



# Pair density functional theory for excited states of Coulomb systems

Á. Nagy<sup>1</sup>

Received: 27 November 2022 / Accepted: 13 July 2023 / Published online: 1 August 2023  
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## Abstract

Pair density functional theory is extended to excited states of Coulomb systems. It is shown that the pair density determines the Hamiltonian of the Coulomb system. A universal kinetic energy functional appropriate for the ground and all bound excited states is defined. The Euler equation can be rewritten as a two-particle auxiliary equation in which the unknown Pauli-like potential should be approximated.

**Keywords** Pair density functional theory · Excited states · Coulomb systems · Pauli potential · Euler equation

## 1 Introduction

One of the most frequently used approach to the electronic structure of many electron systems is the density functional theory (DFT). A similar, though less regularly applied method is the pair density functional theory (PDFT). While in DFT the fundamental variable is the density, in PDFT the basic quantity is the pair density. The Hohenberg-Kohn theorems [1] were extended by Ziesche [2] to give firm foundation to PDFT. There are other approaches [3–7] for the ground state. It was shown [4, 5, 7] that in the ground state the pair density can be determined by solving a single two-particle auxiliary equation, that is, the problem can be reduced to a two-particle problem for an arbitrary system. Further relevant theorems and properties of PDFT can be found in [8–15]. Important extensions and applications are in [16–23].

PDFT can be extended to excited states. While in DFT there are several time-independent excited-state theories (see e.g. [24–37]), in PDFT only one approach was published [38]. This method generalizes the Levy–Nagy theory of a single excited state [30, 31] formalizing a bifunctional theory. The energy is a bifunctional, it depends not only on the pair density, but the external potential, too. Even time-dependent pair density functional theory was formalized [39, 40].

In this paper, the excited-state density functional theory for Coulomb systems [35–37] is extended to pair density. A universal PDFT valid for the ground and all bound excited states of Coulomb systems is constructed. It is shown that the pair density determines the Hamiltonian of the Coulomb system and the degree of excitation. A kinetic energy functional is defined. This sole functional is sufficient to treat any Coulomb excited state. Euler equation is derived and rewritten as a two-particle Schrödinger-like equation in which the unknown Pauli-potential should be approximated.

The paper is organized as follows: the following section presents the important properties of Coulomb pair densities and formalizes the universal PDFT. The last section is devoted to discussion.

## 2 Universal pair density functional theory of Coulomb systems

The Hamiltonian of a Coulomb system has the form

$$\hat{H}^{\text{Coul}} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^N v^{\text{Coul}}(\mathbf{r}_i). \quad (1)$$

$\hat{T}$  and  $\hat{V}_{ee}$  are the kinetic energy and the electron–electron energy operators, while the external Coulomb potential has the form

$$v^{\text{Coul}}(\mathbf{r}) = - \sum_{\beta=1}^M \frac{Z_{\beta}}{r_{\beta}}, \quad (2)$$

Dedicated to Professor Pratim Kumar Chattaraj on the occasion of his 65th birthday.

✉ Á. Nagy  
anagy@phys.unideb.hu

<sup>1</sup> Department of Theoretical Physics, University of Debrecen, Debrecen 4002, Hungary

where  $r_\beta = |\mathbf{r} - \mathbf{R}_\beta|$ .  $N$  and  $M$  are the number of electrons and the nuclei.  $\mathbf{R}_\beta$  and  $Z_\beta$  stand for the position and the charge of the nucleus  $\beta$ .

The pair density  $n$  is defined as

$$n(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \int |\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \mathbf{r}_3, \sigma_3, \dots, \mathbf{r}_N, \sigma_N)|^2 d\sigma_1 d\sigma_2 d\mathbf{r}_3 d\sigma_3 \dots d\mathbf{r}_N d\sigma_N, \quad (3)$$

where  $\Psi$  is the wave function and the integration is for all but two spatial ( $\mathbf{r}$ ) variables and summation for all spin ( $\sigma$ ) variables.

**Theorem 1** *Let  $n$  be a Coulomb pair density. Then,  $n$  determines the external potential.*

**Proof** Shift the origin of the coordinate system to the nucleus  $\beta$  and average  $n$  for the polar angles  $\hat{r}_1$

$$\bar{n}(r_1, \mathbf{r}_2) = \frac{1}{4\pi} \int d\hat{r}_1 n(r_1, \hat{r}_1, \mathbf{r}_2). \quad (4)$$

The following cusp condition holds [9]:

$$\left. \frac{d}{dr_1} \bar{n}(r_1, \mathbf{r}_2) \right|_{r_1=0} = -2Z_\beta n(0, \mathbf{r}_2). \quad (5)$$

That means that the cusps of  $n$  reveal the position of the nuclei and the atomic numbers. The integral of  $n$  yields the number of electrons because

$$\int n(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{N(N-1)}{2}. \quad (6)$$

Consequently, Eqs. (5) and (6) provide the parameters of the Coulomb potential (2), i.e., the Coulomb pair density  $n$  determines the external potential, the Hamiltonian and any property of the system. Kato's theorem is valid for excited states as well. (We mention in passing that  $n$  possesses a somewhat different cusp relation for very highly excited states, but we can still extract the same information from  $n$  [9].) Consequently, the knowledge of  $n$  of the Coulomb system is enough in principle to determine all of its properties. The energy is the functional of  $n$ .

**Theorem 2** *Let  $n$  be a Coulomb pair density (that is, an eigen pair density of  $\hat{H}^{\text{Coul}}$  of Eq. (1)). Then,  $n$  is not an eigen pair density of any other Coulomb potential.*

**Proof** The asymptotic behavior of  $n$  is [41]

$$n(\mathbf{r}_1, \mathbf{r}_2) \rightarrow e^{-2\sqrt{\mu}r_1} e^{-2\sqrt{\mu}r_2}, \quad (7)$$

where

$$\mu = E - E_0^{N-2}. \quad (8)$$

$E$  is the total energy of the given excited state (or ground state) of the system under investigation, while  $E_0^{N-2}$  is the ground-state energy of the  $N-2$ -electron system obtained after removing two electrons from the original  $N$ -electron system. Observe that  $E_0^{N-2}$  does not depend on the degree on excitation. Therefore, the asymptotic decay of  $n$  determines  $E$ .

The energy can be written as the sum of the electron–electron, electron–nucleon and the kinetic terms

$$E^{\text{Coul}}[n] = \int \frac{n(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{N-1} \int [v^{\text{Coul}}(\mathbf{r}_1) + v^{\text{Coul}}(\mathbf{r}_2)] n(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 + T^{\text{Coul}}[n]. \quad (9)$$

Utilizing Theorem 2 the functional

$$T^{\text{Coul}}[n] = E[n] - \int \frac{n(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 - \frac{1}{N-1} \int [v^{\text{Coul}}(\mathbf{r}_1) + v^{\text{Coul}}(\mathbf{r}_2)] n(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (10)$$

can be constructed, where  $n$  is the pair density of a stationary state of any Coulomb system. This functional exists for any bound stationary state arising from Coulomb external potential. But it is unsuitable for practical use, because Coulomb pair densities should be applied to create it. In fact, no approach is available to tell if a given pair density is Coulombic or not, unless we construct the external potential, solve the Schrödinger equation and compare the given pair density with the calculated pair density. But, of course, this is not practicable. After all, there is no point solving the Schrödinger equation in PDFT. Therefore, the way proposed in DFT [35] is now extended to PDFT:  $T$  is defined for all  $n$ , not only for Coulombic  $n$ .

First a bifunctional

$$T[n, n^{\text{Coul}}] = \min_{\substack{\Psi \rightarrow n \\ \{ \langle \Psi | \Psi_i^{\text{Coul}}[n^{\text{Coul}}] \rangle = 0 \}_{i=1}^{k-1}}} \langle \Psi | \hat{T} | \Psi \rangle \quad (11)$$

is taken. The minimization of the kinetic energy is done over the wave functions  $\Psi$  producing the excited-state pair density  $n$  and orthogonal to the first  $k-1$  eigenfunctions of the Coulomb system fixed by  $n^{\text{Coul}}$ . Presume the existence of a unique Coulomb pair density that is closest to the (non-Coulomb) pair density  $n$ . In case more than one Coulomb pair density is found in the same distance from  $n$ , the one generating the smallest  $T$  in Eq. (11), is chosen.

$$T_\epsilon^{\text{Coul}}[n] = \min_{n^{\text{Coul}}} T[n, n^{\text{Coul}}]; \quad \|n^{\text{Coul}} - n\| \leq \epsilon. \quad (12)$$

$\epsilon$  is selected to be large enough for being at least one Coulomb pair density in the distance smaller than  $\epsilon$ . Finally,  $T$  with the smallest  $\epsilon$  is taken:

$$T^{\text{Coul}}[n] = T_{\epsilon_{\min}}^{\text{Coul}}[n]. \quad (13)$$

The minimization leads to the Euler equation

$$\frac{\delta T^{\text{Coul}}[n]}{\delta n} = -\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{N-1} [v^{\text{Coul}}([\mathbf{n}], \mathbf{r}_1) + v^{\text{Coul}}([\mathbf{n}], \mathbf{r}_2)] \quad (14)$$

up to a constant.

It should be stressed that both the functional in Eq. (13), and the Euler Eq. (14) are relevant for the ground and all bound excited states. Different excited states do not have different functionals, one functional does it all.

The Euler Eq. (14) can be rewritten as [38]

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + v_{\text{eff}}^{\text{Coul}}(\mathbf{r}_1, \mathbf{r}_2)\right]n^{1/2}(\mathbf{r}_1, \mathbf{r}_2) = \mu n^{1/2}(\mathbf{r}_1, \mathbf{r}_2), \quad (15)$$

where

$$v_{\text{eff}}^{\text{Coul}}(\mathbf{r}_1, \mathbf{r}_2) = v^{\text{Coul}}(\mathbf{r}_1) + v^{\text{Coul}}(\mathbf{r}_2) + \frac{N-1}{|\mathbf{r}_1 - \mathbf{r}_2|} + v_p^{\text{Coul}}(\mathbf{r}_1, \mathbf{r}_2) \quad (16)$$

This form can be readily obtained partitioning the kinetic energy as

$$T^{\text{Coul}} = T_w + T_p^{\text{Coul}}, \quad (17)$$

where

$$T_w = \frac{1}{N-1} \int n^{1/2}(\mathbf{r}_1, \mathbf{r}_2) \left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2\right] n^{1/2}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (18)$$

is a Weizsäcker-like kinetic energy functional and  $T_p^{\text{Coul}}$  is analogous to the DFT Pauli energy. Here  $T_p^{\text{Coul}}$  is constructed from the pair density instead of the density. The Pauli potential  $v_p^{\text{Coul}}$  is proportional to the functional derivative of the Pauli energy  $T_p^{\text{Coul}}$  with respect to the pair density:  $v_p^{\text{Coul}} = (N-1) \frac{\delta T_p^{\text{Coul}}}{\delta n}$ .

It is interesting to note that there is a relation between  $v_p^{\text{Coul}}$  and the DFT effective potential  $v_{\text{eff}}^{\text{DFT}}$ . The DFT Euler equation can be rewritten as [42]

$$\left[-\frac{1}{2}\nabla^2 + v + v_{\text{eff}}^{\text{DFT}}\right]\rho^{1/2} = \mu^{\text{DFT}}\rho^{1/2}, \quad (19)$$

where  $v$  is the external potential, and  $\mu^{\text{DFT}}$  is the chemical potential. The density  $\rho$  can be obtained from the pair density

$$\rho(\mathbf{r}) = \frac{2}{N-1} \int n(\mathbf{r}, \mathbf{r}') d\mathbf{r}'. \quad (20)$$

$v_{\text{eff}}^{\text{DFT}}$  is related to the DFT Pauli potential  $v_p^{\text{DFT}}$  as

$$v_p^{\text{DFT}} = v + v_{\text{eff}}^{\text{DFT}} - v_{\text{KS}}, \quad (21)$$

where  $v_{\text{KS}}$  is the Kohn–Sham potential.  $n$  can also be written as [40]

$$n(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} |\chi(\mathbf{r}_1, \mathbf{r}_2)|^2 \quad (22)$$

and  $\chi$  can be expressed with the amplitude  $\Phi$

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = 2^{-1/2} \rho(\mathbf{r}_1) \Phi(\mathbf{r}_1, \mathbf{r}_2). \quad (23)$$

The relationship between  $v_p^{\text{Coul}}$  and  $v_{\text{eff}}^{\text{DFT}}$  has already been derived [40]:

$$v_{\text{eff}}^{\text{DFT}} = \frac{1}{2} \int |\nabla_1 \Phi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_2 + \mu^{\text{DFT}} - \mu + \int \Phi^*(\mathbf{r}_1, \mathbf{r}_2) \left[-\frac{1}{2}\nabla_2^2 + v(\mathbf{r}_2) + \frac{N-1}{|\mathbf{r}_1 - \mathbf{r}_2|} + v_p^{\text{Coul}}(\mathbf{r}_1, \mathbf{r}_2)\right] \Phi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2. \quad (24)$$

The functional  $T_p^{\text{Coul}}$  is unknown. If we have an approximation to  $T_p^{\text{Coul}}$  for which the functional derivative  $v_p^{\text{Coul}}$  exists, Eq. (15) can be solved and the pair density can be computed. Then, Eq. (20) yields the density and Eqs. (22) and (23) produce  $\Phi$ . Inverting Eq. (19), the DFT effective potential  $v_{\text{eff}}^{\text{DFT}}$  can be calculated. Therefore, all quantities in Eq. (24) are available and we can check Eq. (24). Obviously, for the exact  $v_p^{\text{Coul}}$  Eq. (24) is satisfied exactly. However, for an approximate  $v_p^{\text{Coul}}$  Eq. (24) is not necessarily fulfilled. Consequently, Eq. (24) is a constraint for the unknown functional  $T_p^{\text{Coul}}$ .

Finally, the virial theorem is presented. The derivation is detailed in ref. [6]. The virial theorem for the Weizsäcker-like functional is

$$T_w = -\frac{1}{2} \int n(\mathbf{r}_1, \mathbf{r}_2) [\mathbf{r}_1 \cdot \nabla_1 + \mathbf{r}_2 \cdot \nabla_2] \frac{\delta T_w}{\delta n} d\mathbf{r}_1 d\mathbf{r}_2. \quad (25)$$

The virial theorem for the potential  $v_p^{\text{Coul}}$  takes the form

$$2T_p^{\text{Coul}} = -\frac{1}{N-1} \int n(\mathbf{r}_1, \mathbf{r}_2) [\mathbf{r}_1 \cdot \nabla_1 + \mathbf{r}_2 \cdot \nabla_2] v_p^{\text{Coul}}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (26)$$

Eq. (26) can also be considered a constraint that is useful to test an approximate functional.

### 3 Discussion

$T[n, n^{\text{Coul}}]$  is a bifunctional similar to the one defined in [38]. Here  $T[n, n^{\text{Coul}}]$  appears only as a step in the construction of  $T^{\text{Coul}}[n]$ . In [38], on the other hand, the kinetic bifunctional depends not only on  $n$  but on the external potential, too.

The very special properties of the Coulomb pair density makes it possible to define universal kinetic energy functional. That is,  $T^{\text{Coul}}[n]$  is a single functional valid for the ground and all bound excited states. The Pauli energy functional  $T_p^{\text{Coul}}$  is also universal. It should be emphasized that the excited-state (or the ground-state) problem can be reduced to Eq. (15), that is, to the solution of a two-electron problem. Of course, the exact form of  $T_p^{\text{Coul}}$  is unknown and should be approximated. The advantage of the present approach is that we have only one unknown functional:  $T_p^{\text{Coul}}$ . A single functional is appropriate for any excited state. However, finding suitable approximation will not be easy, as the functional studied should be free of the N-representability problem [41, 43–59].

It might happen that it is worth to introduce distinct functionals for different states. Functionals  $T_k^{\text{Coul}}[n]$  might be useful if  $T^{\text{Coul}}[n]$  defined above possesses unfavorable properties, for example, it is discontinuous. Introduce first  $T_{\epsilon,k}^{\text{Coul}}[n]$  as

$$T_{\epsilon,k}^{\text{Coul}}[n] = \min_{n^{\text{Coul},k}} T[n, n^{\text{Coul},k}]; \quad ||n^{\text{Coul},k} - n|| \leq \epsilon. \quad (27)$$

$\epsilon$  is picked out so as to guarantee the existence of at least one  $k$ th excited state Coulomb pair density in the distance smaller than  $\epsilon$ . Then, the definition is completed by taking the smallest  $\epsilon$

$$T_k^{\text{Coul}}[n] = T_{\epsilon_{\min,k}}^{\text{Coul}}[n]. \quad (28)$$

The variation leads to the Euler equation of the  $k$ th state

$$\frac{\delta T_k^{\text{Coul}}[n]}{\delta n} = -\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{N-1} [v^{\text{Coul}}([n], \mathbf{r}_1) + v^{\text{Coul}}([n], \mathbf{r}_2)] \quad (29)$$

up to a constant.

After removing the Weizsäcker-like term from  $T_k^{\text{Coul}}$  Eq. (29)) can be rewritten as

$$\begin{aligned} & \left[ -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 + v^{\text{Coul}}(\mathbf{r}_1) + v^{\text{Coul}}(\mathbf{r}_2) \right. \\ & \quad \left. + \frac{N-1}{|\mathbf{r}_1 - \mathbf{r}_2|} + v_{p,k}^{\text{Coul}}(\mathbf{r}_1, \mathbf{r}_2) \right] n^{1/2}(\mathbf{r}_1, \mathbf{r}_2) \\ & = \mu_k n^{1/2}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (30)$$

$v_{pk}^{\text{Coul}}$  is the Pauli potential, the functional derivative of the Pauli energy  $T_{p,k}^{\text{Coul}} = T_k^{\text{Coul}} - T_w$  with respect to the pair density.

In summary, it is shown that the pair density determines the Hamiltonian of the Coulomb system and the degree of excitation. Based on these findings the pair DFT is extended to excited states of Coulomb system. A kinetic energy functional  $T^{\text{Coul}}[n]$  is defined for the ground and all bound excited

states. One functional is enough for treating any Coulomb excited state. The Euler equation can be rewritten as a two-particle Schrödinger-like equation in which the unknown Pauli-potential should be approximated.

**Acknowledgements** This research was supported by the National Research, Development and Innovation Fund of Hungary, financed under 123988 funding scheme.

**Author contributions** I am the only author, the manuscript is my work.

**Funding** Open access funding provided by University of Debrecen.

**Data availability** Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

## Declarations

**Conflict of interest** The author states that there is no conflict of interest.

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