Ensemble Formalism of the Orbital-free Density Functional Theory

Á. Nagy
Department of Theoretical Physics, University of Debrecen, Debrecen, Hungary

Abstract— Ensembles are constructed in the ground-state non-interacting density functional theory. The ensemble Euler equation is formulated as a one-particle Schrödinger-like equation for the square root of the ensemble density. The potential in this equation is the sum of the original Kohn-Sham potential plus the ensemble Pauli potential. The latter satisfies a first-order differential equation. The true electron density can be easily obtained from the ensemble electron density. The ensemble density or the ensemble non-interacting energy density or the ensemble angular momentum density provide a full description of a Coulomb system.

1. INTRODUCTION

Density functional calculations are generally done by solving the Kohn-Sham equations. There are several Kohn-Sham equations for systems with a lot of electrons. In orbital-free density functional theory, on the other hand, one has to solve only a single equation, the Euler equation, which is a huge simplification. Therefore, there is a growing interest in orbital-free methods [1–3]. Unfortunatelly, they are not accurate enough. The main problem is the lack of accurate approximation for the kinetic energy functional. In this paper we discuss a novel approach [4–7] that avoids using approximate kinetic energy functionals.

2. ENSEMBLE FORMALISM

In the construction the original Kohn-Sham equations

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

are made use of. The original ground-state density is given by

$$n_0(\mathbf{r}) = \sum_{i=1}^{M} \lambda_i n_i(\mathbf{r}), \tag{2}$$

where $n_i(\mathbf{r}) = |u_i(\mathbf{r})|^2$ are the one-electron densities. u_i, λ_i and v_{KS} are the Kohn-Sham orbitals, the occupation numbers and the Kohn-Sham potential, respectively. $\varepsilon_1 \leq \varepsilon_2 \leq \ldots \leq \varepsilon_M$ are the one-electron energies. M denotes the number of levels with non-zero occupation numbers. Now, the ensemble density and the ensemble non-interacting energy are defined as

$$n(\mathbf{r}) = \sum_{i=1}^{M} \lambda_i w_i n_i(\mathbf{r}), \tag{3}$$

$$\mathcal{E} = \sum_{i=1}^{M} w_i \lambda_i \varepsilon_i. \tag{4}$$

Note that if all $w_i = 1$, the ensemble density and the ensemble non-interacting energy equal the true density ($n = n_0$) and the non-interacting energy ($\mathcal{E} = \mathcal{E}_0$). The generalized Rayleigh-Ritz variational principle [8] is valid for the ensembles if the weighting factors satisfy the inequalities: $w_1 \geq w_2 \geq \ldots \geq w_M \geq 0$. The generalized variational principle leads to the ensemble Euler equation:

$$\frac{\delta T}{\delta n} + v_{KS} = \mu, \tag{5}$$

where μ is the Lagrange multiplier and the ensemble non-interacting kinetic energy is defined as:

$$T = \int t(\mathbf{r}) d\mathbf{r} = \int \sum_{i=1}^{M} \lambda_i w_i t_i(\mathbf{r}) d\mathbf{r}. \tag{6}$$

The one-electron kinetic energy densities are given by the Laplacian form $t_i(\mathbf{r}) = -\frac{1}{2}u_i^*(\mathbf{r})\nabla^2 u_i(\mathbf{r})$. Note that v_{KS} in Equation (5) is the original Kohn-Sham potential (1).

The total ensemble non-interacting kinetic energy can be partitioned as $T = T_w + T_p$, where T_w is the ensemble Weizsäcker kinetic energy

$$T_w = \frac{1}{8}\int \frac{|\nabla n|^2}{n} d\mathbf{r} \tag{7}$$

and T_p is ensemble Pauli energy. Then the ensemble Euler Equation (5) can be rewritten as

$$\left[-\frac{1}{2}\nabla^2 + v_p + v_{KS}\right] n^{1/2} = \mu n^{1/2}, \tag{8}$$

where $v_p = \frac{\delta T_p}{\delta n}$ is the Pauli potential.

3. ENSEMBLE DENSITY FOR SPHERICALLY SYMMETRIC SYSTEMS

For spherically symmetric systems the ensemble Euler Equation (8) takes the form

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + v_p + v_{KS}\right] \varrho^{1/2} = \mu \varrho^{1/2}, \tag{9}$$

where $\varrho = 4\pi r^2 n$ is the radial ensemble density. It was shown in [6] that with the choice of the weighting factors

$$w_i = e^{\beta\varepsilon_i - \gamma l_i(l_i+1)} \tag{10}$$

(β and γ are real numbers) the ensemble Pauli potential satisfies the first-order differential equation

$$\frac{1}{2}\varrho v_p' + \varrho' v_p = f, \tag{11}$$

where

$$f = -\frac{\partial}{\partial r}\left(\frac{\partial \varrho}{\partial \beta}\right) + \mu\varrho' - \frac{1}{2r^2}\frac{\partial}{\partial r}\left(\frac{\partial \varrho}{\partial \gamma}\right) + \frac{1}{2r^3}\frac{\partial \varrho}{\partial \gamma}. \tag{12}$$

The differential Equation (11) can be solved and the Pauli potential can be written as

$$v_p = \frac{2}{\varrho^2}\int_\infty^r \varrho(r_1) f(r_1) dr_1. \tag{13}$$

Note that

$$\frac{\partial \varrho}{\partial \beta} = \sum_{i=1}^{M} w_i \lambda_i \varepsilon_i \varrho_i = \varrho_E \tag{14}$$

is the ensemble non-interacting energy density and

$$\frac{\partial \varrho}{\partial \gamma} = \sum_{i=1}^{M} w_i \lambda_i l_i \left(l_i + 1\right) \varrho_i = \varrho_L \tag{15}$$

is the ensemble angular momentum density.

The orbital-free solution for spherically symmetric systems can then be obtained in the following steps.

(i) Guess an initial ensemble electron density.
(ii) Using Equation (12) calculate the function f.
(iii) Calculate the ensemble Pauli potential v_p using Equation (13).

(iv) Solve the ensemble Euler Equation (8) to obtain the ensemble electron density ϱ. Note that one needs the original ground-state Kohn-Sham potential. The accuracy of the results will depend on the approximate exchange-correlation functional used in solving the ensemble Euler equation.

(v) Repeat steps (i)–(iv) until convergence. At the end the ground-state density can be obtained from the ensemble density at $\beta = \gamma = 0$.

The procedure seems to be simple, however, because of the β and γ dependence of the ensemble density, novel numerical methods have to be worked out to find the solution. This work is in progress.

4. DESCRIPTORS OF COULOMB SYSTEMS: ENSEMBLE DENSITY, ENSEMBLE NON-INTERACTING ENERGY DENSITY AND ENSEMBLE ANGULAR MOMENTUM DENSITY

It is well-known that the ground-state density determines every property of the system. In case of Coulomb systems, not only the density, but several other quantities possess this attribute. The shape function (density per particle) [9], reactivity indicators [10] as Fukui function, local softness, softness kernel, electrostatic potential, local kinetic energy and local temperature [11] are all capable of fully determining every property of a Coulomb system. The ensemble density and its derivatives with respect to β and γ appearing in Equation (13), are all provide a full description of a Coulomb system.

The external potential of a Coulomb system has the form

$$v(\mathbf{r}) = -\sum_{\alpha} \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|}, \tag{16}$$

where Z_α is the atomic number of the nucleus at the position $\mathbf{R}_\alpha$. Consider a linear combination of one-electron densities: $\xi(\mathbf{r}) = \sum_{i=1}^{M} a_i n_i$, where a_i are real numbers. Using the cusp conditions for the one-electron densities [12], one can readily obtain for the spherical average of ξ around the nucleus α

$$\bar{\xi}'(\mathbf{R}_\alpha) = -2Z_\alpha \bar{\xi}(\mathbf{R}_\alpha). \tag{17}$$

The positions of cusps in ξ locate the nuclei and Equation (17) gives the atomic numbers Z_α. ξ determines also the number of electrons. The asymptotic decay of ξ is given by the highest occupied orbital [9]:

$$\xi(r \to \infty) \sim n_M(r \to \infty) \sim r^{2\left(\frac{Z_{tot}-N+1}{\sqrt{2I}}-1\right)} e^{-2r\sqrt{2I}}, \tag{18}$$

where I is the vertical ionization potential of the system and $Z_{tot} = \sum_\alpha Z_\alpha$ is the sum of the atomic numbers. Then the number of electrons can be obtained as [9]:

$$N = 1 + \left(Z_{tot} + \frac{1}{4} \left[\left(\frac{\partial \ln \xi}{\partial r} \right) \left(\frac{\partial^2 \ln \xi}{\partial r \partial \left(\frac{1}{r}\right)} + 2 \right) \right]_{r\to\infty} \right). \tag{19}$$

Equations (17)–(19) lead to the theorem: For any Coulomb system, ξ determines the external potential v up to an additive constant and the number of electrons.

ξ is the ensemble density if $a_i = \lambda_i w_i$. The choice $a_i = \lambda_i w_i \varepsilon_i$ leads to the ensemble non-interacting energy density. In case of sherically symmetric systems $a_i = w_i \lambda_i l_i(l_i + 1)$ gives the ensemble angular momentum density. That means that if we know the ensemble density or the ensemble non-interacting energy density or the ensemble angular momentum density we can, in principle, determine the external potential, that is, the total Hamiltonian of the true interacting system, therefore any property of the system.

As an illustration, the radial ensemble density, the ensemble non-interacting energy density and the ensemble angular momentum density of the Neon atom are presented as a function of the radial distance for some values of of β and γ. Figure 1 shows the radial ensemble density as for $\beta = 0.00$, $\beta = -0.01$, $\beta = -0.05$ and $\gamma = 0.00$ (a) and $\gamma = 5.00$ (b). Note that the case $\beta = \gamma = 0.00$ corresponds to the ground state (solid line). The negative value of β gives larger weight to the

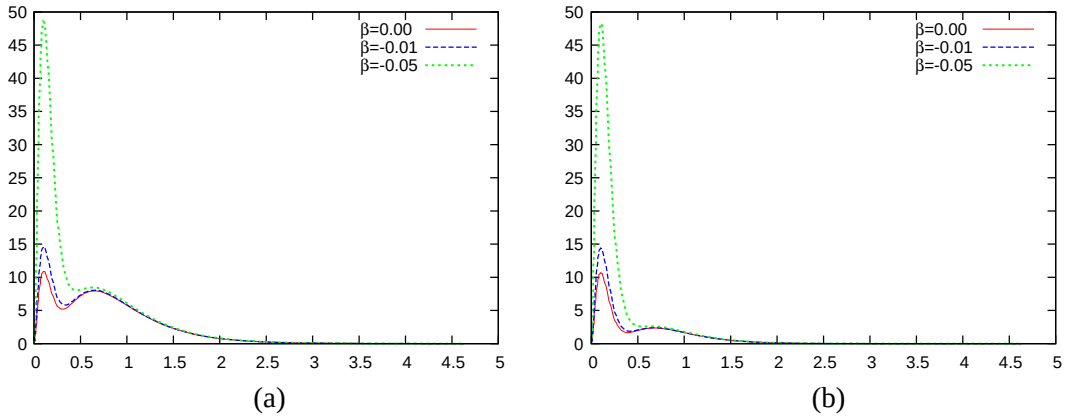

Figure 1: Radial ensemble density for (a) $\gamma = 0$ and (b) $\gamma = 5$ for some values of β as a function of the radial distance for the Neon atom. (Atomic units).

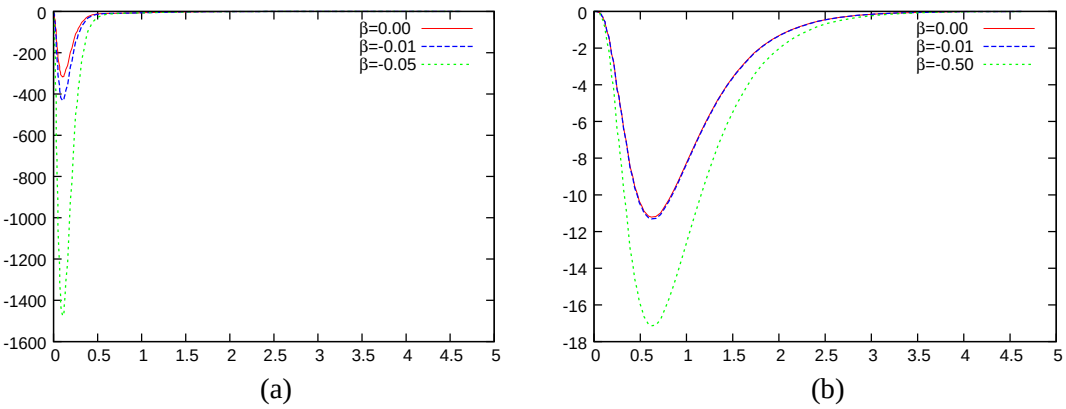

Figure 2: Derivative of the radial ensemble density with respect to (a) β and (b) γ for some values of β and $\gamma = 0$ as a function of the radial distance for the Neon atom. (Atomic units).

lower lying levels (see Equation (3)), therefore the first maximum arising from the $1s$ orbital is increased, while the second maximum is almost disappeared. Figure 2 shows the ensemble non-interacting energy density (a) and the ensemble angular momentum density (b). The ensemble non-interacting energy density, that is the derivative of the ensemble density with respect to β, is presented for $\beta = 0.00$, $\beta = -0.01$, $\beta = -0.05$ and $\gamma = 0.00$. The plots are very similar for larger values of γ. The minimum becomes deeper as β is decreased (see Equation (14)), because β is negative. The ensemble angular momentum density, that is, the derivative of the ensemble density with respect to γ, is presented for $\beta = 0.00$, $\beta = -0.01$, $\beta = -0.50$ and $\gamma = 0.00$. The plots are very similar for larger values of γ. Note that there is no contribution from s orbitals. The minimum becomes deeper as β is decreased (see Equation (15)), because β is negative.

5. CONCLUSION

In the ensemble formulation of the orbital-free density functional theory, the ensemble Euler equation takes the form of a one-particle Schrödinger-like equation for the square root of the ensemble density. The potential in this equation is the sum of the original Kohn-Sham potential plus the ensemble Pauli potential. The latter satisfies a first-order differential equation. The orbital-free problem is reduced to the solution of an equation that contains only the ensemble density and its derivatives. The ground-state problem can be recovered as a special case. The ensemble density, the ensemble non-interacting energy density and the ensemble angular momentum density are all descriptors of a Coulomb system.

ACKNOWLEDGMENT

The work is supported by the TAMOP 4.2.2.A-11/1/KONV-2012-0036 project. The project is co-financed by the European Union and the European Social Fund. Grant OTKA No. K100590 is also gratefully acknowledged.

REFERENCES

1. Chacón, E., J. E. Alvarellos, and P. Tarazona, *Phys. Rev. B*, Vol. 32, 7868, 1985.
2. Huang, C. and E. A. Carter, *Phys. Rev. B*, Vol. 81, 045206, 2010.
3. Trickey, S. B., V. V. Karasiev, and A. Vela, *Phys. Rev. B*, Vol. 84, 075146, 2011.
4. Nagy, Á., *Chem. Phys. Lett.*, Vol. 460, 343, 2008.
5. Nagy, Á., *Int. J. Quant. Chem.*, Vol. 110, 2117, 2010.
6. Nagy, Á., *J. Chem. Phys.*, Vol. 135, 044106, 2011.
7. Nagy, Á., *Recent Advances in Orbital-free Density Functional Theory*, T. A. Wesolowski, and Y. A. Wang, Eds., World Scientific, Singapore, 2013.
8. Gross, E. K. U., L. N. Oliveira, and W. Kohn, *Phys. Rev. A*, Vol. 37, 2805, 1988.
9. Ayers, P. W., *Proc. Natl. Acad. Sci.*, Vol. 97, 1959, 2000.
10. Ayers, P. W., *Chem. Phys. Lett.*, Vol. 438, 148, 2007.
11. Ayers, P. W. and Á. Nagy, *J. Chem. Phys.*, Vol. 126, 144108, 2007.
12. Nagy, Á and K. D. Sen, *J. Chem. Phys.*, Vol. 115, 6300, 2001.