ORBITAL-FREE DESCRIPTION OF COULOMB SYSTEMS

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OUTLINE

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- Descriptors of Coulomb systems
- Construction of 'generalized densities' in the Kohn-Sham system
- Diferential equation for the 'generalized densities'
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- Pauli potential for the 'generalized densities'
- Numerical method of the solution

Alternative descriptors of Coulomb systems

According to the Hohenberg-Kohn theorems the groundstate electron density determines every property of the electron system. In case of Coulomb systems there are other descriptors, e.g. shape function (density per particle), Fukui function, local softness, electrostatic potential, local kinetic energy.

A family of quantities capable of fully determining every property of a Coulomb system

$$\xi(r) = \sum_{i}^{N} \theta_i n_i$$

$\theta_i \geq 0$ for $1 \leq i < N$ and $\theta_N > 0$, n_i are the one-particle densities.

Examples

- If θ_i are the occupation numbers: $\theta_i = \lambda_i$, ξ is the density
- If $\theta_i = \lambda_i/N$, is the shape function
- If $\theta_1 = \cdots = \theta_{N-1} = 0$ and $\theta_N = 1, \xi = n_{homo} \approx f$ Fukui-function
- If $\theta_i = \lambda_i \varepsilon_i, \xi = g = \sum_i \lambda_i \varepsilon_i n_i$ non-interacting energy density
- If $\theta_i = \lambda_i l_i(l_i+1), \xi = g = \sum_i \lambda_i l_i(l_i+1) n_i$ angular momentum density

Coulomb Hamiltonian

$$\hat{H} = \hat{T} + \widehat{V_{ee}} + \sum_{i=1}^{N} v(r_i)$$

kinetic energy:

$$\hat{T} = \sum_{j=1}^{N} (-\frac{1}{2}\nabla_j^2)$$

electron-electron energy:

$$\widehat{V_{ee}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{|r_i - r_j|}$$

external potential:

$$v(r) = -\sum_{\beta=1}^{M} \frac{Z_\beta}{|r - R_\beta|}$$

Alternative descriptors of Coulomb systems

Theorem: For any Coulomb system, ξ determines the external potential *v* up to an additive constant. ξ also determines the number of electrons.

Proof: $\bar{\xi}'(R_\beta) = -2Z_\beta \bar{\xi}(R_\beta)$

The cusp conditions determine the atomic numbers and the positions of cusps in locate the nuclei.

$$\xi(r \to \infty) \sim n_N(r \to \infty) \sim r^{2\left(\frac{Z_{tot}-N+1}{\sqrt{2I_N}}-1\right)} e^{-2r\sqrt{2I_N}}$$

I_N is the highest ionization potential, $Z_{tot} = \sum_\beta Z_\beta$ is the sum of the atomic numbers.

The original Kohn-Sham system

original Kohn-Sham equations:

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

electron density:

$$n_0(r) = \sum_i^N n_i(r)$$

one-electron density:

$$n_i(r) = |u_i(r)|^2$$

one-electron orbitals:

$$\varepsilon_1 \leq \varepsilon_1 \leq \cdots \leq \varepsilon_n$$

Construction of 'generalized densities' in the Kohn-Sham system

'generalized density'

$$\xi = \sum_i \theta_i n_i \text{ , } \theta_i \text{ are constants}$$

'generalized radial density,

$$\tilde{\xi} = 4\pi r^2 \xi = \sum_i \theta_i \varrho_i = \sum_i a_i w_i \varrho_i$$

the weighting factors w_i defined as:

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

If $a_i = \lambda_i$ and $w_i = 1$ the generalized density equals the electron density: $n = n_0$

Differential equation for the 'generalized densities'

Kohn{Sham equations for spherically symmetric systems:

$$-\frac{1}{2}\frac{d^2P_i}{dr^2}+\frac{l_i(l_i+1)}{2r^2}P_i+v_{KS}P_i=\varepsilon_iP_i$$

- $P_i=rR_i(r)$ are the radial wave functions, li are the azimuthal quantum numbers.

Differential equation

$$\tilde{\xi}=8v_{KS}\tilde{\xi'}+4v'_{KS}\tilde{\xi}-8\frac{\partial\tilde{\xi'}}{\partial\beta}+\frac{4\partial\tilde{\xi'}}{r^2\partial\gamma}-\frac{4\tilde{\xi}}{r^3\partial\gamma}$$

'Generalized densities' as descriptors of Coulomb systems

The most important special cases are:

- If a_i are the occupation numbers: $a_i = \lambda_i, \tilde{\xi}$ is the 'generalized radial electron density'.
- If a_i are the orbital energies multiplied with the occupation numbers: $a_i = \lambda_i \varepsilon_i, \tilde{\xi}$ is the $\tilde{g} = \sum_i w_i \lambda_i \varepsilon_i \varrho_i$. It is the partial derivative of the 'generalized radial electron density' ϱ with respect to β: $\tilde{g} = \frac{\partial \varrho}{\partial \beta} = \varrho_\beta$ 'generalized non-interacting energy density,
- If $a_i = \lambda_i l_i(l_i + 1), \tilde{\xi}$ is the $\tilde{q} = \sum_i w_i \lambda_i l_i(l_i + 1) \varrho_i$. It is the negative of the partial derivative of the 'generalized radial electron density' ϱ with respect to : γ: $\tilde{q} = -\frac{\partial \varrho}{\partial \gamma} = \varrho_\gamma$.'generalized angular momentum density'

Euler equation for the 'generalized densities'

Generalized Weizsacker expression

$$S_w = \frac{1}{8}\int \frac{(\nabla\xi)^2}{\xi}\,dr$$

functional derivative of S_w with respect to ξ :

$$\frac{\delta S_w}{\delta\xi} = \frac{1}{8}\left(\frac{\nabla\xi}{\xi}\right)^2 - \frac{1}{4}\frac{\nabla^2\xi}{\xi} = \frac{1}{8}\left(\frac{\widetilde{\xi'}}{\tilde{\xi}}\right)^2 - \frac{1}{4}\frac{\widetilde{\xi''}}{\tilde{\xi}} = -\frac{1}{2}\frac{\nabla^2\xi^{1/2}}{\xi^{1/2}}$$

Dene a generalized potential

$$u = \frac{1}{2}\frac{\nabla^2\xi^{1/2}}{\xi^{1/2}} - v_{KS}$$

Euler equation for the 'generalized densities'

Kohn-Sham potential

$$v_{KS} = -\frac{1}{8}\left(\frac{\widetilde{\xi}'}{\tilde{\xi}}\right)^2 + \frac{1}{4}\frac{\widetilde{\xi}''}{\tilde{\xi}} - u$$

Dierential equation for $\tilde{\xi}$:

$$\frac{1}{2}\tilde{\xi}u' + \widetilde{\xi}'u = F$$

$$F = -\frac{\partial\widetilde{\xi}'}{\partial\beta} - \frac{\partial\widetilde{\xi}'}{2r^2\partial\gamma} - \frac{\partial\widetilde{\xi}}{2r^3\partial\gamma}$$

Euler equation for the 'generalized densities'

The solution

$$u = \frac{2}{\widetilde{\xi^2}} \int_{\infty}^{r} \tilde{\xi}(r_1) F(r_1) dr_1$$

Euler equation

$$-\frac{1}{2} \frac{\nabla^2 \xi^{\frac{1}{2}}}{\xi^{\frac{1}{2}}} + v_{KS} + u = 0$$

$$-\frac{1}{2} \nabla^2 \xi^{\frac{1}{2}} + (v_{KS} + u)\, \xi^{\frac{1}{2}} = 0$$

In the original Euler equation there is a constant on the right-hand side. A constant μ can be added:

$$-\frac{1}{2} \frac{\nabla^2 \xi^{\frac{1}{2}}}{\xi^{\frac{1}{2}}} + v_{KS} + \hat{u} = \mu$$

However, $\hat{u} = u + \mu$ is defined only up to a constant.

Euler equation for the generalized radial density

Euler equation

$$-\frac{1}{2}\frac{d^2}{dr^2}\varrho^{\frac{1}{2}} + (v_{KS}+u)\,\varrho^{\frac{1}{2}} = 0$$

Pauli potential for the generalized radial density

$$u = \frac{2}{\varrho^2}\int_{\infty}^{r} \varrho(r_1)F(r_1)dr_1$$

Euler equation for the generalized non-interacting energy density ϱ_β

Euler equation for ϱ_β

$$-\frac{1}{2}\frac{d^2}{dr^2}\varrho_\beta^{1/2} + (v_{KS} + u^\beta)\,\varrho_\beta^{1/2} = 0$$

Pauli potential for the generalized non-interacting energy density

$$u^\beta = \frac{2}{\varrho_\beta^2}\int_\infty^r \varrho_\beta(r_1)F^{(\beta)}(r_1)dr_1$$

Euler equation for the generalized non-interacting energy density ϱ_γ

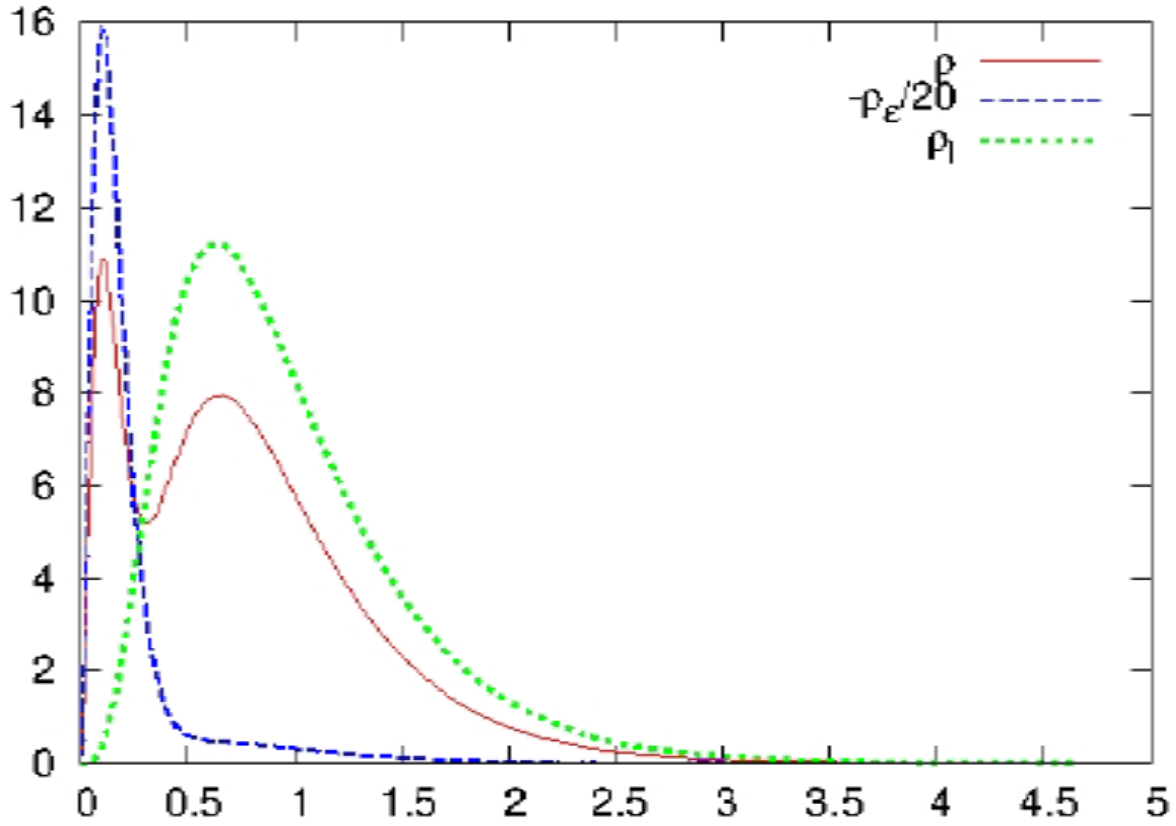
Euler equation for ϱ_γ

$$-\frac{1}{2}\frac{d^2}{dr^2}\varrho_\gamma^{1/2} + (v_{KS} + u^\gamma)\,\varrho_\gamma^{1/2} = 0$$

Pauli potential for the generalized non-interacting energy density

$$u^\gamma = \frac{2}{\varrho_\gamma^2}\int_\infty^r \varrho_\gamma(r_1)F^{(\gamma)}(r_1)dr_1$$

The radial density ϱ, the radial non-interacting density ϱ_ε divided by -20 and the angular momentum density ϱ_l for $\beta = \gamma = 0$ as a function of the radial distance for the Neon atom.



Solution of the orbital-free problem for the density

ASCAM VII

Talk of Henrik Levämäki: Highly accurate orbital-free density functional theory calculations for Beryllium

H. Levämäki - A. Nagy - K. Kokko - L. Vitos: Alternative to the Kohn-Sham equations: The Pauli potential differential equation, Phys. Rev. A 92 (2015) 062502.

Solution of the orbital-free problem

1) Find the 3 variable function $\xi(r,\beta,\gamma)$satisfying the Euler equation

$$-\frac{1}{2}\nabla^2\xi^{\frac{1}{2}} + (v_{KS}+u)\,\xi^{\frac{1}{2}} = 0$$

$$u = \frac{2}{\widetilde{\xi^2}}\int_{\infty}^{r}\tilde{\xi}(r_1)F(r_1)dr_1$$

2) Find the 3 variable function $\xi(r,\beta,\gamma)$satisfying the Euler equation

$$\widetilde{\xi'''} = 8v_{KS}\widetilde{\xi'} + 4v'_{KS}\tilde{\xi} - 8\frac{\partial\widetilde{\xi'}}{\partial\beta} + \frac{4\partial\widetilde{\xi'}}{r^2\partial\gamma} - \frac{4\partial\tilde{\xi}}{r^3\partial\gamma}$$

$$\tilde{\xi} = 4\pi r^2\xi$$

Solution of the orbital-free problem

The solution will depend on the approximation for the exchange-correlation potential.

The Kohn-Sham potential should be calculated with

$$\varrho(r, \beta = 0, \gamma = 0)$$

$$v_{KS} = v + v_j + v_{xc}$$

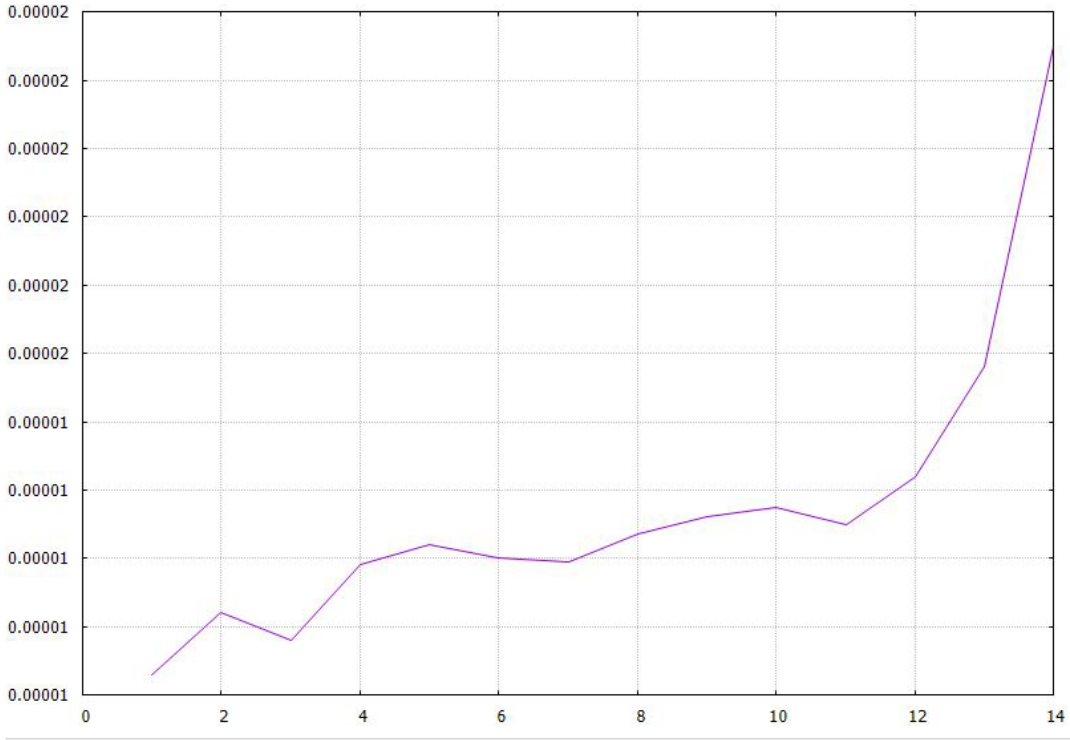
Solution of the orbital-free problem

1) Select an initial guess: $\xi^0(r, \beta, \gamma)$.
2) Calculate $v_{KS}^{(0)}$ (and $u^{(0)}$).
3) Check if the Euler equation is satisfied.
4) Construct $\xi(r, \beta, \gamma)$for the following iteration.

Repeat steps 2-4 until convergence

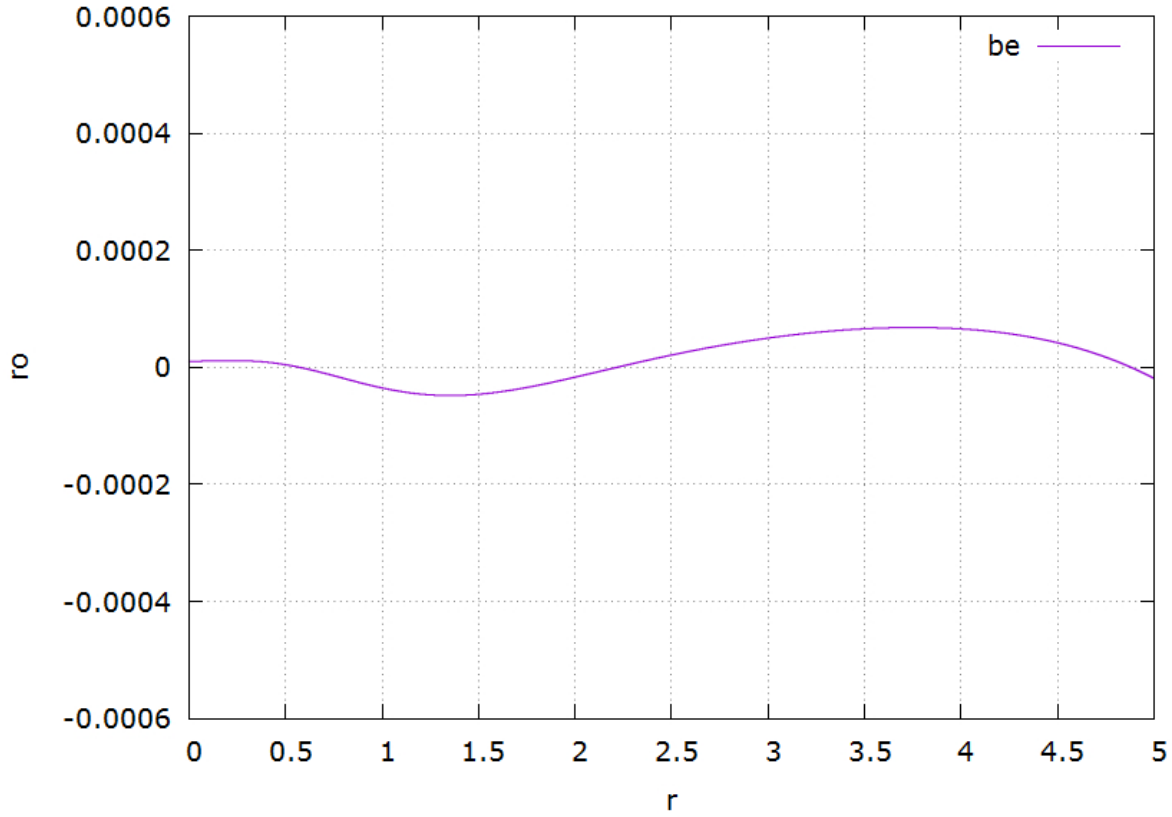
Numerical method of the solution

- exponential bin density
- radial initial point 10^{-7}
- Integration and derivation with variable allocation
- approximation at r = 0, cusp



Numerical method of the solution

- modified Bulirsch-Stoer algorithm
- differentiation by interpolation
- fourth-order Runge-Kutta
- comparison with KS solutions



Summary

Coulomb systems have the very special property that not only the ground-state electron density determines all their properties. There are several other quantities that are also capable of fully determining every property of a Coulomb system.

Though these descriptors have been known and studied for a while, equations for their calculations have not been presented yet.

To fill this gap, Euler equations for a family of descriptors of the spherically symmetric Coulomb systems are derived and discussed. These can be considered the generalizations of the Euler equation of the density functional theory.