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The complete proof of the virial theorem in the refined TFD theory for all electrons of an atom in a solid*

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The complete proof of the virial theorem in refined Thomas–Fermi–Dirac theory for all electrons of an atom in a solid is given.

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1. Introduction

For the structures and properties of nano-materials, and the dynamical behaviour of micro- and nano- systems, the quantum effects are known of importance more or less. The semi-classical Thomas–Fermi–Dirac (TFD) theory is a simplified one of those theories to treat of the quantum effects. In TFD theory, there is no quantum tunnel effect, i.e. there is no possibility of electrons with energy E being checked up in the area where the potential is bigger than E. In the 1990s, Cheng *et al* [1−4] proposed the refined TFD theory, in which the quantum tunnel effect for the atoms in a solid is included, and the tunnel electrons provide a pseudo-potential for the system. Cheng and Cheng[5] have shown that the pseudo-potential will affect the properties of materials, so that the discussion of this theory and its deductions in detail will be useful for the study of the structures and properties of nano-materials, and the behaviours of micro- and nano-systems, as well as the structures and some properties of some general materials and their surfaces.

In Ref.[6], the important virial theorem for the electrons on the atomic surface in the refined TFD theory have been proved. In Ref.[7], the virial theorem for the inner of an atom in the same theory has also been given. As to the virial theorem for all the electrons in an atom in the same theory, although its correct form has been given in Ref.[6], there was some ambiguity in the proof given there. In the present paper, we will show that the proof is incomplete through analysis of the ambiguity, and then give a complete proof by using the virial theorem for the inner of an atom in the same theory. Because of the importance of the virial theorem, it is obviously necessary to do this.

2. The incompleteness of the proof of virial theorem for all electrons inside an atom in Ref.[6]

In Ref.[6], the final result, i.e. the virial theorem for all electrons of an atom in a solid in the refined TFD theory was expressed by Eq.(14) in Ref.[6] as follows:

$$2(\text{total kinetic energy}) + (\text{total potential energy})$$

$$-3p_0V_0 = 0, \qquad (14) \text{ in Ref.}[16]$$

where p_0 and V_0 are the pressure on the outside of the surface of the atom and the volume of it respec-

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tively. This result was reached by integrating Eq.(16) in Ref.[6] over

$$(1/3)(2E_{\mathrm{k}}(r)+E_{\mathrm{ex}}(r))+\int n(r)(\mathrm{d}U(r)/\mathrm{d}r)\mathrm{d}r=0, \qquad (16) \text{ in Ref.[16]}$$

from zero to V_0 and using

$$p_{02}=-\partial\Phi_0/\partial V_0=\Phi_0/3V_0, \quad (22) \text{ in Ref.[6]}$$

$$p_0=p_{01}+p_{02}.$$

Here $n(r)$ is the density of electrons, $U(r)$ is the potential energy of an electron located at r from the nuclei contributed by the nuclei and the other electrons except those of the surface charge, V_0 is the volume of the atom; Φ_0 is the pseudo-potential, which includes the self-energy of the surface charge and the interaction energy between the surface charge and both of the nuclei and all the volume charges; p_{02} is the pressure complement on the outside of the surface of the atom provided by the pseudo-potential; p_{01} is the pressure complement on the surface of the atom provided by all of the energies except the pseudo-potential; E_{k} is the density of kinetic energy of electrons, and E_{ex} is the density of exchange energies of electrons.

In fact, Eq.(16) in Ref.[6] was obtained by an indefinite integral of the product of $\mathrm{d}n(r_1)/\mathrm{d}r_1$ and Eq.(7) in Ref.[6],

$$\begin{aligned}&(3h^2/10m)(3/8\pi)^{2/3}(5/3)n(r_1)^{5/3}\\&-e^2(3/\pi)^{1/3}n(r_1)^{1/3}-Ze^2/r_1\\&+\int_{r_2<r_0}(n(r_2)e^2/r_{12})\mathrm{d}V_2+\lambda=0, \quad (7) \text{ in Ref.[6]}\end{aligned}$$

with r_0 and λ being the radius of the atom and Lagrangian multiplier respectively. Thus Eq.(16) in Ref.[6] should be revised to

$$\begin{aligned}&(1/3)(2E_{\mathrm{k}}(r)+E_{\mathrm{ex}}(r))\\&+\int_0^r n(s)(\mathrm{d}U(s)/\mathrm{d}s)\mathrm{d}s+C_1=0,\end{aligned} \qquad (1)$$

where C_1 is a certain real number independent of r. C_1 can be determined by a definite integral of the product of $\mathrm{d}n(r_1)/\mathrm{d}r$ and Eq.(7) in Ref.[6], and we have no reason for taking C_1=0 to recover Eq.(16) in Ref.[6]. So Eqs.(17), (20) and (23) in Ref.[6] should be revised to, respectively,

$$\begin{aligned}&(1/3)\Big[\int_{r<r_0}(2E_{\mathrm{k}}(r)+E_{\mathrm{ex}}(r))\mathrm{d}V\Big]\\&+V_0\int_0^{r_0}n(r)(\mathrm{d}U(r)/\mathrm{d}r)\mathrm{d}r+C_1V_0\\&-(1/3)\int_0^{r_0}n(r)(\mathrm{d}U(r)/\mathrm{d}r)4\pi r^3\mathrm{d}r=0,\end{aligned} \qquad (2)$$

$$V_0\int_0^{r_0}n(r)(\mathrm{d}U(r)/\mathrm{d}r)\mathrm{d}r=-V_0p_{01}+C_2V_0, \qquad (3)$$

$$\begin{aligned}&2(\text{total kinetic energy})\\&+(\text{total potential energy})\\&-3p_0V_0+(C_1+C_2)V_0=0,\end{aligned} \qquad (4)$$

where C_2 is a certain real number to be determined by the definite integral of

$$-\mathrm{d}p(r)/\mathrm{d}r+nE_r=0, \qquad (5)$$

which is the equation next to Eq.(19) in Ref.[6], and we have no reason for taking C_2=0 to recover Eq.(20) in Ref.[6].

The above analysis shows that the proof given by Ref.[6], when revised, has only proved Eq.(4), which is different from virial theorem (14) in Ref.[6] by an unwanted term $(C_1+C_2)V_0$. In order to complete the proof of virial theorem (14) in Ref.[6], we need to supply the proof of

$$(C_1+C_2)V_0=0. \qquad (6)$$

3. The proof of $(C_1+C_2)V_0=0$

Put $r=r_0$ in Eq.(1), we have

$$\begin{aligned}&(1/3)(2E_{\mathrm{k}}(r_0)+E_{\mathrm{ex}}(r_0))\\&+\int_0^{r_0}n(r)(\mathrm{d}U(r)/\mathrm{d}r)\mathrm{d}r+C_1=0.\end{aligned} \qquad (7)$$

Substituting Eq.(3) into Eq.(7), we obtain

$$(1/3)(2E_{\mathrm{k}}(r_0)+E_{\mathrm{ex}}(r_0))-p_{01}+C_1+C_2=0. \qquad (8)$$

According to the virial theorem for the inner of the atom in a solid,[7] we have

$$p_1(r)=(1/3)[2E_{\mathrm{k}}(r)+E_{\mathrm{ex}}(r)]. \qquad (9)$$

Substituting Eq.(9) with r replaced by r_0 into Eq.(8) and making use of

$$p_1(r_0) = p_{01}, \tag{10}$$

we obtain Eq.(6). This finishes the proof.

This proof looks simple. This attributes to making use of the virial theorem for the inner of the atom in a solid, of which the proof in Ref.[7] was not so simple.

Another way to prove Eq.(6) is to use the definite integral of the product of $\mathrm{d}n(r_1)/\mathrm{d}r_1$ and Eq.(7) in Ref.[6] to obtain some terms in Eq.(2) instead of C_1V_0 and to use that of Eq.(5) to obtain a term in Eq.(3) instead of C_2V_0, and then prove the sum of these terms is zero. However, this way, although is right, is not so simple as what we have done above.

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