PHYSICAL REVIEW A

GENERAL PHYSICS

THIRD SERIES, VOLUME 24, NUMBER 5 NOVEMBER 1981

Thomas-Fermi atom in n dimensions

G. F. Kventsel and J. Katriel

Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

(Received 24 February 1981)

The n-dimensional Thomas-Fermi equation is derived and some of its properties are studied. An analytic solution is obtained in two dimensions for both neutral atoms and positive ions. It is shown that for $n \geq 4$ the density is too singular at the origin to be normalizable.

The Thomas-Fermi model[1] had been considered a crude, virtually obsolete description of the many-electron atom. The recent proof by Lieb and Simon[2] that the Thomas-Fermi results correspond to the $N \to \infty$ limit of the exact solution of the nonrelativistic atom, such that $N/Z = \text{constant} \leq 1$, has provided new significance to this model. In particular, it has rigorously established that the Thomas-Fermi term is the leading term in the density-functional formalism.[3] In this context it is remarkable that the Thomas-Fermi density behaves qualitatively differently from the density of a finite many-electron atom, both close to the nucleus and at asymptotically large distances.

In view of this situation it is of interest to extend our knowledge of the properties of the Thomas-Fermi model. One avenue of investigation, which has been demonstrated to be fruitful in other contexts, involves the examination of the effect of space dimensionality.[4,5]

In an obvious extension of the standard treatment in three dimensions[1] we relate the electron charge density $\rho(r)$ and the potential $\Phi(r)$ via an n-dimensional Poisson's equation

$$\nabla_n^2 \Phi(r) = -4\pi\rho(r) , \tag{1}$$

where $\nabla_n^2 = \partial^2/\partial r^2 + [(n-1)/r]\partial/\partial r + (1/r^2) \times \Lambda(\Theta_1, \Theta_2, \ldots, \Theta_{n-1})$ is the n-dimensional Laplacian. Because of the spherical symmetry of $\Phi(r)$ the angular terms in Eq. (1) vanish.

The maximum local momentum is given by

$$\frac{p_F(r)^2}{2m} = e[\Phi(r) - \Phi_0] \equiv e\Psi(r) , \tag{2}$$

where m is the electron mass and Φ_0 is a constant to be determined. For an N-electron atom the phase-space integration yields

$$2V_n \frac{\Omega_n}{n} p_F^n = Nh^n , \tag{3}$$

where the first factor of 2 is due to the spin degeneracy, V_n is the occupied volume in configuration space and the rest is the occupied volume in momentum space, $\Omega_n = n\pi^{n/2}/\Gamma(n/2+1)$ being the area of the n-dimensional unit hypersphere.

For the charge density we obtain

$$\rho = -eN/V_n = -e\frac{2\Omega_n}{n}\frac{p_F^n}{h^n} = -\frac{\beta_n}{4\pi}\Psi^{n/2} , \tag{4}$$

where $\beta_n = [8\pi e/\Gamma(n/2+1)](\sqrt{2\pi me}/h)^n$.

Substituting Eq. (4) in Eq. (1) we get

$$\frac{\partial^2\Psi}{\partial r^2} + \frac{n-1}{r}\frac{\partial\Psi}{\partial r} = \beta_n \Psi^{n/2} . \tag{5}$$

Before attempting a solution we point out that the fundamental solution of Poisson's equation for the potential corresponding to a point charge Ze, $\nabla_n^2 \phi(r) = -4\pi Ze\delta(r)$, is[6]

$$\phi(r) = \begin{cases} \dfrac{4\pi Ze}{(n-2)\Omega_n} r^{2-n} , & n \geq 3 \\ -2Ze \ln r , & n = 2 \\ -2\pi Zer , & n = 1 . \end{cases} \tag{6}$$

For $n = 3$ we obtain the conventional Coulomb potential. The potentials obtained for $n = 1$ and $n = 2$ were used by Lenard[7] and Dyson,[8] respectively, in studies of the one- and two- dimensional Coulomb gas. These potentials have only discrete

spectra, and as such have recently been extensively studied in the context of the confinement models of quarks.[9,10] For $n \geq 4$ we obtain singular potentials whose bound spectrum is continuous, extending to arbitrarily negative energies.[11] To the extent that Poisson's equation is the appropriate route towards generalizing the three-dimensional Coulomb potential to an arbitrary dimensionality, the three-dimensional space appears to be unique, possessing both a discrete spectrum within a certain finite range of energies and a continuum above that range.

Furthermore, from Gauss's theorem, which is a consequence of Poisson's equation, it follows that close to the origin the potential has to approach the bare nuclear potential,

$$\Psi(r) \simeq \phi(r) . \tag{7}$$

Consequently, close to the nucleus the density behaves like $\phi^{n/2} \sim r^{(2-n)n/2}$, a singularity which for $n \geq 4$ cannot be compensated by the shrinking volume element $d\tau = \Omega_n r^{n-1} dr$. This means that $\int \rho(r) d\tau$ diverges for $n \geq 4$, a feature which should be expected for a singular potential,[11] but which precludes further discussion of the Thomas-Fermi model in four and higher dimensions.

We note in passing that insisting on the $1/r$ behavior of the potential for $n \neq 3$, though of some interest in the context of the one-electron atom [e.g., preserving $O(n+1)$ symmetry[12]], results in sacrificing Gauss's theorem, which is the source of considerable mathematical simplification and physical transparency in the treatment of many-electron atoms.

For the total kinetic energy we obtain

$$E_k = \int d\tau \int^{p_F} \Omega_n p^{n-1} \frac{p^2}{2m} dp \sim \int d\tau |\rho|^{(n+2)/n} .$$

In the limit $n \to \infty$ $E_k \sim \int d\tau |\rho| = Ne$, i.e., the total kinetic energy is proportional to the number of particles. For a finite dimensional space we obtain a higher than linear increase of the kinetic energy with the number of particles. This is a consequence of the Pauli principle, which ceases to be effective when the number of spatial degrees of freedom is infinitely large.

The n-dimensional Thomas-Fermi equation, Eq. (5), has a Sommerfeld-type particular solution of the form $\Phi_S = A_n r^s$, where $s = 4/(2-n)$ and $A_n = [4n(4-n)/\beta_n(2-n)^2]^{2/(n-2)}$, for all odd n. This is so because $A_2 = \infty$, $A_4 = 0$, and $A_{2n}(n > 2)$ is imaginary. For $n = 3$ we obtain Sommerfeld's solution $\Phi_S = (12/\beta_3)^2 r^{-4}$. Only for $n > 2$ can the Sommerfeld-type solution be used as a starting point for constructing a solution which is physically acceptable at large r. These properties of the Sommerfeld-type solution are in harmony with the previous observations concerning the uniqueness of $n = 3$.

In analogy with Jensen's three-dimensional results,[1] it can be shown formally that in any number of dimensions the charge density is continuous at the radius r_0 beyond which it vanishes, i.e.,

$$\rho(r_0) = 0 . \tag{8}$$

From this result and Eq. (4) it follows that $\Phi_0 = \Phi(r_0)$. From Gauss's theorem it follows that

$$\left.\frac{d\Phi}{dr}\right|_{r_0} = (Z-N)\frac{1}{Z}\left.\frac{d\phi}{dr}\right|_{r_0} . \tag{9}$$

For a neutral atom ($Z = N$) we must therefore have $r_0 = \infty$ and $\Phi_0 = 0$.

For $n = 2$ the Thomas-Fermi equation obtains the linear form

$$\frac{d^2\Psi}{dr^2} + \frac{1}{r}\frac{d\Psi}{dr} = \beta_2 \Psi , \quad \beta_2 = 4me^2/\hbar^2 . \tag{10}$$

Defining $R = r 2e\sqrt{m}/\hbar$ we obtain

$$\Phi = C_1 I_0(R) + C_2 K_0(R) , \tag{11}$$

where I_0 and K_0 are the modified Bessel functions.[13] Their asymptotic behavior is given by $I_0 \sim 1$; $K_0 \sim -\ln R$ for $R \to 0$ and $I_0 \sim e^R/\sqrt{2\pi R}$; $K_0 \sim \sqrt{\pi/2R} e^{-R}$ for $R \to \infty$. To satisfy Eq. (7), i.e., $\Phi \sim -2Ze \ln R$ for $R \to 0$, we have to choose $C_2 = 2Ze$. For a neutral atom the large R behavior will be satisfied by choosing $C_1 = 0$, hence $\Phi = 2ZeK_0(R)$ and $\rho = -(2mZe^3/\pi\hbar^2)K_0(R)$. Note that $\int_0^\infty \rho 2\pi r dr = -Ze$, as it should be. The long-range asymptotic form of the density is exponential, unlike the three-dimensional $1/r^6$ behavior.

For a positive ion we determine R_0 and C_1 using Eqs. (8) and (9) which result in the set of equations

$$C_1 I_0(R_0) - 2ZeK_0(R_0) = 0$$

and

$$[C_1 I_0'(R_0) - 2ZeK_0'(R_0)] 2\sqrt{me}/\hbar = (Z-N)e2/r_0 .$$

Noting that $I_0' = I_1$ and $K_0' = -K_1$ we obtain for R_0 the equation

$$R_0\left(K_0(R_0)\frac{I_1(R_0)}{I_0(R_0)} + K_1(R_0)\right) = 1 - q ,$$

where $q = N/Z$.

For $q \to 0$ we must have $R_0 \to 0$. Using the small argument forms of the modified Bessel functions we obtain $R_0 \simeq 2q^{1/2}$. The corresponding result in three dimensions is[14] $R_0 \sim q^{2/3}$.

For $q = 1 - \epsilon$, where $0 < \epsilon \ll 1$, we use the asymptotic forms of the modified Bessel functions to derive $\sqrt{2\pi R_0} e^{-R_0} \simeq \epsilon$ or $R_0 \simeq -\ln\epsilon$. The corresponding result in three dimensions would be of considerable interest.

[1]P. Gombas, *Die Statistische Theorie des Atoms* (Springer, Wien, 1949).
[2]E. H. Lieb, Rev. Mod. Phys. 48, 553 (1976); E. H. Lieb and B. Simon, Adv. Math. 23, 22 (1977).
[3]R. G. Parr, S. R. Gadre, and L. J. Bartolotti, Proc. Natl. Acad. Sci., U.S.A. 76, 2522 (1979).
[4]E. H. Lieb and D. C. Mattis, *Mathematical Physics in One Dimension* (Academic, New York, 1966).
[5]M. E. Fisher, Rev. Mod. Phys. 46, 597 (1974).
[6]I. M. Gel'fand and G. E. Shilov, *Generalized Functions* (Academic, New York, 1964), Vol. I.
[7]A. Lenard, J. Math. Phys. 2, 682 (1961).
[8]F. Dyson, J. Math. Phys. 3, 140 (1962).
[9]A. F. Antippa and A. J. Phares, J. Math. Phys. 19, 308 (1978).
[10]H. J. W. Muller-Kirsten and S. K. Bose, J. Math. Phys. 20, 2471 (1979).
[11]R. M. Spector, J. Math. Phys. 8, 2357 (1967).
[12]G. I. Kuznetsov, Zh. Eksp. Teor. Fiz. 51, 216 (1966) [Sov. Phys.—JETP 24, 145 (1967)].
[13]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (N.B.S., Washington, 1970).
[14]Y. Tal and M. Levy, Phys. Rev. A 23, 408 (1981).