

A New Approximation Method in the Problem of Many Electrons

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surprising, since reaction (1a) is endothermic. Unfortunately, it is not feasible to extend the measurements below the range of pH used.

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¹ Fricke and Morse, *Phil. Mag.* 7, 129 (1929).

A New Approximation Method in the Problem of Many Electrons

The principles of an approximation method have been recently published by the author for systems consisting of closed shells and of valence electrons.¹ The method consists in treating simultaneously the atom kernels according to Thomas-Fermi and the valence electrons according to Schroedinger. It is possible to obtain an approximated Schroedinger equation for the valence electrons from the variation principle for the whole energy. There are no additional exclusion conditions for the valence electrons, arising from the states occupied by paired electrons. But the potential field for the valence electrons contains, besides the familiar electrostatic action of the charge of closed shells on the valence electrons, an additive term of the form $\partial T/\partial \rho$, where T is the kinetic energy per unit of volume of the paired electrons, ρ their density. (The theory of Thomas-Fermi gives $\partial T/\partial \rho = (\hbar^2/8m)[(3/\pi)\rho]^{2/3}$.)

There is nothing to prevent the use of better distributions of electrical density ρ than those obtained from the Thomas-Fermi method. But even the use of the latter gives the right order of magnitude, e.g., for a univalent ion the potential function is, in the region from $r = \infty$ to $r = r_0 (= 4.6\text{\AA})$, the pure Coulomb potential, i.e., $-e^2/r$, and then the value $eV + \partial T/\partial \rho$ is constant, being equal to $-e^2/r_0$.² If we put the valence electron into this potential hole, then its energy will be somewhat higher than the potential $-e^2/r_0$ at the bottom of the hole, namely, -3.1 volts. For caesium, where the application of the Thomas-Fermi solutions for the atomic kernels is better justified than in other cases, the experimental value is -3.9 volts. Without an additive potential and without the exclusion principle the valence electron would fall into the K -shell with many thousand volts of ionization energy.

The practical value of the method lies in that it allows us to obtain the entire potential function $eV + \partial T/\partial \rho$ from experimental data. The potential field and the corresponding eigenfunctions of the valence electrons can be obtained from the spectra so that the lowest state of the valence electrons corresponds to the lowest level obtained in the potential field without any additional conditions. These data enable us to enter upon the problem of boundary. Thus both the electrostatic and the exclusion principle

influences of the atomic kernels on all the valence electrons are taken into consideration and the Ritz method may be used for the valence electrons alone.

For potassium a preliminary calculation suggested the expression $-1/r + (2.74/r)e^{-1.10r}$ for the complete potential for the valence electron, and the corresponding eigenfunction $\psi \sim e^{-0.29r}$ (approximated by means of the Ritz method expressed in atomic units). Then the Heitler-London method will give for K_2 an equilibrium distance of about 4\AA (exp.: 3.9\AA) and an energy of about 37 percent of the experimental value. It is this result which agrees very well with the results obtained by James³ for Li_2 who considered the effects produced by closed shells in detail. We must also assume, that the greater part of the binding energy appears first in higher approximations. The accordance of the results of Rosen and Ikehara⁴ and of others with experimental data must be ascribed to their being arbitrary assumptions. The decrease in the value of the triplet under the influence of the closed shells, emphasized by James, comes quite naturally in our calculation, for the additional potential changes not only the Coulomb interaction but also the exchange integrals. A diminution in the exchange integrals produces an increase in the singlet and a decrease in the triplet term. However, our having obtained more favorable results than may have been expected from James's calculations may be explained first by our having omitted the mutual interaction between atomic kernels and, secondly, by our having partially included the polarization forces with the closed shells in our empirical potential function.

For KH a rough approximation including, however, the homopolar and ionic states gives an equilibrium distance of about 2\AA and an energy of -0.8 volt. The share of the ionic state in the molecule is 80 percent. The difference as compared with the experimental value of -2.06 volts must be again explained by polarization forces. In the extreme case of pure ionic binding we can avail ourselves of the result of Hylleraas⁵ for the internal polarization interaction of H^- . Then, in the subsequent calculation, only the resulting density (not the eigenfunctions) of the H^- atom plays a part. This was assumed approximately as $\sim e^{-11r/8}$. Thus we find an equilibrium distance of 1.9\AA and a binding energy of 1.95 volts.

A detailed account of the subject will shortly appear in the *Acta Physicochimica U. R. S. S.* The approximation method is being further elaborated for the alkaline molecules and its hydrides in this institute. The method shall be extended for polyvalent atoms.

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November 26, 1934.

¹ H. Hellmann, *Comptes rendus de l'Académie des sciences de U.R.S.S.* In print.

² A. Sommerfeld, *Zeits. f. Physik* 78, 283 (1932).

³ M. James, *J. Chem. Phys.* 2, 794 (1934).

⁴ N. Rosen and S. Ikehara, *Phys. Rev.* 43, 5 (1933).

⁵ E. A. Hylleraas, *Zeits. f. Physik* 65, 209 (1930).