From dispersion to commutation relations

(A short guide by P. Hraskó)

The Phenomenon of Dispersion

The basic feature is the light spectrum: the angle of refraction depends on the colour (Newton 1672), it increases from red toward violet (normal dispersion).

In terms of the colour-frequency correspondence one can say that normal dispersion consists in the (slow) increase of the refractive index n_Ω with frequency Ω.

Sometimes the refractive index decreases with frequency (anomalous dispersion, Le Roux 1862). In the neighborhood of spectral lines — i.e. at frequencies where light absorption takes place — always this is the case.

The Mathematical Form of the Dispersion Curve

The physical picture (Zeelmeyer 1871): The electric field, acting in a condensator or propagating in light, polarizes the charges of the neutral molecules of the medium. The dipole moment p of the molecule is equal to ex, where $\pm e$ are the charges at the poles and x is the distance between them. For small x the newtonian equation of motion of x is

$$\ddot{x} + 2\lambda\dot{x} + \omega^2 x = \frac{eE_\Omega}{m} \cdot e^{i\Omega t}, \tag{1}$$

where $\omega = \sqrt{\dfrac{k}{m}}$ is the (circular) frequency of the free oscillations and the term proportional to $\dot{x}$ describes dissipation. The expression on the r.h.s. is the force — divided by m — by which the electric field in the light wave acts on the charges.

In the general solution the forced oscillation is given by the expression (Landau-Lifschitz, Mechanics §§25,26)

$$\delta x = \delta x_\Omega \cdot e^{i\Omega t},$$

where

$$\begin{aligned} \delta x_\Omega &= \frac{e \cdot e^{i\delta_\Omega}}{m\sqrt{(\omega^2-\Omega^2)^2+4\lambda^2\Omega^2}} \cdot E_\Omega \\ \tan\delta_\Omega &= \frac{2\lambda\Omega}{\Omega^2-\omega^2}. \end{aligned} \tag{2}$$

The dipole moment is, therefore, equal to

$$p = \alpha_\Omega \cdot E_\Omega e^{i\Omega t},$$

where the polarizability α_Ω is given by the expression

$$\alpha_\Omega = \frac{e^2 \cdot e^{i\delta_\Omega}}{m\sqrt{(\omega^2-\Omega^2)^2+4\lambda^2\Omega^2}}. \tag{3}$$

When the dissipation is small which is the case for an isolated molecule the simpler expression

$$\alpha_\Omega = \frac{e^2}{m}\frac{1}{\omega^2-\Omega^2} \tag{4}$$

is valid except in the close vicinity of the resonance frequency ω.

The macroscopic Maxwell-equations contain dispersion properties of the medium in the form of the dielectric permittivity

$$\epsilon_\Omega = 1 + 4\pi N\alpha_\Omega, \tag{5}$$

where N is the density of the molecules. The dependence of the permittivity on Ω is determined by that of the polarizability and either of these functions may be taken for the dispersion curve. This curve gives excellent fit to the experiments if one allows for several kind of molecules with different resonance frequencies ω_i. In this case for $\Omega \not\approx \omega_j$ we have

$$\alpha_\Omega = \sum_j \frac{e_j^2}{m_j}\frac{w_j}{\omega_j^2-\Omega^2} \tag{6}$$

($w_j = N_j/N$ and N_j is the j-type molecules' density.)

The refractive index n_Ω which appears in the Descartes-Snellius law is equal to the square root of ϵ_Ω. In the neighborhood of the resonances ϵ_Ω is a complex number. In this case $n_\Omega = \sqrt{\Re\epsilon_\Omega}$.

Why just dispersion?

a) The place of the dispersion formula in the classical theory of electromagnetic phenomena:

The formula (6) describes correctly the dependence of the polarizability on the frequency Ω of the exciting light wave provided

i) the quantities ω_i are set equal to the experimentally observed resonance frequencies (spectral lines), and

ii) for each i an appropriate value for $N_i e_i^2/M_i$ is chosen.

These constants are the properties of the medium but, since we choose them empirically through best fit, the utilization of the dispersion formula does not presuppose knowledge of the molecular structure. It, however, rests heavily on the assumption that the shape (time dependence) of the field is intimately related to the motion of the charges, or — more precisely — *the spectrum of the emitted or absorbed light contains only those frequencies which appear in the Fourier-decomposition of* $p(t)$. We will call this fundamental postulate *Spectral Similarity Principle* (SSP) and note that its validity is abundantly proved by radio and television broadcasting. Mathematically SSP is introduced into the theory via the electric force between the charges and the field in the newtonian equations of motion of the charges which in the vicinity of each of the resonances reduce to the simple form of *1).

b) The role of the dispersion formula in the genesis of quantum mechanics:

The critical years are the middle 20-ths. By this time the validity of Bohr's quantum theory of the planetary hydrogen atom was already firmly established but it became also evident that the theory fails for any atom, containing more but one electron. Though Einstein's theory of the light quanta was already 20 years old, practically nobody accepted it. The basis for the rejection was the wavelike nature of the light which clearly manifested itself in the phenomenon of interference.

In retrospective one can discern two different routes by which people tried to clarify the situation:

1) Searching for new principles in calculating atomic spectra (i.e. the resonance frequencies in the dispersion formula). This approach led to the improvement of the Bohr quantization rules by Sommerfeld and Einstein, the prediction of the matter-waves by De Broglie and, finally, to the discovery of the Schroedinger-equation.

2) Reconciliation of the quantum theory of matter with the field theory of light. The point is that the Planck-rule

$$\hbar\omega = E_i - E_f, \tag{7}$$

by which the frequency of the emitted (or absorbed) light in the transition $i \longrightarrow f$ (or $f \longrightarrow i$) is to be calculated in the Bohr-model, sharply contradicts SSP (this will be shown later)[1]. Coppenhagen school felt that the *kinematical* problem of replacing SSP by a truly quantum interaction principle conceptually precedes the spectrum problem which is essentially of *dynamical* nature. The only field of physical knowledge which was both successful empirically and sensitive mainly just to this kinematical aspect was light dispersion. Since dispersion formula had been derived decades ago on the basis of SSP alone, without having the slightest idea about molecular structure, it seemed reasonable to hope that this same formula would be helpful again in giving just enough insight into the quantum form of SSP, prior to understanding molecular spectra.

This highly intuitive expectation was indeed realized in the matrix mechanics of Heisenberg. His basic paper of 1925 contained the formulation of the new principle, and its detailed mathematical form (the form of the basic commutation relations) was extracted from the dispersion formula. In this approach the hydrogen spectrum was calculated by Pauli only a year later.

On the contrary, the main result of Schroedinger's basic paper was the rederivation of the hydrogen-spectrum. However, the fact that quantum theory presupposed completely new kind of kinematics remained largely hidden in this theory since the formalism of the Schroedinger-equation strongly resembled that of continuum mechanics and mathematically the spectrum emerged like eigenfrequencies in the theory of e.g. membranes. This difference in approach survived in the protagonists' beliefs toward quantum physics throughout their whole lives and is still discernible in the different interpretations of quantum theory.

SSP is deeply rooted in intuition.

Waves of small intensity take their energy directly from their source and together with the energy they inevitably inherite the *profile* of the motion of

[1]The only exception is the radiation of a harmonic oscillator which was the only case considered by Planck in his theory of black body radiation (1900).

the source too — this is the essential content of SSP. Any particular process of wave generation may serve as an illustration: excitation of surface waves on water or sound generation by loudspeakers. The problem is that light emission of atoms violates this principle while emission of radio-waves by currents certainly obeys it.

Heisenberg's approach started from the recognition that intuition might validate SSP only in the macroscopic domain accessible to senses. Thinking of microphysics, one is justified to criticise the concepts, occurring in the formulation of the principle, including even the concept of the motion itself. Any concept may be called to be devoid of physical meaning if it never enters into relevant physical statements, i.e. if it never shows up in sensible equations of physical processes. In particular, to assume that in microphysics motion has no physical significance means that, instead of the function $x(t)$, occurring naturally in the newtonian equations of motion (see (1)), the true dynamical equations contain position in some other way.

Below we briefly recapitulate Heisenberg's reasoning. The starting point is Bohr-theory (1913) in the form given by Sommerfeld (1915) and Einstein (1917).

Bohr-theory

The theory is applicable only to the limited motion of conservative separable systems, for which the physical quantities (i.e. functions of the coordinates, momenta and — possibly — of time) depend quasi-periodically on time (see Landau-Lifschitz, Mechanics, §52):

$$a = \sum_k A_k(I) e^{i(k \cdot \omega)t}. \tag{8}$$

In this formula

$$a \equiv a(p,q) \quad q \equiv q_1, ...q_f \quad p \equiv p_1, ...p_f,$$

$$k \equiv k_1, ...k_f \qquad \text{integers},$$
$$k \cdot \omega = k_1\omega_1 + ... + k_f\omega_f.$$

The frequencies ω_r are given as partial derivatives of the Hamiltonian expressed in terms of the action-variables:

$$\omega_r = \frac{\partial H(I)}{\partial I_r}. \tag{9}$$

The action variables $I \equiv I_1, ...I_f$ which are constants of motion can be expressed as functions of the separation constants

$$\alpha \equiv \alpha_1, ...\alpha_f$$

through the integrals

$$I_r = \frac{1}{2\pi} \oint p_r(q_r, \alpha) dq_r. \tag{10}$$

The integration is taken along independent closed contours defined by the given set of the α-s (invariant torus).

The functional form of the coefficients $A_k(I)$ is determined by the type of the physical quantity $\mathcal{A}$, whose time dependence $a(t)$ is meant in (8) for given values of the constants of motion I.

In Bohr-theory the allowed motions are selected by the quantization of the action variables according to the rule

$$I_r = \hbar \left(n_r + \frac{\gamma_r}{4} \right) \qquad (r = 1, ...f), \tag{11}$$

in which the n_r-s are integers and γ_r is the Maslov-index which we will disregard[2]. Through (10), this condition establishes the possible values of the separation constants among which we always find the energy E of the system.

Quantum states are, therefore, characterized by the set

$$n \equiv n_1, ...n_f$$

of integers. In the process of light emission the system "jumps" from an initial state n into some final state n'. The frequency of the emitted light must be calculated by the Planck-formula

$$\omega_{nn'} = \frac{1}{\hbar}(E_n - E_{n'}). \tag{12}$$

This rule violates SSP, since the system's motion contains frequencies of the form $k \cdot \omega$, while $\omega_{nn'}$ in general cannot be expressed as linear combination of the ω_r-s with integer coefficients. In short, no relation of the type

$$k \cdot \omega = \omega_{nn'} \tag{13}$$

[2]This term was not known in the period we are considering.

is satisfied with integer k_r-s.

According to the Maxwell-theory, the electromagnetic wave generated by the system contains only frequencies $k \cdot \omega$, occurring in (8). The intensity emitted at $k \cdot \omega$ is given by the expression

$$\frac{4(k \cdot \omega)^2 e^2}{3c^3} \left| X_k(I) \right|^2, \tag{14}$$

in which c is the light velocity and $X_k(I)$ is the coefficient in the (8)-type expansion of the coordinate x which, as we have seen, is the parameter of the system, entering into the theory of dispersion. This formula, conforming to SSP, is the starting point of antenna calculations.

The Correspondence Principle

In the limit of low frequencies (the range of radio waves) the results of the true microscopic theory must coincide with those of the classical Maxwell-theory — this is the essential content of the Correspondence Principle (Bohr 1918) whose necessity is dictated by the success of classical physics in the macroscopic domain.

Bohr-theory obeys this principle. In particular, in this limit it satisfies SSP. To show this, we choose in (12) $n' = n - k$ and suppose that $k_r \ll n_r$. Then

$$\begin{aligned} E &\equiv H(I') \overset{(11)}{=} H(\hbar n') \approx H(\hbar n) - k \cdot \frac{\partial H(\hbar n)}{\partial n} \equiv \\ &\equiv E_n - k \cdot \frac{\partial H(\hbar n)}{\partial n}, \end{aligned} \tag{15}$$

hence

$$\omega_{nn'} = \frac{1}{\hbar}(E_n - E_{n'}) = k \cdot \frac{\partial H(\hbar n)}{\partial(\hbar n)} \overset{(11)}{=} k \cdot \frac{\partial H(I)}{\partial I} \overset{(9)}{=} k \cdot \omega. \tag{16}$$

In this limit, therefore, (13) is fulfilled with $k = (n - n')$ and SSP is indeed satisfied. In addition, the formula (14) for the intensity of the transitions $n \longrightarrow n'$ turned out to be empirically valid in the low frequency limit, as required by the Correspondence Principle.

The dispersion formula in the generale case

We now derive the generalized form of the classical dispersion formula which is valid for systems considered in the previous section (Kramers 1924). The hamiltonian function of the system put into the field of a monochromatic electromagnetic wave is given by the expression

$$\mathcal{H} = H - exE_\Omega e^{i\Omega t}, \tag{17}$$

where, as before, H is the hamiltonian function of the isolated system. We will work with action-angle variables I_r, w_r (Landau-Lifschitz, Mechanics, §52):

$$H \equiv H(I)$$

$$x = \sum_k X_k(I) e^{ik \cdot w} \qquad (X_{-k} = X_k^*)$$

$$k \cdot w \equiv k_1 w_1 + ...k_f w_f.$$

The quantity ex is the x-component of the dipole moment (it is best to think of a single particle of charge e and x as the component of its position.)

The canonical equations of motion are

$$\begin{aligned} \dot{I}_r &= -\frac{\partial H}{\partial w_r} = e\frac{\partial x}{\partial w_r} E_\Omega e^{i\Omega t} \\ \dot{w}_r &= +\frac{\partial H}{\partial I_r} = (9) = \omega_r - e\frac{\partial x}{\partial I_r} E_\Omega e^{i\Omega t}. \end{aligned}$$

To first order in E_Ω we have

$$\begin{aligned} \dot{I}_r &= ie\left(\sum_k k_r X_k e^{ik \cdot \omega t}\right) E_\Omega e^{i\Omega t} \\ \dot{w}_r &= \omega_r - e\left(\sum_k \frac{\partial X_k}{\partial I_r} e^{ik \cdot \omega t}\right) E_\Omega e^{i\Omega t}, \end{aligned}$$

whose solution, corresponding to (2), is given by the formulae

$$\begin{aligned}\delta I_r &= e\left(\sum_k \frac{k_r X_k e^{ik\cdot\omega t}}{k\cdot\omega+\Omega}\right) E_\Omega e^{i\Omega t} \\ \delta w_r &= ie\left(\sum_k \frac{\dfrac{\partial X_k}{\partial I_r} e^{ik\cdot\omega t}}{k\cdot\omega+\Omega}\right) E_\Omega e^{i\Omega t}.\end{aligned}$$

From these we obtain

$$\begin{aligned}\delta x_\Omega &= \frac{\partial x}{\partial I_r}\delta I_r + \frac{\partial x}{\partial w_r}\delta w_r = \\ &= e\sum_{k,k'} e^{[(k+k')\omega+\Omega]\,\cdot}\left(\frac{\delta X_k}{\delta I'}X_{k'} - \frac{\delta X_{k'}}{\delta I}X_k\right)\frac{1}{k'\cdot\omega+\Omega}E_\Omega, \qquad (18)\end{aligned}$$

where the notations

$$\frac{\delta}{\delta I} \equiv k_r\frac{\partial}{\partial I_r} \qquad \frac{\delta}{\delta I'} \equiv k'_r\frac{\partial}{\partial I_r}$$

have been introduced.

Dispersion is determined by those terms of the sum which are coherent with the exciting field ($k+k'=0$). From this part we extract the expression for the polarizability in that state of motion which is characterized by the action variables I:

$$\alpha_\Omega(I) = e^2\sum_k \frac{1}{k\cdot\omega-\Omega}\cdot\frac{\delta|X_k|^2}{\delta I} = 2e^2\sum_{k>0}\frac{(k\cdot\omega)}{(k\cdot\omega)^2-\Omega^2}\cdot\frac{\delta|X_k|^2}{\delta I}. \qquad (19)$$

In the last sum the condition $k>0$ means $\omega\cdot k>0$.

For the special case of the harmonic oscillator (without damping) we have

$$X_k = X_{-k} = \sqrt{\frac{I}{2m\omega}}\cdot\delta_{1k}.$$

In this case no incoherent terms occur and we arrive at (4) again.

The physical quantities as matrices

Let us denote the "name" of the physical quantity to which (8) refers by $\mathcal{A}$. On the l.h.s. of (8) $a(t)$ is the time dependence of $\mathcal{A}$ — this is the representation of $\mathcal{A}$ which, according to Heisenberg, must be purged out of the theory. Instead, the coefficients $A_k(I)$ are those which do have physical meaning. The $X_k(I)$-s, for example — the coefficients of the quantity $\mathcal{X}$ whose name is "the component of the position in the x direction" —, enter into (14) which is a correct formula at least in the domain of the Correspondence Principle. In his fundamental paper of 1925 Heisenberg postulated the universal validity of (14) but assumed that, outside the domain of the Correspondence Principle, it leads to predictions numerically different from those of the Bohr theory, because the coefficients $X_k(I)$ are to be calculated in a radically new manner.

The new dynamical equations Heisenberg had in mind were to satisfy the following two basic requirements:

a) They had to contain the coefficients $A_k(I)$ of the physical quantities $\mathcal{A}$ in such a form that they never combine into the sum $a(t)$. This requirement served to make SSP devoid of physical meaning, by discrediting the concept of the motion as incorporated in the quantity $a(t)$.

b) Their structure had to be "maximally similar" to the structure of the equations of classical physics in the hope to meet the requirements of the Correspondence Principle.

Symbolically, Heisenberg proposed to replace the identification

$$\mathcal{A} \Longleftrightarrow a(t)$$

by the new correspondence

$$\mathcal{A} \Longleftrightarrow \left\{ A_k(I) e^{i(k \cdot \omega)t} \right\}. \tag{20}$$

The set k consists of integers but the elements of the set I in classical physics may be any numbers. However, in Bohr-theory $I = \hbar n$, the set of integers n being the label of some allowed quantum state. As we have seen, in the domain of the correspondence principle the set $n' = n - k$ refers also to a quantum state, that with $I' = \hbar n'$. So, for a given n, k and n' are equivalent labels and, using (16), we can put (20) into a more symmetric form in which both sets of indices refer to some quantum state:

$$\mathcal{A} \Longleftrightarrow \{A_{nn'}(t)\} \equiv \left\{ A_{nn'} \cdot e^{i\omega_{nn'}t} \right\}. \tag{21}$$

This step which at first seems merely a notational improvement turned out to be crucial — it allowed to map the algebra of physical quantities into that of matrices.

Take another physical quantity

$$\mathcal{B} \Longleftrightarrow \{B_{nn'}(t)\} \equiv \left\{B_{nn'} \cdot e^{i\omega_{nn'}t}\right\}.$$

The representative of the the product of $\mathcal{A}$ and $\mathcal{B}$ is the coefficient $C_{nn'}(t)$ in the (8)-type expansion of $a(t) \cdot b(t)$. This calculation does not lead authomatically to a coefficient of the form of (21), but Heisenberg pointed out that only a minor modification of it is needed to ensure this form:

$$C_{nn'}(t) = \sum_m A_{nm}(t) \cdot B_{mn'}(t) = \left(\sum_m A_{nm}B_{mn'}\right) e^{i\omega_{nn'}t},$$

which is the matrix multiplication rule (which Heisenberg was actually not aware of).

Notice that conserved quantities, for which (8) reduces to the single term $k = 0$, are represented by time independent diagonal matrices. In particular[3]

$$\mathcal{H} \Longleftrightarrow \{H_{nn'} = E_n\delta_{nn'}\}.$$

So we arrived at the representation

$$\mathcal{A} \Longleftrightarrow \hat{A}(t)$$

of the physical quantities by matrices which are in general time dependent[4]. The form (21) together with the property $\omega_{nn'} = -\omega_{n'n}$ suggest that they are hermitean ($A^*_{nm} = A_{mn}$), but this was not made explicite in Heisenberg's paper. In order to prove that this is the *true* representation of the physical entities one has to show that the empirically correct dynamical equations are matrix equations. Both this demand and requirement b) above may be satisfied if the new equations have the structure of the hamiltonian equations of the classical mechanics with the Poisson bracket $\{,\}$ replaced by $(i\hbar)^{-1}$-times commutator $[,]$ and the representatives $a(q,p)$ of the physical quantities

[3]Today this particular form of the matrix-mechanics is called energy-representation.

[4]This so-called Heisenberg-picture is unitarily equivalent to the Schroedinger-picture in which the matrices of the physical quantities are independent of time.

by matrices $\hat{A} = a(\hat{Q}, \hat{P})$. Hence, for the fundamental commutation relations we have

$$\Big[\hat{Q}_r,\ \hat{Q}_s\Big] = \Big[\hat{P}_r,\ \hat{P}_s\Big] = 0$$
$$\Big[\hat{Q}_r,\ \hat{P}_s\Big] = i\hbar\hat{1} \tag{22}$$

where $\hat{1}$ is the unit matrix. In the remaining sections we discuss the role dispersion formula played in the discovery of (22).

The dispersion formula in the Bohr-theory

We delayed the transcription of (19) into Bohr theory up to this section because it looks simpler in Heisenberg's symmetric notation which is the only form we need it. This transcription actually preceded Heisenberg's paper discussed above (Heisenberg-Kramers 1925).

The problem consists in transcription of the derivative $\dfrac{\delta|X_k(I)|^2}{\delta I}$. In the discussion of the Correspondence Principle we used for $H(I)$ the rule

$$\frac{\delta H(I)}{\delta I} \longrightarrow \frac{1}{\hbar}\Big[H\big(\hbar n\big) - H\big(\hbar(n-k)\big)\Big],$$

i.e. the differential change was replaced by a difference.

We apply the same recipe to

$$\frac{\delta|X_k|^2}{\delta I} = k\frac{\partial(X_{-k}\cdot X_k)}{\partial I} = X_{-k}\left(k\frac{\partial X_k}{\partial I}\right) + X_k\left(k\frac{\partial X_{-k}}{\partial I}\right)$$

in which

$$k\frac{\partial X_k(I)}{\partial I} \longrightarrow \frac{1}{\hbar}\Big[X_k\big(\hbar(n+k)\big) - X_k\big(\hbar n\big)\Big]$$
$$k\frac{\partial X_{-k}(I)}{\partial I} \longrightarrow \frac{1}{\hbar}\Big[X_{-k}\big(\hbar n\big) - X_k\big(\hbar(n-k)\big)\Big].$$

This special symmetric choice of arguments is justified by the simplicity of the final formula:

$$\frac{\delta|X_k|^2}{\delta I} = \frac{1}{\hbar}\Big[X_{-k}\big(\hbar n\big)X_k\big(\hbar(n+k)\big) - X_k\big(\hbar n\big)X_{-k}\big(\hbar(n+k)\big)\Big].$$

In matrix notation this same formula is

$$\begin{aligned}\frac{\delta|X_k|^2}{\delta I} &= \frac{1}{\hbar}\Big[X_{n,n+k}X_{n+k,n} - X_{n,n-k}X_{n-k,n}\Big] = \\ &= \frac{1}{\hbar}\Big[|X_{n,n+k}|^2 - |X_{n,n-k}|^2\Big].\end{aligned}$$

At the same time we have

$$k\cdot\omega = \frac{\delta H(I)}{\delta I} \longrightarrow \pm\frac{E_n - E_{n\mp k}}{\hbar} = \pm\omega_{n,n\mp k},$$

and for the polarizability we obtain

$$\alpha_\Omega(n) = \frac{2e^2}{\hbar}\sum_{k>0}\left(\frac{\omega_{n+k,n}|X_{n,n+k}|^2}{(\omega_{n+k,n})^2 - \Omega^2} - \frac{\omega_{n,n-k}|X_{n,n-k}|^2}{(\omega_{n,n-k})^2 - \Omega^2}\right). \tag{23}$$

Now $k>0$ means $\omega_{n+k,n}>0$ and it is assumed that if k is positive then $-k$, if allowed,[5] is negative.

In order to simplify this formula we first introduce the symmetric positive quantities

$$f_{lm} = \frac{2m}{\hbar}|\omega_{lm}|\cdot|X_{lm}|^2 \tag{24}$$

called *oscillator strenghts*. In addition, we change n to i (initial) and the summation over k we replace by $j = n+k$ in the first term and $j' = n-k$ in the second. We obtain

$$\alpha_\Omega(n) = \frac{e^2}{\hbar}\left(\sum_j \frac{f_{ji}}{\omega_{ji}^2 - \Omega^2} - \sum_{j'}\frac{f_{j'i}}{\omega_{j'i}^2 - \Omega^2}\right). \tag{25}$$

The sum in the first (second) term extends over those states whose energy E_j ($E_{j'}$) is larger (smaller) then E_i.

Though (25) refers to a single molecule its form is that of (6) rather than (4) — at least for the ground state $i=g$ when the second term is absent. In the framework of the Bohr-theory it was thought that it describes the response of a set of oscillators with frequencies $|\omega_{jg}|$ excited with probabilities

[5] That is, if $n-k$ is a label of some quantum state.

f_{jg} (this interpretation explains the name of the f-s). This picture is to some extent corroborated by the TRK (Thomas-Reiche-Kuhn) sum rule

$$\sum_j f_{ji} - \sum_{j'} f_{j'i} = 1 \tag{26}$$

proved within Bohr-theory which for $i = g$ reduces to $\sum_j f_{jg} = 1$.

The physical significance of the TRK sum rule is best seen in the limit when the frequency Ω of the field of excitation is much larger than any of the frequencies ω_{gj} or, in other words, the binding of the charges within molecules is negligible as compared to the photon energy $\hbar\Omega$. In that case α_Ω must reduce to the polarizability of the free charge e

$$\alpha_\Omega(e) = -\frac{e^2}{m\Omega^2}, \tag{27}$$

which, owing to the TRK sum rule, is indeed the case.

Connection with the commutation relation

Let us first reconsider the simple case of the harmonic oscillator in the hamiltonian form. The hamiltonian is given by (17) specified to the oscillator:

$$\mathcal{H} = \frac{1}{2m}(p^2 + m^2\omega^2 x^2) - exE_\Omega e^{i\Omega t} = H - exE_\Omega e^{i\Omega t}.$$

According to hamiltonian mechanics we have

$$\ddot{x} = \big\{\{x, \mathcal{H}\}, \mathcal{H}\big\},$$

where $\{,\}$ is the Poisson-bracket. Linear approximation in E_Ω gives

$$\ddot{x} = \big\{\{x, H\}, H\big\} - \big\{\{x, H\}, x\big\}eE_\Omega e^{i\Omega t}.$$

The first term on the r.h.s. is equal to $-\omega^2 x$, hence

$$\ddot{x} + \omega^2 x = \big\{x, \{x, H\}\big\}eE_\Omega e^{i\Omega t}.$$

For the forced oscillation we obtain

$$\delta x_\Omega = \frac{\big\{x, \{x, H\}\big\} \cdot e}{\omega^2 - \Omega^2} E_\Omega e^{i\Omega t},$$

and for the polarizability we have

$$\alpha_\Omega = \frac{e^2}{m}\frac{f}{\omega^2 - \Omega^2} \tag{28}$$

where

$$f = m\big\{x, \{x, H\}\big\}.$$

The expression (28) must coincide with (4), i.e. the "TRK sum rule" $f = 1$ must be satisfied. This requirement determines the value of the fundamental PB:

$$m\big\{x, \{x, H\}\big\} = \frac{1}{2}\big\{x, \{x, p^2\}\big\} = \{x, p\} = 1.$$

Turning now to the formula (25), we note that

i) its form is again empirically true for the experimentally important case $i = g$,

ii) it contains the coefficients $X_k(I)$ only and though derived in the correspondence limit its validity, like that of (14), may also be postulated in the new theory and, finally

iii) the TRK sum rule, owing to its clear physical meaning, must also be retained.

These expectations are strongly supported by the fact that (25), taken as a valid formula in matrix mechanics, naturally leads to an interrelation between the value of the TRK sum and that of the fundamental commutator, structurally very similar to the connection between f and $\{x, p\}$ in the classical theory. In order to see this we perform a series of transformations of the l.h.s. of (26) in which the fundamental commutator (22) will be exploited:

$$\begin{aligned}
\sum_j f_{ji} \;-\; \sum_{j'} f_{j'i} &\overset{(24)}{=} \frac{2m}{\hbar}\Big(\sum_j \omega_{ji}|X_{ji}|^2 + \sum_{j'} \omega_{j'i}|X_{j'i}|^2\Big) = \\
&= \frac{2m}{\hbar}\sum_n \omega_{ni}|X_{ni}|^2 = \frac{2m}{\hbar^2}\sum_n (E_n - E_i)X_{in}X_{ni} = \\
&= -\frac{m}{\hbar^2}\sum_n \big(X_{in}(X_{ni}E_i - E_nX_{ni}) - (X_{in}E_n - E_iX_{in})X_{ni}\big) = \\
&= -\frac{m}{\hbar^2}\big[\hat{X}, [\hat{X}, \hat{H}]\big]_{ii} = -\frac{1}{2\hbar^2}\big[\hat{X}, [\hat{X}, \hat{P}^2]\big]_{ii} = \\
&= -\frac{(i\hbar)}{\hbar^2}[\hat{X}, \hat{P}]_{ii} = -\frac{(i\hbar)^2}{\hbar^2}\hat{1}_{ii} = 1
\end{aligned}$$

(we assumed that $\hat{H}$ contains momentum only in the kinetic energy term).

The lines above show the role dispersion formula played in the specification of the form of the fundamental commutation relation. This important technical result, however, need not hide the fact that they are based on the deep analysis of the ambiguities, which may arise in the representation of fundamental physical concepts in the mathematical framework of theoretical physics.