Derivation of von Weizsäcker Equation Based on Green–Gauss Theorem

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A simple and short derivation of von Weizsäcker equation for kinetic energy functional is presented. The derivation is based on the Green–Gauss theorem and is valid for one-electron systems. In the proof the asymptotic behavior of wave function for the finite systems was used. Two results important for kinetic energy functional evaluation are also derived as consequences of the Green–Gauss theorem.

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1. Introduction

The density functional theory (DFT) [1–3] is a powerful tool to study the molecular systems. First main theorem of this theory states that the ground state of the system can be fully described by electron density $\rho(\mathbf{r}): \mathbb{R}^3 \to \mathbb{R}$. Second theorem states that the total energy of the system can be obtained by minimization of the functional $E[\rho]$ subject to the constraint $\int_{\mathbb{R}^3} \rho(\mathbf{r}) d\mathbf{r} = N$, where N is total number of electrons in the system. The DFT theory is the powerful tool, however it has one drawback: the exact kinetic energy functional and exact exchange-correlation functional are unknown and hence the total energy functional is approximated only.

The research in construction of the exchangecorrelation functionals has been successful and many precise (although approximate) functionals based on local (LDA) and gradient (GGA) approximation have been proposed [4]. However, the progress in construction of the kinetic energy functionals is not so fruitful. The review of the orbital-free kinetic energy density functionals (OF-KEDF) is presented by Wang [5]. The availability of accurate orbital-free kinetic energy density functionals could avoid the solution of the Kohn–Sham eigenproblem. It has not been constructed and, therefore, the algorithm solving Kohn–Sham eigenproblem based on the linear combination of atomic orbital (LCAO) leads to algebraic generalized eigenvalue problems with solving cost scaling as $O(n^3)$.

In the classical approach based on the Kohn–Sham eigenproblem one must store the set of eigenfunctions $\{\Psi_i(\mathbf{r}): \mathbb{R}^3 \to \mathbb{R}\}_{i=1}^N$. If the eigenfunction $\Psi_i(\mathbf{r})$ is represented by M basis functions, then MN coefficients must be evaluated holding the orthogonality constraints $\int_{\mathbb{R}} \Psi_i(\mathbf{r}) \Psi_j(\mathbf{r}) d\mathbf{r} = \delta_{i,j}$. The availability of OF-KEDF could reduce the dimension of the problem to \mathbb{R}^3 . Moreover, if electron density $\rho(\mathbf{r})$ was represented by M atomic orbitals, only M coefficients could be evaluated without the orthogonality constraint. Further, one could avoid solving eigenvalue problem and solve the minimization problem with constraints only, where the efficient algorithms are available [6].

There are two classical results proved by Thomas– Fermi and von Weizsäcker [5, 3] concerning OF-KEDF. Based on these models more sophisticated results were presented in Refs. [7–9]. The key point is that Thomas– Fermi model is exact only for the free electron gas. The Thomas–Fermi model applied to molecular systems gives quite poor results [10, 11]. More reliable model was introduced by von Weizsäcker, which is derived using the density matrix formalism. For instance von Weizsäcker model is exact for one-electron systems.

In this paper we present the derivation of von Weizsäcker relation for one-electron systems. The derivation is based on the definition of kinetic energy. Additionally, we prove that the kinetic energy functional for many-electron system cannot include $\int_{\mathbb{R}^3} \nabla^2 \rho(\mathbf{r}) d\mathbf{r}$. The derivation is based on the Green–Gauss theorem.

2. Consequences of the Green–Gauss theorem

There are many formulations of the Green–Gauss theorem [12], one of them is the following. Let $f, g: \Omega \subset \mathbb{R}^3 \to \mathbb{R}$ be two integrable functions and Σ be the surface (boundary) of the closed volume Ω . Then it holds

$$\int_{\Omega} f(\boldsymbol{r}) \nabla^2 g(\boldsymbol{r}) d\boldsymbol{r} = -\int_{\Omega} \nabla f(\boldsymbol{r}) \nabla g(\boldsymbol{r}) d\boldsymbol{r} + \oint_{\Sigma} f(\boldsymbol{r}) \nabla g(\boldsymbol{r}) \cdot \boldsymbol{n} d\sigma, \qquad (1)$$

where \boldsymbol{n} is a normal unit vector to the surface $\boldsymbol{\Sigma}$, directed outwards and $\boldsymbol{\phi}$ denotes the surface integral. For

the special case $f(\mathbf{r}) \equiv 1$ this theorem reduces to

$$\int_{\Omega} \nabla^2 g(\boldsymbol{r}) d\boldsymbol{r} = \oint_{\Sigma} \nabla g(\boldsymbol{r}) \cdot \boldsymbol{n} d\sigma.$$
⁽²⁾

Let assume that $g(\mathbf{r}) \equiv \varrho(\mathbf{r})$ is the electron density of many-electron finite system, hence the integral $\int_{\mathbb{R}^3} \varrho(\mathbf{r}) d\mathbf{r}$ must be finite and equal to the number of electrons in the system.

Let us denote by $||\boldsymbol{v}||$ the length of vector $\boldsymbol{v} \in \mathbb{R}^3$. It is well known [3, 13] that for finite systems and for large $r = ||\boldsymbol{r}||$ the wave function $\Psi(\boldsymbol{r})$ decreases exponentially, i.e. $\Psi(\boldsymbol{r}) = Ce^{-\alpha r}$, where $C, \alpha > 0$. Hence, the electron density behaves as $\varrho(\boldsymbol{r}) = \Psi^2(\boldsymbol{r}) = C^2e^{-2\alpha r}$. If Ω is a ball of radius r, then the surface Σ is a sphere of radius r. For this case the integral on the right hand side of Eq. (2) can be easily obtained

$$I(r) = \oint_{\Sigma} \nabla g(\mathbf{r}) \cdot \mathbf{n} \mathrm{d}\sigma = -8\pi\alpha C^2 r^2 \mathrm{e}^{-2\alpha r}.$$
 (3)

The limit of this integral is

$$\lim_{r \to \infty} I(r) = -8\pi\alpha C^2 \lim_{r \to \infty} r^2 e^{-2\alpha r} = 0.$$
(4)

Moreover, if the radius of the ball Ω is increased, then $\Omega \to \mathbb{R}^3$. Hence, based on the above relation, we obtain

$$\int_{\mathbb{R}^3} \nabla^2 \varrho(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} = 0.$$
(5)

It means that the kinetic energy functional T for manyelectron system does not need to account explicitly the term proportional to $\int_{\mathbb{R}^3} \nabla^2 \varrho(\mathbf{r}) d\mathbf{r}$. As a consequence, in the gradient expansion of the kinetic energy functional

$$T \approx T_0[\varrho] + T_1[\nabla \varrho] + T_2[\nabla^2 \varrho] + \dots$$
(6)
the terms proportional to $T_2[\nabla^2 \varrho]$ can be omitted.

3. One-electron system

Let us denote by $\Psi(\mathbf{r}): \mathbb{R}^3 \to \mathbb{R}$ the real wave function of one-electron system. Then, the kinetic energy of this system is given by

$$T = -\frac{1}{2} \int_{\mathbb{R}^3} \Psi(\mathbf{r}) \,\nabla^2 \Psi(\mathbf{r}) \,\mathrm{d}\mathbf{r},\tag{7}$$

and the electron density is defined as

$$\varrho(\boldsymbol{r}) = \Psi^2(\boldsymbol{r}). \tag{8}$$

Applying the ∇^2 operator to both sides of the above relation one obtains

$$\nabla^2 \varrho(\boldsymbol{r}) \equiv \nabla^2 \Psi^2(\boldsymbol{r}) = 2||\nabla \Psi(\boldsymbol{r})||^2 + 2\Psi(\boldsymbol{r}) \nabla^2 \Psi(\boldsymbol{r}),$$
(9)

where $||\nabla \Psi(\mathbf{r})||$ denotes length of vector $\nabla \Psi(\mathbf{r})$. Integrating the above equation over \mathbb{R}^3 and substituting Eq. (7) we obtain

$$\int_{\mathbb{R}^3} \nabla^2 \varrho(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} = 2 \int_{\mathbb{R}^3} ||\nabla \Psi(\boldsymbol{r})||^2 \mathrm{d}\boldsymbol{r} - 4T, \qquad (10)$$
hence

$$T = \frac{1}{2} \int_{\mathbb{R}^3} ||\nabla \Psi(\mathbf{r})||^2 \mathrm{d}\mathbf{r} - \frac{1}{4} \int_{\mathbb{R}^3} \nabla^2 \varrho(\mathbf{r}) \mathrm{d}\mathbf{r}.$$
(11)

Let us apply ∇ operator to both sides of Eq. (8)

$$\nabla \varrho(\mathbf{r}) \equiv \nabla \Psi^2(\mathbf{r}) = 2 \Psi(\mathbf{r}) \nabla \Psi(\mathbf{r}). \tag{12}$$

Taking square of both sides in the above equation and

substituting Eq. (8) we obtain

$$||\nabla \varrho(\boldsymbol{r})||^2 = 4 \Psi^2(\boldsymbol{r}) ||\nabla \Psi(\boldsymbol{r})||^2$$

$$= 4\varrho(\mathbf{r}) ||\nabla \Psi(\mathbf{r})||^2.$$
(13)

Inverting this relation we get

$$||\nabla \Psi(\mathbf{r})||^2 = \frac{||\nabla \varrho(\mathbf{r})||^2}{4\varrho(\mathbf{r})}.$$
(14)

Finally, substituting Eq. (14) into Eq. (11) we get the kinetic energy functional

$$T = \frac{1}{8} \int_{\mathbb{R}^3} \frac{||\nabla \varrho(\boldsymbol{r})||^2}{\varrho(\boldsymbol{r})} d\boldsymbol{r} - \frac{1}{4} \int_{\mathbb{R}^3} \nabla^2 \varrho(\boldsymbol{r}) d\boldsymbol{r}.$$
 (15)

This is an exact kinetic energy functional for one-electron system where the electron density is defined by function $\varrho(\mathbf{r}): \mathbb{R}^3 \to \mathbb{R}$. It follows from Eq. (15) that kinetic energy functional depends on electron density $\varrho(\mathbf{r})$, length of gradient $||\nabla \varrho(\mathbf{r})||$ and laplacian $\nabla^2 \varrho(\mathbf{r})$. From Sect. 2 it follows that the second term is equal to zero. Dropping the second term in Eq. (15), the von Weizsäcker equation is derived

$$T = \frac{1}{8} \int_{\mathbb{R}^3} \frac{||\nabla \varrho(\boldsymbol{r})||^2}{\varrho(\boldsymbol{r})} \mathrm{d}\boldsymbol{r}.$$
 (16)

¿From the above discussion it follows that von Weizsäcker equation is valid for any one-electron system.

4. Kinetic energy in DFT

In this section we provide the derivation of kinetic energy formula commonly applied in DFT. The derivation is based on equations presented in the previous sections. In DFT the kinetic energy of system containing N electrons is given by

$$T = -\frac{1}{2} \sum_{i=1}^{N} \int_{\mathbb{R}^{3}} \Psi_{i}(\boldsymbol{r}) \nabla^{2} \Psi_{i}(\boldsymbol{r}) \mathrm{d}\boldsymbol{r}, \qquad (17)$$

where $\Psi_i(\mathbf{r}): \mathbb{R}^3 \to \mathbb{R}$ for i = 1, ..., N is set of occupied one-electron Kohn–Sham eigenfunctions [2, 1, 11, 10, 3]. If each eigenfunction $\Psi_i(\mathbf{r})$ is occupied by one electron, then the electron charge distribution is defined as

$$\varrho(\boldsymbol{r}) = \sum_{i=1}^{N} \Psi_i^2(\boldsymbol{r}).$$
(18)

Since the Laplace operator is linear, applying ∇^2 to both sides of the above equation, we obtain the analogous relation to Eq. (9):

$$\nabla^{2} \varrho(\boldsymbol{r}) = 2 \sum_{i=1}^{N} ||\nabla \Psi_{i}(\boldsymbol{r})||^{2}$$
$$+ 2 \sum_{i=1}^{N} \Psi_{i}(\boldsymbol{r}) \nabla^{2} \Psi_{i}(\boldsymbol{r}).$$
(19)

Integrating over the space \mathbb{R}^3 and applying Eq. (5) one obtains

$$\sum_{i=1}^{N} \int_{\mathbb{R}^{3}} \Psi_{i}(\boldsymbol{r}) \nabla^{2} \Psi_{i}(\boldsymbol{r}) \mathrm{d}\boldsymbol{r}$$
$$= -\sum_{i=1}^{N} \int_{\mathbb{R}^{3}} ||\nabla \Psi_{i}(\boldsymbol{r})||^{2} \mathrm{d}\boldsymbol{r}.$$
(20)

Using Eq. (17) we get

$$T = \frac{1}{2} \sum_{i=1}^{N} \int_{\mathbb{R}^3} ||\nabla \Psi_i(\boldsymbol{r})||^2 \mathrm{d}\boldsymbol{r}.$$
 (21)

The above formula is more convenient than Eq. (17), since the degree of the differential operator is one (as compared to ∇^2 in Eq. (17)). This reformulation is important when finite element method [14] or spectral method [15] are applied to solve the Kohn–Sham equation [16].

5. Summary

We provided the short derivation of the von Weizsäcker formula. The derivation is based on the definition of the kinetic energy valid for any one-electron system. The derivation does not use the matrix density formulation. Moreover, it was shown that for finite system, containing any number of electrons, it holds $\int_{\mathbb{R}^3} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} = 0$. Hence, the kinetic energy functional T for any system does not need to account this term explicitly. Additionally, convenient formula for kinetic energy is provided which is particularly useful in finite element or spectral method.

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