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DIPOLE MOMENTS IN THOMAS–FERMI–DIRAC AND THOMAS–FERMI THEORIES

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It is shown that the electronic contribution to the dipole moment, calculated from a solution to the Thomas–Fermi–Dirac or Thomas–Fermi equations, should be equal and opposite to the nuclear contribution. Thus, the Thomas–Fermi–Dirac and Thomas–Fermi theories predict vanishing dipole moments for all molecular systems.

Recently, we have been performing calculations of molecular electronic charge distributions according to the Thomas–Fermi–Dirac theory. Our method [1] permits treatment of any cylindrically symmetric molecule; only for homopolar diatomic systems [2, 3] have accurate solutions to the TFD equation been presented so far. For the heteropolar diatomic molecules we treated, we found an electric dipole moment (nuclear minus electronic contributions) of zero, within the estimated accuracy of our calculations. In the present article, it is shown that the moment should be exactly zero for the TFD density of a neutral system.

Brinkman and Peperzak [4], after finding zero moments from Thomas–Fermi calculations on H_2O, presented a proof that the Thomas–Fermi (TF) density always gives zero moments. The proof has been criticized [5], since it assumes that the potential goes as r^{-4} when r, the distance from the nuclei, is large. This assumption permits one to state that a certain integral over a sphere of radius r approaches zero as r approaches infinity. However, assuming that the potential goes as r^{-4} is equivalent to assuming the nonexistence of a dipole moment. The Thomas–Fermi–Dirac (TFD) electron density is finite in extent, so that integrals over infinitely large surfaces will not occur in our proof. Having proved the theorem for TFD, we will show how it may be extended to cover TF.

In our proof, we will require some results given by Sheldon [2]. Some of his proofs will also be repeated in a notation more convenient for our use. In the TFD

theory, the electron density ρ is chosen to minimize the energy functional

$$W = \int dr(e\rho V_N + \kappa_k \rho^{5/3} - \kappa_a \rho^{4/3})$$
$$+ \tfrac{1}{2}e^2 \int dr_1 \int dr_2 \, \rho(r_1)\rho(r_2)|r_1 - r_2|^{-1}, \qquad (1)$$

with the normalization constraint

$$N = \int dr\rho . \qquad (2)$$

Here, V_N is the potential due to the nuclei, $\kappa_k = \tfrac{3}{10}(3\pi^2)^{2/3}e^2 a_0$, $\kappa_a = \tfrac{3}{4}(3/\pi)^{1/3}e^2$, and N is the number of electrons. Let nucleus A, with charge Z_A, be located at r_A, with

$$\sum_M Z_M = N, \qquad (3)$$

for a neutral system. By making $W - \lambda N$ stationary, with λ a Lagrange multiplier, one finds

$$\tfrac{5}{3}\kappa_k \rho^{2/3} - \tfrac{4}{3}\kappa_a \rho^{1/3} + e\Phi = \lambda , \qquad (4)$$

where

$$\Phi(r) = V_N(r) + e \int dr' \rho(r')|r - r'|^{-1} . \qquad (5)$$

Sheldon [2] shows one must consider the possibility of a discontinuous solution, i.e., $\rho = 0$ outside a boundary surface C.

The boundary is chosen to make the energy a

minimum, by considering another solution, differing slightly from the first, and being bounded by a surface c. Its properties are distinguished by primes. Letting subscripts C and v refer to the volumes within C and between C and c respectively, Sheldon noted that

$$W' - W = W'_C - W + W'_v = \lambda(N - N'_C) + W'_v \qquad (6)$$

because of the stationary principle obeyed by the first solution within C. Since v is small,

$$W'_v = \int_v dr\rho(\kappa_k \rho^{2/3} - \kappa_a \rho^{1/3} + e\Phi_1)$$

$$\approx N'_v(\kappa_k \rho^{2/3} - \kappa_a \rho^{1/3} + e\Phi_1), \qquad (7)$$

where $N'_v = N - N'_C$. Now, using (4) and (7) in (6),

$$W' - W = N'_v(-\tfrac{2}{3}\kappa_k \rho^{2/3} + \tfrac{1}{3}\kappa_a \rho^{1/3}).$$

This will be negative if $\rho^{1/3}$ is greater than $\tfrac{1}{2}\kappa_a/\kappa_k$. Therefore, the boundary surface is defined by

$$\rho_C = (\tfrac{1}{2}\kappa_a/\kappa_k)^3. \qquad (8)$$

The TFD equations, then are

$$\nabla^2\Phi_1 = -4\pi e\rho, \qquad \rho \geqslant \tfrac{1}{2}\kappa_a/\kappa_k; \qquad (9a)$$

$$\nabla^2\Phi_1 = 0, \qquad \rho < \tfrac{1}{2}\kappa_a/\kappa_k, \qquad (9b)$$

where Φ_1 is given in terms of ρ by eq. (4). The boundary conditions are, for a neutral system,

$$\Phi_1 \to 0 \qquad \text{as} \quad r \to \infty,$$

$$\Phi_1 \to -Z_M e/r_M \quad \text{as} \quad r_M \to 0, \qquad (10)$$

where r_M is the distance to nucleus M. Eqs. (9) are actually satisfied everywhere that the nuclear charge density vanishes.

If eq. (9a) is used in eq. (2), with the volume of integration the volume of the molecule, excluding small spheres centered at the nuclei, Green's theorem may be used to give a surface integral:

$$N = -(1/4\pi e) \int_S \nabla\Phi_1 \cdot dS. \qquad (11)$$

The contribution of the sphere centered on nucleus M is Z_M. This means, because of the neutrality condition (2), that the surface integral over the boundary of the

molecule is zero. According to (4), Φ_1 is constant on the boundary, i.e., the boundary is an equipotential, so that $\nabla\Phi_1$ is normal to the boundary, and the normal component of $\nabla\Phi$ is of the same sign at all points on the boundary. Since the surface integral of $\nabla\Phi \cdot dS$ vanishes, the normal component of $\nabla\Phi_1$ is zero on the boundary, and

$$\nabla\Phi_1 = 0 \quad \text{on the boundary of the molecule}. \qquad (12)$$

Outside the boundary, ρ vanishes. Since there are no lines of force extending out of the molecule, one can integrate Φ_1 to infinity, starting at the boundary, to show $\Phi_1(\infty) = \Phi_1(\text{boundary})$. Then, using (10),

$$\Phi_1 = 0 \quad \text{on the boundary of the molecule}. \qquad (13)$$

Inserting (8) and (13) in (4), we have

$$\lambda = -\tfrac{1}{4}\kappa_a^2/\kappa_k. \qquad (14)$$

The electronic contribution to the dipole moment in the x direction is

$$\int x\rho dr = -(1/4\pi e) \int x\nabla^2\Phi_1 \, dr$$

$$= -(1/4\pi e) \int [\nabla^2(x\Phi_1) - 2d\Phi_1/dx] \, dr, \qquad (15)$$

where we integrate over the region where ρ is non-zero, except for small volumes around the nuclei. If these volumes are taken as small cylinders of radius R with axes in the x direction, $d\Phi_1/dx$ may be integrated immediately over x, with y and z fixed, to give Φ_1 at the limits of the integration, which may be the boundary of the molecule, or a face of a small cylinder. In the former case, $\Phi_1 = 0$; the contributions of the faces give zero as $R \to 0$. Converting the remainder of (15) to a surface integral, we have

$$\int x\rho dr = (1/4\pi e) \int_S \nabla(x\Phi_1) \cdot dS. \qquad (16)$$

The contribution of the outer boundary surface vanishes because of (12) and (13). The contribution of the cylinder about nucleus M may be calculated exactly as follows.

Let the cylinder have radius R and extend from $x = \zeta_1$ ($\zeta_1 < x_M$) to $x = \zeta_2$ ($\zeta_2 > x_M$). Then the surface integral of $\nabla(x\Phi_1) \cdot dS$ is

$$\int_{\substack{0 \\ (x=\zeta_2)}}^{R} 2\pi r dr(-dxV/dx) + \int_{\substack{0 \\ (x=\zeta_1)}}^{R} 2\pi r dr(dxV/dx)$$

$$+ \int_{\substack{\zeta_1 \\ (r=R)}}^{\zeta_2} 2\pi r dx(-dxV/dR)$$

$$= 2\pi e Z_M \{-2[(\zeta_2 - x_M)^2 + R^2]^{1/2} + 2[(\zeta_1 - x_M)^2 + R^2]^{1/2}$$

$$+ [2\zeta_2 - x_M][\zeta_2 - x_M][(\zeta_2 - x_M)^2]^{-1/2}$$

$$- [2\zeta_1 - x_M][\zeta_1 - x_M][(\zeta_1 - x_M)^2]^{-1/2}\},$$

after some algebra. Note that

$$[(\zeta_1 - x_M)^2]^{1/2} = |\zeta_1 - x_M| = x_M - \zeta_1$$

and $[(\zeta_2 - x_M)^2]^{1/2} = \zeta_2 - x_M$. Letting R approach 0, and ζ_1, and ζ_2 approach x_M from the left and the right, the first two terms in the above integral vanish, and one obtains

$$2\pi Z_M [(2\zeta_2 - x_M) + (2\zeta_1 - x_M)] \rightarrow 4\pi Z_M x_M e.$$

Now the total dipole moment is

$$-e \sum_M Z_M x_M + e \int x\rho dr = 0. \tag{17}$$

Therefore, the net dipole moment for the Thomas–Fermi–Dirac electron density vanishes. To extend this result to the Thomas–Fermi electron density, we have only to note the well-known fact that the TFD model goes over to the TF model when electronic exchange energy is neglected. This corresponds to neglecting the third term in (1), or to putting $\kappa_a = 0$. The surface C is at infinity, and $\rho_C = 0$ [eq. (8)]. Now all the results above are independent of the value of κ_a. There-

fore, the result (17) holds for the TF model as well. It also holds for modifications like that of Gombás [6, section 11], which include some of the effect of correlation, but involve a change in the value of κ_a.

It is interesting to note that the chemical potential [6, pp. 38, 58] of the Thomas–Fermi atom is zero for all neutral atoms. In the TFD theory, the chemical potential is

$$\partial W/\partial N = \delta W/\delta N = -\lambda,$$

which also has the same value $(-\frac{1}{4}\kappa_a^2/\kappa_k)$ for all neutral systems. Thus, there is no tendency for charge transfer from one atom to another: all atoms have the same electronegativity. This helps to explain the absence of dipole moments.

In our calculations, as in calculations performed by other methods, the errors in the electron density are likely to be largest on the periphery. The density at the periphery has a great effect on the expectation value of x, because of the weighting by the operator. Thus, large errors are likely to occur in calculations of dipole moments. The deviation of the electronic contribution to the dipole moment from the nuclear contribution should be interpreted as a measure of the numerical error in the calculation, since we have shown that the exact TFD or TF density must give a net dipole moment of zero.

References

[1] J. Slezak and J. Goodisman, to be submitted for publication.
[2] J.W. Sheldon, Phys. Rev. 99 (1955) 1291.
[3] J. Goodisman, Phys. Rev. 3 (1971) 1819.
[4] H.C. Brinkman and B. Peperzak, Physica 21 (1955) 48.
[5] N.H. March, Advan. Phys. 6 (1957) 1, see p. 44.
[6] P. Gombás, Die statistische Theorie des Atoms und ihre Anwendungen (Springer, Berlin, 1949).