Numerical Calculation of the Electron Density at the Wigner–Seitz Radius Based on the Thomas–Fermi–Dirac Equation

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The fourth order Runge–Kutta method was used to solve the Thomas–Fermi–Dirac (TFD) equation. This method simplifies solving the TFD equation and improves the solution accuracy. The electron density of Cu at the Wigner–Seitz atomic radius was calculated as an example, using the TFD equation. The same method was used to calculate electron densities of other 24 elements at the Wigner–Seitz radius. These results demonstrate a successful application of the Thomas–Fermi–Dirac model in materials research.

Keywords: Electron Density, Thomas–Fermi–Dirac (TFD) Equation, Runge–Kutta Method, Wigner–Seitz Radius.

1. INTRODUCTION

Thomas in 1926[1] and Fermi in 1928[2] independently created the statistical model describing the distribution of electrons in an atom, called the Thomas–Fermi (TF) model (equation). In 1930 Dirac[3] had introduced the exchange interaction into the Thomas–Fermi model, and then the Thomas–Fermi–Dirac (TFD) model was built, known as the electronic statistical theory. A successful solution of the TFD equation is helpful to describe the shell structure of atoms. The numerical solutions of the TFD equation include the second order Runge–Kutta method, Taylor series expansions, and the Cheng et al. method. Cheng et al.[4] applied the numerical method, given by Latter,[5] to solve the TFD equation.

The TFD model has been constantly improved. Cheng et al.[6] further modified the TFD model. The modified TFD electron theory is known as the Thomas–Fermi–Dirac–Cheng (TFDC) model. The TFDC model proposed two important boundary conditions at the interface (including atomic interfaces): the electron densities and the chemical potentials must be continuous in accordance with the quantum principles. Density functional theory (DFT) and TFDC both originated from the TFD model. Currently, DFT is the most powerful tool for electronic structure

calculations. In recent years, the method combining DFT with molecular dynamics simulations has been widely used in design, synthesis and performance evaluation of materials, being the basic core technology in computational materials science. Hao et al.[7] studied interactions between an oxygen atom and $C_{70}(D_{5h})$, while Weng et al.[8] looked at the mechanism of O_2 adsorption and dissociation on the W (111) surface. Ono et al.[9] used the first principles calculation methods for obtaining scattering waves to investigate transport properties of nanostructures.

Since the use of TFDC is quite simple and convenient, it has also attracted some attention. In the TFDC model, Cheng et al. proposed a new concept of "electron density of atomic surface,"[6] and calculated the electron densities of some elements at the Wigner–Seitz atomic radius, based on the numerical solution of the TFD equation.[6, 10] Based on the TFDC model, researches addressed many applications in condensed materials, such as calculating internal stress in thin film,[10] or the dislocation limiting size in some pure metals,[11] along with interpreting the superconducting mechanism.[12] Li[13] had established the atomic phase diagram, and experimentally demonstrated it. Ren et al.[14, 15] explained the softening of nanometer Ag/Cu and Cu/Ni metallic multilayers.

Based on only four computed items of the power series expansion, Cheng et al. solved the TFD equation, and calculated electron density, which is different in their

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own Refs. [6 and 10]. It is possible that the accuracy of this solution is low, and a more accurate solution of the TFD equation is desired. Runge–Kutta is an important explicit or implicit iterative method, which is often used to solve common differential equations, due to its high accuracy and steady convergence. In this paper, the fourth order Runge–Kutta method was applied to solve the TFD equation. Using this method, the numerical solution of the TFD equation for Cu was obtained as an example, and the electron densities of some other elements at the Wigner–Seitz radius were calculated. These results aid the TFDC electron theory applications in materials research and design.

2. TFD EQUATION

In the TF model, built by Thomas and Fermi,[1,2] the electron density $n(x)$ was expressed as

$$n(x) = \frac{Z}{4\pi\mu^3}\left[\frac{\psi(x)}{x}\right]^{3/2} \tag{1}$$

The effect of electron exchange interactions was brought into the TF model by Dirac,[3] and the electron density $n(x)$ can be expressed at absolute zero as

$$n(x) = \frac{Z}{4\pi\mu^3}\left[\varepsilon + \left(\frac{\psi(x)}{x}\right)^{1/2}\right]^3 \tag{2}$$

Here, $\mu = a_0((9\pi^2)/(128Z))^{1/3}$, $\psi(x)$ is the TFD function, $n(x)$ is the electron density, a_0 is the first Bohr's radius of hydrogen atom, Z is the atomic number, x is the non-dimensional atomic radius, $r = \mu \cdot x$ is the real atomic radius, and $\varepsilon = (3/(32\pi^2))^{1/3}Z^{-2/3}$ is a term of electron exchange interactions, which was brought by Dirac.

By using Eq. (2) in the Poisson's equation, the TFD equation at absolute zero can be written as

$$\frac{d^2\psi}{dx^2} = x\left[\left(\frac{\psi(x)}{x}\right)^{1/2} + \varepsilon\right]^3 \tag{3}$$

For a non-isolated neutral atom, the following boundary conditions can be defined

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

$$\left(\frac{d\psi}{dx}\right)_{x=x_0} = \frac{\psi(x_0)}{x_0} \tag{5}$$

The Poisson's equation assumes that the electron cloud is spherically symmetric, based on which the TFD model has been successfully applied to calculate the atomic scattering factor in X-ray diffraction.[4] Thus, the electron density at the atomic radius can be calculated, as long as the atomic radius is known.[13]

3. RUNGE–KUTTA METHOD

The ordinary differential system, expressed as the following, can be transferred to the fourth order Runge–Kutta

formula by a series of mathematical transformations:

$$\begin{cases} \dfrac{dy}{dx} = f(x, y) \\ y(x_0) = y_0 \end{cases}$$

where y and f are vectors.

The fourth order Runge–Kutta formula can be expressed as

$$\begin{cases} y_{n+1} = y_n + \dfrac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4) \\ k_1 = f(x_n, y_n) \\ k_2 = f\left(x_n + \dfrac{1}{2}h, y_n + \dfrac{1}{2}hk_1\right) \\ k_3 = f\left(x_n + \dfrac{1}{2}h, y_n + \dfrac{1}{2}hk_2\right) \\ k_4 = f\left(x_n + h, y_n + hk_3\right) \end{cases}$$

The Runge–Kutta method has the advantage of high calculation accuracy and stability, and can be conveniently programmed. The local truncation error is $O(h^5)$.

4. THE NUMERICAL SOLUTION OF TFD EQUATION

Equation (3) is a second order ordinary differential equation. While its analytical solution can not be determined, it can be solved by means of numerical integration. Since $\psi''(0) = \infty$, the $\psi(x)$ function around the null point can not be expanded in the Taylor's series, but it can be expanded in a semi-convergent expansion, expressed as in:[16]

$$\psi(x) = 1 + a_1 x^{1/2} + a_2 x + a_3 x^{3/2} + a_4 x^2 + a_5 x^{5/2} + \cdots \tag{6}$$

and

$$\psi'(x) = \frac{1}{2}a_1 x^{-1/2} + a_2 + \frac{3}{2}a_3 x^{1/2} + 2a_4 x + \frac{5}{2}a_5 x^{3/2} + \cdots \tag{7}$$

By plugging Eq. (6) into Eq. (3), a series of coefficients in the expansion can be obtained by comparing coefficients of the terms with the same power exponent on both sides of the equation. Coefficient formulas of the top 13 terms are:

$$a_1 = 0$$

$$a_3 = \frac{4}{3}$$

$$a_4 = \frac{3}{2}\varepsilon$$

$$a_5 = \frac{2}{5}a_2 + \frac{4}{5}\varepsilon^2$$

Table I. r and Ψ corresponding to a_2 in the numerical solutions of the TFD equation for Cu.

$-a_2$	1.6245	1.6230	1.62241	1.6224	1.6220	1.6210
$r \times 10^{-10}$/m	Ionic	Ionic	1.415	1.391	1.057	0.861
Ψ	Imaginary	Imaginary	0.028633	0.02964	0.072146	0.117281

$$a_6 = \frac{1}{3} + \frac{a_2\varepsilon}{2} + \frac{\varepsilon^3}{6}$$

$$a_7 = \frac{6}{35}a_2\varepsilon^2 + \frac{3}{70}a_2^2 + \frac{5}{7}\varepsilon$$

$$a_8 = \frac{2}{15}a_2 + \frac{77}{120}\varepsilon^2$$

$$a_9 = \frac{14}{45}\varepsilon^4 - \frac{1}{42}a_2^2\varepsilon^2 + \frac{41}{210}a_2\varepsilon - \frac{1}{252}a_2^3 + \frac{2}{27}$$

$$a_{10} = \frac{17}{200}\varepsilon^4 + \frac{137}{1400}a_2\varepsilon^2 + \frac{5}{28}\varepsilon + \frac{1}{175}a_2^2$$

$$a_{11} = \frac{\varepsilon^5}{99} + \frac{37}{3465}\varepsilon^3 a_2 + \frac{15397}{83160}\varepsilon^2 + \frac{1}{132}a_2^3\varepsilon^2$$
$$+ \frac{83}{9240}a_2^2\varepsilon^2 + \frac{31}{1485}a_2 + \frac{1}{1056}a_2^4$$

$$a_{12} = \frac{4}{405} + \frac{509}{5040}\varepsilon^3 + \frac{1}{21}a_2\varepsilon - \frac{2}{175}a_2\varepsilon^4$$
$$+ \frac{8}{525}a_2^2\varepsilon^2 + \frac{4}{1575}a_2^3$$

$$a_{13} = \frac{272}{9009}\varepsilon + \frac{149}{6600}\varepsilon^4 + \frac{21457}{40040}a_2\varepsilon^2 - \frac{1}{286}a_2\varepsilon^5$$
$$+ \frac{557}{100100}a_2^2 + \frac{41}{4004}a_2^2\varepsilon^3 + \frac{47}{48048}a_2^3\varepsilon$$
$$- \frac{15}{4576}a_2^4\varepsilon^2 - \frac{5}{4576}a_2^5$$

The formula for the a_2 coefficient doesn't appear above, since a_2 is defined as the initial slope, which is equal to $\psi'(0)$. For the convenience of calculation, an independent variable w was introduced, defined as $x = w^2/2$. The value of the initial slope a_2 is between -1.7 and -1.5,[17] so its initial value was taken in this interval for the beginning of the calculation. Once the initial slope $a_2 = \psi'(0)$ was determined, the other coefficients were calculated.

By using these coefficients in Eqs. (6) and (7), one can get the values of $\psi(w)$ and $\psi'(w)$ at $w = 0.48$, corresponding to $x = 0.1152$ near the null point. Subsequently, solving the TFD equation can be transformed into finding the initial value of the first-order ordinary differential equation. When $w < 0.48$ (corresponding to $x < 0.1152$, x can be seen to be very near the null point), the method of solving for $\psi(w)$ is same as that at $w = 0.48$. When $w > 0.48$, the numerical solution of $\psi(w)$ can be obtained by the fourth order Runge–Kutta method using a computer program. In our computation, w interval step was taken as 0.0001. Although the accuracy of the fourth order Runge–Kutta method for the TFD equation cannot be determined, it is definitely higher than that of the second order Runge–Kutta method.

5. ELECTRON DENSITY CALCULATIONS FOR Cu AND SOME OTHER ELEMENTS

Equation (5) is the boundary condition for the TFD equation of the non-isolated neutral atom, and an x_0 solution, obeying this boundary condition, can be determined from the numerical solution of the TFD equation. If the difference between both sides of Eq. (5) was less than 10^{-6}, they were considered approximately equal. For different initial slopes, a_2, the boundary conditions can be obeyed at different atomic radii, r. A series of numerical solutions of $\psi(w)$, corresponding to different atomic radii can be solved for each element, and then an initial slope, a_2, corresponding to the Wigner–Seitz radius, r_{ws}, can be picked out. Finally, by using the initial slope and $\psi(r_{ws})$ numerical solution in Eq. (2), one can get the electron density.

In the TFDC theory, the Winge–Seitz radius, which is different than the usual atomic radius, is often used. The Wigner–Seitz radius can be determined from lattice constants for any element with the known crystal structure. The relationships between the Winger–Seitz radius, r_{ws}, and the lattice constant, a, are: $r_{ws} \approx 0.3908a$ for the face centered cubic lattice, $r_{ws} \approx 0.4924a$ for the body centered cubic lattice, and $r_{ws} \approx 0.4693a$ for the hexagonal close packed lattice.[13, 18]

Table II. Electron densities of some elements at the Wigner–Seitz radius.

Element	$r_{ws} \times 10^{-10}$/m	Electron density $\times 10^{29}$/m^{-3}	Element	$r_{ws} \times 10^{-10}$/m	Electron density $\times 10^{29}$/m^{-3}
Li	1.728	0.232	Zn	1.537	1.96
Be	1.246	1.454	Sr	2.378	0.157
Na	2.113	0.173	Zr	1.771	1.073
Mg	1.77	0.5495	Nb	1.625	1.728
Al	1.582	1.045	Mo	1.549	2.246
Ca	2.181	0.207	Rh	1.486	2.877
Sc	1.775	0.754	Pd	1.520	2.591
Ti	1.616	1.277	Ag	1.597	2.027
V	1.496	1.939	Cd	1.727	1.348
Cr	1.420	2.572	Cu	1.413	2.931
Fe	1.411	2.739	C	1.106	3.283
Co	1.3827	3.132	Ni	1.377	3.261

A larger difference between Cu electronic densities exists in Refs. [6 and 10], so Cu element was taken as an example in this paper to show the solution process for the electron density at the atomic boundary. In the computer program, a_2 was set as a variable, and the corresponding r and Ψ were determined, with some of the a_2 values listed in Table I ($a_2 = -1.6245$ or -1.6230, corresponding to the boundary condition of the ionic atom, to be discussed in another paper). The Winger–Seitz radius, r_{ws}, was determined as 1.413×10^{-10} m from the lattice constant, and the r value, closest to r_{ws}, was picked out from a series of r values. The atomic radius of 1.412992 Å, obeying the boundary condition of Eq. (5) is the closest to r_{ws}, only when a_2 equals -1.6224093. The value of ψ under this condition is used in Eq. (3), allowing to determine the electron density of Cu as 2.931×10^{29} m^{-3}, which is close to the result in Ref. [6]. The Winger–Seitz radii and electron densities of the 24 common elements were determined using this method, shown in Table II. The lattice constants of the 24 elements were taken from Refs. [19 and 20].

6. CONCLUSION

(1) The fourth order Runge–Kutta method was applied to solve the TFD equation numerically. The method can be conveniently programmed.
(2) Based on the numerical solution of the TFD equation, the electron densities of 24 elements at the Wigner–Seitz radius were calculated.

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