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1960

SovietRxiv

Abstract

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A MEASURE OF ELECTRON DELOCALIZATION IN AN ATOMIC-MOLECULAR SYSTEM

(Presented by Academician I. V. Obreimov, December 7, 1959)

On the basis of M. Born's interpretation of the square of the modulus of the wave function of a system of n particles as the probability density of the configuration of the system, it is possible to apply to the description of a quantum-mechanical system the general concept of the entropy of a random variable that has developed in probability theory in recent years.

Let, for example, the Schrödinger equation (not containing time) be given for a system Σ of n particles,

$$\hat{H}\psi = E\psi, \tag{1}$$

where $\psi = \psi(x_1, y_1, z_1, \ldots, x_n, y_n, z_n)$, $\int |\psi|^2 d\tau = 1$, $d\tau = d\tau_1 \ldots d\tau_n$, $d\tau_i = dx_i dy_i dz_i$, and R is the configuration space in which the function ψ is defined.

Then, applying the concept of the entropy of a continuous random variable [1,2], we may define for the stationary state ψ_k of the system Σ the entropy H_k by the equality

$$H_k = -\int |\psi_k|^2 \lg |\psi_k|^2 d\tau, \tag{2}$$

where lg denotes a logarithm to an arbitrarily chosen base, which must be chosen the same when different entropies are compared (just as the origin is also chosen) *.

We regard the quantity H_k as a measure of the uncertainty in the positions of the particles.

In considering atomic-molecular systems, we shall regard the nuclei as fixed in space. In the case of a one-electron system it is quite natural to call the quantity H_k the delocalization of the electron. But in the case of a many-electron system one can also define the quantity h_k for one electron (the wave function is assumed to take account of electron exchange); for this purpose, instead of $|\psi|^2$, i.e., the square of the modulus of the many-electron eigenfunction, we take as the probability density [3,4] **

$$\Phi_k(\tau_i) = \int |\psi_k|^2 d\tau_1 \dots d\tau_{i-1} d\tau_{i+1} \dots d\tau_n. \tag{3}$$

* The chosen definition of H_k could be supplemented on its right-hand side by an additive term, $-\lg l_\tau$, defining the origin on the entropy scale; in principle it is arbitrary, but when entropies are compared it must necessarily be fixed.

** The probability density of finding an electron in a system of n electrons at the point (x_i, y_i, z_i) is equal to $n\Phi_k(\tau_i)$; we define the delocalization calculated per electron. The quantity $\Phi_k(\tau_i)$ is the diagonal matrix element of the corresponding density matrix.

Then

$$h_k = -\int \Phi_k \lg \Phi_k d\tau_i \tag{4}$$

Thus it is possible to determine the delocalization of an electron also in a many-electron system. It is obvious that delocalization, so defined, is a characteristic essential for describing the electronic structure of an atomic-molecular system and, moreover, one whose definition is not connected with any approximate methods of quantum-mechanical calculations*; on the other hand, the numerical value of H_k or h_k, calculated with the aid of some wave function of the system, depends, of course, on whether the wave function used is exact or approximate, and in the latter case—on the degree of approximation. One may further define the delocalization of an electron in an atomic-molecular system with respect to a chosen coordinate or coordinates. Thus, for example, the delocalization of an electron with respect to the coordinates x_i, y_i may be defined, using the probability density

$$\Phi_k(x_i, y_i) = \int \Phi_k(\tau_i)\, dz_i \tag{5}$$

as follows

$$h_{k,x_i,y_i} = \int \Phi_k(x_i, y_i) \lg \Phi_k(x_i, y_i)\, dx_i dy_i. \tag{6}$$

The quantity h_{k,x_i,y_i} does not depend on the choice of the value of the index i $(i = 1, 2 \dots)$, if the original wave function ψ_k takes into account permutations of the electrons, and therefore it may be written simply in the form $h_{k,x,y}$.

These latter quantities make it possible to refine the picture of electron delocalization in atomic-molecular systems.

As an illustration of the definitions introduced, let us present a calculation of the delocalization for several of the simplest systems**.

The delocalization of an electron in the ground state of the hydrogen atom is equal to

$$H_{1s\mathrm{H}} = \ln \pi a_0^3 + 3.$$

The delocalization of an electron in the excited $2s$- and $2p$-states is, naturally, greater than in the ground state; moreover, for the $2s$-state, which has no distinguished direction in space, it is greater than for the $2p$-state. Namely, the values of the entropy integral for an electron in the $2s$- and $2p$-states of the hydrogen atom are, respectively,

$$H_{2s\mathrm{H}} = \ln \pi a_0^3 + 6.966, \qquad H_{2p\mathrm{H}} = \ln \pi a_0^3 + 6.12.$$

It is obvious that in the ground state of the helium ion the delocalization of the electron must be considerably smaller than in the ground state of the hydrogen atom. Indeed, the entropy integral of the electron in the $1s$-state of the helium ion He^+ is equal to

$$H_{1s\mathrm{He}} = \ln \pi a_0^3 + 0.92.$$

The formation of a bond between two hydrogen atoms leads to an increase in the delocalization of the electron: the entropy integral for an electron on the ground molecular orbit of the hydrogen molecule (calculated in the one-electron approximation without taking into account electron interaction by the LCAO method

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* In contrast to characteristics constituting what are called molecular diagrams in quantum chemistry (bond orders, free-valence indices, atomic charges), the very definitions of which depend on the choice of an approximate method of calculation.

** E. S. Bogatova took part in the calculations.

MO with allowance for the overlap integral) is somewhat greater than for an electron in the ground state of the hydrogen atom:

$$H_{1\sigma_{\mathrm{H2}}} = \ln \pi a_0^3 + 3.24.$$

On the antibonding orbital, by contrast, the delocalization is smaller:

$$H_{1\sigma^*_{\mathrm{H2}}} = \ln \pi a_0^3 + 2.75.$$

In calculating the entropy integrals we used natural logarithms,

$$H = -\int |\varphi|^2 \ln |\varphi|^2 \, d\tau.$$

Their value includes the constant $\ln \pi a_0^3$ (a_0 is the Bohr radius), which depends on the choice of system of units.

From the point of view of the concepts defined above, a new approach is possible to a number of problems of the electronic structure of atomic-molecular systems and, in particular, to the problem of conjugation.

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Received
27 XI 1959

CITED LITERATURE

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