

# Alternative to the Kohn-Sham equations: The Pauli potential differential equation

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A recently developed theoretical framework of performing self-consistent orbital-free (OF) density functional theory (DFT) calculations at Kohn-Sham DFT level accuracy is tested in practice. The framework is valid for spherically symmetric systems. Numerical results for the Beryllium atom are presented and compared to accurate Kohn-Sham data. These calculations make use of a differential equation that we have developed for the so called Pauli potential, a key quantity in OF-DFT. The Pauli potential differential equation and the OF Euler equation form a system of two coupled differential equations, which have to be solved simultaneously within the DFT self-consistent loop.

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## I. INTRODUCTION

Conventionally density functional theory (DFT) calculations involve a group of Kohn-Sham (KS) single-particle equations. Solving these equations becomes prohibitively cumbersome as the number of electrons in the system grows past a few hundred. This difficulty is related to the fact that the computational time scales cubically as a function of the electron number. Such a bottleneck is circumvented in orbital-free (OF) DFT, which consequently scales linearly with the volume. OF-DFT can hence treat very large systems comprised of as many as millions of electrons. In OF-DFT one traditionally only needs to solve a single Euler equation for the square root of the electron density. In addition to the KS potential, the Euler equation contains an extra potential, the so-called Pauli potential [1–6], which emerges from the fermionic anti-symmetry requirement of the many-electron wave function.

Despite the great promise of the OF-DFT, it has yet to become a mainstream research tool due to the lack of satisfactorily accurate approximations for the kinetic energy functional (or the Pauli potential). This situation is nonetheless expected to improve in the future, as better approaches are being developed [7,8]. Some systems, such as warm dense aluminum [9], can already be modeled to a high degree of accuracy using existing OF-DFT implementations.

A fundamentally different approach, valid for spherically symmetric systems, was recently developed by Nagy [10–12] to address the difficulties with the current kinetic energy functionals mentioned above. This new framework allows one, in principle, to perform OF calculations with an accuracy tantamount to that of KS-DFT. We accomplish this by avoiding the need to approximate the kinetic energy functional, by introducing an additional differential equation for the Pauli potential. This Pauli potential differential equation (PPDE) can be solved to provide the exact Pauli potential (in the

KS sense). The system is now described by two coupled differential equations, one of which is the Euler equation and the other the differential equation for the Pauli potential. Being coupled, they have to be solved simultaneously. As the Pauli potential is not approximated in our method, the individual energy components and, especially, the obtained shell structure practically coincide with those of KS-DFT. We formulate the problem in terms of the so-called ensemble densities, which are needed to obtain the Pauli potential of the true DFT ground-state density. Using the formulation for the ensemble densities the OF electronic structure of a spherically symmetric system can be solved self-consistently.

In this paper, the method of combining the Euler equation with the differential equation for the Pauli potential is tested in practice. So far, one simple spherically symmetric test system, the beryllium atom, has been solved successfully. The existence of  $p$ ,  $d$ , and  $f$  orbitals in heavier atoms has been found to cause numerical problems. Partly these problems are connected to the difficulty of describing the asymptotic behavior of the Pauli potential both near the nucleus and in the tail part of the density, where only the two outermost KS orbitals are left. A cusp relation for the Pauli potential was recently reported by us [6], but the asymptotic behavior of the Pauli potential tail, which is a function of the spatial overlap of the two outermost KS orbitals, is not known. Efforts to overcome the above problems and stabilize the methodology for larger systems are considered and discussed in future publications.

## II. THEORY AND METHODS

The variational principle ensures that the ground-state total energy of a system can be found by minimizing the total energy functional  $E[n]$  of the system. This procedure leads to the Euler equation,

$$\frac{\delta T_s}{\delta n} + v_{\text{KS}} = \mu, \quad (1)$$

where  $T_s$  is the noninteracting KS kinetic energy,  $v_{\text{KS}}$  is the KS potential, and  $\mu$  is the chemical potential. The KS potential

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itself is the sum of three contributions,

$$v_{\text{KS}} = v_{\text{ext}} + v_H + v_{\text{xc}}, \quad (2)$$

where the subscripts on the right-hand side are the external potential, Hartree potential, and exchange-correlation potential, respectively. For isolated atoms the external potential is simply  $-Z/r$ , where  $Z$  is the atomic number.  $T_s$  is customarily divided into two contributions,

$$T_s = T_W + T_p, \quad (3)$$

where  $T_W$  is the von Weizsäcker kinetic energy functional

$$T_W = \frac{1}{8} \int \frac{|\nabla n|^2}{n} d\mathbf{r} \quad (4)$$

and  $T_p$  is an always non-negative remainder, known as the Pauli kinetic energy. To facilitate numerical calculations, Eq. (1) is often rewritten (using atomic units of Hartree and bohr) as

$$\left[-\frac{1}{2}\nabla^2 + v_p + v_{\text{KS}}\right]n^{1/2} = \mu n^{1/2}, \quad (5)$$

which is a single KS-like equation for the square root of the total density of the system. Here  $v_p$  is the Pauli potential, which is, by definition, a functional derivative of the Pauli kinetic energy:

$$v_p = \frac{\delta T_p}{\delta n}, \quad v_p \geq 0. \quad (6)$$

The representation of Eq. (5) is useful when implementing OF schemes in existing KS codes [13,14].

Equation (5) serves as the starting point for our numerical implementation. In conventional OF-DFT approaches Eq. (5) or direct minimization of the total energy functional together with some kind of approximation for the kinetic energy, or the Pauli potential, would provide all the necessary framework for practical OF calculations.

As stated before, sufficiently accurate OF kinetic energy approximations have remained elusive despite many decades of research. This reality has motivated us to explore an avenue where the Pauli potential is not approximated but obtained exactly for spherically symmetric systems without the need to solve the KS system explicitly. In order to obtain the Pauli potential exactly we present a differential equation for it below. The derivation of the PPDE relies on the so-called ensemble densities formalism, which is briefly described in the following. For a comprehensive account of the ensemble densities formalism, the reader is referred to Refs. [10–12].

Due to spherical symmetry, it is convenient to define the radial electron density,

$$\rho = 4\pi r^2 n. \quad (7)$$

Using the radial density and exploiting the properties of the spherical coordinate system, Eq. (5) can be written in the following form:

$$-\frac{1}{2}\varphi'' + (v_{\text{KS}} + v_p)\varphi = \mu\varphi, \quad \varphi^2 = \rho. \quad (8)$$

The notation  $f'$  is used for the radial derivative, viz.,  $f' = df/dr$ . In the ensemble densities formalism the ground-state

density  $\rho$  is replaced by a more general quantity of the form

$$\rho(\beta, \gamma, r) = \sum_i \lambda_i w_i(\beta, \gamma) \rho_i(r), \quad (9)$$

where, in practice, the sum is chosen to have as many components as the system has occupied KS orbitals.  $w_i$ ,  $\lambda_i$ , and  $\rho_i$  are the weighting factor, occupation number, and electron density of the ensemble member  $i$ , respectively. This ensemble density is therefore a linear combination of the occupied orbitals, each weighted by a factor  $w_i$ . These weight factors introduce two new dimensions into the problem and for them we choose the definition

$$w_i(\beta, \gamma) = e^{\beta\epsilon_i - \gamma l_i(l_i+1)}, \quad (10)$$

with  $\epsilon_i$  being the KS energy eigenvalue of orbital  $i$ . We also choose each  $\rho_i(r)$  to be the radial KS density of orbital  $i$ . In that case, when all  $w_i \equiv 1$ ,  $\rho(\beta, \gamma, r)$  in Eq. (9) reduces to the conventional KS radial density. Accordingly, the true ground state is accessed when both  $\beta$  and  $\gamma$  are set to 0. The significance of the  $\beta$  and  $\gamma$  dimensions is to provide the needed derivatives  $\partial\rho/\partial\beta$  and  $\partial\rho/\partial\gamma$ , which will appear in the expression of the PPDE. With the help of the so-called ensemble differential virial theorem from Ref. [11] and some algebra, we arrive at the PPDE:

$$\frac{1}{2}\rho v_p' + \rho' v_p = \mu\rho' - \frac{\partial\rho'}{\partial\beta} - \frac{1}{2r^2}\frac{\partial\rho'}{\partial\gamma} + \frac{1}{2r^3}\frac{\partial\rho}{\partial\gamma}. \quad (11)$$

The Pauli potential of spherically symmetric systems can thus be computed, without resorting to approximations, using the PPDE, provided that the  $\beta$  and  $\gamma$  derivatives of the density can be handled with sufficient accuracy. Using Eqs. (9) and (10) it can be seen that the derivatives  $\partial\rho/\partial\beta$  and  $\partial\rho/\partial\gamma$  have the definitions

$$\frac{\partial\rho}{\partial\beta} = \sum_i \lambda_i w_i(\beta, \gamma) \epsilon_i \rho_i(r) \quad (12)$$

and

$$\frac{\partial\rho}{\partial\gamma} = - \sum_i \lambda_i w_i(\beta, \gamma) l_i(l_i + 1) \rho_i(r), \quad (13)$$

where  $l_i$  is the azimuthal quantum number of orbital  $i$ .

The Pauli potential, as solved from Eq. (11), clearly depends on the density. On the other hand, the density depends on the Pauli potential, as it is solved from Eq. (8). Equations (8) and (11) therefore form a system of two coupled differential equations, which have to be integrated simultaneously.

As Be only has 1s and 2s orbitals with two electrons each ( $\lambda_{1s} = \lambda_{2s} = 2$ ),  $l_i$  is always 0. From Eq. (13) it can be seen that in this case  $\partial\rho/\partial\gamma$  vanishes, simplifying the equations presented above. It should be noted that the existence of a nontrivial  $\gamma$  dimension in systems more complicated than Be by itself is not expected to cause problems. In fact, in principle, the  $\gamma$  dimension should be easier to handle than the  $\beta$  dimension, because the azimuthal quantum numbers  $l_i$  can be taken as known *a priori*.

For Be the coupled system now reads

$$-\frac{1}{2}\varphi'' + [v_{\text{KS}} + v_p]\varphi = \mu\varphi, \quad (14a)$$

$$v_p' = \frac{2}{\rho} \left[ (\mu - v_p)\rho' - \frac{\partial \rho'}{\partial \beta} \right]. \quad (14b)$$

Note that  $v_{\text{KS}}$  or  $\mu$  never depends on either  $\beta$  or  $\gamma$ . Equation (14a) is further split into two first-order differential equations by defining the variables  $P(\beta, r) = \varphi(\beta, r)$  and  $Q(\beta, r) = P'(\beta, r)$ . We, finally, arrive at a form which is amenable to numerical integration:

$$P'(\beta, r) = Q(\beta, r), \quad (15a)$$

$$Q'(\beta, r) = 2[v_{\text{KS}}(r) + v_p(\beta, r) - \mu]P(\beta, r), \quad (15b)$$

$$v_p'(\beta, r) = 4 \frac{[\mu - v_p(\beta, r)]P(\beta, r)Q(\beta, r) - \frac{\partial P}{\partial \beta}(\beta, r)Q(\beta, r) - P(\beta, r)\frac{\partial Q}{\partial \beta}(\beta, r)}{P^2(\beta, r)}. \quad (15c)$$

Standard integration algorithms, such as the Runge-Kutta and implicit Adams methods [15,16], can be used to solve Eqs. (15). Due to their coupled nature, predictor-corrector iterations are needed to converge  $P(\beta, r)$ ,  $Q(\beta, r)$ , and  $v_p(\beta, r)$  at each radial point  $r$ . A logarithmic radial mesh [15] has been used to improve the accuracy of the integration near the nucleus. The starting point for the mesh was  $r_{\text{min}} = 10^{-7}$  Bohr, and the end point, the practical infinity, was  $r_{\text{max}} = 50$  Bohr. The number of mesh points was  $N_r = 2001$ , which was found to guarantee sufficient numerical accuracy. To describe the exchange-correlation effects we have used the local-density approximation [17] with Vosko-Wilk-Nusair parametrization [18] for the correlation term. The initial guess for the density was constructed of a linear combination of hydrogen-like orbitals, and a simple linear mixing scheme was employed to converge the density and the KS potential self-consistently.

The  $\beta$  dimension can be taken into account by performing the calculations on a linear  $\beta$  mesh. Equations (15) are simultaneously integrated for each  $\beta$  value. At each radial point  $r$ , the  $\beta$ -dependent solutions are then compared to determine the  $\beta$  derivatives needed in Eq. (15c). The simplest approach to calculating the derivatives is by means of finite-differenceschemes. However, we have found that even very high-order finite-difference formulas (up to nine-point  $\beta$ -mesh stencils were tested) tend to be too unstable, even for Be. In our experience, this is mostly due to the  $\partial Q/\partial \beta$  term in Eq. (15c), which is a mixed second-order derivative. Also, choosing a good step size for the finite-difference scheme is challenging.

Better results can be obtained by constructing the derivative exactly by way of an analytical fit. This is achieved using Eq. (9); for a two-point  $\beta$  mesh  $\{\beta_1, \beta_2\}$ , at each radial point  $r$ , the  $\beta$ -dependent densities enter the right-hand side of a  $2 \times 2$  linear system:

$$\lambda_{1s} e^{\beta_1 b_1} a_1(r) + \lambda_{2s} e^{\beta_1 b_2} a_2(r) = \rho(\beta_1, r), \quad (16a)$$

$$\lambda_{1s} e^{\beta_2 b_1} a_1(r) + \lambda_{2s} e^{\beta_2 b_2} a_2(r) = \rho(\beta_2, r). \quad (16b)$$

The mesh points  $\{\beta_1, \beta_2\}$  were chosen to be  $\{0.0, 0.1\}$ . Equations (16) can be routinely solved to find  $a_1(r)$  and  $a_2(r)$  at each  $r$ . This, however, requires the parameters  $b_1$  and  $b_2$  to be known. These parameters in fact define the initial  $\beta$

dependence when the integration of Eqs. (15) is started. We therefore adopt a shooting method [15,16] to solve for them. Within the shooting method, inward and outward integrations are performed and the two solutions meet at some radial point  $\tilde{r}$ . The correct  $b_2$  (and also  $\mu$ ; see the next paragraph) has been found when  $\rho'(\beta_i, \tilde{r})$  are continuous.  $b_1$  is determined by exploiting the condition that  $v_p(\beta, r)$  should have the correct asymptotic decay to 0 far from the nucleus.

It should be noted that when the correct solution has been found,  $a_1(r)$  and  $a_2(r)$  in fact coincide with the KS orbital densities  $\rho_{1s}(r)$  and  $\rho_{2s}(r)$ . Furthermore, in the correct solution, the parameters  $b_1$  and  $b_2$  reduce to the KS orbital energies, i.e.,  $b_1 \rightarrow \epsilon_{1s}$  and  $b_2 \rightarrow \epsilon_{2s} = \mu$ . Indeed, when utilizing the analytical fit of Eqs. (16), the KS orbitals and energies of the system are reproduced as a “by-product.”

### III. SELF-CONSISTENT SOLUTION FOR BERYLLIUM

Using Eqs. (15), we have calculated the electronic structure of the Be atom self-consistently. In terms of numerical performance the conventional KS solution can be considerably faster. This is due to the fact that in the case of Be, both our method and the KS method have two equations to solve. Consequently, as the two equations are coupled in our method, our solution is numerically heavier than that of KS-DFT. Also, our implementation is at the beginning of its development and therefore not fully optimized. Our hope is that future developments can prove our method to be numerically faster than KS-DFT for large electron numbers  $N$ , because the number of equations in our method will always remain at two. Currently, the bulk of the numerical complexity in our method arises from the use of the analytical fit of Eqs. (16) and we aim to replace it with a more efficient approach in the future. The system of linear equations part of the analytical fit is a well-known problem and formally scales as  $N^3$ . The determination of the  $b_j$  parameters in Eqs. (16) is, in principle, described by a multidimensional boundary value problem, the scaling of which is trickier to estimate. However, it should be possible to treat the  $b_j$  parameters as being independent, in which case the  $b_j$  part of the analytical fit scaling would be linear times some overhead.

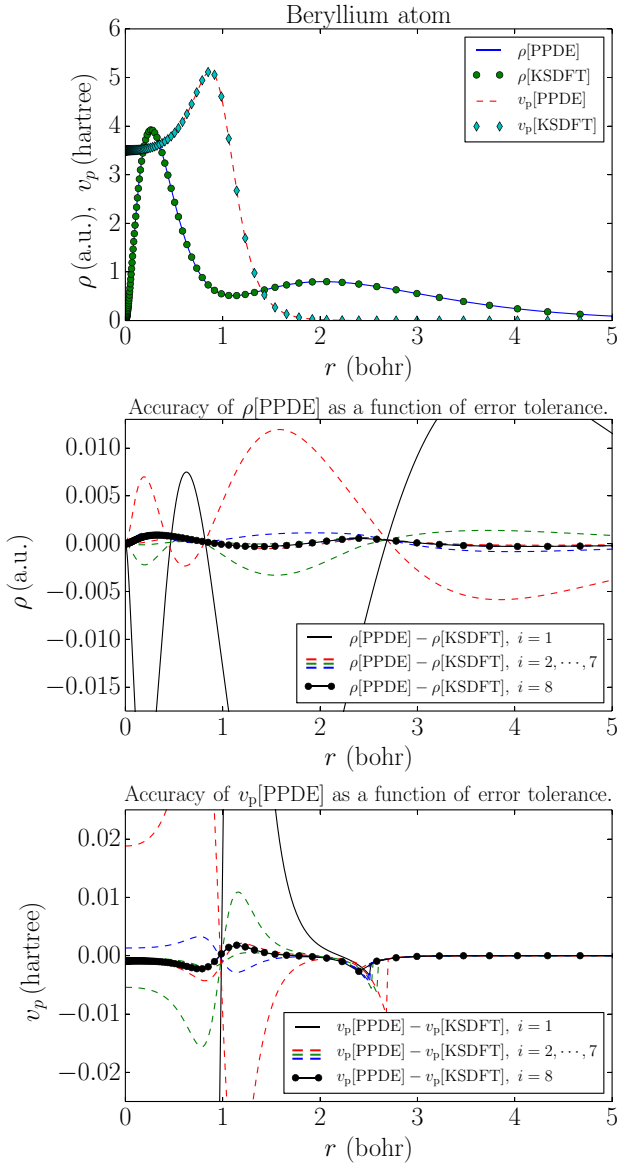


FIG. 1. (Color online) Top: Converged radial electron density  $\rho$  (solid line) and Pauli potential  $v_p$  (dashed line) of the Be atom, obtained using the Pauli potential differential equation (PPDE). Kohn-Sham (KS) results are also presented for comparison (circles and diamonds). Middle and bottom: Difference between the PPDE and the KS-DFT for  $\rho$  (middle) and  $v_p$  (bottom) using eight values for the PPDE self-consistent loop error tolerance in the range  $1.0 \times 10^{-i}$ ,  $i = \{1, \dots, 8\}$ . Solid black curve,  $i = 1$ ; dashed colored curves,  $i = 2, \dots, 7$ ; black circles,  $i = 8$ .

The top panel in Fig. 1 shows the PPDE and KS-DFT radial densities  $\rho$  and Pauli potentials  $v_p$  for the Be atom. Ideally, the electron structure of a given system, as calculated from Eqs. (15), should exactly agree with that calculated in the KS-DFT. The differences between the two solutions on the scale of the plot are indeed unnoticeable. In practice, however, some numerical discrepancies can be expected due to the differing numerical implementations of the two approaches. Also, other sources of error, such as the number of points in the radial

TABLE I. Calculated energy components and orbital energies of the Be atom for the Pauli potential differential equation (PPDE) method. KS-DFT results from Refs. [19] and [20] are also listed for comparison. Hartree energy units have been used.

|                    | Be ( $2s^1 2s^2$ ) |                 |
|--------------------|--------------------|-----------------|
|                    | PPDE               | KS-DFT          |
| $E_{\text{Tot}}$   | -14.447 225        | -14.447 209     |
| $E_{\text{Kin}}$   | 14.309 439         | 14.309 424      |
| $E_{\text{Coul}}$  | 7.115 267          | 7.115 257       |
| $E_{\text{E-Nuc}}$ | -33.357 068        | -33.357 034     |
| $E_{\text{xc}}$    | -2.514 863         | -2.514 856      |
| $b_1$              | -3.856 409         | $\epsilon_{1s}$ |
| $b_2$              | -0.205 779         | $\epsilon_{2s}$ |
|                    |                    | -0.205 744      |

mesh and the strictness of the error tolerance of the main self-consistent loop, may contribute.

For example, the effect that the aforementioned error tolerance can have on the accuracy of the PPDE solution, compared to the KS-DFT solution, is illustrated in the middle and bottom panels in Fig. 1. Both panels have eight curves calculated by varying the value of the error tolerance in the range  $1.0 \times 10^{-i}$ ,  $i = \{1, \dots, 8\}$ . It can be seen that the PPDE solution indeed converges to the KS-DFT solution provided that the value of the error tolerance of the self-consistent loop is chosen with care. Similar behavior is observed with respect to other parameters governing the numerical accuracy. It should be noted that in the bottom panel in Fig. 1, continuity of  $v_p$  or  $v'_p$  at  $\tilde{r}$  has not been enforced, causing the curves to spike around 2.5 bohr. Finally, the convergence behavior of the self-consistent loop itself is very similar to KS-DFT; with a mixing parameter of  $\alpha = 1.0$  ( $\rho_{n+1} = \alpha \rho_{\text{new}} + [1 - \alpha] \rho_n$ ), both methods reach convergence in 18 iterations, with the error tolerance being  $1.0 \times 10^{-10}$ . Here, the error is measured by computing the norm of the residual  $\int_{r_{\min}}^{r_{\max}} (\rho_{n+1} - \rho_n)^2 dr$ .

Table I lists our results for the Be atom. In the table,  $E_{\text{Tot}}$ ,  $E_{\text{Kin}}$ ,  $E_{\text{Coul}}$ ,  $E_{\text{E-Nuc}}$ , and  $E_{\text{xc}}$  are the total energy, electron kinetic energy, electron Hartree energy, electron-nucleus Coulombic energy, and exchange-correlation energy, respectively. It can be seen that the KS results in Refs. [19] and [20] are reproduced within an accuracy of three to four decimals, depending on the quantity in question.

#### IV. CONCLUSIONS

We have shown that it is possible to solve the KS electronic structure of spherically symmetric systems without explicitly solving the KS equations. This is made possible by solving a differential equation for the Pauli potential instead. Together this PPDE and the OF Euler equation form a system of two coupled differential equations. Numerical results for one simple model system, the beryllium atom, have been presented. It is observed that our results coincide, within the expected numerical accuracy, with those calculated using the conventional KS approach. Our work should also be helpful in learning how better approximations for the Pauli potential

could be developed. Further generalization of the present OF approach to more complicated systems is in progress.

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