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Oscillations in the Thomas-Fermi-Dirac Electron Density

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It is shown that there can be no local maxima (except at nuclei) in the electron density predicted by models, such as the Thomas-Fermi-Dirac theory, which make the electron density a monotonic function of the electrostatic potential.

Key words: Density oszillations – Thomas-Fermi-Dirac model.

It is well known [1] that the Thomas-Fermi and Thomas-Fermi-Dirac models predict, for atoms, an electron density lacking the oscillations associated with shell structure. We have been interested in assessing the utility of these models for calculation of molecular electron densities. In this note, we show that, for a molecule, these models cannot give rise to local maxima in the electron density, or to points in space at which the electron density is constant along one or two perpendicular spatial directions and a maximum in those remaining, except at a nucleus (where the Thomas-Fermi-Dirac electron density is infinite). Hohenberg and Kohn [2] have discussed the impossibility of density fluctuations by considering properties of the polarizability in momentum space.

Here, we prove the impossibility of local maxima from the condition that the electron density ϱ be a monotonic function of the electrostatic potential Φ. In the Thomas-Fermi-Dirac theory

$$\varrho = f(\Phi) = \left[\frac{2\kappa_a}{5\kappa_k} + \left(\frac{-3e\Phi}{5\kappa_k} + \frac{16\kappa_a^2}{100\kappa_k^2}\right)^{\frac{1}{2}}\right]^3$$

where κ_a and κ_k are constants. It is easily seen that $f(\Phi)$ is monotonic.

Suppose that, at some point where ϱ is finite, one has

$$\partial\varrho/\partial x = \partial\varrho/\partial y = \partial\varrho/\partial z = 0 \tag{a}$$

and

$$\partial^2\varrho/\partial x^2 \leqq 0; \quad \partial^2\varrho/\partial y^2 \leqq 0; \quad \partial^2\varrho/\partial z^2 \leqq 0\,. \tag{b}$$

Since $\partial\varrho/\partial x = (df/d\Phi)(\partial\Phi/\partial x)$, we have

$$\partial\Phi/\partial x = \partial\Phi/\partial y = \partial\Phi/\partial z = 0\,.$$

Since

$$\frac{\partial^2\varrho}{\partial x^2} = \frac{d^2 f}{d\Phi^2}\left(\frac{\partial\Phi}{\partial x}\right)^2 \quad \frac{df}{d\Phi}\left(\frac{\partial^2\Phi}{\partial x^2}\right)$$

and the first term vanishes, the conditions (b) imply

$$\frac{df}{d\Phi}\left(\frac{\partial^2\Phi}{\partial x^2}+\frac{\partial^2\Phi}{\partial y^2}+\frac{\partial^2\Phi}{\partial z^2}\right)\leqq 0\,.$$

But $df/d\Phi$ is positive, and $\nabla^2\Phi$ is positive since the potential satisfies the Poisson equation.

Therefore, (a) and (b) cannot hold. Thus, local maxima in ϱ are impossible (except at the nuclei), and there can be no density fluctuations.

References

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