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Effective Size in Quantum-mechanical Systems

D.A.Bochvar, I.V.Stankevich, and A.L.Chistyakov

The review presents the results of a number of studies where various integral characteristics of the effective dimensions of quantum-mechanical systems have been derived and justified by interpreting the square of the modulus of the wave function using probability theory. The concepts of the types of electron delocalisation in atoms and molecules and quantities which can serve at its measure as well as hypotheses concerning the integral characteristics of the charge distribution between the effective volume of an atomic-molecular system and the surrounding space are discussed.
The above characteristics have been calculated for a number of specific quantum-mechanical systems, in particular for some of the simplest atoms and molecules.
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I. INTRODUCTION

This paper presents the result of a number of studies in which various integral characteristics of the effective dimensions of quantum-mechanical systems were derived and their validity was proved. These concepts are related primarily to hypotheses concerning the types and quantities used as measures of electron delocalisation in atoms and molecules and integral characteristics of charge distribution between the effective volume of an atomic-molecular system and the surrounding space.

One of the significant changes introduced by quantum mechanics into the description of an atomic-molecular system was the elimination of the classical concept of an atom or molecule having a specific volume. The square of the modulus of a normalised wave function of an n-particle system is interpreted as the probability density of a $3n$-dimensional continuous random quantity. The electrons of atoms and molecules can be located with a finite non-zero probability in any volume element in a three-dimensional space. For this reason, the pre-quantum-mechanical concept of a definite volume is no longer applicable to an atom or molecule.

Nevertheless the concept of quantities characterising the "effective" dimensions or "effective" volumes of quantum-mechanical systems retains its physical significance and usefulness. As a rule, the methods adopted for the determination of quantities of this kind are related to specific methods for the experimental investigation of the structure of matter.

At the same time it is also possible to justify theoretically the concept of the effective dimensions of an atomic-molecular system. The definition of such concepts uses the generally accepted interpretation of the square of the modulus of the wave function on the basis of probability theory as the probability density of the configuration of the system. In order to characterise completely the distribution, it is generally speaking necessary to know the entire infinite series of its moments. The definition of the concept of the effective dimensions of an atomic-molecular system employs only some of the integral characteristics of the distributions. We shall consider briefly the most important of these characteristics.

Suppose that the state of an n-electron system is described by a normalised function $\psi(\mathbf{x})$, where $\mathbf{x} = (\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n)$ denotes a set of cartesian coordinates of n electrons and $\mathbf{x}_i = (x_{i1}, x_{i2}, x_{i3})$ denotes the coordinates of the ith particle. We put

$$\rho(\mathbf{x}) = |\psi(\mathbf{x})|^2$$

$\rho(\mathbf{x})$ can then be treated as the density of the distribution of a $3n$-dimensional random vector $\mathbf{X} = (\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n)$. whose components $\mathbf{X}_i = (X_{i1}, X_{i2}, X_{i3})$ are three-dimensional random quantities with the distribution densities

$$\rho_i(\mathbf{x}_i) = \int \rho(\mathbf{x})\, d\mathbf{x}_1 \ldots d\mathbf{x}_{i-1}\, d\mathbf{x}_{i+1} \ldots d\mathbf{x}_n.$$

Each of the densities $\rho_i(\mathbf{x}_i)$ describes the distribution of the coordinates of the individual ith particle with all other particles in their average positions. We shall denote by $K(\mathbf{X})$ the covariance matrix of the n-particle system:

$$K(\mathbf{X}) = \begin{pmatrix} \mathcal{K}_{11}\mathcal{K}_{12} \ldots \mathcal{K}_{1n} \\ \mathcal{K}_{21}\mathcal{K}_{22} \ldots \mathcal{K}_{2n} \\ \ldots\ldots\ldots \\ \mathcal{K}_{n1}\mathcal{K}_{n2} \ldots \mathcal{K}_{nn} \end{pmatrix},$$

where $\mathbf{K}_{ij}$ is the covariance matrix of the ith and jth particles (see Section III, 5).

The quantity $D(\mathbf{X}) = \det K(\mathbf{X})$ is termed the general variance of the n-electron system. In model problems where the theoretical probability characteristics of a one-dimensional particle are investigated, this quantity is

identical with the variance of a one-dimensional distribution generated by the corresponding wave function. The quantity

$$H(\mathbf{X}) = -\int \rho(\mathbf{x}) \ln \rho(\mathbf{x})\, d\mathbf{x}$$

is termed the entropy of the quantum-mechanical distribution with a density $\rho(\mathbf{x})$ for an n-particle system†. We put $v = \exp H$ and $V = \sqrt{(2\pi e)^{3n} D}$. These quantities are termed respectively the internal and external effective volumes of the n-particle system.

The entropy and external and internal volumes for the distribution of the ith particle or a subsystem of particles with all other particles in their average positions can be defined similarly.

The introduction of general variances makes it possible to extend the concept of the correlation coefficient (describing the relation between two one-dimensional random quantities) to cases where the correlation of particles (i.e. of multidimensional random quantities) is investigated. Namely, if $D(\mathbf{X}_i)$ is the general variance of the ith particle and $D(\mathbf{X}_i, \mathbf{X}_j)$ the general variance of a system of two particles (the ith and jth particles) in an n-particle system, the general correlation coefficient $r(\mathbf{X}_i, \mathbf{X}_j)$ (or the correlation coefficient of two particles) is given by the formula (see Section III, 5)

$$r(\mathbf{X}_i, \mathbf{X}_j) = \sqrt{1 - D(\mathbf{X}_i, \mathbf{X}_j)/D(\mathbf{X}_i)\, D(\mathbf{X}_j)}.$$

Like the usual correlation coefficient, the above coefficient represents a measure of linear correlation. Similarly, the internal correlation coefficient $r_i(\mathbf{X}_i, \mathbf{X}_j)$, introduced in Section III, 6 and defined in terms of the internal volume, also takes into account non-linear correlation.

The entropy and variance reflect, generally speaking, different features of the distribution, significantly supplementing one another. The usefulness of the entropy of a quantum-mechanical distribution together with the variance for the characterisation of the effective size is confirmed by the close relation between this quantity and Heisenberg's uncertainty principle. This principle, together with its variance expression, also permits a formulation in terms of the entropy of distributions. The entropy expression, which is logically stronger and physically more significant, makes it possible to exclude the occurrence of certain situations which are not ruled out by the variance formulation (see Section III, 8).

The formulation of the uncertainty principle is not restricted to a pair of canonically coupled one-dimensional particles such, as, for example, the components of the vector-coordinate $\mathbf{r}_i$ and the corresponding components of the momentum-vector $\mathbf{p}_i$. The uncertainty in the position of a particle or a system of particles can be described not only by one-dimensional characteristics (variances along the coordinate axes), but also by the available volume characteristics such as the covariance matrix, the general variances, and the internal and external volumes. As shown in Section III, 8, the uncertainty principle can be expressed also in terms of all the above volume characteristics. This formulation of the uncertainty principle is stronger than the corresponding one-dimensional formulations.

The calculations of the effective volumes for the simplest atoms and molecules show that these quantities are fairly close to the values found from experimental studies on the viscosities of gases and vapours, which also demonstrates the usefulness of the theoretical definitions of the effective volumes of quantum-mechanical systems.

The variance of the distribution has been used for a long time in quantum mechanics to characterise the uncertainty of the position of the particles. However, the usefulness of the concept of entropy in quantum mechanics was considered for the first time in 1960 by Segal[1]. Hirschman[2] showed that Heisenberg's uncertainty principle can be formulated in terms of the entropies of quantum-mechanical distributions in the coordinate and momentum representations.

Bochvar, Gambaryan, Stankevich, and Chistyakov[3-5] used the concept of the entropy of the distribution to characterise the measures of the delocalisation of electrons and the effective size in atomic-molecular systems.

In a study of studies by Rubanov, Stepanov, and Sedoi[6-9] certain general properties of the entropy functional were investigated and the entropies of the distributions, associated with the wave functions of the simplest quantum-mechanical systems were found.

We shall now consider briefly the contents of this review. Section II deals with the available results of the calculations of the effective volumes of the simplest atomic-molecular systems. The reader interested only in the application of the above concepts of internal and external volumes to specific systems need peruse only this part of the article.

Section III presents a detailed analysis of the concepts of entropy and general variance for the case of many particles. The entropy formulation of the uncertainty principle is discussed in Subsection 8 of Section III.

II. EFFECTIVE DIMENSIONS OF SIMPLEST ATOMIC AND MOLECULAR SYSTEMS

The effective theoretical dimensions of quantum-mechanical systems are interesting from different points of view. One of the significant aspects of the formation of a chemical bond is the redistribution of electron density in the vicinity of atomic nuclei. This redistribution is accompanied by a change in the effective dimensions of the system, its effective internal and external volumes, and the associated change in the normality coefficient N‡.

It is important to have a correct idea concerning the charge distribution in the electron shells of the atoms and molecules between the inner part of the atom or a molecule included in the effective volume and the infinite space external to such volume.

It is interesting to compare the effective theoretical dimensions of atoms and molecules with their effective dimensions determined by the application of various experimental research techniques.

However, one should bear in mind that the entropy H and the general variance D of the distribution are sensitive to the type of wave function employed in the calculation. Therefore serious limitations in the choice of data for the calculations are inevitable. Only fairly accurate wave functions, a further refinement of which no longer has a significant influence on the calculated entropy H and general variance D of the distribution, are suitable for

†We emphasise that this concept must not be confused with the concept of entropy in thermodynamics, as is done, for example, in the book "Dialektika Razvitiya Khimii" (Dialectics of the Development of Chemistry) by V. I. Kuznetsov, Izd. Nauka, Moscow, 1973, pp. 198–199.

‡For a definition of the normality coefficient N, see Section III, 1.

the calculation of the effective dimensions of quantum-mechanical systems.

In this Section the concepts of the entropy and variance refer to the three-dimensional electron density. The information contained in the effective atomic and molecular dimensions, which is of interest primarily from the quantum-chemical point of view, is presented and discussed below. Table 1 gives the results of the calculation of the effective volumes in the ground states of one-electron systems (the H atom, the He^+ ion, and the H_2^+ molecular ion) and the ground states of two-electron systems (the H^- ion, He, Li^+, and H_2). Table 1 also includes the values of v for the H(2s) atom.

Table 1. Effective volumes of the simplest quantum-mechanical systems[a].

System[b]	References	$v\ (a_0^3)$	$V\ (a_0^3)$	N	$r\ (X_1, X_2)$
H (1s)		63.1	70.59	0.894	—
H (2s)		3330.7	3697.6	0.901	—
He^+		7.89	8.82	0.895	—
H_2^+	10	45.15	—	—	—
H^-	11	300.60	443.45	0.678	0.1201
He	11	14.89	17.50	0.851	0.0947
He	12, 13	—	17.71	—	0.0939
He	14	14.88	17.77	0.837	0.0867
Li^+	11	3.50	4.03	0.869	0.0672
H_2	15	50.91	—	—	—
H_2	16	—	54.38	0.936[c]	0.1860

[a] A number of the calculations were made by S. S. Abdullaev.
[b] In the calculation of the effective volumes different approximate wave functions were employed. References are given to studies in which these wave functions were found. Where there are no references, the calculation was made using the exact wave functions. The characteristics of all the systems, with the exception of the H atom, are quoted only for the ground states.
[c] The normality coefficient was found using the internal volume calculated from James and Coolidge's function [15].

The data in Table 1 permit a number of conclusions.

1. For two-electrons spherically symmetrical neutral or positively charged systems, the difference between the external and internal effective radii (R_{ext} and R_{int} respectively) is insignificant. For He and Li^+, $R_{ext}/R_{int} \simeq \simeq 1.05$. With a negative charge, this ratio must of course be somewhat greater than for the corresponding neutral or positively charged systems. Thus $R_{ext}/R_{int} \simeq 1.14$ for H^-. For the hydrogen molecule, the ratio of the average lengths of the effective half-axes of the ellipsoids bounding v is $R_{ext}/R_{int} \simeq 1.02$.

2. For one-centre systems, the addition of a second electron to a one-electron system gives rise to a marked increase of the effective volume v, which also depends on the nuclear charge.

Comparison of H_2^+ and H_2 in the ground states also leads to the conclusion that v increases, although to a smaller extent than for one-centre systems. In this more complex case an effect involving the contraction of the internuclear distance obtains, which partly cancels the increase of v due to electron-electron repulsion.

3. In one-centre two-electron systems an increase of nuclear charge causes a marked decrease of v and V, as can be seen in the series of H^-, He and Li^+ in their ground states. The coefficient N increases—the distribution approaches significantly the normal distribution.

4. The formation of an H_2 molecule from two H atoms entails an appreciable decrease of v compared with the value for the 1s state of the H atom, namely by $11.89a_0^3$.

The fact that $v = 50.91a_0^3$, calculated by Bochvar et al. [17] using the James–Coolidge function [15], is much smaller than the value derived from the wave function of the simple MO-LCAO method [4] ($79.84a_0^3$) merits attention. Table 1 shows that the latter actually exceeds the value of v for the 1s state of the H atom. Hence it follows that the wave functions of the LCAO method in all its versions employing rigid atomic orbitals are unsuitable for a quantitative description of the properties of the electron density distribution in molecules.

5. $v = 45.15a_0^3$ for the ground state of H_2^+, i.e. is smaller by $5.76a_0^3$ than v for the ground state of the H_2 molecule. The overall positive charge and the absence of electron-electron repulsion surpass the effect of the increase in the internuclear distance R due to the weakening of the bond.

6. Comparison of the H_2 and He two-electron systems shows that, whereas v for the He atom in the ground state decreases almost by a factor of two on single ionisation (from $14.88a_0^3$ to $7.89a_0^3$, i.e. by a factor of 1.87), on removal of one electron from the H_2 molecule in the ground state with conversion into H_2^+ also in the ground state v decreases only by $5.7a_0^3$.

The explanation of this fact is that, in the vertical ionisation of H_2, v is reduced by $18.12a_0^3$, i.e. to $32.79a_0^3$ (by a factor of 1.55), but this contraction is partly compensated by the increase of R from $1.4a_0$ to $2a_0$, which leads to an increase of v from $32.79a_0^3$ by $12.36a_0^3$, i.e. to $45.15a_0^3$.

7. The correlation coefficients $r(X_1, X_2)$ for electrons in two-electron systems listed in the last column of Table 1 make it possible to infer the correlation of electrons from the standpoint of probability theory. We note in the first place that, in contrast to the correlation energy, the correlation coefficient of electrons is estimated for any approximate function (poor or satisfactory) without resorting to experimental data or the exact wave function. As the exact wave function is approached, the correlation coefficients should tend to a limit. Calculations show that the values of $r(X_1, X_2)$ for all three fairly satisfactory wave functions of the helium atom yield, to within 0.01, the same value $r(X_1, X_2) = 0.09$. It is noteworthy that (in the present authors' view) the internal correlation coefficient $r_H(X_1, X_2)$ defined by Eqn. (6, 1) allows more completely for the correlation of electrons. According to this hypothesis, $r_H(X_1, X_2)$ calculated from the Hylleraas function [14] is 0.20, which greatly exceeds $r(X_1, X_2) = 0.09$.

Proceeding now to a comparison of the correlations in different systems, we note that in many isoelectronic systems (H^-, He, Li^+) $r(X_1, X_2)$ decreases with increase of the nuclear charge. Its values are respectively 0.12, 0.09, and 0.07. The correlation coefficient of the electrons in the H_2 molecule is 0.186 and is largely determined by the correlations of the z components (directed along the lines of the bond) of both electrons: $|r(z_1, z_2)| = 0.156$.

In many systems the negative charges in regions within and outside the effective volume v were calculated from the data in Table 1. [18] The surfaces bounding the effective volumes v for one-centre systems were naturally regarded as spherical, while for the two-centre systems H_2^+ and H_2 they were assumed to be ellipsoids of rotation with the foci located at the atomic nuclei. The calculation reduced to the integration of the three-dimensional probability

density (corresponding to the three-dimensional charge density) over the corresponding regions. The calculated charges Z_{int} within the effective volumes v and the charges Z_{ext} outside the effective volumes are listed in Table 2. For the two-electron systems He and H_2, Table 2 also includes the unit probabilities defined as the probability sums

$$1 = P^{(2,0)} + P^{(1,1)} + P^{(0,2)}, \qquad (*)$$

where $P^{(2,0)}$ is the probability of finding both electrons within the volume v, $P^{(1,1)}$ the probability of finding one electron in the volume v and the other electron outside this volume, and $P^{(0,2)}$ the probability of finding both electrons outside the volume v. When calculating the charges within and outside the volume v, Eqn. (*) must be multiplied by two and account must be taken of the fact that the situation where one electron is within the volume v and the other is outside it, which has a probability $P^{(1,1)}$, makes different contributions to the charge within the volume v and the charge distributed in the space outside v.

Table 2. Charge distributions for the simplest quantum-mechanical systems (in the ground state).

System	$v\,(a_0^3)$	Z_{int}[a]	Z_{ext}	$P^{(2,0)}$[b]	$P^{(1,1)}$	$P^{(0,2)}$
He^+	7.89	0.871	0.129			
H_2^+	45.15	0.893	0.103			
H (1s)	63.1	0.870	0.130			
He	14.88	1.6956	0.3044	0.7080	0.2796	0.0125
H_2	50.91	1.744	0.256	0.7525	0.1280	0.0085

[a] Z_{int} is the charge (in electronic units) in the effective volume v; Z_{ext} is the charge (in electronic units) outside the effective volume v.
[b] $P^{(2,0)}$ is the probability of finding two electrons in the volume v, $P^{(1,1)}$ the probability of finding one electron in the volume v and another electron outside this volume, and $P^{(0,2)}$ the probability of finding two electrons outside the volume v.

The comparatively small range of values of Z_{ext} (per electron) in Table 2, despite the significant differences between many systems, is striking (only from 10.7 to 14.0%). For the H(1s), He^+, and H_2 systems, Z_{ext} (per electron) is almost constant. This finding suggests the hypothesis that significant differences in charge distribution occur only within the effective volumes. Outside the effective volumes, the distributions are similar for different systems, and a spherical distribution is approached more closely the further away one moves from the system of nuclei.

As mentioned above, for the surfaces bounding the internal effective volumes of one-centre systems it is natural to adopt the geometry of the sphere with the centre at the atomic nucleus and, for homonuclear two-centre systems with cylindrical symmetry (H_2^+ and H_2), the geometry of an ellipsoid of rotation with the foci at the atomic nuclei. With these assumptions, it is possible to calculate the effective linear dimensions of the systems.

Table 3 lists the effective diameters d_{ef} of the H and He atoms in their ground states and the effective lengths of the axes $2a_{ef}$ and $2b_{ef}$ of the ellipsoids of rotation for the molecular ion H_2^+ and the molecule H_2, also in their ground states. The average values of d_{ef} obtained from the effective axes of the ellipsoids are also listed for H_2^+ and H_2.

Table 3 also contains (the extreme right-hand column) the effective diameters of He and H_2 calculated from the experimental viscosities of the gases [19] at high temperatures by Chapman's formula [20]:

$$\eta = \frac{1}{\pi\sigma_\infty^2}\sqrt{\frac{kTm}{\pi}},$$

where η is the viscosity of the ideal gas and σ_∞^2 the effective diameter of the species (atom or molecule) of the ideal gas which is assumed to be spherical. The effective external diameter of helium (1.72 Å) is closer to σ_∞ (1.91 Å) than the internal diameter.

Table 3. Effective linear dimensions for the ground states of H, He, H_2^+, and H_2 calculated from the internal volumes.

System	d_{ef}, Å	$2a_{ef}$, Å	$2b_{ef}$, Å	d_{ef}, Å	σ_∞, Å
H	2.62	—	—	—	—
He	1.61	—	—	—	1.91
H_2^+	—	2.50	2.26	2.38	—
H_2	—	2.51	2.39	2.45	2.42

We may note that r_{ef} for the hydrogen atom in the ground state, which is 1.31 Å, exceeds somewhat the van der Waals radius of hydrogen (1.17–1.20 Å). This is quite reasonable, since r_{ef} = 1.31 Å refers to an isolated atom in the ground state, while the van der Waals radius (1.20 Å) corresponds to the state of a hydrogen atom bound in the crystal.

The figures quoted in Table 3 indicate the possibility of interesting relations between the internal (and also external) effective volumes v and the approximate effective volumes of atoms and molecules from other sources (the viscosities of gases, vapours, and liquids, mean free paths in gases, etc.).

According to the foregoing considerations, the internal effective volumes v of the molecular ion H_2^+ and the molecule H_2 in their ground states are smaller than the effective volume v of the H atom in the 1s state. This is understandable, since the formation of a chemical bond should lead to a decrease of the entropy of the three-dimensional distribution of electron density.

However, it is at the same time reasonable to suppose that in each case where a chemical bond is formed there is a certain characteristic one-dimensional density distribution the entropy of which in fact increases. A test of this hypothesis [21] for the ground state of the molecular ion H_2^+ with the exact wave function [10] and for the ground state of the molecule H_2 with the James–Coolidge function [15], in relation to the ground state of the hydrogen atom, is consistent with the above hypothesis, as can be seen from Table 4. In the Table h denotes the entropies of the one-dimensional distribution of entropy density in the H_2^+ and H_2 systems in a direction parallel to the z axis passing through the protons, while for the hydrogen atom it denotes, in view of its spherical symmetry, the entropy of the one-dimensional distribution of electron density in a direction parallel to an arbitrarily chosen diameter.

The situation in the H_2 molecule is more complicated than in the ion H_2^+, since there is the additional effect of the electron-electron repulsion. This last factor tends to increase h and v. On the other hand, in contrast to the attraction of one-electron in H_2^+, the attraction of two electrons to two protons results in a decrease of the distance R between the protons, which tends to reduce h and v. As a result, the effective volume v in the ground state of the H_2 molecule is somewhat smaller than for the ground state of the H_2^+ ion, remaining, however, greater than v for the ground state of the hydrogen atom.

Table 4. One-dimensional effective volumes for the ground states of H, H_2^+ and H_2.

System	h	$v = \exp h$ (a_0)
H	1.39	4.01
H_2^+	1.47	4.35
H_2	1.43	4.18

The entropy of the distribution and the internal volumes for the wave functions in the electron gas model (the lateral cylindrical surface model) for molecules with a "sandwich" type structure were investigated by Bochvar et al.[22] In this study the entropy of the distribution was used as a qualitative characteristic of the degree of conjugation between the carbon rings in molecules of the dibenzene-chromium and ferrocene type.

In conclusion we may mention a number of studies in which the concept of the entropy of a discrete distribution is used for quantum-mechanical systems.

In conformity with studies by Daudel and coworkers[23], who were the first to introduce the concept of the "loge", Aslangul[24] employed the entropy of a discrete distribution to characterise the information which can be extracted from the wave function by considering arbitrary subdivisions of the coordinate space into regions and by assigning to each such region the probability of finding a definite number of electrons in it. The applications of certain properties of the entropy of spin operators have been considered[25].

The definition of the information contained in the state of one quantum-mechanical system relative to the state of another has been discussed[26]. In Zhdanov's book[27] the entropy is used to obtain information about the relative reactivities of conjugated molecules. Primas[28] suggested that the criterion of a minimum in the entropy function be used in certain cases for the derivation of approximate wave functions.

III. THEORY OF EFFECTIVE DIMENSIONS OF QUANTUM-MECHANICAL SYSTEMS

1. Effective Size in a One-Dimensional Quantum-Mechanical System

In order to elucidate the significance of the principal definitions of the theory of the effective volumes of quantum-mechanical systems without complicating the treatment with cumbersome mathematical formulae, we shall consider initially the simplest and most evident case of one-dimensional probability density on the coordinate of a single particle located on an infinite straight line. In this case the wave function $\psi(x)$ is a function of a single variable. Then

$$\rho(x) = |\psi(x)|^2 \tag{1.1}$$

is the probability density of the coordinate for point x on the straight line. The general variance is identical with the usual variance:

$$D = \int_{-\infty}^{\infty} (x - m)^2 \rho(x)\, dx, \tag{1.2}$$

where $m \int_{-\infty}^{+\infty} x\rho(x)dx$ is the expectation value of the coordinate for the distribution $\rho(x)$ and the entropy H is§

$$H = -\int_{-\infty}^{\infty} \rho(x) \ln \rho(x)\, dx. \tag{1.3}$$

Both the quantities D and H characterise the uncertainty in the coordinate of the one-dimensional particle. In order to emphasise the differences between these quantities, we shall resort to an example. Fig. 1*a* represents the density $\rho_1(x)$ of the uniform distribution along a section $[a, b]$ of length L. Fig. 1*b* represents the density of the distribution $\rho_2(x)$ concentrated uniformly on two sections $[a_1, b_1]$ and $[a_2, b_2]$ with an overall length L. The entropies of the distributions $\rho_1(x)$ and $\rho_2(x)$ are equal for any values of $t = a_2 - b_1 > 0$, while the corresponding variances are different, that of $\rho_2(x)$ increasing with increase of the parameter t. This example shows that the entropy is an absolute¶ characteristic of the distribution which reflects the scatter within the regions of the localisation of the distribution regardless of the relative positions of these regions. The variance of the distribution also depends on the relative scatter of the localisation regions. In this sense the variance can be regarded as a relative characteristic of the distribution.

In real problems one can encounter cases more complex than those illustrated in Fig. 1. The distribution densities may not become zero and may have several maxima (corresponding to the localisation regions). The entropy of the distribution characterises, to a rough

§For the logarithmic term in the integrand to be significant, it is necessary that the integrand should be dimensionless. To achieve this, the definition of H must be reformulated as follows[29]:

$$H = -\int_{-\infty}^{+\infty} \rho(x) \ln [\rho(x)\, l]\, dx\ ,$$

where l is a certain length. We shall assume (without restricting the generality of the treatment) that this length is unity. Then H has the significance of the average logarithm of a certain length; in the n-dimensional case H has the significance of the average value of an n-dimensional volume.

¶The absolute nature of the entropy is expressed by the fact that the integrand depends on the coordinate only through the density. This is in fact the cause of the property of entropy considered in this example.

approximation, the overall scatter within the localisation regions and the variance also takes into account the scatter of the localisation regions. The entropy and the variance each reflect the degree of delocalisation of the particle.

Entropy and variance can be used to characterise the effective dimensions of a one-dimensional particle. For this purpose, it is convenient to introduce the concept of effective volumes: the internal effective volume v defined in terms of the entropy by the formula

$$v = \exp H \tag{1.4}$$

and the external effective volume defined in terms of the variance by the formula

$$V = \sqrt{2\pi e D}. \tag{1.5}$$

We may note that, for a uniform distribution on the section $[a, b]$ with a length L (Fig. 1*a*), the internal volume is equal to the length of the section: $v = L$.

For any one-dimensional distribution, the following inequality is valid:

$$H \leqslant \frac{1}{2}\ln(2\pi e D). \tag{1.6}$$

Hence it follows that always $v \leqslant V$†. The equality of these volumes holds only for normal‡ (Gaussian) distribution.

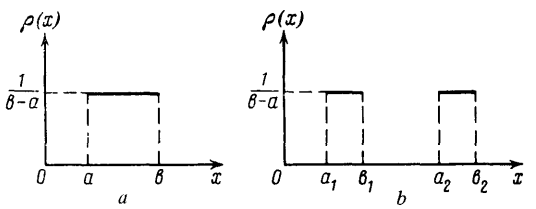


Figure 1.

Fig. 2 presents a plot of D as a function of $H = -\int \rho(x)\ln\rho(x)dx$ for normal distributions. The points located above the curve represent non-Gaussian one-dimensional distributions. When the variance is specified (for example D_0 in Fig. 2), the maximum entropy H_0 holds for the normal distribution. When the entropy is specified (for example H_0, Fig. 2) the minimum variance D_0 holds also for the normal distribution.

Evidently the following inequality is valid for any distribution:

$$v/V \leqslant 1. \tag{1.7}$$

The sign of equality in Eqn. (1.7) holds for normal distributions and only for normal distributions. Therefore it is reasonable to introduce the definition

$$N = v/V$$

and to term the quantity N $(0 \leqslant N \leqslant 1)$ the coefficient of the normality of the distribution. For all normal distributions, $N = 1$. For a uniform distribution, the normality coefficient is a constant quantity of about 0.7. The normality coefficient can be interpreted as the average "degree of population" of the external effective volume of the system with the given distribution. This interpretation presupposes a spatial localisation of the effective volumes v and V involving certain assumptions. These assumptions are chosen in accordance with the nature of the system for which the given distribution is observed. It is noteworthy that, in contrast to the effective volume V, the geometrical interpretation of the effective volume v may show it to be unconnected. We shall consider several examples.

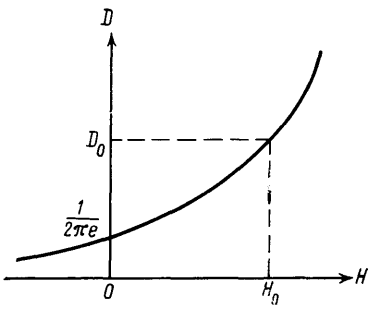


Figure 2.

A one-dimensional particle in a potential well with a finite length L, an infinitely high wall, and a constant potential within the well has a normalised wave function of the type

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{\pi n x}{L}, \quad (0 \leqslant x \leqslant L),$$

where n is the quantum number. The entropy H of the electron density distribution $|\psi_n(x)|^2$ is $\ln(2L/e)$ and therefore it depends only on L and is independent of the quantum number n. The variance of the electron density distribution $D(|\psi_n|^2)$ depends on L and n:

$$D(|\psi_n|^2) = L^2\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right).$$

The limiting value of $D(|\psi_n|^2)$ when $n \to \infty$ is $\frac{1}{12}L^2$. Table 5 lists the values of v, V, and the normality coefficient N.

Table 5. Effective volumes of the wave functions of a particle in a one-dimensional potential well.

n	v/L	V/L	N
1	0.736	0.747	0.985
2	0.736	1.098	0.670
30	0.736	1.192	0.617

It shows that the normality coefficient decreases with increase of n and almost attains its limiting value when $n = 30$.

†This relation justifies the terms "external" and "internal" for v and V.

‡The normal distribution has the density $\rho_N(x) = (2\pi D)^{1/2}\exp[-(x-m)^2/2D]$.

As a second example, we present in Table 6 analogous data for the first ten eigenstates of the harmonic oscillator. Evidently the normality coefficient gradually decreases with increase n.

Consider now, a particle localised at the point x_0. Its distribution density is given by the δ-function $\delta(x-x_0)$, the variance is zero, and the entropy is strictly speaking undefined. Nevertheless it is convenient to attribute $H[\delta(x-x_0)] = -\infty$ and the internal volume $v = 0$ to the δ-function, since the entropy tends to $-\infty$ for sequences of the type $\rho_1(x)$ and $\rho_2(x)$ which tend to the δ-function when $L \to 0$ and $D \to 0$. To ensure the validity of the treatment, it will be necessary to show that the entropy tends to $-\infty$ in any δ-sequence.

The introduction of the terms "internal" and "external" for the effective volumes is based on the fact that for specific geometrical interpretations of these quantities, the part of the space representing the entropy volume is contained within the part of the space representing the variance volume or is identical with it for normal distributions§.

Table 6. Effective volumes of the wave functions of a harmonic oscillator.

n	v	V	N
0	2.92	2.92	1.00
1	3.83	5.06	0.76
2	4.47	6.53	0.68
3	4.98	7.73	0.64
4	5.40	8.76	0.62
5	5.79	9.69	0.60
6	6.13	10.54	0.58
7	6.45	11.32	0.57
8	6.72	12.05	0.56
9	6.98	12 74	0.55

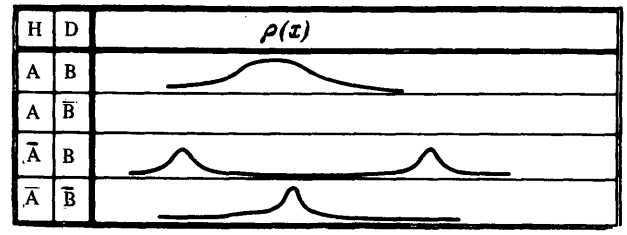
As stated above, in order to characterise fully the distribution it is necessary to know all its moments. However, a rough and purely qualitative classification of one-dimensional distributions with respect to entropy and variance can be formulated as follows: (a) each distribution belongs to one and only one of two classes $\mathbf{A}(H \geqslant 0)$ or $\bar{\mathbf{A}}(H < 0)$; (b) each distribution belongs to one and only one of two classes $\mathbf{B}[D \geqslant (2\pi e)^{-1}]$ or $\bar{\mathbf{B}}[D < (2\pi e)^{-1}]$. Four combinations of the above criteria, corresponding to four classes (one of these classes is empty), are presented in Table 7. The $\rho(x)$ column of Table 7 lists fairly typical distributions of three classes (A, B), ($\bar{\mathbf{A}}$, B), and ($\bar{\mathbf{A}}$, $\bar{\mathbf{B}}$). The normal or Gaussian distribution and a uniform distribution can belong to either of the two classes (A, B), and ($\bar{\mathbf{A}}$, $\bar{\mathbf{B}}$) depending on their parameters. Linear combinations of Gaussian or uniform distributions are encountered (depending on the parameters) in all non-empty classes. Among the examples of the three classes, two correspond to two sharply different extreme types of particle delocalisation and one to a marked localisation at one centre.

Between the extreme types of delocalisation, there is a continuous series of transitional cases referring, depending on the parameters, to class (A, B) or to ($\bar{\mathbf{A}}$, B).

§Thus the internal effective volume v of the distribution is equal in magnitude to the effective volume of the isentropic normal distribution, which is uniquely defined.

Next we proceed from the one-dimensional case to the consideration of real multidimensional (one- and many-particle) systems. The generalisation of the concept of the internal effective volume does not require additional justification, since the above definition of entropy changes on being extended to the multidimensional case only with respect to the interpretation of the variable integration symbol. However, the usual definition of variance quoted above is essentially one-dimensional. Therefore the concept of the external effective volume cannot be generalised to include multidimensional systems and it is necessary to define not only a more general but formally also a more complex concept.

Table 7. Classification of one-dimensional distributions with respect to the entropies and variances.



2. The Covariance Matrix and General Variance of a particle

We shall now consider a real physical object (the electron¶) in a potential field. Suppose that the state of the electron is described by the wave function $\psi(x_1, x_2, x_3)$ normalised to unity ($\int |\psi(x_1, x_2, x_3)|^2 d\mathbf{x} = 1$)†.

We put

$$\rho(\mathbf{x}) = |\psi(x_1, x_2, x_3)|^2, \tag{2.1}$$

where $\mathbf{x} = (x_1, x_2, x_3)$ are the coordinates of the electron. Then $\rho(\mathbf{x})$ can be treated as the probability density of a three-dimensional random quantity $\mathbf{X} = (X_1, X_2, X_3)$. Its components are one-dimensional random quantities X_1, X_2, X_3, which correspond to the coordinates x_1, x_2, x_3. The densities of the distribution of these one-dimensional random quantities are defined by the formulae

$$\rho_1(x_1) = \iint \rho(\mathbf{x})\, dx_2 dx_3, \quad \rho_2(x_2) = \iint \rho(\mathbf{x})\, dx_1 dx_3, \quad \rho_3(x_3) = \int\int \rho(\mathbf{x})\, dx_1 dx_2. \tag{2.2}$$

We shall employ the probability theory for the description of the delocalisation of a three-dimensional particle. We first recall the definition of the covariance matrix which characterises the deviation of a random quantity $\mathbf{X}$ from a point $M(m_1, m_2, m_3)$ the coordinates of which are given by the formulae

$$m_s = \int x_s \rho(\mathbf{x})\, d\mathbf{x} \quad (s = 1, 2, 3). \tag{2.3}$$

¶Or any other quantum-mechanical particle.

†For brevity we put $dx = dx_1 dx_2 dx_3$ and omit the integration limits. Here and henceforth the integration is from $-\infty$ to $+\infty$ with respect to each one-dimensional variable.

The radius-vector of the point M is called the expectation value of the random quantity X and is designated by $M(\mathbf{X})$. The covariance matrix (or the second moment matrix) is defined as

$$\mathscr{K}(\mathbf{X}) = \begin{pmatrix} k_{11} & k_{12} & k_{13} \\ k_{21} & k_{22} & k_{23} \\ k_{31} & k_{32} & k_{33} \end{pmatrix}, \tag{2.4}$$

the elements of which are

$$k_{st} = \int (x_s - m_s)(x_t - m_t)\rho(\mathbf{x})\, d\mathbf{x}. \tag{2.5}$$

The matrix K(X) is symmetrical ($k_{ts} = k_{st}$). Its diagonal elements are the variances $D(X_s) = \sigma_s^2$ of the components X_s and the non-diagonal elements $k_{st} = \mathrm{Cov}(X_s, X_t)$ are the covariances of the components X_s and X_t. The covariance characterises the statistical correlation between the random quantities X_s and X_t. It depends on the choice of scale. In order to eliminate this dependence, the concept of the normalised correlation or the correlation coefficient of two one-dimensional random quantities X_s and X_t is introduced. It is defined by the formula

$$r_{st} = r(X_s, X_t) = \frac{\mathrm{Cov}(X_s, X_t)}{\sqrt{D(X_s)\,D(X_t)}}. \tag{2.6}$$

It can be shown[30] that the following inequality always holds:

$$|r_{st}| \leqslant 1. \tag{2.7}$$

The equality is attained only when the variables X_s and X_t are linearly related. On the other hand, if the random quantities X_s and X_t are independent, then $r_{st} = 0$‡. We shall now determine what information about the delocalisation of the particle can be derived from the matrix K. As already mentioned, the diagonal elements characterise the scatter of the coordinates x_1, x_2, and x_3. In order to determine the scatter in the direction of an arbitrary vector $\mathbf{c}(c_1, c_2, c_3)$, it is necessary to calculate the scaler product of K(X)c and c, i.e.,

$$D_{\mathbf{c}}(\mathbf{X}) = (\mathscr{K}(\mathbf{X})\mathbf{c}, \mathbf{c}) = \sum_{i=1}^{3}\sum_{j=1}^{3} k_{ij}c_j c_i. \tag{2.8}$$

Thus the covariance matrix contains the full information about the delocalisation of the particle in any direction. However, together with the matrix characteristic of the scatter, scalar quantities describing the scatter of a random vector quantity X in terms of a single integral number are of interest.

Before stating these characteristics, we shall elucidate the requirements which they must satisfy. Hitherto, the coordinate system was fixed. On passing to a new coordinate system x_1, x_2, x_3 by an orthogonal transformation (including rotations and reflections)

$$\mathbf{x}' = U\mathbf{x} \tag{2.9}$$

the random quantity X will have the distribution density

$$\tilde{\rho}(\mathbf{x}') = \rho(U^{-1}\mathbf{x}'). \tag{2.10}$$

The substitution (2.9) may be treated as a change to a new random vector (in the old coordinate system)

$$\mathbf{X}' = U\mathbf{X} \tag{2.11}$$

with distribution density

$$\tilde{\rho}(\mathbf{x}) = \rho(U^{-1}\mathbf{x}). \tag{2.10'}$$

The covariance matrix of the random vector X′ (or, what amounts to the same thing, the covariance matrix of the initial random vector in the new coordinate system) is

$$\mathscr{K}(\mathbf{X}') = U\mathscr{K}(\mathbf{X})U^{-1}. \tag{2.12}$$

Since the entire class of random vectors X′ obtained from the initial vector X by all possible orthogonal transformations describes the same state of the particle, the required scalar characteristics must be invariant in the above transformations. Such invariant characteristics are the "spur" of the matrix K(X) (the sum of its diagonal elements)

$$\mathrm{Sp}\,\mathscr{K}(\mathbf{X}) = D(X_1) + D(X_2) + D(X_3) \tag{2.13}$$

and the determinant§

$$D(\mathbf{X}) = \det \mathscr{K}(\mathbf{X}), \tag{2.14}$$

called the general variance of a random quantity X.[30] We shall also call it the general variance of the coordinates of the particle [in the state $\psi(\mathbf{x})$]. We shall now consider the geometrical significance of the above quantities. If we denote by $\Delta\mathbf{X}$ the random vector $\mathbf{X} - M(\mathbf{X})$, then it is readily seen that the spur of the matrix K(X) represents the expectation value of the quantity $|\Delta\mathbf{X}|^2$, i.e. $M(|\Delta\mathbf{X}|^2)$. This quantity has the dimensions of the square of a length. Therefore $\sqrt{M(|\Delta\mathbf{X}|^2)}$ characterises the scatter of the values in the direction of the radius-vector drawn from a point and cannot provide an answer to the question of whether the particle is localised in the vicinity of a plane or a straight line. We emphasise that the quantity $M(|\Delta\mathbf{X}|^2)$ is essentially a one-dimensional characteristic.

In contrast to the quantity $M(|\Delta\mathbf{X}|^2)$ the general variance $D(\mathbf{X})$ characterises a multidimensional scatter. In order to elucidate the geometrical significance of this quantity, we shall consider further the quantity

$$D^*(\mathbf{X}) = D(X_1)\,D(X_2)\,D(X_3). \tag{2.15}$$

The standard deviation $\sigma^*\sqrt{D^*}$ corresponding to this quantity is equal to the volume of a rectangular parallelepiped with the sides $\sigma(X_i) = \sqrt{D(X_i)}$ $(i = 1, 2, 3)$. Thus the quantity $D^*(\mathbf{X})$ characterises the three-dimensional scatter in the direction of all the coordinate axes at once, but it does depend on the choice of the coordinate system. The minimum value of $D^*(\mathbf{X})$ is attained in the coordinate system the unit vectors of which are the eigenvectors of the covariance matrix K(X) and is equal to $D(\mathbf{X})$¶. The coordinate system formed by the eigenvectors of the matrix will be called the intrinsic system of the particle

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‡The converse assertion is incorrect. It does not follow from the equality $r_{st} = 0$ that the random quantities are independent. There are random quantities which are actually linked by a non-linear functional relation, whose correlation coefficient is zero. Therefore Eqn. (2.6) can characterise only a linear relation.

§The remaining invariant characteristics are not considered here.

¶A maximum value of D^* also exists and is $D_{\max}(\mathbf{X}) = (\frac{1}{3}\mathrm{Sp}\mathbf{K})^3$. With the aid of the quantities $D_{\max}(\mathbf{X})$ and $D(\mathbf{X})$, it is possible to define a measure of the anisotropy of the distribution: $[D_{\max}(\mathbf{X}) - D(\mathbf{X})]\sqrt{D_{\max}(\mathbf{X})D(\mathbf{X})}$.

coordinates†. In this coordinate system the covariance matrix is of the diagonal form, i.e. the components of the random vector X are not correlated.

Thus the geometrical significance of the quantity $D(\mathbf{X})$ becomes clear: it is the general variance of the particle equal to the product of the one-dimensional variances in the directions of the axes of the intrinsic coordinate system of the particle, i.e. to the product of the eigennumbers of the covariance matrix. It follows from the condition for an extremum in $D^*(\mathbf{X})$ that the following inequality always holds:

$$D(\mathbf{X}) \leqslant D(X_1) D(X_2) D(X_3), \tag{2.16}$$

where the equality sign obtains only when the components X_1, X_2, and X_3 are not correlated.

3. The Covariance Matrix of an n-Particle System

We shall now consider a quantum-mechanical system of n particles. Suppose that the state of the system is described by the normalised wave function $\psi(\mathbf{X})$, where $\mathbf{x} = (\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n)$ denotes a set of cartesian coordinates of n particles and $\mathbf{x}_i = (x_{i1}, x_{i2}, x_{i3})$ denotes the coordinates of the ith particle. We put

$$\rho(\mathbf{x}) = |\psi(\mathbf{x})|^2. \tag{3.1}$$

Then $\rho(\mathbf{x})$ can be treated as the probability density of a $3n$-dimensional random vector:

$$\mathbf{X} = (\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n). \tag{3.2}$$

The components of the vector are three-dimensional random quantities $\mathbf{X}_i = (X_{i1}, X_{i2}, X_{i3})(i = 1, 2, \ldots, n)$ with the distribution densities

$$\rho_i(\mathbf{x}_i) = \int \rho(\mathbf{x})\, d\mathbf{x}_1 \ldots d\mathbf{x}_{i-1} d\mathbf{x}_{i+1} \ldots d\mathbf{x}_n. \tag{3.3}$$

Each density describes the distribution of the coordinates of the individual ith particle with all other particles in their average positions. The expectation value of the sth component of the ith particle is given by the formula

$$m_{is} = \int x_{is} \rho(\mathbf{x})\, d\mathbf{x}, \tag{3.4}$$

and the covariance matrix $\mathbf{K}_{ii}$ of the ith particle is defined by formulae of type (2.4) and (2.5). The covariance of the sth component of the ith particle and of the tth component of the jth particle is given by the formula

$$\mathrm{Cov}(X_{is}, X_{jt}) = \int (x_{is} - m_{is})(x_{jt} - m_{jt}) \rho(\mathbf{x})\, d\mathbf{x}. \tag{3.5}$$

Thus the covariance matrix of the coordinates of a system of n particles [i.e. of the random vector (3.2)] is of order $3n$ and can be represented by the block matrix

$$K(\bar{\mathbf{X}}) = \begin{pmatrix} \mathcal{K}_{11} & \mathcal{K}_{12} & \ldots & \mathcal{K}_{1n} \\ \mathcal{K}_{21} & \mathcal{K}_{22} & \ldots & \mathcal{K}_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ \mathcal{K}_{n1} & \mathcal{K}_{n2} & \ldots & \mathcal{K}_{nn} \end{pmatrix}, \tag{3.6}$$

where $\mathbf{K}_{ij}$ is the covariance matrix of the ith and jth particles comprising the elements of the matrix (3.5) with $s = (1, 2, 3)$ and $t = (1, 2, 3)$. The matrix $K(\mathbf{X})$ is symmetrical. Therefore the "elements" symmetrical relative to the main diagonal are linked by the relation $\mathbf{K}_{ij} = \mathbf{K}'_{ii}$, where the prime denotes transposition. On the basis of the considerations set out in Section III, 2, one can speak of the general variance of the coordinates of an individual particle $\mathbf{x}_i$ in an n-particle system. This variance is given by the formula

$$D(\mathbf{X}_i) = \det \mathcal{K}_{ii}. \tag{3.7}$$

The general variance of the coordinates of the entire system,

$$D(\mathbf{X}) = \det K(\mathbf{X}) \tag{3.8}$$

and the general variance of the coordinates of an arbitrary subsystem of μ particles,

$$D(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_\mu) = \det K_\mu, \tag{3.9}$$

where K_μ is a block matrix comprising the elements of the matrix $\mathbf{K}_{ij}$ designated by the numbers of the isolated particles, can be defined by analogous formulae.

For the system as a whole (as well as for any of its subsystems), it is possible to select the intrinsic coordinate system, i.e. the coordinate system in the $3n$-dimensional space in which the covariance matrix of the entire system (called the subsystem) is diagonal. If not all the elements of the matrix $\mathbf{K}_{ij}$ are zero, the set of the intrinsic coordinate systems of the individual particles need not coincide with the intrinsic coordinate system of the n-particle system (or subsystem).

4. Effective Volumes of Quantum-Mechanical Systems

Just as the uncertainty of the position of a one-dimensional quantity is described by the variance D and the entropy H, the uncertainty of the position of a real particle or a system of n particles is described by the general variance (3.8) and the entropy:

$$H(\mathbf{X}) = H(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n) = -\int \rho(\mathbf{x}) \ln \rho(\mathbf{x})\, d\mathbf{x}. \tag{4.1}$$

As in the one-dimensional case, the entropy characterises the uncertainty of the position of the particles in the regions of their "localisation", while the general variance takes into account also the scatter of the localisation regions. Therefore the concepts of the internal and external volumes can be naturally extended to the multidimensional case as follows. The internal volume of an n-particle system is given by the formula

$$v(\mathbf{X}) = v(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n) = \exp H(\mathbf{X}), \tag{4.2}$$

and the external volume by the formula

$$V(\mathbf{X}) = V(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n) = \sqrt{(2\pi e)^{3n} D(\mathbf{X})}. \tag{4.3}$$

The usefulness of the definition of the internal volume by Eqn. (4.2) is confirmed by the following facts. If the system is concentrated in a finite region Ω and the density of its distribution is uniform, then the internal volume of such a system is equal to the volume of the region Ω. On the other hand, if the distribution of the system in the region Ω is non-uniform, its internal volume is smaller than that of the region Ω.

It follows from the properties of the general variance and the definition of the one-dimensional external volume (size) that the external volume of the particle is equal to the product of the one-dimensional external sizes in the

†It is assumed that the particle is in a fixed state $\psi(\mathbf{x})$.

directions specified by the intrinsic coordinate system of the particle. The following inequality for the external volume follows from inequality (2.16):

$$V(\mathbf{X}) \leqslant V(X_1)\,V(X_2)\,V(X_3). \tag{4.4}$$

A similar assertion is valid also for a system of n particles. It is then found that the external volumes of the particles‡ and of the system as a whole are linked by the inequality

$$V(\mathbf{X}) = V(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n) \leqslant V(\mathbf{X}_1)\,V(\mathbf{X}_2) \ldots V(\mathbf{X}_n), \tag{4.5}$$

where the equality sign obtains only when the particles are not correlated, i.e., all the elements of all the matrices $\mathbf{K}_{ij}$ $(i \neq j)$ are zero.

The situation is somewhat different when one-dimensional and multidimensional internal volumes are compared. We shall demonstrate this using as an example a single particle. If $\rho(x_1, x_2, x_3)$ is the distribution density of the particle, the distribution densities of the components X_i are given by Eqns. (2.2) and the one-dimensional entropies and internal volumes are given by the equations

$$H(X_i) = -\int \rho_i(x_i) \ln \rho_i(x_i)\, dx_i \tag{4.6}$$

and

$$v(X_i) = \exp H(X_i). \tag{4.7}$$

The quantity $v^*(\mathbf{X}) = v(X_1)v(X_2)v(X_3)$ depends on the choice of the coordinate system. It has a minimum $v^0(\mathbf{X})$ which satisfies the inequality

$$v^0(\mathbf{X}) \geqslant v(\mathbf{X}), \tag{4.8}$$

where the equality sign is obtained for normal distributions. Thus the relation between one-dimensional and multidimensional internal volumes is given by the inequality

$$v(\mathbf{X}) \leqslant v(X_1)\,v(X_2)\,v(X_3). \tag{4.9}$$

Similarly the internal volume of an n-particle system is linked to the volumes of its constituent particles§ by the inequality

$$v(\mathbf{X}) = v(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n) \leqslant v(\mathbf{X}_1)\,v(\mathbf{X}_2) \ldots v(\mathbf{X}_n). \tag{4.10}$$

The last two inequalities are of the same form as inequalities (4.4) and (4.5). However, the equality sign is not generally speaking attained in formulae (4.9) and (4.10) even for non-correlated components¶. This finding suggests that the entropy (and hence the internal volume) is a more refined concept which takes correlation into account more fully. We shall consider this in greater detail in Section III, 6.

As already mentioned, among distributions concentrated in a restricted region Ω the uniform distribution has the maximum internal volume. Among distributions which are not concentrated in a limited region and have a specified external volume V, the normal distributions have the maximum internal volume v (equal to V). The converse is also true; among distributions which are not concentrated in a restricted region and have a specified internal volume v, the normal distributions have the minimum external volume (equal to v).

‡The external volume of an individual particle in a system of n particles is defined in terms of the variance $D(\mathbf{X}_i)$ given by Eqn. (3.7).

§The internal volume of an individual (ith) particle is defined in terms of the entropy of the distribution with density $\rho_i(\mathbf{x}_i)$ specified by Eqn. (3.3).

¶Systems with the normal distribution density are an exception.

5. The General Covariance Matrix

The introduction of the concepts of a general variance and an external volume makes it possible to assign a definite geometrical significance to covariance and the correlation coefficient. Consider a covariance matrix $\mathbf{K}(\mathbf{X})$ specified by Eqns. (2.4) and (2.5). An arbitrary non-diagonal element k_{ij} $(i \neq j)$ of this matrix expresses the correlation of the coordinates x_i and x_j of a particle [in a state with the distribution density $\rho(x_1, x_2, x_3)$]. The covariance matrix of a two-dimensional random vector (X_i, X_j) has the form

$$\begin{pmatrix} D(X_i) & k_{ij} \\ k_{ij} & D(X_j) \end{pmatrix}. \tag{5.1}$$

The general variance of an arbitrary t-dimensional random vector is defined as the determinant of its covariance matrix [Eqns. (2.14), (3.8), and (3.9) represent special cases of this definition]. The general variance of the two-dimensional random vector (X_i, X_j) is thereby expressed by the formula

$$D(X_i, X_j) = D(X_i)\,D(X_j) - k_{ij}^2 .$$

Hence it follows that the covariance modulus k_{ij} can be put in the form

$$|\operatorname{Cov}(X_i, X_j)| = |k_{ij}| = \sqrt{D(X_i)\,D(X_j) - D(X_i, X_j)}, \tag{5.2}$$

and the modulus of the correlation coefficient in the form

$$|r(X_i, X_j)| = \frac{|\operatorname{Cov}(X_i, X_j)|}{\sqrt{D(X_i)\,D(X_j)}} = \sqrt{1 - \frac{D(X_i, X_j)}{D(X_i)\,D(X_j)}}. \tag{5.3}$$

By analogy with Eqn. (4.3), the external volume of a two-dimensional random quantity is given by the formula $V(X_1, X_2) = 2\pi e\sqrt{D(X_1, X_2)}$. It is therefore possible to express the modulus of the correlation coefficient in terms of the external volumes:

$$|r(X_i, X_j)| = \sqrt{1 - \left[\frac{V(X_i, X_j)}{V(X_i)\,V(X_j)}\right]^2}. \tag{5.3'}$$

We shall now elucidate somewhat the geometrical interpretation of covariance and the correlation coefficient using as an example two one-dimensional random quantities.

Suppose that $\rho(x_1, x_2)$ is the distribution density of a two-dimensional random quantity. In order to express the nature of the distribution, it is useful to outline the lines of the $\rho(x_1, x_2)$ density levels on the plane of the variables x_1 and x_2. As an example, Fig. 3 presents the density levels for a two-dimensional normal distribution. The point O' with the coordinates $(m_{\mathbf{X}_1}, m_{\mathbf{X}_2})$ characterises the "centre of gravity" of the distribution and the uncertainty of the position of the two-dimensional random quantity in the directions x_1 and x_2 is characterised by the standard deviations $\sigma(X_1) = \sqrt{D(X_1)}$ and $\sigma(X_2) = \sqrt{D(X_2)}$. The "volume" characteristic of the uncertainty of the position of the two-dimensional random quantity can be expressed, without taking into account the correlation of the components,

by the area of the rectangle $ABCD$, the "centre" of which is at point O', the sides are parallel to the coordinate axes, and their lengths are $2\sigma(X_1)$ and $2\sigma(X_2)$.

We shall now find the eigenvectors of the matrix (5.1) and, assuming them to be the unit vectors of a new coordinate system with origin at the point O', we obtain the intrinsic coordinate system (x_1^0, x_2^0) of the two-dimensional random quantity. The uncertainty of its position with respect to the intrinsic directions is characterised by the standard deviations $\sigma(x_1^0)$ and $\sigma(x_2^0)$, while the "volume" uncertainty is expressed by the area of the rectangle $A^0B^0C^0D^0$ with the centre at the point O' having sides with lengths $2\sigma(x_1^0)$ and $2\sigma(x_2^0)$ which are parallel to the axes x_1^0 and x_2^0 (respectively). If such rectangles are plotted for any orthogonal coordinate system, it is found that among them there is one whose area is an extremum. The area of the rectangle $A^0B^0C^0D^0$ is the smallest of all the possible values. This follows from the following inequality for a two-dimensional random quantity X:

$$D(\mathbf{X}) \leqslant D(X_1)\, D(X_2). \tag{5.4}$$

which is analogous to inequality (2.16).

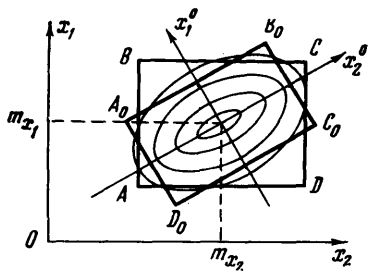


Figure 3.

We may mention further that the length of the sides of the triangles may be made proportional to the standard deviations. In particular they can be made equal to the external dimensions $\mathbf{V}(X_i)$. In all cases the ratio of the areas of the rectangles $A^0B^0C^0D^0$ and $ABCD$ will be the same and equal to

$$s = \frac{\sigma(X_1, X_2)}{\sigma(X_1)\,\sigma(X_2)} = \frac{V(X_1, X_2)}{V(X_1)\,V(X_2)}. \tag{5.5}$$

The quantity s will be called the non-correlation coefficient. It is readily seen that its values lie in the range

$$0 \leqslant s \leqslant 1. \tag{5.6}$$

The quantity s is a maximum for non-correlated components. Indeed, in this case the equality sign obtains in formula (5.4) and consequently $s = 1$. The minimum value of s occurs when there is a linear correlation between X_1 and X_2. The minimum eigenvalue $D(X_1^0)$ of the covariance matrix then becomes zero, so that $s = 0$.

Formula (5.3) or (5.3′) shows that the relation between the correlation coefficient r and the non-correlation coefficient s is given by

$$r^2 + s^2 = 1. \tag{5.7}$$

If one remembers further that $\sigma(X_1, X_2) = \sigma(X_1^0)\sigma(X_2^0)$ and $V(X_1, X_2) = V(X_1^0)V(X_2^0)$ characterises the "volume" of the scatter of the non-correlated random quantities X_1^0 and X_2^0, one may conclude that the quantities r and s reflect the change in the "volume" uncertainty of the position of the two-dimensional random quantity on passing to the intrinsic coordinate system.

We shall now turn to the consideration of an n-particle system with the distribution density $\rho(\mathbf{x}) = \rho(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n)$. As already mentioned, the covariance matrix $K(\mathbf{X})$ of such a system has the form of the block matrix (3.6). This matrix contains the complete information about the uncertainty of the position of the $3n$-dimensional random vector $\mathbf{X}(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n)$ in terms of the approximation defined by the second moments. However, in order to estimate the correlation between the particles (ith and jth), it is useful to have a scalar quantity as well as the matrix $\mathbf{K}_{ij}$. From physical considerations, it should be independent of the choice of the coordinate system of the particles and should reflect the correlation between the particles†.

The above considerations suggest the necessity to extend the concept of correlation based on probability theory to the case of a pair of particles or a system of particles. Therefore our immediate problem is to construct the covariance matrix Q of quantum-mechanical particles in an n-particle system which would constitute a natural extension of the usual covariance matrix‡.

One of the possible generalisations (seemingly the most natural generalisation) was proposed by Del-Re et al.[31] It is based on Eqn. (2.5), where the vectors $\mathbf{x}_s$ and $\mathbf{x}_t$ must be substituted in place of the variables x_s and x_t and the vector product must be regarded as a scalar quantity. As will be shown below, this definition of covariance is defective as regards physical significance.

Another possible generalisation of the covariance matrix was proposed by ourselves on the basis of the concept of general variance. Indeed the general variances $D(\mathbf{X}_i)$ characterising the uncertainty of the position of the coordinates of the ith particle

$$q_{ii} = D(\mathbf{X}_i), \tag{5.8}$$

are adopted as the diagonal elements of the matrix Q. The non-diagonal elements q_{ij} of the matrix Q, i.e. the covariances of the coordinates of the ith and jth particles, are determined, by analogy with Eqn. (5.2), from the formula

$$q_{ij} = \mathrm{Cov}(\mathbf{X}_i, \mathbf{X}_j) = \sqrt{D(\mathbf{X}_i)\,D(\mathbf{X}_j) - D(\mathbf{X}_i, \mathbf{X}_j)}, \tag{5.9}$$

where the plus sign was chosen for the square root term, since the correlation interaction is characterised by the

---

†We may note that in the term "correlation energy" employed in quantum chemistry the word correlation means in fact the part of the electron correlation which depends significantly on the choice of the approximate method of calculation used and the term "correlation energy" itself denotes a correction to the energy calculated by the approximate method. The correlation energy is usually understood as the difference between the energy calculated by the Hartree–Fock method and the exact energy of the system.

‡In contrast to the initial covariance matrix K of order $3n$, the generalised covariance matrix Q is of order n.

modulus of the correlation coefficient. The term correlation coefficient for two particles in an n-particle system ($n \geq 2$) will be given to the quantity

$$r(\mathbf{X}_i, \mathbf{X}_j) = \frac{\mathrm{Cov}(\mathbf{X}_i, \mathbf{X}_j)}{\sqrt{D(\mathbf{X}_i) D(\mathbf{X}_j)}} = \sqrt{1 - \frac{D(\mathbf{X}_i, \mathbf{X}_j)}{D(\mathbf{X}_i) D(\mathbf{X}_j)}}. \qquad (5.10)$$

Using Eqn. (4.3), it is possible to express the correlation coefficient in terms of external volumes:

$$r(\mathbf{X}_i, \mathbf{X}_j) = \sqrt{1 - \left[\frac{V(\mathbf{X}_i, \mathbf{X}_j)}{V(\mathbf{X}_i) V(\mathbf{X}_j)}\right]^2}. \qquad (5.10')$$

Therefore r will also be called the external correlation coefficient in contrast to the internal correlation coefficient defined below. Eqns. (5.10) and (5.10′) constitute natural extensions of Eqns. (5.3) and (5.3′). The concept of the non-correlation coefficients can also be evidently extended to the case of a pair of particles:

$$s(\mathbf{X}_i, \mathbf{X}_j) = \frac{\sigma(\mathbf{X}_i, \mathbf{X}_j)}{\sigma(\mathbf{X}_i)\sigma(\mathbf{X}_j)} = \frac{V(\mathbf{X}_i, \mathbf{X}_j)}{V(\mathbf{X}_i) V(\mathbf{X}_j)}. \qquad (5.11)$$

Therefore the correlation coefficient of the particles $r(\mathbf{X}_i, \mathbf{X}_j)$ and the non-correlation coefficients $s(\mathbf{X}_i, \mathbf{X}_j)$ have the same significance as the usual coefficients r and s: they reflect the degree of condensation of the two-particle subsystem. It is easy to verify the following properties of the correlation coefficient.

1. $r(\mathbf{X}_i, \mathbf{X}_j) = 0$ if the ith and jth particles are independent, i.e. their density is represented by the product $\rho(\mathbf{x}_i)\rho(\mathbf{x}_j)$.

2. $r(\mathbf{X}_i, \mathbf{X}_j) = 1$ if there is a linear relation between the coordinates of the ith and jth particles§; the converse assertion is also valid: if $r(\mathbf{X}_i, \mathbf{X}_j) = 1$, there is at least one linear relation between the coordinates.

3. The correlation coefficient satisfies the inequality

$$0 \leqslant r(\mathbf{X}_i, \mathbf{X}_j) \leqslant 1.$$

The above properties are fully analogous to those of the usual correlation coefficient. Thus, for the usual correlation coefficient property(1) is irreversible, i.e. when $r(\mathbf{X}_i, \mathbf{X}_j) = 0$, the given particles need not necessarily be independent. There can even be a functional relation between them. This factor and property (2) suggest that the correlation coefficient (the usual and extended coefficient) should be more correctly called the linear correlation coefficient.

The analogue of the correlation coefficient for the approximation of a non-linear functional relation is discussed in Section III, 6.

In conclusion of this subsection we emphasise that the quantities $D(\mathbf{X}_i)$, $D(\mathbf{X}_i, \mathbf{X}_j)$, $\mathrm{Cov}(\mathbf{X}_i, \mathbf{X}_j)$ and $r(\mathbf{X}_i, \mathbf{X}_j)$ satisfy the requirement of invariance in relation to the orthogonal transformations of the coordinate systems of the individual particles. We may note that the definitions of covariance and correlation coefficient proposed by Del-Re et al.[31] do not satisfy this invariance condition.

§This means that there is a functional relation of the type:

$$a_1 x_{i1} + a_2 x_{i2} + a_3 x_{i3} + b_1 x_{j1} + b_2 x_{j2} + b_3 x_{j3} = 0.$$

6. Non-Linear Correlation. Internal Correlation Coefficient

When we speak of a statistical relation for random quantities, we are interested primarily in the possible similarity of the given statistical relation to a functional relation. To assess this similarity, it is necessary to determine a quantity characterising its measure. The linear correlation coefficient cannot serve as such a measure since, as already shown, there exist distribution in which the variables are linked by a functional relation, while the correlation coefficient is zero.

We recall that the modulus of the correlation coefficient defined by Eqn. (2.6) for two one-dimensional random quantities is expressed in terms of the external volumes by Eqn. (5.3′). The formal replacement of the external by internal volumes permits the introduction of the quantity

$$r_H(X_i, X_j) = \sqrt{1 - [v(X_i, X_j)/v(X_i)v(X_j)]^2}, \qquad (6.1)$$

which we shall call the internal correlation coefficient¶. The subscript H means that this quantity is defined in terms of the entropy, namely

$$r_H(X_i, X_j) = \sqrt{1 - \exp[2H(X_i, X_j) - 2H(X_i) - 2H(X_j)]}.$$

We shall now consider the properties of the internal correlation coefficient. In the first place it follows from the inequality[29] $H(X, Y) \leqslant H(X) + H(Y)$ that the quantity $r_H(X, Y)$ also varies in the range $0 \leqslant r_H \leqslant 1$. The minimum value is reached for independent X and Y, i.e. when the probability density of the two-dimensional random quantity is a product of the densities of the quantities X and Y: $\rho(x, y) = \rho_1(x)\rho_2(y)$. Indeed for the independent quantities $H(X, Y) = H(X) + H(Y)$, $\exp[2H(X, Y) - 2H(X) - 2H(Y)] = 1$ and hence $r_H(X, Y) = 0$. On the other hand, if the random quantities are linked by a functional relation $Y = \varphi(X)$, then $r_H(X, Y) = 1$.

We shall prove this assertion. For simplicity, we shall assume that the function φ has a converse function $X = \theta(Y)$. Then the density of the joint distribution of two random quantities is of the form

$$\rho(x, y) = f(x)\,\delta(y - \varphi(x)) = f(x)\,\delta(x - \theta(y)), \qquad (6.2)$$

where the function f satisfies the condition $\int f(x)dx = 1$. In addition the convergence of the integrals is postulated:

$$H[f] = -\int f(x) \ln f(x)\, dx, \quad H[f(\theta)] = -\int f[\theta(y)] \ln f[\theta(y)]\, dy.$$

The functional of the entropy has not been defined for the density (6.2). It must be additionally defined as the limit of the functionals of the entropy H_n for the densities $\rho_n(x, y) = f(x)g_n[y - \varphi(x)]$, where g_n is a δ-sequence. We have

$$H_n = -\int\int \rho_n(x, y) \ln \rho_n(x, y)\, dx\, dy = -\int\int f(x)\, g_n(y - \varphi(x)) \ln f(x)\, dx\, dy -$$
$$- \int\int f(x)\, g_n(y - \varphi(x)) \ln g_n(y - \varphi(x))\, dx\, dy = -\int f(x) \ln f(x)\, dx -$$
$$- \int f(x)\, dx \int g_n(y - \varphi(x)) \ln g_n(y - \varphi(x))\, dy = H[f] + H[g_n].$$

By virtue of the hypothesis made in Section III, 1 concerning the entropy of the δ-function and the condition for $H(f)$, we have $\lim_{n\to\infty} H_n = H[f] + \lim_{n\to\infty} H[g_n] = -\infty$.

¶On the other hand the usual correlation coefficient, which is expressed in terms of the external volumes, can also be reasonably called the external correlation coefficient.

Moreover, $\rho_1(x) = \int f(x)\delta[y - \varphi(x)]dy = f(x)$ and $\rho_2(y) = \int f(x)\delta[x - \theta(y)]dx = f[\theta(y)]$. Therefore $H(X) = H[f]$ and $H(Y) = H[f(\theta)]$. Since both these quantities are finite, it follows that $\exp[2H(X, Y) - 2H(X) - 2H(Y)] = 0$ and therefore $r_H(X, Y) = 1$.

The definition (6.1) can be naturally extended to the multidimensional case. The internal correlation coefficient of two particles will be defined as

$$r_H(X_i, X_j) = \sqrt{1 - [v(X_i, X_j)/v(X_i)\,v(X_j)]^2}. \qquad (6.1')$$

The properties of this quantity are as follows.

1. $r_H(X_i, X_j) = 0$ if the quantities X_i and X_j are independent, i.e. $\rho(x_i, x_j) = \rho_i(x_i)\rho_j(x_j)$.

2. If there is a functional relation between the coordinates of the vectors x_i and x_j, then $r_H(X_i, X_j) = 1$; conversely if $r_H = 1$, the internal volume of a system of two particles (the ith and jth particles) is zero.

3. For any distribution density $\rho(x_i, x_j)$, the quantity $r_H(X_i, X_j)$ satisfies the inequalities

$$0 \leqslant r_H(X_i, X_j) \leqslant 1.$$

The equality $r_H(X_i, X_j) = 1$ is not a characteristic property of the functional relation. It is characteristic of the situation where the internal volume becomes zero.

7. Many-Particle Correlation

As stated above, electron correlation is usually estimated from the energy standpoint. Below we quote formulae for the estimation of many-electron correlation in the language of the concepts of probability theory. They are obtained by a natural extention of the formulae for two-particles.

The external correlation coefficient of a subsystem of μ particles ($2 \leqslant \mu \leqslant n$) will be defined as

$$r(X_1, X_2, \ldots, X_\mu) = \left[1 - D(X_1, X_2, \ldots X_\mu) \Big/ \prod_{i=1}^{\mu} D(X_i)\right]^{1/2}. \qquad (7.1)$$

This quantity can evidently be expressed also in terms of external volumes:

$$r(X_1, X_2, \ldots, X_\mu) = \left\{1 - \left[V(X_1, X_2, \ldots, X_\mu) \Big/ \prod_{i=1}^{\mu} V(X_i)\right]^2\right\}^{1/2}.$$

The internal correlation coefficient is defined similarly:

$$r_H(X_1, X_2, \ldots, X_\mu) = \left\{1 - \left[v(X_1, X_2, \ldots, X_\mu) \Big/ \prod_{i=1}^{\mu} v(X_i)\right]^2\right\}^{1/2}. \qquad (7.2)$$

The properties of these quantities are as follows.

1. If one of the particles $x_1, x_2, \ldots, x_\mu$ is independent of the others, then $r(X_1, X_2, \ldots, X_\mu) = r_H(X_1, X_2, \ldots, X_\mu) = 0$.

2. If there is a functional relation between the coordinates of the particles $x_1, x_2, \ldots, x_\mu$, then $r_H(X_1, X_2, \ldots, X_\mu) = 1$†; if this relation is linear, then also $r(X_1, X_2, \ldots, X_\mu) \leqslant 1$.

3. Both quantities satisfy the inequalities $0 \leqslant r(X_1, X_2, \ldots, X_\mu) \leqslant 1$ and $0 \leqslant r_H(X_1, X_2, \ldots, X_\mu) \leqslant 1$.

†Nothing can be said about the quantity $r(X_1, X_2, \ldots, X_\mu)$. It may even be zero.

8. The Uncertainty Principle

As noted in the introduction, the concepts of entropy, variance, and effective volumes are very closely related to one of the most important principles of quantum mechanics—the uncertainty principle.

For a quantitative expression of the uncertainty principle, the variances (or standard deviations) of canonically coupled quantities are usually employed as measures of their uncertainty. We shall consider initially the case of a one-dimensional particle and shall examine two quantities: the coordinate x and momentum p‡. Heisenberg's uncertainty principle is expressed in terms of Weyl's inequality:

$$D_x D_p \geqslant \tfrac{1}{4}(\text{at. units}) \qquad (8.1)$$

where D_x and D_p are the variances of the coordinate and the momentum respectively. Suppose that D_x is "small" which corresponds to the localisation of the coordinate of the particle; then the variance of the momentum must be large, i.e. $D_p \geqslant 1/4D_x$. Otherwise inequality (8.1) will not hold. However, the method of expressing the uncertainty principle in the form of inequality (8.1) suffers from an important disadvantage.

Suppose that is it known that the particle is localised in fairly small regions around two or a greater (finite) number of centres. The variance of this distribution can have any value, as can be seen, for example, from Fig. 4. Weyl's inequality will not rule out in this case the possibility of determining the momentum with a fairly high degree of accuracy. Nevertheless this type of situation is in reality excluded. The uncertainty principle formulated in the entropy form [2,32,33],

$$H_x + H_p \geqslant C > 0 \qquad (8.2)$$

shows that in our example the distribution density of the momentum not only cannot be fully concentrated in a small region around a certain point but it cannot be localised even in the vicinity of a finite number of points.

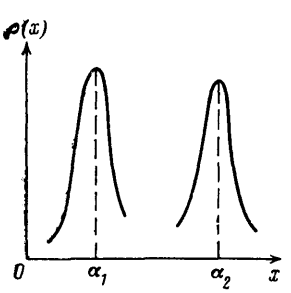


Figure 4.

Indeed if the particle is localised in a small region Ω around a certain point, then $f(x) > 1$ for $x \in \Omega$ and $f(x) = 0$ for $x \notin \Omega$. Therefore $f(x)\ln f(x) \geqslant 0$ and consequently the entropy integral is negative. The greater the degree of localisation the smaller the entropy and the smaller the

‡If the state of the one-dimensional particle in the coordinate representation is described by a wave function $\psi(x)$, then in the momentum representation it corresponds to the wave function $\psi(p) = (1/\sqrt{2\pi})\int \psi(t)e^{-ipx}dx$.

effective size. It follows from inequality (8.2) that the quantities H_x and H_p cannot assume simultaneously values so small that $H_x + H_p < C (C > 0)$.

In the general case the functionals D and H do not define one another unambiguously. However, they are linked to one another by inequality (1.6). It follows from this inequality that the expression of the uncertainty principle in the entropy form (8.2) is stronger than in the variance from (8.1), since

$$0 < C \leqslant H_x + H_p \leqslant \frac{1}{2} \ln (2\pi e D_x D_p). \qquad (8.3)$$

This factor in fact makes it possible to investigate certain general physical aspects of the uncertainty principle which are not embraced by Weyl's inequality.

The problem of the value of the constant $C (C > 0)$ in inequality (8.2) is of fundamental importance. If $C = \ln \pi e$, the implication is that the two characteristics of uncertainty in the phase space $D_x D_p$ and $v_x v_p / 2\pi e$ assume identical minimum values. There is every reason to suppose that this does indeed happen and that the minimum uncertainty is achieved with Gauss functions. However, there is at present no rigorous proof of this assertion.

The derivation of inequality (8.1) has been frequently discussed in the literature and therefore we shall not consider it in detail. We shall only mention that, in order to prove Weyl's inequality, it is sufficient to employ the most general properties of the Fourier transformation in the Gilbertian space $L_2(-\infty, \infty)$§.

We shall consider briefly the proof of inequality (8.2). Let $\varphi(x) \in L_r(-\infty, \infty)$ and let $\psi(t)$ be its Fourier transform. Then $\psi(p) \in L_q(-\infty, \infty)$, where $q = r/(r-1)$. Babenko[34] showed that for even values of q the following inequality holds

$$\| \psi \|_q \leqslant M(r) \| \varphi \|_r,$$

where

$$M(r) = \left(\frac{r}{2\pi}\right)^{\frac{1}{2r}} \left(\frac{q}{2\pi}\right)^{\frac{1}{2q}}.$$

Using the Riesz theorem, the present authors showed[32] that for $r \in [4/3, 2]$ we have

$$\| \psi \|_q \leqslant M^{2(r/2-1)} \| \varphi \|_r, \qquad (8.4)$$

where $M = 0.592$¶. On taking logarithms in inequality (8.4), we obtain

$$\frac{1}{q} \ln \int |\psi|^q \, dp \leqslant 2 (2/r - 1) \ln M + \frac{1}{r} \ln \int |\varphi|^r \, dx. \qquad (8.5)$$

Consider the function

$$\chi(r) = \frac{1}{q} \ln \int |\psi|^q \, dp - \frac{1}{r} \ln \int |\pi|^r \, dx - 2 \left(\frac{2}{r} - 1\right) \ln M.$$

§Henceforth the following notation will be employed: $L_r(-\infty, \infty)$ is defined as a set of functions $f(x)$ of a single real variable x for which the values of the integral $\int |f(x)|^r dx = I_r$ are finite. The quantity $(I_r)^{1/r}$ is designated by $\| f(x) \|_r$ and is called the norm of the function $f(x)$.

¶The constant is quoted to within 0.001.

Then it follows from inequality (8.5) that $\chi(r) \leqslant 0$ for $4/3 \leqslant r \leqslant 2$. Moreover, $\chi(2) = 0$. Therefore $\chi'(2 - 0) \geqslant 0$. Formal differentiation of the function $\chi(r)$ leads to the expression

$$\chi'(r) = \frac{1}{r^2} \ln \int |\psi|^q \, dp - \frac{1}{r(r-1)} \frac{\int |\psi|^q \ln |\psi| \, dp}{\int |\psi|^q \, dp} +$$

$$+ \frac{1}{r^2} \ln \int |\varphi|^r \, dx - \frac{1}{r} \frac{\int |\varphi|^r \ln |\varphi| \, dx}{\int |\varphi|^r \, dx} + \frac{4}{r^2} \ln M.$$

Bearing in mind that $\| \varphi \|_2 = \| \psi \|_2 = 1$ we obtain for $r = 2$ the inequality

$$- \int |\psi|^2 \ln |\psi|^2 \, dp - \int |\varphi|^2 \ln |\varphi|^2 \, dx + 4 \ln M \geqslant 0.$$

and hence the entropy expression for the uncertainty principle can be formulated as $H_x + H_p \geqslant C$, where $C \simeq 2.100$.

We have considered hitherto the uncertainty principle in terms of a one-dimensional treatment. We shall now proceed to a real physical system—a quantum-mechanical particle or a system of such particles.

The uncertainty of the position of the coordinates of an n-particle system [in the state $\psi(\mathbf{x}_1, \ldots, \mathbf{x}_n)$] is characterised by the covariance matrix $K(\mathbf{X})$, the general variance $D(\mathbf{X})$, and the entropy $H(\mathbf{X})$. The one-dimensional uncertainty in the direction of the $3n$-dimensional vector $\mathbf{c}$ is expressed by the quantity $[K(\mathbf{X})\mathbf{c}, \mathbf{c}]$ and the "volume" uncertainty is expressed by the quantities $D(\mathbf{X})$ and $H(\mathbf{X})$.

In the momentum representation the same state of the n-particle system is described by the wave function $\tilde{\psi}(\mathbf{p}) = \psi(\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_n)$, which is a Fourier transform of the initial function

$$\tilde{\psi}(\mathbf{p}) = \frac{1}{(2\pi)^{n/2}} \int e^{-i(\mathbf{p}, \mathbf{x})} \psi(\mathbf{x}) \, d\mathbf{x}.$$

The distribution density of the momenta $|\tilde{\psi}(\mathbf{p})|^2$ is also normalised to unity, which makes it possible to treat it as the distribution density of a $3n$-dimensional random quantity $\mathbf{P} = (\mathbf{P}_1, \mathbf{P}_2, \ldots, \mathbf{P}_n)$, where the random three-dimensional vector $\mathbf{P}_j$ corresponds to the momentum of the jth particle. The covariance matrix $K(\mathbf{P})$ of the random vector $\mathbf{P}$ characterises the uncertainty of the positions of the momenta in the n-particle system and the general variance $D(\mathbf{P})$ and the entropy $H(\mathbf{P})$ characterise their "volume" uncertainty.

The above characteristics of multidimensional quantum-mechanical systems based on probability theory permit the formulation of the Heisenberg uncertainty principle directly in the multidimensional form. Indeed, it is possible to prove the validity of the inequalities

$$H(\mathbf{X}) + H(\mathbf{P}) \geqslant \ln (2\pi)^{3n} \qquad (8.6)$$

and

$$D(\mathbf{X}) D(\mathbf{P}) \geqslant (1/4)^{3n} \text{ (at. units)} \qquad (8.7)$$

which constitute natural generalisations of inequalities (8.2) and (8.1) respectively. The uncertainty relations, expressed in terms of the internal and external volumes

$$v(\mathbf{X}) v(\mathbf{P}) \geqslant (2\pi)^{3n} \text{ (at. units)} \qquad (8.8)$$

and

$$V(\mathbf{X}) V(\mathbf{P}) \geqslant (\pi e)^{3n} \text{ (at. units)} \qquad (8.9)$$

follow from inequalities (8.6) and (8.7). All the inequalities (8.6)–(8.9) express the fact that the volume uncertainty of an n-particle system cannot

be fairly small in the coordinate and momentum representations simultaneously. We may note that inequality (8.2) or, what amounts to the same thing,

$$D(\mathbf{X}) - {}^1/_4 D^{-1}(\mathbf{P}) \geqslant 0$$

can be generalised also in terms of the covariance matrices. It is found that the matrix

$$T = K(\mathbf{X}) - {}^1/_4 K^{-1}(\mathbf{P})$$

is positively defined, i.e. for any $3n$-dimensional vectors c we have the inequality

$$(Tc, c) \geqslant 0. \qquad (8.10)$$

It is possible to show that inequality (8.10) follows from the uncertainty relation in the variance form for each pair of canonically coupled variables (one-dimensional variables).

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Institute of Organic Derivatives of the Elements,
USSR Academy of Sciences, Moscow