

# Self-consistent mean-field approximation in the density functional theory of many-electron unbounded systems

A. Ya. Shul'man

V.A. Kotel'nikov Institute of Radio Engineering and Electronics of the RAS

The density functional approach is based on the minimal property of the ground-state energy of finite  $N$ -electron system relative to the electron density variations. Evidently, this formulation does not make sense in the case of an unbounded electron system. Nevertheless, the set of 'Self-Consistent Equations Including Exchange and Correlation Effects' derived by Kohn and Sham with making use of an variational procedure is widely applied to infinite electron systems. As noted in [1], at that two new difficulties arise: the normalization problem of the continuous-spectrum eigenfunctions of the single-particle Hamiltonian, and unstable convergence (or divergence at all) of the iterative solution of these equations while achieving self-consistency. The workaround of these difficulties was achieved by introducing of a countable Hilbert space with Hamiltonian eigenfunctions as complete basis and by conversion of the Hartree term in the electrostatic energy functional in order to provide due account of boundary problem for Poisson equation [1]. The stable iterative solution of Kohn-Sham equations was obtained using these means for several inhomogeneous unbounded many-electron systems [2].

In this report the further development of the density functional theory for unbounded systems is presented. It is shown that the countable Hilbert space is strictly equivalent to Gelfand's rigged Hilbert space (Gelfand triplet [3]) in the form  $\mathcal{S} \subset \mathcal{H}(L_2) \subset \mathcal{S}'$ , where  $\mathcal{S}$  is the Schwartz space of the ground functions. It allows one to define computationally convenient scalar productions for any pair of slowly growing distributions in the  $\mathcal{S}'$ -space, including continuous-spectrum eigenfunctions which are normalized to  $\delta$ -function.

For the density functional to be extended to include unbounded systems, the Hartree energy term of the usual density functional was rearranged in the following manner

$$V_H \equiv 2\pi \iint_{all\ space} d^3\mathbf{r}d^3\mathbf{r}'\rho(\mathbf{r})G_0(|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}') \rightarrow \int_{system\ subspace} d^3r \left[ \rho(\mathbf{r})u(\mathbf{r}) + \frac{1}{8\pi}u(\mathbf{r})\Delta u(\mathbf{r}) \right],$$

which describes the Coulomb interaction of selected part of the unbounded system both with itself and the rest of the environment via non-variable boundary conditions. Here  $\rho(\mathbf{r}) = n_+(\mathbf{r}) - n(\mathbf{r})$  is the mean charge density,  $u$  is the mean electrostatic potential,  $G_0 = (4\pi|\mathbf{r}-\mathbf{r}'|)^{-1}$  is the Green function of Laplace operator  $\hat{L} = -\Delta$  in the free space. The Poisson equation results now from the variational equality  $\delta V_H/\delta u = 0$  with predetermined boundary values of  $u$ . These boundary conditions are changing the inverse Laplace operator  $\hat{L}^{-1} \equiv G \neq G_0$  and, therefore, interelectron interaction in the system. The derivation of the expression for  $V_H$  has shown that the exact mean electrostatic energy is the sum of electrostatic energy of the mean density and the density fluctuations

$$\langle V_{ee} \rangle = V_H + 2\pi \iiint_{system\ subspace} d\mathbf{r}d\mathbf{r}' \left[ G(\mathbf{r},\mathbf{r}') \langle \delta\hat{n}(\mathbf{r})\delta\hat{n}(\mathbf{r}') \rangle - G_0(0_+)n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \right],$$

where the exchange-correlation energy is presented as the electrostatic energy of the density fluctuations and the self-interaction is removed. The fluctuation-dissipation theorem allows the density-density correlation function to be expressed in terms the linear response function accounting for the mean field reaction (screening effect). In the independent-particle approximation, the total density matrix is replaced by the production of the single-particle density matrices  $\hat{f}$ , the  $\langle \delta\hat{n}(\mathbf{r})\delta\hat{n}(\mathbf{r}') \rangle$  correlation function can be explicitly expressed in terms of eigenfunctions  $\phi_\lambda$  of the  $\hat{f}$  (natural orbitals), and we obtain the energy functional as the functional of eigenfunctions  $\phi_\lambda$  and the mean potential  $u$ . The variations of this functional over  $\phi_\lambda$  and  $u$  lead to the set of the self-consistent mean-field (SCMF) equations with the interaction energy of density fluctuations partly accounted for and self-interaction removed. The further simplifications allows one to derive from the SCMF functional several semi-empirical approximations such as Fermi-Amaldi correction to the Thomas-Fermi equations for many-electron atoms, exact exchange and screened-exchange generalizations of Kohn-Sham method [4].

## References

- [1] A.Ya. Shul'man. J. Phys.: Conf. Ser. **35**, 163 (2006)
- [2] D.V. Posvyanskii and A.Ya. Shul'man. JETP **109**, 145 (2009) [Zh. Eksp. Teor. Fiz. **136**, 169 (2009)]
- [3] A. Bohm, M. Gadella. *Dirac Kets, Gamow Vectors, and Gel'fand triplets*, LN in Phys., v. 348, Springer, 1989
- [4] S. Kuemmel and L. Kronik. *Orbital-dependent density functionals*, Rev. Mod. Phys. **80**, 3 (2008)