Approximate solutions of the Thomas-fermi equations for molecules.

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APPROXIMATE SOLUTIONS OF THE THOMAS-FERMI EQUATION FOR MOLECULES. II

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Synopsis

The method of solving the Thomas-Fermi equation, developed in a previous paper [1]), is applied to the H_2O-molecule. The electronic density is calculated.

A proof is given that the Thomas-Fermi method, ~~or generally any method, which treats the electrons as a continuous cloud of electricity obeying the Poisson equation,~~ gives a zero value for the electric dipole moment of any molecule.

§ 1. *The H_2O-molecule.* In a previous paper [1]) the equation of Thomas and Fermi was solved approximately in an analytic form for atoms and for the N_2-molecule. In this paper the same method is applied to the H_2O-molecule. The Thomas-Fermi equation reads:

$$\Delta V = 4\pi\sigma e V^{3/2} \tag{1}$$

where V is the electric potential

               e is the electron charge

               $\sigma = 2^{3/2}/3\pi^2 \, e^{3/2} \, a_0^{3/2}$

               a_0 is the radius of the first electron orbit of the hydrogen atom.

For the H_2O molecule V is written as a sum of three terms:

$$V = V_0(r_1) + V_H(r_2) + V_H(r_3) \tag{2}$$

where r_1 is the distance from the O-atom and r_2, resp. r_3 are the distances from the first, resp. the second H-atom. The following new variables are introduced:

$$\varphi_0 = (r_1/8e) \, V_0 \, (r_1) \tag{3}$$

$$\varphi_H = (r_2/e) \, V_H(r_2) \text{ resp. } = (r_3/e) \, V_H(r_3) \tag{4}$$

$$x_1 = r_1/\mu_0 \tag{5}$$

$$x_2 = r_2/\mu_H, \; x = r_3/\mu_H$$

$$\mu = (4\pi\sigma)^{-2/3} \, e^{-1} \, Z^{-1/3}$$

Z is the nuclear charge. The introduction of these varaibles in (1) yields:

$$64\frac{\varphi_0''(x_1)}{x_1} + \frac{\varphi_H''(x_2)}{x_2} + \frac{\varphi_H''(x_3)}{x_3} = \left[16\frac{\varphi_0(x_1)}{x_1} + \frac{\varphi_H(x_2)}{x_2} + \frac{\varphi_H(x_3)}{x_3}\right]^{3/2} \quad (6)$$

Now equation (6) is separated in such a way as to yield equations which are approximately linear. By trial and error it was found that the following equations give good results:

$$4\varphi_0''(x_1) = \sqrt{A}\, x_1^{5/3}\, \varphi_0(x_1)/x_1^{5/6} \quad (7a)$$

$$\varphi_H''(x_2) = \sqrt{A}\, \varphi_H(x_2) \quad (7b)$$

$$\varphi_H''(x_3) = \sqrt{A}\, \varphi_H(x_3) \quad (7c)$$

where $\qquad A = 16\varphi_0(x_1)/x_1 + \varphi_H(x_2)/x_2 + \varphi_H(x_3)/x_3$

Combination of (7a, b, c) yields (6).

The factor $\sqrt{A}x_1^{5/3}$ proves to be reasonnably constant throughout the molecule. This was ascertained by substituting the atomic functions for φ_0 and φ_H, which gives a sufficient approximation. The factor $\sqrt{A}$ is reasonnably constant near the H-atoms, where the function φ_H is important. A check was obtained by trying a different equation instead of (7a), viz.:

$$4\varphi_0''(x_1) = \sqrt{A x_1^{4/3}}\, \varphi_0(x_1)/x_1^{2/3} \quad (7a)'$$

The factor $\sqrt{A x_1^{4/3}}$ shows a larger fluctuation in the molecule than the factor $\sqrt{A x_1^{5/3}}$, as used in (7a). However, the final results obtained by (7a) and (7a)' differ only slightly. Apparently, slight variations in the factor, which is treated as a constant, do not influence the results.

The solution of (7a) is:

$$\varphi(x_1) = C\sqrt{x_1}\, K_{6/7}\left(\tfrac{6}{7}\sqrt[4]{A x_1^{5/3}}\, x^{7/12}\right) \quad (8)$$

where $K_{6/7}$ is the modified Bessel function of the second kind of order 6/7. It was obtained by interpolation between $K_{3/4}$ and K_1.

The approximately constant factor $\sqrt{A x_1^{5/3}}$ has the value 2,7. The factor C was chosen in such a way that the potential approximates the potential of atomic O near the O–nucleus: $C = 22{,}61$.

In a similar way the solution of (7a)' is:

$$\varphi(x_1) = C\sqrt{x_1}\, K_{3/4}\left(\tfrac{3}{4}\sqrt[4]{A x_1^{4/3}}\, x^{2/3}\right) \quad (9)$$

with: $\sqrt{A x_1^{4/3}} = 2{,}6$

and $\qquad C = 2{,}49 . \sin \tfrac{3}{4}\pi/(\pi/2)$.

The solution of (7b, c) is:

$$\varphi(x) = C\, e^{-\sqrt[4]{A}x} \quad (10)$$

with $\sqrt{A} = 1{,}1$ and $C = 0{,}98$.

From the solution of (1) obtained in this way, the electronic density ϱ was calculated from

$$\varrho = \sigma V^{3/2} \tag{11}$$

The results are given in fig. 1. In this figure curves of constant electronic density are given. Fig. 1a shows these curves in a plane through the atomic nuclei. The distance H–O is 0,958 Å, OA = 0,587 Å, HA = 0.758 Å. Only the left half of the plane is reproduced, because of the symmetry of the H_2O molecule. Figures 1b and 1c represent planes parallel to the plane of the atomic nuclei at distance of 0,2525 resp. 0,505 Å. In order to facilitate the orientation the projection of the H- and O-nuclei in these planes is given too.

§ 2. *Electric dipole moments*. From the electronic charge distribution, as calculated in the previous paragraph, the electric dipole moment of the molecule may be calculated. However, it may be shown generally that for any molecule the electronic cloud, as calculated by the Thomas-Fermi method, yields a zero value for the electric dipole moment. This proof will be given.

Consider a molecule consisting of a number of atomic nuclei with charges Z_i at distances $\mathbf{r}_i$ from an arbitrarily chosen center of coordinates and of an electronic cloud distributed according to the Thomas-Fermi equation. Now the electric dipole moment of the electron cloud may be defined as

$$\mathbf{M} = - e \int \varrho \mathbf{r} \, dv \tag{12}$$

dv is an element of volume.

The minus sign occurs because of the negative charge of the electrons. Substitution of the Poisson-equation:

$$\Delta V = + 4\pi\varrho e \tag{13}$$

leads to:

$$\mathbf{M} = - (4\pi)^{-1} \int \mathbf{r} \, \Delta V \, dv \tag{14}$$

Green's equation is applied to the space between a large sphere (radius R) with its center at the center of coordinates and a number of small spheres (radii ϱ_i) with their centers at the atomic nuclei. Green's equation may then be written as

$$\int (x\Delta V - V\Delta x) \, dv = \oint (x \, \mathrm{grad} \, V - V \, \mathrm{grad} \, x) \, df \tag{15}$$

where x is the x-component of $\mathbf{r}$ and where the integration in the right hand member is extended over the surfaces of the large sphere and the small spheres.

As $\Delta x = 0$ we conclude that:

$$M_x = - (4\pi)^{-1} \int x \, \Delta V \, dv = - 1/4\pi \oint (x \, \mathrm{grad} \, V - V \, \mathrm{grad} \, x) \, df \tag{16}$$

Now, far from the atomic nuclei, where the electron cloud may be treated as resulting from an atom with a nuclear charge equal to that of the
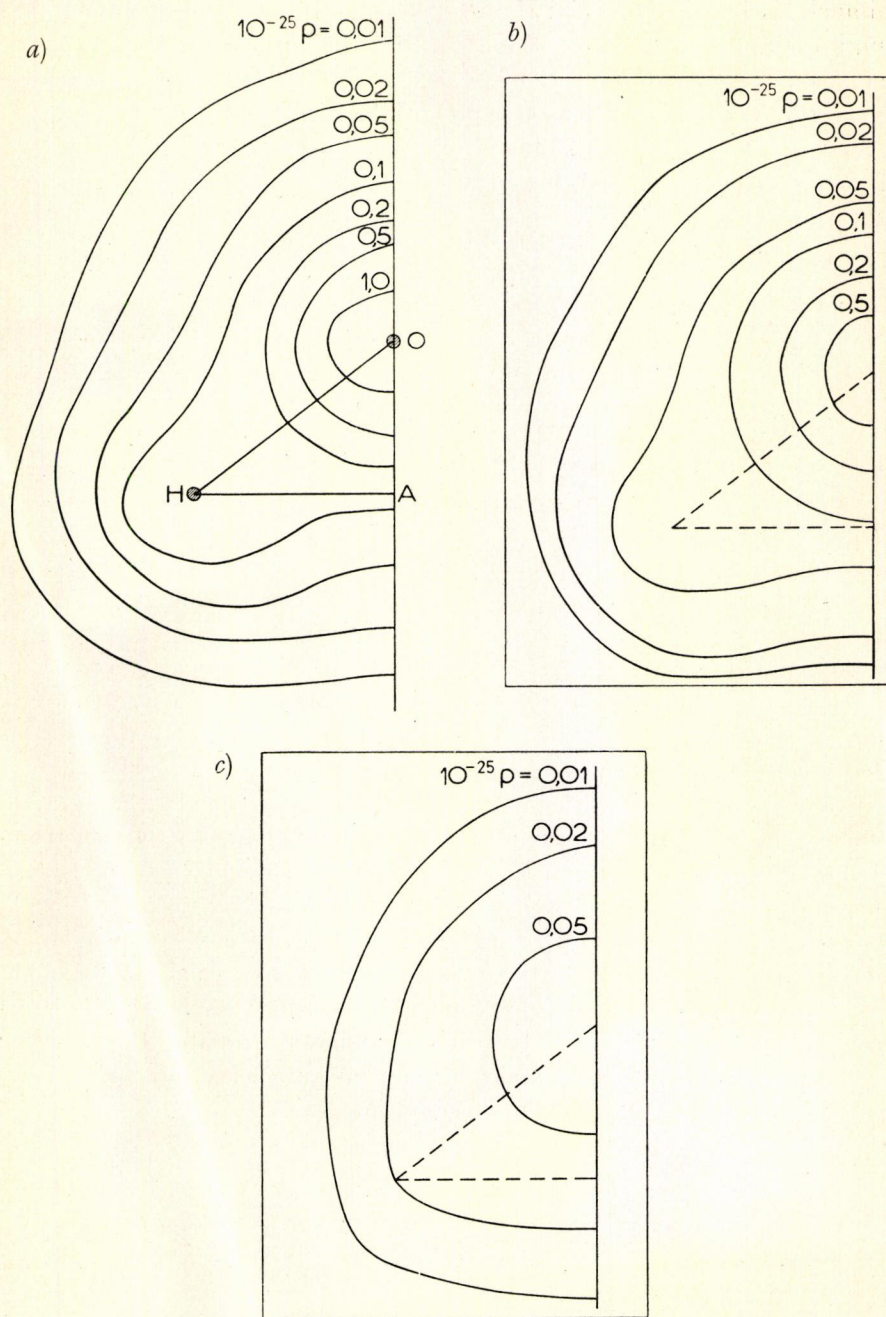
Fig. 1. Electron density in the H_2O-molecule in cm^{-3}

a) In the plane of the atomic nuclei.

b) In a plane parallel to and at a distance of 0,2525 Å from *a*).

c) In a plane parallel to and at a disatnce of 0,505 Å from *a*).

combined nuclei, the potential $V \propto 1/r^{3/2}_i$, as may be seen from Sommerfeld's asymptotic approximation [1]). If follows that the surface integral over the large sphere gives a zero result for $R \to \infty$.

Near the ith atomic nucleus the potential V is approximately equal to $V = Z_i e/\varrho_i$, where ϱ_i is the distance from that nucleus.

It follows that for $\varrho_i \to 0$ the surface integral over the ith small sphere is equal to:

$$\oint x \operatorname{grad} V \, \mathbf{df} = (Z_i e/\varrho_i^2) \, x_i \int \mathrm{d}f = 4\pi Z_i \, e x_i \tag{17}$$

where x_i is the x-coordinate of the ith atomic nucleus.

And

$$\oint V \operatorname{grad} x \, \mathbf{df} = (Z_i e/\varrho_i) \int \mathbf{i} \, \mathbf{df} = 0 \tag{18}$$

where $\mathbf{i}$ is the unit vector in the x-direction.

It follows from (16), (17) and (18) that

$$\mathbf{M} = - e \, \Sigma_i \, Z_i \, \mathbf{r}_i \tag{19}$$

On the other hand the electric dipole moment of the atomic nuclei is:

$$\mathbf{M} = + e \, \Sigma_i \, Z_i \, \mathbf{r}_i \tag{20}$$

It follows from (19) and (20) that the electric dipole moment of a molecule is zero. This result is of course in contradiction with experiment. It may be pointed out, however, that the electric dipole moment is due to a second order effect. Therefore the charge distribution as given in fig. 1 may be a good approximation notwithstanding the fact that it yields a zero dipole moment. This was found in practice too. Very slight changes in the electronic distribution result in relatively large differences in the values of the electric dipole moment as found by numerical integration.

On the other hand the question arises what causes the electric dipole moment in actual molecules. It follows from our discussion that a model containing a continuous electron cloud governed by the classical Poisson-Thomas Fermi equation can never yield non zero dipole moments. Probably the fact that the electron is a point charge subject to quantum laws is the cause of non zero dipole moments. For the water molecule a model in accordance with these principles was given by Lennard Jones and Pople [2]).

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