

Research Article

Examination of Minimizer of Fermi Energy in Notions of Sobolev Spaces

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Abstract: This study examines the well-known Thomas-Fermi equation as a Euler-Lagrange equation associated with the Fermi energy. The first integral of Thomas-Fermi equation and the behaviour of the solution near the saddle point of the equation has been determined. Then, drawing upon advanced ingredients of Sobolev spaces and weak solutions, an exact 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 have 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 the more general Euler-Lagrange equation with more singularities are proposed.

Keywords: Euler-lagrange equation, fermi energy, sobolev space, thomas-fermi equation, weak solution

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 (Lieb and Simon, 1977; Lieb, 2000; Schwabl, 2007). This physical approach gives again the self-consistent Thomas-Fermi equation. In this manner, an energy functional extremization 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 study. 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 the analytic solution to the Thomas-Fermi equation (Pearson and Richardson, 1983; Liao, 2003; Fatoorehchi and Abolghasemi, 2014; Hasan-Zadeh and Fatootehchi, 2017) encourage to refer the analytic approach.

Many of solutions of this equation consist of the approximate or numerical solutions of it (Parker, 1988; Zaitsev *et al.*, 2004; Turkyilmazoglu, 2012) for example refer to Baaquie (1997), Bahuguna *et al.* (2002) and Fatoorehchi and Abolghasemi (2014). This problem for natural atoms has been examined by integral curves of

an infinitesimal version of the corresponding differential equation (Baaquie, 1997; Lieb, 2000; Hagen, 2009) which we collect all of them in Theorem 1. In effect, some results about the procedure have been defined as the integration of the problem.

For quantum correction near the origin of Thomas-Fermi equation, in Theorem 2, 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, the structure of the proof of the Theorem 2 can be extended to the Euclidean space \mathbb{R}^n and then Euler-Lagrange partial differential equation for no smooth functions with the singularities on the sets with the nonzero measure.

APPROXIMATE EXAMINATION OF THOMAS-FERMI EQUATION

This study was conducted in Fouman Faculty of Engineering, College of Engineering, University of Tehran, Iran.

Preliminaries of thomas-fermi equation: As mentioned in the works of Pearson and Richardson (1983) and Schwabl (2007) the Thomas-Fermi equation

is a spherically symmetric version of the Poisson equation for the electric potential $\frac{V_1}{e}$ outside the nucleus of a many-electron atom:

$$\nabla V_1 = -4\pi e^2 \rho \tag{1}$$

here $V_1 = V - \xi$, $-\frac{V}{e}$ is potential, ξ is the energy of the most energetic electrons, e is electronic charge and $-e\rho$ is charge density. By statistical considerations, the Eq. (1) becomes a nonlinear ordinary differential equation:

$$\frac{1}{r} \frac{d^2}{dr^2} (rV_1) = -\frac{4e^2}{3\pi\hbar^3} (-2mV_1)^{\frac{3}{2}} \tag{2}$$

The solution of (2) is sought for $r > 0$, but as $r \rightarrow 0$, the potential of the concentrated source (nucleus) at the origin is $Z \rightarrow -\frac{Ze^2}{r}$, where Z is the atomic number. For neutral free atoms, a boundary condition at infinitely is also defined. The surface of the atom corresponds to $r \rightarrow \infty$ where $\rho \rightarrow 0$ ($\xi = 0$). No net charge demands; $rV_1 \rightarrow 0$ as $r \rightarrow \infty$. Thus, for neutral atoms the problem is:

$$\frac{d^2y}{dx^2} = \frac{y^{\frac{3}{2}}}{\sqrt{x}}, 0 < x < \infty \tag{3}$$

$$y(0) = 1 \tag{4}$$

$$y(\infty) = 0 \tag{5}$$

Of Eq. (3) the differential equation for the infinitesimal difference $\delta y = u$ is:

$$\ddot{u} = \frac{3}{2} x^{-\frac{1}{2}} y^{\frac{1}{2}} u \tag{6}$$

where, $u(\infty) = 0$. We can show that if $u(0) > 0$, then $u(x) \geq 0$ for all x .

The infinitesimal version of thomas-fermi equation:

All of the collection from the numerical approaches of Thomas-Fermi equation (Parker, 1988; Baaquie, 1997; Lieb, 2000; Zaitsev *et al.*, 2004; Hagen, 2009; Turkyilmazoglu, 2012) it can be expressed the following result.

Theorem 1: The first integral of Thomas-Fermi Eq. (3) with boundary conditions (4) and (5), also the path which satisfies the boundary condition (5) and the behaviour of the solution near the saddle point of the equation can be determined. In effect, it can be given an algorithm which defines the integration of the problem (3) with boundary conditions (4) and (5).

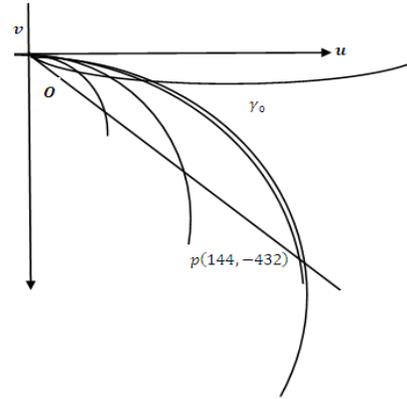


Fig. 1: First integrals of thomas-fermi equation

Proof: The Eq. (3) scales under stretching transformations as $\frac{y}{x} \sim \frac{y^{\frac{3}{2}}}{x^{\frac{3}{2}}}$, the group is $y_1 = a^3y$, $x_1 = \frac{x}{a}$. The corresponding invariant coordinates are $u = x^3y$, $v = x^4y'$. Then $\frac{du}{dx} = x^3y' + 3x^2y = \frac{v+3u}{x}$, $\frac{dv}{dx} = x^4y'' + 4x^3y' = \frac{4v+u^{\frac{3}{2}}}{x}$. The first order equation to be studied is:

$$\frac{dv}{du} = \frac{4v+u^{\frac{3}{2}}}{v+3u} \tag{7}$$

And the mapping to x along an integral curve of (7) is:

$$\frac{dx}{x} = \frac{du}{v+3u} = \frac{dv}{4v+u^{\frac{3}{2}}} \tag{8}$$

The general solution of the first order differential Eq. (6) is a one-parameter family of curves $\varphi(u, v) = \gamma$. Only one curve of this family corresponds to the family $y(x)$ of positive solutions of the Thomas-Fermi Eq. (6) for which $y(\infty) = 0$; for any one of these curves $y(x)$ is uniquely determined by its value $y(0)$ at $x = 0$. For the desired curve in the (u, v) -plane, it can be concentrated on the fourth quadrant, shown in Fig. 1. The isoclines of zero slope $4v + u^{\frac{3}{2}} = 0$ are drawn as well as some representative paths. There is one singular point p of interest where $4v_p + u_p^{\frac{3}{2}} = 0$, $4v_p + 3u_p = 0$, or $u_p = 144$ and $v_p = -432$. The locus of zero slope γ_0 is the curve $4v + u^{\frac{3}{2}} = 0$ and the locus of infinite slope γ_∞ is the line $3u + v = 0$ (the transverse line in Fig. 1).

The intersections of these loci are the singular points of the differential equation. They are a node at the origin O and a saddle point at $p(144, -432)$. In the lenticular region between these two loci, the slope $\frac{dv}{du} < 0$; to either side of this region $\frac{dv}{du} > 0$. As usual, the singular point represents one exceptional solution y_E of (3), $y_E = \frac{144}{x^3}$.

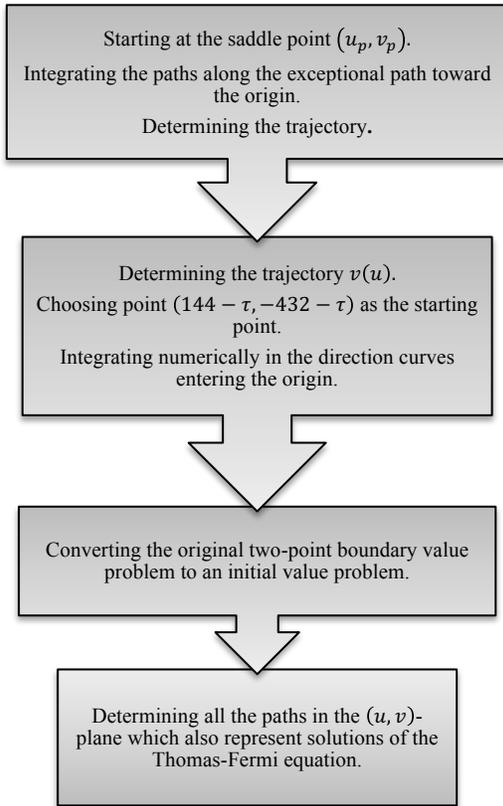


Fig. 2: An algorithm of integration of thomas-fermi problem

The behaviour near the origin can be obtained from the local form of (7). Many paths run into the origin between the isoclines and (it turns out) that on these paths $v \gg u^2$, so that (7) is approximated by $\frac{dv}{du} = \frac{4v}{3u} + \dots$, thus, near the origin, on all these paths:

$$v = c_0 u^{\frac{4}{3}} + \dots \quad (9)$$

where, c_0 to be determined. Integrating of the mapping formula (8), $\frac{dx}{x} = \frac{du}{3u}$ result in $u = a_0 x^3 + \dots = yx^3$. Thus, the origin of (u, v) corresponds to $x = 0$ and the boundary condition (4) determines the constant of integration in the mapping back to x , namely $a_0 = 1$. The only path which has a chance to satisfy the boundary condition at infinity is the exceptional path running from the origin to the saddle point at p . For the study of the behaviour as the solution approaches the saddle point along this path, let $u = u_p + u^*$, $v = v_p + v^*$. So of (9), $\frac{dv^*}{du^*} = \frac{4v^* + \frac{3}{2}u_p^{\frac{1}{2}}u^*}{v^* + 3u^*}$, $u_p^{\frac{1}{2}} = 12$.

The singular point is a saddle point and the exceptional paths can be found by letting $v^* = ku^*$. Then $k = \frac{4k+18}{k+3}$. The roots are $k_{1,2} = \frac{1}{2} \pm \sqrt{\frac{1}{4} + 18}$. Let $-k_2 = \lambda = 3.76$. Thus, along the exceptional path

running from the origin to the singular point p , $v^* = -\lambda u^*$ and the mapping formula (8) shows that $\frac{dx}{x} = -\frac{du^*}{(\lambda-3)u^*}$. Integration leads to:

$$x = a_\infty (u^*)^{\frac{1}{\lambda-3}} \quad (10)$$

so that, in fact, $x \rightarrow \infty$ as $u^* \rightarrow 0$. The constant a_∞ in the mapping formula is not arbitrary but has already been found from the considerations near the origin. The form of corrections to (9) is found from (10), $y \rightarrow \frac{1}{x^3} \left\{ 144 + \left(\frac{a_\infty}{x}\right)^{\lambda-3} + \dots \right\}$.

The final algorithm for a definition of integration of the problem (3) with boundary conditions (4) and (5) has been depicted in Fig. 2.

PHYSICAL NOTIONS OF THOMAS-FERMI EQUATION

As the notations of the works of Liao or Hagen (Liao, 2003; Hagen, 2009), 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 $n(\vec{x})$ calculated from the classical local density $\rho_{cl}(E; \vec{x}) = \frac{s_D M_p^D(E; \vec{x})}{\rho^2(E; \vec{x})(2\pi\hbar)^D} = \frac{2M\{2M[E-V(\vec{x})]\}^{\frac{D}{2}-1}}{(4\pi\hbar^2)^{\frac{D}{2}}\Gamma(\frac{D}{2})}$ over all negative energies, yielding the Thomas-Fermi density of states:

$$\rho_{cl}^{(-)}(\vec{x}) = \int_{V(\vec{x})}^0 \rho_{cl}(E; \vec{x}) dE = \left(\frac{M}{2\pi\hbar^2}\right)^{\frac{D}{2}} \frac{[-V(\vec{x})]^{\frac{D}{2}}}{\Gamma(\frac{D}{2}+1)} \quad (11)$$

At each point \vec{x} , the electrons occupy all levels up to a Fermi energy $E_F = \frac{p_F(\vec{x})^2}{2M} + V(\vec{x})$. The associated local Fermi momentum is equal to the local momentum function $\rho(E; \vec{x}) = \sqrt{2M[E-V(\vec{x})]}$ at $E = E_F$; $p(E; \vec{x}) = \sqrt{2M[E_F - V(\vec{x})]}$.

For neutral atoms, the Fermi energy is zero and the density (11) will be recovered. By occupying each state of negative energy twice, the classical electron density is:

$$n(x) = 2\rho_{cl}^{(-)}(\vec{x}) \quad (12)$$

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

$$E_{potTF}^{(-)}(\vec{x}) = V(\vec{x})\rho^{(-)}(x) = -\left(\frac{M}{2\pi\hbar^2}\right)^{\frac{D}{2}} \frac{1}{\Gamma(\frac{D}{2}+1)} [-V(\vec{x})]^{\frac{D}{2}+1} \quad (13)$$

To find the kinetic energy density should be integrated:

$$E_{kinTF}^{(-)}(\vec{x}) = \int_{V(\vec{x})}^0 [E - V(\vec{x})] \rho_{cl}(E; \vec{x}) dE = \frac{\frac{D}{2}}{\frac{D}{2}+1} \left(\frac{M}{2\pi\hbar^2} \right)^{\frac{D}{2}} \frac{1}{\Gamma(\frac{D}{2}+1)} [-V(\vec{x})]^{\frac{D}{2}+1} \quad (14)$$

The sum of the two is the Thomas-Fermi energy density $E_{TF}^{(-)}(\vec{x}) = \int_{V(\vec{x})}^0 E \rho_{cl}(E; \vec{x}) dE = -\frac{(\frac{M}{2\pi\hbar^2})^{\frac{D}{2}}}{(\frac{D}{2}+1)\Gamma(\frac{D}{2}+1)}$. 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:

$$\Delta V(x) = 4\pi e^2 [Z\delta^3(\vec{x}) - n(\vec{x})] \equiv 4\pi e^2 [n_c(x) - n(\vec{x})] \quad (15)$$

It is convenient to describe the screening effect of the electron cloud upon the Coulomb potential (14) by a multiplicative dimensionless function $f(\vec{x})$. Restricting our attention to the ground state, which is rotationally symmetric, the solution of the Poisson Eq. (15) can be written as $V(x) = -\frac{Ze^2 f(r)}{r}$. At the origin, the function $f(r)$ is normalized to unity:

$$f(0) = 1 \quad (16)$$

To make sure that the nuclear is not changed by the electrons, where has been obtained in Eq. (12) with boundary conditions (13) and (14).

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 (13) becomes simply $n(x) = -\frac{(2Ze^2M)^{\frac{3}{2}}}{3\pi^2\hbar^3} \left(\frac{f(\xi)}{a_{TF}\xi} \right)^{\frac{3}{2}} = \frac{Z}{4\pi a_{TF}^3} \left(\frac{f(\xi)}{\xi} \right)^{\frac{3}{2}}$. The left-hand side of the Poisson Eq. (15) reads $\Delta V(\vec{x}) = \frac{1}{r} \frac{d^2}{dr^2} V(\vec{x}) = -\frac{Ze^2}{a_{TF}^3 \xi} f''(\xi)$.

So that will be obtained the self-consistent Thomas-Fermi equation:

$$f''(\xi) = \frac{1}{\sqrt{\xi}} f^{\frac{3}{2}}(\xi), \xi > 0 \quad (17)$$

The condition $\xi > 0$ excludes the nuclear charge from the equation, whose correct size is incorporated by the initial condition (16). Near the origin, the Eq. (17) starts out like $f(\xi) = 1 - s\xi + \dots$, with a slope $s \sim 1.58807$. For large, it goes to zero like $f(\xi) \sim \frac{144}{\xi^3}$.

This power falls 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 (17) but does not satisfy the desired boundary condition (16).

It can be derived as an energy functional whose functional extremization yields the Thomas-Fermi Eq. (17), (Baaquie, 1997; Lieb, 2000; Schwabl, 2007; Hagen, 2009).

IMPROVEMENTS IN THE QUANTUM EFFECTS NEAR THE SINGULARITY

Statement of the problem: The Thomas-Fermi energy with exchanges corrections which obtained in above Section 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 are necessary to account for the quantum effects near the singularity, based on the other observation (Baaquie, 1997). This problem can be solved in Theorem 1 by analytic ingredients, especially weak solutions.

METHODOLOGY

Weak solution: For approximate approaches, the Fermi energy and the Poisson Eq. (15) which result in the Thomas-Fermi Eq. (17) will be reviewed in the notions of functional analysis. For the quantum correction near the origin, in general, suppose $U \subseteq (0, \infty)$ is a bounded, open interval and $L: \mathbb{R} \times \mathbb{R} \times \bar{U} \rightarrow \mathbb{R}$; $L = L(p, z, x)$ is a smooth Lagrangian. Also, it should be assumed that the function $I[.]$ have the explicit form:

$$I[\omega] := \int_U L(D\omega(x), \omega(x), x) dx \quad (18)$$

for smooth functions $\omega: \bar{U} \rightarrow \mathbb{R}$ 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, the nonlinear ODE, i.e., the Euler-Lagrange equation associated with the energy functional $I[.]$ defined by (18) can be solved by u :

$$-\left(L_p(Du, u, x) \right)_x + L_z(Du, u, x) = 0 \quad (19)$$

So, on the contrary, it can be tried to find a solution of (19) by searching for minimizers of (18).

Let the Sobolev space $W^{k,p}(U)$ consists of all weak derivations of the locally summable functions $u: U \rightarrow \mathbb{R}$ such that for each multi-index α with $|\alpha| \leq k$ and for all test functions $C_c^\infty(U)$, $\int_U u D^\alpha \varphi dx = (-1)^{|\alpha|} \int_U v \varphi dx$ which the weak derivation belongs to $L^p(U)$. Suppose the closure of $C_c^\infty(U)$ in $W^{k,p}(U)$ is denoted by $W_0^{k,p}(U)$ (Bahuguna *et al.*, 2002; Maz'ya, 2008).

Theorem 2: Singularity near the origin of Thomas-Fermi equation (and then singularity of the Coulomb potential) as a 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 to this enigma.

As the notions of above, let $f: \mathbb{R} \rightarrow \mathbb{R}$ 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 $I[\omega] := \int_U \frac{|D\omega|^2}{2} - F(\omega) dx$ 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 above Section.

Now, focus on Lagrangian L which can be exposed to some awkward singularities other than ones of Thomas-Fermi energy.

Fix any $v \in W_0^{1,q}(U)$ and set $i(\tau) = I[u + \tau v]$, $\tau \in \mathbb{R}$. It can be checked that the Lagrangian L verifies the growth conditions:

$$\begin{aligned} |L(p, z, x)| &\leq C(|p|^q + |z|^q + 1), \\ |D_p L(p, z, x)| &\leq C(|p|^{q-1} + |z|^{q-1} + 1), \\ |D_z L(p, z, x)| &\leq C(|p|^{q-1} + |z|^{q-1} + 1) \end{aligned} \quad (20)$$

For some constant C , $1 < q < \infty$ and all $p, z \in \mathbb{R}$ and $x \in U$. In view of (20), it can be seen that $i(\tau)$ is finite for all τ . Let $\tau \neq 0$ and write the difference quotient:

$$\begin{aligned} \frac{i(\tau) - i(0)}{\tau} &= \int_U \frac{L(Du + \tau v, u + \tau v, x) - L(Du, u, x)}{\tau} dx = \\ &= \int_U L^\tau(x) dx \end{aligned} \quad (21)$$

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

$$\begin{aligned} L^\tau(x) &\rightarrow L_p(D_{u,u,x})v_x + L_z(Du, u, x)v, \tau \rightarrow 0, a.e \\ L^\tau(x) &:= \frac{1}{\tau} \times \int_0^\tau L_p(Du + sDv, u + sv, x)v_x \\ &\quad + L_z(Du + sDv, u + sv, x)v ds \end{aligned} \quad (22)$$

Then since $u, v \in W^{1,q}(U)$, inequality (11) and Yong inequality imply after some elementary calculations that for each $\tau \neq 0$, $|L^\tau(x)| \leq C(|Du|^q + |u|^q + |Dv|^q + |v|^q + 1) \in L^1(U)$.

Consequently, it can be invoked the Dominated Convergence Theorem to conclude from (21) and (22) that $i'(0)$ exists and equals $\int_U L_p(Du, u, v)v_x + L_z(Du, u, v)v dx$.

But then since $i(\cdot)$ has a minimum for $\tau = 0$, $i'(0) = 0$; and $u \in T = \{\omega \in W^{1,q}(U) | \omega = g \text{ on } \partial U \text{ in the trace sense}\}$ is a solution of the boundary-value problem:

$$\begin{cases} -\left(L_p(Du, u, x)\right)_x + L_z(Du, u, x), \text{ in } U \\ u = g, \text{ on } \partial U \end{cases} \quad (23)$$

For the Euler-Lagrange equation means is the weak solution. Also the mapping $(p, z) \rightarrow L(p, z, x)$ is convex. Then $I[u] + \int_U D_{Du}(Du(x), u(x), x) \cdot (Dw - Du) + D_u L(Du(x), u(x), x) \cdot (w(x) - u(x)) dx \leq I[\omega]$, for the weak solution u and any $\omega \in T$.

In view of (23) the second term on the right is zero and therefore $I[u] \leq I[\omega]$ for each $\omega \in T$. Then this solution is unique, too.

CONCLUSION

In this study, the first integral of Thomas-Fermi equation and the behaviour of the solution near the saddle point of the equation was determined which result to an algorithm for the numerical procedure. Also, a novel method 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 method is to offer a general solution to the problem that can be applied to the nonlinear Poisson equation. The proposed approach for Euler-Lagrange equations corresponding to multivariate functions can be used with a large set of singularities of that functions.

CONFLICT OF INTEREST

It should be noted that there is no financial support and there is no competitive interest in this area.

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