LETTERS TO THE EDITOR

ON THE INTERPRETATION OF SLATER'S APPROXIMATION OF ATOMIC ORBITALS

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In the theory of chemical bonds one assumes in general, (following Slater (1930)), the following form for the eigenfunction of an electron in the atom

$$\psi = N r^{n^\star - 1} \cdot e^{-Z^\star r / n^\star a_0} \cdot Y_{lm}(\vartheta, \varphi), \tag{1}$$

where n^* in this formula denotes the effective quantum number, Z^* is the effective nuclear charge, and $Y_{lm}(\vartheta, \varphi)$ is the angular part of the hydrogen-like function. Some authors of basic monographs on quantum chemistry (Gombash 1953, Eyring, Walter, and Kimball 1954) give an erroneous (in our opinion) interpretation of this approximation which is moreover not in agreement with the views of Slater (1930)[1]. Thus e. g. Gombash (1953) writes:

„...Eigenfunctions (1) are a solution to the problem of the one-electron atom with a potential energy of

$$U = -\frac{Z^* e^2}{r} + \frac{1}{2} e^2 a_0 \frac{n^*(n^* - 1)}{r^2}. \tag{2}$$

...For the electron energy we obtain, by (1) and (2),

$$E = -\frac{1}{2} \frac{Z e^2}{n^{*2} a_0}. \text{"} \tag{3}$$

It may be shown that function (1) is an eigenfunction of problem (2) for eigenvalue (3) if and only if $l = 0$, i. e. for s electrons. Thus, knowing the eigenfunction and the eigenvalue we can uniquely determine the potential corresponding to them from the Schroedinger equation. From this there results for (1) and (3) the following potential:

$$U = -\frac{Z^* e^2}{r} + \frac{1}{2} e^2 a_0 \frac{n^*(n^* - 1) - l(l + 1)}{r^2}. \tag{4}$$

This is in agreement with (2) if and only if $l = 0$.

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[1] The same mistake is contained in Preuss's Tables (1957).

In the cited paper by Slater (1930) the justification for approximation (1) is not the same. On the basis of the results of Zener and the method of Hartree he arrives at the conclusion that the influence of the nodes in the radial port of trial function is not significant. The density distribution for hydrogen-like function and its term of the highest power in r, i. e. (1), is, in general, nearly the same. Slater therefore keeps the most important term of the hydrogen-like function. Eq. (3) is then an approximate expression for the energy. As follows from (4), this formula contains an approximation exept where $n^* = l + 1$.

In the monograph *Quantum Theory of Matter* Slater (1953) goes somewhat further by applying the rules which he gave for Z^* and n^* to hydrogen-like functions. Eq. (3) is then an exact eigenvalue in this approximation.

REFERENCE

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