Chapter 21
Orbital-Free Density Functional Theory: Pauli Potential and Density Scaling

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Abstract In orbital-free density functional theory only a single equation, the so-called Euler equation, has to be solved for any system instead of the Kohn–Sham equations. The Euler equation is a Schrödinger-like equation for the square root of the density. This equation contains an extra potential, the so-called Pauli potential, in addition to the usual Kohn–Sham potential. Equations for the Pauli potential, the relationship of the Pauli potential and Pauli energy are reviewed. A derivation of the Euler equation via density scaling is presented.

21.1 Introduction

Nowadays, electron structure calculations are usually done with density functional theory. The history of density functional theory started with the fundamental works of Thomas [1], Fermi [2], Dirac [3] and Gombás [4]. The theory was rigorously established by Hohenberg and Kohn [5]. They derived the Euler equation

$$\frac{\delta E}{\delta n} = \mu, \tag{21.1}$$

where $E[n]$ is the total energy functional and the Lagrange multiplier μ is the chemical potential. The solution of the variational problem gives the electron density. However, the energy functional $E[n]$ is unknown and even accurate approximations are unavailable. $E[n]$ can be regarded as a sum of several terms. The most troublesome is the kinetic energy term. Both the kinetic energy functional and its functional derivative appearing in the Euler equation are difficult to approximate. Kohn and Sham (KS) [6] gave a genuine solution to this problem with the invention of the non-interacting system. In this fictitious system the electrons move independently in a common, local potential. The density

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$$n(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \tag{21.2}$$

is the same as the true interacting electron density. The orbitals ϕ_i satisfy the Kohn–Sham equations

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \tag{21.3}$$

where N, ε_i, ϕ_i, and v_{KS} are the number of electrons, the one-electron energies, orbitals and the Kohn–Sham potential, respectively.

Nowadays, in the great majority of density functional calculations, the Kohn–Sham equations are solved. The original Hohenberg-Kohn theory would have the great advantage that only one equation, the Euler equation, Eq. (21.1), should be solved instead of several Kohn–Sham equations. It is very important in case the system considered has a lot of electrons. Therefore, there is a growing interest in this so-called orbital-free density functional theory.

The non-interacting kinetic energy

$$T_s = -\frac{1}{2}\sum_i^N \int \phi_i^* \nabla^2 \phi_i d\mathbf{r} \tag{21.4}$$

can be partitioned as $T_s = T_w + T_p$. T_w is the Weizsäcker kinetic energy [7]

$$T_w = -\frac{1}{2}\int n^{1/2}\nabla^2 n^{1/2} d\mathbf{r}. \tag{21.5}$$

The Pauli energy is defined as $T_p = T_s - T_w$ [8–24]. The Euler equation, Eq. (21.1), can be rewritten as

$$\left[-\frac{1}{2}\nabla^2 + v_P + v_{\mathrm{KS}}\right] n^{1/2} = \mu n^{1/2}, \tag{21.6}$$

where

$$v_p = \frac{\delta T_p}{\delta n} \tag{21.7}$$

is the Pauli potential, the functional derivative of the Pauli energy T_p. It was Norman March who first wrote the Euler equation in the form of Eq. (21.6) [10]. The Schrödinger like equation for the square root of the density n appeared a bit earlier in the literature [8, 9], but the partition of the effective potential as sum of the Kohn–Sham and Pauli potentials was first presented in [10]. Norman March used first the notation Pauli potential, because this term emergies owing to the Pauli principle.

As he wrote this term "... distinguishes the fermionic system, with its associated Exclusion Principle, from the Boson problem..." [10].

The Pauli potential has a very important role in the orbital-free density functional theory. Professor March addressed this issue in several important papers [9–11, 14, 15, 17–21, 23].

21.2 Differential Virial and Force-Balance Equations

The differential virial theorem goes back to March and Young [25] in one dimension and is generalized first to spherically symmetric systems by Nagy and March [26], then to three dimensions by Holas and March [27]. In the non-interacting system it reads

$$-\frac{\partial v_{\mathrm{KS}}}{\partial r} = -\frac{1}{4n(r)}\frac{\partial}{\partial r}\nabla^2 n(r) + \frac{\hat{\mathbf{r}}\cdot\mathbf{z}^{(s)}(\mathbf{r})}{n(r)}. \tag{21.8}$$

Here, $\hat{\mathbf{r}}$ denotes the radial unit vector, while the vector field $\mathbf{z}^{(s)}(\mathbf{r})$ is defined via the non-interacting kinetic energy density tensor $t^{(s)}_{\alpha\beta}(\mathbf{r})$ [27]

$$t^{(s)}_{\alpha\beta}(\mathbf{r}) = \frac{1}{4}\left[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta}\gamma^{(s)}(\mathbf{r}',\mathbf{r}'') + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\gamma^{(s)}(\mathbf{r}',\mathbf{r}'')\right]_{\mathbf{r}''=\mathbf{r}'=\mathbf{r}} \tag{21.9}$$

as

$$z^{(s)}_\alpha(\mathbf{r}) = 2\sum_\beta \frac{\partial t^{(s)}_{\alpha\beta}(\mathbf{r})}{\partial r_\beta}. \tag{21.10}$$

Here, $z^{(s)}_\alpha$ is the α component of the vector $\mathbf{z}(\mathbf{r})$. The non-interacting kinetic energy density tensor $t^{(s)}_{\alpha\beta}(\mathbf{r})$ is defined in terms of the non-interacting one-particle density matrix $\gamma^{(s)}(\mathbf{r}',\mathbf{r}'')$ in Eq. (21.9). Using the differential virial theorem, Eq. (21.8), the force $\langle F\rangle$ can be calculated

$$\langle F\rangle = -\int n(r)\frac{\partial v_{\mathrm{KS}}(r)}{\partial r}d\mathbf{r} = -\frac{1}{4}\int \frac{\partial}{\partial r}\nabla^2 n(r)d\mathbf{r} + \int \hat{\mathbf{r}}\cdot\mathbf{z}^{(s)}(\mathbf{r})d\mathbf{r}. \tag{21.11}$$

One can find useful equations for the external and exchange-correlation forces in [28].

Consider now spherically symmetric systems. Using the Laplacial form $t_L(r)$ of the kinetic energy density for the appropriate general level occupancy, we multiply Eq. (21.3) by ϕ_i^* and sum over occupied levels to find

$$t_L(r) + n v_{\mathrm{KS}}(r) = \sum_{\text{occupied } i} \varepsilon_i|\phi_i|^2 \equiv g(r). \tag{21.12}$$

Forming the gradient of Eq. (21.12) we find

$$\nabla t_L(r) + n(r)\nabla v_{\mathrm{KS}}(r) + v_{\mathrm{KS}}(r)\nabla n(r) = \nabla g(r). \tag{21.13}$$

Equation (21.8) can be rewritten as

$$z_s(r) = \frac{1}{4}\frac{\partial}{\partial r}\nabla^2 n(r) + \frac{\partial t_L}{\partial r} + v_{\mathrm{KS}}(r)\frac{\partial n(r)}{\partial r} - \frac{\partial g(r)}{\partial r}. \tag{21.14}$$

Replacing $t_L(r)$ by the positive definite gradient form $t_G(r)$ of kinetic energy density, we obtain

$$z_s(r) = \frac{\partial t_G(r)}{\partial r} + v_{\mathrm{KS}}(r)\frac{\partial n(r)}{\partial r} - \frac{\partial g(r)}{\partial r}. \tag{21.15}$$

Equation (21.15) can also be written as

$$z_s(r) = 2\frac{\partial t_W}{\partial r} + 4\frac{t_W}{r} + \frac{\partial t_P}{\partial r} + \mu n' - \frac{\partial g(r)}{\partial r} - v_P(r)n'. \tag{21.16}$$

The Pauli potential can also be expressed as

$$v_P(r) = \frac{t_P(r)}{n(r)} + \mu - \frac{g(r)}{n(r)}, \tag{21.17}$$

therefore Eq. (21.16) takes the form

$$z_s(r) = 4\frac{t_W}{r} + 2t_W'(r) + n(r)v_P'(r). \tag{21.18}$$

The final expression, Eq. (21.18), connects z_s to the Weizsäcker kinetic energy density and the Pauli potential. Equation (21.17) establishes a relation between the Pauli potential and the Pauli energy density.

21.3 Pauli Potential via Density Scaling

It has recently been shown that Pauli potential can be constructed via density scaling [29]. In density scaling we immagine another non-interacting system having a scaled density $n_\zeta(\mathbf{r}) = n(\mathbf{r})/\zeta$. Here, $\zeta = N/N_\zeta$ is a positive number. We recover the original non-interacting (Kohn–Sham) system if $\zeta = 1$. Suppose that the original real system has N electrons. Then the Kohn–Sham system with the scaled density n_ζ has N_ζ electrons:

$$\int n_\zeta(\mathbf{r})d\mathbf{r} = N_\zeta. \tag{21.19}$$

While N is always an integer, N_ζ is generally non-integer. Therefore the grand canonical ensemble [30–34] is constructed. A zero temperature grand canonical density matrix Γ in the Fock space takes the form

$$\Gamma = \sum_N \sum_i f_{Ni} |\Psi_{Ni}\rangle\langle\Psi_{Ni}|, \tag{21.20}$$

where Ψ_{Ni} is the ith N-particle eigenfunction of the Hamiltonian. The occupation numbers f_{Ni} should satisfy the conditions $0 \le f_{Ni} \le 1$ and $\sum_N \sum_i f_{Ni} = 1$. Apply now the constrained search for the kinetic energy over the density matrices Γ as

$$T_\zeta[n] = \zeta \min_{\Gamma \to n_\zeta} Tr[\hat{\Gamma}\hat{T}], \tag{21.21}$$

where the scaled density is given by

$$n_\zeta = Tr[\hat{\Gamma}\hat{n}]. \tag{21.22}$$

$T_\zeta[n]$ is a convex functional and the functional derivative exists [30, 35, 36].

Consider the case $N_\zeta = 2$ and denote this value of ζ as $\zeta_d = N/2$. It corresponds to a non-interacting system with two electrons. The constrained search [37, 38] minimizes the scaled kinetic energy

$$-2\frac{1}{2}\int \phi^*(\mathbf{r})\nabla^2\phi(\mathbf{r})d\mathbf{r} \tag{21.23}$$

with a fixed scaled density

$$n_{\zeta_d} = 2|\phi|^2 :$$
$$\min\left(-\int \phi^*(\mathbf{r})\nabla^2\phi(\mathbf{r})d\mathbf{r} + \int n_{\zeta_d}(\mathbf{r})v_{\zeta_d}(\mathbf{r})d\mathbf{r} + \mu\int n_{\zeta_d}(\mathbf{r})d\mathbf{r}\right). \tag{21.24}$$

The minimization is done with fixing the density n_{ζ_d} and its norm, Eq. (21.19), using the Lagrange multipliers $v_{\zeta_d}(\mathbf{r})$ and μ, respectively. The minimization leads to the equation

$$-\frac{1}{2}\nabla^2\phi + v_{\zeta_d}\phi = \mu\phi \tag{21.25}$$

that can also be written as

$$\left(-\frac{1}{2}\nabla^2 + v_{\zeta_d}\right)n_{\zeta_d}^{1/2} = \mu n_{\zeta_d}^{1/2} \tag{21.26}$$

or

$$\left(-\frac{1}{2}\nabla^2 + v_{\zeta_d}\right) n^{1/2} = \mu n^{1/2}. \tag{21.27}$$

Comparing Eq. (21.27) with the Euler equation, Eq. (21.6), we obtain the Pauli potential as

$$v_P = v_{\zeta_d} - v_{\mathrm{KS}}. \tag{21.28}$$

According to this remarkable expression the Pauli potential is the difference of the scaled and the original Kohn–Sham potential. To derive another important expression for the Pauli potential consider now the relation between the original non-interacting kinetic (T_s) and exchange-correlation (E_{xc}) and the scaled non-interacting kinetic (T_ζ) and exchange-correlation ($E_{\zeta xc}$) energies [30–32]:

$$T_s + E_{xc} = T_\zeta + E_{\zeta xc}. \tag{21.29}$$

The functional derivation provides an expression between the original and scaled exchange-correlation potentials:

$$\frac{\delta T_s}{\delta n} + v_{xc} = \frac{\delta T_\zeta}{\delta n} + v_{\zeta xc}. \tag{21.30}$$

In our case $\zeta = \zeta_d$, and using the partition $T_s = T_w + T_p$ we obtain

$$T_w + T_p + E_{xc} = T_w + E_{\zeta_d xc}, \tag{21.31}$$

that is, the Pauli energy is the difference of the scaled and the original exchange-correlation energies:

$$T_p = E_{\zeta_d xc} - E_{xc}. \tag{21.32}$$

The functional derivative of Eq. (21.32) gives the Pauli potential

$$v_p = v_{\zeta_d xc} - v_{xc} \tag{21.33}$$

as the difference of the scaled and original exchange-correlation potentials.

21.4 Discussion

Nowadays, there is a growing interest in orbital-free density functional theory. Avoiding the solution of the Kohn–Sham equations – solving the Euler equation instead – would result an enormous simplification and would make it possible to treat systems with large number of electrons.

Pauli potential is a key quantity in orbital-free density functional theory. As it is responsible for the fulfillment of the Pauli principle, its presence in the Euler equation is essential. Unfortunately, its exact form is unknown, therefore, we have to approximate it in calculations. Exact relations might be very useful in constructing adequate approximate potentials. The exchange-correlation part of the Kohn–Sham potential is also unknown. There are, however, several important exact relations for the exchange, correlation and exchange-correlation potentials and energies. Some of them turned to be extremely useful in constructing and improving approximate functionals. It is expected that exact relations for the Pauli potential and energy might be similarly valuable in designing approximate forms. Equations (21.18) and (21.17) seem to be beneficial in modeling the Pauli potential and the Pauli energy density or checking approximations.

Density scaling provides a constructive way of obtaining approximations for the Pauli potential. The Pauli potential (energy) of the density functional theory is expressed as the difference of the scaled and original exchange-correlation potentials (energies). Further, Eqs. (21.32) and (21.33) make it possible to seek alternative approximations for the Pauli energy and potential.

Finding adequate approximation for the Pauli potential is a very hard problem. Density scaling induces a hope of constructing good approximate Pauli potentials. It should be the subject of further research.

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