A new approach to the problem of existence and uniqueness of the minimizer of Fermi energy

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Abstract— *This paper deals with Thomas-Fermi equation which is formulated as an Euler-Lagrange equation associated with the Fermi energy functional. Drawing upon advanced ingredients of Sobolev spaces and weak solutions, an analytic methodology is presented for the quantum correction near the origin of Thomas-Fermi equation. By this approach the existence and uniqueness of the minimizer for the energy functional of the Thomas-Fermi equation has been proved. It has been demonstrated that by the definition of such a functional and the relevant Sobolev spaces, the Thomas-Fermi equation, particularly of a neutral atom, extends to the nonlinear Poisson equation. Accordingly, weak solutions for more general Euler-Lagrange equation with more singularities are proposed.*

Keywords— *Euler-Lagrange equation, Fermi energy, Thomas-Fermi equation, Weak solution.*

I. INTRODUCTION

Thomas–Fermi equation as a special case of nonlinear Poisson equations arises from a statistical model of many electron atoms. Physical notions of Thomas-Fermi equation result to local Fermi momentum, Fermi sphere, Thomas-Fermi energy density, and finally, Thomas-Fermi model applied to ions [1-3]. All of them will be reviewed in Section 2 of this article. This physical approach gives again the self-consistent Thomas-Fermi equation. In this manner, an energy functional extermization yield Thomas-Fermi equation can be derived.

Near the origin, however, (Columb) potential is singular and the Thomas-Fermi energy is no longer reliable for the large nuclear charges and it is the main problem of this paper. On the other hand, one special Euler-Lagrange equation as a minimizer of energy functional gives a nonlinear Poisson equation which is an extended version of Thomas–Fermi equation. This fact and in the sequel of applying the differential technique for analytic solution to the Thomas–Fermi equation (e.g. in [4-7]) encourage to refer the analytic approach.

For quantum correction near the origin of Thomas-Fermi equation, in Theorem 1, the minimizer of the energy functional will be found by some notions of Sobolev spaces. Also, this minimizer is a solution of a boundary–value problem for the Euler–Lagrange equation associated with the Fermi energy functional which satisfies in the condition for the existence of the solution in the weak sense. This approach is a motivation for the definition of weak solution which can be applied to the general Euler-Lagrange equation with more singularities, sometimes awkward. Also, structure of the proof of the Theorem 1 can be extended to the Euclidean space $\mathbf{R}^n$ and then Euler–Lagrange partial differential equation for no smooth functions with the singularities on the sets with nonzero measure.

II. PHYSICAL NOTIONS OF THOMAS-FERMI EQUATION

As the notations of [6] or [8], if an atom has a large nuclear charge Z, most of the electrons move in orbits with large quantum numbers. Filling up all negative energy states with electrons of both spin directions produces some local particle density $n(\vec{x})$ which is calculated from the classical local density $\rho_{cl}(E;\vec{x}) = \left(S_D M p^D(E;\vec{x})\right) \Big/ \rho^2(E;\vec{x})(2\pi\hbar)^D = \left(2M\{2M[E-V(\vec{x})]\}^{\frac{D}{2}-1}\right) \Big/ \left(\left(4\pi\hbar^2\right)^{\frac{D}{2}}\Gamma\left(\frac{D}{2}\right)\right)$ over all negative energies, yielding the Thomas-Fermi density of states

$$\rho_{cl}^{(-)}(\vec{x}) = \int_{V(\vec{x})}^{0} \rho_{cl}(E;\vec{x})dE = \left(\frac{M}{2\pi\hbar^2}\right)^{\frac{D}{2}} \frac{1}{\Gamma\left(\frac{D}{2}+1\right)}[-V(\vec{x})]^{\frac{D}{2}}. \quad (1)$$

At each point $\vec{x}$, the electrons occupy all levels up to a Fermi energy $E_F = p_F(x)^2 \big/ (2M) + V(\vec{x})$.

The associated local Fermi momentum is equal to the local momentum function $\rho(E;\vec{x})=\sqrt{2M[E-V(\vec{x})]}$ at $E=E_F$; $p_F(\vec{x})=p(E;\vec{x})=\sqrt{2M[E_F-V(\vec{x})]}$. The electrons fill up the entire Fermi sphere $|\vec{p}|\le p_F(\vec{x})$:

$$\rho_{cl}^{(-)}(x)=\int_{|\vec{p}|\le p_F(x))}\frac{d^Dp}{(2\pi\hbar)^D}=\frac{1}{(2\pi\hbar)^D}S_D\int_0^{p_F(x)}p^{D-1}dp\frac{1}{(2\pi\hbar)^D}\frac{2\pi^{\frac{D}{2}}}{\Gamma\left(\frac{D}{2}\right)}\frac{p_F^D(x)}{D} \tag{2}$$

For neutral atoms, the Fermi energy is zero and the density (1) will be recovered. By occupying each state of negative energy twice, the classical electron density is

$$n(x)=2\rho_{cl}^{(-)}(\vec{x}), \tag{3}$$

the potential energy density associated with the levels of negative energy is

$$E_{pot\ TF}^{(-)}(\vec{x})=V(\vec{x})\rho^{(-)}(x)=-\left(\frac{M}{2\pi\hbar^2}\right)^{\frac{D}{2}}\frac{1}{\Gamma\left(\frac{D}{2}+1\right)}[-V(\vec{x})]^{\frac{D}{2}+1}. \tag{4}$$

To find the kinetic energy density should be integrated

$$E_{kin\ TF}^{(-)}(\vec{x})=\int_{V(x)}^0[E-V(\vec{x})]\rho_{cl}(E;\vec{x})dE=\frac{\frac{D}{2}}{\frac{D}{2}+1}\left(\frac{M}{2\pi\hbar^2}\right)^{\frac{D}{2}}\frac{1}{\Gamma\left(\frac{D}{2}+1\right)}[-V(\vec{x})]^{\frac{D}{2}+1}. \tag{5}$$

The sum of the two is the Thomas-Fermi energy density $E_{TF}^{(-)}(\vec{x})=\int_{V(\vec{x})}^0 E\rho_{cl}(E;\vec{x})dE=-\left(M/\left(2\pi\hbar^2\right)\right)^{\frac{D}{2}}/(((D/2)+1)\Gamma((D/2)+1))$. The total electrostatic potential energy $V(\vec{x})$ caused by the combined charges of the nucleus and the electron cloud is found by solving the Poisson equation

$$\Delta V(x)=4\pi e^2\left[Z\delta^3(\vec{x})-n(\vec{x})\right]\equiv 4\pi e^2[n_C(x)-n(\vec{x})]. \tag{6}$$

It is convenient to describe the screening effect of the electron cloud upon the Coulomb potential (5) by a multiplicative dimensionless function $f(\vec{x})$. Restricting our attention to the ground state, which is rotationally symmetric, the solution of the Poisson equation (6) can be written as $V(x)=-\left(Ze^2/r\right)f(r)$. At the origin the function $f(r)$ is normalized to unity

$$f(0)=1 \tag{7}$$

to ensure that the nuclear is not changed by the electrons, where has been obtained in equation (3) with boundary conditions (4) and (5). All length scales of the electrons will now be specified in units of a_{TF}, i.e., $r=a_{TF}\xi$. In these units, the electron density (4) becomes simply $n(x)=-\left(\left(2Ze^2M\right)^{\frac{3}{2}}/\left(3\pi^2\hbar^3\right)\right)\left(f(\xi)/\left(a_{TF}\xi\right)\right)^{\frac{3}{2}}=\left(Z/\left(4\pi a_{TF}^3\right)\right)\left(f(\xi)/\xi\right)^{\frac{3}{2}}$. The left-hand side of the Poisson equation (6) reads $\Delta V(\vec{x})=(1/r)d^2/dr^2\,(V(\vec{x}))=-\left(\left(Ze^2\right)/\left(a_{TF}^3\xi\right)\right)f''(\xi)$. So that will be obtained the self-consistent Thomas-Fermi equation

$$f''(\xi)=\frac{1}{\sqrt{\xi}}f^{\frac{3}{2}}(\xi),\quad \xi>0. \tag{8}$$

The condition $\xi>0$ excludes the nuclear charge from the equation, whose correct size is incorporated by the initial condition (7). Near the origin, the equation (8) starts out like $f(\xi)=1-s\xi+\ldots$ with a slope $s\approx 1.58807$. For large ξ, it goes to zero like $f(\xi)\approx 144/\xi^3$. This power fall off is a weakness of the model since the true screened potential should fall off exponentially fast. The right–hand side by itself happens to be an exact solution of (8), but does not satisfy the desired boundary condition (7). It can be derived an energy functional whose functional extremization yields the Thomas-Fermi equation (8). For more details refer to [1-3] and [8].

III. ANALYTIC APPROACH

A. Statement of the problem

The Thomas-Fermi energy with exchanges corrections which obtained in Section 2 would be reliable for large Z only if the potential was smooth so that the semiclassical approximation is applicable. Near the origin, however, the Coulomb potential is singular and this condition is no longer satisfied. Some more calculational efforts is necessary to account for the quantum effects near the singularity, based on the other observation (e.g., refer to [9]). This problem can be solves in Theorem 1 by analytic ingredients, especially weak solutions.

B. Our methodology: Weak solution

For approximation approach, Fermi energy and Poisson equation (6) which result to the Thomas-Fermi equation (8) can be sketched in the functional analysis framework. For the quantum correction near the origin, in general case suppose $U \subseteq (0,\infty)$ is a bounded, open interval and $L : \mathbf{R}\times\mathbf{R}\times\bar{U} \to \mathbf{R}$; $L=L(p,z,x)$ is a smooth Lagrangian. Also, it should be assumed that the function $I[.]$ have the explicit form

$$I[\omega] := \int_U L(D\omega(x), \omega(x), x)dx, \tag{9}$$

for smooth functions $\omega : \bar{U} \to \mathbf{R}$ satisfying the boundary condition $\omega=g$ on ∂U . Also, suppose some particular smooth function u , satisfying the requisite boundary condition $u=g$ on ∂U , happens to be a minimizer of $I[.]$. In this way, it can be shown that u solve the nonlinear ODE, i.e., the Euler-Lagrange equation associated with the energy functional $I[.]$ defined by (9)

$$-\left(L_p(Du,u,x)\right)_x + L_z(Du,u,x)=0, \tag{10}$$

thus conversely, it can be tried to find a solution of (10) by searching for minimizers of (9). Consider the Sobolev space $W^{k,p}(U)$ consists of all locally summable functions $u : U \to \mathbf{R}$ such that for each multiindex α with $|\alpha| \le k$, $D^\alpha U$ exists in the weak sense which means that for all test functions $C_c^\infty(U)$, $\int_U uD^\alpha \varphi dx = (-1)^{|\alpha|}\int_U v\varphi dx$ and the weak derivation belongs to $L^p(U)$. Denote by $W_0^{k,p}(U)$ the closure of $C_c^\infty(U)$ in $W^{k,p}(U)$. More details can be found in analysis books, for example [10-11].

Theorem 1. Singularity near the origin of Thomas-Fermi equation (and then singularity of the Coulomb potential) as an Euler-Lagrange equation associated with the Fermi energy can be improved in the sense of nonsmooth potential.

Proof. In fact, it will be shown that the weak solution of the Lagrangian which is a minimizer of the Euler-Lagrange equation is the key for this enigma.

As the notions of above, let $f : \mathbf{R} \to \mathbf{R}$ be a smooth function and $F(z)=\int_0^z f(y)dy$ is its antiderivative. Then the Euler-Lagrange equation associated with the functional $I[\omega] := \int_U \left(\left(|D\omega|^2/2\right) - F(\omega)\right)dx,$ is the nonlinear Poisson equation $\Delta u = f(u)$ in U , which Thomas-Fermi equation is a special case of it and studied this equation in Section 2. Now, focus on Lagrangian L which can be exposed some awkward singularities other than ones of Thomas-Fermi energy. Fix any $v \in W_0^{1,q}(U)$ and set $i(\tau)=I[u+\tau v]$, $\tau \in \mathbf{R}$. It can be checked that the Lagrangian L verifies the growth conditions

$$|L(p,z,x)| \le C\left(|p|^q + |z|^q + 1\right), \tag{11}$$

$$\begin{aligned} \left|D_p L(p,z,x)\right| &\le C\left(|p|^{q-1} + |z|^{q-1} + 1\right), \\ \left|D_z L(p,z,x)\right| &\le C\left(|p|^{q-1} + |z|^{q-1} + 1\right), \end{aligned} \tag{12}$$

for some constant C , $1 < q < \infty$ and all $p, z \in \mathbf{R}$ and $x \in U$. In view of (11), it can be seen that $i(\tau)$ is finite for all τ . Let $\tau \neq 0$ and write the difference quotient

$$\frac{i(\tau) - i(0)}{\tau} = \int_U \frac{L(Du+\tau v, u+\tau v, x) - L(Du,u,x)}{\tau}dx = \int_U L^\tau(x)dx, \tag{13}$$

where $L^\tau(x) := \frac{1}{\tau}\left[L(Du(x)+\tau v(x), u(x)+\tau v(x), x) - L(Du(x), u(x), x)\right]$ for almost everywhere $x \in U$. Clearly

$$L^{\tau}(x) \to L_p\begin{pmatrix} D \\ u,u,x \end{pmatrix} v_x + L_z(Du,u,x)v, \quad \tau \to 0. \quad a.e$$
$$L^{\tau}(x) := \frac{1}{\tau}\int_0^{\tau} L_p(Du+sDv,u+sv,x)v_x + L_z(Du+sDv,u+sv,x)v ds. \tag{14}$$

Then since $u,v \in W^{1,q}(U)$, inequality (13) and Yong inequality imply after some elementary calculations that for each $\tau \neq 0$, $\left|L^{\tau}(x)\right| \le C\left(|Du|^q + |u|^q + |Dv|^q + |v|^q + 1\right) \in L^1(U)$.

Consequently, it can be invoked the Dominated Convergence Theorem to conclude from (13) and (14) that $i'(0)$ exists and equals $\int_U L_p(Du,u,v)v_x + L_z(Du,u,x)v dx$. But then since $i(.)$ has a minimum for $\tau=0$, $i'(0)=0$; and $u \in T = \left\{\omega \in W^{1,q}(U))\,|\ \omega = g \ \text{on}\ \partial U \ \text{in the trace sense}\right\}$ is a solution of the boundary-value problem

$$\begin{cases} -\left(L_p(Du,u,x)\right)_x + L_z(Du,u,x) = 0 & \text{in } U \\ u = g & \text{on } \partial U \end{cases} \tag{15}$$

for the Euler-Lagrange equation means is the weak solution. Also the mapping $(p,z) \mapsto L(p,z,x)$ is convex. Therefore $I[u] + \int_U D_{Du}(Du(x),u(x),x)(Dw-Du) + D_u L(Du(x),u(x),x)(w(x)-u(x))dx \le I[\omega]$, for the weak solution u and any $\omega \in T$. In view of (15) the second term on the right is zero, and therefore $I[u] \le I[\omega]$ for each $\omega \in T$. Then this solution is unique, too.

IV. CONCLUSIONS

In this paper, a novel methodology for the quantum correction near the origin presented. This consists of finding the (weak) solution of the Lagrangian associated with Thomas-Fermi equation which has the singularities, especially in the origin. Also, since the Lagrangian mapping corresponded to the Thomas-Fermi equation is convex then each weak solution is in fact a minimizer. The main advantage of the proposed methodology is that it provides the analytic solution of the problem and it can be applied to the partial differential of Euler-Lagrange equations and the nonlinear Poisson equation in more variables and the multivariable functions with the big set of singularities.

REFERENCES

[1] E. H. Leib, *A brief review of Thomas–Fermi theory*, Princeton University, 2000.
[2] E. H. Leib, and B. Simon, "The Thomas–Fermi theory of atoms, molecules and solids", *Advances in Mathematics*, 23, pp. 22–116, 1977.
[3] F. Schwabl, *Quantum mechanics*, Springer , 2007.
[4] A. Hasan-Zadeh, and H. Fatoorehchi, "Some analytic efforts for the quantum effects near the singularity of Thomas-Fermi equation", *1th National Conference on Applied Researches in Science and Engineering*, Mashhad, and Islamic World Science Citation Center, 2017.
[5] H. Fatoorehchi, and H. Abolghasemi, "An explicit analytic solution to the Thomas Fermi equation by improved differential transform method", *Acta Physica Polonica A*, 125, pp. 1083–1087, 2014.
[6] S. Liao, "An explicit analytic solution to the Thomas–Fermi equation", *Applied Mathematics and Computation*, 144, pp. 495–506, 2003.
[7] R. A. Pearson, and S. M. Richardson, *Computational analysis of polymer processing*, Applied Science Publishers LTD, 1983.
[8] H. Kliener, *Path integrals in quantum mechanics, statistics, polymer physics, and finanical markets*, World Scientific, 5th edition, 2009.
[9] B. E. Baaquie, "A path integral approach to optic princing with stochastic volatility: some exact results", *J. de Physique I*, 7, pp. 17–33, 1997.
[10] D. Bahuguna, V. Raghavendra, and B. V. Rathish Kumar, *Topics in Sobolev Spaces and Applications*, Alpha Science, 2002.
[11] V. Maz'ya, "Sobolev space in Mathematics II: Applications in analysis and partial differential equation", *International Mathematical Series*, vol. 9, Tamara Rozhkovslaya Publisher, 2009.