Variational method is used to show that a density, ρ-dependent functional $\approx c\rho^{1/3}$ approximates the exchange potential including self exchange. Thomas-Fermi atomic number, Z, dependent scaling transformation is used to find functionals for the potential field and particle density of neutral atoms, transforming them into universal functionals of the scaled distance. Simple analytical expressions for these quantities are given, and it is demonstrated that they yield orbitals in good agreement with those of the Hartree-Fock theory. [The *SCI*® indicates that this paper has been cited in more than 405 publications.]

---◆◆◆---

Density-Dependent Exchange Potential and the Many-Electron Schrödinger-Equation

Rezsö Gáspár
Institute of Theoretical Physics
Kossuth Lajos University
H-4010 Debrecen
Hungary

In the Hartree-Fock theory of atoms, molecules, and solids, the electron-electron interaction terms may be reduced to the sum of the coulombic self energy of the electrons containing the density ρ of electrons and the exchange energy which is the sum of numerous terms of complicated expressions, the so-called exchange terms. The number of these exchange terms grows as $N \approx \frac{1}{8} n^4$, where n is the number of basis functions, a multiple of the number of electrons. If n is large, N grows very rapidly. In a solid where the number of electrons is $\approx 10^{23}/cm^3$ the numerical value of the exchange energy cannot be computed. The necessity of finding a simple approximate expression for the exchange energy and its potential was trivial until the advent of solid-state devices in the early 1950s.

In a 1952 paper,[1] I demonstrated that the reduced effective nuclear charges Z_p/Z of neutral atoms determined by the SCF method without exchange, as functions of the Thomas-Fermi scaled variable, are nearly independent of the atomic number Z, and they make possible the determination of the joint electrostatic potential field of the nucleus and electrons by a transformation. Looking for an appropriate expression for the exchange term of the potential field, I developed an equation by a variational treatment. In the Thomas-Fermi theory, this term was introduced earlier by Dirac. Nearly 10 years later, in 1965, W. Kohn and L.J. Sham[2] independently reinvented this exchange potential, and, with computers, they demonstrated its great utility. J.C. Slater, who also invented a similar expression for the exchange potential but with a different numerical factor, further developed the theory by introducing an adjustable numerical factor α into the potential and summarized the results of the application to various atomic, molecular, and solid-state problems in the paper.[3] A summary on the theoretical foundation of the α factor may be seen in a work I published with A. Nagy.[4]

The local density functional theory has been further developed with refinements of the self-interaction correction and the gradient correction. The correlation of the motion of the electrons by their coulomb-field may be taken into account by the density functional theory, too. All the developments have been reviewed in detail by the paper of R.O. Jones and O. Gunnarsson.[5]

1. Gáspár R. An analytical method for the approximate determination of the eigenfunctions and energies of electrons in atoms. *J. Chem. Phys.* 20:1863-5, 1952.
2. Kohn W & Sham L J. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* 140:A1133-8, 1965. (Cited 3,255 times.)
3. Slater J C. Statistical exchange-correlation in the self-consistent field. (Löwdin P O, ed.) *Advances in quantum chemistry.* New York: Academic Press, 1972. Vol. 6. p. 1-92. (Cited 630 times.)
4. Gáspár R & Nagy A. The chemical bond and model exchange-correlation potentials. (Maruany J, ed.) *Molecules in physics, chemistry and biology.* Dordrecht, The Netherlands: Kluwer, 1989. Vol. 3. p. 93-110.
5. Jones R O & Gunnarsson O. The density functional formalism, its applications and prospects. *Rev. Mod. Phys.* 61:689-746, 1989.
Received April 10, 1991

PC 765