CHEMICAL BOND AND ENTROPY OF THE ELECTRON DENSITY DISTRIBUTION IN MOLECULES
II. CHARACTERISTIC OF THE ELECTRON DENSITY DISTRIBUTION IN THE MOLECULAR H$_2^+$ ION

D. A. Bochvar and A. V. Tutkevich

The entropy of the one-dimensional electron density distribution along the axis through the protons has been calculated for the 1s$_g^2$ state of the molecular H$_2^+$ ion. This entropy is somewhat higher than the entropy of the one-dimensional electron density distribution for the 1s state of the hydrogen atom.

In paper [1] we calculated the entropy of the electron density distribution $H$ and the effective molecular volume of the H$_2^+$ ion. It was found that for H$_2^+$ the entropy $H = 3.81$, i.e., considerably lower than that ($H = 4.14$) for the ground state of the hydrogen atom, which, of course, is explained by the presence of a second proton and the formation of a chemical bond. Essential in this connection is that the value of $H$ refers to the electron density distribution in the three-dimensional space.

As seen from the angle of the entropy of the electron density distribution in [2], the results of an analysis regarding conjugation permit the supposition that, although a bond should lead to a decrease in entropy of the three-dimensional distribution, the entropy of some characteristic one-dimensional distribution may, on the other hand, increase during formation of a bond. It was of interest to check this assumption in the simplest case allowing of a sufficiently accurate calculation.* In the present study, using the functions taken from [4], we calculated the entropy $h$ of the one-dimensional electron density distribution along the axis through the protons for the case the H$_2^+$ ion is in the ground state 1s$_g^2$, and the equilibrium distance between the protons equals $R = 2.0$ a.u.

It was found that the value of $h$ for the 1s$_g^2$ state is somewhat larger than the entropy of the one-dimensional electron density distribution for the 1s-state of the hydrogen atom. The values $h(H_2^+)$ and $h(H)$ thus found equal 1.467 and 1.395, respectively. The difference between $h(H_2^+)$ and $h(H)$ equals 0.072.†

Consequently, we may state that our result agrees with the above assumption.

Calculation of the Entropy of the One-Dimensional Electron Density Distribution in the H$_2^+$ Ion

In the elliptic coordinates $(\lambda, \mu, \phi)$

\[
\lambda = \frac{1}{R} \left[ \sqrt{x^2+y^2+(z-R/2)^2} + \sqrt{x^2+y^2+(z+R/2)^2} \right],
\]

*Since wavefunctions of the electron gas model [3] were employed in [2], the results obtained there are, of course, only useful for a comparison.
†This value can be considered a reliable value of the difference $h(H_2^+)-h(H)$.

where $R$ denotes the distance between the protons, the wavefunction of the ground state of the $H^+$ ion has the shape \[4\]:

$$
\Psi(\lambda, \mu, \varphi) = \Lambda(\lambda) M(\mu).
$$

If the density of the probability density distribution of the coordinates $\Psi^2$ is normalized to unity, i.e., if

$$
\int \Psi^2(\lambda, \mu, \varphi) dV = 1, \quad dV = \frac{R^3}{8}(\lambda^2 - \mu^2) d\lambda d\mu d\varphi
$$

then, taking into account Eqs. (1) and (2), we get a nonnegative function $\rho(z)$ ($-\infty < z < +\infty$), which is defined in all points of the axis connecting the protons and is normalized to unity according to [3]:

$$
\int_{-\infty}^{\infty} \rho(z) dz = 1,
$$

where

$$
\rho(z) = 2\pi \int_0^\infty \Lambda^2(\lambda(r, z)) M^2(\mu(r, z)) r dr,
$$

and the dependence of $\lambda$ and $\mu$ on $r$ and $z$ is defined in accordance with [1].

A plot of the function $\rho = \rho(z)$ at $z \geq 0$ for the $1s\sigma_g$ state is shown in Fig. 1.

We calculated the integral

$$
h = -\int_{-\infty}^{\infty} \rho(z) \ln \rho(z) dz
$$

for the ground state $1s\sigma_g$ of the molecular hydrogen ion (distance between the protons $R = 2$ a.u.) and also for the $1s$-state of the hydrogen atom. In the latter case the function $\rho(z)$ has the simple shape:

$$
\rho(z) = \left(|z| + \frac{1}{2}\right) e^{-|z|}
$$

and the integral (5) can be easily calculated:

$$
h = 1 + \ln 2 - \frac{1}{2} e^{\int_1^\infty e^{-t} dt} = 1.395.
$$

The integration necessary for calculating the function $\rho(z)$ and the entropy $h$ was carried out numerically. The functions $\Lambda$ and $M$ in Eq. (2) read

$$
\Lambda(\lambda) = (\lambda + 1)^\nu e^{-\mu} \sum_{r} g_r \left(\frac{\lambda - 1}{\lambda + 1}\right)^r,
$$

and the dependence of $\lambda$ and $\mu$ on $r$ and $z$ is defined in accordance with [1].

A plot of the function $\rho = \rho(z)$ at $z \geq 0$ for the $1s\sigma_g$ state is shown in Fig. 1.