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D. A. BOCHVAR, I. V. STANKEVICH, and A. L. CHISTYAKOV

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Abstract

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D. A. BOCHVAR, I. V. STANKEVICH, and A. L. CHISTYAKOV

LOCALIZATION ENTROPY AND EXTENT IN A QUANTUM-MECHANICAL SYSTEM

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In joint work with N. P. Gambaryan ([1]), one of us proposed defining the delocalization of a particle in a stationary state of a quantum-mechanical system as the localization entropy, calculated by means of the corresponding eigenfunction of the system. Namely, if $\psi(x_1, y_1, z_1, \dots, x_n, y_n, z_n)$ is a stationary state of a system of n particles, we define the probability distribution density for the position of the i-th particle as

$$\Phi(\tau_i) = \int_{R_{3n-3}} |\psi|^2 \, d\tau_1 \dots d\tau_{i-1} \, d\tau_{i+1} \dots d\tau_n$$

and, further, the localization entropy of the i-th particle in the given stationary state of the quantum-mechanical system as

$$h_i = -\int_{R_3} \Phi(\tau_i) \log \Phi(\tau_i) \, d\tau_i,$$

where R, with the corresponding index, is the space over which the integral is taken, $d\tau_i = dx_i \, dy_i \, dz_i$.

We shall consider systems consisting of $m + k$ particles, where m is the number of fixed particles of one type (for example, positively charged nuclei) and k is the number of identical particles (for example, electrons). In this case the index i may be omitted.

The question arises: to what extent is it natural, with such a definition, to associate the notion of extent?

Since for a quantum-mechanical system one cannot speak of volume in the ordinary sense, various experimental data are used to characterize extent (van der Waals radius, covalent radius, etc.).

In the present article an attempt is made to introduce a certain theoretical characteristic of extent in a quantum-mechanical system.

It is obvious that, under a mathematically reasonable definition of extent, for the simplest distribution laws that admit application of the usual concept of volume, the extent must coincide with the volume in the ordinary sense.

It is easy to show that, in the case of a uniform distribution (with density ρ) specified on some finite region D of a space R, with volume V_D (in the ordinary sense), the localization entropy h, defined as

$$h = -\int_D \rho \log_b \rho \, d\tau,$$

is nothing other than $\log_b V_D$ (b is the chosen base of the logarithms), i.e.,

$$V_D = b^h.$$

Proceeding from the above considerations, we shall now define, in general, the h-extension V_h of a particle in a quantum-mechanical system (in the given state) as

$$V_h = e^h \text{ units of volume.}$$

It is easy to verify that the value of the h-extension is independent of the choice of the base of the logarithm, which indicates the correctness of our definition. In the specific calculations we used the base e.

Let us illustrate the above with several examples.

In the case of such a system as a particle in a one-dimensional potential box of length L, with constant potential inside the box and infinitely high walls, the one-dimensional h-extension in any stationary state is equal to $0.836L$, i.e., the one-dimensional h-extension is somewhat less than the length of the potential box, which is naturally associated with the presence of nodes in all eigenfunctions.

If the walls of the potential box are finite, then, generally speaking, the h-extension will exceed the length of the potential box by some amount depending on the parameters of the potential box and on the stationary state. Thus, for example, for a well depth equal to 1.0 en. units and a width equal to 0.1 length units, the h-extension of the ground state is equal to 4.035 length units.

In ([1]) the value of h was given for the hydrogen atom in the 1s-state with the position of the nucleus fixed; namely, $h = \ln \pi + 3$ (when calculated in atomic units). If in this case the h-extension is interpreted as the volume of a sphere centered at the nucleus, it turns out that its radius is 1.31 Å, which is quite close to the experimental value of the van der Waals radius of hydrogen (equal, according to crystallochemical data, to 1.20 Å). Since the value 1.31 Å refers to an isolated atom, while the value 1.20 Å is of crystallochemical origin, such a result is quite natural.

The calculations of particle entropies in potential boxes were carried out by N. P. Gambaryan and E. S. Bogatova.

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REFERENCES

1. D. A. Bochvar, N. P. Gambaryan, DAN, **131**, 532 (1960).

Note: Figure translations are in progress. See original paper for figures.