l increases from l_1 to l_t. We thus obtain:

$$\zeta(X, l_t)=O\left[\tfrac{1}{2}W_A{}^{(1)}(X)\left(1-\frac{l_1(l_1+1)}{l_t(l_t+1)}\right)^{\frac{1}{2}}\right]. \tag{50}$$

Now

$$\frac{l_1(l_1+1)}{l_t(l_t+1)}=\frac{(l_t-\Delta l)(l_t-\Delta l+1)}{l_t(l_t+1)} \approx 1-\frac{(2l_t+1)\Delta l}{l_t(l_t+1)}. \tag{51}$$

Putting $\Delta l=b\kappa(l_t)$, where the factor $b>1$ may be chosen large enough to give a sufficient margin of safety, we obtain from (40), (49)–(51)

$$W^{(1)}(X)=W_A{}^{(1)}(X)\left[1-O\left(\frac{1}{2}\frac{b}{[l_t(l_t+1)]^{\frac{1}{2}}}\right)\right], \tag{52}$$

and thus

$$I(\omega)=I_A(\omega)\left[1-O\left(\frac{1}{2}\frac{b}{[l_t(l_t+1)]^{\frac{1}{2}}}\right)\right]. \quad (53$$

The term $b/2[l_t(l_t+1)]^{\frac{1}{2}}$ represents the presumed order of magnitude of the proportion of $I_A(\omega)$ which may be considered as uncertain. Its dependence on l_t is rather slight, and thus it does not influence considerably the *slope* of the intensity curve. It vanishes for $l_t\rightarrow\infty$, and thus the asymptotic distribution becomes equal to the true one for $l_t=\infty$; nevertheless, even for Hg+A at 1000°K (large l's) it reaches 0.4 for $r_c=3.3$A if value $b=10$ is assumed. Possibly our estimate is overpessimistic (as the experimental results seem to indicate), but until more exact calculations are carried out, there is no reason to be more optimistic. Certainly a still larger degree of uncertainty is involved in the results of all theories describing the nuclear movements classically.

The second source of error which may be discussed here is the approximate computation of integral (36). We therefore extended the limits of integration from $-\infty$ up to $+\infty$ (instead of O and R). This may be justified only in the case when the phase of $\cos(\alpha+\beta\xi)$ grows rapidly enough with ξ; in any case it is necessary that the phase should increase by at least π while ξ grows from 0 to r_c. Thus, the necessary condition for the applicability of the above procedure is that $|\beta r_c{}^2|>\pi$ or

$$r_c>\left(\frac{2\pi\hbar p(r_c)}{\mu|dX/dr|_{r=r_c}}\right)^{\frac{1}{2}}. \tag{54}$$

For $|X|=\hbar K/r^\eta$, this becomes

$$r_c<\left(\frac{\eta K\mu}{2\pi p(r_c)}\right)^{1/(\eta-1)}. \tag{55}$$

Expression (55) shows that our approximation ceases to be valid for large r_c, i.e., for the region of the center of the line. In the case of Hg+A and $T=1000$°K, (55) leads to the restriction of the asymptotic distribution to the frequencies corresponding to the transitions in $r_c<6.4\times 10^{-8}$ cm in agreement with experimental results of

Kuhn.[38] For Hg+H_2 at the same temperature $r_c < 2.1 \times 10^{-8}$ cm.

One could suppose that for very large r_c (large l's) the perturbation theory could be successfully applied[39] in order to obtain the intensity distribution of the central part of the broadened line, but, presumably, sufficiently accurate calculations by this method would be as tedious as those carried out by means of (20) and (21) or (20a) and (21a) and certainly less accurate.

The shift of the maximum of the intensity is not considered here. It would result from (14) for high densities of perturbers if calculations of particular cases involving the effect of multiple encounters were carried out. Apart from this, a shift may also be caused by the displacement of translational motion energy levels due to the perturbations of these levels by mutual potential energy of the radiator and the perturbers. The last effect, however, is not included in our approximation.

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[38] K., reference 10.

[39] J.2, reference 1.

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A Generalization of the Dielectric Ellipsoid Problem

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The classical problem of the dielectric ellipsoid involves the determination of the field within a homogeneous, isotropic, dielectric ellipsoid when it is placed in a uniform electric field. In the present generalization, both the ellipsoid and the medium in which it is placed, although still homogeneous, are anisotropic and also possess conductivities which are anisotropic. The principal axes of the ellipsoid, of the two dielectric tensors, and of the two conductivity tensors, may all be differently oriented. The external field, although uniform in space, varies sinusoidally with time. The condition specified in the last sentence is consistent with the electromagnetic field equations only in a region whose maximum dimension is small compared with $\lambda/2\pi$ where λ is the wave-length which corresponds to the frequency in question. Thus the solution given here is restricted by the condition that the maximum dimension of the ellipsoid must be small compared with $\lambda/2\pi$.

INTRODUCTION

In the application to practical problems of Wiener's general theory[1] of the electrical and optical properties of heterogeneous materials, the writer has found it desirable to have the solution of a generalization of the dielectric ellipsoid problem. The solution of this generalized problem is presented in this paper.

The classical problem of the dielectric ellipsoid[2] involves finding the field within a homogeneous, isotropic, dielectric ellipsoid when the ellipsoid is placed in a uniform electric field. In the present generalization, the ellipsoid is anisotropic and has a finite electric conductivity, and the medium in which it is imbedded is likewise anisotropic and conducting. Furthermore, the electric field, which is uniform except for the disturbance produced by the presence of the ellipsoid, varies sinusoidally with time. The conditions that the electric field be uniform in space and that it vary sinusoidally with time are evidently inconsistent with the electromagnetic field equations, but the conditions may be satisfied to any desired degree of approximation by making the dimensions of the ellipsoid sufficiently small compared with the wave-length which corresponds to the frequency in question. Accordingly, the solution obtained here holds only for the case in which the maximum dimension of the ellipsoid is small compared with c/ω where c is the velocity

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[1] Otto Wiener, Abhandl. d. Sächs. Ges. d. Wiss. **32**, 509–604 (1912).

[2] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 211–213.