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Thomas-Fermi Theory Revisited

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We show that the Thomas-Fermi theory is exact for atoms, molecules, and solids as $Z \to \infty$.

The Thomas-Fermi (TF) theory of atoms and molecules[1] is now more than 45 years old. The literature on the subject is vast[2] yet there remain more than a few unresolved problems both of principle and interpretation. Can one show that there is an electron density function ρ which actually minimizes the TF energy expression and that it satisfies the TF equation? Does this ρ represent the true electron density as computed from the Schrödinger equation as $Z \to \infty$? If so, there appear to be some "paradoxes": For atoms the density falls off exponentially with distance, while in TF theory[3] it falls off as r^{-6}; in TF theory atoms shrink in size as $Z^{-1/3}$ instead of growing; the electron density in TF theory is infinite at the nuclei instead of being finite; in TF theory molecules never bind.[4]

Recently, considerable progress has been made in showing that TF theory is applicable to high-density matter,[5] but the questions raised above are of a different nature, especially in the fact that a parameter in the problem, Z, becomes infinite; it is that which causes the electron density to become infinite. We report here the results of our analysis[6] of the above questions, and the main conclusion is that TF theory, when correctly interpreted, is rigorously exact as $Z \to \infty$. We also show that TF theory is rigorously exact for solids in this limit and leads to a periodic ρ which satisfies the TF equation with the *periodic* Coulomb potential. This $Z \to \infty$ limit is related to, but is not the same as, the high-density limit with fixed Z, a case to which TF theory is often applied.[7] We make no statements about this latter situation.

The TF energy functional in the presence of k nuclei of positive charges and positions (z_i, R_i), $i = 1, \ldots, k$, in units such that $h^2(3/8\pi)^{2/3}(2m)^{-1} = 1$ and $|e| = 1$, is

$$E(\rho; z_1, \ldots, z_k; R_1, \ldots, R_k) = \tfrac{3}{5}\int \rho(x)^{5/3}\, d^3x + \tfrac{1}{2}\iint \rho(x)\rho(y)|x-y|^{-1}\, d^3x\, d^3y - \int \rho(x) \sum_{i=1}^{k} z_i |x - R_i|^{-1}\, d^3x. \quad (1)$$

The electric potential is defined to be

$$\varphi(x) = -\int \rho(y)|x-y|^{-1} d^3y + \sum_{i=1}^{k} z_i |x-R_i|^{-1}. \quad (2)$$

The subsidiary condition is that $\rho(x) \geq 0$ and

$$\lambda \equiv \int \rho(x) d^3x = \text{electron number}, \quad (3)$$

but we may consider λ to be an arbitrary constant. Finally,

$$Z = \sum_{i=1}^{k} z_i . \quad (4)$$

The cases $\lambda = Z$, $\lambda < Z$, and $\lambda > Z$ are the neutral-molecule, the positive-ion, and the negative-ion cases, respectively. While it is easy to see[8] that for a given λ, $E(\rho)$ is bounded below and is strictly convex in ρ, the crucial question is whether there is a ρ that actually minimizes E and whether it is unique. For all $\lambda \geq 0$ we define E_λ to be the infimum of (1) under condition (3).

Theorem 1: (a) If $\lambda \leq Z$, E has a unique minimizing ρ. If $\lambda > Z$ there is no such ρ. E_λ is convex and monotone decreasing, and $E_\lambda = E_Z$ for $\lambda \geq Z$. (b) If $\lambda = Z$, $\rho(x) \to 1728|x|^{-6}$ as $|x| \to \infty$, $\rho(x) > 0$ for all x, $\rho(x)$ is C^∞ away from the nuclei, and $\rho(x)^{2/3} = \varphi(x)$. (c) If $\lambda < Z$, $\rho(x)$ has compact support and is C^∞ where $\rho > 0$; $\rho(x)$ is C^1 and $\varphi(x)$ is C^2 everywhere. There is a $C > 0$ such that $\rho(x)^{2/3} = \varphi(x) - C$ when $\varphi(x) \geq C$, and $\rho(x) = 0$ when $\varphi(x) \leq C$. In particular, φ satisfies the TF differential equation. (d) The constant C above is the negative of the chemical potential (Fermi energy), i.e., $dE_\lambda/d\lambda = -C$. (e) $\varphi(x) \to z_i|x-R_i|^{-1} + \text{const}$ as $x \to R_i$. Hence $\rho(x) \sim z_i^{3/2}|x-R_i|^{-3/2}$ near R_i.

The next two theorems refer to the neutral case and we denote the minimizing ρ by $\rho(x; z_1, \ldots, z_k; R_1, \ldots, R_k)$. The TF energy plus the nuclear Coulomb energy,

$$E_Z + \tfrac{1}{2} \sum_{i \neq j}^{k} z_i z_j |R_i - R_j|^{-1},$$

will be denoted by $E(z_1, \ldots, z_k; R_1, \ldots, R_k)$. The following result[9] is due to Teller[4] and is important in the proofs of Theorems 1 and 3.

Theorem 2: (a) If $R_1, \ldots, R_k$ are fixed and $z_i^* \geq z_i$, $i = 1, \ldots, k$ with some $z_j^* > z_j$, then $\rho(x; z^*; R) > \rho(x; z; R)$ for all x. Moreover, if $z_i^* = z_i$ then

$$\lim_{x \to R_i} \rho(x; z^*; R) - \rho(x; z; R)$$

exists and is strictly positive. (b) Molecules never bind in TF theory, i.e.,

$$E(z_1, \ldots, z_{n+k}; R_1, \ldots, R_{n+k}) > E(z_1, \ldots, z_k; R_1, \ldots, R_k) + E(z_{k+1}, \ldots, z_{n+k}; R_{k+1}, \ldots, R_{n+k}). \quad (5)$$

The following theorem about the thermodynamic limit for solids in TF theory holds for arbitrary Bravais lattices with any distribution of nuclei in a unit cell, but for simplicity we state it for a simple cubic lattice.

Theorem 3: Let z be fixed. For each subset Λ of the lattice of integral points, let ρ_Λ denote the solution of the neutral TF theory with nuclei of charge z at each point of Λ, and let E_Λ be the TF energy. Then (a) as $\Lambda \to \infty$ in the sense of van Hove, $\rho_\Lambda(x)$ converges pointwise to a function $\rho(x)$ and $E_\Lambda/|\Lambda|$ converges to an intensive energy e. (b) ρ is periodic with unit period. (c) ρ is the solution to the neutral TF problem in a unit cell in which $|x|^{-1}$ is replaced by the periodic[10] Coulomb potential $G_p(x)$. e is the corresponding TF energy.

Unlike the neutral-molecule case, the Lagrange multiplier C will be negative for solids; it is related to the compressibility. The basic tool in the proof of Theorem 3 is Theorem 2, e.g., (5) implies that E_Λ is superadditive in Λ.

We turn next to the question of how TF theory is related to the solution of Schrödinger's equation. We first note that TF theory has a simple scaling relation: Let $E_N[\rho_N(x)]$ denote the TF energy [function] for k nuclei of charges and positions $z_i N$, $R_i N^{-1/3}$ $(i = 1, \ldots, k)$, and $\int \rho_N(x) d^3x = \lambda N$, with $\lambda \leq Z = \sum z_i$. Then

$$E_N = N^{7/3} E_1, \quad \rho_N(x) = N^2 \rho_1(N^{1/3}x). \quad (6)$$

This relation allows us to relate the quantum problem for large N (electron number) to an N-independent TF problem.

Theorem 4: For $\lambda \leq Z$, let E_N^0 and $\rho_N^0(x)$ denote the ground-state energy and one-electron distribution function for N spin-$\frac{1}{2}$ electrons obeying the Pauli principle and interacting with k nuclei as described above. Then (a) $N^{-7/3} E_N^0 \to E_1$ as $N \to \infty$; (b) $N^{-2} \rho_N^0(N^{-1/3}x) \to \rho_1(x)$ as $N \to \infty$, where convergence in (b) means that for any domain $D \subset R^3$, the expected fraction of electrons in $N^{-1/3}D$ approaches $\int_D \rho_1(x) d^3x$.

The methods employed to prove Theorems 1, 2, and 3 include L^p space techniques, the theory of convex functions, and the theory of harmonic functions. The basic fact used in Theorem 4 is that the introduction of Neumann (Dirichlet) boundary conditions on subdomains lowers (raises) the ground-state energy. This fact has been used before.[11] In two places problems arise that do not appear in the theory of gravitating fermions.[5,12]

From the above theorems a picture of large-Z

atoms that resolves the aforementioned "paradoxes" can be formulated. The electron cloud is divided into five regions:

(1) An inner core of size $\sim Z^{-1/3}$ described by TF theory in which the density is $\sim Z^2$ and in which there are $\sim Z$ electrons.

(2) The mantle of the core in which $\rho \sim 1728|x|^{-6}$ independently of Z. The length scale of the mantle is also $Z^{-1/3}$ and the core and the mantle contain 100% of the electrons as $Z \to \infty$.

(3) A complicated intermediate region.

(4) The outer shells. Crude models, in which one takes into account screening, suggest that this region has a size of order 1 and contains $\sim Z^{2/3}$ electrons. Chemistry takes place here.

(5) The outside of the atom where the density falls off exponentially with distance.

In understanding TF theory, then, one principle must be borne in mind: TF theory describes the atomic core and mantle, and only those. These two regions contain almost all the electrons, but their size shrinks like $Z^{-1/3}$. There is no difficulty reconciling the $|x|^{-6}$ falloff here with the exponential falloff in region (5). The shell region, which is what one sees chemically, is enormously large compared to the TF region but it contains a negligible fraction of electrons. It is not surprising that molecules fail to bind in TF theory, because to do so would require core binding and, as Teller noted,[4] this would imply that molecular sizes would shrink as $Z^{-1/3}$ and binding energies would grow as $Z^{7/3}$. Instead, binding occurs in the shell region.

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[9]Some concern has been expressed about the role of the self-energy in Teller's proof; this has led to some questioning of the validity of his results. For this reason, we have provided a rigorous proof of Teller's results (see Ref. 6). We emphasize that the basic idea in our proof is Teller's. Because L^p techniques allow us to handle an unsmeared nuclear charge, our proof is somewhat more direct then Teller's and no self-energies enter.

[10]G_ρ is a periodic solution of $-\nabla^2 G_\rho(x) = \delta(x) - 1$. While such a solution is only unique up to a constant, the addition of a constant to G_ρ does not affect the TF energy because of neutrality.

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